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PhD Thesis
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Preface

The work presented in this PhD thesis was conducted from September 2010 to August 2014 at the Department of Environmental Engineering of the Technical University of Denmark (DTU) under the supervision of Professor Peter Kjeldsen and co-supervision of Associate Professor Charlotte Scheutz. The PhD project was funded by the 3R PhD school and the Danish landfill network for sustainable landfill (DepoNet).

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

I Mou, Z.S., Scheutz, C., Kjeldsen, P., 2014. Evaluating the biochemical methane potential (BMP) of low-organic waste at Danish landfills. Waste Management, in press. DOI: 10.1016/j.wasman.2014.06.025.

II Mou, Z.S., Scheutz, C., Kjeldsen, P., 2014. Evaluating the methane generation rate constant (k value) of low-organic waste at Danish landfills. Waste Management, in press.

III Mou, Z.S., Scheutz, C., Kjeldsen, P., 2014. Evaluation and application of site-specific data to revise the first order decay model to estimate landfill gas generation and emissions at Danish landfills. Submitted to Journal of the Air & Waste Management Association.

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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I want to thank all my Chinese friends in this department and DTU for making my life here more colorful. Last but not the least, I would like to express my gratitude to my wife and my entire family for their unconditional love and support.

Summary

Methane (CH_4) is one of the most important greenhouse gases (GHG) with a 100-year global warming potential 28 times that of carbon dioxide (CO_2). Waste degradation at landfills is one of the major anthropogenic resources of CH_4 generation and emissions in the world. According to the EU Council Directive 1999/31/EC on the landfill of waste, landfilling in Europe is limited to inert materials that are not biodegradable or combustible on a national level. According to the European Pollutants Release and Transfer Registers (PRTR) Regulation 166/2006/EC, operators of landfills with a total capacity of 25,000 ton or receiving more than 10 ton per day must quantify and report their pollutant emissions to the general public and their national government. Therefore it is important for landfill operators to have a reliable guideline to measure, calculate and estimate landfill gas (LFG) emissions for the PRTR reporting. Due to difficulties in precisely monitoring a whole site's CH_4 emissions, first order decay (FOD) landfill gas generation models are currently widely used to estimate CH_4 emissions from landfills.

FOD models are recommended by both researchers and state regulators for estimating CH_4 generation from waste degradation. Most of the models are based on two primary parameters, a biochemical CH_4 potential (BMP) and an FOD rate constant (k) of the landfilled material. This study reviewed several currently used FOD LFG models in terms of their default parameter values and defined waste categories. Depending on whether various k values were defined for different waste categories, there are two major kinds: multi- and single-phase FOD models. The single-phase model has no function for distinguishing various decay rates between different waste categories. The multi-phase model required waste amount by fractions as input data.

Three FOD models were selected to estimate LFG generation from Danish landfills. The single-phase LandGEM model was developed by the US EPA and was intended to model the LFG generation from traditional municipal solid waste (MSW) disposal sites with relative homogeneous waste fractions. The IPCC (developed by the Intergovernmental Panel on Climate Change) and Afvalzorg (developed by a Dutch company) model are multi-phase, which defined waste fractions into traditional MSW and low-organic waste categories, respectively. For running the models, actual waste data from four Danish landfills (AV Miljø, Audebo, Glatved, and Odense) were used as input data. Most disposed waste at Danish landfills had insignificant or very low organic fractions. Original waste data were translated into various frac-

tions to fit the multi-phase model. By applying default values for the BMPs and k values, the annual and normalized CH_4 generation (kg CH_4 ton^{-1} waste) from the beginning of disposal until year 2020 and year 2100 at the four landfills were estimated by three FOD models (using both default and revised parameter values).

In comparison to the multi-phase model outcomes, the LandGEM model estimated significantly larger CH_4 generation because it defined only one relatively high BMP value (122 CH_4 ton^{-1} waste, wet weight) for low-organic waste. The IPCC model estimated only 1/4–1/3 of the annual CH_4 generation estimated by the LandGEM model until year 2020. The Afvalzorg model estimated only approximately 10% of the annual CH_4 generation estimated by the LandGEM model. Moreover, in comparison to the IPCC model, the Afvalzorg model could better show the influence of not only the total disposed waste amount, but also various waste categories. Therefore, it is more suitable to estimate LFG generation from landfills receiving low-organic waste.

To further calibrate the BMPs and k values of Danish waste fractions, four major disposed waste categories (mixed bulky, shredder, dewatered sludge and street cleansing waste) and temporarily stored combustible waste were sampled and were characterized in terms of TS, VS, TC, and TOC. In general, waste samples showed lower TOC contents than traditional MSW fractions. The same category of waste samples from different landfills showed similar results. By incubation experiments at 55 ^{o}C over 77 days, the BMPs of all waste samples were determined. As main fractions at Danish landfills, mixed bulky and shredder waste had similar BMPs, which was in the range of 5.4-9.1 kg CH_4 ton^{-1} waste (wet weight) on average. The sludge waste and temporarily stored combustible waste showed BMP values of 51.8-69.6 and 106.6-117.3 kg CH_4 ton^{-1} waste on average, respectively.

For determining k values, anaerobic degradation experiments were set up in duplicate and incubated for 405 days, during which the cumulative CH_4 generation was continuously monitored. Applying FOD equations to the experimental results, k values of all waste samples were determined. Likewise, similar waste categories obtained from different Danish landfills showed similar results. Sludge waste had the highest k values, which were in the range 0.156-0.189 yr^{-1}. The combustible and street cleansing waste showed k values of 0.023-0.027 yr^{-1} and 0.073-0.083 yr^{-1}, respectively. The lowest k values were obtained for mixed bulky and shredder wastes ranging from 0.013 to 0.017 yr^{-1}. Most low-organic waste samples showed lower BMPs and k values in comparison to the default numeric values in current FOD models. By using lab-determined results, the Afvalzorg model was revised and estimated smaller cumulative CH_4 generation results in comparison to default values. Based on CH_4 recovery data (provided by the landfill operators) and estimated CH_4 oxidation factor of 10%, fugitive CH_4 emissions from whole-sites and a specific cell for shredder waste at the Odense landfill were aggregated based on the revised Afvalzorg model outcomes. Former studies have established a tracer dispersion method as a reliable and accurate approach for quantifying whole-site fugitive landfill CH_4 emissions, which were applied at the same landfills. Aggregated CH_4 emissions were in good agreement with field measurements, indicating that the revised FOD model with site-specific data could provide a practical and accurate estimation for LFG emissions. Additionally, by using only one k value for each waste category instead of identifying various degradable fractions, the Afvalzorg model could be revised as a less complicated and more practical model for the Danish scenario.

Dansk sammenfatning

Metan (CH_4) er en af de vigtigste drivhusgasser (DHG) med en 100-årig global opvarmning potentiale 28 gange så kraftig som kuldioxid (CO_2). Lossepladser udgør en af de største menneskeskabte kilder til metan i atmosfæren, idet der dannes store mængder biogas – også kaldet deponigas (LFG) - grundet anaerob nedbrydning af organnisk affald. I henhold til EU-Rådets direktiv 1999/31/EC om affaldsdepoter, skal lossepladser i Europa kun modtage inaktive materialer, som ikke er biologisk nedbrydelige eller brændbare. Ifølge den europæiske Pollutants Release and Transfer Registers (PRTR) Regulation 166/2006/EC, skal operatører af lossepladser med en samlet kapacitet på 25.000 ton eller med modtagelse af mere end 10 ton om dagen kvantificere og rapportere deres forurenende emissioner til offentligheden og deres nationale regering. Derfor er det vigtigt for lossepladsers operatører at have en pålidelig procedure for måling, beregning og skøn af deponigas-emissioner med henblik på rapportering til PRTR-registret. Da det har været vanskeligt at måle CH_4 emissioner fra en hel losseplads, har modeller baseret på første ordens nedbrydning(FOD) til estimation af dannelse af deponigas fået vid udbredelse.

FOD modeller anbefales af både forskere og offentlige administratorer til at estimere dannelsen af CH_4 fra affaldsnedbrydning. De fleste af modellerne er baseret på to primære parametre, et biokemisk CH_4 potentiale (BMP) og en FOD hastighedskonstant (k) for de deponerede materialer. I dette studie blev flere benyttede FOD modeller gennemgået - herunder benyttede "default" parametre og indeholdte affaldstyper. De benyttede modeller kan opdeles i to typer; multi- og enkeltfase FOD modeller. Enkeltfasemodeller kan ikke skelne mellem forskellige nedbrydningsforhold for modtagne affaldstyper, hvor multifasemodeller har "default" parametre for flere affaldstyper og kræver input af årlige affaldsmængder for alle modtagne affaldstyper.

Tre FOD-modeller blev udvalgt for at estimere gasdannelse på danske lossepladser: 1) Enkeltfasemodellen, LandGEM, udviklet af US EPA med henblik på at modellere gasdannelsen på traditionelle lossepladser der modtager homogene affaldsfraktioner primært bestående af husholdningsaffald (MSW), 2) IPCC-modellen (udviklet af Intergovernmental Panel on Climate Change) og 3) Afvalzorg-modellen (udviklet af et hollandsk affaldsselskab), som begge er multi-fasemodeller med mulighed for input af både traditionelle MSW affaldstyper og affald indeholdende lavt indhold af organisk materiale. De tre modeller blev benyttet med inputdata fra fire danske lossepladser (AV Miljø, Audebo, Glatved og Odense). De fleste affaldstyper, som modtages på danske lossepladser har ubetydeligt eller lavt indhold af organiske fraktioner. De originale indsamlede affaldsdata på lossepladserne blev tilpasset de forskellige affaldsfraktioner defineret i modellerne. Ved benyttelse af modellernes "default" værdier for BMP og rate-konstanten, k, blev den årlige normaliserede metandannelse (kg CH_4 ton^{-1} affald) beregnet fra begyndelsen af affaldsdeponering til hhv. år 2020 og 2100 for alle de fire lossepladser og med brug af alle tre modeller.

