Temporal and spatial variability of soil gas transport parameters, soil gas composition and gas fluxes in methane oxidation systems

Dissertation

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Summary

In this study temporal and spatial variability of soil gas transport parameters, soil gas composition, fluxes and oxidation efficiency in landfill methane oxidation systems were examined.

The work consists of three parts: (1) A laboratory experiment on gas diffusion and gas permeability, exploring gas transport parameters at low water tensions; (2) A case study on properties and genesis of and gas migration through the cover soil at an emission hotspot on an old landfill; (3) A field study of a large scale methane oxidation test field, examining performance and variability of fluxes of such systems in real size application.

(1) Gas transport parameters for advective and diffusive flux were determined in the laboratory for a sandy and a loamy landfill cover soil. Measurements were carried out at water tensions between 2 kPa and 30 kPa. For the determination of diffusion coefficients (D_{eff}) and gas conductivity (k_{gas}) a single chamber apparatus was constructed, by means of which diffusion through undisturbed soil samples, retrieved using 100 cm³ core cutters, could be observed. Gas conductivity was determined on the same samples in a pressure loss experiment. For diffusion coefficients a good accordance with existing models was found while gas permeability could not be described by a mathematical function at an adequate statistical level of significance. Field flux scenarios were calculated for a range of concentration and pressure gradients. Potential advective fluxes exceeded the potential diffusive fluxes already at pressure gradients as low as 1 Pa. D_{eff} was reduced much stronger from increasing soil moisture than k_{gas}. Hence, advective flux would theoretically dominate over diffusive flux already at very low driving pressure gradients especially in wet soils. The gas conductivity did not change a lot with drying of the samples. This emphasized the importance of the very coarse macro pores > 1 mm diameter as determining feature for advective gas fluxes. As these (usually secondary macropores) are a heterogeneous, randomly distributed feature, the spatial heterogeneity is high and the predictability is low.

(2) A case study was carried out on the cover soil at a methane point source (hotspot) on an old landfill in northern Germany. The hotspot was identified in previous field observations on the landfill cover that was characterized by heterogeneous emissions and soil gas concentrations. Soil gas phase composition and methane surface concentration were monitored over a period of six months. For the hotspot area (approx. 1 m²) a constant spatial pattern of surface and soil gas methane concentration was found proposing a cone-shaped zone of elevated methane concentration. The site was excavated along a transect arranged from the outer, non-emissive zone though the emissive center. The area of high surface and soil methane concentrations showed reduced features such as grey and black colors, extending into the subsoil. At this point of the transect, the soil was classified as *Reduktosol*. Soil physical analyses revealed an increased porosity of the central hotspot structure. Organic carbon, nitrogen and electric conductivity were found to be increased in

the hotspot samples compared to the non-hotspot samples. Total porosity and air capacity were highest in the hotspot samples.

(3) A large-scale methane oxidation cover ("biocover") test field was monitored over a period of 30 months with respect to emission, soil gas concentration, oxidation efficiency and rates, with a special focus on their temporal and spatial variability. Emissions were quantified employing a novel, large static emission chamber with a footprint of 17 m². At loads of up to 42.5 g CH₄ m⁻² d⁻¹ over the investigation period, an average oxidation efficiency of 84% was achieved. The spatial heterogeneity of emissions, base fluxes, oxidation efficiency and soil gas concentration was high on the scale of the test field. The variability of the gas transport parameters of the test field material was found to be high even on a scale of a few decimeters. The principal pattern of gas distribution within the test field was found to be determined by the capillary barrier that was used as gas distribution layer. The compaction of the methane oxidation layer had an influence on the evenness of the gas distribution within the test field, with a higher compaction and hence reduced permeability of the methane oxidation layer resulting in a more even spatial distribution of the base flux. A simple predictive model (Methane Oxidation Tool, MOT) for the determination of the methane oxidation potential of landfill cover soils was tested against field data. It seemed to be promising in the prediction of the achievable oxidation potential if the prerequisite of a homogeneous gas distribution is given. The temporal pattern was reflected correctly while the spatial pattern could not be reproduced due to the lack of spatially refined input data. Most of the time the base flux was too low to challenge the MOT predictions.

The work contributes to the understanding of processes, phenomena and applicability of methane oxidation as a landfill gas remediation technology.

Based on laboratory data it was found that diffusive gas fluxes can vary by a factor of two already on the scale of a few decimeters. It could be shown that advective gas transport through the macro- and coarse pore system exceeds diffusive fluxes if pressure gradients occur.

The examination of a hotspot on the cover of an old landfill showed that the soil pore structure could explain the focused gas emission. Further, an influence of the hotspot on soil physical and chemical properties was shown which was attributed to soil organisms which were favored by the high methane availability.

Measurements on a methane oxidation test field showed spatial and temporal heterogeneity of emissions and oxidation rates. Spatial heterogeneity was principally determined by the combined use of the capillary block as gas distribution layer and by the heterogeneity of gas permeability resulting from differences in soil moisture. Temporal variability was determined by seasonal moisture and temperature fluctuations. The mean oxidation efficiency of the system was 84% over a time of two and a half years, while maximum oxidation rates of 39.6 g CH₄ m⁻² d⁻¹ were obtained. Lowest rates were 8.5 g CH₄ m⁻² d⁻¹ which is a discussed threshold value for shifting from active to passive

landfill gas aftercare. Using the field data, a simple model (Methane Oxidation Tool, MOT) for the estimation of potential oxidation rates was validated. It could be shown that using only very few input parameters a realistic estimation of the test field performance could be obtained. Validation of the model was complicated by the heterogeneous loading of the test field.

All in all, it could be shown that methane oxidation systems can be an important component in landfill aftercare. The range of applicability starts considerably above the lower limits for flaring. Hence, a seamless transition from active to passive landfill gas aftercare can be realized. In the planning process it has to be considered that constructional features can influence the gas distribution. Especially when using capillary barrier systems an asymmetric gas distribution has to be expected. If methane oxidation systems are operated at an adequate range of methane loads, they can be expected to work over long term on a highly effective level.

Zusammenfassung

In dieser Studie wurde die räumliche und zeitliche Variabilität von Gastransportparametern, der Bodengaszusammensetzung, der Gasflüsse und der Oxidationseffizienz in einem Methanoxidationssystem auf einer Deponie untersucht.

Die Arbeit besteht aus drei Teilen: (1) einem Laborversuch zu Gasdiffusions- und Konvektionsparametern speziell bei niedrigen Wasserspannungen; (2) einer Fallstudie zu den Eigenschaften und der Entstehung eines Hotspots auf der Abdeckschicht einer Altablagerung; (3) einer Feldstudie an einem großmaßstäbigen Methanoxidations- Testfeldes an dem die Leistungsfähigkeit und die Variabilität der Flüsse in einem solchen System unter realen Bedingung untersucht wurden.

(1) Im Labor wurden die bestimmenden Parameter für diffusiven und konvektiven Gasfluss durch einen sandigen und einen lehmigen Boden aus Deponieabdeckschichten bestimmt. Die Messungen wurden bei Wasserspannungen zwischen 2 kPa und 30 kPa durchgeführt. Für die Bestimmung des Diffusionskoeffizienten (Deff) und der Permeabilität (kgas) wurde eine Diffusionsmesskammer mit einer Kammer entwickelt, mit der Diffusion an ungestörten 100 cm³ Bodenproben gemessen werden konnte. Die Gasleitfähigkeit wurde an denselben Proben mittels eines Druckabbauversuchs ermittelt. Die ermittelten Diffusionskoeffizienten zeigten eine gute Übereinstimmung mit bestehenden Modellen, während die Permeabilität nicht durch eine mathematische Funktion mit hinreichender statistischer Signifikanz beschreibbar war. Flussszenarien wurden für eine Reihe von real möglichen Druck- und Konzentrationsgradienten berechnet. Die Diffusivität wurde hierbei erheblich stärker vom steigenden Gehalt an Bodenfeuchtigkeit beeinträchtigt als die Permeabilität. Letztere blieb relativ konstant über den Wasserspannungsbereich des Versuchs. Die potentiellen konvektiven Flüsse überstiegen schon bei sehr geringen Druckgradienten von nur 1 Pa die potentiellen diffusiven Flüsse. Folglich würden konvektive Flüsse dominieren, besonders bei hoher Bodenfeuchte. Die Ergebnisse betonen die Bedeutung der Grobporen >1 mm als bestimmend für den konvektiven Gastransport. Da diese Poren normalerweise sekundäre Makroporen sind ist von einer heterogenen, zufälligen Verteilung auszugehen womit die räumliche Variabilität dieser präferentiellen Fließwege hoch und die Vorhersagbarkeit gering wird.

(2) Es wurde ein Fallstudie an einer Methanpunktquelle (Hotspot) auf der Abdeckung einer Altablagerung im Norddeutschland durchgeführt. Der Hotspot wurde in vorausgehenden Untersuchungen auf der Abdeckschicht identifiziert, welche durch ein heterogenes Emissionsgeschehen und eine hohe Variabilität der Bodengaszusammensetzung gekennzeichnet war. Die Bodengaszusammensetzung und die Methanoberflächenkonzentration wurde in dieser Studie über einen Zeitraum von sechs Monaten regelmäßig beprobt. An dem Hotspot (ca. 1 m²) wurde ein konstantes räumliches Muster der Oberflächen- und Bodengaskonzentration gefunden, dass eine kegelförmige Zone erhöhter Methankonzentration im Boden nahelegte. Die Stelle wurde aufgegraben wobei die Profilwand vom nicht emissiven, äußeren Bereich durch das Hotspotzentrum gelegt wurde. Der Bereich der erhöhten Methankonzentration in der Bodengasphase und an der Oberfläche zeigte reduzierte Merkmale in Form grauer und schwarzer Verfärbungen, die sich bis in den Unterboden erstreckten. Der Boden am Hotspotzentrum wurde als *Reduktosol* klassifiziert. Bodenphysikalische Analysen zeigten eine erhöhte Porosität im zentralen Hotspotbereich. Organischer Kohlenstoff, Stickstoff und elektrische Leitfähigkeit waren in den Hotspotproben erhöhte im Vergleich zu den Referenzproben aus dem Nicht-Hotspot Bereich.

