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Published in:
Science of the Total Environment

Link to article, DOI:
[10.1016/j.scitotenv.2018.03.289](https://doi.org/10.1016/j.scitotenv.2018.03.289)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Delre, A., Mønster, J., Samuelsson, J., Fredenslund, A. M., & Scheutz, C. (2018). Emission quantification using the tracer gas dispersion method: The influence of instrument, tracer gas species and source simulation. *Science of the Total Environment*, 634, 59-66. <https://doi.org/10.1016/j.scitotenv.2018.03.289>

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Emission quantification using the tracer gas dispersion method: the influence of instrument, tracer gas species and source simulation

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Highlights

- Emission rates varied up to 18% when multiple analytical instruments were used
- The analytical instrument should have good precision and high detection frequency
- The ratio of the tracer gas release rate to instrument precision should be high
- Upwind tracer gas misplacement results in emission measurement errors of up to 50%

ABSTRACT

The tracer gas dispersion method (TDM) is a remote sensing method used for quantifying fugitive emissions by relying on the controlled release of a tracer gas at the source, combined with concentration measurements of the tracer and target gas plumes. The TDM was tested at a wastewater treatment plant for plant-integrated methane

emission quantification, using four analytical instruments simultaneously and four different tracer gases. Measurements performed using a combination of an analytical instrument and a tracer gas, with a high ratio between the tracer gas release rate and instrument precision (a high release-precision ratio), resulted in well-defined plumes with a high signal-to-noise ratio and a high methane-to-tracer gas correlation factor. Measured methane emission rates differed by up to 18% from the mean value when measurements were performed using seven different instrument and tracer gas combinations. Analytical instruments with a high detection frequency and good precision were established as the most suitable for successful TDM application. The application of an instrument with a poor precision could only to some extent be overcome by applying a higher tracer gas release rate. A sideward misplacement of the tracer gas release point of about 250 m resulted in an emission rate comparable to those obtained using a tracer gas correctly simulating the methane emission. Conversely, an upwind misplacement of about 150 m resulted in an emission rate overestimation of almost 50%, showing the importance of proper emission source simulation when applying the TDM.

Keywords: Diffusive emissions, multiple analytical instruments, release precision ratio, tracer misplacement error, emission factors, wastewater treatment

45 **Graphical abstract**

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1. Introduction

Anthropogenic methane emissions into the atmosphere are important drivers of climate change (IPCC, 2013). Quantifying these methane emissions is important for assessing the contribution of various methane emission sources as well as forming the basis for emission mitigation actions. Recently, the tracer gas dispersion method (TDM) has been adopted for quantifying fugitive methane emissions from area sources in both Europe and the United States (Delre et al., 2017; Jakober et al., 2014; Mitchell et al., 2015; Mønster et al., 2015; Reinelt et al., 2017), and the Danish Environmental Protection Agency currently recommends its use for landfill methane emission quantification, resulting in a method that is routinely applied (DEPA, 2006). The United States Environmental Protection Agency also promotes TDM development (designated EPA Category C “other test method” (OTM) 33B) as a standard method for plant-integrated and area source emission measurements (Foster-Wittig et al., 2015). The TDM combines tracer gas release and downwind gas concentration measurements across the plume, and thus long-lived atmospheric tracer gases are required, in order to maintain a constant concentration ratio between the target and tracer gases during atmospheric dispersion (Lamb et al., 1995; Stiversten, 1983). The target gas emission rate is obtained by multiplying three factors, namely the tracer gas mass release rate, the downwind concentration ratio of the target and tracer gases above background level and the ratio of the target and tracer gases’ molecular weights (Galle et al., 2001). Originally, a TDM was employed by using static atmospheric sampling points across the plume, followed by subsequent gas sample analysis (Stiversten, 1983). Recently, analytical instrument developments have led to real-time concentration measurements using mobile analytical platforms performing several traverses across the plume, thus

allowing one to quickly adjust the traverse location in response to changes in wind direction (Scheutz et al., 2011). The TDM has been applied at different area sources, including petrochemical refineries (Stiversten, 1983), natural gas facilities (Mitchell et al., 2015; Lamb et al., 1995), landfills (Börjesson et al., 2009; Foster-Wittig et al., 2015; Mønster et al., 2015; 2014), biological waste treatment facilities (Andersen et al., 2010; Jensen et al., 2017; Reinelt et al., 2017) and wastewater treatment plants (Delre et al., 2017; Yoshida et al., 2014; Yver Kwok et al., 2015).

