

Quantifying greenhouse gas emissions from waste treatment facilities

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Quantifying greenhouse gas emissions from waste treatment facilities



Jacob Mønster

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PhD Thesis
July 2014

DTU Environment
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The synopsis part of this thesis is available as a pdf-file for download from the DTU research database ORBIT: <http://www.orbit.dtu.dk>

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Preface

The thesis is organized in two parts: the first part puts the findings of the work into context in an introductory review; the second part consists of the papers listed below. These papers will be referred to in the first part by their paper number written with the Roman numerals **I-VI**.

- I** Mønster, J., Samuelsson, J., Kjeldsen, P., Rella, C. W., Scheutz, C. (2014). Quantifying methane emission from fugitive sources by combining tracer release and downwind measurements – a sensitivity analysis based on multiple field surveys. *Waste Management*, in press (doi:10.1016/j.wasman.2014.03.025)
- II** Mønster, J., Samuelsson, J., Kjeldsen, P., Scheutz, C. Quantification of methane emissions from 15 Danish landfills using mobile tracer dispersion method. Accepted (with revision) by *Waste Management*.
- III** Mønster, J., Kjeldsen, P., Scheutz, C. Emission measurements methodologies for measuring fugitive methane emission from landfills – a review. Manuscript in preparation.
- IV** Scheutz, C., Pedersen R. B., Petersen, P. H., Jørgensen J. H. B., Uccendo, I. M. B., Mønster, J. G., Samuelsson, J. and Kjeldsen, P. (2014). Mitigation of methane emission from an old unlined landfill in Klintholm, Denmark using a passive biocover system. *Waste Management*, in press (doi:10.1016/j.wasman.2014.03.015)
- V** Yoshida, H., Mønster, J., Scheutz, C. (2014). A plant-integrated measurement of greenhouse gas emissions from a municipal wastewater treatment plant. *Water Research* 61 (2014) 108-118.
- VI** Yver-Kwok, C. E., Müller, D., Caldow, C., Lebegue, B., Mønster, J.G., Rella, C.W., Scheutz, C., Schmidt, M., Ramonet, M., Warneke, T., Broquet, G., Ciais, P. (2013). Estimation of waste water treatment plant methane emissions: methodology and results from a short campaign. *Atmos. Meas. Tech. Discuss.*, 6, 9181-9224, 2013. In review.

In this online version of the thesis, the papers are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Miljøvej, Building 113, 2800 Kgs. Lyngby, Denmark, reception@env.dtu.dk.

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A great thank goes to Lisbet and Torben for helping with layout and illustrations for the thesis and articles.

I also thank friends and family who supported me during the years and told me that everything was going to be alright. Thanks to Søren for correcting the thesis. Finally, I would like to thank Letizia for the support, both privately in good and bad times of the PhD, and for providing a nice drawing for the thesis.

Summary

Methane is a greenhouse gas (GHG) and the anthropogenic emission of methane to the atmosphere contributes to global warming. There are several anthropogenic methane sources, and the quantification of methane from these emission sources are often based on emission factors and model calculations making reporting uncertain. Reducing the methane emission is an effective way of reducing the overall greenhouse gas emission. Methane reductions can often be difficult to quantify and document, as accurate measurements methods are lacking and not commercial available.

The methane emission from the waste sector is a significant part of the global anthropogenic methane emission, and landfills are responsible for the majority of the GHG emission. Several initiatives have been taken to minimize the methane emission from landfills, e.g. by methane recovery followed by flaring or utilization, or by constructing mitigation installations such as a cover material with enhanced methane oxidizing capability. Due to a series of factors, methane from landfills is emitted very heterogeneous in both time and space, challenging methane quantification. Several methods have been developed to quantify methane emissions from landfills, but none of these have been accepted internationally as the best way to perform emission measurements.

The overall aim of this PhD study was to identify, develop, document and apply an optimal method for quantifying fugitive GHG emissions from waste treatment facilities such as landfills and wastewater treatment plants. The primary objective was to identify a potential measurement method, build the associated analytical platform and document and verify the method. The secondary objective was to apply the method to quantify emissions from Danish landfills and from wastewater treatment plants.

The PhD study reviewed and evaluated previously used methane measurement methods and found the tracer dispersion method promising. The method uses release of tracer gas and the use of mobile equipment with high analytical sensitivity, to measure the downwind plumes of methane and tracer gas. The method was chosen as it enable measurements of the emission from whole landfill areas, including possible hotspot emissions occurring at the landfill.

A fast response and high resolution analytical equipment was purchased and tested. An analytical platform was build, enabling the instrument to be in-

stalled in any vehicle and thereby enabling measurements wherever there were roads. The validation of the measurement method was done by releasing a controlled amount of methane and quantifying the emission using the release of tracer gas. The validation test showed that even in areas with large turbulence, such as urban areas, the measured emission could be quantified within a few percent of the released methane. The sensitivity of incorrect location of tracer gas release was also tested, showing the possibility of a significant over-/underestimation of the methane emission by misplacing the tracer gas, and that this error becomes smaller with increasing measurement distance.

A measurement protocol was developed and the methane emission was quantified from a series of landfills with different size, age and gas recovery and mitigation conditions. The landfills were measured between one and four times and the emissions ranged from 2.6 to 60.8 kg methane per hour, with the lowest emissions from the oldest and smallest landfills and the highest emissions from the bigger landfills. It was not possible to correlate the measured emission with a single factor such as landfill age, size or mitigation actions. As an example the highest emission was measured at a landfill with active methane recovery and utilization. Compared with national and European greenhouse gas reporting schemes the measurement showed a large difference, with reporting ranging a factor of 100 above to a factor of 10 below the measured methane emission. The average reporting was three times higher than the average measured emission, even when including the two landfills without reporting. The landfills recovering methane for utilization showed a methane recovery efficiency ranging between 41 and 81%, excluding a possible methane oxidation in the top layer of the landfills.

To expand the application of the developed analytical platform to also cover fugitive emissions of other gasses, an additional instrument for measuring nitrous oxide (greenhouse gas) and ammonia (causes eutrophication) was developed and tested in collaboration with the manufacturer. The development was done in two stages. The first stage was optimization and field testing done during an external research stay at the instrument manufacturer in USA. The second stage was field measurements conducted in Denmark with subsequent tuning of the spectroscopy in the instrument. The implementation of nitrous oxide measurements were done by intensive measurements at a Danish wastewater treatment plant. The measurement campaigns showed that the nitrous oxide emission mainly occurred from the aeration tanks during aeration. The nitrous oxide emission showed high temporal variations ranging from

below quantifiable and up to 10.3 kg nitrous oxide per hour. The methane emission from the wastewater treatment was also quantified and the majority (99%) was emitted from the sludge treatment processes, including anaerobic digestion and open air storage of digested sludge. The methane emission ranged from 10 to 92 kg per hour and was found to change in even short timescales of a few hours. The periods with large emissions correlated with a drop in methane utilization, indicating that emissions came from the digesters tanks or gas storage/use. The measurements indicated that the main emissions occurred in elevated heights, but theoretically calculation showed that this only resulted in a 2% underestimation, although measurement conditions could make the error more significant.

Besides the extensive emission research, the outcome of the PhD study is a mobile analytical platform implementable on any means of transportation able to carry approximately 100 kg, including batteries, inverter, weather station, GPS, pumps, analyzers and screens. The mobile analytical platform can measure real time atmospheric concentrations of methane, nitrous oxide and ammonia and measure concentration changes in parts per billion levels, enabling the use of dynamic tracer dispersion method for quantifying fugitive emissions from various sources. The analytical setup was proven applicable for measuring methane emissions from landfills and methane and nitrous oxide emission from wastewater treatment plants. The flexibility of the analytical platform allows many setups, including short term mobile measurements and long term, stationary measurements, opening up for a large range of applications both for emission quantification and concentration monitoring.

Dansk sammenfatning

Med et drivhusgaspotential på 25 er metan en potent drivhusgas, hvis udledning bidrager væsentligt til den globale opvarmning. Metan bliver udledt fra flere antropogene kilder og bestemmelse af udledningen fra disse er ofte baseret på emissionsfaktorer og modelberegninger, hvilket gør resultaterne meget usikre. Reduktion af metanudledningen er en effektiv måde at reducere det totale antropogene udslip af drivhusgasser. Det kan dog være svært at dokumentere en sådan reduktion særligt fra diffuse kilder, da dette kræver metoder, der præcist kan måle emissionen før og efter reduktionen.

Udledning af metan fra affaldssektoren bidrager væsentligt til den globale antropogene udledning af metan og lossepladser står for hoveddelen af denne udledning. Der er blevet igangsat flere initiativer for at minimere metanudledningen fra lossepladser. Allerede for flere årtider siden begyndte man at indvinde metanen fra lossepladser. Metanen blev efterfølgende enten brændt af i en fakkellampe eller i en gasmotor, som kan producere varme og/eller strøm. En nyere teknologi til reduktion af metan fra lossepladser indbefatter etablering af et afdækningslag, der er designet med henblik på at opnå en høj oxidation af metanen ved hjælp af metanoxiderende bakterier. Ofte anvendes kompost, som lægges over et gas distributionslag, der hjælper til at fordele gassen til kompostlaget. Denne teknologi kaldes for biocover eller biovinduer. Udledning af metan fra lossepladser er meget heterogen, både mht. tid og sted, hvilket gør det vanskeligt at kvantificere størrelsen af udledningen. Dette kompliceres yderligere af lossepladseres store størrelse (ofte >5 ha).

En anden vigtig drivhusgaskilde er spildevandsrensningsanlæg, hvorfra der frigives metan og lattergas. Metanen kommer hovedsageligt fra behandlingen af slam imens lattergas kommer i forbindelse med biologisk fjernelse af nitrogen fra spildevandet. Disse udledninger af drivhusgasser er ligeledes vanskelige at bestemme.

Der er blevet udviklet flere metoder til at kvantificere metanudledningen fra lossepladser, men ingen af metoderne er internationalt anerkendt som den måde, man bør foretage målingerne på.

Det overordnede formål med dette PhD studie var at identificere, udvikle, dokumentere og applikere en optimal metode til kvantificering af drivhusgas udledninger fra affaldsbehandlingsanlæg som lossepladser og spildevandsrensningsanlæg. Det primære formål var at identificere en potential målemetode, opbygge den analytiske platform samt dokumentere og verificere meto-

den. Det sekundære formål var at applikere metoden til at bestemme udledningen af drivhusgasser fra Danske lossepladser samt fra anlæg til spildevandsrensning.

Den første del af dette PhD-studie indbefattede en litteraturgennemgang med formålet at vurdere målemetoder, som tidligere havde været brugt til at kvantificere udledningen af metan fra lossepladser, samt at identificere en lovende metode til brug på lossepladser i Danmark. Det blev vurderet, at den bedste metode ville være en mobil sporgas metode, som anvender frigivelse af en sporgas, og mobilt udstyr med høj analytisk følsomhed, til at måle fanerne af metan og sporgas nedvinds fra kilden. Metoden blev valgt, da den kan måle emissionen fra hele lossepladsen inklusiv hotspots, brønde og boringer med store emissioner.

Til opbygning af en ny analytisk platform blev nyt analytisk udstyr indkøbt og testet. Udstyret blev sat op, så det kunne installeres i et hvilket som helst køretøj. Det gav fleksibilitet og gjorde det muligt at måle på kilder med forskellige adgangsforhold. For at validere metoden blev der udført en test med en kontrolleret frigivelse af metan. Testen viste at selv i områder med stor turbulens så som byområder, var den målte udslip indenfor et par procent af den kontrollerede metanfrigivelse. Metodens følsomhed overfor placeringen af sporgas blev også testet, og viste en mulig over-/underestimering ved fejlplacering af sporgassen, samt at denne fejlestimering blev mindre ved anvendelse af en større måleafstand til udledningsområdet. På baggrund af tesforsøgene blev der udviklet en protokol for hvorledes en emissionsmåling bedst udføres.

Den udviklede mobile platform og sporgasmetode er blevet anvendt til at kvantificere metanudledningen fra mere end 15 danske lossepladser af forskellige størrelse, alder, gasindvinding og gasreduceringsforhold. Resultatet viste, at alle de målte lossepladser havde kvantificerbare metanudledninger. Hver enkelt losseplads blev målt mellem en og fire gange, og udledningen varierede mellem 2,6 og 60,8 kg metan per time. De laveste emissioner blev målt fra de ældste og mindste lossepladser mens de højeste emissioner blev målt fra de større lossepladser, både med og uden aktiv metanindvinding og udnyttelse. En sammenligning med indrapportering af drivhusgasser på både nationalt og europæisk niveau viste en stor afvigelse, med rapporteringer på plus en faktor 100 til minus en faktor 10 på de målte udledninger. Den gennemsnitlige indrapportering var tre gange højere end det målte udslip, inklusiv to lossepladser uden rapportering. Lossepladserne, som indvandt og ud-

nyttede metan, viste en indvindelsesgrad på mellem 41 og 81%. Dette er dog uden at medregne en eventuel oxidering af metan i de øvre jordlag, hvilket vil medføre en lavere indvindelsesgrad.

I samarbejde med det amerikanske firma Piccaro, blev den analytiske platform udvidet med et ekstra instrument. Det nye instrument kunne måle lattergas og ammoniak, hvor sidstnævnte er en kilde til eutroficerende. Udviklingen blev gjort ved et forskningsophold hos Piccaro i USA, hvor der blev foretaget optimering og testning af instrumentet i felten samt af behandlingen af selve spektroskopien i instrumentet, efterfulgt af en række feltmålinger i Danmark. Metoden til kvantificering af lattergas blev indkørt ved intensive målinger på et spildevandscenter. Resultaterne fra spildevandsrensingsanlægget viste stor tidslig variation i udledningen af lattergas, som primært skete fra beluftningstankene. Udslippet varierede fra under detektionsgrænsen og op til 10,3 kg lattergas per time. Der blev også målt metan fra spildevandsbehandlingen, og det viste sig at hoveddelen (>99%) kom fra behandlingen af slam, anaerob udrådning af slam samt udendørs opbevaring af udrådet slam. Metanudledningen varierede mellem 10 og 92 kg per time og store ændringer i udledningen blev observeret inden for få timer. De høje metanudledninger korrelerede med perioder med fald i metanudnyttelsen til strøm. Det indikerede, at emissionen kom fra rådnetankene eller fra brug og/eller opbevaring af metanen. Yderligere undersøgelser indikerede, at metanemissionen kom fra udluftningsventiler placeret ca. 30 meter over jordoverfladen på anaerobtankene. Ventilerne bruges til at udlufte metan f.eks. når der er skumdannelse i beholderne.

Det primære produkt af denne PhD er udviklingen af en mobil analytisk platform som kan implementeres i ethvert transportmiddel der kan bære ca. 100 kg, inklusiv batterier, inverter, vejrstation, GPS, pumper, analyseinstrumenter samt skærme. Den mobile analytiske platform kan måle den aktuelle atmosfæriske koncentration af metan, lattergas og ammoniak og gøre dette ned til koncentrationsændringer i milliardtedele (ppb). Udstyret har en høj målefrekvens (2 Hz). Samlet giver dette mulighed for at bruge en dynamisk sporgasmetode til at kvantificere emissioner fra forskellige diffuse kilder, som ellers ville være svære at kvantificere. I dette PhD studie blev det dokumenteret at den analytiske platform kunne bruges til at kvantificere metanudledning fra lossepladser samt udslip af metan og lattergas fra spildevandsrensning. Flexibiliteten af den analytiske platform giver mulighed for at anvende udstyret til en lang række målinger, både til kvantificering af udledning af drivhusgasser fra diffuse kilder samt til monitorering af atmosfæriske koncentrationer.