LandGEM-modellen estimerede i sammenligning med de to multifasemodeller signifikant højere metandannelse grundet brugen af en relativ høj BMP-værdi (122 m^3 CH_4 ton^{-1} affald, våd vægt) for affald med lavt indhold af organisk affald. IPCC-modellen estimerede kun 1/4 - 1/3 af den årlige metandannelse estimeret af LandGEM-modellen indtil 2020, hvor Afvalzorg-modellen estimerede kun 10% af LandGEM-estimatet. Herudover kunne Afvalzorg-modellen bedre tage hensyn til betydningen af at der modtages forskellige affaldstyper og er derfor mere velegnet til brug på lossepladser som modtager affald med lavt indhold af organisk materiale.

Med henblik på yderligere kalibrering af BMP- og k-værdier for danske affaldsfraktioner, fire væsentlige affaldstyper (blandet affald, shredderaffald, afvandet slam, affald fra gadeopfej og midlertidig lagret brændbart affald) blev prøvetaget og karakteriseret for TS, VS, TC og TOC. Generelt indeholdte de prøvetagede affaldstyper fra alle de fire lossepladser et lavere indhold af organisk stof (karakteriseret som TOC) i forhold til traditionelle MSW fraktioner. BMP-værdier for de prøvetagne affaldstyper blev bestemt ved inkubation ved 55 ^{o}C i 77 dage. For de to største affaldstyper (blandet affald og shredderaffald) blev der fundet BMP-værdier i det samme niveau fra 5,4 til 9,1 kg CH_4 ton^{-1} affald (våd vægt) i gennemsnit. Afvandet slam og det midlertidige lagrede brændbare affald viste BMP værdier på henholdsvis 51,8-69,6 og 106,6-117,3 kg CH_4 ton^{-1} affald i gennemsnit.

Til bestemmelse af metandannelsesrater (k-værdier) for de prøvetagne affaldstyper blev der opsat duplikate anaerobe gasdannelses-eksperimenter, som blev udført med en 405 dages varighed. Under forsøget blev den akkumulerede metandannelse bestemt for hvert forsøg. Ved at fitte de eksperimentelle resultater med FOD-ligningen blev k-værdier for alle inkuberede affaldstyper bestemt. Der sås generelt en lille variation i k-værdier for den samme affaldstype mellem de fire lossepladser. Afvandet slam havde de højeste k-værdier, som lå i området 0,156-0,189 $år^{-1}$. Midlertidig lagret brændbart affald og affald fra gadeopfej viste k-værdier på henholdsvis 0,023-0,027 år^{-1} og 0,073-0,083 år^{-1}. De laveste k-værdier blev opnået for blandet affald og shredder affald, og spændte fra 0,013 til 0,017 år^{-1}. De fleste af affaldsprøverne med lavt indhold af organisk materiale viste lavere BMP og k-værdier i forhold til "default" - værdierne i de benyttede FOD-modeller. Afvalzorg-modellen blev revideret ved input af de nye laboratorie-bestemte værdier. Brugen af den reviderede model resulterede i signifikant lavere akumuleret gasdannelse sammenlignet med modellen og default-værdier. Estimerede metandannelser ved brug af den reviderede Afvalzorg-model blev sammenlignet med udregnede metandannelse baseret på måling af opsamlet metan, estimeret matanoxidation (10%) og målte total metanemissioner fra de fire lossepladser og en specifik affaldsetape indeholdende shredderaffald. Total metanemissionerne var målt med sporstof dispersions metoden, som er dokumenteret som en præcis og robust metode. Der var generelt god overensstemmelse mellem de model-estimerede metandannelser og de beregnede gasdannelser baseret på målinger. Dette viser at en FOD-model revideret med lokal-specifikke input data kan give realistiske model output for metandannelsen. Samtidig er der opnået en mere simple FOD-model indholdende én k-værdi for hver enkelt affaldstype i stedet for en model med flere teoretiske fraktioner havende forskellige nedbrydningsgrader. Den reviderede Afvalzorg-model anses som velegnet for fremtidig estimation af gasdannelse for danske affaldsdeponeringsanlæg som modtager affald med lavt indhold af organiske materilaer.

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1 Introduction

1.1 Landfill Gas Generation

Landfilling has been the only method for final disposal of solid waste for many years (Mc Dougall et al., 2001). In many parts of the world, it is still the main management route for industrial and municipal solid waste (MSW). Since the 1950s, landfills have developed from open polluting dumps to modern, highly engineered facilities with sophisticated control measures and monitoring routines (Christensen, 2011). However, in spite of all the new approaches and technological advancement, landfilling is a long-lasting accumulation of waste, and may pose negative impacts to the environment (Niskanen et al., 2013). Landfill gas (LFG) generated from organic waste degradation contributes significantly to global warming in terms of 55-60% of methane (CH_4) and 40-45% of carbon dioxide (CO_2). The amount of gas generated in a landfill depends on the amount, the composition (such as organic content, moisture content, nutrient content, presence of inhibitory compounds), and the age of the waste (Scheutz et al., 2009a). The generation will continue for decades after the waste is deposited, until the majority of the organic material has been degraded. The rate of LFG generation depends on the composition of the organic waste and the biochemical environment in the landfill (temperature, moisture, waste compaction, landfill cover design, etc.) (Christensen, 2011). Landfill is one of the three major anthropogenic sectors (animal husbandry and agriculture are the others), which emit large amounts of CH_4 over shorter time horizons (20 yr). The recent assessment report from the intergovernmental panel on climate change (IPCC) suggests new global warming potential for CH_4 of 28, or 34, if the change in carbon storage due to climate change is included (IPCC, 2013).

The generated LFG will tend to build up inside the landfill. However, diffusion and advection processes make the generated gas escape from the landfill. In 2011, landfills contributed to 4,907 and 3,052 Gg fugitive CH_4, accounting for 17.5 and 19.6% of anthropogenic CH_4 emission in the US and Europe, respectively (EEA, 2013; US EPA, 2013). On a global basis, landfills have been estimated to emit 5-10% of an estimated annual global emission of 600 Tg CH_4 (Bogner et al., 2008). To reduce fugitive LFG emission and lower the global warming impact, LFG can be recovered for heat and electricity production. Research has increased on developing CH_4 mitigation technologies;

e.g. biocover has been applied to landfills without a gas extraction system (Barlaz et al., 2004; Scheutz et al., 2009a). Additionally, the European Union (EU) implemented a directive on landfill of waste, setting targets for phasing out landfill of organic materials and other combustible waste (EU, 1999). In 1997, Denmark, as one of the first countries in the EU, implemented a ban on landfilling of organic waste to reduce LFG generation.

1.2 Danish Waste Disposal Sites

According to the EU Council Directive 1999/31/EC on the landfilling of waste, most countries have set up national strategies for reducing biodegradable waste going to final disposal sites (EU, 1999, 2002). Landfills in Europe are about to be limited to inert materials, which are not biodegradable or combustible (waste not containing significant fractions of organic matter). Consequently, more and more EU member states (e.g. the Netherlands as of 1996, Denmark as of 1997, and Germany as of 2005) have banned landfilling of organic waste (Manfredi et al., 2010). In Europe, CH_4 emission from landfills have to be registered nationally if the landfill receives more than 10 ton of waste per day or has a capacity above 25,000 ton (CEC, 2006). If the emission is greater than 100 ton CH_4 annually, it should be reported to the European Pollutant Release and Transfer Register (E-PRTR) (CEC, 2006). Between 1990 and 2011, the reported CH_4 emission from Danish landfills has decreased 53%, and the estimated annual emission is 33.3 Gg CH_4, which corresponds to approximately 1% of the total landfill LFG emission from the EU-15 countries (EEA, 2013; Nielsen et al., 2013). There are 134 registered landfills in Denmark, and the Danish emission estimates are based on LFG generation model calculations using waste information as input. Only 52 of the landfills are included in the national reporting, of which 16 have gas recovery installed, which is subtracted in the CH_4 emission estimate (Nielsen et al., 2013).

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. Therefore, it is important for landfill operators to have a reliable guideline to measure, calculate, and estimate LFG emission for the PRTR reporting (Scheutz et al., 2009b). Over the years, a number of methods have been developed to measure fugitive CH_4 emission; likewise, various models are applied to estimate CH_4 generation from organic waste degradation (Jacobs and Scharff, 2001).

Due to difficulties in precisely monitoring whole site's CH_4 emission (Scheutz et al., 2011b), first order decay (FOD) models are currently widely used to estimate CH_4 generation and emission from landfills. FOD models are recommended by both researchers and state regulators for estimating CH_4 generation from waste degradation. Calibration of numerical values for primary parameters by site-specific data is reported to be essential for the application of FOD models (Amini et al., 2012; Börjesson et al., 2000; Sormunen et al., 2013). To precisely estimate LFG generation and emission at Danish landfills, this research was approached with the co-operation of four Danish landfills between 2010 and 2014.