Previous studies applied various tracer gases and analytical instruments (Galle et al., 2001; Lamb et al., 1995; Mosher et al., 1999; Mønster et al., 2014; Scheutz et al., 2011; Stiversten, 1983), but their performances in terms of plume description (e.g. peak height, signal-to-noise ratio, etc.) and emission rate quantification were never compared directly. The TDM was investigated in previous studies by performing a controlled release test (Mønster et al., 2014) and numerical simulations (Taylor et al., 2016), focusing on the importance of tracer gas placement, minimum measurement distance and ways to obtain the tracer to target gas concentration ratio (Mønster et al., 2014; Taylor et al., 2016).

This study investigates the influence of analytical instrument properties and tracer gas species on the TDM results, to outline the properties of the most suitable analytical instrument for TDM application. For this purpose, plant-integrated methane emissions from a wastewater treatment plant were measured simultaneously, using different analytical instruments with varying precisions and measurement frequencies as well as different tracer gases. Furthermore, this study investigates the influence of tracer gas misplacement on methane emission quantification.

2. Materials and methods

2.1. Site description

The TDM was applied at a wastewater treatment plant near Lund, Sweden (Section S1 in the Supplementary Material (SM)), which treats about 11,290,000 m³ of wastewater annually, corresponding to a population equivalent (PE) of 120,000. The plant is divided into three operational lines: a wastewater treatment line, a sewage sludge treatment line and a biogas line. The wastewater line involves mechanical treatments, activated sludge reactors for biological pollutant removal and an advanced form of treatment effected by flocculation and clarification ponds. Sewage sludge removed from the wastewater line is stabilised in the sludge line through anaerobic digestion, producing digestate and biogas. The digestate is dewatered and sent daily to an external facility, and the biogas is upgraded on-site and sold partly as vehicle fuel and partly to the natural gas supply grid.

2.2. Application of the tracer gas dispersion method

In this study, the TDM was applied using three vehicles equipped with analytical instruments, global navigation satellite system devices and monitors for real-time concentration readings. Atmospheric air was sampled continuously through tubes from the roofs of the vehicles and led to the analytical instruments, where gas concentrations were measured in real time. Prior to tracer gas release and methane emission quantification, off-site screenings were performed to ensure the absence of interfering sources in the vicinity of the plant. On-site screenings were used to identify the main methane sources at the facility for subsequent correct tracer gas placement at the centroid of the emitting area, thereby ensuring proper methane emission simulation. Tracer gases were released from gas cylinders using calibrated flowmeters, which were

monitored continuously to guarantee constant flow rates. In addition, the weight loss from the gas cylinders was measured and used for the methane emission rate calculation. During emission quantification, downwind concentrations of methane and tracer gases were measured by performing multiple traverses across the plume at suitable downwind distances away from the plant – far enough to allow an appropriate mixing of methane and tracer gases, and close enough for the analytical instrument to distinguish the plume from the background concentration. Vehicle speeds were kept constant during individual plume traversing, which was only considered successful if the plume was completely crossed and the background concentration identified on both sides of the plume (Fig. 1). Further details on TDM application can be found in the literature (Delre et al., 2017; Mønster et al., 2014).

The fugitive methane emission rate was calculated for each plume traverse by following the formula:

$$E_{CH_4} = Q_{tr} \cdot \frac{\int_{plume\ start}^{plume\ end} C_{CH_4} dx}{\int_{plume\ start}^{plume\ end} C_{tr} dx} \cdot \frac{MW_{CH_4}}{MW_{tr}} \quad (1)$$

where E_{CH_4} is methane emission in mass per time; Q_{tr} is tracer gas release in mass per time; C_{CH_4} and C_{tr} are measured downwind concentrations of methane and tracer gas in parts per billion (ppb) above the plume traverse baseline (Fig. 1); MW_{CH_4} and MW_{tr} are the molecular weights of the methane and tracer gas, respectively (Scheutz et al., 2011). Methane and tracer gas concentrations were integrated over the plume detected in the plume traverse (Fig. 1) so that possible improper target and tracer gasses mixing, and possible improper emitting source simulation would be minimised (Mønster et al., 2014).

In this study, methane and tracer gas plume traverses were described through four parameters: peak height (PH), the Gaussian coefficient (GC), the signal-to-noise ratio (SNR), and the plume correlation factor (R^2). PH is the maximum concentration above the baseline measured in the plume (Fig. 1), while GC is the coefficient of determination of the fitted Gaussian curve on the measured plume concentrations. GC ranges between 0 and 1, and the closer the plume shape is to Gaussian distribution, the higher the GC is. The SNR indicates how well within a traverse the plume can be distinguished from the background concentration. The SNR is calculated as suggested by Shrivastava and Gupta (2011):

$$SNR = \frac{PH}{0.5 h} \quad (2)$$

where h is the difference between the highest and the lowest background concentrations (Fig. 1). Finally, R^2 is the coefficient of determination of the linear regression of methane-to-tracer gas concentrations within a plume traverse, and thus R^2 ranges between 0 and 1. It indicates how well methane and tracer gases are mixed in the plume. R^2 and GC were calculated using a build-in function of OriginPro 2016 ® (OriginLab, 2016).