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1 Introduction

1.1 Introduction to greenhouse gasses

The average temperature of the Earth has been increasing the last many decades (IPCC, 2013). There is a strong consensus among atmospheric scientists that this change is mainly due to human activities and especially due to the increase in anthropogenic emission of gasses absorbing the outgoing radiation from the Earth, enhancing the so-called greenhouse effect (IPCC, 2013). The greenhouse gasses (GHGs) of main concern are carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). These gasses are emitted from various anthropogenic activities and international initiatives and protocols have been initiated to reduce the global emission. CH₄ and N₂O are more powerful greenhouse gases (per mass) than CO₂ due to their higher ability to absorb infrared radiation. The timescale of the global warming potential (GWP) of the GHGs is often set to 100 years at which CH₄ and N₂O are respectively 25 and 310 times as effective as CO₂ (IPCC, 2007). The recent assessment report from the intergovernmental panel on climate change (IPCC) suggests new GWPs for CH₄ and N₂O of 28 and 265, or 34 and 298 if the change in carbon storage due to climate change is included (IPCC, 2013). The knowledge of the carbon storage effect is still limited and thus uncertain and these latest numbers are yet to be implemented in estimating GHG emissions. The global atmospheric concentration of all the three main emitted GHGs have been increasing since industrialization started, and although the increase in CH₄ concentration has flatten the last decade (IPCC, 2013), the size of the total GHG concentration increase is still alarming regarding the greenhouse effect. Anthropogenic CH₄ and N₂O emissions come from many different sources such as agriculture, oil and gas drilling and transport and waste management and reductions can be obtained by implementation of reduction technologies at the individual emission sources.

1.2 Greenhouse gas emission and reporting

The European Union (EU) and its member countries have committed themselves to reduce their GHG emissions. In order to evaluate if the commitments are being met, GHG emissions from all known, significant, anthropogenic sources are being collected and summarized in annual inventory reports. To estimate the total national GHG emission, the Intergovernmental Panel on Climate Change (IPCC) has published a guideline on how to obtain the GHG inventories on a national level (IPCC, 2006). The IPCC guideline gives ad-

vices on how to estimate GHG emissions from seven sectors including energy, agriculture, industry, and waste. On a global scale, the waste sector contributes with approximate 3% of the total GHG emission, of which 90% is due to CH₄ emissions from landfills and wastewater treatment plants, equal to approximately 18% of the global anthropogenic CH₄ emission (Bogner et al., 2008). In Denmark, CH₄ from landfills and wastewater treatment accounts for 70% and 7%, respectively, of the total GHG emission from the waste sector (Nielsen et al., 2013). Reducing emissions of CH₄ and N₂O has become an important tool for reaching the GHG emission reduction targets, and although the waste sector only accounts for a minor part of the total GHG emission mitigation initiatives will still improve the GHG accounting. In addition, GHG reduction cost for the waste sector is relatively low in comparison with the reduction costs for other sectors (IPCC, 2007). When a landfill receives more than 10 Mg waste per day or have a disposal capacity of more than 25.000 Mg, CH₄ emissions should be registered (CEC, 2006), and if the emission is above 100 Mg CH₄ per year, then it must be reported to the European Pollutant Release and Transfer Register (CEC, 2006). GHG emissions reported in national inventory reports are obtained using best available knowledge of the individual processes leading to the emission, but high uncertainty is associated with the reported emission numbers. The emission from Danish landfills and wastewater treatment plants are mainly estimated using models and regional or site specific emission factors. These models and emission factors are based on older research often done under conditions very different from Danish conditions, and thus a significant difference could be expected. Recent studies conclude that the total US CH₄ emission is between 1.25 to 1.75 times the GHG estimates reported in the national inventory by the US EPA (Brandt et al., 2014).

1.3 Aim of the study

The overall aim of this PhD study was to identify, develop, document and apply an optimal method for quantifying fugitive GHG emissions from waste treatment facilities such as landfills and wastewater treatment plants. The primary objective was to identify a potential measurement method, build the associated analytical platform and document and verify the method. The secondary objective was to apply the method to quantify emissions from Danish landfills and from wastewater treatment plants.

A review of methods for quantifying CH₄ from landfills is presented in Mønster et al. (III) identifying the dynamic tracer dispersion method as a suitable

method for the applications in this PhD study. After construction of the analytical platform, the application, sensitivity and uncertainty of the method was explored in Mønster et al. (I). The total CH₄ emissions from a number of Danish landfills were quantified in Mønster et al. (II) as well as the emission from individual landfill areas (Mønster et al., I; Scheutz et al. IV). The method was applied to wastewater treatment plants for quantifying the CH₄ and N₂O emissions (Yoshida et al. V) and a comparison study for CH₄ emission quantification were performed together with a other research groups at a wastewater treatment plant in Valence, France (Yver-Kwok et al. VI).

2 GHG generation and emissions from landfills and wastewater treatment plants

The global generation of solid waste and wastewater is increasing (IPCC, 2007), setting high demands on the waste management sector to mitigate the sectors negative influence on the global environment. Landfilled solid waste and treatment of wastewater result in significant GHG production and emission to the atmosphere. This chapter gives a short introduction to the processes causing emission of GHGs emission during waste and wastewater treatment.

2.1 Landfills

Solid waste containing organic materials will, when disposed in landfills, undergo anaerobic microbial degradation resulting in generation of landfill gas consisting mainly of CH_4 (55-60%) and CO_2 (40-45%). The generation will continue for decades after the waste is deposited, until the majority of the organic material has been degraded (Scheutz et al., 2009). The amount of gas generated in a landfill depends on the amount of waste in the landfill, the waste composition (such as organic content, moisture content, nutrient content, presence of inhibitory compounds), the age of the waste, and the landfill conditions (temperature, moisture, waste compaction, landfill cover design, etc.) (Scheutz et al., 2009). The generated landfill gas builds up a pressure inside the landfill. This pressure, together with diffusion and advection, makes the generated gas escape from the landfill. The emission of CH_4 from a landfill occurs through many different escape routes (see Fig.1) and measuring the individual or total emission rate from these routes is a challenging task, which will be further discussed in chapter 3. The generated gas can be recovered by engineered recovery systems and the collected gas can be utilized for heat and electricity production and thereby prevent it from entering the atmosphere. The landfill gas has a biogenic origin and the CO_2 is therefore considered GHG neutral, while the CH_4 contributes to the GHG accounting. To lower the CH_4 emission from landfills, recovery and utilization plants have been made mandatory at many new landfills. The recovery and utilization in combination with a decrease in landfilling of organic waste has lowered the CH_4 emission from landfills in the EU (Bogner et al., 2008). Additionally, research has increased on developing CH_4 mitigation technologies at existing landfills without gas extraction (e.g. Barlaz et al. 2004, Stern et al. 2007, Scheutz et al., 2011, Scheutz et al., IV). For evaluating the efficiency

of mitigation initiatives such as gas collection or methane oxidation in biocovers, reliable measurements for methane emissions quantification are needed.

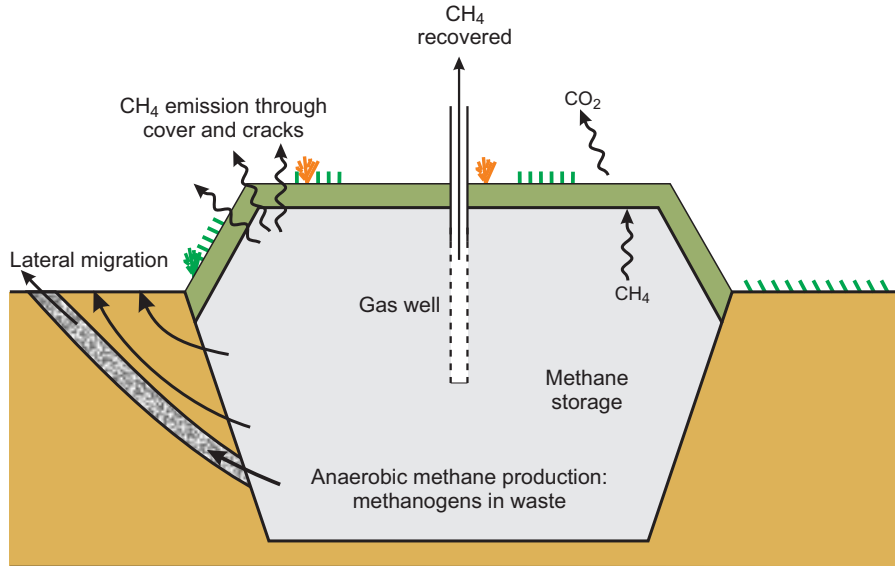


Figure 1. CH₄ production, transport and emission from a landfill.

On a global basis, landfills have been estimated to emit between 5 and 10% of an estimated annual global emission of 600 Tg CH₄ (Bogner et al. 2008). Landfill CH₄ production is expected to increase significantly in the future due to global population growth, economic growth and implementation of better waste management practices using controlled landfilling especially in developing countries (Bogner et al., 2008). The US EPA have estimated that the total landfill CH₄ emission in 2005 was 37.8 Tg, making up 12% of the total anthropogenic CH₄ emission that year or 7% of the total non-CO₂ GHG emission (US-EPA, 2013). In Europe, the annual CH₄ emission from managed landfills in the EU15 countries were reported to 5.7 Tg in 1990 (EEA, 2013). These CH₄ emissions are estimates based on CH₄ production rates applied to national statistics for landfilled solid waste, and a substantial uncertainty is expected. Due to these emissions, the European Union implemented a directive on landfill of waste, setting targets for phasing out landfill of organic materials and other combustible waste (EC, 1999). The European implementation of the directive has contributed to an emission reduction of 47% between 1990 and 2011 from the EU15 countries and recent national GHG reporting from these countries shows an annual CH₄ emission from landfills of 3.0 Tg, making up 75% of the total GHG emission from the waste sector (EEA, 2013). In 1997 Denmark as the first country in the European Union

implemented a ban on landfilling of organic waste. The reported emission from Danish landfills has decreased 53% between 1990 and 2011. The estimated annual emission is 33.3 Gg CH₄, corresponding to approximately 1% of the total landfill gas emission from the EU15 countries (EEA, 2013; Nielsen et al., 2013). There are 134 registered landfills in Denmark and the Danish emission estimates are based on landfill gas generation model calculations using waste information as input. Only 52 of the landfills are included in the national reporting, whereof 16 have gas recovery installed, which is subtracted in the CH₄ emission estimate (Nielsen et al., 2013).

2.2 Wastewater treatment plants

Treatment of wastewater leads to formation of both CH₄ and N₂O. CH₄ is generated through the anaerobic degradation of organics, whereas N₂O is formed during biological removal of nitrogen through enhanced nitrification and denitrification (e.g. Kampschreur et al., 2009, Law et al., 2012). The GHGs are emitted to the atmosphere during different steps of wastewater and sewage sludge treatment. The amount of both CH₄ and N₂O emitted highly depends on the individual operation processes in the treatment facility. Figure 2 illustrates typical operation processes during wastewater treatment and identifies the processes where emission of CH₄ and N₂O can occur.

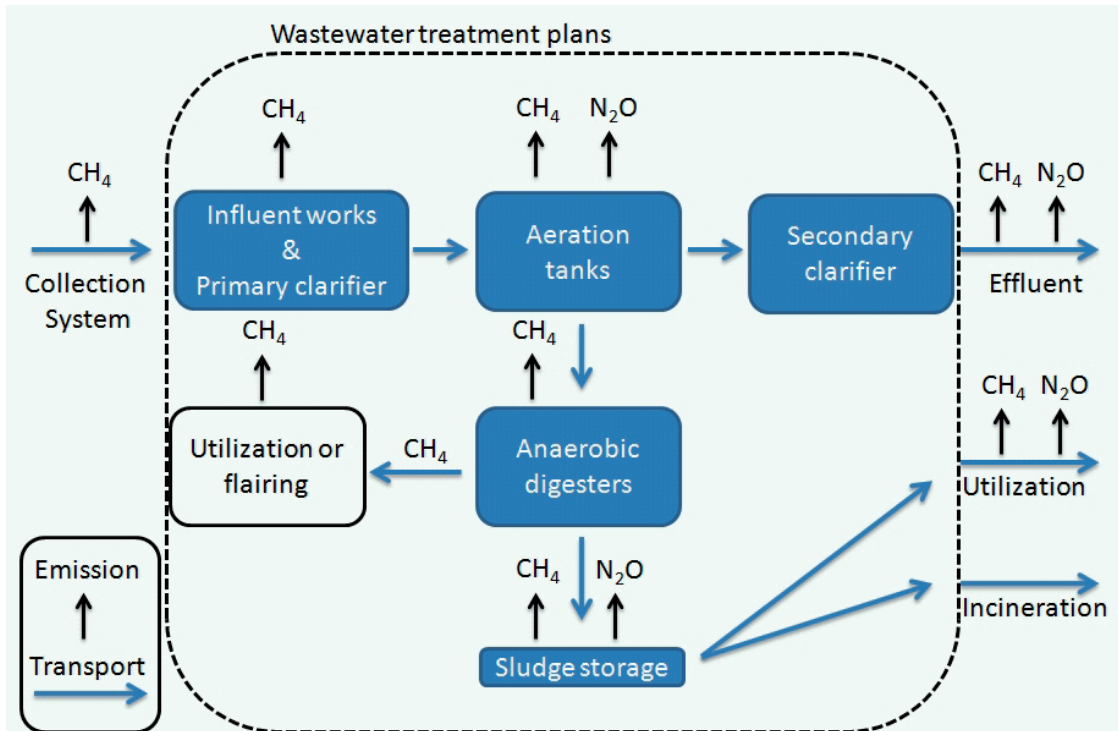


Figure 2 Schematic overview of the typical unit processes during wastewater treatment and the possible CH₄ and N₂O emission pathways.

It should be noted that CO₂ emissions also occurs from the treatment but are considered biogenic and therefore GHG neutral, although recent research have discussed this issue after finding that wastewater contains fossil carbon (Law et al., 2013; Yoshida et al., 2014). Better understanding of the microbial processes and process controlling factors leading to N₂O emissions focusing on optimizing nitrogen removal without increasing the N₂O emission is an ongoing research area. Therefore, quantifying full scale N₂O emission is essential for identifying the size of the emission at open wastewater treatment plants and to document if changes in the process will increase or decrease the total emission of N₂O. Stabilization of sewage sludge via anaerobic digestion and utilization of the produced CH₄ can minimize the carbon footprint of the wastewater treatment plant. However fugitive emissions from the digestion process, the utilization unit (e.g. gas engine generating heat and/or electricity, gas upgrading system (for producing gas with a sufficient quality (high CH₄ content) for use as vehicle fuel), and sludge storage could alter the positive effect of CH₄ production and utilization (Yoshida et al., V). Additionally, current GHG reporting at plant or national scale is based on emission factors established many years ago (e.g. Czepiel et al., 1995), which might not correspond to more recent wastewater treatment systems.