1.3 Research Objective

The overall aim of this PhD project was to study CH_4 generation from low-organic waste disposed at Danish landfills and to provide new guidelines for estimating CH_4 emission from modern landfills to report to the E-PRTR. In this research, four categories of waste (street cleansing, mixed bulky, shredder, and sludge waste) with a low-organic content and temporarily stored combustible waste were sampled from four Danish landfills (AV Miljø, Audebo, Glatved and Odense) and characterized in the lab. FOD models are based on two primary parameters: a biochemical CH_4 potential (BMP) and an FOD rate constant (k) of the landfilled material (Faour et al., 2007; Cho et al., 2012). BMP and k values of all sampled waste were quantified and presented in Paper **I** and **II**, respectively. By applying site-specific data, CH_4 generation and emission estimated by original and revised FOD models were evaluated and compared in Paper **III**. Recent studies have established a tracer dispersion method as a reliable and accurate approach for quantifying whole-site fugitive landfill CH_4 emission (Scheutz et al., 2011a; Mønster et al., 2014a, 2014b). Field measurements of four Danish landfills were used to test the applicability of the revised Afvalzorg model, which was also presented in Paper **III**.

The structure of this thesis is, a) based on review of current FOD LFG generation models, their applicability for Danish landfills was identified (section 2); b) main categories of waste were sampled and analyzed in terms of physical characteristics and primary parameters (section 3); c) by using laboratory determined values, one FOD model (Afvalzorg) was revised, estimates of CH_4 generation and emission were presented and compared to field measurements (section 4); and d) last but not least, section 5 highlights the conclusions of the whole PhD study, and discusses issues and topics suitable for further scientific investigation.

2 First Order Decay Models

The MSW degradation and LFG generation is affected by many factors including, among others, the amount of waste disposed, waste composition, moisture content, temperature, and landfill operation (Christensen, 2011). Therefore, it is very difficult to estimate this process by deterministic mathematical approaches. Although several investigators highlighted their achievements in recent years, advanced models are still highly uncertain, because they were based on the stochastic method, e.g. the Monte Carlo method (Zacharof and Butler, 2004) or the fuzzy synthetic evaluation method (Garg et al., 2006), both of which lack realistic data support. Today, numerical approaches based on decay models (including zero, first, and second-order approaches) are still popular. However, second-order models are not commonly used because the required parameters in each model are often so uncertain that they negatively affect the accuracy of the model outcomes (Tintner et al., 2012). Likewise, zero-order models do not reflect the biological LFG generation processes (Amini et al., 2012). Because of these limitations, simplified approaches based on first order decay (FOD) of organic waste are widely used for research and industrial purposes (Scharff and Jacob, 2006; Weitz et al., 2008), and are officially regulated as the methodology for LFG emission estimation (CEC, 2006; IPCC, 2006; US EPA, 2005).

2.1 Formulas and Key Parameters

The FOD model assumes that the degradable organic carbon (DOC) in waste decays by following the first order reaction kinetics as shown in Eq.1.

$$N_t = N_0 \cdot e^{-kt} \qquad \text{(Eq. 1)}$$

where N_t is the quantity (kg) of DOC after a period of time (t); N_0 is the initial quantity (kg) of DOC (i.e., when t = 0); t is the organic carbon (OC) degradation time (yr), and k is the FOD rate constant (yr^{-1}).

By assuming a certain amount of degraded OC in any kind of waste would generate constant CH_4, Eq. 2 could be calculated based on the derivation of t in Eq. 1.

$$\alpha_t = \delta \cdot \frac{d(N_0 - N_t)}{dt} \qquad \text{(Eq. 2)}$$

$$\alpha_t = \delta \cdot N_0 \cdot k \cdot e^{-kt} \quad \text{(Eq. 3)}$$

where α_t is the annual CH_4 generation (kg CH_4 yr^{-1}); δ is the dissimilation factor, which equals to the ratio between CH_4 generation and degraded OC. In most cases, degraded OC in waste generates LFG with equal fractions of CH_4 and CO_2 (Cavaleiro et al., 2013; Elfadel et al., 1996). Only material including substantial amounts of fat or oil can generate gas with substantially more than 50% CH_4. Therefore, in most FOD models, δ is calculated based on Eq. 4 and 5. Under the Ideal Gas Law, δ is sometimes also presented as 0.933 m^3 CH_4 or 1.87 m^3 LFG per kg C (Scharff and Jacob, 2006).

$$C \rightarrow \frac{1}{2}CH_4 + \frac{1}{2}CO_2 \quad \text{(Eq. 4)}$$

$$\delta = 50\% \cdot 16/12 \quad \text{(Eq. 5)}$$

where 16 and 12 are the molar masses of CH_4 and carbon, respectively. In most FOD LFG generation models, $\delta \times N_0$ is calculated based on Eq. 6.

$$\delta \cdot N_0 = W \cdot L_0 \quad \text{(Eq. 6)}$$

where W is the total raw weight of disposed waste in the landfill (ton), and L_0 is the BMP (kg CH_4 ton^{-1} waste, wet weight). Since the amount of disposed waste (A) is always recorded by the landfill operators, the BMP (L_0) is an essential parameter in most FOD models (Cho et al., 2012).

Based on the integration of Eq. 1, the FOD rate constant (k, yr^{-1}) could be calculated in Eq. 7.

$$k = -\ln{(N_t/N_0)}/t \quad \text{(Eq. 7)}$$

When N_t is 50% of N_0, the corresponding time is defined as half-life time ($t_{½}$, yr), as shown in Eq. 8.

$$k = -\ln(50\%)/t_{½} \quad \text{(Eq. 8)}$$

Assuming that the DOC in the waste material could be entirely converted to CH_4 and CO_2 with equal fractions during a long period of time (presented as t_∞), the theoretical CH_4 potential (kg) can be determined by Eq. 9.

$$\text{Theo. CH}_4 \text{ Poten.} (t_\infty) = N_0 \cdot 50\% \cdot 16/12 \qquad \text{(Eq. 9)}$$

Assuming duration of a certain period of time (presented as t_1, yr), the actual cumulative CH_4 generation (kg) can be determined by 10.

$$\text{Cumu. CH}_4 \, (t_1) = (N_t - N_0) \cdot 50\% \cdot 16/12 \qquad \text{(Eq. 10)}$$

Therefore the decay rate constant (k, yr^{-1}) can be calculated by Eq. 11 and 12 (De Gioannis et al., 2009; De la Cruz and Barlaz, 2010).

$$k = -\ln[\text{Theo. CH}_4 \text{ Poten.} (t_\infty) - \text{Cumu. CH}_4 \, (t_1)] / t_1 \qquad \text{(Eq. 11)}$$

$$k = -\ln[(W \cdot L_0) - \text{Cumu. CH}_4 \, (t_1)] / t_1 \qquad \text{(Eq. 12)}$$

The decay rate constant (k) is another primary parameter. Together with BMP, their values are significantly important for FOD models (Bogner and Matthews, 2003; Faour et al., 2007). A major challenge for precisely estimating of LFG generation is the high uncertainties of practical BMPs and k values when applying current FOD models to actual waste disposal sites (Amini et al., 2013).

2.2 Single and Multi-phase Models

In this research, various FOD LFG generation models were studied, as shown in Table 1 in terms of their default parameter values. The LandGEM, IPCC and Afvalzorg model were selected to estimate CH_4 generation based on actual waste data at Danish landfills (Paper **III**).

Table 1. Overview of various FOD models in terms of BMPs and k values.

FOD model	Country	Latest version	Waste/Landfill	BMP (kg CH^4 ton^{-1} waste)	k (yr^{-1})	Data resource	Reference
E-PRTR (Fr)	France	France	fast degradable	56 for MSW, sludge and yard waste; 28 for industrial, commercial and bio-chemical pre-treated waste	0.5	k values were determined based on field measurements in approximately 50 French landfills	ADEME, 2003; Oonk, 2010; Scharff and Jacob, 2006
			moderate degradable		0.1		
			slow degradable		0.04		
LandGEM [a]	US	2005	wet area landfill	69	0.7	k values were determined by US Clean Air Act 1990.	US EPA, 1990, 2005
			conventional landfill	72 / 122	0.05		
			arid area landfill		0.02		
IPCC [b]	International	2011	Food	100	0.185	default values were determined by international experts and cited from various literature	IPCC, 2006, 2011
			Garden	133	0.1		
			paper/wood	267	0.06		
			Textile	160	0.06		
			Sludge	33	0.185		
			Industrial	67	0.09		

a. The default value of 122 kg CH_4 ton^{-1} waste was based on requirements for U.S. landfills as specified in the Clean Air Act. The default value of 72 kg CH_4 ton^{-1} waste was based on results of an inventory by the US EPA In this research. In this research, BMP = 122 kg CH_4 ton^{-1} waste and k = 0.05 yr^{-1} were used for Danish landfills.

b. The IPCC model defined four groups of k values applied to different climatic conditions. Default values for wet temperate climate were used for Danish landfills (as shown here).

Table 1 (continued). Overview of various FOD models in terms of BMPs and k values.

FOD model	Country	Latest version	Waste/Landfill	BMP (kg CH_4 ton_{-1} waste)	k (yr^{-1})	Data resource	Reference
GasSim	UK	2012	incinerator ash	3	fast degradable 0.116 moderate degradable 0.076 slow degradable 0.046	k values were determined based on water satura-tion level of different waste categories	Arnold and Yang, 2005; GasSim, 2012; Gregory, 1999; Scharff and Jacob, 2006
			Sludge	24			
			composted organic material	34			
			civic amenity	47			
			domestic (household)	79			
			Commercial	121			
Afvalzorg	Holland	2014	contaminated soil	3	fast degradable 0.187 moderate degradable 0.099 slow degradable 0.03	k values were determined based on IPCC model default values and field measurements in Dutch landfills	Afvalzorg, 2014; Scheutz et al., 2011a; Scharff and Jacobs, 2006
			C&D waste	11			
			Commercial	56			
			Shredder	13			
			street cleansing	19			
			mixed bulky	80			
			Sludge	25			

Depending on whether various k values were defined for different waste categories, there are two major kinds, multi- and single-phase FOD models. The single-phase model has no function for distinguishing various decay rates between different waste categories. The LandGEM model, developed by the US EPA, also only defines one BMP value for all waste categories. It is intended to model the LFG generation from traditional MSW disposal sites with relative homogeneous waste fractions. Therefore, it only requires the users to input the total annual weight of disposed waste for modeling. Although the E-PRTR (Fr) model defines three k values, it only applies one decay rate for the fast, moderate and slow degradable period at 0, 5 and 10 years after landfilling, respectively. In the old (2007) version of the IPCC model, there was a single-phase sheet named IPCCb, which applied only one k value for each selected climate type (one of dry temperate, wet temperate, dry tropical, and moist and wet tropical) to both MSW and the industrial waste.