2.3. Analytical instruments and tracer gases

Plant-integrated methane emissions from the wastewater treatment plant were quantified using four tracer gases (acetylene, ethene, nitrous oxide and propane) and measured with four analytical instruments (A, B, C and D) installed in three vehicles (AB, C and D). Two cavity ring-down spectroscopy analysers were placed in vehicle AB, namely analytical instrument A, which simultaneously measured acetylene and methane (G2203, Picarro, Inc., Santa Clara, CA), and analytical instrument B, which measured acetylene and nitrous oxide (S/N JADS2001, Picarro, Inc., Santa Clara, CA)

(Mønster et al., 2014; Yoshida et al., 2014). Vehicle C contained analytical instrument C, which was a Fourier Transform infrared spectroscopy analyser (IRCube Matrix-M, Bruker Optics GmbH, Ettlingen, Germany) for the simultaneous measurement of acetylene, ethene, methane, nitrous oxide and propane (Galle et al., 2001; Scheutz et al., 2011). Vehicle D contained analytical instrument D, which was the same model as analytical instrument A. Table 1 provides an overview of measured gases, analytical instrument properties and gas release rates during the two tests in the measurement campaign. Although activated sludge reactors at wastewater treatment plants are known to emit nitrous oxide, emissions during the measurement campaign were below the TDM detection limit ($0.4 \text{ kg N}_2\text{O h}^{-1}$), corresponding to less than 2% of the nitrous oxide release rate when nitrous oxide was used as a tracer gas (Table 1). The TDM detection limit was calculated according to the literature (Delre et al., 2017).

On-site atmospheric pressure, atmospheric temperature and wind speed were recorded at four metres above ground level by a weather station placed in open terrain on the southern border of the plant.

2.4. Measurement campaign

The measurement campaign was performed at a wastewater treatment plant in Lund (SE) during the night and between August 4th and 5th, 2016. It was decided to perform measurements during night-time due to the likelihood of lower atmospheric gas dispersion and less interference by traffic. During the night, the vertical dilution in the atmosphere of any gas emitted/released is usually lower than during the day. This means that, at the same distance from the emitting/releasing location, the downwind signal of the plume is stronger when the dilution is lower. This is an advantage when applying the TDM because downwind measurements can be performed further away from the source,

and still obtain a plume traverse where the plume is well distinguished from the background (Fig. 1). Additionally, less traffic allows downwind measurements with a speed independent from other vehicles using the same road.

The campaign consisted of two tracer gas release tests. In Test 1, four tracer gases (acetylene, ethene, nitrous oxide and propane) were released from the sludge treatment area (Fig. 2), which was identified as the main methane emission source at the plant during on-site screening. In Test 2, acetylene and ethene were still released from the sludge treatment area, but nitrous oxide and propane were placed at two opposite locations away from the main methane source (Fig. 2). Test 1 lasted 1 hour and 20 minutes (from 21:45 to 23:05), while Test 2 lasted 2 hours (from 01:45 to 03:45). During both tests, atmospheric pressure was about 1005.5 hPa, and atmospheric temperature was about 16°C. Wind speed, measured at 4 m above the ground, was between 0.5 and 1 m s⁻¹ during Test 1, and about 0.6 m s⁻¹ during Test 2. During both tests, wind direction changed, moving the plume between NE and N-NW from the plant. Analytical instruments A, B and C traversed the plume together, while analytical instrument D traversed the plume at different distances and at different driving speeds. Instrument D measured only during Test 1. Analytical instruments A, B and C performed 12 and 17 plume traverses in Test 1 and Test 2, respectively. Analytical instrument D performed 18 plume traverses in Test 1. Fig. 2 shows the location of the performed plume traverses (more details are available in Table S1 in the SM).