Wastewater in industrialized countries is often treated at large centralized treatment plants. Globally, wastewater treatment is estimated to emit approximately 264 Gg N₂O annually, which is 2.4% of the total anthropogenic N₂O emission, and 22.7 Tg CH₄, which is 7% of the total anthropogenic CH₄ emission (US EPA, 2012). In total, wastewater treatment accounts for 5.2% of the global non-CO₂ GHG emission and the emission is expected to increase relatively by 28% between 2005 and 2030 (US EPA, 2012). The rise in global emission is mainly due to population increase in developing countries and implementation of centralized wastewater treatment (US EPA, 2012), while in Europe, the emission projection has the opposite trend and emissions are expected to decrease (EEA, 2013). The GHG emission in 2011 from wastewater treatment in the EU15 countries was estimated to 33.7 Gg N₂O and 431 Gg CH₄. In Denmark, around 90% of all households and 80% of all industries are connected to municipal wastewater treatment plants allowing advanced treatment of approximately 86% of the all wastewater at 1558 treatment plants (EEA, 2005). The Danish emission in 2011 was estimated to 0.26 Gg N₂O and 3.2 Gg CH₄ or 0.8% and 1.5% of the respective emissions from the EU15 countries (EEA, 2013).

3 Quantification of fugitive CH₄ emissions from landfills

The annual amount of emitted CH₄ from individual landfills is often needed for green accounting and national GHG reporting. However as the emission is influenced by a number of factors, obtaining realistic emission estimates is a challenging task. Often the emission is estimated by theoretical gas generation models using standard conditions of waste composition and surface CH₄ oxidation (e.g. El-Fadel et al., 1997). Many models have been developed, but are yet to be validated, making it highly uncertain whether they describe the actual CH₄ emission from the landfill (Scharff and Jacobs, 2006). The amount and composition of waste are important input parameters in these models but such data are often of poor quality or even unknown at many older landfills. No model is applicable at all landfills due to the large variation in landfill design (construction, finish and aftercare) and composition of the deposited waste. As a consequence, some countries have developed their own model, to estimate the CH₄ emissions from the landfills in their country or region. As an alternative to the landfill gas models, the landfill CH₄ emission can be quantified using different measurement methods. Measurements have the advantage of being independent of the waste amount and composition and can also be used to evaluate the efficiency of a mitigation initiative, such as a gas recovery system and CH₄ oxidation installation. Furthermore, such emission quantifications can give more accurate emission numbers and help to evaluate the performance of the models currently applied.

3.1 Methods for CH₄ quantifying

A number of measurement techniques are currently available, but none of them has been recognized as an international reference method to measure annual landfill CH₄ emissions. Also, few are commercially available and only in a handful of countries. New methods have been developed in the last few decades and a few of these have been compared to previous methods (e.g. Tregoures et al., 1999; Babilotte, 2011) and in one case to the CH₄ generation models used in different countries (Scharff and Jacobs, 2006). The main challenge in measuring CH₄ emissions from landfills is the temporal and spatial variability of the emissions. Emission rates can vary up to seven order of magnitude within a few meters due to cracks or holes in the soil cover leading to emission hotspots (Bogner et al., 1997). Temporal variability of the CH₄ emission is often caused by changes in atmospheric conditions, and it

has been reported how both pressure change and the absolute pressure can lead to a change in the CH₄ emission from landfills (e.g. Christophersen et al., 2001, Czepiel et al., 2003; Fredenslund et al., 2010). This temporal and spatial emission variation combined with the large size and challenging topography of a landfill makes CH₄ emission quantification a difficult task. The following section provides an overview of the different available methodologies for measuring the flux of CH₄ from landfills. Figure 3 show the most commonly used methods to identify and quantify CH₄ emission from landfills. Advantages and disadvantages of the individual methods are discussed and an overall comparison is presented and evaluated. Further details on the individual methods can be found in Mønster et al., (III).

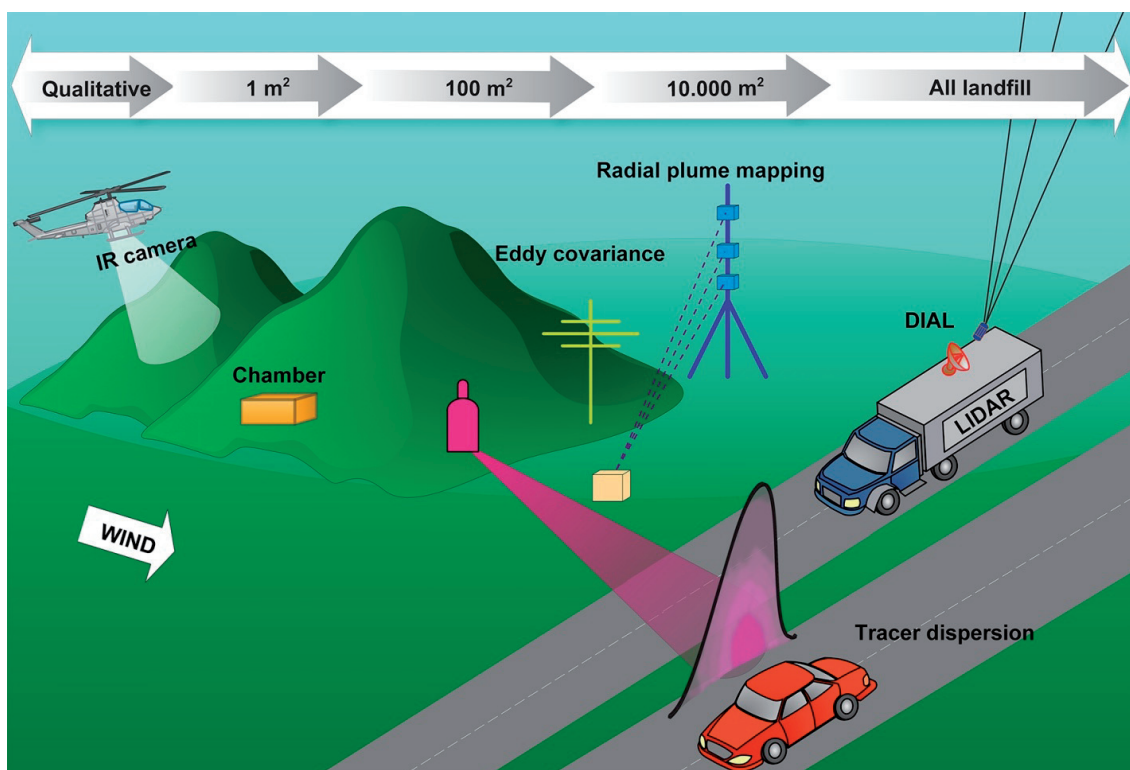


Figure 3 Overview of the most commonly used methods to identify and quantify CH₄ emission from landfills.

3.1.1 Closed surface chamber methods

The closed chamber method is based on direct measurements of gas escaping from the surface of a landfill cover. The gas is captured inside a chamber and the CH₄ flux through the surface enclosed by the chamber is calculated based on chamber CH₄ concentrations measured over a time interval. The setup is adapted from soil emission measurements where emissions occur much more homogeneously across the surface. The closed chamber method has two basic

setups; a static and a dynamic. In the static setup, the increase of gas concentration inside the chamber is measured with time and the flux from the covered area can be calculated (e.g. Reinhart et al., 1992). The dynamic setup resembles the static but have a continuous gas flow through the chamber. The constant flow through the chamber prevents CH₄ build-up, which could influence the emission. The CH₄ flux is calculated from the continuous gas flow through the chamber and the inlet and outlet concentrations (Tregoures et al., 1999). The closed chamber methods are simple, fairly straightforward and relatively cheap in terms of instrumentation, and have thus been widely used for measuring CH₄ emission from landfills e.g. (Bogner and Scott, 1995; Kjeldsen & Fischer, 1995; Czepiel et al., 1996, Scheutz et al., 2008). The UK EPA have implemented the closed chamber method for use in the UK and developed a guideline on how to measure the whole landfill emission rate by creating a network of chamber measurements and integrating the individual flux measurements (Environment Agency, 2010).

The main advantage of the method is the simplicity and its low cost. However, the large number of measurements needed makes it a labour intensive and time consuming method, and as the emission can change in relatively short time due to changes in atmospheric conditions, the emission rates quantified in the beginning of the measurement campaign can differ significantly from emissions from the end of the measurement campaign. The chamber method can be used to improve the mechanistic understanding of the factors controlling the emission from landfills. Several studies have used surface flux chambers to observe the influence of change in CH₄ emission as a result of atmospheric pressure change (e.g. Kjeldsen & Fischer, 1995; Christophersen & Kjeldsen, 2001; Czepiel et al., 2003; Gebert & Gröngröft, 2006; Fredenslund et al., 2010), and to investigate CH₄ emission and oxidation in biocovers (Gebert & Gröngröft, 2006; Abichou et al., 2006; Scheutz et al., 2011a). Besides the temporal emission variation, also the spatial variation is difficult to capture using the chamber method. Even when many systematic or random chamber measurements are made, the covered area represents less than a percent of the total landfill area and the chances are high for missing significant hotspots of emission. Additionally, known emission areas such as steep slopes and leachate wells are difficult to impossible to measure using surface chambers.

3.1.2 Micrometeorological methods

Micrometeorological methods to quantify fugitive emissions rely on local meteorological conditions. The main approaches used for landfills are the mass-balance method and eddy covariance. Both approaches use a small tower where CH₄ measurements are taken place at a known height (typically 1-15 m) above the landfill surface. In the mass-balance method, the CH₄ concentrations are measured at different heights above the landfill surface and by using simultaneously measured vertical wind velocities at the different heights, the total horizontal flux of CH₄ can be calculate. The eddy covariance approach is using an anemometer for measuring three dimensional wind direction and speed and fast CH₄ measurements (10 to 20 Hz). These measurements are done at one height only and results in the horizontal flux of CH₄. Both approaches use inverse dispersion modeling for determining the surface area contributing to the measured emission. The mass-balance approach has been used in the Netherlands (Oonk and Boom, 1995) and was, in a comparison study with an inverse modeling method using tracer emission for gas calibration, found to give similar emission results (Scharff et al., 2003). Eddy covariance is a frequently used method for quantifying fluxes from/to soil, water, snow and forest (e.g. Garratt, 1984; Flechard & Fowler, 1998), and has been applied at landfills in several studies (Tregoures et al., 1999; Laurila et al., 2005; Lohilla et al., 2007; McDermitt et al., 2013). Tregoures et al. (1999) found in a method comparison study that both mass-balance and eddy covariance gave much lower emission rates than chamber and tracer gas methods, while Lohilla et al. (2007) found good agreement between chamber and eddy covariance. The main advantage of the micrometeorological methods is that they can be setup for continuous measurements over weeks or months obtaining a spatially averaged measurement and capture temporal emission variations. Another advantage is that, which the right analytical equipment, the methods can be used to measure fluxes of other gasses such as CO₂ and thereby be used to obtain additional information of the emission from the landfill and potentially oxidation in the landfill cover. The disadvantages are related to determine the surface area from where the measured emission comes from. This area is found by inverse modeling, which can be a challenging task at areas with highly changing topography such as landfills. The surface area included depends on the height of the tower. Under average meteorological conditions, a tower will cover an upwind distance of approximately 100 times the height (McDermitt et al., 2013), while the width of covered area depends on the topography and turbulence. To measure the emission from a whole landfill several measurement cam-

paigns have to be conducted or extrapolation models or assumptions have to be applied. Long time series are needed to make sure the whole landfill is measured, as the measured area is depending on the wind direction. Additionally, a landfill with a complex topography can create local turbulence influencing the measured concentration fluxes (Laurila et al., 2005).

3.1.3 Radial plume mapping methods

Radial plume mapping (RPM) uses a combination of concentration measurements and wind profiles to obtain a surface emission factor from an upwind area. For landfills, this is done by measuring the mass of CH₄ crossing a vertical plane located immediately downwind from the landfill area using multiple laser beam paths reflected by mirrors at the other side of the landfill, so the laser beams cross the downwind plume of CH₄. RPM gives information about the two-dimensional distribution of the CH₄ concentrations (Hashmonay and Yost, 1999, Wu et al., 1999, Hashmonay et al., 2001, Hashmonay et al., 2008). The measured concentrations are then combined with local wind direction and speed to obtain the CH₄ flux across the vertical measurement plane. The CH₄ flux data are eventually used to estimate the CH₄ emission rates from the whole landfill or the part of the landfill upwind from the vertical plane, by assigning the flux to the emission area using a multiple linear regression model. The parameters for this model are based on field measurements using tracer gas release (Thoma et al. 2010). The laser/reflector can also be set up on the landfill measuring the emission from individual parts of the landfill, as well as upwind from the landfill to measure the background concentration of CH₄. The US-EPA has proposed the method for quantifying the CH₄ emission from landfills and has given the method the name Other Test Method-10 (OTM-10) and it has been tested and used for quantification of 20 landfills around USA (Abichou et al., 2010, Goldsmith et al., 2012). The advantages of RPM are that the emission can be measured without access to the landfill and that it can be done in a few days. In general, the output from RPM can be used to identify emission hotspots, which makes this method convenient for performing site surveys before initiating remediation activities on a landfill. One disadvantage is that the area contributing to the flux measured needs to be determined either by using a model including measured and assumed factors, which add uncertainty to the method. Another disadvantage is that the RPM laser/reflector has a range of approximately 200 m and can therefore not cover the whole transect of a normal sized landfill, forcing multiple measurement points or an extrapolation of the emission rate assuming similar emission from the rest of the landfill. Although the RPM

system can be moved around the landfill, it is a time consuming process. Atmospheric conditions play an important role in the estimation of the whole site emission. Abichou et al. (2010) found that a change in wind direction could introduce an uncertainty of 20% and that the area contributing to the measured flux is a function of the atmospheric stability class and has an uncertainty of 10-30%. Hashmonay et al., (2001) found that the gas mass flux was significantly (up to 34%) underestimated under unstable atmospheric conditions and 10-15% under stable conditions. Goldsmith et al. (2012) found that only 31% of they collected data fulfilled the quality requirements. The method is further challenged by the complex topography of a landfill and there are landfill areas where the method is not applicable. Finally, measurement for hours or up to a few days is also the relative short measurement time, not able to capture temporal emission variations.

3.1.4 Tracer dispersion methods

Tracer dispersion methods use simultaneous measurements of atmospheric concentrations of CH₄ and a tracer gas. The tracer gas is released at the emission source at a known rate and it is assumed that CH₄ and tracer gas have the same fate (dispersion, chemical/photochemical reaction) in the atmosphere within the time span of the measurement. For this reason, tracer gasses with relatively long atmospheric lifetimes have to be used. The measurements are done downwind from the source/release and the concentration ratio can be used to calculate the CH₄ emission from the source. The tracer dispersion method is generally divided into a stationary and dynamic approach. The stationary approach relies on measurements in a single or in multiple points stationary in the downwind plume. This approach have had many applications and was first applied on landfills by Czepiel et al. (1996) using a mobile instrument to locate the downwind plume followed by placement of evacuated canisters across the plume transect for air sampling. Similar setup has been used in other studies (e.g. Tregoures et al. 1999, Jacobs et al., 2007). Galle et al. (2001) developed a similar method based on measurements in a single point and letting the change in wind direction ensure capture of CH₄ from the whole landfill. The method was then further developed into a dynamic plume method, based on performing transects of the downwind plume and thereby measure the CH₄ and trace gas concentration near ground level across the whole plume with subsequent integration of the plumes. For applying the dynamic approach, a sensitive and relatively fast analytical instrumentation is needed. A Swedish group developed a Fourier transform infrared spectroscopy (FTIR) instrument stable enough to be driven around in a van, enabling

many successful studies of CH₄ emissions from landfills (e.g. Samuelsson et al., 2005; Börjesson et al., 2009; Scheutz et al., 2011a). A newly developed instrument for dynamic tracer dispersion is based on cavity ring-down spectroscopy (CRDS) and measuring CH₄ and acetylene (tracer gas). This CRDS instrument is smaller, lighter, more stable and easier to mount in a car than an FTIR. This CRDS has recently been successfully used for dynamic plume measurements at two Californian landfills (Green et al., 2010) and in a stationary plume approach using gas sampling of the plume lifted above the ground by a weather balloon enabling to measure the horizontal downwind plume (Zhou et al., 2012). The application and limitations of the CRDS instrument has recently been explored and compared with FTIR instrument (Mønster et al. (I)), and used for quantifying the CH₄ emission at a large number of Danish landfills (Mønster et al. (II)). The dynamic tracer approach was further developed into using special tracer gas placement or multiple tracer gasses for quantifying CH₄ emissions from different sources close to each other (Scheutz et al., 2011b, Mønster et al., I, Scheutz et al., IV). A disadvantage for the static approach is that it is sensitive to change in wind direction, when air is being sampled without online measurements. A disadvantage of the dynamic approach is its dependence on the right weather conditions combined with good road access, which makes it difficult to measure at some landfills with limited access and few surrounding roads. Additionally, the method alone cannot identify local on-site emission sources and care has to be taken of the presence of other CH₄ sources, which can cause an error in the whole landfill site quantification. The instrumentation is expensive and requires expertise for operation. An additional disadvantage is that measurements are usually done in hours or during a few days and thus the temporal variation of landfill gas emission can be a challenge to capture. One advantage of the tracer dispersion method is the simplicity of its approach. When the CH₄ and tracer gas plumes are fully mixed, the analysis and calculation are relatively straightforward. The dynamic approach enable measurement of the whole downwind plume and a change in wind direction will be noticed immediately and can be adjusted for. Additionally, emissions from hotspots, onsite installations or weak landfill structures such as steep slopes, can all be measured using the dynamic approach. The method can also be used for improving input data for inverse modeling (e.g. Piccot et al., 1996, Scharff et al., 2003), or as a small-scale tracer dispersion method (Fredenslund et al., 2010).