(3) Eine großmaßstäbiges Methanoxidationsschicht – Testfeld wurde über einen Zeitraum von 30 Monaten untersucht. Emissionsmessungen, Bodengaskonzentrationen, Oxidationseffizienz und -rate wurden mit einem besonderen Augenmerk auf räumliche und zeitliche Variabilität untersucht. Emissionen wurden mit einer neu entwickelten großen statischen Haube mit einer Grundfläche von 17 m² gemessen. Bei einer Befrachtung von bis zu 42.5 g CH₄ m⁻² d⁻¹ wurde eine mittlere Oxidationseffizienz von 84% erreicht. Die räumliche Teilflächenbefrachtungen, Heterogenität der Emissionen, Oxidationseffizienz und Bodengaskonzentration innerhalb des Testfeldes war groß. Die für das verwendete Material ermittelten Gastransportparameter variierten war schon auf einer Skala von wenigen Dezimetern um den Faktor zwei. Die dominanten Muster der räumlichen Variabilität der Gasflüsse des Testfeldes wurden durch die Kapillarsperre geprägt, deren Kapillarblock als Gasverteilung fungierte. Die Verdichtung der Methanoxidationsschicht hatte einen Einfluss auf die gleichmäßige Verteilung das Gases innerhalb des Testfeldes, wobei eine höhere Verdichtung und damit eine reduzierte Permeabilität der Methanoxidationsschicht zu einer größeren Gleichmäßigkeit der teilflächenspezifischen Befrachtung führte. Ein einfaches Modell (Methane Oxidation Tool, MOT) zur Bestimmung des Oxidationspotentials von Deponieabdeckschichten wurde anhand der Felddaten überprüft. Die Vorhersagefähigkeit der erreichbaren Oxidationsleistung erschien vielversprechend wenn eine gleichmäßige Gasverteilung gegeben ist. Der zeitliche Verlauf des Emissionsgeschehens wurde korrekt abgebildet während die räumlichen Muster nicht reproduziert werden konnten, da hierfür keine räumlich ausreichend aufgelösten Eingangsdaten zur Verfügung standen. Über die meiste Zeit des Versuchs waren die Frachten zu gering um das vorhergesagten Oxidationspotential in Frage zu stellen.

Die Arbeit trägt zum Verständnis der Prozesse, Phänomene und Anwendbarkeit von Methanoxidationssystemen als Minderungsstrategie für Gasemissionen in der Deponienachsorge bei.

Basierend auf Laborergebnissen konnte gezeigt werden, dass diffusive Flüsse schon auf einer räumlichen Skale von wenigen Dezimetern um den Faktor zwei variieren können. Konvektive Anteile der Gasflüsse waren maßgeblich an die Grob- und Makroporenstruktur gekoppelt. Beim Auftreten von Druckgradienten übertrafen die potentiellen konvektiven Flüsse die potentiellen diffusiven Flüsse bei weitem.

Die Überprüfung eines Hotspots auf der Abdeckung einer Altablagerung ergab, dass die Porenstruktur des Bodens den punktförmigen Gasaustritt erklären konnte. Weiterhin wurde eine Beeinflussung der physikalischen und chemischen Eigenschaften des Bodens am Hotspot aufgezeigt, welche den durch das hohe Methanangebot begünstigten Organismen zugeschrieben wurde.

Die Messungen an dem Testfeld zeigten eine räumliche und zeitliche Heterogenität der Emissionen und Oxidationsleistung. Die räumliche Heterogenität wurde maßgeblich durch die kombinierte Nutzung des Kapillarblocks als Gasverteilungsschicht und durch die aus der Heterogenität der Bodenfeuchte entstehenden Unterschiede in der Gasleitfähigkeit bestimmt. Die zeitliche Variabilität wurde durch jahreszeitlich bedingte Feuchte- und Temperaturschwankungen bestimmt. Die mittlere Oxidationseffizienz des Systems wurde mit 84% über den Zeitraum von zweieinhalb Jahren bestimmt, wobei maximale Raten von 39.6 g CH₄ m⁻² d⁻¹ erzielt wurden. Die niedrigste gemessene Rate lag bei 8.5 g CH₄ m⁻² d⁻¹ was der diskutierten Methan - Grenzfracht zum Übergang in die passive Nachsorge entspricht. Anhand der Messdaten wurde ein einfaches Model (Methane Oxidation Tool, MOT) zur Abschätzung der potentiellen Oxidationsleistung von Methanoxidationssystemen überprüft. Es konnte gezeigt werden, dass das Modell anhand von wenigen Eingangsdaten eine realistische Einschätzung der Leistung des Testfeldes liefert wobei die Modellvalidierung durch die heterogene Befrachtung der Fläche verkompliziert wurde.

Insgesamt konnte herausgearbeitet werden, dass Methanoxidationssysteme eine wichtige Komponente der Deponiegasnachsorge sein können. Ihr Einsatzbereich beginnt wesentlich oberhalb der Betriebsuntergrenze von Gasfackeln, damit kann gasseitig ein nahtloser Übergang aus einer aktiven Nachsorge in die passive Nachsorge erfolgen. Bei der Planung ist zu beachten, dass bautechnische Merkmale die Gasverteilung beeinflussen können, besonders bei der Nutzung von Kapillarsperren muss mit einer asymmetrischen Verteilung der Gasfracht gerechnet werden. Die Heterogenität von Bodenmaterial, auch in technisch aufgebauten Schichten, kann maßgeblich zur räumlichen Variabilität der Gasflüsse und damit zur Bildung von Hotspots beitragen. Bei einer Befrachtung im Zielanwendungsbereich ist aber mit einem dauerhaft leistungsfähigen, wartungsarmen Betrieb zur rechnen.

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List of abbreviations

BQS	Bundeseinheitlicher Qualitätsstandard
b.s.	Below surface
СНР	Combined heat and power plants
D _{eff}	Effective diffusion coefficient
EPS	Exopolysaccharide
FDR	Frequency domain reflectometry
FID	Flame ionizing detector
FOP	Factorized oxidation potential
GWP	Global warming potential
HDPE	High density polyethylene
ID	Identifier
IPCC	Intergovernmental Panel on Climate Change
KA5	Bodenkundliche Kartieranleitung 5 (German soil classification, 5 th ed.)
k _{gas}	Gas permeability coefficient
kPa	kilo Pascal
MOS	Methane oxidation system
MOT	Methane Oxidation Tool
NDIR	Non-dispersive Infrared
NI	Liter at normal conditions (0°C, 1013 hPa)
pF	Logarithmic value of the suction in hPa
PVC	Polyvinylchloride
RMSE	Root mean square error
RTO	Regenerative thermal oxidation
SD	Standard deviation
SOP	Standardized oxidation potential
WRB	World Reference Base for Soil Resources

1 Introduction

Landfill gas is a major contributor to anthropogenic greenhouse gas emissions accounting for 3% of the overall greenhouse gas emission (Barros and Field, 2015). Emission reduction and remediation of emissive sites is a societal and political task and therefore target to scientific investigation and engineering practice. Landfill gas consists of mainly methane and carbon dioxide with typical concentrations of 55-60% methane and 40-45% carbon dioxide (Scheutz et al., 2009). As methane has a global warming potential (GWP₁₀₀) 28 times as high as carbon dioxide (Barros and Field, 2015) it a primary target to emission abatement strategies. One removal strategy is the microbial methane oxidation within the landfill cover soil, a biowindow or a biofilter. In the oxidation process methanotrophic soil bacteria convert methane and oxygen into carbon dioxide. Previous studies described the necessary prerequisites a soil must meet to obtain a high oxidation performance (Boeckx and van Cleemput, 1996; Börjesson et al., 1998; Gebert, 2004; Rachor et al., 2011). A critical point for the performance of Methane oxidation systems (MOS) is the even spatial distribution of the gas at the base of the MOS. In the past, it has been frequently shown that emissions occur along preferential pathways which form by swelling and shrinking of the soil resulting in secondary soil pores, by root channels and animal burrows and by settling resulting in shear cracks, further along interfaces and along borders of building structures (Giani et al., 2002; Jung et al., 2011; Rachor et al., 2009). At these sites, the locally elevated methane load to the cover is higher than the methane oxidation capacity of the soil, thus resulting in emissions. These locally confined emissive sites are referred to as hotspots.

Soil is a three-phase system consisting of a solid, a liquid and a gaseous phase. Naturally, the liquid phase consists of water. At contaminated sites a fourth, non-aqueous liquid phase could occur, which is not considered in this study. The soil matrix consisting of the solid phases can be seen as a porous medium with the pore space containing the liquid and the gaseous phase. In general, water filled pore space is not available for the gaseous phase. The pore space consists of pores of different diameters and geometries. Larger pores drain with gravity thus they are available for gas transport most of the time while very fine pores are water filled most of the time. Pores are not straight but tortuous. The higher the tortuosity the longer is the pathway for a gas molecule to pass a distance through the soil. Landfill gas moves through the soil within the water free pore space, which is mainly the larger pores. The moister a soil is the less pore space is available for gas transport. Due to the blocking of narrow points, the tortuosity usually increases with water saturation. The transport regime of the landfill gas is critical for methane oxidation. Gas can move along concentration gradients by diffusion or along pressure gradients by advection. Advective transport is affected more by soil pore structure than diffusive transport (Moldrup et al., 2001). It is hypothesized that gas transport through hotspots occurs mainly advective, hence the emission regime of a hotspot site is to a large proportion governed by variations of soil water saturation.

The parameters describing the gas transport characteristics of the soil are D_{eff} for diffusion and k_{gas} for advection. For methane oxidation the diffusive influx of oxygen into the soil is as

important as the transport of methane from the waste body or gas inlet upwards. Oxidation can happen only at the soil depth where both gases are present. In a system that is dominated by advective fluxes it is important for effective oxidation that the efflux is not disabling the diffusive influx of oxygen. In both cases the methane fluxes must not exceed the oxidation potential of the soil.

With respect to the importance of gas transport in soils for the performance of the investigated methane oxidation system, the following three work packages and corresponding working hypotheses were identified:

(1) Relevance of pore size distribution for gas transport in differently saturated soil samples at low water tensions.

Hypotheses:

- a. At higher degrees of water saturation, the change of gas transport parameters for diffusion (D_{eff}) and advection (k_{gas}) with available water-free pore volume is highest and nonlinear.
- b. The ratio of diffusion to advection decreases with increasing degrees of water saturation.
- c. Small differences in soil water content convert equal concentration or pressure gradients into considerably different diffusive and advective fluxes depending on the initial saturation of the soil.
- (2) Spatial emission patterns and properties from a hotspot in a non-optimized cover soil of an old landfill.