2.5. Release precision ratio (RPR)

Table 1 reports the amount of tracer gas released in both tests, and introduces the release precision ratio (RPR), which is the ratio between molar release (mol h⁻¹) and analytical instrument precision (ppb). RPR indicates the strength of the downwind

signal for a given instrument and gas combination. A higher RPR is obtained using an analytical instrument with good precision (low precision value) when the tracer gas release rate is kept constant. Conversely, an analytical instrument with a specific precision has a higher RPR for a given tracer gas when more of this tracer gas is released. Therefore, when different analytical instruments simultaneously traverse the plume at the same distance away from the source, analytical instruments' performances can be compared using the RPR. Table 1 also reports the methane emission rates measured using A_C₂H₂, which was the instrument and gas combination used in Test 1 and Test 2, where the tracer gas was correctly placed at the main methane emission source.

3. Results and discussion

3.1. Description of the plume traverses

Fig. 3 shows the GC, PH and SNR of methane and tracer gas plume traverses measured simultaneously at the same distance away from the plant by instruments A, B and C. PHs were similar when different instruments measured the same gases at approximately the same time and the same distance. However, when the analytical instruments measured the same gas, higher GC and SNR were obtained for instrument and gas combinations with a higher RPR. This difference in plume description was attributed to the RPR and not to the specific tracer gas, as shown in Fig. 3 through a comparison of instruments B and C, measuring acetylene and nitrous oxide. Plume traverses of acetylene and nitrous oxide had high GC and SNR when they were measured by instrument and gas combinations with high RPR (e.g. B_C₂H₂ and C_N₂O in Fig. 3); conversely, plume traverses had low GC and SNR when RPR was low

(e.g. C_C₂H₂ and B_N₂O in Fig. 3). In other words, GC and SNR of plume traverses measured in Test 1 by B_C₂H₂ (RPR equal to 48) were on average 15% and 63% higher than GC and SNR of plume traverses measured by C_C₂H₂ (RPR equal to 18), respectively. Similarly, GC and SNR of plume traverses measured in Test 1 by C_N₂O (RPR equal to 542) were on average 8% and 83% higher than GC and SNR of plume traverses measured by B_N₂O (RPR equal to 18), respectively. Similar results were obtained in Test 2. In general, higher GC was seen for instrument and gas combinations with a higher RPR (Fig. 3). However, this result does not imply that a higher GC produces better quantification measurements. This analysis only shows that the description of a plume traverse depends on the used instrument gas combination. A high RPR also resulted in a high SNR, which is important in order to distinguish the plume from the background concentration in each plume traverse (Fig. 1). Furthermore, a high SNR increases the accuracy of baseline determination and thus reduces errors in determining emission rates caused when subtracting background concentrations (Eq. 1).

Fig. 4 shows the correlation values (R^2) of the methane and tracer gas plume traverses obtained by different instrument and tracer gas combinations measuring simultaneously and at the same distance away from the plant. Since all analytical instruments had similar RPRs when detecting methane (Table 1), the instruments differed by tracer gas RPR and detection frequency. When tracer gases were released from the same location, analytical instruments and tracer gas combinations with high RPR (e.g. A_C₂H₂ in Test 1 and Test 2, and C_N₂O in Test 1) gave high R^2 . Generally, low R^2 -values were obtained when, in Test 2, the placement of the two tracer gas (nitrous oxide and propane) release points was moved away from the main methane source (Fig. 4). However, exceptions were when the tracer gas became aligned with the

methane emission source, due to changes in wind direction (e.g. nitrous oxide placed about 150 m upwind of the main methane source and plume traverses performed along NE_1100 (Test 2 in Fig. 2)).

The combination of wind speed, plume traverse distances, and correct tracer gas placement resulted in a sufficient mixing of methane and tracer gases, which was confirmed by the very high R^2 -value (0.86-0.98) of A_C₂H₂ obtained in Tests 1 and 2 (Fig. 4). The instrument and gas combination A_C₂H₂ was used as an example because this combination had a high RPR and acetylene was released from the main methane source in both tests. In general, the other instrument and tracer gas combinations also had high R^2 -values, the only exceptions were traverses where R^2 was below 0.75, which were caused by a low RPR (Fig. 4). A previous study considered R^2 high when it is larger than 0.75 (Roscioli et al., 2015).

The influence of RPR on the description of the plume traverse was also addressed by studying the 12 plume traverses recorded by analytical instrument C in Test 1. In this case, the analysed plume traverses differed only by RPR, as analytical instrument C measured all gases with the same frequency (Table 1). An analysis was performed ranking SNR, GC and R^2 of the plume traverses for all tracer gases. A low rank was assigned to a low parameter value, whereas a high rank was assigned to a high parameter value. Table 2 describes the ranking procedure and reports the ranking results for all investigated parameters. This analysis confirmed that analytical instrument and tracer gas combinations with higher RPRs provided plume traverses with higher SNR, GC and R^2 (Table 2: instrument C using nitrous oxide as tracer gas).