3.1.5 Inverse modelling methods

Inverse modeling is based on combining downwind concentration measurements with meteorological data. By knowing the concentration downwind from a source, the location of the source, and the meteorological factors controlling the atmospheric dispersion, the emission rate from the source can be calculated. Inverse modeling can be divided into two approaches using stationary or dynamic measurements. In the stationary approach, measurements are done in one or multiple measurement points at the landfill or downwind from the landfill. Measurements are done by continuous concentration measurements or by sampling for a fixed amount of time with subsequent analysis in the laboratory. Applying concentration measurements to an appropriate model, considering the landfill as a single point source or as a network of multiple sources, together with information on atmospheric conditions can provide an estimate of the emission rate from the landfill. Different approaches have been applied; by using long term measurements at one or multiple fixed points or by using multiple, continuous measurements (e.g. Figueroa et al., 2009, Abichou et al., 2012). Different models have been developed based on Gaussian dispersion of gasses. An example is the steady-state plume model AERMOD, developed by the US-EPA, which models the atmospheric dispersion in the boundary layer. The model can deal with both ground level and elevated sources, and different types of terrain. AERMOD is not specially targeted towards landfills but have been used in different studies to evaluate the emission of dust (Westbrook et al., 2007) or CH₄ from a Canadian landfill (Wyles et al., 2010). Dynamic inverse modeling relies on concentration measurements across a downwind plume from an emission source. The method is equivalent to the dynamic tracer dispersion method, but done without the release of tracer gas. The measured concentration profiles are used in combination with data on atmospheric conditions (wind speed, stability class, topography) to fit into a standard Gaussian dispersion equation and solved by matrix method to retrieve the emission rate (Figueroa et al., 2009; Mønster et al., I). Measurements are typically done from 500 m to several km depending on the size of landfill and the emission rate. The analytical equipment for these kinds of measurements needs to be able to measure a concentration difference of down to a few ppb with a background concentration of CH₄ normally between 1800 and 2000 ppb. Current available and capable instruments are quantum cascade laser spectroscopy, tunable diode laser spectroscopy (TDL) or CRDS, all having advantages and disadvantages in terms of temporal resolution and number of species measurable. Hensen and Scharff (2001) used inverse Gaussian modeling, measuring the plumes with a

mobile TDL instrument and calibrated the model using controlled emission of N_2O as a tracer gas, making their method similar to a tracer dispersion method, but with subsequent inverse modeling. They measured three landfills in the Netherlands and found emissions of 3.6 to $16 \text{ m}^3 \text{ ha}^{-1} \text{ h}^{-1}$.

The disadvantage of reverse modeling is the amount of high quality input data needed to get a good emission estimate. Excellent atmospheric condition input from the exact area of emission is very important and can be difficult to obtain. Additionally, stationary measurements are dependent on the wind direction and correct placement of air sampling devices is of utmost importance. The disadvantages of dynamic approach are the need for specialized analytical equipment, a detailed emission model of the landfill and access to downwind roads. For optimal conditions, the landfill should be located in a relatively flat area with a road crossing the downwind plume at a suitable distance. Also accurate measured and relatively stable meteorological conditions are needed, such as stable wind direction and speed, minimum change in atmospheric pressure, and stable atmospheric conditions regarding turbulence. The advantage of static inverse modeling is the possibility for long time series overcoming the temporal variation of the emission. The dynamic approach has the advantage of giving the emission plume from the whole landfill site, regardless of the size of the landfill. The measured plume will also include emission from the landfill slopes and leachate collection systems. General for the modeling methods is that a large number of input parameters are needed and the quality of these inputs highly influences the outcome of the model calculations. Needed factors like wind speed and wind direction and atmospheric turbulence are highly variable in time and the proper values are difficult to obtain for accurate model calculation.

3.1.6 The DIAL method

The differential absorption lidar (DIAL) method uses pulsed tuneable laser radiation transmitted into the atmosphere. A part of the radiation is backscattered and can be measured by a detector. DIAL measurements can be used to determine the CH_4 concentration by tuning the laser to the appropriate absorption lines. The laser can be pointed in any direction and for landfill application measurements are done along several lines-of-sight obtaining a vertical concentration distribution downwind from the landfill. This allows a capture of the whole vertical profile of the CH_4 plume and the emission from the landfill can be calculated by combining the vertical concentration profile with the wind speed in different heights (Babilotte et al., 2010, 2011, Robinson et al., 2011). Measurements are done downwind, close to the landfill in

combination with upwind measurements to check for interfering sources and background concentration. Individual landfill areas can also be measured by “shooting” the laser in vertical plan above the actual landfill (Babilotte, 2011). A moveable DIAL system is a large setup mounted in a truck and very few are available worldwide. The DIAL method has mainly been applied for quantification of fugitive emissions from petrochemical processes, while the use at landfills is still fairly limited (Babilotte et al., 2010, 2011, Robinson et al., 2011, Bourn & Browell, 2013). The main disadvantage of the DIAL method is the size of the analytical setup and the complexity of the data handling. The truck transporting the setup requires good roads and measurements are therefore depending on the wind direction and the infrastructure. Also stable and accurate measured wind conditions are needed for precise flux quantification. As other remote sensing measurements, the DIAL is sensitive to possible interfering sources. Measurements are conducted in hours or days and temporal variation can therefore be difficult to capture. The advantages of the DIAL method are that it can measure CH₄ at a distance of 400-800 m, often enabling measurements of the total vertical concentration plane from a landfill eliminating the effect of spatial emission variation. Additionally, the DIAL have the option of measuring other atmospheric species scattering light in infrared or ultraviolet spectra, such as ethane, hydrogen, sulfur oxide, ozone and benzene at a sub parts per million level (Babilotte et al., 2010).

3.1.7 Method comparison

The methods listed above are the methods most frequently used for quantifying CH₄ emissions from landfills. However, other methods have also been suggested such as using the soil gas pressure gradient in combination with the porosity of the soil or using airborne infrared cameras. The latter one cannot quantify the emission, but identify emission areas, which is a useful alternative to full site screening before initiating mitigation initiatives. All the methods reviewed here have advantages and disadvantages, and one method could be superior in one type of research while others could to be preferred for another landfill application. For quantifying the total emission from a landfill, a method is needed that is able to encounter the spatial variation of the emission. Babilotte et al., (2010) conclude from their method comparison study, that methods able to measure the total mass flux (DIAL and dynamic tracer dispersion, and RPM at smaller landfills) are needed for obtaining whole landfill CH₄ quantification, including a confidence interval. Methods measuring the emission from the surface (chamber, micrometeorological and partly RPM) have problems with emission hotspots such as slopes and wells at the

landfill, as they only cover a fraction of the landfill and an extrapolation to the full area is needed. In order to obtain an average or annual emission from a landfill, the temporal variation needs to be addressed. The suggested methods from Babilotte et al., (2010) are usually conducted over relatively short time and thus do not provide much information on the temporal variation of the emission.

After evaluating the methods, it was decided to acquire analytical equipment for building up an analytical platform able to perform the dynamic tracer dispersion method. Given the latest development within the instrumentation, it was evaluated that this was the most flexible method for landfill studies, and could be used for many applications such as CH₄ surveys as well as small and large scale tracer dispersion methods. Additionally, specialized equipment such as the DIAL is rather expensive and requires its own vehicle while the analytical platform for the dynamic tracer dispersion method can be mounted and dismounted in existing vehicles at each measurement campaign.

3.2 Implementation of a tracer dispersion method

The Technical University of Denmark (DTU) had previously used the dynamic tracer dispersion method with success by collaboration with the Swedish company Fluxsense using a mobile FTIR instrument (Andersen et al. 2010, Scheutz et al. 2011a, 2011b). New development within analytical instruments for trace gas concentration measurements opened up for smaller and faster instruments using the cavity ring-down approach (Crosson, 2008), and decision was made to purchase such a CRDS instrument able to measure CH₄ and acetylene concentration changes down to a few parts per billion (ppb). Further details on the specifications of the instrument are given in Mønster et al. (I). The analytical platform was then expanded with two additional CRDS instruments: an instrument measuring CO and CO₂ and one measuring N₂O and NH₃, both able to measure small concentration changes. The latter instrument was a prototype, developed and tested in the field during a collaboration research stay at Picarro Inc., the manufacture of the CRDS instruments, during summer 2012. The prototype was then employed in parallel with the CH₄/acetylene analyzer, enabling quantification of N₂O and NH₃ from fugitive sources. The specifications of this new analytical setup and the application for quantifying N₂O and CH₄ emissions from a wastewater treatment plant is described in Yoshida et al. (V).

The following section gives an introduction to the mobile tracer dispersion method and how the work in this PhD developed and implemented the

method at DTU. The configuration of the analytical platform is described together with the development of measurement routine, data treatment, and reproducibility and uncertainty evaluation.

3.2.1 Introduction to tracer dispersion method

Using the release of tracer gas is far from being a new approach. Previous studies have used the release of SF₆ to evaluate atmospheric dispersion models for highway emissions (Eskridge et al 1979) and industrial sources (Lamb et al., 1978) and ventilation of mines (Timko et al., 1984). The release of SF₆ was later combined with quantification of CH₄ emissions from natural gas facilities and urban areas (Lamb et al., 1995), barns with ruminants (Marik & Levin 1996; Kaharabata et al., 2000) and landfills (Czepiel et al., 1996).

For the application to landfills, the first tracer methods were initially done as static measurements in the downwind plume, either by sampling across the downwind plume (Czepiel et al., 1996, Jacobs et al., 2007)) or use the mobility of the analytical instrument to locate the plume and then perform static, online measurements of the CH₄ and tracer concentrations (Börjesson et al., 2009). Hensen and Scharff (2001) introduced dynamic plume measurements on landfills for the use with a Gaussian plume model, while releasing tracer gas for calibrating the model. The dynamic plume measurements with tracer release (Figure 4) were later used without modelling for quantification of CH₄ emission from whole landfill sites (Scheutz et al., 2011a, Goldsmith et al., 2012), individual landfill cells (Mønster et al., I, Scheutz et al., 2011b, IV) and individual on-site such as composting facilities (Andersen et al, 2010, Mønster et al., II).

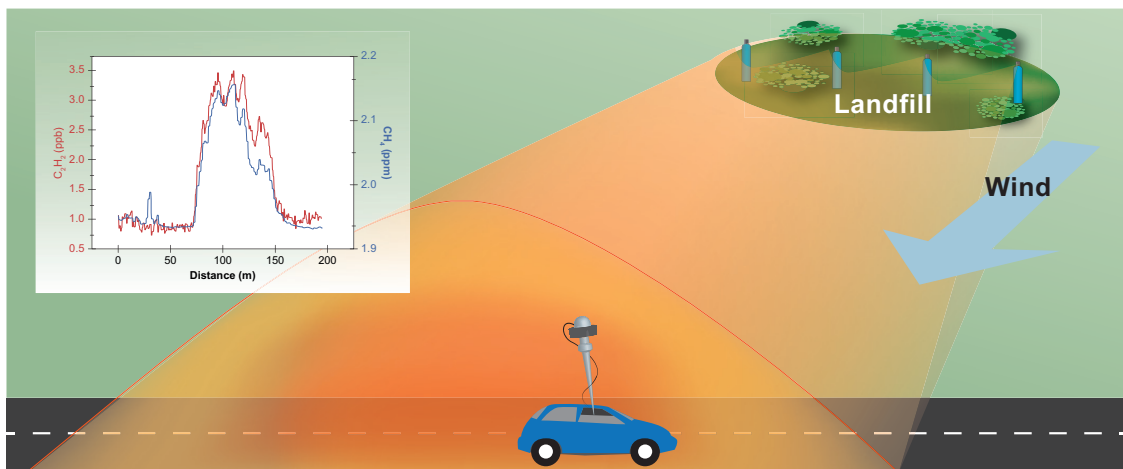


Figure 4 Schematic view of the dynamic dispersion method applied at a landfill.

In general, the tracer dispersion method is based on the assumption that a tracer gas released at an emission source, will disperse during transport in the atmosphere in the same way as the CH₄ emitted from the source. Assuming that the wind direction is defined and conditions in the air above the landfill are well mixed, the CH₄ emission rate can be calculated as a function of the ratio of CH₄ to tracer gas. In the dynamic tracer dispersion method, the ratio of the integrated cross-plume concentration of CH₄ emitted and the integrated cross-plume concentration of the tracer gas is used and the CH₄ emission rate (E_{gas}) can be calculated as follows:

$$E_{gas} = Q_{tracer} \cdot \frac{\int_{Plumeend1}^{Plumeend2} C_{gas} dx}{\int_{Plumeend1}^{Plumeend2} C_{tracer} dx} \cdot \frac{MW_{gas}}{MW_{tracer}} \quad (\text{Eq. 1})$$

where Q_{tracer} is the release rate of the tracer gas (kg h^{-1}), C_{gas} and C_{tracer} denote cross-plume concentrations above the background concentration, MW denotes molecular weight and x corresponds to the distance across the plume.

The choice of tracer gas used for tracer dispersion tests have changed over time. Initial studies used SF₆, which is a strong greenhouse gas with a GWP of 23,500 (IPCC, 2013) and thus is not an environmental friendly gas to release into the atmosphere. N₂O was introduced as a substitute tracer gas in the dynamic tracer dispersion method (Börjesson et al., 2009), and with a GWP of 298 (IPCC, 2013) it is far better than SF₆ but still not well-suited for environmental studies of GHG emissions. Recent tracer dispersion studies at landfills have used C₂H₂ as tracer gas (Green et al., 2010, Goldsmith et al., 2012, Thoma et al., 2012, Mønster et al., I, II). C₂H₂ has no reported direct GWP, and it can therefore be assumed that the only influence the Earth's radiation balance is that the C₂H₂ eventually will be oxidized to CO₂ in the atmosphere, giving C₂H₂ an indirect GWP of approximately three times CO₂. Whether this small effect should be accounted for depends on the origin of the C₂H₂. Using C₂H₂ also enable the quantification of N₂O emission without using SF₆ or CO, the latter one being a toxic gas. C₂H₂ is highly flammable and care should be taken to avoid any open fire near the tracer gas release.