The IPCC, GasSim and Afvalzog model are multi-phase models, which operate with a number of more detailed waste categories (Mata-Alvarez et al., 2011; Thompson et al., 2009). In the new (2011) version of the IPCC model, there is only one version—named IPCCa in 2007, developed by an international team of experts involved in the International Panel of Climate Change (IPCC)—which is to give guidance to national authorities in the quantification of CH_4 generation from all landfills at a national level. Therefore, it defined waste categories as traditional MSW such as food, garden, paper, and other high-organic content fractions. The GasSim model was developed for the Environment Agency of England and Wales and does not provide the complete set of equations in the software program.

The Afvalzorg model, developed by a Dutch waste management company, holds datasets for different low-organic waste fractions, such as soil (contaminated with oil and other residues), construction and demolition (C&D) waste, commercial waste, shredder waste (shredded pieces of abandoned vehicles or machines), street cleansing waste (residues from street cleansing), mixed bulky waste (i.e. coarse household waste), and sludge waste. Above all, the shredder, street cleansing, mixed bulky, and sludge waste are also main fractions of disposed organic waste at current Danish landfills.

Because different types of waste contain different fractions of organic matter that degrade at different rates, for each waste category in the Afvalzorg model, various fractions of DOC is defined as fast, moderate, slow degradable and inert, respectively, with corresponding k values of 0.187, 0.099, 0.030, and 0 yr^{-1} (Table 1). For each DOC fraction in each waste category, the LFG generation is calculated separately based on FOD equation (Scharff and Jacob, 2006). In the old version (before 2013), a minimum and a maximum amount of organic matter was attributed to each fraction of each waste category, which resulted in minimum and maximum annual LFG generation for model estimates. Since March 2014, the new version of Afvalzorg multi-phase model calculates one result for each year (Afvalzorg, 2014).

2.3 Application of Original FOD Models

2.3.1 Translation of Waste Data

Four Danish landfills (AV Miljø, Audebo, Glatved and Odense), geographically distributed throughout Denmark, were selected to represent modern landfill scenarios. All the landfills, which are described in more detail in Paper **III**, Paper **I** and Mønster et al. (2014b) (the Glatved landfill was also presented under the name of Reno Djurs), were still in service and at that time only received low-organic waste fractions for permanent disposal. They had different ages and provided waste data from various beginnings of disposal until year 2012. Two sites, AV Miljø and Audebo, have special cells for combustible waste such as paper, plastic, and wood. The combustible waste is stored temporarily before being sent to incineration plants in the winter for energy recovery. Original data about the deposited waste categories are similar at all four sites, including shredder waste, dewatered sludge, mixed bulky waste, contaminated soil, and C&D waste. Only one landfill, Audebo, does not receive any shredder waste. To estimate CH_4 generation by FOD models (multi-phase), users are required to input disposed weight for each specific model-defined waste category. According to landfill operators' information and the method developed by Scheutz et al. (2007), translation of landfill-recorded waste data into model-defined categories was carried out. Only one landfill, AV Miljø, was able to provide full waste data from its beginning of disposal (year 1989). For the other three landfills, estimated amounts of annual waste for the early disposal period were obtained by using the assumed waste density and the approximate volume of the covered landfill cells. Thereafter, the annual disposed amount for each waste category at the landfills was determined by assuming 1) a constant increasing rate of annual disposed waste amount, and 2) constant waste fractions according to each landfill's actual data over recent years. Detail information on translated waste data fitting the IPCC and Afvalzorg models can be found in the Supplemental Information in Paper **III**.

2.3.2 Comparison of Original Model Estimations

In Paper **III**, annual CH_4 generation at each landfill was estimated until year 2100 based on waste data from the beginning of disposal until year 2012, as shown in Fig. 1 (a)-(d), in which the left Y axis applies to the IPCC and Afvalzorg model and the right Y axis only applies to the LandGEM model estimates. For each model, the fraction of CH_4 in LFG was set as 50% and the CH_4 oxidation factor was set as 0. Cumulative CH_4 generation (k ton) and normalized results to the amount of disposed waste (kg CH_4 ton^{-1} waste, wet weight) until year 2020 and year 2100 were calculated and are shown in Table 2. Moreover, at each landfill, CH_4 generation from shredder, sludge, mixed bulky, and street cleansing waste was also estimated and presented respectively.

The LandGEM model estimated larger CH_4 generation than the other two models over the whole time period. Because of applying high BMP value (122 kg CH_4 ton^{-1} waste, wet weight) to disposed low-organic waste categories, the single-phase model resulted in significant overestimation. The IPCC model defined several fractions as industrial waste and plastic/inert waste, which had default BMP values of 67 and 0 kg CH_4 ton^{-1} waste, respectively. Therefore, the IPCC model estimated only 1/4-1/3 of the annual CH_4 generation estimated by the LandGEM model. In Denmark, landfills categorize disposed waste in more than 40 categories, approximately one third of which were defined as inert in the Afvalzorg model (Scheutz et al., 2007). At the AV Miljø and Odense landfill, where the largest disposed waste fractions were shredder, inert and contaminated soil, the Afvalzorg model estimated only approximately 10% of the annual CH_4 generation estimated by the LandGEM model until year 2020.

In Fig. 1, curves of the IPCC and the Afvalzorg estimations have a point of intersection geometrically, which indicates that the Afvalzorg model estimated a larger result of annual CH_4 generation in a later period. It was because larger k values are used in the IPCC model, which means that the organic matter will degrade faster and result in faster CH_4 generation in the IPCC model in comparison to the Afvalzorg model (Tolaymat et al., 2010; Wang et al., 2013). By using larger default k values, the IPCC model would show an accelerated process of CH_4 generation. E.g. at the Glatved landfill, weight fractions of mixed bulky and sludge waste were 13.2% and 18.3%, respectively, which for both fractions were the highest among the four landfills. For sludge waste, the k value was 0.185 yr^{-1} in the IPCC, but was only 0.075 yr^{-1} in the Afvalzorg model. Moreover, mixed bulky waste was defined as MSW with larger BMPs and k values in the IPCC model. In Fig 1. (c), it can be seen that the IPCC and Afvalzorg curves crossed each other in 2009, which was also earlier than in other figures. Consequently, default k values would affect CH_4 generation rates in FOD model estimations. This is important for landfill operators if FOD models were used to estimate CH_4 generation amounts in a certain time period (Themelis and Ulloa, 2007; Zietsman et al., 2008). E.g. if the FOD model was used for designing an LFG extraction system in the early period, or estimating fugitive CH_4 emissions for the landfill's aftercare, proper estimates of k values would reduce the uncertainties significantly.

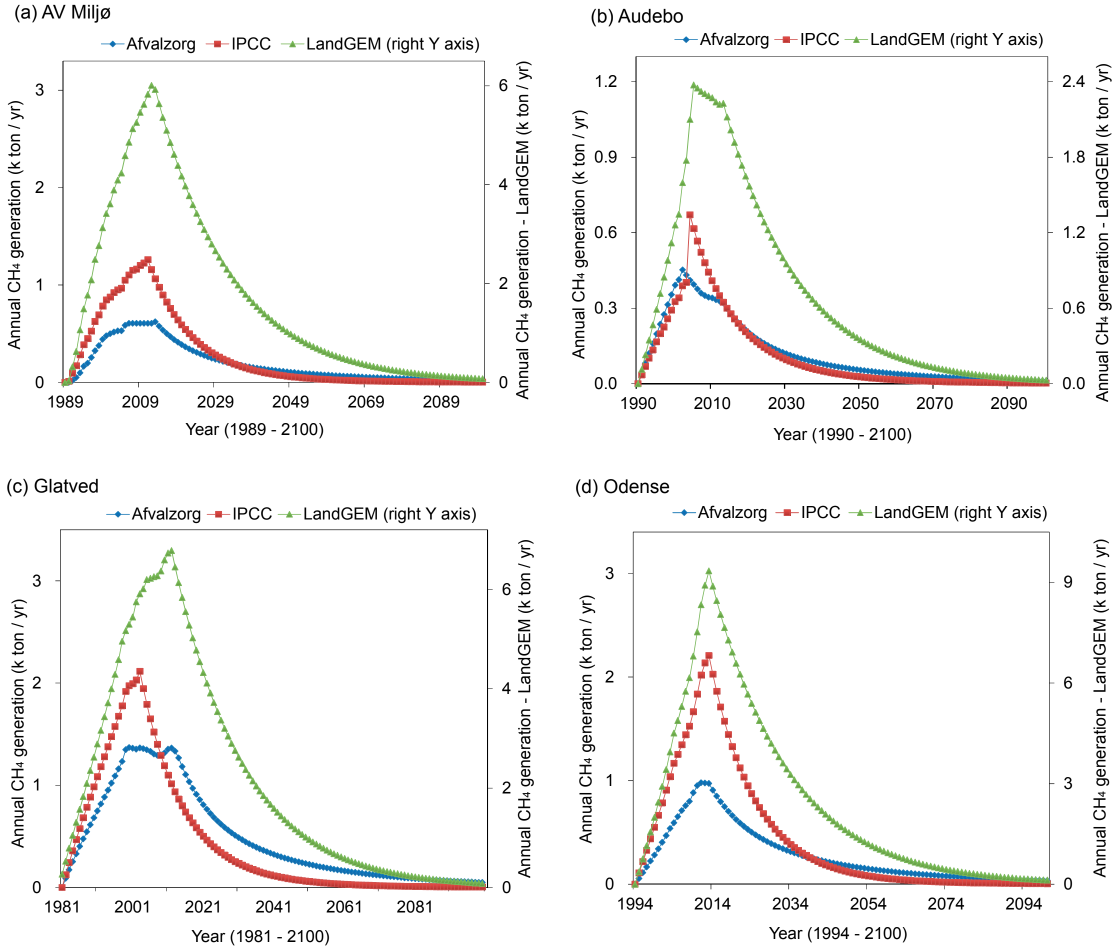


Figure 1. Annual CH_4 generation rates as functions of time at the (a) AV Miljø; (b) Audebo; (c) Glatved; and d) Odense landfill, estimated by the original Afvalzorg, IPCC and LandGEM models with default parameter values (the right Y axis only applies to the LandGEM curve in all four figures).