Hypotheses:

- a. The spatial soil gas and surface concentration pattern of hotspots is caused by small-scale differences in soil pore size distribution of the cover soil.
- b. The preferential gas flow through the soil, leading to prolonged exposure of soil to reducing gas, influences the soil's physical and chemical properties.
- (3) Spatial and temporal patterns of base flux, methane oxidation and methane emission in a large-scale methane oxidation cover test field and their relation to topography and soil properties.

Hypotheses:

- a. Spatial patterns of soil moisture on sloped areas lead to gas emission patterns with predominant emission in the upslope area.
- b. Spatial emission patterns are constant but vary over time as a result of changing environmental conditions affecting physical gas transport and biological oxidation processes.
- c. Compaction of topsoil results in a more homogeneous distribution of the soil gas phase.

- d. In situ the advective transport is most dominant at high water saturations (see hypothesis 1a).
- e. Using a simple model, oxidation potential of methane oxidation systems can be predicted.

For the investigation of the abovementioned work packages and the validation of the related hypotheses, three systems covering different spatial scales were examined: (1) laboratory studies using undisturbed soil samples of 100 cm^2 , (2) an emission hotspot with a spatial dimension of 1 m^2 on an abandoned landfill and (3) a 1060 m^2 test field designed as optimized methane oxidation cover system.

2 State of knowledge

2.1 Preferential gas flow in landfill cover soils

Gas migration through soil happens within the air-filled pore space. This is the share of the total pore space which is not filled with water. Pore content and structure of a soil are dependent on soil texture, natural or engineered compaction, organic content and biotic factors like root channels or soil dwelling micro and macro fauna. The degree of water saturation of the total pore space is determined by its topographic position, its permeability, its distance to groundwater table or an impermeable layer and the micro climatic conditions. Thus pore space it is a highly complex and dynamic system.

Essential for water retention and water and gas flow through soil is the pore size distribution and the structure of the pore space, namely its tortuosity and connectivity. Tortuosity can be defined as the ratio of the length of the flow path through the pores of a medium to the length of the direct line across the medium (Ghanbarian et al., 2013). The concept of connectivity describes the inter-connection between pores. The pore network can be blocked by water menisci in the bottlenecks of the pore system resulting in isolated pores.

The pore size distribution is determined by the texture and organic content of the soil material and its density. In general, coarse material has a higher share of large pores while finely textured soils have a high share of fine pores. According to German soil classification fine pores are pores with an equivalent diameter of $\leq 0.2 \,\mu$ m. The equivalent water tension is 1500 kPa. Plants usually cannot extract water from these pores. That is why the point is also known as permanent wilting point derived from experiments with sunflowers. Medium pores are classifies as pores from >0.2 μ m up to 10 μ m equivalent diameter. Water in these pores is held against gravitational force and is accessible for plants. Its lower equivalent water tension is 30 kPa. Pores from >10 μ m up to 50 μ m equivalent diameter are classified as narrow coarse pores. Water within these does drain with gravity but slow enough to be accessible for plant roots. The lower water tension equivalent of this compartment is 6 kPa .The water content at 6 kPa defined as field capacity. Coarse wide pores are pores wider than 50 μ m. They drain with gravity. Water it not accessible to plants and the pores are usually air-filled if free drainage is given. The pore space share of wide coarse pores is defined as air capacity. Fine coarse pores and middle pores sum up to the plant available field capacity (Ad-hoc-AG Boden, 2005).

The pores resulting from the grain size distribution is referred to as primary pores. Pores that form by pedogenetic processes like swelling and shrinking, freezing and thawing or bioturbation are referred to as secondary pores. Swelling and shrinking of clay-rich soil results in the formation of cracks. As a result, finely textured soil can have coarse secondary pores available for gas and water transport.

Organic material content and compaction influence the water retention characteristic of soils. Field capacity both, total and plant available, increase with organic matter content. Air

capacity tends to decrease with increasing organic matter content in sandy soils while it increases in finer textures. As an example a loamy sand (German classification: Su2; WRB: LS) soil with 3% w/w organic content has 4 percentage points more available field capacity and 6 percentage points more field capacity while its air capacity decreases by 1 percentage point with reference to the organic free material. Compaction decreases pore space in all soil textures. A loamy sand at a density of 1.3 g cm⁻³ has an air capacity of 30% which decreases to 23% at 1.5 g cm⁻³, to 18% at 1.7 g cm⁻³ and to 12% at 1.9 g cm⁻³ (Wessolek et al., 2009).

As a result of small scale differences of the mentioned characteristics the resulting pore space and pore structure is heterogeneous and hence water and gas migration through soil is heterogeneous as well. For water, preferential flow or fingering is the normal form of percolation through soil (Flury et al., 1994). The pores of the soil are not or to a much lesser extent available for gas transport if filled with water. Thus, heterogeneous flow patterns of water cause spatially heterogeneous soil gas permeability and diffusivity (Cabral et al., 2010b). The concentration of gas fluxes to small areas may cause areas of elevated methane emissions or surface concentrations compared to their surroundings. In the following, these emissive sites are referred to as hotspots. The hotspot phenomenon is often found on landfill covers (Bogner et al., 2007; Giani et al., 2002; Rachor, 2012; Rachor et al., 2013). Hotspots can be very small with only some centimeters in diameter up to several square meters. Hotspots can contribute a major part of the overall methane emission of a landfill while covering only a fraction of its surface. Czepiel et al. (1996a) found 50% of the total methane emissions to originate from about 5% of the surface of a landfill in New Hampshire. A share of 70% of total emissions via cracks was reported by Bergamaschi et al. (1998). The soil gas composition at hotspot sites is different form the surrounding area. While in the surroundings usually no methane is found in the topsoil or at the surface, the hotspot soil gas profile shows methane up to the top. The typical shift of the carbon dioxide- methane ratio at sites with oxidation is only very small or does not happen at all (Gebert and Perner, 2015; Gebert et al., 2011c). If the shift is small, it indicates an overload of the oxidation capacity of the soil. If the ratio does not shift at all or neglectably no methane oxidation happens. This can happen if the gas efflux is too fast to allow counter diffusion of oxygen. The resulting emissions can be labeled 'direct emissions' as the gas involved does not or hardly not interact with the soil material but bypassing it (Gebert et al., 2011d).

Spatial heterogeneity can be observed on different scales. Small scale variability on a scale of few centimeters to decimeters (Geck, 2011; Rachor et al., 2009) can be found as well as variability over some decameters (Röwer, 2014). Driving factors can be the variability of soil properties, for instance cracks, root channels or animal burrows (Allaire et al., 2008; Giani et al., 2002), for small scale effects and variability of gas generation of the underlying waste, differences in cover type, slopes or obstacles like gas wells, roads or built-up areas for variability on larger scales.

The spatial pattern of hotspots seems to be relatively stable while the emission intensity changes over time (Rachor et al., 2013). This implies that the preferential flow path of the soil causing the hotspot is stable over time.

Continuous exposition to methane or absence of oxygen can cause reduced soil features. Prolonged exposition may lead to the formation of a Reduktosol (Blume, 2002). According to the German soil classification, a Reduktosol is a soil with a reduced horizon beginning within 4 dm below surface whose reduced properties originate from reducing or oxygen displacing gases. Above the reduced horizon, an oxic horizon can be present. At the surface, typically a humic topsoil horizon is found, except at sites with recently deposited material. This is in contrast to gley soil where reduction happens by water saturation. Reduktosols may form naturally over post volcanic mofettes or anthropogenic over leaking gas pipes or in soils exposed to gases formed in waste or sludge with high degradable organic content (Ad-hoc-AG Boden, 2005). Formation of Reduktosol soil can happen within months. Above intense sources like gas pipes formation might happen within days. The black color of the reduced horizon comes from metal sulfides. The persistence of the soil type depends on the duration and strength of the causing gas source (Blume, 2002).

In the *World Reference Base for Soil Resources* (WRB, Food an Agricultural Organization) since 2006 gleyic properties of gleysols may result from reductic gases while in *US Soil Taxonomy* no adequate soil types exist to describe the specific conditions of natural soil material with reduced properties causes by exposure to non-oxic gas.

2.1.1 Soil gas transport

2.1.1.1 Gas transport processes in soils

Gas transport in soil is realized through the soil pore space. It can be driven (1) by concentration gradients resulting in diffusive flux or (2) pressure gradients resulting in advective flux. In both cases along with the pore size distribution the soil structure characteristics mentioned above, tortuosity and connectivity, are important geometric properties of the pore space. The air-filled porosity at the considered water content is important for both transport processes. For advective fluxes, the pore diameter is important. Advective permeability is influenced by the power of four by the pore diameter while diffusion depends on air-filled pore volume without being influenced by the pore diameter (Kühne et al., 2012). Moldrup et al. (2001) found that soil structure strongly affect air permeability but not diffusivity.

(1) The diffusive transport of a substance is the net movement of molecules of the substance along a concentration gradient from higher concentration toward lower concentration. The driving motion is the thermal motion of the molecules. Diffusion in a closed system results in an even distribution of all substances. As diffusive transport is a very slow process in solids and liquids, the diffusive gas transport in soils can be considered to practically happen only through air-filled pores. Diffusion velocity of methane in air (0.196 cm² s⁻¹) is four orders of magnitude higher than in water (1.4×10^{-5} cm² s⁻¹) because the solubility of methane in water is very low (26 ml L⁻¹ at standard conditions (IFA)). Hence diffusive methane transport

through water saturated soil or between pores separated by water films is usually neglected (Maier and Schack-Kirchner, 2014).

Three forms of diffusion are known: Knudsen diffusion, binary molecular diffusion and nonequimolar flux. If the pore radius is much smaller than the mean free path length wallmolecule collisions dominate over molecule-molecule collisions. **Knudsen regime** is at a ratio of mean free path length to pore radius (Knudsen number) of ten and above (Scanlon et al., 2002)). At 10°C the mean free path length of methane is about 53.4 nm (Lide, 2007), thus pore radius must be around 5.3 nm. As fine pores in soils are defined as pores with an equivalent diameter smaller 0.2 μ m i.e. 200 nm, Knudsen diffusion might become important in soils only if they are very finely textured and absolutely dry. These conditions are not to be found in landfill cover soils.