3.2. Plant-integrated methane emission quantifications

Table 3 reports on plant-integrated methane emission quantifications, using different instrument and tracer gas combinations when tracer gases were released from the main methane-emitting source at the plant. The analysis included analytical instruments A, B and C, which traversed the plumes simultaneously and at the same distance away from the plant. Different instrument and tracer gas combinations provided emission rates between 8.7 and 11.3 kg h⁻¹ in Test 1, and between 6.5 and 10.2 kg h⁻¹ in Test 2 (Table 3). Considering emission rates from all instrument and tracer gas combinations in Table 3, the corresponding mean emission rate was 10.3 kg h⁻¹ in Test 1, and 7.9 kg h⁻¹ in Test 2.

Emission rates obtained by individual instrument and tracer gas combinations differed from the mean emission rate by 1 to 15% in Test 1, and by 4 to 18% in Test 2 (Table 3). The variation of the methane emission rates, through multiple plume traverses, was reported as standard error of means (SEM), which was between 3 and 6% in Test 1, and was equal to 2% in Test 2. The size of the SEM was caused by three factors: real variations in the methane emission rates from the plant, non-systematic measurement uncertainty and the number of samples (plume traverses). However, the individual contribution from the real variations and measurement uncertainty were not quantifiable.

Table 3 also compares emission rates obtained by each instrument and tracer gas combination with the emission rate obtained by A_C₂H₂, which was chosen as a reference because it had a high tracer gas RPR and acetylene was released from the main methane source in both tests. The difference in emission rates compared to the methane emission rates quantified by A_C₂H₂ tended to be larger with a lower tracer

gas RPR, e.g. the highest emission rate difference (26%) was seen when quantification was performed using C₂H₄, which had the lowest tracer gas RPR (16) (Table 3).

3.3. Properties of a suitable analytical instrument

Besides proper atmospheric gas transportation and mixing, the success of any TDM application is mainly a combination of three factors: the analytical instrument's detection frequency, the analytical instrument's precision in measuring target and tracer gas, and the tracer and target gas release/emission rates. A suitable analytical instrument should have good precision and sufficient high detection frequency. Regarding precision, an analytical instrument with good precision can distinguish the plume better from the background concentration than an instrument with poor precision. Good instrument precision becomes important when measurements are performed in unfavourable conditions, i.e. situations with high atmospheric dispersion. Furthermore, better precision allows for measurements at a greater distance away from the source, thereby increasing the chance of having fully mixed conditions in the plume at the measurement distance. Additionally, a more precise analytical instrument allows a lower tracer gas release rate. An example is reported in Table 1, illustrating analytical instruments B and C measuring nitrous oxide. In Test 1, an nitrous oxide release rate of 16.7 kg h⁻¹ was just enough to produce an RPR of 18 for instrument B, whereas it produced an RPR equal to 542 for instrument C. Releasing less nitrous oxide, however, would have lowered the RPR of the plume traverses measured by both instruments, thereby resulting in very low RPRs for instrument B and still high RPRs for instrument C (Table 1). Additionally, a lower tracer gas release rate permits longer measurement periods without replacing tracer gas cylinders, thus resulting in lower costs. The use of an analytical instrument with poor tracer gas precision is still possible, though, by

increasing the release rate of the tracer gas, with the consequence of a higher RPR. The use of an analytical instrument with poor target gas precision, however, may be impossible in some cases. An instrument with better target gas precision allows for quantifying smaller emission rates than an instrument with a worse target gas precision.

An analytical instrument with high frequency has three important benefits. First, it provides a more defined plume within the traverse, making it easier to distinguish the studied plume from other interfering sources, which would be seen as additional peaks/plumes (Fig. S2 in SM). Second, an analytical instrument with a higher detection frequency can perform more plume traverses within a specific time interval, thus obtaining an emission rate with smaller variation (SEM). An example of this is given in Table 3, showing a smaller SEM in Test 2 than in Test 1, where 17 and 12 plume traverses were performed, respectively. Third, an analytical instrument with a higher detection frequency can reduce the measurement time required and thus reduce costs.