3.2.2 Cavity Ring-Down Spectroscopy

Measuring small concentration changes across a plume downwind from an emission source requires an instrument, which is mobile and stable. Previously used instrumentation for the dynamic tracer dispersion method are Tunable

Diode Laser (TDL) (Hensen and Schaff, 2001) and Fourier Transform Infrared (FTIR) (Galle et al., 2001, Scheutz et al., 2011a). The instrumentation chosen in this study is based on CRDS, an optical technology with direct measurement of infrared absorption loss in a sample cell used to quantify the concentration of the gas. The main features are the small size (flow cells of less than 10 cm³) and a very long optical path length (15-20 km) allowing uncertainty in parts per billion (ppb) and parts per trillion (ppt) levels. Measurement of the targeted gasses are done approximately every second, and the CRDS instrument has a stability allowing accurate measurements and little need for calibration relative to other analytical approaches measuring gasses in these concentration ranges. The analytical approach of this product line has previously been reported (Crosson, 2008), and further description of the two instruments can be found in Mønster et al. (I) and Yoshida et al. (V). The stability of the CRDS analyzer due to its simple approach, compact size and minimum of movable parts makes it an ideal instrument for the dynamic tracer dispersion method. The fixed and narrow spectra lasers give the instrument the disadvantage of only being able to measure a few gasses per instrument. This disadvantage is not an issue for CH₄ quantification using the tracer dispersion method, but it limits the applications of the instrument for other atmospheric studies, where multiple instruments are needed to obtain the concentration of many atmospheric trace species.

3.2.3 Analytical platform

An important part of the method development was to build up the mobile analytical platform for quantification of fugitive GHG emissions. Initially, the focus was set at the CH₄ emissions from landfills and in spring 2011, a C₂H₂/CH₄/H₂O CRDS analyzer from Picarro Inc. was purchased and tested in the lab. The analyzer was made mobile using two marine batteries and connecting these to the car battery extended the operational time of the analyzer. A high precision GPS and a weather station were connected and all data was stored in an incorporated computer enabling the measured concentrations to be plotted on mapping software in real-time visual view during the measurements. An earlier prototype of the analyzer had previously been used for landfill emission studies (Goldsmith et al., 2012; Green et al., 2012; Thoma et al., 2012), while this analyzer's performance, setup and use was described for the first time in Mønster et al., (I). The analytical platform was then expanded during summer 2012 with an N₂O/NH₃/H₂O analyzer. This analyzer was a prototype and was developed in close collaboration between the Technical University of Denmark (DTU) and Picarro Inc. in California, USA, including

a seven weeks research stay at Picarro for laboratory testing and calibration and field testing at actual N₂O and NH₃ sources. Upon return, the analyzer was implemented in the mobile analytical platform, enabling real-life measurements and quantifications of N₂O emissions. The performance of the analyzer is described in Yoshida et al., (V).

3.2.4 Controlled gas release

An accurate, controlled release of tracer gas is crucial in order to minimize the uncertainty in the tracer dispersion method. A flow meter with a rotating, floating ball was chosen for the controlled gas releases, as this type of flow meter have the advantage of not requiring a power source. The flow meters were calibrated by the manufacture under controlled conditions (gas type, temperature, pressure) and their use for CH₄ and acetylene was adjusted knowing the gasses density and viscosity. Flow meters with two different diameters, but the same length was used for the two gasses. Laboratory test was performed measuring mass loss of CH₄ and acetylene gas bottles. The CH₄ or acetylene bottle was placed on a scale with a resolution of 2 g and the change in mass at three different readings on the flow meter was plotted and the slope of this was compared with the calibration from the manufacture. The mass loss plotted against flow meter reading were all linear with $r^2 = 0.98$ or higher and the combined flow rate was within 2% of the manufacture calibration. The calibrations (manufacture and laboratory) were done at standard temperature and pressure ($T = 293$ K and $P = 101.3$ kPa), whereas the controlled releases often were done at different temperatures and pressures. At these different conditions, the actual release rates Q_{actual} (L min⁻¹) were calculated according to:

$$Q_{actual} = Q_{calibrated} \times \sqrt{\frac{T_{calibrated}}{T_{actual}}} \times \sqrt{\frac{P_{actual}}{P_{calibration}}} \quad (\text{Eq. 2})$$

where $Q_{calibrated}$ is the release rate calculated from the manufacture calibration, $T_{calibrated}$ (K) and $P_{calibrated}$ (P) are the temperature and pressure during calibration and T_{actual} (K) and P_{actual} (Pa) are the actual temperature and pressure during the gas release.

At each measurement campaign, acetylene from one or more bottles was released and at a test to verify the tracer dispersion method, release of both CH₄

and the tracer gas acetylene was controlled. For controlled CH₄ release, 50 L bottles with purity of 96% were used with a two-stage regulator connected to a 150 mm flow meter (Sho-rate from Brooks), calibrated for measuring between 0 and 5000 L per minute. At the controlled release test and at all measurement campaigns, 21 L acetylene gas bottles containing 3.92 kg acetylene with a purity >99.5% was used. The acetylene was dissolved in acetone in a ratio 25:1 allowing a stable and safe release, but also limiting the release rate to approximately 1 kg per hour as the acetylene needs time to go from being dissolved in the acetone to be a gas in the headspace of the gas bottle. Acetylene has a much higher vapor pressure than acetone, resulting in <1% acetone in the released gas. The acetylene flow was controlled by a two-stage regulator, with a safety valve for back-flush, connected to a 150 mm flow meter (Sho-rate, Brooks) calibrated for measuring between 0 and 1500 L per minute. The uncertainty of the flow meters was given from the manufacture to be 5% on the maximum value (150 mm), although the laboratory test showed a difference less than 2% on maximum value (150 mm).

3.2.5 Controlled release tests

A controlled release test was performed to validate the tracer dilution method and to determine the accuracy of the quantification. In addition, the measurement campaign was used for assessing the uncertainty of the measurements as a result of a misplacement of the tracer gas bottles. To do this, three tracer gas configurations were used. The first was where CH₄ and tracer gas were placed right next to each other. The second configuration was with CH₄ in the middle and tracer gas bottles “misplaced” to each side compared to the CH₄ and the wind direction. In a third test configuration, the tracer gas bottles were placed upwind from the CH₄ release point. Figure 5 shows the test setup and the corresponding downwind plumes, 370, 775 and 1200 m away during the first tracer gas configuration.

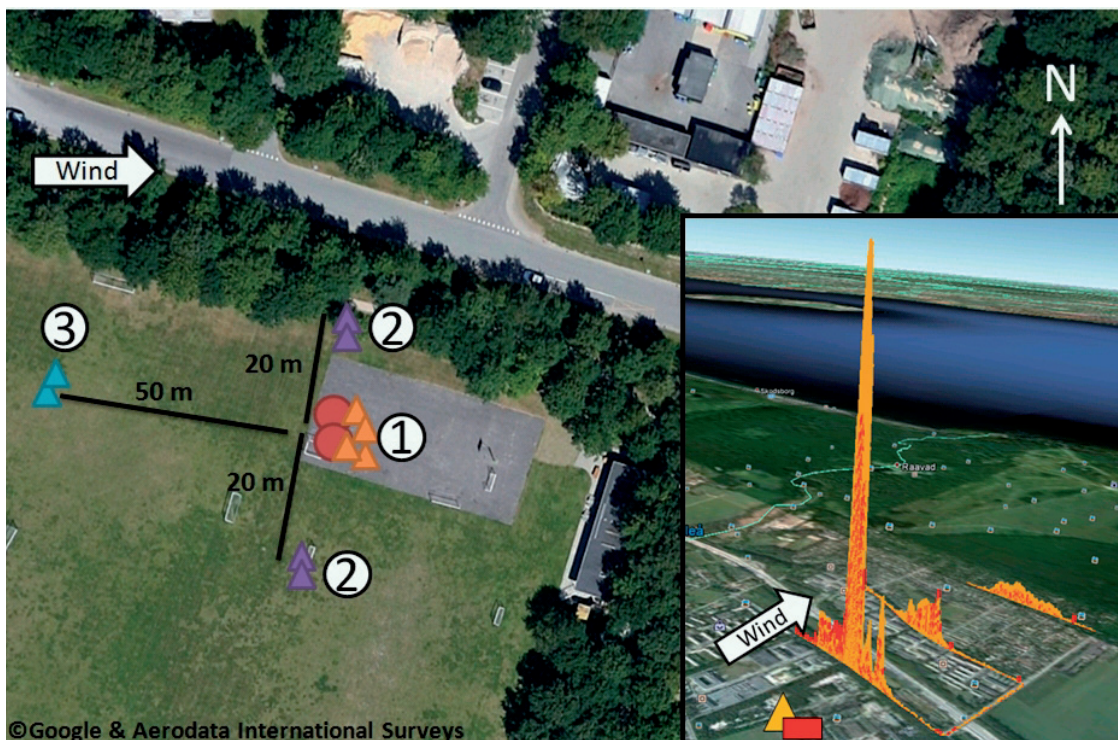


Figure 5 CH₄ (circles) and acetylene (triangles) placement during the controlled release test (main picture) and the downwind plumes of CH₄ (red) and acetylene (yellow) at 370, 775 and 1200 meters distance (inserted picture).

The results from the controlled release test showed that the method was well-suited for quantifying the emission when the CH₄ and tracer gas were released at the same spot, while the emission quantification became more uncertain when the tracer gas bottles were moved away from the CH₄ release point. Moving the tracer gas bottles upwind resulted in a clear overestimation of the emission at a short measurement distance, but the effect became less important with increasing measurement distance (Mønster et al., I).

3.2.6 Development of measurement routine

The dynamic tracer dispersion method is a rather new approach for quantifying fugitive CH₄ emission from landfills and no best-practise guideline had been developed for how a quantification campaign should be performed. In collaboration with the Swedish company Fluxsense, the following protocol was developed: (1) Possible roads for quantification are located on a map. Roads should be approximate 5 times further away than the size of the emission source and no interfering CH₄ sources should be between the landfill and the road. (2) The measurement day is chosen when a matching wind direction is being foreseen by the local weather forecast and the wind speed is between 2 and 10 m s⁻¹ and the atmospheric pressure is stable around the average pres-

sure of the area. (3) Initial screening measurements are done on all accessible roads on and around the landfill to locate emission hotspots for accurate tracer gas placement as well as possible interfering CH₄ sources in the area. If there is limited site access, then screening with handheld CH₄ analyzer, e.g. a Flame Ionization Detector (FID), is used to help locate on-site hotspot areas. The measurements around the landfill includes a background measurement immediately upwind from the landfill area. 4) Tracer gas bottles are placed at the main emission areas (typically 2 to 4 bottles) with a total C₂H₂ release rate of 1-2 kg h⁻¹ (with the accurate release rates known). A release of maximum 0.5 kg h⁻¹ will give a stable release rate for minimum 4 hours when using standard 21 L C₂H₂ bottles. As an extra check, the tracer gas bottles are weighted on a scale before and after the measurement to check with the calculated release rate from the flow meters. (5) The downwind plume of CH₄ and C₂H₂ is located using mobile analyzer and a minimum of 10 traverses of the plume are performed. Great care is taken to pass the whole plume before turning around. (6) After the measurements and the tracer gas releases were stopped, an additional upwind measurement is done to check for changing background concentration. The background concentration should be measured in between series of traverses during long measurement campaigns.

3.2.7 Data treatment

Obtaining whole site emission rates from a tracer dispersion method has previously been done using different approaches. Galle et al. (2001) used the mobility of their instrument to locate the plume and performed then stationary measurements letting the change in wind direction control, which part of the plume that was measured. This method was also used to estimate the CH₄ emission from Swedish landfills (Börjesson et al., 2009). Henson and Scharff (2001) used the fully integrated CH₄ plume, but used the tracer gas plume to calibrate their Gaussian plume model, as they were measuring too close to the landfill for a fully mixed CH₄ and tracer plume. Traversing the “close to” fully mixed CH₄/tracer plume at a far distance was introduced to insure the capture of the whole plume and avoid the uncertainties introduced to Gaussian plume modelling by temporal and spatial change in atmospheric stability (e.g. Samuelsson et al., 2005; Andersen et al., 2009; Scheutz et al., 2011a, 2011b; Goldsmith et al., 2012; Green et al., 2012). The latter approach was taken in this PhD work and a comparison of data treatment using four different approaches to determine the CH₄ to tracer ratio was conducted (Figure 6).

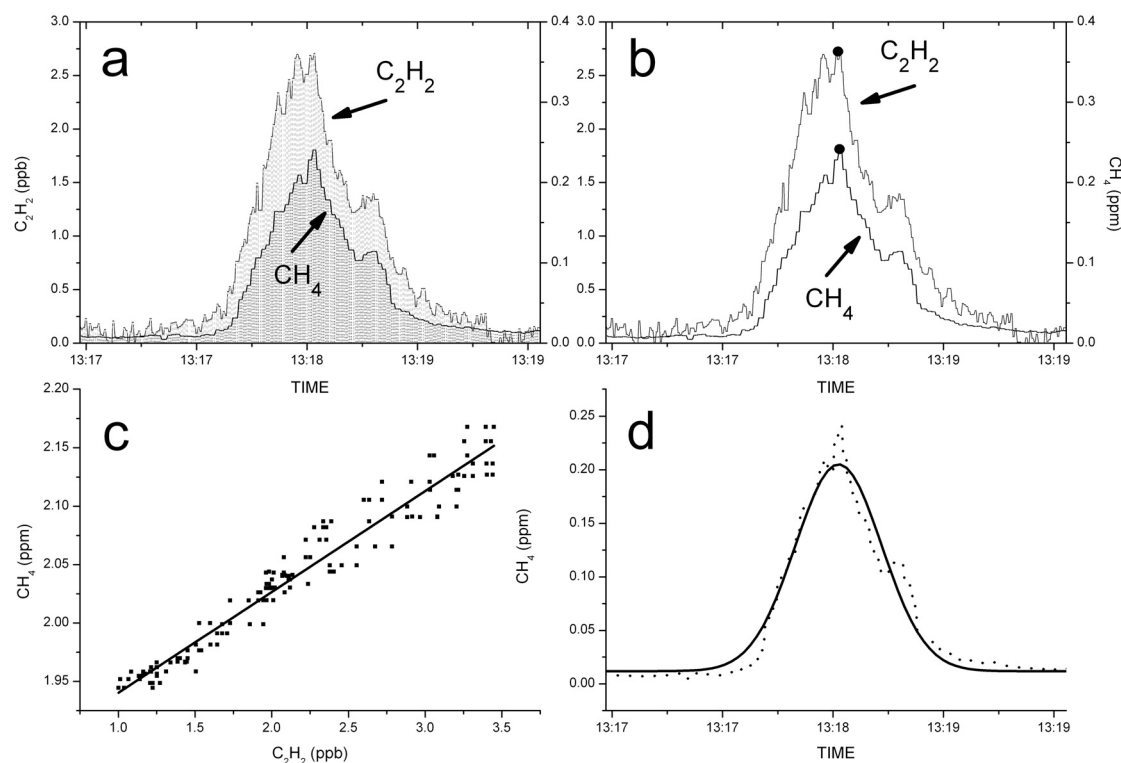


Figure 6 Typical plume transect 1200 m downwind from a landfill giving a graphical view of the four approaches to determining the CH₄ to tracer ratio; a) ratio of the integrated plume transects, b) peak height ratio, c) plume concentrations scatter plot and d) Gaussian model using the concentration at the center of the Gaussian curve fitted to the plume.