If only two gases are present, **binary molecular diffusion** is the prevailing transport process. It occurs under isobaric, isothermal conditions with equimolar pairs of gases. If the gases are not equimolar thus having a different molar weight the faster movement of the lighter molecules results in a faster diffusion of the lighter component. This establishes a pressure gradient. The resulting flux is called **nonequimolar flux** or diffusive slip flux (Cunningham and Williams, R. J. J., 1980; Scanlon et al., 2002).

(2) Pressure driven gas flow through soils is called advection. Pressure gradients can be induced by changing ground water levels, passing weather systems, temperature gradients, formation or depletion of gases and in technical applications by pumping. In soils, the pressure gradient is usually equilibrated instantly except for situations with blocked pore space or in technical applications like pumping with high flow rates (Schack-Kirchner, 2002).

Mostly gas migration through soils is assumed to happen direction-independent. Nevertheless anisotropy was reported for air permeability (Dörner and Horn, 2006; Peng and Horn, 2008) and for diffusion (Kühne et al., 2012). Anisotropic transport might be important for landfill cover systems especially when the soils are heavily compacted or capillary barriers are in use. Compaction can cause a platy soil structure that can cause anisotropic air permeability (Dörner and Horn, 2006). Elevated soil moisture content is found at the border between two layers of differently textured materials (Berger et al., 2005). This horizontal seam of reduces pore space can increase the vertical resistance against gas movement through the wetter material while the horizontal resistance above and below stays unchanged.

2.1.1.2 Experimental determination of diffusive gas transport

The gas diffusion coefficient *D* describes the transport of a substance by thermal motion. It is dependent on the substances diffusing into each other. For the diffusion of gas 1 into gas 2 a diffusion coefficient $D_{1,2}$ can be identified that is often named D_0 because no diffusion resistance exists. Diffusion coefficients can be taken from tables (Marrero and Mason, 1972). If the diffusion occurs through a porous medium like soil D_p describes the diffusion through the porous medium. D_p is also referred to as apparent diffusion coefficient. The relative

diffusivity D_p/D_0 describes the diffusion through the porous medium in relation to the diffusion without a resistance D_0 . D_p can be empirically determined by diffusion experiments. Experimental setups can be differentiated into one- and two-chamber experiments. In one-chamber experiments, the soil core connects a flushable chamber with the surrounding atmosphere. The concentration of the gases in the chamber is monitored over time. The atmosphere functions as an infinite sink. In two-chamber experiments, the soil sample to be examined is placed between two chambers that can be flushed with two specific gases. For details on diffusion experiments reference is made to Rolston and Moldrup (1994).

In this study, a one chamber experimental setup was employed. Rolston and Moldrup (1994) identify the potential errors associated with the one-chamber or Currie method. These are (1) drying of sample (2) convective flow (3) reaction of gas with soil or chamber and (4) diffusion though chamber parts.

From the change of concentration over time the sample geometry and the chamber volume the diffusion coefficient can be calculated from Fick's first law (Equation 1) (Rolston and Moldrup, 1994).

 $J_d = -D_{eff} \frac{dc}{dx}$ Equation 1

with $J_d = diffusive Flux [mol m^{-2} s^{-1}]$ $D_{eff} = effective diffusion coefficient [m^2 s^{-1}]$ dx = length of diffusion way [m] $dc = concentration gradient [mol m^{-3}]$

2.1.1.3 Experimental determination of advective gas transport

The gas permeability coefficient (k_{gas}) describes the resistance of a porous medium to a pressure driven gas flux. It can be determined by steady state methods or non-steady state method. For steady state measurement either a constant pressure gradient over the soil sample is established and the resulting flux is measured (Janse and Bolt, 1960; Tanner and Wengel, 1957) or a constant flux is applied and the resulting pressure is measured (Groenevelt and Lemoine, 1987; McCarthy and Brown, 1992). For non—steady state measurement pressure from a stock vessel can be equilibrated though the soil sample while recording the pressure over time and calculating the advective flux (Gebert and Gröngröft, 2010). In both cases from flux, pressure, time, cross section and length of the sample the permeability coefficient can be calculated according to Darcy's law in analogy to the saturated water flux through porous media (Equation 2).

$$k_{gas} = Q \times \frac{dl}{dp} \times \frac{1}{A} \times t$$

Equation 2

with k_{gas} = coefficient of permeability [m s⁻¹] Q = flux [m³s⁻¹] dl/dp = pressure loss over soil column [m m⁻¹] A = area of soil column [m²] t = time [s]

2.1.1.4 Diffusive gas transport models – an overview

The experimental determination of the diffusivity is complex therefore models are developed to derive the value from a less complex variable. One of the first attempts to find a relationship describing D_p/D_o was made by Buckingham (1904). From empirical data measured on granular materials, he established the Equation 3.

$$\frac{D_p}{D_0} = \varepsilon^2$$
 Equation 3

with

$$\begin{split} D_p &= gas \mbox{ diffusion coefficient in soil } \\ D_0 &= gas \mbox{ diffusion coefficient in air } \\ \epsilon &= air-filled \mbox{ porosity } [m^3 \ m^{-3}] \end{split}$$

The relation is determined only by the air-filled porosity (ε). Other authors developed similar models using only one parameter (Marshall, 1959; Millington, 1959; Penman, 1940).

In 1960 and 1961 with models proposed by Millington and Quirk total porosity was integrated into modeling, thus including effects of soil texture and compaction (e.g. Equation 4 (Millington and Quirk, 1961)). They based the model on data from different porous materials.

Equation 4

Equation 5

with

 $\frac{D_p}{D_0} = \varepsilon^{10/3} / \phi^2$

 ε = air-filled porosity [m³ m⁻³] Φ = total porosity [m³ m⁻³]

Different authors published models for repacked (Deepagoda et al., 2011a; Moldrup et al., 2005a), or undisturbed (Moldrup et al., 2005b) soils. Some authors point to include bimodal soil pore structures (Deepagoda et al., 2011a) or to improve the density correction (Deepagoda et al., 2011b). An overview is given in (Allaire et al., 2008).

Some models focusing intact soil material include soil water retention characteristics such as Equation 5 (Moldrup et al., 2005b) where the porosity at 10 kPa is uses as a shape factor.

$$\frac{D_p}{D_0} = \phi^2 \left(\frac{\varepsilon}{\phi}\right)^{X_{10}} \quad with \ X_{10} = 2 + \frac{\log(\varepsilon_{10}^{1/4})}{\log(\varepsilon_{10}/\phi)}$$

with

$$\label{eq:eq:expansion} \begin{split} \epsilon &= \text{air-filled porosity } [m^3 \, m^{\text{-3}}] \\ \epsilon_{10} &= \text{air-filled porosity at 10 kPa soil water tension } [m^3 \, m^{\text{-3}}] \\ \Phi &= \text{total porosity } [m^3 \, m^{\text{-3}}] \end{split}$$

Details on coupling diffusivity models to water retention models are given in Moldrup et al. (2005b).

A non-predictive function that has to be fitted to the data is proposed by Troeh et al. (1982). Two parameters have to be set for fitting the function (Equation 6). Parameter 'u' can be interpreted as initial threshold for diffusion to start while 'v' defines the shape of the curve.

$$\frac{D_p}{D_0} = \left(\frac{\phi - u}{1 - u}\right)^{\nu}$$

Equation 6

with

 Φ = total porosity [m³ m⁻³] u,v fitting parameters

Allaire et al. (2008) state that a priori no best relationship can be chosen to describe a soils diffusivity. The decision for one model must be supported by a few measurements of the namely soil material.

2.1.1.5 Modelling gas permeability

In contrast to gas diffusion prediction the modelling of the gas permeability is much more unreliable. The high dependence of gas permeability on soil pore size and pore geometry results in an increased importance of soil structure. Moldrup et al. (2001) discuss the link between soil structure and air permeability. A parameter characterizing soil structure is needed. Ball (1981) used the equivalent pore diameter implying that the pores behaves like a bundle of parallel tubes. Ghanbarian and Hunt (2014) found that due to the more complex structure of natural porous media this assumption is wrong. In Klute et al. (1994) attempts of predicting air permeability are summarized. It is proposed to measure air permeability at least at 10 kPa as a reference value. Others use air-filled porosity, total porosity and Campbell's factor *b* (Moldrup et al., 1998). As soil structure is highly complex, prediction accuracy for gas permeability remains as vague as one order of magnitude (Klute et al., 1994).

2.1.2 Methane oxidation systems

In this section the relevant aspects of methane oxidation systems (MOS) are being characterized. First, the process of microbial methane oxidation is described and the range of applicability is given along with a short description of other landfill gas management technologies. Following the possible setups of MOS are described and details on constructional requirements for optimized MOS are given. Afterwards an overview on landfill gas emission measurement methods is given. Concluding methods for performance estimation of MOS are described.

The terminology to describe methane oxidation systems is not universally applied. Some authors employ the term *biomitigation systems* (Bour et al., 2015). Others employ terms like *passive methane oxidation biocover* (Cabral et al., 2010a) for systems herein called biofilters and biowindows. In that case, *passive* refers to the form of gas supply working without a pump. The term *bio system* is meant to delimit these systems from thermal oxidation systems like flares.

2.1.2.1 Process of microbial methane oxidation

Methanotrophic bacteria are ubiquitous in soils. They use methane as carbon and energy source. This is being done by the enzyme methane monooxygenases. This enzyme is one defining characteristic for methanotrophic bacteria. The methanotrophs are grouped in type I and type II methanotrophs. Type I methanotrophs assimilate formaldehyde by the ribulose monophosphate pathway (RuMP) while type II methanotrophs use the serine pathway (Hanson and Hanson, 1996). Both types are able to oxidize methane under a wide range of environmental conditions according to the following Equation 7.

$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O + 780 \text{ kJ mol}^{-1}CH_4$ Equation 7

For landfill cover soil with its high methane concentrations in contrast to natural environments type II methanotrophs prevail (Gebert, 2004).

The activity of the bacteria depends on environmental factors. The process is highly dependent on temperature. Experiments yielded highest oxidation rates at 30 °C (Park et al., 2009; Scheutz and Kjeldsen, 2004; Stein and Hettiaratchi, 2001). Warming to 40 °C resulted in a strong decrease while further warming up to 50 °C resulted in complete stop of oxidation due to denaturation of proteins (Scheutz and Kjeldsen, 2004). At 2°C still some activity was registered with an exponential increase of oxidation rates with rising temperatures up to 25 °C (Scheutz and Kjeldsen, 2004). Other experiments indicated thermal optima at 31-36°C (Whalen et al., 1990) and 35-38°C (Gebert, 2004). As a measure of the influence of rising temperatures on microbiological process rates, the Q_{10} value indicates the factor by which the activity increases with the warming of 10 K while the process is still below its thermal optimum. From 10 °C to 30 °C oxidation rates had Q_{10} values of 1.7 to 4.1 (Scheutz et al., 2009).