Table 2. Model estimated cumulative CH_4 generation (k ton) until 2020 and 2100, numbers given parenthetically were normalized CH_4 generation (kg CH_4 ton^{-1} waste, wet weight), which was calculated by using whole-site CH_4 generation divided by the total disposed waste amount (wet weight).

Landfill	Waste	Afvalzorg (original)		LandGEM		IPCC	
		2020	2100	2020	2100	2020	2100
AV Miljø	whole-site generation	13	22	118	198	24	31
	(total waste 1.6 * 10^6 ton)	(8.1)	(13)	(72)	(121)	(14)	(19)
	street cleansing [a]	0.76	1.1	5.5	7.7	1.9	2.1
Audebo	whole-site generation	8.8	13	47	77	9.4	12
	(total waste 6.4 * 10^5 ton)	(14)	(21)	(74)	(121)	(15)	(19)
	mixed bulky [b]	0.39	0.63	4.2	6.4	1.9	2.6
Glatved	whole-site generation	39	58	174	261	45	52
	(total waste 2.2 * 10^6 ton)	(18)	(26)	(79)	(118)	(21)	(24)
	shredder [c]	0.77	1.8	2.1	3.5	1.3	2.6
Odense	whole-site generation	16	30	140	266	33	47
	(total waste 2.2 * 10^6 ton)	(7.5)	(14)	(65)	(122)	(15)	(22)
	sludge [d]	0.83	1.3	2.8	4.2	0.78	1.1

a. The weight fraction of street cleansing waste at AV Miljø is 4.9%. In the IPCC model, it was set as garden and inert waste with an equal fraction.

b. The weight fraction of mixed bulky waste at Audebo is 13.1%. In the IPCC model, it was set as MSW with default sub-category fractions.

c. The weight fraction of shredder waste at Glatved is 9.2%. In the IPCC model, it was set as industrial waste.

d. The weight fraction of sludge waste at Odense is 3.4%. In the IPCC model, it was set as sludge waste.

3 Characterization of Low-organic Waste

3.1 Waste Sampling and Characterizing

3.1.1 Materials and Methods

From four Danish landfills, samples of shredder (consisting mainly of metals, plastic, rubber, wood, and foam), sludge (dewatered excess activated sludge from sewage treatment plants), mixed bulky, street cleansing and temporary stored combustible waste were collected and described in detail in Paper **I**. For each sample, approximately 300 kg of wet waste was collected as raw material, either from same-day-deposited waste piles or waste transporting trucks when they arrived at the site. When sampling sludge and combustible waste, the top or cover layer was removed to avoid unrepresentativeness. The combustible waste was covered daily with wood pieces and soil at AV Miljø landfill, or packed in large plastic bags at Audebo landfill by the landfill operators. Therefore, samples of combustible waste were quite dry when deposited at the landfills. Glatved and Odense landfills do not dispose street cleansing waste in separate cells; therefore, samples were obtained only from the AV Miljø landfill. Over a period of approximately 24 days in October 2011, 14 waste samples in total were obtained, as shown in Table 3. The waste was collected in plastic bags (100 L, 0.07 mm in thickness) and placed in sealed steel drums (115 L and 60 L) for transportation. All waste samples were kept at 4 ^{o}C in the dark before pre-treatment.

Within seven days after sampling, mass and size reduction of the samples was approached. Except for sludge waste, each sample was spread out on a large plastic sheet placed on the floor and was mixed manually. Then, using a grid method (Jansen et al., 2004; Laine-Ylijoki et al., 2009), about 50% of the samples were retained for a large-scale incubation test aimed at determining k values; about 20% of the sample was retained and then shredded in a cutter mill machine (SM 2000, Retsch). About 5-6 kg of samples for analysis of total solid (TS) and volatile solids (VS) were taken. About 20% of the machine's outcome was collected using the same grid method and then dried at 80 ^{o}C until a constant weight was achieved. The dry sample was afterwards milled in a small hammer mill (Macsa 300, Eriez) with a 2 mm screen. The material was thoroughly mixed for BMP assay and the finely grained sample was smashed into powder manually with a mortar and pestle for analyzing total carbon (TC) and total organic carbon (TOC).

Waste samples were characterized in terms of TS, VS, TC, and TOC following standard procedure. The moisture content was measured by oven-drying 2-4 kg of the samples at 105 ^{o}C for at least 24 h until a constant weight was achieved. Ash from each sample was obtained by heating the dry samples in an oven at 550 ^{o}C for at least 2 h until no further weight loss was obtained. All experiments were run in triplicate. Dry powder from each sample was used to test TC and TOC in solid state using a LECO CS-200 oven. When testing TOC, 2 ml 5% H_2SO_3 solution was added to approximately 0.5 g of powder to remove inorganic carbon. Each experiment was run in triplicate and the systemic error was ± 2%. All results of TS, VS, TC, and TOC are presented as mass fraction of wet waste (%) in Table 3.

Table 3. Waste characterization in terms of TS, VS, TC, and TOC (%, kg/kg waste, wet weight).

Waste	Landfill	TS	VS	TC	TOC
Combustible	AV Miljø	84	70	32	28
	Audebo	86	69	29	26
Shredder	AV Miljø	87	30	12	10
	Glatved	86	31	12	10
	Odense	90	29	13	11
Sludge	AV Miljø	20	17	11	10
	Glatved	18	15	9	9
	Odense	19	17	10	9
	Audebo	21	19	12	11
Mixed bulky	AV Miljø	82	7	4	3
	Glatved	81	7	4	3
	Odense	80	8	5	4
	Audebo	84	8	4	4
Street cleansing	AV Miljø	82	3	2	1

3.1.2 Results and Discussion

Table 3 shows the average results for TS, VS, TC and TOC of all the waste samples obtained from triplicate experiments with a relative error less than ± 5%. In general, samples showed lower TOC values than traditional MSW fractions waste (Bolan et al., 2013; De la Cruz et al., 2013; Jones et al., 2013; Yang et al., 2013). Disposed sludge waste at Danish landfills was dehydrated and had a much lower moisture content (80-82%, calculated from TS results). Traditional sludge waste deposited at MSW landfills has a moisture level of 90-95% (Astals et al., 2013; Kim and Townsend, 2012; Seng et al., 2010). The shredder and sludge waste showed similar TC and TOC values, but different VS values because of their lower moisture contents and various characteristics of the dry fractions. Combustible and mixed bulky waste samples contained the highest and the lowest carbon fractions, which were 29-32% and 4-5%, respectively. Theoretically, the DOC value of waste must be lower than the TOC value because some fractions such as the fossil carbon is non-degradable and results in carbon storage at landfills (De la Cruz et al., 2013; Law et al., 2013). The default DOC values in the Afvalzorg and IPCC model, for instance, are 15-40% and 10-20% for MSW waste, respectively (Afvalzorg, 2014; IPCC, 2011). Single-phase models use default DOC values of 8% and 11-18% in the E-PRTR (Fr) and LandGEM models (ADEME, 2003; EU EPA, 2005). However, the TC and TOC values of mixed bulky waste at Danish landfills are only 3-5% as tested, which was even lower. Therefore, these default DOC values in FOD models were obviously not suitable for Danish LFG generation estimation.

3.2 Determining the BMPs and k values of Waste Samples

By incubating pre-treated waste samples, lab scale experiments were approached to determine the BMPs and k values. The set-up of experiments and determined results were described in detail in Paper **I** and **II**, respectively.

3.2.1 Materials and Methods

The BMP assay was conducted in triplicate by following the method developed by Hansen et al. (2004). Sealed glass bottles were used as reactors, full flushed with N_2 and placed in the incubator at 55 ^oC for over nine weeks. Thermophilically (55 ^oC) digested material from a full-scale biogas plant, located at Vegger (Nibe, Denmark) was used as inoculum. The Vegger biogas plant co-digests mainly cattle manure (80%) together with different wastes from the food industry (20%). The organic load (weight of TOC in substrate per unit volume of inoculum) was set as 0.5 g OC L^{-1} for mixed bulky waste to avoid inhibition (Scheutz et al., 2007), and as 2 g OC L^{-1} for other samples. Blank and control experiments with the same set up (starting and running date, inoculum, and reactor volume) were also performed in triplicate.

Blank experiments, which contained only water and inoculum, were used to measure CH_4 generation originating from the inoculum alone, and to indicate the detection limit of BMP in this method. Control experiments, which also contained standard substrate, were used to test the quality of the inoculum (i.e. to address the variation among triplicates), and to indicate if the incubation method for determining BMP was functioning as expected. In this method, Avicel (Fluka, Sigma-Aldrich, Vallensbæk Strand, Denmark), which is a microcrystalline cellulose powder, was used as the standard substrate in the control experiments. The CH_4 concentration in reactors was monitored by gas chromatograph (Shimadzu GC 14A) 2-3 times per week. Based on the difference of CH_4 concentration before and after release of excess gas from the reactors, the generated CH_4 amount was calculated. The experiments stopped when cumulative CH_4 generation curves (changing with time) asymptotically approaching to a constant level and calculated BMP results were presented as kg CH_4 ton^{-1} waste (wet weight).