The first approach applied a fully integration of both plumes to obtain the CH₄ to tracer ratio, the second approach used the peak height of the plumes, the third used a scatter plot of the concentrations, and finally the last approach included a Gaussian fitting of the CH₄ plume and subsequent inverse modelling. In an ideal situation with a point source giving perfect mixing of CH₄ and tracer gas, undisturbed Gaussian distribution of the plume and known atmospheric stability parameters, all four approaches would yield the same result. The results presented in Mønster et al., (I), showed that the plume integration is the best approach and significant over- and underestimation of the emission rate can occur using the other approaches especially when the tracer gas bottles are misplaced compared to the CH₄ emission area. The study also showed that even with nice, Gaussian shaped plumes as in Figure 6, an overestimation between 9 and 18% was obtained using the last three calculation approaches. Using the plume integration approach gave the lowest uncertainty.

3.2.8 Reproducibility and uncertainty.

It is important to assess the reproducibility and uncertainty for any analytical setup sampling rationale, and data treatment, in order to understand the strength and weaknesses of the obtained results. For the dynamic tracer dispersion method the uncertainty of the “true emission rate” is a combination of the individual uncertainties, which can be divided into the analytical uncertainty, uncertainty in tracer gas release, data treatment uncertainty and tracer, source and transect geometry errors. A previous study using a mobile FTIR instrument estimated that the overall uncertainty was $\pm 18\%$ at a 95% confidence interval (CI), while the precision of the method was 7.5% (95% CI) over a two days period (Samuelsson et al., 2005). In this PhD work, an overall analytical uncertainty for the CRDS analyzer was estimated to be less than 10% mainly origin from the uncertainty of the C_2H_2 calibration gas. The uncertainty of the tracer gas release was experimentally determined to be maximum 2% while the producer of the flow meters gave an uncertainty of 5% on the full reading. The uncertainty in transect analysis is highly depending on the stability of the background concentration and the signal-to-noise ratio. Measurements showed a reproducibility uncertainty, including the transect analysis, of 1-2% under normal conditions and emissions above $50 \text{ kg CH}_4 \text{ h}^{-1}$ at a 1.2 km distance from the source (Mønster et al., I). At lower signal-to-noise ratios, an error in the integrated plume due to an erroneous determination of the baseline can become significant. The baseline uncertainty is not necessarily the raw noise of the data, but can be less if the baseline is stable and an average of multiple baseline points can be used to determine the baseline. Changes of background concentration during a measurement can lead to a larger uncertainty on the baseline (Mønster et al., I). Geometry errors induced by misplaced tracer gas bottles was also tested in Mønster et al., (I), both by controlled release test of both CH_4 and C_2H_2 and theoretically using a simple Gaussian plume model for reverse modelling. The release test showed that misplacing the tracer gas bottle 50 m upwind from the emission point induced an error of up to 36% depending on the distance to the measurement road, with smaller errors at increasing distances. The theoretical model calculations were done for various atmospheric stability situations and for both urban and open country conditions, using:

$$C(x, y, z) = \frac{Q}{2\pi V \sigma_y \sigma_z} e^{\frac{-y^2}{2\sigma_y(x)^2}} \left(e^{\frac{-(z-H)^2}{2\sigma_z(x)^2}} + e^{\frac{-(z+H)^2}{2\sigma_z(x)^2}} \right) \quad (\text{Eq. 3})$$

Where C is the concentration (g m^{-3}) in any given point (x, y, z) in the plume, Q is the emission rate (g s^{-1}), V is the wind speed (m s^{-1}), σ_y and σ_z are the dispersion coefficients (m) and H is the emission height (m) above ground level. For the dispersion coefficients, the neutral atmospheric stability class D is used (Mohan, 1997), which is assumed in typical Danish conditions. Figure 7 shows how the theoretical errors of an upwind misplacement of the tracer gas decrease with increasing measurement distance. It shows that there is no big difference in the expected error between the urban and the open country conditions at this stability class (meaning that weather induced turbulence is the main mixing mechanism) and that an error smaller than 10% can be expected, even at a significant misplacement of the tracer gas (up to 100 m upwind) if measurements are done minimum 2 km from the source.

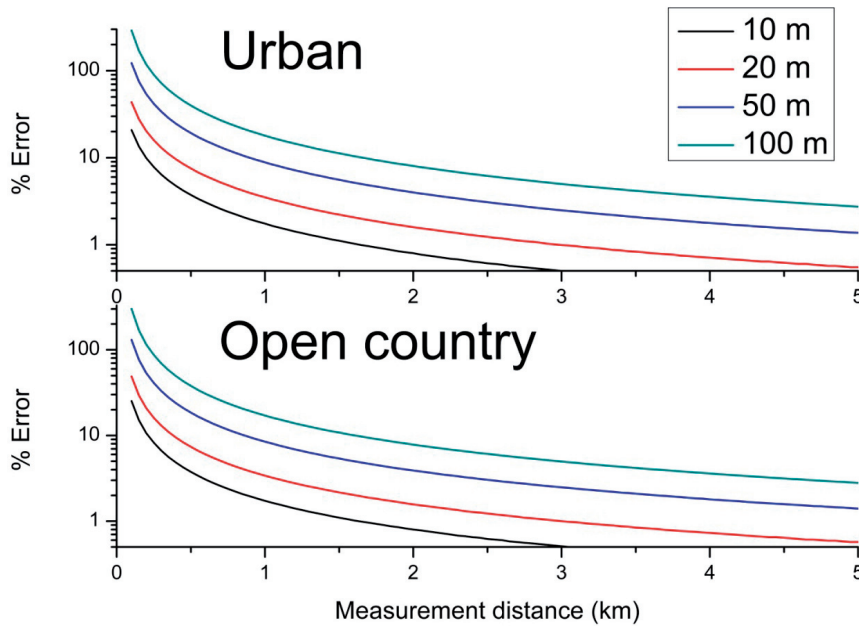


Figure 7 The theoretical error in plume concentration at different distances to the source by placing the trace gas 10, 20, 50 and 100 meters upwind from source. The model assumes Gaussian plume dispersion with urban and open-country conditions and atmospheric stability class D.

4 Quantification of CH₄ emission from Danish landfills

After implementing the dynamic tracer dispersion method and exploring the method's possibilities and limitations, the setup was applied at different landfills in Denmark. Some of the landfills were measured several times in order to address temporal emission variation at the individual landfills, while others were only measured once. In general, measurements were conducted during stable atmospheric conditions, aiming for a period with minimum changes in the atmospheric pressure in the days before the measurements, and with a pressure close to the average pressure during the measurements. Additionally, variations of the tracer dispersion method were developed and used for quantifying the emission from individual areas of landfills and other CH₄ emitting activities at the landfill site areas. The whole landfill site emissions and the emission from onsite activities are presented in Mønster et al., (II). The methodology of identifying and quantifying individual sources in an area with multiple emission sources are presented in Mønster et al., (I), while several examples of using this methodology at a number of landfills and for evaluation of a specific CH₄ mitigation project is presented in Mønster et al., (II) and Scheutz et al., (IV).

4.1 Emission from whole landfill sites

Emissions were quantified at old closed landfills, newer landfills, partly or fully in operation, landfills with gas recovery systems and landfills employing biocovers to reduce the escape of CH₄. The results presented in Mønster et al., (II) includes measurements at four landfills measured using mobile FTIR instrumentation. Three of these were quantified before the start of this PhD work, but included in the study for a more complete emission dataset. The last FTIR measurement campaign was done in parallel with a campaign using the analytical platform based on CRDS. Figure 8 shows a typical plume measurement downwind from a landfill during tracer gas release. Where possible, a minimum of 10 transects were performed at each landfill.

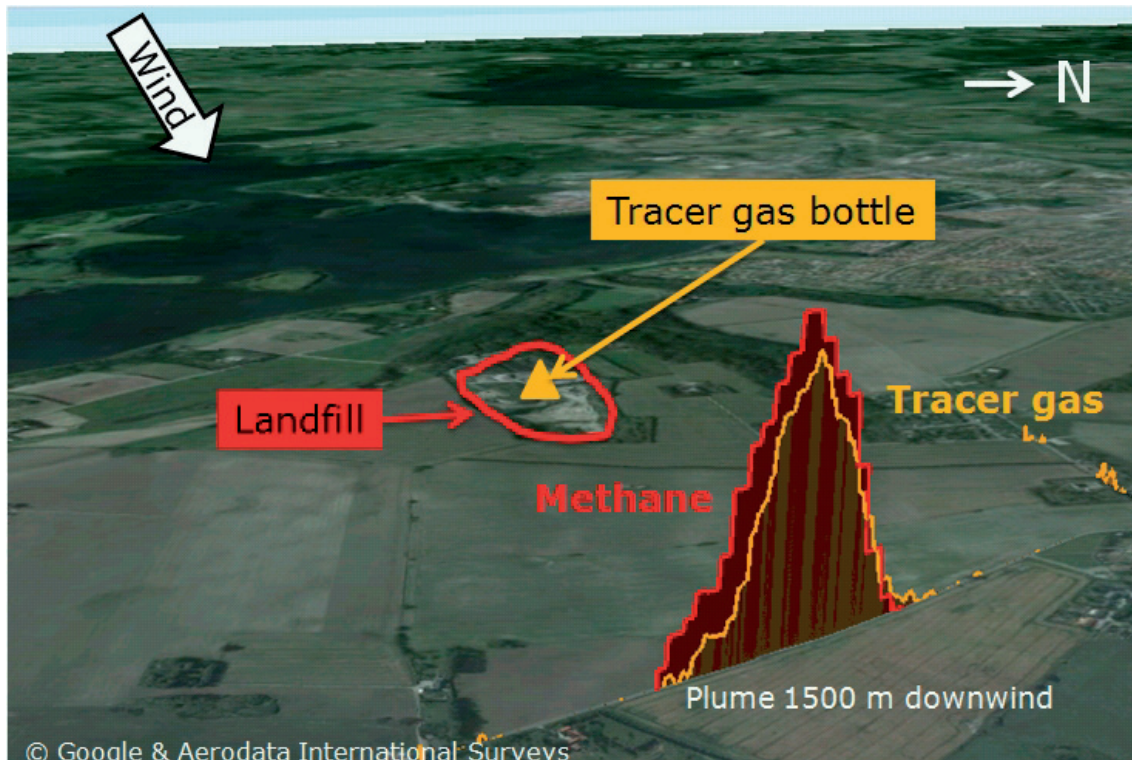


Figure 8: Measurement transect downwind from an active landfill. Only concentrations of CH₄ and tracer gas above background concentration are shown. Background concentration was 1910 ppb and 0.2 ppb and peak concentrations were 2030 ppb and 5.0 ppb for CH₄ and tracer gas respectively.

The measured CH₄ emissions were normalised by considering the area of the landfill, the amount of waste received, the age of the waste and the type of aftercare. This was done in order to evaluate emissions from different sizes and ages of landfill and to suggest contributory factors, where possible. The goal was to obtain estimations of overall CH₄ emissions, by measuring at landfills representing the diverse range of Danish sites, and subsequently compare these with official estimates. Table 1 show an overview of the measured emission rates and compare with previous studies using similar quantification methods.

Table 1: Landfill overview and whole-site CH₄ emission measured by tracer dispersion method from selected landfills.

Landfill	Disposal period (Year)	Area (ha)	Waste amount (10 ⁶ m ³)	Waste amount (10 ⁶ tons)	Gas recovery (kg CH ₄ h ⁻¹)	CH ₄ emission (kg CH ₄ h ⁻¹)	CH ₄ emission (g CH ₄ m ⁻² d ⁻¹)	CH ₄ emission (g CH ₄ ton ⁻¹ d ⁻¹)	Reference
Nashua, US	1971 → (1999)	25.3	2.56	2.23	No	822/643	78/61	8.85/6.92	(Mosher et al., 1999)
PLF-A, US	1962-1996	23	5.7	4.96*	No	1246	130	6.03	
PLF-B, US	1973 → (1999)	34	8.7	7.57*	Yes	1289	91	4.09	
PLF-C, US	1973-unknown	17.8	3	2.61*	Yes	377/170	51/23	3.47/1.56	
PLF-D, US	1930s → (1999)	46.5	5.7	4.96*	Yes	899	47	4.35	
Höbytorp, Sweden	1964 → (2003)	40	1.69	1.47	211	344	20.6	5.62	(Börjesson et al., 2009 and Samuelsson et al., 2005)
Filborna, Sweden	1951 → (2003)	51	1.18	1.03	892	357	16.8	8.32	
Heljestorp, Sweden	1975 → (2003)	25	0.61*	0.53	198	164	15.7	7.43	
Hagby, Sweden	Unknown-1995	32	0.26*	0.23	84	104	7.80	10.9	
Kristianstad, Sweden	1966 → (2003)	8	0.70*	0.61	117	43	12.9	1.69	
Sundsvall, Sweden	1970 → (2003)	22	0.47*	0.41	58	34	3.71	2.00	
Visby, Sweden	Unknown-1997	8.5	0.09	0.08	40	20	5.65	6.00	
Falköping, Sweden	1960 → (2001)	25	0.33	0.29*	Yes	38	3.65	3.14	(Galle et al., 2001)
AV Miljø, Denmark	1989 →	30	1.49*	1.3	No	32.4	2.59	0.60	(Scheutz et al., 2011b) and this study
Fakse, Denmark ^a	1981-1997	13	0.76*	0.66	Yes ^b	32.6	6.02	1.19	(Scheutz et al., 2011a)
Audebo, Denmark	1990 →	4.7	0.70*	0.61	No ^c	16.0	8.17	0.63	This study
Eskelund, Denmark	1950-1980	15.0	0.85	0.74*	No	6.1	0.98	0.20	
Feltengård, Denmark	1983 →	10.3	0.58	0.50*	5.9	3.8	0.89	0.18	
Frederiksværk, Denmark	1950-2009	7.5	-	-	No	8.9	2.85	-	
Glatved, Denmark	1981 →	14.0	1.38*	1.2	43	60.8	10.4	1.22	
Hedeland, Denmark	1978-2009	10.0	1.72*	1.5	13	3.1	0.74	0.05	
Klintholm, Denmark	1978 →	6.5	0.76*	0.66	No ^d	15.0	5.54	0.55	
Odense, Denmark	1994 →	6.0	1.25*	1.09	35	33.1	13.2	0.73	
Skovsted, Denmark	1987 →	4.0	0.37*	0.325	No	2.6	1.56	0.19	
Skårup, Denmark	1980 →	8.9	0.59	0.51*	No	11.9 ^f	3.20	0.56	
Uggeløse, Denmark	1970-1989	11.0	1.15*	1.0	No ^e	9.5	2.07	0.23	
Viborg, Denmark	1989-2009	3.5	0.63*	0.55	27	11.1	7.61	0.48	
Ærø, Denmark	1985-2005	5.0	0.27*	0.233	No	6.9	3.31	0.71	

* Estimated based on an assumed average density of the compacted waste of 870 kg/m³ (Campbell, 1982).

a) Only the older part of Fakse landfill is included.

b) Gas recovery installed in 2011 after the measurements, and in 2012 an average of 11 kg h⁻¹ was recovered.

c) Gas recovery installed but not in use.

d) Biocover installed on oldest part of the landfill.

e) Wells with compost for CH₄ oxidation installed on newest part of the landfill.

f) Including emission from composting.