Soil moisture is another important parameter for methane oxidation. With increasing water content available soil pore space for gas transport is reduced and continuity of pores decreases. As gas diffusion through water is four orders of magnitude smaller than through air higher water contents impede oxygen supply and hence oxidation. Pore size distribution of the soil material and its water content result in a specific water tension. It is expressed as pF value, which is the logarithmic value of the suction in hPa. Field capacity is pF 1.8 (6.3 kPa, equivalent to 50 µm coarse pores) and permanent wilting point is at pF 4.2 (1500 kPa, equivalent to 2 µm fine pores). As the availability of water for plants and microorganisms at one gravimetric water content is different for different soil textures, it is reasonable to use the water potential instead of the water content to indicate moisture optima (Spokas and Bogner, 2011). An influence of the water tension on oxidation activity was found by Gebert (2004) where it could be shown that a pF value of 1.8 is an optimum for microbial methane. This was confirmed by Spokas and Bogner (2011). Lower pF values indicate that drainage of the soil is hindered, thus less pores are available for gas transport hence oxygen supply will be restricted. When oxygen concentration in soil air drops below 1.7-2.6% v/v hardly any methane oxidation occurs (Gebert et al., 2003). At increasing pF values, the microorganisms are exposed to growing drought stress. At about pF 4.2 oxidation comes to a halt (Spokas
and Bogner, 2011). After drought periods methanotrophs seem to have difficulties to come back to their previous activity (Scheutz and Kjeldsen, 2004). In Rachor et al. (2013) the in situ effect of soil moisture from strong precipitation events is described. Blockage of the pathways can cause the temporal reduction or stop of emissions.

Exposition to methane stimulates the growth of methanotrophic bacteria. It was shown that the oxidation potential at methane exposed sites is elevated (Röwer et al., 2011). In batch tests, methane oxidation rates of >100 μ g CH₄ g_{dm}⁻¹ h⁻¹ are reported and in column studies rates >200 g CH₄ m⁻² d⁻¹ were found (Scheutz et al., 2009). Incubation temperatures were usually above 20 °C, optima were found around 30 °C.

After installing a MOS, a lag time was observed before a methanotrophic community establishes (Jugnia et al., 2008). The same was observed for an increase of the load. It needs some time of adaption while the microbial community grows. Gebert (2004) showed that methanotrophic population could restore oxidation performance within a few weeks after a periods of up to 25 weeks of starvation. A similar observation was made by Einola et al. (2007) who could not state a decrease in oxidation rates after 13 to 20 weeks of starvation.

2.1.2.2 Application range of MOS

If the gas generation of a landfill is still high, the gas is extracted and utilized in a gas engine or flared. For energy recovery in combined heat and power plants (CHP) methane concentration must be above 35-40% and gas production rates must exceed 30-50 m³ h⁻¹. Otherwise CHP treatment becomes infeasible economically and technically (Haubrichs and Widmann, 2006). Flares can treat lower concentrations. There are different types of flares. The operational range of low calorific value high temperature flare begins at 40 m³ h⁻¹ at a methane concentration of 25% or 100 $m^3 h^{-1}$ at a methane concentration of 10%. Regenerative thermal oxidation (RTO) units can treat methane concentration ranges of 0.4 – 27% at flow rates of 500 to 50,000 m³ h⁻¹ (EPA, 2011). In a review of studies on methane oxidation rates of MOS Chanton et al. (2009) found rates of about 6 NI CH₄ m⁻²h⁻¹ for sandy soils. For a landfill of one hectare, that is equivalent to 60 m³ CH₄ h⁻¹. The flux ranges of the applicability for flaring and MOS overlap. As a basis for dimensioning MOS the expected flux has to be measured which is possible for systems where gas is collected in a gas well and distributed from there. Otherwise, the gas flux has to be modeled with gas generation models. An estimate concerning the methane flux every soil even of non-optimized systems can oxidize is 0.5 NI CH₄ m⁻² h⁻¹ (Stegmann et al., 2006). The percentage of methane in the gas is not limiting the applicability of such system. Hence, MOS are especially suitable for the decades of low activity aftercare when gas generation still happens but thermal treatment or energy recovery are no longer options for mitigation of methane emissions (Figure 1). This time of low gas generation can extend over decades and up to a hundred years and beyond (Huber-Humer et al., 2008). The gas flux and composition can be influenced by techniques like landfill aeration or rewetting. In sealed landfills, the decomposition may be very low or come to a halt due to dry conditions. In this case the controlled intrusion of water can increase or re-establish the gas generation bringing the flux back in a usable range and reducing the remaining pool of biodegradable carbon. The aim of landfill aeration is to stimulate the aerobic decomposition of organic material in situ (Scharff et al., 2010). For this purpose, atmospheric oxygen is pumped into the waste body. Different approaches exist with regard to the pressure used to bring the aeration gas into the landfill and with regard to the treatment of the off-gas. Due to the aerobic conditions, no methane formation happens. Yet a gas generation potential will remain within the waste body after aeration. Gas generation potential of landfills is expected to decrease to nearly stable conditions. Ritzkowski and Stegmann (2012) report the reduction of biodegradable organic carbon of more than 90% over four and six years of aeration. In contrast to technical gas treatment, MOS need only little care which makes them more cost efficient if a suitable material (see section 2.1.2.4.1) for methane oxidation is used in cover construction right away. On old landfills without gas extraction system and capping biocovers are a methane mitigation option (Sadasivam and Reddy, 2014).



Figure 1: Schematic course of methane production, capturing and gas handling options over a landfill life cycle. Adapted from Huber-Humer et al. (2008).

2.1.2.3 Principal setups of MOS

The process of microbial methane oxidation is used in engineered systems for the abatement of methane emissions from landfills at a time where energy recovery or flaring is not suitable any more. This can be due to economical or technical reasons. In the previous chapter, the application ranges of the technical treatments are described. In this section the three different forms of employment of biotic mitigation systems are described.

(1) Biofilters (or methane oxidation filters) are contained reactors filled with a substrate to host the methane oxidizing bacteria (Figure 2). They can be supplied actively (Streese and

Stegmann, 2003) or passively (Gebert, 2004) with gas. At the top, they can be open or closed. If open oxygen can enter the filter by diffusion, if the filter is closed oxygen has to be added to the gas to be treated. This requires an active gas supply but would expand the oxidation process to the whole depth of the filter and thus increase oxidation efficiency (Barlaz et al., 2004; Haubrichs and Widmann, 2006). Open biofilters can be covered with vegetation. If oxidation rates are high exopolysaccharide (EPS) formation can occur clogging the filters pore system (Wilshusen et al., 2004). Desiccation due to the treated gas stream is unlikely because the gas from landfills or compost piles is water saturated. Additionally water is produced in the oxidation process. That is why open and closed filter systems need a leachate drain. The potential of biofilters to remove methane was proofed in in-situ systems. Gebert and Gröngröft (2006b) found oxidation rates of 80 g CH₄ m⁻³ h⁻¹ in a passively vented upflow biofilter using expanded clay covered with topsoil. Streese and Stegmann (2003) reported oxidation rates of 20 - 40 g CH₄ m⁻³ h⁻¹ where the lower level was achieved in a system filled with yard waste compost, wood fibers and peat and the higher level in a system filled with compost. Hernández et al. (2015) published results from a biofilter experiment with maximum methane oxidation capacities of 11 g CH₄ m⁻³ h⁻¹.



Figure 2: Schematic of a biofilter.

(2) Biowindows (or methane oxidation windows) are areas within landfill covers designed and optimized for methane oxidation (Figure 3). The sizes of biowindows typically range from some square meters (Röwer, 2014) up to 480 m² (10 biowindows with a total area of 4800 m²) (Scheutz et al., 2014). The area of a biowindow has a lower resistance to gas movement, i.e. a higher permeability, than the surrounding. Gas supply is passive from the underlying waste body. Containment does not exist. As the surrounding is less permeable or impermeable, the gas load of a larger area concentrates to the area of the biowindow. With regard to vegetation and leachate control, the window is not different to the rest of the landfill cover. Scheutz et al. (2011a) reported average oxidation rates of 20.4 g CH₄ m⁻² h⁻¹ for a biowindow set up with a 15 cm gravel gas distribution layer and a 100 cm compost layer for methane oxidation. At an old uncapped landfill, biowindows were built upon hotspot sites as remediation action. For these mean oxidation rates of 2 – 45 g CH₄ m⁻² d⁻¹ with maximum rates of 278 g CH₄ m⁻² d⁻¹ were reported (Röwer, 2014). Implementation of best available technology is mandatory for gas treatment on German landfills regulated by the landfill regulation. For weak emissions methane oxidation can be implemented if its efficiency can be proved to the authorities (DepV, 2012). A large-scale project (3000 m²) is currently executed in Hamburg/Germany for a landfill of dredged material.



Figure 3: Schematic of a biowindow.

(3) If the whole landfill cover is optimized for methane oxidation, it is referred to as biocover (or methane oxidation cover) (Figure 4). As biocovers spread over the whole area of a landfill, the methane load to area is much smaller than in biofilters or –windows. Homogeneity of gas distribution over the biocover area is highly linked to high removal rates thus thorough attention has to be paid to the gas distribution system (Huber-Humer et al., 2008). The air-filled porosity of the cover material was identified as another central parameter for a good oxidation performance (Huber-Humer et al., 2008) because it ensures the diffusive supply with atmospheric oxygen. Increased oxygen availability was identified to enhance methane oxidation (Barlaz et al., 2004). In contrast to biofilters and to smaller biowindows the substrate of biocovers cannot be replaced without disproportional costs. In spite of the scarce experience with full-scale biocovers several field studies showed their potential to mitigate methane efficiently. Bogner et al. (2010) found oxidation efficiencies of 20-70% on a 576 m² biocover. Stern et al. (2007) reported 64% oxidation for a 58 m² biocover cell. In the IPCC FAR (Fourth Assessment Report) biocovers are considered an important secondary control on landfill methane emissions (Bogner et al., 2007).