The k values of sampled waste fractions were determined by large-scale and long-term (405 days) anaerobic degradation experiments. Steel drums with airtight lids (Scandrums, Søndersø, Denmark) were used as reactors and full flushed with N_2. To reduce sampling errors caused by heterogeneity of the waste samples, 115 L drums were used for combustible and mixed bulky waste; 60 L drums for shredder waste; and 12 L drums for sludge and street cleansing waste. The moisture content of the waste material (except for sludge) was adjusted to 40% (based on dry matter) by adding water after placement in the reactors. The control of water content was based on average moisture level of Danish landfills (Kjeldsen and Beaven, 2011) and was intended to avoid either inhibition or acceleration (due to low or high water content, respectively). All drums were painted to prevent corrosion. The drums were placed upside down in a large water pool to prevent air diffusion. The generated gas was collected in 20 L SKC Tedlar Sampling Bags (SKC Inc., Eighty Four, PA, US). Volume of excess gas from reactors was determined by timing the emptying of gas sample bags using a Fluid Metering Inc.

laboratory pump set (QG, Fluid Metering Inc., Syosset, NY, US). Once a week, a 5 mL gas sample was extracted by a syringe and injected into evacuated glass vials fitted with pierceable rubber septa (Exetainer Vail, Labco Ltd, Lampeter, UK). The gas composition was determined by a 490-PRO Micro GC (Agilent Technologies Denmark Aps, Glostrup, Denmark) equipped with two columns (PoraPLOT Q PLOT, 0.25 mm, 10 m, and Molecular Sieve 5A PLOT, 0.25 mm, 20 m) and used for analyzing gas concentrations. The detection limit of the Micro GC was 0.1% for CH_4 based on a 5 mL injection volume. For the whole experimental period, CH_4 generation curves (changing with time) of all waste samples showed a linearly increasing trend. Based on incubated waste weight, the BMPs and monitored CH_4 generation amounts, k values and half-life time ($t_{½}$, yr^{-1}) of each waste fraction were calculated by Eq. 8 and 12.

3.2.2 Results and Discussion

CH_4 generation curves were presented in Paper **I** and **II**, respectively, as the results of the incubation experiments determining the BMPs and k values. Curves of the mixed bulky waste samples are shown in Fig. 2 (a) and (b) as an example. Calculated results of the BMPs and k values for all waste samples are shown in Table 4.

In general, curves within the same waste category showed similar trends over time. In the BMP assay, CH_4 generation from the blank experiments was lower than those from control and other incubation experiments with waste. Curves of the blank and control experiments have the same trend as other waste samples. No unexpected changes were observed during the whole CH_4 generation process. Over 77 days, the inoculum in blank experiments generated 606 g CH_4, and by subtracting this, the mixed bulky waste samples generated 38-53 g CH_4. The detection limit was 23g CH_4 in this assay. If normalizing the CH_4 generation amount by the wet weight of substrate, 5.4-7.0 kg CH_4 ton^{-1} waste was calculated as the BMPs for mixed bulky waste at Danish landfills. In comparison to default values in current FOD models as listed in Table 1, the mixed bulky waste shows much lower BMP values, which is also quite special and different from traditional MSW fractions. If curves in Fig. 2 (a) were considered as linear trends in the first 55 days, rates of 67 mg CH_4 kg^{-1} waste day^{-1} could be fitted after subtraction of the blank experiments. As presented in Paper **I**, incubation time for mixed bulky waste was also longer than others, which indicated that the CH_4 generation from such low-organic waste categories would be a slow and long-term process.

Fig. 2 (b) shows the cumulative CH_4 generation curves with average result of duplicate experiments. The mixed bulky waste samples show constant gas generation trends over the whole period, and the correlation coefficient is no less than 0.97 across all linear regression curves. It is reasonable since low-organic waste degradation is a long-term process that normally lasts for decades. Therefore, it was more reliable to determine the CH_4 generation rate based on first-order rather than zero-order decay equations (Amini et al., 2012; Scheutz et al., 2011a). By day 405, CH_4 was still being generated at constant rates in all reactors. The normalized CH_4 generation rates were in the range of 0.2-0.4 mg CH_4 kg^{-1} waste day^{-1}, which is much lower than the BMP assay but is comparable to the results reported by Scheutz et al. (2011a). Although the trend of CH_4 generation curves was different from that reported in the literature (De Gioannis et al., 2009; De la Cruz and Barlaz, 2010), it is most likely due to the difference between the tested waste fractions and the incubation conditions. Because of a lower BMP content in our waste samples, a longer biodegradation time is expected. Furthermore, to simulate an actual landfilling environment, our reactors were run under less-optimal conditions in comparison to the reported studies, where they used small-scale reactors incubated under optimal conditions (e.g. controlled temperature, leachate circulation, adjusted NH_3-N and PO_4-P, etc.), which would accelerate the degradation process (Eleazer et al., 1997; Rhew and Barlaz, 1995). In the incubation experiments determining k values, no inoculum was added. Therefore, results were more realistic to simulating waste degradation and LFG generation process at Danish landfills receiving only low-organic waste.

As shown in Table 4, k values of mixed bulky waste was 0.013-0.014 yr^{-1}, which was lower than all the default k values provided in the FOD models listed in Table 1. Applying current FOD models directly to landfills receiving low-organic waste categories would thus result in an overestimation of the CH_4 generation for the early disposal period. A similar conclusion was reported in the literature, e.g. an overestimation by the LandGEM model was observed by Amini et al. (2013), Lamborn (2012) and Thompson et al. (2009). For waste samples at AV Miljø, multi-phase models (IPCC, GasSim, and Afvalzorg) also showed higher estimates of CH_4 generation in comparison to measured results based on lab research (Scheutz et al., 2011a). Therefore, it is necessary to calibrate key parameters such as the BMPs and k values of local waste categories with site-specific values when applying current FOD models to low-organic waste landfill scenarios.

As shown in Table 4, sludge waste samples show relatively higher BMPs and k values in comparison to other waste fraction. The lab-determined BMP values of Danish landfill sludge waste were actually higher than the default values (Table 1) in the IPCC and Afvalzorg model. This is due to the dehydration process, which would enhance the VS and TOC content (weight fraction) as well as the BMP values. The lab-determined k values were close to the default values reported for fast degradable waste categories in the IPCC model and the Afvalzorg model. It was most likely due to higher contents of active microorganisms and easily degradable organic matter in the sludge waste (Yan et al., 2013).

The street cleansing waste showed a k value of 0.078 yr^{-1}. As shown in Table 1, in the Afvalzorg model 11, 21, 35 and 33% of DOC in street cleansing waste was defined as fast, moderate, slow degradable, and inert, respectively, and their corresponding k values were 0.19, 0.099, 0.030, and 0 yr^{-1}. If calculating a weighted average k value based on Afvalzorg default fractions for DOC and k values, the result is 0.077 yr^{-1}, which is very similar to our results. Because it is difficult to determine k values for individual DOC fractions within one waste category, and similar DOC fraction in different waste could show various degradation rates (e.g. cellulose in wood waste has a much slower rate of dissolution and hydrolysis than in paper waste due to the composite structure) (Zhao et al., 2014), it is more practical to use only one k value for each category of low-organic waste when estimating the CH_4 generation, as well as for estimation of LFG generation at a whole landfill.