3.4. Tracer gas placement and emission source simulation

In Test 2, nitrous oxide and propane were moved from the main on-site methane source, as shown in Fig. 3, to study the importance of tracer gas placement in the application of the TDM. Acetylene and ethene were still released from the main methane source, in order to simulate methane emissions properly. The analysis of the tracer gas placement was carried out on 12 plume traverses, performed by analytical instrument C along NE_1100 (Fig. 2), so that emission rates would be calculated using the same instrument performing the most plume traverses at the same distance. Nitrous oxide was misplaced about 150 m upwind, whereas propane was misplaced about 250 m sideward (Fig. 2). The tracer gas misplacement was measured from the centroid of the methane emitting area, which was approximately 1,250 m² large (considering the sludge

treatment line). Table 4 presents the results of the tracer gas placement analysis. The mean methane emission rate obtained using acetylene (C_2H_2) and ethene (C_2H_4), which were correctly placed, was 6.7 kg h^{-1} . Methane emission rates obtained with combinations C_ C_2H_2 and C_ C_2H_4 differed by only 9% from the mean emission rate (Table 4). When the tracer gas was misplaced about 250 m sideward (C_ C_3H_8), the methane emission rate was comparable to those quantified using correct tracer gas placement (Table 4). Conversely, a high methane emission rate overestimation (almost 50%) was obtained when the tracer gas was misplaced about 150 m upwind, due to different travel distances for the methane and the tracer gas, which resulted in higher tracer gas dispersion compared to methane (C_ N_2O in Table 4). These findings are in line with previous studies highlighting the importance of tracer gas placement and the ability to minimise errors caused by a sideward misplacement when applying Eq. 1 rather than other formulas for emission rate quantifications (Mønster et al., 2014; Taylor et al., 2016). When tracer gases were placed correctly (C_ C_2H_2 and C_ C_2H_4), the variation (SEM) of the emission rates was smaller than variation reported using misplaced tracer gases (C_ C_3H_8 and C_ N_2O) (Table 4). The overestimation and increased variation indicated that emission rates obtained through proper emission simulation are more accurate and precise than emission rates obtained through poor emission simulation.

3.5. Varying measurement team

Each measurement team (person or persons operating each analytical instrument) decided on measurement distances, vehicle speeds, etc. mainly based on previous experiences using their respective analytical instruments. During Test 1, analytical instrument D performed 18 plume traverses at other distances, driving speeds, etc. in the

same time interval as the other analytical instruments (Table S1 in SM), which performed 12 plume traverses. As reported in Table 1, instrument D had higher detection frequency and better acetylene precision than instrument C. These properties allowed the collection of more plume traverses, and plume traverse measurements further away (e.g. NNW_1900) (Table S1). The methane emission rate obtained with the instrument and tracer gas combination D_C₂H₂ was 10.6 kg h⁻¹, which was similar to the emission rates measured in closer vicinity to the plant with instrument and tracer gas combinations with high RPRs reported in Table 3 (C_N₂O: 11.0 kg h⁻¹, C_C₂H₂: 10.2 kg h⁻¹). This result demonstrated a negligible difference in emission rate quantification when different measurement teams measured in the same time interval, even when using different instruments allowing collection of different numbers of plume traverses at different distances from the emission source.

4. Conclusions

The tracer gas dispersion method (TDM) was applied at a wastewater treatment plant to investigate the influence of analytical instrument properties and tracer gas species on TDM results. Plant-integrated methane emissions were quantified simultaneously using four analytical instruments with varying precisions and detection frequencies, as well as four tracer gases. Two tracer gas releasing tests were carried out. In Test 1, all tracer gases were released from the main on-site methane-emitting source, to simulate correctly emissions from the plant. In Test 2, two tracer gases were still correctly placed, while the other two were moved to two places opposite to the main on-site methane-emitting source, thereby allowing for investigating the effect of tracer gas misplacement on the methane emission rate.

The combination of an analytical instrument and a tracer gas resulting in a high ratio between the tracer gas release rate and instrument precision (high tracer gas release precision ratio (RPR)) resulted in well-defined plumes close to a theoretical Gaussian atmospheric plume dispersion (a Gaussian coefficient closer to 1), and with a high signal-to-noise ratio (SNR) – the latter reducing the risk of over- or underestimating the plume baseline, which is important for calculating the target gas emission rate. Finally, an instrument and tracer gas combination with a high release precision ratio provided plume traverses with a higher methane-to-tracer gas correlation factor (R^2), thereby indicating better mixing between the two gases at the measurement point.

Measured plant-integrated methane emission rates varied between 8.7 and 11.3 kg h⁻¹ in Test 1, and between 6.5 and 10.2 kg h⁻¹ in Test 2, when measurements were performed under the same conditions (distance and tracer gas release configuration) but using seven different instrument and tracer gas combinations. Methane emission rates differed from the mean value by up to 15% in Test 1, and by up to 18% in Test 2.