The current CH₄ emissions from Danish landfills are in general much smaller than CH₄ emissions observed from US landfills in the mid-1990s (Mosher et al., 1999) and from Swedish sites in the early 2000s (Galle et al., 2001, Börjesson et al., 2009). The Danish landfills with the highest CH₄ emissions are comparable to the Swedish landfills with the lowest emissions. Additionally, the emission per area and per waste mass are significantly different compared to CH₄ emissions reported for American and Swedish tracer dispersion studies. Mosher et al. found landfill CH₄ emissions ranging from 23 to 130 g CH₄ m⁻² d⁻¹, while the landfill emissions varied between 0.74 and 13.2 g CH₄ m⁻² d⁻¹ in this study. The Swedish study did not scale emissions to landfill area, but the per waste mass figures ranged between 0.05 and 1.22 g CH₄ ton⁻¹ d⁻¹, which was significantly lower than the 1.69 to 10.9 g CH₄ ton⁻¹ d⁻¹ that Börjesson et al. (2009) found and 1.56 to 8.85 g CH₄ ton⁻¹ d⁻¹ found by Mosher et al. (1999). The low Danish emissions are likely due to the lower organic content of the waste being disposed during the last two decades due to the 1997-ban on disposal of municipal solid waste and other waste types with high organic content.

Six of the measured Danish landfills had gas recovery and the effectiveness of the recovery ranged between 41 and 81%. The oxidation in the top layer of the landfill was not included, which would lead to lower gas collection efficiencies. Börjesson et al. (2009), who found a recovery efficiency of 14-78% at seven Swedish landfills, and Bourn and Browell, (2013) found a variation between 23 and 85% at nine British landfills. Both these studies included CH₄ oxidation, which was found to vary between 5 and 43%.

Table 2 compare the measured emissions to the emissions reported in European Pollutant Release and Transfer Register (E-PRTR) or in the register of the Danish EPA, and reveals a large discrepancy. Most landfills have a higher reported emission (up to two orders of magnitude) in comparison to the actual measured emission, while a few landfills have smaller (up to one order of magnitude) reported emission. The reported emission depends highly on the method used for calculating and on the degree of knowledge about the waste (amount and composition/organic content). The average reported CH₄ emission (793 tons y⁻¹) is more than four times higher than the average measured emission (154 tons y⁻¹).

Table 2: Comparison of measured whole landfill site CH₄ emissions and the emissions reported to the European Pollutant Release and Transfer Register (E-PRTR) or the Danish EPA.

Landfill	CH ₄ emission measured		CH ₄ emission reported
	(kg CH ₄ h ⁻¹)	(tons CH ₄ y ⁻¹)	(tons CH ₄ y ⁻¹)
Audebo	16.0	140	664 ^d (C)
AV Miljø	32.4	284	28 ^f (C)
Eskelund	6.1	53	NR
Fakse	42.2	370	129 ^b (C)
Feltengård	3.9	34	298 ^a (E)
Frederiksværk	8.9	78	17 ^e (E)
Glatved	60.8	533	3490 ^d (C)
Hedeland	3.1	27	3390 ^d (M)
Klintholm	15.0	131	1490 ^b (E)
Odense	33.1	290	487 ^d (C)
Skovsted	2.6	23	500 ^c (C)
Skårup	11.9	104	24 ^f (C)
Uggeløse	9.5	83	NR
Viborg	11.1	97	1260 ^a (E)
Ærø	6.9	60	118 ^f (E)
Average	17.6	154	793 [*]

- a) E-PRTR 2007. b) E-PRTR 2009. c) E-PRTR 2010. d) E-PRTR 2011. All E-PRTR data obtained from the E-PRTR database. e) Danish EPA 2011. f) Danish EPA 2012. All Danish EPA data obtained from Danish EPA PRTR database. NR: No reporting. (C): Calculated. (E): Estimated. (M): Measured. *) NR counted as zero emission.

4.2 Emission from individual sources

The mobility, flexibility and high time resolution of the analytical setup enabled quantification of CH₄ from small on-site emission areas. Previously, quantification of on-site sources were conducted using two different trace gasses placed at the different sources and measuring down-wind CH₄ and trace gas concentrations using an FTIR analyser (Scheutz et al., 2011b). The significantly increased time resolution of the CRDS compared to the FTIR enabled a source split-up with the use of only one kind of tracer gas and carefully choose measurement road and wind direction. This approach was applied for quantifying the emission from a landfill cell with engineered biocover installed and having other sources (landfill cells and windrow composting) physically close by (Scheutz et al. (IV)). At one of the measurement campaigns in Scheutz et al. (IV), the FTIR instrumentation was operated by the Swedish company Fluxsense using multiple tracer gasses and the CRDS instrumentation was operated in a separate car by DTU. The emissions from the biocover was found close to each other (0.7 and 1.3 kg h⁻¹), using the two analytical approaches, but while the tracer gas release for the FTIR system included the strong GHGs N₂O and SF₆, the CRDS relied solely on C₂H₂.

Landfills with organic waste treatment such as windrow composting resulted in significant CH_4 emissions $2.9 - 16.8 \text{ kg CH}_4 \text{ h}^{-1}$. Landfill cells containing solely shredder waste emitted up to $19.7 \text{ kg CH}_4 \text{ h}^{-1}$ suggesting an emission of $0.02 \text{ g CH}_4 \text{ h}^{-1}$ per tons of shredder waste, comparable with Scheutz et al. (2011a) who used incubation studies and found an emission factor of $0.031 \text{ g CH}_4 \text{ h}^{-1}$ tons of shredder waste.

An additional application of the CRDS analytical platform included a slightly modified version of a tracer method for quantification of CH_4 emission from leachate wells suggested by Fredenslund et al. (2010). The difference from Fredenslund et al. (2010) is that the CH_4 and tracer gas is measured 10 to 25 m downwind from the well, which insures a complete mix of the gasses before measuring the ratio for emission quantification. Figure 9 shows (left) the setup with controlled tracer gas flow into the leachate well and stationary measurements downwind from the well and (right) the measured concentration and the linear regression of the relationship of the two gasses.

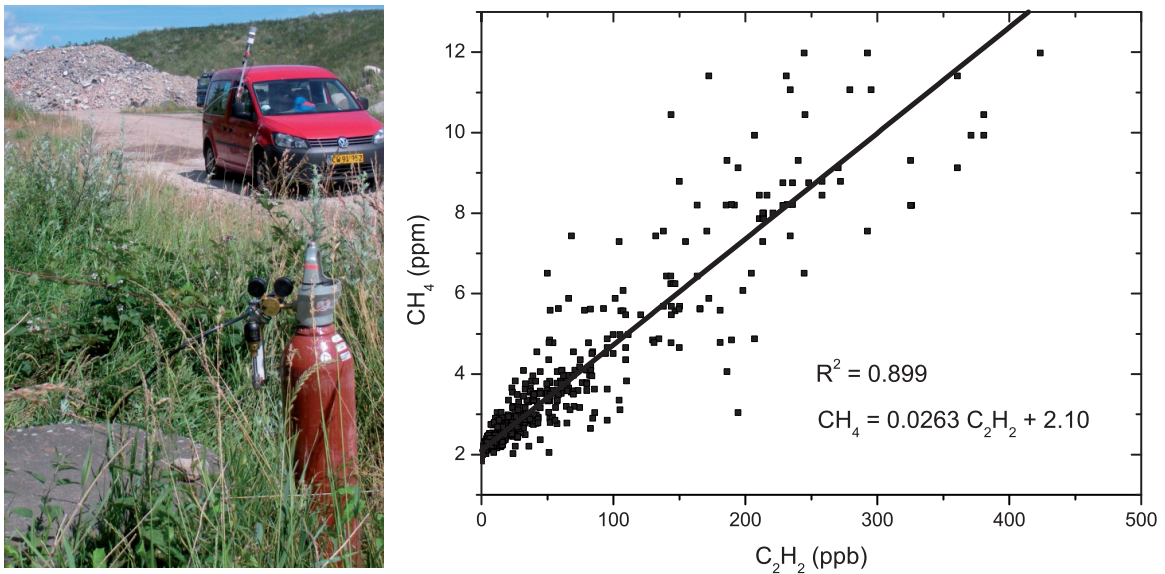


Figure 9 Experimental setup (left) and data treatment (right) for CH_4 emission quantification from a leachate well. Wind is carrying the gasses from the well to the car with the analytical platform.

Measurements from leachate wells at the different landfills showed emissions from close to zero and up to 5.3 kg h^{-1} . The leachate well emitting 5.3 kg h^{-1} contributed with 77% of the total emission from that landfill, showing the significance of being able to include these hotspots in the quantification of the emission rate from a landfill when estimating the whole site emission.

5 Quantification of CH₄ and N₂O emissions from wastewater treatment plants

Wastewater treatment plants can have GHG emissions, but due to its spatial and temporal variation of these emissions, whole plant characterization of GHG emissions can be a challenge to obtain. Floating chamber methods, equivalent to the chamber methods for landfills described in chapter 1, have been used for open tanks with liquids, while possible point sources such as sludge storage and leaks at anaerobic digesters are difficult to access (e.g. Czepiel et al., 1995, Foley et al., 2010, Aboobarkar et al., 2013). Additionally, current Danish GHG reporting from anaerobic digestion of sewage sludge is determined by emission factors, assuming a CH₄ recovery efficiency of 99%, and thereby not taking individual plant operations into account (Nielsen et al., 2013). Using the analytical platform developed in this PhD study could help to identify emission sources at individual wastewater plants and applying the dynamic tracer dispersion method could quantify these emissions, which has not previously done in the literature. For testing this, Avedøre wastewater treatment plant was chosen as additional information about the plant was already being collected as a part of another PhD study. Whole site emissions were performed at the site in a series of measurement campaigns (Yoshida et al., V), which proved the use of the tracer dilution method and led to initial measurements at five wastewater treatment plants in Denmark and Sweden. The five measurements were a part of a bigger project “LaGas” which was initiated in spring 2013, with the aim to identify the processes to production and emission of N₂O.

5.1 Whole site quantification of CH₄ and N₂O

Initial site screenings with the mobile analytical platform around various wastewater treatment plants showed the ability to identify fugitive emission sources. As an example, Figure 10 shows the screening measurements at Sjölanda wastewater treatment plant. N₂O emissions from both the nitrogen removal processes and from the storage of digested sludge were observed, while CH₄ emission was identified from both the stored digested sludge and from the sludge handling area.

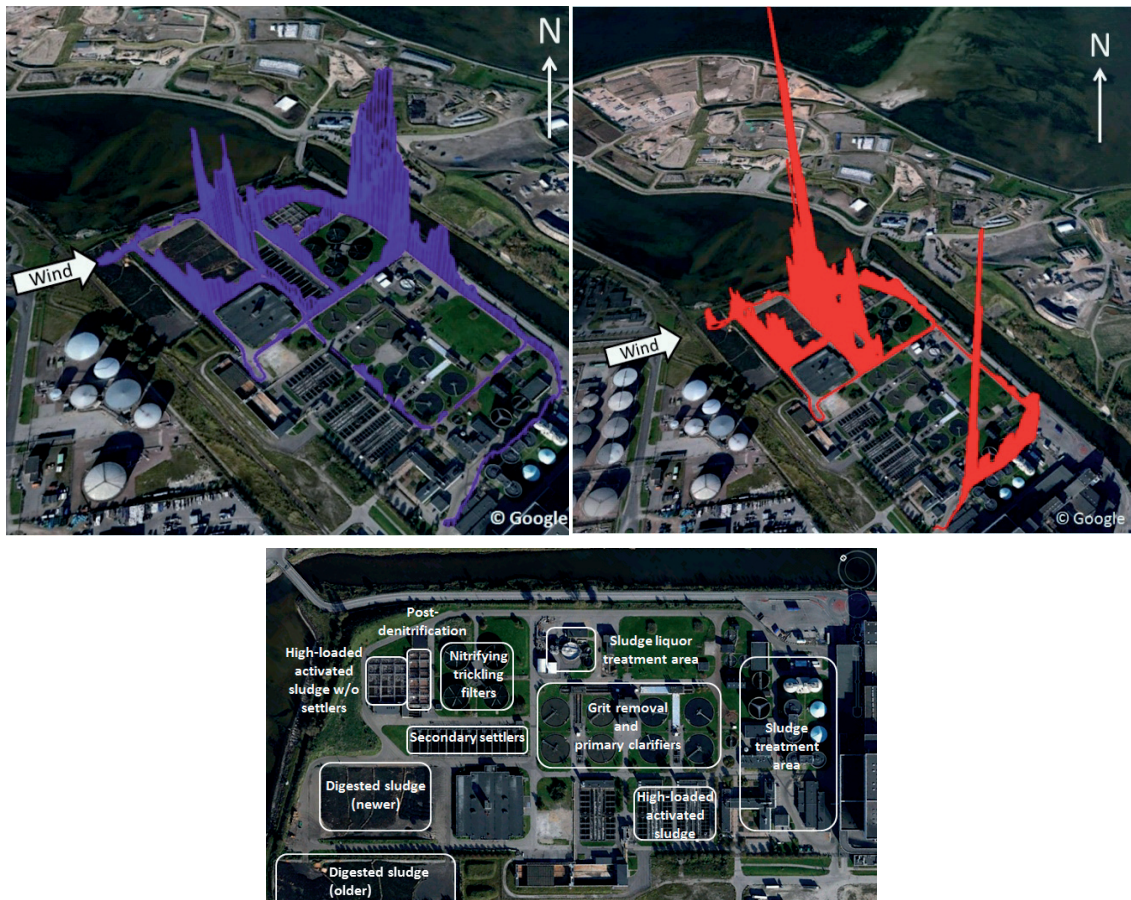


Figure 10 N₂O (top left, blue) and CH₄ (top right, red) concentrations above background concentrations at Sjölanda wastewater treatment plant. Lower picture shows an aerial photo with positions of important process steps.

The emission from the individual processes depends on the operation conditions. At Avedøre wastewater treatment plant, the only significant source of N₂O emissions was found to be the aeration tanks, while CH₄ emissions came from areas around the anaerobic digester. Higher concentrations of CH₄ were detected approximately 100 m downwind from the digester in comparison to measurement conducted closer to the digester, indicating emissions from an elevated source. The top of the anaerobic digester was 30 m above ground and was suspected to be the source. It was calculated using reverse Gaussian dispersion modelling that at the given location and atmospheric conditions, such an elevated source would theoretically lead to a 2% underestimation when measured at a distance of 1200 m, which was the distance used at Avedøre wastewater treatment plant. The underestimation could become greater if measured at shorter distances or different atmospheric and turbulence conditions, leading to more significant underestimations. A further discussion on underestimation caused by elevated sources can be found in Yo-

shida et al., (V). The quantifications were performed 400-600 m (N_2O) and 1200 m (CH_4) downwind from the source and were done at different wind directions (see Figure 11).