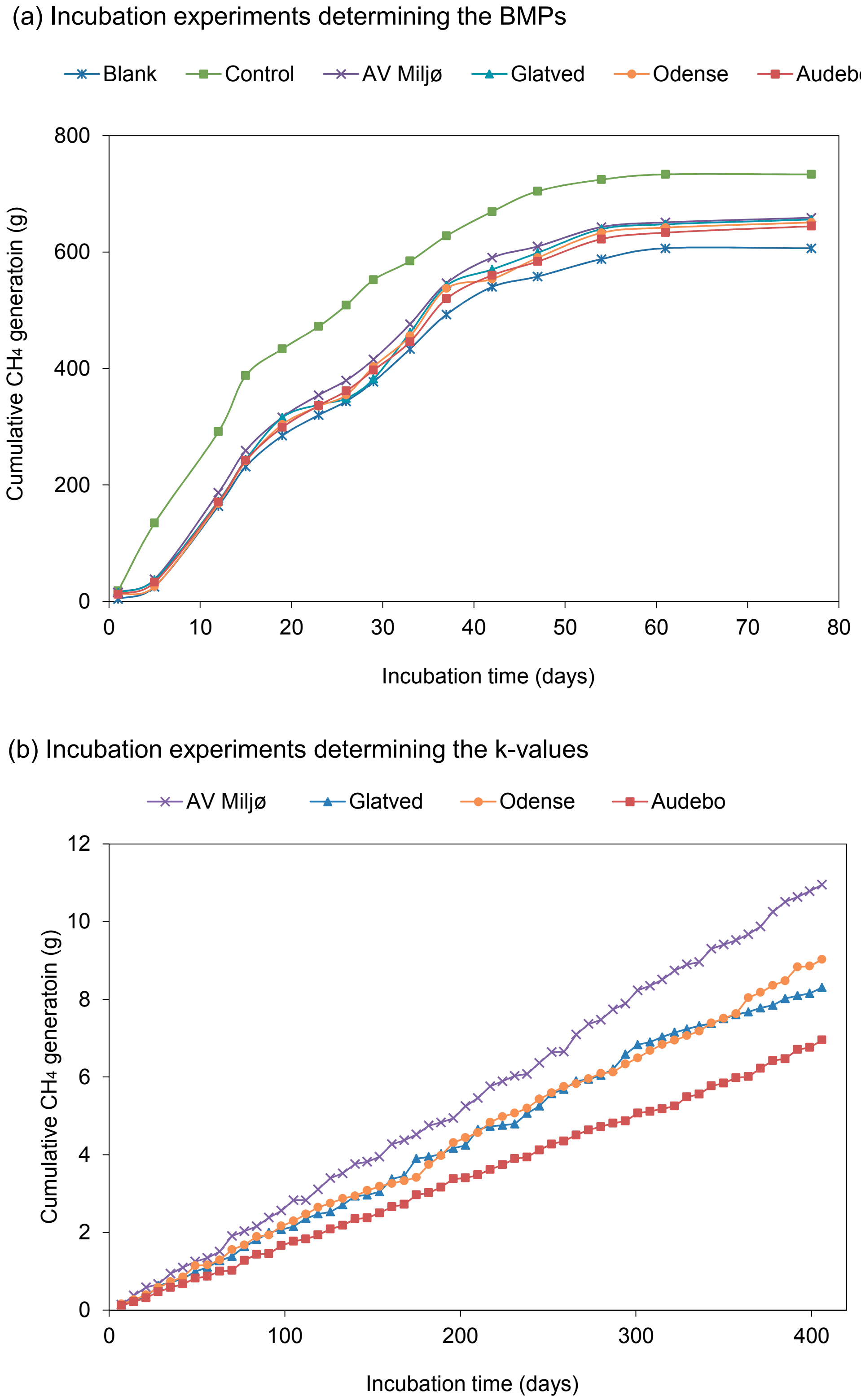


Figure 2. CH_4 generation curves for the mixed bulky waste samples from four Danish landfills during the incubation experiments determining (a) the BMPs and (b) the k values.

Table 4. The lab-determined BMPs and k values of waste samples.

Waste	Landfill	BMP (kg CH_4 ton^{-1} waste, wet weight) [a]	k value (yr^{-1})	$t_{½}$ (yr)
Combustible	AV Miljø	117 (1.7)	0.024	28.5
	Audebo	107 (2.6)	0.025	28.1
Shredder	AV Miljø	6.2 (1.9)	0.017	40.0
	Glatved	7.3 (2.6)	0.017	40.1
	Odense	9.1 (2.2)	0.016	41.9
Sludge	AV Miljø	63.7 (2.5)	0.189	3.7
	Glatved	59.6 (2.0)	0.187	3.7
	Odense	51.8 (1.9)	0.156	4.4
	Audebo	69.6 (2.0)	0.163	4.4
Mixed bulky	AV Miljø	7.0 (1.1)	0.014	47.7
	Glatved	5.9 (1.3)	0.013	51.9
	Odense	6.6 (1.2)	0.013	52.4
	Audebo	5.4 (1.1)	0.013	54.2
Street cleansing	AV Miljø	7.3 (1.6)	0.078	8.9

a. Digits given parenthetically present the relative error (%) determined based on triplicate batch experiments.

4 Methane Generation and Emissions at Danish Landfills

4.1 Methane Generation Estimated by Revised Afvalzorg

In Paper **III**, the Afvalzorg model was revised by using site-specific BMPs and k values (Table 4) instead of the default values for shredder, sludge, mixed bulky and street cleansing waste. At each landfill, CH_4 generation from the above four categories was estimated again. For other waste categories, the default parameter values in the original Afvalzorg model were used. By summing up the above two parts, whole-site CH_4 generation was calculated. Consequently, CH_4 generation curves were updated as shown in Fig. 3. In comparison to the original model outcomes of both whole-site and specific waste categories (Table 2), the applicability of calibrated BMPs and k values were evaluated.

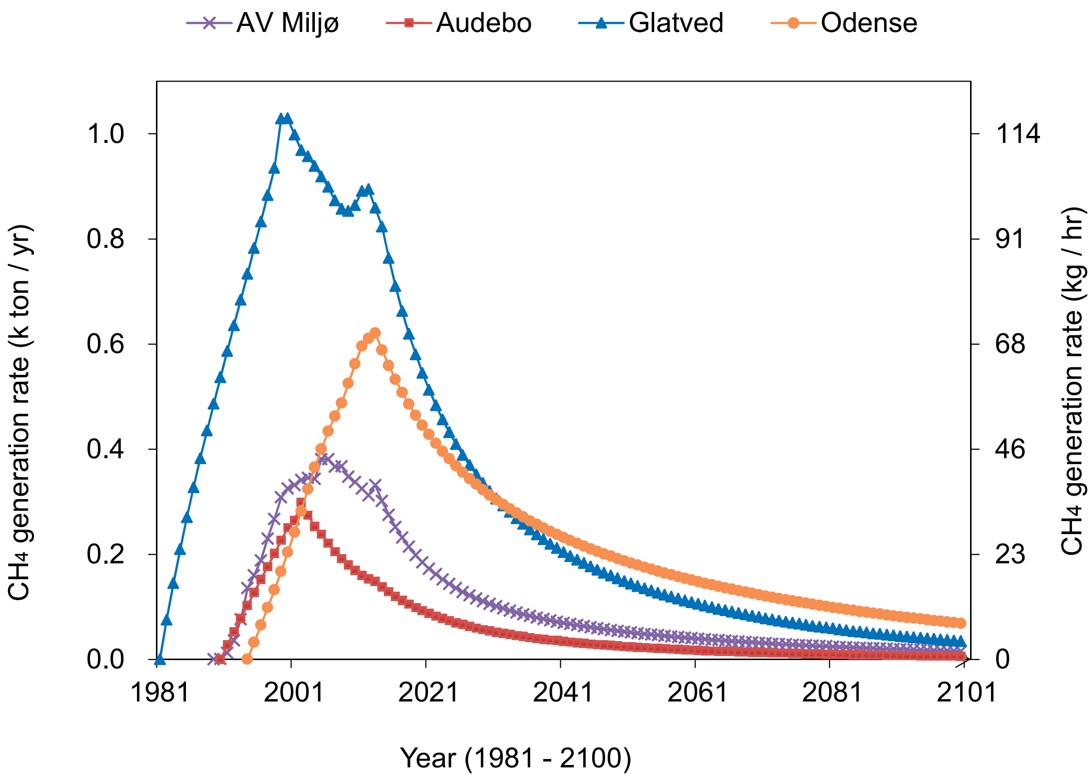


Figure 3. CH_4 generation rates as functions of time estimated by the revised Afvalzorg model using site-specific waste input data (both Y axes apply to all curves).

Curves in Fig. 3 show similar trends as the original Afvalzorg model estimations in Fig. 1, but smaller annual CH_4 generation rates could be observed due to the revised lower BMPs and k values. The Audebo landfill showed the lowest estimation results due to a relatively low total disposed mass (about $6.4 * 10^5$ ton) in comparison to the Glatved and Odense landfills ($2.2 * 10^6$ ton). However, those two landfills also showed quite different curves because the fractions of disposed shredder waste were very different (9.2% at Glatved and 60.3% at Odense, respectively). Shredder waste consisting mainly of metals, plastic, rubber, wood, and foam, had relatively low BMPs and k values, as listed in Table 4. Besides, at the Odense landfill, sludge waste was only 3% of the total disposed waste mass, whereas at the Glatved landfill, sludge waste constituted about 18% of the total disposed waste mass. Fig. 3 also shows that the AV Miljø and Glatved landfill CH_4 generation curves have a relatively larger variation over time compared with the other two landfills. This was mainly due to sudden changes of waste composition (see Supplemental Information in Paper **III**). Additionally, it can be seen that in Fig. 1 the LandGEM and IPCC model showed more similar curves to each other, while the Afvalzorg model showed more various trends with time. In conclusion, the Afvalzorg model can better distinguish the influence of various waste categories rather than those only affected by the total disposed waste amount. This is consistent with the findings of Scharff and Jacobs (2006) when applying the Afvalzorg model to Dutch landfills, which had similar waste composition to those in Denmark.

4.2 Aggregated Methane Emissions at Danish landfills

4.2.1 Materials and Methods

With the assumption of a constant CH_4 density, a landfill CH_4 mass flow balance can be expressed volumetrically, as shown in Eq. 13 (Jacobs and Scharff, 2001; Amini et al., 2013).

$$A = G - R - O \qquad \text{(Eq. 13)}$$

where, A is aggregated fugitive CH_4 emission, G is CH_4 generation estimated by FOD models, R is the recovered CH_4 by the LFG extraction system, and O is oxidized CH_4 when crossing the landfill covering soil. The unit for all parameters in Eq. 13 is kg/hr.