A suitable analytical instrument for TDM application should preferably have good precision and high detection frequency when measuring target and tracer gas. It is important that the combination of an analytical instrument and tracer gas release can produce a high RPR, as this will result in a high SNR. Setting aside cost and environmental issues, the choice of tracer gas species is not important. As long as tracer gas release and analytical instrument precision can produce a high SNR, any long-lived atmospheric gas can be used as a tracer gas in the TDM application. However, it should be emphasised that costs and environmental effects vary highly between different potentially usable tracer gas species, whereby the choice of tracer gas should be done considering those factors.

The analysis of tracer gas misplacement showed that an upwind misplacement of about 150 m led to an overestimation of the plant-integrated emission rate by almost 50%. Conversely, a sideward misplacement of about 250 m led to an emission rate comparable to quantifications obtained using a tracer gas correctly simulating the methane emission source.

Finally, a 4% difference in emission rate quantification was found when three measurement vehicles measured in the same time interval using four different instruments, which allowed for the collection of different numbers of plume traverses at different distances away from the plant.

Acknowledgements

This work was funded in part by the Innovation Fund Denmark (IFD) (Project LaGAS, File No. 0603-00523B) and Veolia Water Technologies (Krüger, AnoxKaldnes, The Veolia Group). Support from the wastewater utilities (Biofos, DK; VA SYD, SE; Lyngby-Taarbæk forsyning, DK; FORS A/S, DK; Växjö, SE) and Unisense Environment, DK, is acknowledged. The authors wish to thank the plant managers for their assistance during the whole study as well as staff at the plant for facilitating the measurements.

Supplementary Material

The Supplementary Material (SM) contains detailed information about the investigated site, quantifying analytical instrument precision, the measurement campaign, analytical instrument detection frequency and plant-integrated methane emission factors.

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539 FIGURES

540

541 Fig. 1. Example of a plume traverse, showing baseline, background concentration, peak
542 height (PH) and integrated plume concentrations.

Fig. 2. Plume traverse positions during Test 1 and Test 2 are marked with blue lines. Plume traverse positions are named using cardinal directions and distance (m) away from the sludge treatment area of the wastewater treatment plant. In Test 1, the tracer gas release location is marked with a yellow circle for all tracer gases. In Test 2, the tracer gas release location is marked with a yellow circle for acetylene and ethene, with white and red circles for nitrous oxide and propane, respectively. The wastewater treatment plant is marked with a green circle.

Fig. 3. Description of plume traverses performed simultaneously at the same distance away from the plant by analytical instruments A, B and C. Parameters shown include the Gaussian coefficient (GC), peak height (PH), and signal-to-noise-ratio (SNR). RPR stands for “release precision ratio.” A description of all instrument and gas combinations is available in Table 1.

Fig. 4. Methane and tracer gas plume traverse correlation factor (R^2) of all analytical instrument and tracer gas combinations measuring simultaneously and at the same distance away from the plant. RPR stands for “release precision ratio.”

561 **Table 1.** Measured gases, analytical instrument properties and gas release rates during the two test campaigns.

Gas		Analytical instrument properties			Gas release rate				Release precision ratio (RPR)	
Name and chemical formula	Molecular weight (g mol ⁻¹)	Instrument and gas	Frequency (Hz)	Precision (ppb)	Mass release (kg h ⁻¹)		Molar release (mol h ⁻¹)		precision ratio (RPR) (mol h ⁻¹ ppb ⁻¹)	
					Test 1	Test 2	Test 1	Test 2	Test 1	Test 2
Acetylene C ₂ H ₂	26	A_C ₂ H ₂	2	0.5					153	153
		B_C ₂ H ₂	0.3	1.6					48	48
		C_C ₂ H ₂	0.06	4.2	2.0	2.0	77	77	18	18
		D_C ₂ H ₂	2	0.3					256	NA
Ethene C ₂ H ₄	28	C_C ₂ H ₄	0.06	10.7	5.4	4.8	193	171	18	16
Methane CH ₄	16	A_CH ₄	2	2.6					245	211
		B_CH ₄	0.3	2.6					245	211
		C_CH ₄	0.06	3.8	10.2	8.8	637.5	550.0	167	144
		D_CH ₄	2	3.2					205	NA
Nitrous oxide N ₂ O	44	B_N ₂ O	0.3	21.1					18	17
		C_N ₂ O	0.06	0.7	16.7	16.0	380	364	542	519
Propane C ₃ H ₈	44	C_C ₃ H ₈	0.06	3.7	9.7	9.7	220	220	59	59

A: Cavity ring down spectroscopy (CRDS) analyser detecting acetylene and methane placed in vehicle AB. B: CRDS analyser detecting acetylene and nitrous oxide placed in vehicle AB. C: Fourier Transform infrared spectroscopy analyser detecting acetylene, ethene, methane, nitrous oxide, and propane placed in vehicle C. D: CRDS analyser detecting acetylene and methane placed in vehicle D. B_CH₄ is methane measured with instrument A and coupled to tracer gases measured by instrument B. NA: Not available. The methane gas releases are the emission rates measured using A_C₂H₂ (the instrument and tracer gas combination used in Test 1 and Test 2, where the tracer gas was placed at the main methane emission source). Precision is defined as three times the standard deviation of six minutes' constant concentration reading (Section S2 in SM).