Figure 4: Schematic of a biocover.

The principle of all three forms mentioned above is that they need an active or passive gas supply, a gas distribution layer and a methane oxidation layer. Biowindows and biocovers need a topsoil to establish vegetation which is also true for biofilters if they are open to the environment and integrated into the landfill cover.

2.1.2.4 Requirements for setup of optimized MOS

Basic components of MOS are from top to bottom: (1) methane oxidation layer topsoil and subsoil and (2) a gas distribution layer. The oxidation process is meant to takes place in the methane oxidation layer. The depth of the main oxidation horizon changes seasonally and depends on the intensity of the gas flux from below and the influx of oxygen from the atmosphere. Typically, it is situated within the first 50 cm a has a thickness of one to three decimeters (Humer and Lechner, 1999). The topsoil layer is necessary for the establishment of a vegetation cover. The task of the gas distribution layer is to homogenize the gas flux from below over the entire area. The construction of MOS has to be accomplished in the frame of other requirements to landfill cover layers defined by local regulations for landfill cover design (e.g Deponieverordnung (DepV, 2012)). In the following central prerequisites for each layer are described.

2.1.2.4.1 Methane oxidation layer

The basic material parameter for a functioning system is the soil texture as it governs the pore size distribution and hence gas transport and water retention parameters as well as soil mechanical properties. The following is stated for mineral soil material. A short comment on organic materials is given afterwards.

Air capacity should be as high as possible. As it can be derived from Equation 3, Equation 4 and Equation 5 gas diffusion is primarily a function of air-filled pore space. Soil pores >50 μ m equivalent diameter drain with gravity thus they are void at field capacity (pF 1.8). This pore space is defined as air capacity. Except in cases of strong or prolonged precipitation, it is available for gas transport. German legislation prescribes minimum requirements for the air

capacity in methane oxidation layers. In the long run, an air capacity of more than 10% v/v must be achieved. Constructional target should be 14% v/v (LAGA Ad-hoc AG "Deponietechnik", 2011c).

Plant available field capacity should be high enough to support the growth of vegetation on the system. German legislation prescribes levels of plant available field capacity of 140 mm over the total depth of at least 1 m for recultivation layers (LAGA Ad-hoc AG "Deponietechnik", 2011a). For water balance layers 220 mm over the total depth of at least 1.5 m are mandatory (LAGA Ad-hoc AG "Deponietechnik", 2011b). If the methane oxidation layer is integrated into one of the afore-mentioned, it needs to meet these standards as well (DepV, 2012). In the BQS 7-3 (Federal quality standard for MOS (LAGA Ad-hoc AG "Deponietechnik", 2011c)) the plant available field capacity for MOS is defined as 140 mm over the total depth of at least 1 m hence following the prescription for recultivation layers.

The texture is defining the tendency of a soil material to form cracks. The higher the clay content, the more likely cracks will form upon drying. As cracks are pathways for direct emissions, they are to be avoided. According to the BQS 7-3 (Federal quality standard for MOS (LAGA Ad-hoc AG "Deponietechnik", 2011c)) the clay content has to be below 17%. Loamy to clayey textures are not suitable for methane oxidation layers not only because of a tendency to form cracks but for the low diffusive and advective gas transport properties of these materials (Gebert et al., 2011a).

Compaction is another mechanical phenomenon that has to be avoided. Compaction due to mechanical stress from machinery during construction reduces pore space and with it air capacity and connectivity of the pore system (Gebert et al., 2011a). To keep the negative effect of construction works as small as possible the material should be handled in a dry to moist but not wet state with the least possible pressure applied by the used machinery (< 15 kN m⁻²) to avoid compaction (LAGA Ad-hoc AG "Deponietechnik", 2011c)

Less prone to handling and construction are the chemical properties of the used soil material. To support environmental conditions favorable for methanotrophic bacteria the pH value should range from 5.5 - 8.5 (Scheutz et al., 2009). Humus content should be above 2% and up to 8% (Gebert, 2013). In this range, it supports available field capacity. Humus content contributes to cation exchange capacity which is important for the vegetation cover. Salinity should be below 6000 μ S cm⁻¹ as higher levels induce increased osmotic stress to the bacterial community (Gebert et al., 2003).

Organic materials like compost or wood chips are often suggested as materials for MOS (Humer and Lechner, 1999; Lisovitskaya et al., 2015; Scheutz et al., 2014). They feature a high porosity and provide a good environment for microbiota as nutrients and water are highly available. Organic materials, however, have some drawbacks which can make them unsuitable for biocovers and depending on size and maintenance intensity biowindows. For biofilters they can work fine.

Major disadvantage is the degradability of the material. Microbial degradation of part of the organic matter will change the material's physical properties. For example, bulk density will

increase and pore volume will be lost, decreasing gas permeability. Combined with its high water retention potential it may hinder the oxidation performance (Jugnia et al., 2008).

Another drawback to methane oxidation is the oxygen consumption due to the decomposition of the material. Anaerobic areas can form, even producing methane (Mei et al., 2015). The oxygen demand for decomposition and methane oxidation are competitive thus methane oxidation cannot be as effective as it would be with the whole oxygen at its disposition (Scheutz et al., 2011b). The latter is a disadvantage for all types of MOS. The former is not so much a problem in biofilters because the substrate here can be exchanged after some time of employment without too much effort and cost. The same is true for biowindows if they are comparatively small. It is not the case for biocovers, which are more extensive. Constructional target of the latter is durability and low to no maintenance and operation costs.

If compost is used it is recommended to use mature compost with a 7-day oxygen demand below 8 mg O_2 g⁻¹ dry matter (Humer and Lechner, 2001).

2.1.2.4.2 Gas distribution layer

As it is crucial to load the methane oxidation layer with an evenly distributed gas load, a gas distribution layer is needed. It has to be (1) filter stable to the overlying methane oxidation layer, (2) far more permeable than the methane oxidation layer and (3) about 20-50 cm thick (Gebert, 2013).

The filter stability prevents clogging due to particles transported with the percolating water from above. The leap in permeability between gas distribution and methane oxidation layer is meant to force the gas into the plane. The flow resistance in vertical direction through gas distribution layer and methane oxidation layer has to exceed the horizontal resistance through the gas distribution layer alone over the desired range of gas distribution. The thickness of the gas distribution layer has to ensure continuity. Layers of 30 - 50 cm yielded good results (ÖVA Arbeitsgruppe, 2008). Scheutz et al. (2011a) found a 15 cm gravel gas distribution layer to work insufficiently.

2.1.2.5 Performance estimation of MOS

This section gives an overview on performance quantification of MOS. Parameters of interest are the absolute oxidation rates and the relative oxidation efficiencies of MOS. In both cases, the load to the system and the emission from the system has to be known or estimated. The oxidation rate gives the amount of methane oxidized per time and area or volume while the oxidation efficiency gives the share of oxidized methane in relation to the load in percentage.

The load of MOS can be measured if the gas influx is monitored which is possible in biofilters. If the system is passively supplied with gas, as in biocovers and biowindows, the load has to be modelled. A short overview of available models is given in the first subsection of this chapter (2.1.2.5.1).

To balance carbon fluxes through a MOS additionally the emission has to be quantified. Methods for emission quantification and fields of application and restrictions are given in the following section 2.1.2.5.2.

2.1.2.5.1 Estimating system loads

Load to cover can be estimate as the gas generated minus the gas recovered for utilization. The gas generation is usually estimated by gas generation models not being subject to this study. The models consider degradable carbon content of certain waste types in combination with decay models and the time passed since deposition. The TNO (The Netherlands Organization of Applied Scientific Research) First Order Model, Intergovernmental Panel on Climate Change (IPCC) FOD (First Order Decay) Tier 2 Model and the Landfill Gas Emission Model (LandGEM, United States Environmental Protection Agency, US-EPA) are examples for models in use. For a review see Oonk (2010) and for model comparison with measurement data for different landfills see Scharff and Jacobs (2006). The load is obtained if the resulting flux is related to the area of the MOS.

One approach used in this study is to calculate the oxidation efficiency from soil gas concentration data using the carbon shift method (description see section 2.1.2.5.3) and emission data from chamber measurements (2.1.2.5.2) and to calculate the influx at the bottom of the MOS by back-calculating the emission according to the calculated oxidation efficiency to the initial load (Christophersen et al., 2001).

2.1.2.5.2 Measurements of landfill gas emission

Different approaches exist to measure the gaseous emission from landfill surfaces. They are very different in their spatial resolution and representability. The method has to be chosen depending on the aim of the investigation. Plume measurements are methods to quantify the emissions of whole sites. Chamber measurements measure only the emissions of their own footprint while surface screenings are a method to detect emissive areas on a site without quantifying them. Rachor et al. (2009) showed that surface screenings relying on a static grid sampling design highly underestimate emissive areas. Röwer et al. (2016b) showed that emissions determined with chamber measurements cannot be extrapolated to larger areas. Thus chamber measurements can be applied on biofilters or small biowindos as used for hotspot remediation purpose (Röwer, 2014) but not for the emission measurement of whole landfills. For that application, plume measurements with tracer release, micrometeorological methods or laser adsorption technologies are more suitable while these are limited in quantifying point sources.

Beside the spatial representation of the measurement method, temporal variability has to be taken into account for all methods (Giani et al., 2002; Poulsen et al., 2003; Rachor et al., 2013). Depending on the seasonal conditions, emissions from one spot may be high in winter or at falling barometric pressure (Poulsen et al., 2003) but non-detectable in summer or at rising barometric pressure. Therefore, sampling strategy has to be designed with respect to ambient conditions and representativeness of the locations.

In the following, a short description of each method is given.

Plume measurements capture the total emission of a site or a part of a site. A tracer is released on the site of interest at a defined rate and the downwind plume is analyzed with a Fourier Transformed Infrared (FTIR) adsorption spectrometer mounted on a vehicle (Galle et al., 2001; Scheutz et al., 2011c) or air from the plume is sampled and analyzed off site (Galle et al., 2001). From the ratio of the tracer and the gas of interest, the emission rate can be computed. Applying this method, a challenge arises: The analytic equipment is usually mounted on a vehicle, which has to drive through the downwind plume. Thus, the possibility to pass the site of interest in an adequate distance in downwind direction has to be given. No other source of gas must be in upwind direction and no obstacles should be present to disturb the wind field. Quantification of multi-source sites can be done using different tracers. This was done by Scheutz et al. (2011c) using two tracers.