In this study, G was estimated by the revised Afvalzorg model using site-specific parameter values. According to the information provided by four landfill operators, an LFG extraction system was operational at only two landfills, Glatved and Odense, with an average extraction capacity of 35 and 43 kg/hr, respectively. In general, a default fraction of 10% for O (as shown in Eq. 14) is recommended for thin landfill cover soils by state regulators (IPCC, 2000; DEA, 2001; US EPA, 2004). It is also widely applied by researchers when there is a lack of information (Aronica et al., 2009; Kim and Yi, 2009; Di Bella et al., 2011). Consequently, A was calculated by Eq. 15.

$$O = (G - R) \times 10\% \qquad \text{(Eq. 14)}$$

$$A = (G - R) \times 90\% \qquad \text{(Eq. 15)}$$

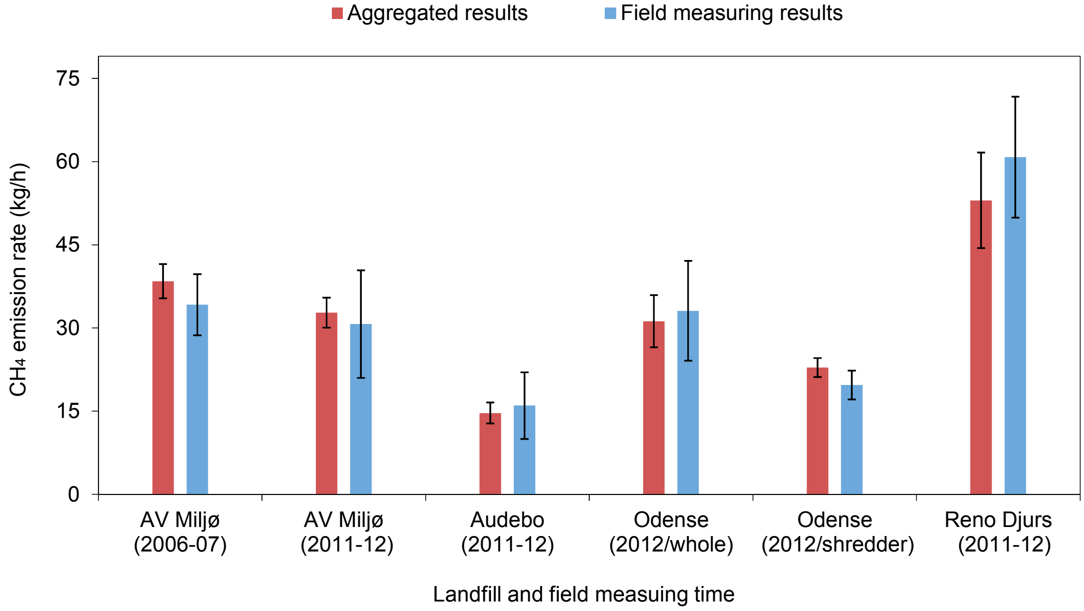
In Paper **III**, various A results were obtained for four Danish landfills and one specific waste cell for shredder waste at the Odense landfill. From 2006 to 2012, several field measurements of whole-site CH_4 emissions at the four Danish landfills (as well as some specific landfill cells) were conducted using the tracer dispersion method (Scheutz et al., 2011a; Mønster et al., 2014a, 2014b). In comparison to A values, measured results were used to test and to evaluate the applicability of the revised Afvalzorg model for Danish landfills receiving low-organic waste fractions.

4.2.2 Results and Discussion

Fig. 4 shows the aggregated (A) and field measured (M) CH_4 emissions in terms of columns with error bars. The standard deviation of A was determined by the uncertainties of BMPs and k values (Paper **I** and **II**). The M was average results from field measurements that were taken over several days during a specific year (Scheutz et al., 2011a; Mønster et al., 2014b). Nevertheless, it can still be concluded that A and M were in good agreement. For every group of compared results, columns overlapped each other for most parts with acceptable error bars. If calculating the ratio between A and M, all results were in the range of 0.87-1.16. Therefore, the field measurements at four Danish landfills confirmed that the lab-determined BMPs and k values of low-organic waste samples were practical, and the revised Afvalzorg model could be used for a more accurate estimation of CH_4 generation and emissions from low-organic waste degradation.

Gas emission measurements conducted at the Odense landfill showed that about 19.7 out of the total emission of 33.1 kg CH_4 / hr (i.e. 60%), was emitted from the cell with shredder waste (Mønster et al., 2014b). Estimated by the revised Afvalzorg model, only 36% (25.4 out of 69.7 kg CH_4 / hr) of the total CH_4 generation came from the shredder waste. However, previous studies have also reported CH_4 emissions from similar landfill cells at AV Miljø (Scheutz et al., 2011a; Mønster et al., 2014b). Although the fractions of shredder waste at AV Miljø and Glatved were much less than at Odense, fugitive CH_4 emissions are still significant, and implementing of proper mitigation methods are needed to reduce their global warming impact.

Above all, it can be concluded that the FOD models based on default parameter values are not suitable for applying correctly, but tend to significantly overestimate LFG generation. FOD LFG generation models can be used to practically estimate CH_4 generation and emissions if only site-specific input data are used, e.g. in this case, the Afvalzorg model for Danish landfills receiving low-organic waste. Since 2009, a tier-based PRTR model was initiated and used by Danish landfill operators to report LFG emissions to Danish EPA (Scheutz et al., 2009b). In the PRTR model, the original Afvalzorg model and a zero order decay approach were used for LFG estimation. Achievements of this study provide a valuable database and a potential guideline for developing an updated version of the PRTR model in terms of improving BMPs and k values in the Afvalzorg model.



	AV Miljø (2006-07)	AV Miljø (2011-12)	Audebo (2011-12)	Odense (2012/whole)	Odense (2012/shredder)	Glatved (2011-12)
G	42.7	36.4	15.9	69.7	25.4	101.9
R	0	0	0	35	0	43
A	38.4	32.7	14.3	31.2	22.9	53
M [a]	34.2	30.7	16	33.1	19.7	60.8

a. M presents the measuring results of the whole-sites CH_4 emissions using a tracer dispersion method and the results were presented in detail in Mønster et al. (2014b) and Scheutz et al. (2011b).

Figure 4. Comparison of aggregated fugitive CH_4 emissions (kg/hr) and measured whole-site CH_4 emissions at four Danish landfills and one specific waste cell for shredder waste at the Odense landfill.

5 Conclusions and Perspectives

This PhD project studied several FOD LFG generation models in terms of their formulas, waste categories, and default parameter values. Based on FOD equations, the BMPs and k values were primary parameters that played a key role for the accuracy and practicality of model outcomes. The single-phase model LandGEM, the multi-phase model IPCC, which focus on traditional MSW fractions, and the Afvalzorg model, which focuses on low-organic waste, were selected for further study.

To test their applicability for the Danish scenario, actual waste data provided by four Danish landfills (AV Miljø, Audebo, Glatved and Odense) were used as input data. All landfills were still in use and only received low-organic waste for permanent disposal. Therefore, the waste data were representative for modern landfills in Europe. For running the multi-phase models, waste data were translated into various categories to fit the definition of the IPCC and Afvalzorg model (Paper **III**).

For each landfill, the CH_4 generation curves from the beginning of disposal until year 2100 were estimated by three models using default parameter values. In general, the LandGEM model estimated significantly larger CH_4 generation than the other two models. The IPCC model defined waste into traditional MSW fractions with higher BMPs, which resulted in larger cumulative CH_4 generation estimates until year 2020 and 2100. Moreover, larger k values would show an accelerated process of LFG generation. In comparison to the IPCC model, the Afvalzorg model could better show the influence of not only the total disposed waste amount, but also various waste categories. Consequently, the Afvalzorg model was more suitable for modeling Danish landfills.

For further calibration of FOD models, mixed bulky, shredder, sludge, street cleansing waste and temporarily stored combustible waste were sampled from four landfills and were characterized in terms of TS, VS, TC, and TOC (Paper **I**). Danish waste samples showed lower TOC contents than traditional MSW fractions. By incubation experiments over 77 days, the BMPs of all waste samples were determined. As main fractions at Danish landfills, mixed bulky and shredder waste had similar BMPs, which was in the range of 5.4-9.1 kg CH_4 ton^{-1} waste (wet weight) on average. By anaerobic degradation experiments over 405 days, cumulative CH_4 generation was monitored and k values were calculated (Paper **II**). The lowest k values were obtained for mixed bulky and shredder wastes ranging from 0.013 to 0.017 yr^{-1}. Consequently, most waste samples had lower BMPs and k values than traditional waste fractions, as well as default values in current FOD models.

By using lab-determined BMPs and k values for the four above waste categories, the Afvalzorg model was revised and estimated smaller cumulative CH_4 generation results. Through a CH_4 mass balance approach, fugitive CH_4 emissions from whole-sites and a specific cell for shredder waste at Odense landfill were aggregated based on the revised Afvalzorg model outcomes. Aggregated results were in good agreement with field measurements, indicating that the revised FOD model with site-specific data could provide a practical and accurate estimation for LFG emissions. Additionally, by using only one k value for each waste category instead of identifying various degradable fractions, the Afvalzorg model could be revised as a less complicated and more practical model for the Danish scenario. This study is valuable for researchers and engineers who are aiming to precisely estimate CH_4 generation from landfills receiving low-organic waste. The results also provide a new guideline for the PRTR reporting of Danish LFG emissions.

According to the model estimation, low-organic waste at Danish landfills would generate LFG slowly but continuously over a long period of time. For instance, at the Odense landfill, 60% of fugitive CH_4 emission was emitted from the cell with shredder waste. Due to the slow process of waste degradation, active LFG collection system would result in low efficiency. Therefore, a cost-efficient method (e.g. the biocover technology) for mitigating a global warming impact should be studied and developed for both daily operation of running landfills and aftercare of closed landfills.

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7 Papers

I Mou, Z.S., Scheutz, C., Kjeldsen, P., 2014. Evaluating the biochemical methane potential (BMP) of low-organic waste at Danish landfills. Waste Management, in press. DOI: 10.1016/j.wasman.2014.06.025.

II Mou, Z.S., Scheutz, C., Kjeldsen, P., 2014. Evaluating the methane generation rate constant (k value) of low-organic waste at Danish landfills. Waste Management, in press.

III Mou, Z.S., Scheutz, C., Kjeldsen, P., 2014. Evaluation and application of site-specific data to revise the first order decay model to estimate landfill gas generation and emissions at Danish landfills. Submitted to Journal of the Air & Waste Management Association.

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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The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four sections:
Water Resources Engineering, Urban Water Engineering,
Residual Resource Engineering and Environmental Chemistry & Microbiology.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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