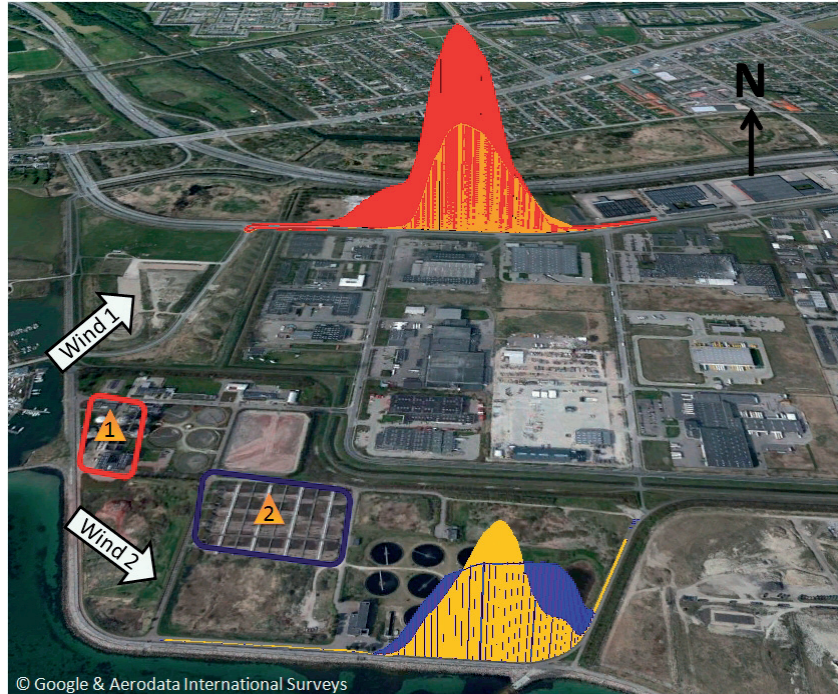


Figure 11 CH_4 (red), N_2O (blue) and tracer gas (yellow) concentration downwind at two different wind directions. Concentrations are the relative concentrations above background. Red square marks the main CH_4 source and blue square marks the N_2O source. Yellow triangle shows the location of tracer gas release during each of the two wind situations.

The CH_4 and the N_2O emissions from Avedøre wastewater treatment plant were changing, both during the individual measurement campaigns (Figure 12) and between the different campaigns.

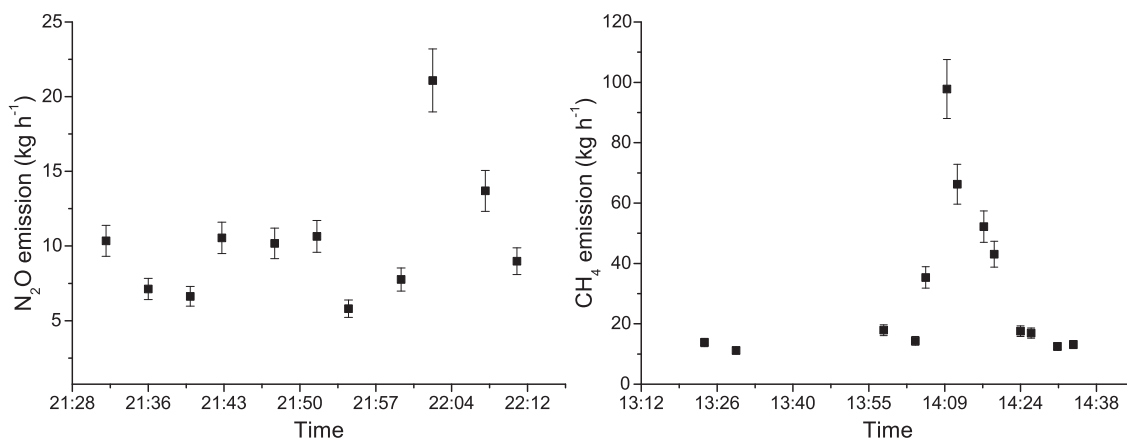


Figure 12 The variation of N₂O (left) and CH₄ (right) emissions during a measurement campaign. The measurements are from two different days.

The N₂O emissions ranged from below detection limit (the detection limit is not constant, but a function of the atmospheric conditions – in this study it was approximately 0.4 kg h⁻¹) and up to 10.5 kg h⁻¹. They were found almost exclusively around the aeration basins and occurred mainly during aeration, which could be a pure physical effect, rather than the chemical reaction forming the N₂O during the nitrogen removal processes (Yoshida et al., V). The CH₄ emissions also showed large fluctuations over short time periods, with emissions varying from around 10 kg h⁻¹ to over 120 kg h⁻¹. The variation could be due to foaming problems inside the anaerobic digesters leading to a biogas release to the atmosphere. The high emission periods correlated with decreasing biogas utilization (Yoshida et al., V).

5.2 CH₄ quantification: comparison of methods

At short time scales, different methods for quantifying CH₄ emission from wastewater treatment plants were compared at a plant in Valence, France. Three methods were used: 1) Dynamic tracer dispersion method 2) open and closed floating chamber method and 3) ²²²Radon method. The chamber method is described in section 3.1.1 in this thesis. The ²²²Radon method relies on simultaneous measurements of CH₄ and ²²²Radon accumulating in the lowest part of the troposphere. ²²²Radon is emitted from the Earth at a known constant rate, and when the concentration increase of ²²²Radon and CH₄ correlate, then the CH₄ emission can be calculated. The three methods measure at different scales. The chamber method measure a specific area of a single wastewater treatment process, while the dynamic tracer dispersion method measure the whole plant emission. Finally, the ²²²Radon method measures the CH₄ emission from the whole region, in this case a grid of 90 x 90 km. See

Yver et al., (VI) for a further description on the tested methods. The comparison shows that the chamber methods can capture the CH₄ emission from the different wastewater treatment basins but fail to catch the main emission from the sludge treatment, as site screenings using the mobile CRDS analyzer indicated relatively large emission from the sludge storage and incineration house. Comparing the whole site emission measured by the dynamic tracer dispersion method to the chamber method, showed that only 6% of the CH₄ was emitted from the ponds, indication that relying on chamber measurements alone would not give a reliable whole site emission at the measured wastewater treatment plant. The ²²²Radon method gives a regional emission, and an emission for the whole Valence area was estimated to be around 1500 kg CH₄ per day, which made the wastewater treatment plant contribute with approximately 3% of the regional emission (Yver et al., VI).

6 Discussion

The work in this PhD study consisted of three parts; (1) identifying the best suitable method for quantifying GHG from fugitive emissions and building up an analytical platform including laboratory tests. (2) Test and validate the chosen method in field conditions using controlled release and measuring at fugitive sources. (3) Quantify GHG emissions from waste treatment facilities including landfills and waste water treatment plants. Careful considerations were taken at each step of the process ensuring reliable results as an outcome. The following is a discussion of the development process and the results obtained, followed by a reflection on the implication of the results and future possibilities to use the results and the measuring method.

6.1 Methodology for CH₄ emission quantification

Various methods have been applied for quantifying CH₄ emission from fugitive emission sources such as landfills. Based on literature review we found the tracer dilution method promising. A new, compound specific analytical instrument made it possible to build up an analytic platform that could be installed in a vehicle. In one day, one can install the analytical platform, perform tracer dilution method measurements and uninstall the equipment from the vehicle. This provides flexibility as the analytical platform can be employed at any available vehicle. The RPM method was also considered, but not being able to cover a whole landfill made us go for the tracer dispersion method. Additionally would the purchase of a CRDS analyzer open up for many other applications and future projects. Measuring methods that are deployed on-site like mass balance and Eddy covariance were disregarded due to the uncertainty in assessing the area they cover and the heterogeneous nature of the emission from a landfill. The DIAL is a promising method, which also has many applications due to the possibility to measure multiple gasses, but the equipment is large and expensive not within the economic frame of a university PhD project. The US-EPA developed a method and guideline for how to measure CH₄ from landfills using the RPM method (Thoma et al., 2010), but have recently started working on the tracer dispersion method. All methods have advantages and disadvantages, but the easy approach and flexibility of the dynamic tracer dispersion method combined with the new and fast CRDS analyzers makes it a strong candidate for a quantification method that could be applied in many future landfill emission measurements, both for research purposes and for GHG emission reporting to the appropriate authorities.

6.2 Applications of the tracer dispersion method

A large effort in this PhD work was put into implementing the tracer dispersion method in order to quantify the emission from Danish landfills. Some older Danish landfills have very small emissions compared to measurements in e.g. Sweden and USA, but the analytical sensitivity of the CRDS instrumentation enabled measurements of landfill site emissions down to 1 kg CH₄ per hour. Many old landfills are left without aftercare, and are still emitting CH₄ to the atmosphere. At these landfills, CH₄ mitigation initiatives such as engineered biocovers for CH₄ oxidation have proven to be effective. The tracer dispersion method would be an obvious choice to identify which old landfills are having significant emissions and to validate the effect of mitigation actions such as a biocover installation. The tracer dispersion method can also be used to quantify multiple emission sources located close to each other by either using different tracer gasses and/or use the exact right combination of wind direction, measurement distance and tracer gas placement. Additionally, a small-scale tracer dilution method enables the emission quantification from point sources such as leachate wells, even if these are located on a landfill with various sources nearby. This opens up for quantification of CH₄ from various other sources where the emissions are uncertain, unknown or simply thought to be insignificant. During the many field campaigns at landfills and wastewater treatment plants, various other sources have given significant CH₄ plumes when passing by downwind from the source including composting facilities, pig farms, slurry tanks, and anaerobic digesters. Such fugitive emissions have been studied and emission factors are used for GHG reporting, but the tracer dispersion method could contribute with more local or site specific emission factors. Additionally, efforts for minimizing the CH₄ emission from various sources could be validated by before/after measurements, to prove the environmental benefit of a mitigation initiative. Also biogas producers could benefit from the tracer dispersion method to address how much of the produced CH₄ they emit to the atmosphere and thereby loose in potential income.

Helping the company Picarro to develop the spectroscopic specification for measuring N₂O with a low concentration resolution in field conditions and with unnatural high concentrations of acetylene (due to being used as tracer gas), enabled to expand the application of the tracer dispersion method to also cover fugitive N₂O emissions. Emission hotspots of N₂O are rare, but the analytical platform was proven useful at wastewater treatment plants, where it

could be used for both locating N₂O emission sources and for quantifying the magnitude of the emission.

6.3 Greenhouse gas emission rates

The emission of GHGs is of great concern in most countries around the world and many initiatives are taken to lower these emissions. The results from the work in this PhD study have shown that the GHG emission reported to national and international inventories might differ significantly from the actual emission. The current study mainly focus on landfills and to a smaller extend on wastewater treatment plants, and shows in both cases that improved site specific emission rates are needed for more accurate GHG reporting. The results also show an inconsistency of the assumed 99% utilization effectiveness of the biogas produced by anaerobic digestion of sludge.

The normal timescale to compare GHGs is on a 100 years scale. The 100 years effect of CH₄ and N₂O are then calculated into CO₂ equivalents to give a comparable total GHG emission. An interesting aspect in the procedure is the chosen timescale. A shorter timescale would significantly change the GHG emission rates for CH₄ emitting sources. CH₄ has a GWP of 25 (or 34 including carbon storage) on a 100 years scale but has, due to its shorter lifetime in comparison to CO₂, a GWP of 86 on a 20 years scale (IPCC, 2013). Looking at global warming at a shorter and maybe more realistic time scale, the CH₄ emission change the radiation balance 3 times more than accounted for in the current GHG accounting.

6.4 Outlook and recommendations

Emission of CH₄ from various anaerobic environments cannot be prevented, but an effort should be given to minimize the anthropogenic part of the emission. There is no doubt that we are currently changing the temperature of the Earth and thereby changing the conditions for where and how human live (IPCC, 2013). International initiatives to slow down the global change are essential and international agreements with national, regional and local obligations are an obvious path towards a smaller human influence on the global temperature. GHG emissions need to decrease further in order to follow these initiatives and live up to national and international agreements. But in order to know in which sector the most cost-efficient GHG emission reduction is obtained, it is essential to have accurate knowledge about the emissions. Especially CH₄ emission is one of the areas where better knowledge could be obtained.

The research done in this PhD study shows that the tracer dispersion method can act as a useful tool for identifying and quantifying fugitive GHG emissions from landfills and wastewater treatment plants and the simple approach of the method imply that it can be applied at many other fugitive GHG sources for expanding the current level of knowledge. The method provides a unique opportunity to quantify whole site emissions and thereby include sources that might be missed by other measurement techniques.

The measured landfill gas emissions show a significant difference from those reported to the national GHG inventory, which opens up for more research in identifying the actual emission and how to best obtain true emission values. Changing atmospheric conditions are known for influencing the emissions from landfills and systematic research on this at various types of landfills is recommended for obtaining better knowledge of this effect.

The implementation of N_2O in the tracer dispersion method is unique and will be used in a project studying the processes determining the N_2O emission from wastewater treatment.

Ammonia (NH_3) emission from agriculture is of great concern and it can be difficult to quantify the NH_3 emission, but since the N_2O CRDS instrument was also developed for NH_3 , future studies could include these emissions using the tracer dispersion method or variants of the method.

7 Conclusion

This PhD project developed a mobile analytical platform that can be used to measure atmospheric plumes of CH₄ from diffusive sources. Combined with tracer gas releases and simultaneous gas concentration measurements, emissions from diffusive sources can be quantified. This PhD project tested, and validated and applied the method to quantify CH₄ emissions from landfills. The analytical platform was expanded to also include analysis of N₂O, enabling quantification of fugitive N₂O emissions. The tracer dilution test was used for the first time to quantify N₂O emissions from wastewater treatment plants.

The test of the analytical platform showed an improved time resolution compared to previously used analytical approaches, giving measurements with higher spatial resolution enabling quantification of individual emission sources using a single tracer gas type. In addition, the fast response of the analytical instrument combined with high concentration resolution enabled measurements of relatively low emission rates, down to 1 kg CH₄ h⁻¹, allowing before/after measurements at landfills having mitigation initiatives installed.

Based on the emission measurement campaigns conducted at a number of Danish landfills it was concluded that at landfill with gas recovery, the collection efficiency is far from 100% and most likely closer to 41-81%. In addition it was shown that the CH₄ emissions reporting to the national GHG inventory is far from the measured emission rates – some of the landfills emit more than reported and some emit less. Measurements showed that anaerobic digesters at waste water treatment plants have significant fugitive CH₄ emissions, which are not properly accounted for in the GHG reporting.

The flexibility and simple approach of the tracer dispersion method opens up for a wide range of applications to obtain better knowledge of fugitive emissions from various sources.

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9 Papers

- I** Mønster, J., Samuelsson, J., Kjeldsen, P., Rella, C. W., Scheutz, C. (2014). Quantifying methane emission from fugitive sources by combining tracer release and downwind measurements – a sensitivity analysis based on multiple field surveys. *Waste Management*, in press (doi:10.1016/j.wasman.2014.03.025)
- II** Mønster, J., Samuelsson, J., Kjeldsen, P., Scheutz, C. Quantification of methane emissions from 15 Danish landfills using mobile tracer dispersion method. Accepted (with revision) by *Waste Management*.
- III** Mønster, J., Kjeldsen, P., Scheutz, C. Emission measurements methodologies for measuring fugitive methane emission from landfills – a review. Manuscript in preparation.
- IV** Scheutz, C., Pedersen R. B., Petersen, P. H., Jørgensen J. H. B., Uendo, I. M. B., Mønster, J. G., Samuelsson, J. and Kjeldsen, P. (2014). Mitigation of methane emission from an old unlined landfill in Klintholm, Denmark using a passive biocover system. *Waste Management*, in press (doi:10.1016/j.wasman.2014.03.015)
- V** Yoshida, H., Mønster, J., Scheutz, C. (2014). A plant-integrated measurement of greenhouse gas emissions from a municipal wastewater treatment plant. *Water Research* 61 (2014) 108-118.
- VI** Yver-Kwok, C. E., Müller, D., Caldow, C., Lebegue, B., Mønster, J.G., Rella, C.W., Scheutz, C., Schmidt, M., Ramonet, M., Warneke, T., Broquet, G., Ciais, P. (2013). Estimation of waste water treatment plant methane emissions: methodology and results from a short campaign. *Atmos. Meas. Tech. Discuss.*, 6, 9181-9224, 2013. In review.

In this online version of the thesis, the papers are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from.

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