Further, **micrometereological methods** as Eddy-Covariance can be employed. This technique uses a gas analyzer and a 3-D ultrasonic anemometer both mounted on a tower. As gas analyzer, usually a tunable diode laser, is used. Laurila et al. (2005) tested the use of a Flame lonization Detector (FID). Peltola et al. (2014) found that the selection of the instrument does not bias the result a lot as long as the data post processing is done appropriately. At a logging interval of about 10 Hz, wind direction and concentration data is recorded. From these the vertical net flux can be computed. The height of the tower determines the footprint of the measurement. Towers of only a few meters might not integrate the whole area of interest while high towers might detect sources outside of the target region (Peltola et al., 2015). The footprint is modeled probabilistically. To match the measured turbulent flux with the mean surface flux the site should not be too complex (Laurila et al., 2005). Eddy-Covariance measurement is widely applied in climate and environmental science.

A further technology to quantify plumes is **open path tunable laser** measurements. In this method, the adsorption of a laser tuned to the specific adsorption frequency of the targeted gas is integrated over a path length. This can be done upwind and downwind and combined with basic wind information (Groth et al., 2015). An alternative setup is to combine downwind measurements with 3-D wind field data (Hrad et al., 2014).

Differential Absorption Lidar (DIAL) uses laser pulses of two different wavelengths. One wavelength that is absorbed by the target substance and one that is not. From the difference of absorption of the backscattering signal, the concentration can be computed and from the time lag between pulse and backscattering the distance can be calculated. By applying this method, a two dimensional cross-section of the plume can be measured. In combination with a wind vector the flux can be calculated (Robinson et al., 2011)

To cover small footprints **chamber measurements** can be employed. Emission chambers have typical dimensions of 0.2 m in diameter up to 0.6 m with round or rectangular shape (Pihlatie et al., 2013). In this study, a quadratic static chamber with 17 m² was used which is, as far as we know, the largest chamber ever applied.

The basic concept of emission measurements with a static camber is simple. A box is placed on the surface only open to the bottom. The concentration increase over time is monitored. From the box volume, covered surface and increase of concentration, the flux from the surface covered by the chamber is calculated. Other than the methods above the flux from a relatively small distinct area is measured. As emissions from landfills show high spatial variability it is not possible to interpolate emission data from a few measurement points to a whole landfill (Czepiel et al., 1996b; Rachor et al., 2009; Röwer, 2014).

A first hint to possible emissive sites can be obtained from **surfaces screenings** with a mobile FID. For FID-surface-screenings, air is sampled from the soil surface with a sampling rod and analyzed. Sites of elevated methane concentration are mapped. FID-surface screenings are mandatory for landfill monitoring in Germany and details on surface screening procedure are given in the guideline for landfill surface screenings (VDI, 2008). However, the magnitude of methane surface concentration cannot be correlated with the magnitude of emission at the same spot but emissive sites show elevated methane concentrations on the surface (Rachor, 2012; Röwer et al., 2016b).

2.1.2.5.3 Measuring efficiencies

If a load to the cover is known or modeled and the emissions can be determined in a manner representative for the whole, area a **methane mass balance** can be made up setting in relation both parameters. Usually this can be done for test fields and biofilters only because the gas load of these is known and due to the small spatial extend the emission can be quantified reliably.

The in situ oxidation potential can be determined with the **gas push-pull test**. Hereby a mixture of methane and an inert tracer gas and usually air or oxygen is injected into the soil at a constant flow rate. After a while, gas flux is reversed and gas is extracted from the soil at a constant flow rate. Gas samples are taken continuously during the gas extraction. From the ratio of methane and the inert tracer gas concentration, methane oxidation rates can be calculated. This method measures the oxidation potential of the soil without substrate limitation because methane and oxygen are supplied. It gives point information for the specific site. The in situ gas push-pull test measurement depicts the oxidation potential in the undisturbed pores space at field conditions. The injected gas distributes within the soil pore space and comes into contact with the soil inner surface. This is an advantage to batch tests where the pore space is disturbed. The background methane concentration within the soil has to be constant, otherwise the measurement result will be faulty. A drawback of the method is that the result cannot be attributed to a defined depth and soil volume because the injected gas distributes unisotrop along the pores. (Gómez et al., 2009, 2009; Gonzalez-Gil et al., 2007; Schroth et al., 2011; Streese-Kleeberg et al., 2011).

Another method to quantify the oxidation efficiency is described by Gebert et al. (2011c). As one mol of methane is converted into one mol of carbon dioxide, the volume of the carbonaceous gases remains the same through the process. The shift of the **carbon dioxide** -

methane ratio over the soil profile is used to calculate the oxidation efficiency (for more detailed description see chapter 4.6). This method provides point information.

It is also proposed to use **stable isotopes** to quantify methane oxidation (Chanton et al., 2008; Chanton et al., 1999; Liptay et al., 1998). As ¹²C methane is preferred over ¹³C methane, the isotopic signature shifts during the oxidation process. From the shift, the methane oxidation efficiency is calculated using the fractionation factors for oxidation and transport (α_{ox} and α_{trans} , respectively). Gebert et al. (2013) found a strong influence of the oxidation rate on the fractionation factor and a high variability between different sites and within one site. Additional uncertainty for this method arises from the fact that fractionation occurs in the diffusive transport process as well. Usually it is not known exactly how large the share of diffusive respectively advective transport is. Thus the contribution of transport processes in the fractionation is uncertain (Chanton et al., 2009; Gebert et al., 2013).

One methodological problem to all methods using point information about oxidation efficiency is the interpolation of highly heterogeneous data to the area of interest. It was shown by geostatistical analysis that emission pattern often lack a spatial correlation (Geck, 2011; Spokas et al., 2003) which makes interpolation of point information highly unreliable. High efficiencies at many spots with very low fluxes do not contribute that much to the overall efficiency of a MOS as few other spots with low efficiencies and very high fluxes. Thus on extrapolating from point data to a whole site the efficiencies derived from field methods must be considered with regard to the load of the measured spot and its share in the overall load.

Modelling is an attempt to avoid uncertainties stemming from sampling design and hence unrepresentative sampling. Oxidation efficiencies can be derived from empirical or semiempirical relationships between environmental parameters and oxidation rates. The oxidation efficiency can be measured in column studies or batch tests (overview given in Scheutz et al. (2009)). Batch tests are not dynamic and the results are difficult to transfer to the field as they give oxidation rates in mol oxidized per mass unit soil material. Usually it is not known how much soil mass participates in the oxidation process. Column studies are closer to the natural conditions but usually are operated under constant environmental conditions and loads. In addition, they usually do not provide preferential flow paths. That makes them different from actual landfill covers. Nevertheless with some knowledge about influencing factors and an estimate of the share of direct emissions an estimate for a MOS can be made. CALMIM is a model developed by the US department of agriculture. It integrates site-specific soil properties and soil microclimatic conditions coupled to a 0.5 ° scale global climate model. It considers the type of cover, the coverage of gas recovery systems, 1-D gas transport processes and methane oxidation but does not provide a gas generation model. It integrates empirical data (Spokas et al., 2011). One other more simple semi-empirical tool for the estimation of methane oxidation is the Methane Oxidation Tool (MOT) (Gebert et al., 2011d) described in section 4.7. Supplemented with an estimate of the load to the cover the oxidation efficiency can be calculated from the models.

3 Description of study sites

3.1 Landfill K

The spatial pattern of a hotspot and the related soil properties were subject to examination. In previous studies the landfill K was monitored showing several constantly present hotspots (Gebert and Perner, 2015; Rachor, 2012; Röwer, 2014). The site is an old landfill situated in northwestern Germany. The former sand and gravel pit was filled and piled up until overtopping the surrounding by 13 m. The base of the waste body is above the ground water table. The landfill closed operations in the 1980s. It covers an area of 1.5 ha and contains approx. 180,000 m³ of household and demolition waste. The site does not provide any base or top sealing and no gas extraction system in operation. On landfill K, the surface methane concentration and the soil gas concentration was monitored on a site were preferential emissions of up to 4.4 mol d⁻¹ (70.6 g d⁻¹) occurred (Rachor et al., 2013) (Further work on landfill K is to be found in Rachor et al. (2013), Röwer et al. (2011) and Röwer (2014)). The examined emissive area (hotspot 13) had a dimension of less than a square meter. Subsequent to gas surface screenings and soil gas composition measurements, the site was excavated and some of the physical and chemical parameters of the soil were recorded in a cross section profile through the emissive site (chapter 4.4).

3.2 Landfill Wieringermeer

For the assessment of the oxidation efficiency of methane oxidation covers, measurements were performed on a large scale test field that was also subject to studies of Röwer (2014). The test field is situated on a 1:5 sloped edge of a landfill in the northwest of The Netherlands. It covers an area of 1060 m². It is integrated into the cover layer but separated from the waste body by a high-density polyethylene (HDPE) membrane so that only the purposely injected gas enters the test field. A catchment of 510 m² was installed to monitor the water balance of the field (not subject to this study). The catchment consists of a 40 cm high HDPE bevel welded to the base sealing. Gas injection is realized by six inlet ports situated on the base sealing. The controllable gas supply to the field is monitored with respect to gas quality and quantity within the gas supply station and the data is logged in an interval of 10 min.

To monitor the environmental conditions of the soil temperature (Pt1000) and moisture (EC5, Decagon) probes were installed downslope, midslope and upslope in the depth of 40 cm. The probes were connected to a data logger and recorded with a resolution of one hour.

The field consists of a capillary barrier (capillary block: 20 cm gravel (2-8 mm), capillary layer: 30 cm sand (1-2 mm)) and a methane oxidation layer (topsoil: 20 cm loam (WRB: L), subsoil: 80 cm loamy sand (WRB: LS) (Figure 5). The oxidation layer was initially constructed in 2009 with a long stick excavator without driving over the material to avoid soil compaction. In the

subsoil, a bulk density of 1.34 g cm⁻³ and an air capacity of 22.1% v/v were achieved (topsoil: bulk density 0.98 g cm⁻³ and an air capacity of 21.2% v/v). Three years after construction (2011) the subsoil had a bulk density of 1.35 g cm⁻³ and an air capacity of 26.0% v/v (topsoil: bulk density 1.23 g cm⁻³ and an air capacity 10.3% v/v) (melchior + wittpohl Ingenieurgesellschaft, 2011). The soil material was mainly aggregated in clumps.