Table 2. Ranking results of parameters describing plume traverses in the analytical instrument precision analysis. Gaussian coefficient (GC), signal-to-noise ratio (SNR) and the plume correlation factor (R^2) are reported for the 12 plume traverses performed by analytical instrument C in Test 1.

Tracer gas	Rank			RPR
	SNR	GC	R^2	
C ₂ H ₂	18	15	15	18
C ₂ H ₄	20	22	23	18
C ₃ H ₈	34	35	38	59
N ₂ O	48	48	44	542

The ranking procedure was carried out by comparing the parameter values (GC, SNR and R^2) of the four tracer gases in each plume traverse. The tracer gas having the lowest and the highest parameter value scored 1 and 5, respectively, whereas the tracer gas with parameter values in between scored 2, 3, and 4, accordingly. The final score assigned to each dataset was the sum of the scores of the 12 plume traverses.

Table 3. Plant-integrated methane emission quantifications using different instrument and tracer gas combinations when tracer gases were released from the main methane emitting source at the wastewater treatment plant.

Instrument and tracer gas combination	Test 1 Emission rate		Test 2 Emission rate		Relative difference in emission rate compared to the mean CH ₄ emission rate quantified by all combinations (10.3 kg h ⁻¹ in Test 1, and 7.9 kg h ⁻¹ Test 2)				Relative difference in emission rate compared to the CH ₄ emission rate quantified by A_C ₂ H ₂		Tracer gas RPR	
					Test 1		Test 2		Test 1	Test 2	Test 1	Test 2
	Average (kg h ⁻¹)	SEM (kg h ⁻¹)	Average (kg h ⁻¹)	SEM (kg h ⁻¹)	Average (%)	SEM (%)	Average (%)	SEM (%)	Average (%)	Average (%)		
C_N ₂ O	11.0	0.7	NA	NA	7	3	NA	NA	8	NA	542	519
A_C ₂ H ₂	10.2	0.8	8.8	0.3	-1	4	11	2	0	0	153	153
C_C ₃ H ₈	8.7	0.8	NA	NA	-15	4	NA	NA	-15	NA	59	59
B_C ₂ H ₂	10.6	0.9	8.7	0.3	3	4	10	2	4	-1	48	48
C_C ₂ H ₂	9.1	0.8	7.6	0.3	-12	4	-4	2	-11	-13	18	18
C_C ₂ H ₄	11.3	1.2	6.5	0.3	10	6	-18	2	11	-26	18	16
B_N ₂ O	11.2	0.7	NA	NA	9	4	NA	NA	10	NA	18	17

The average emission rate was given as the average value of all plume traverses, and the corresponding variation of the methane emission rates, through multiple plume traverses, was expressed as standard error of the means (SEM). Instrument and tracer gas combinations are ordered from the highest to the lowest RPR. NA: not applicable. Relative difference in emission rate: (Measured emission rate – Average emission rate)/Average emission rate

Table 4. Tracer gas placement analysis. Comparison of plant-integrated methane emission rates using different tracer gas placements. Twelve plume traverses performed in Test 2 by instrument C along NE_1100 were used.

Instrument and tracer gas	Tracer gas placement	Emission rate		Relative difference in emission rate compared to the mean emission rate quantified with C_ C ₂ H ₂ and C_ C ₂ H ₄ (6.7 kg h ⁻¹)	
		Average (kg CH ₄ h ⁻¹)	SEM (kg CH ₄ h ⁻¹)	Average (%)	SEM (%)
C_ C ₂ H ₂	Correct	7.3	0.4	9	3
C_ C ₂ H ₄	Correct	6.1	0.4	-9	3
C_ C ₃ H ₈	Sideward misplacement	7.5	0.7	12	5
C_ N ₂ O	Upwind misplacement	10.0	0.8	49	6

Correct tracer gas placement was at the main on-site methane source.

The average emission rate was given as the average value of all plume traverses, and the corresponding variation of the methane emission rates, through multiple plume traverses, was expressed as standard error of the means (SEM).

Relative difference in emission rate: (Measured emission rate – Average emission rate)/Average emission rate.