In July 2013, the test field was reconstructed. The upper 60 cm of the field were excavated and reconstructed using a crawler instead of a long stick excavator. This was done to achieve a higher compaction. A survey directly after the measure yielded a bulk density of 1.37 g cm^{-3} in 5 cm (topsoil), 1.49 g cm^{-3} in 35 cm, 1.42 g cm^{-3} in 50 cm and 1.38 g cm^{-3} in 68 cm depth with respective air capacities of 6.4% v/v (5 cm b.s), 19.5% v/v (30 cm b.s.), 24.1% v/v (50 cm b.s.) and 27% v/v (68% v/v b.s.) (data averaged from two profiles (upslope and downslope) (melchior + wittpohl Ingenieurgesellschaft, 2014). The capillary block was meant to function as gas distribution layer, distributing the gas over the entire base area of the catchment before it moves upwards evenly through the oxidation layer.

On the surface of the test field, a grid was marked permanently with pegs. The grid fields had a size of 4.25 m x 4.25 m. The grid was used to ensure consistent positioning of emission chamber and surface screenings (Figure 6). IDs were assigned to the grid fields with columns indicated by letter A-F and rows indicated by numbers 1-10.



Figure 5: Setup of Wieringermeer test field, cross section.



Figure 6: Setup of Wieringermeer test field, bird's view. Lines signify grid fields of 4.25 x 4.25 m².

3.3 Landfill Eckerkoppel

Soil material from a well-established recultivation layer with a sandy soil was needed to conduct diffusion and permeability experiments in comparison to the loamy material from Wieringermeer. A suitable site was found in Eckerkoppel, an old landfill in Hamburg/Germany covering about 1.1 ha containing about 78.000 m³ of industrial and demolition waste. During remediation activities a new recultivation layer was built in 2002 (Hirschmann et al., 2003). For topsoil (0.3 m) and subsoil (1.7-2 m) material loamy sand (WRB: LS) was used. Topsoil material had a loss on ignition of 2.5% w/w, subsoil of 0.7% w/w. After completion, topsoil density was 1.35-1.65 g cm⁻³ and density in approx. 90 cm depth was 1.36-1.55 g cm⁻³ (melchior + wittpohl Ingenieurgesellschaft 2002, unpublished report). The soil material was of a homogeneous appearance without pronounced aggregate formation. The sand fraction appeared to be medium to fine sand.

3.4 Soil observation area Amsinckpark

Soil gas composition on the engineered site Wieringermeer should be compared with a natural site featuring a sandy soil without groundwater influence. These conditions were found at "Amsinckpark". Amsinckpark is a public park in Hamburg/Germany where long term soil monitoring is performed (Witt and Wichmann, 1993). The area in the park is dominated by soils with little or no material or construction debris added to the topsoil (Wiesner et al., 2015). Hence, the area was considered to be composed of native soil. Within the five hectare park, one campaign mapping soil gas concentrations and soil water content was conducted. The grid size of the survey was the same as at Wieringermeer test field. The area was vegetated with a meadow and did not have a pronounced topography.

4 Material and methods

In this chapter the laboratory and field methods employed in this study are described. Section 4.1 presents the laboratory methods for determination of the diffusion coefficient and gas permeability. In sections 4.2 to 4.5 field data acquisition is described and in section 4.6 methods of field data processing are presented. In section 4.7 a model for oxidation estimation is presented and its application in this context is described.

4.1 Gas transport parameters

4.1.1 Sample preparation

Two sites were selected for taking undisturbed samples. They were chosen because both are landfill cover soils and their soil textures are within the recommendations for methane oxidation systems (see chapter 2.1.2.4.1). The Eckerkoppel cover soil was sampled ten years after its construction, the Wieringermeer cover test field was sampled three years after construction, thus both are expected to be stable in terms of initial settlement and establishment of vegetation. The undisturbed soil samples were taken using 100 cm³ steel cylinders from topsoil and 95 cm below surface of the cover of the Eckerkoppel landfill in Hamburg/Germany (chapter 3.3). From the Wieringermeer test field (chapter 3.2) samples were taken from the topsoil and from 35 cm below surface. At each location and depth, five parallel samples were taken (Table 1). The resulting four groups of five samples each were water saturated to 0.3 kPa in a sandbox. Then the samples were drained by pressure plate extraction to 2, 4, 6, 20 and 30 kPa. Pressure plate extraction was done according to DIN EN ISO 11274 (2014). At each pressure head diffusivity (D_{eff}) and gas permeability (k_{gas}) were determined as described in the following sections. Finally, the samples were oven dried at 105 °C and total porosity was determined. Corg was determined by loss on ignition at 450 °C for five hours (DIN ISO 10694, 1996). Bulk density was determined with a pycnometer on about 100 g of dried sample material using nitrogen.

Site	Sampling depth	Texture	Bulk density n=5	Total porosity	Corg
	[cm]	[WRB]	[g cm ⁻ ³] ± SD	[vol-%] ± SD	[mass%]
Eckerkoppel	5 (topsoil)	Loamy sand (LS)	1.39 ± 0.08	47.5 ± 2.9	2.5
Eckerkoppel	95 (subsoil)	Loamy sand (LS)	1.52 ± 0.01	43.7 ± 0.5	0.7
Wieringermeer	5 (topsoil)	Loam (L)	1.07 ± 0.05	59.3 ± 1.8	7.7
Wieringermeer	35 (subsoil)	Loamy sand (LS)	1.22 ± 0.03	54.7 ± 1.0	2.2

Table 1: Soil data of samples for laboratory experiment.

4.1.2 Determination of effective diffusion coefficient

A single chamber diffusion apparatus was constructed consisting of two main parts (Figure 7). One part held the sample, the other one was the chamber itself equipped with two sensors. Both parts were separated with a steel slider. The chamber components were made from PVC. The chamber volume was 550 cm³. It was equipped with an oxygen sensor (SK 25 F, GS Yuasa) and a Pt1000 resistor for temperature measurement. The oxygen sensor was selected according to the device built by Schjønning et al. (2013). The parts were sealed with O-rings to the surrounding. The chamber could be flushed by two 8 mm self-closing vents.



Figure 7: Two diffusion chambers. Top: Chamber open with sensors visible through the sample adapter. Bottom: rear view of the chamber with the two blue ports for flushing, sensors and data cable. The chamber is closed and the opening in the steel slider is visible.

A gas chromatography survey revealed a linear relation between the sensors output signal and oxygen concentration ($R^2 > 0.99$) in a way that a linear interpolation could be done to convert the sensors signals into oxygen content. Before each measurement, a calibration was performed with ambient air and pure argon. The data from the sensors were recorded using a DL2e (Delta-T-Devices Ltd., Cambridge, UK) logger in intervals of five seconds. The comparability of the five chambers was confirmed using the same sample of a porous material in each chamber. As porous material aerated concrete was used that was fitted into a 100 cm³ steel cylinder used for soil sampling. The standard deviation of the variability between the chambers was determined as 3.6%.



Figure 8: The five diffusion chambers in operation. The three chambers to the left carry a sample, the two to the right are still closed and not loaded with samples.

For the actual measurement, the chamber was flushed with argon for about three minutes while the slider was closed sealing the chamber. After flushing ten minutes, time was given to check if the chambers were sealed properly. If so, the samples were inserted and the sliders were opened (Figure 8). Now the argon from the chamber could diffuse through the soil sample into the atmosphere and air could diffuse through the sample into the chamber. The oxygen content in the chamber was monitored. A typical oxygen increase is displayed in Figure 9. Depending on the permeability of the sample, the duration of the experiment was 30 minutes to two hours. Samples were scaled before and after the measurement to quantify desiccation. This procedure was repeated for each pressure head (2, 4, 6, 20 and 30 kPa, see section 4.1.1).

From logged sensor output data, a function was derived to convert the output signal into an oxygen concentration. Therefore minimum and maximum sensor output for each chamber and each measurement was equalized to zero and 20.9% oxygen concentration. For the purpose of flux calculation, the gas volume was corrected according to the actual temperature within the diffusion chamber. From the change of concentration over time, the diffusion coefficient D_{eff} was calculated according to Fick's first law (Equation 1). To do so, concentration gradients of a moving time frame of five minutes were calculated assuming linearity within this time interval. The resulting D_{eff} values from five-minute intervals over the length of the experiment were averaged and the standard deviation was determined as an indicator of accuracy.



Figure 9: Typical course of oxygen increase in the diffusion chamber during the experiment. For the first approx. 15 minutes it was proven that the chamber was properly sealed. At approx. minute 15 the slider was opened resulting in a mixing of the chamber atmosphere with the air between slider and sample.

4.1.3 Determination of gas permeability coefficient

The gas permeability coefficient (k_{gas}) was measured with the pressure loss experiment described in Gebert and Gröngröft (2010). A stock vessel of 0.452 m³ was pressurized up to about 1 kPa. Afterwards the vessel was connected to the diffusion chamber by one of its vents (Figure 10). After opening the valve, the pressure was allowed to equilibrate with the atmosphere by an air flux through the soil sample. Meanwhile time and pressure were logged on a DL2e (Delta-T-Devices Ltd., Cambridge, UK) logger at an interval of one second. The experiment was done directly after the diffusion experiment at each pressure head (2, 4, 6, 20 and 30 kPa, see section 4.1.1).



Figure 10: Schematic of gas permeability experiment.

To determine k_{gas} from the pressure loss experiment, the data were smoothed with a moving window over three seconds. Fluxes and pressure differences were calculated for a moving window time interval of 20 seconds. k_{gas} was calculated according to Darcy's law for saturated flow in porous media (Equation 7). For each sample, the calculated k_{gas} values for the 20 seconds intervals over the relevant time of the experiment were averaged and the standard deviation was determined.

4.2 Surface gas concentration

After the description of the laboratory methods in the previous section, the methods of field data acquisition are described in the following chapter. Surface screening of methane concentration is a method to detect emissive sites on landfill covers. Elevated surface concentrations indicate the likeliness of emissions. On landfill K the method was used to map small scale surface concentration pattern of one square meter. On the Wieringermeer test field, surface surveys were performed with a grid size of about four square meters.

4.2.1 Hotspot 13 on Landfill K

For mapping the methane concentration on soil surface, a grid of eight by eight cells was spread out over 1 m by 1 m (Figure 11a). The cells were sampled with a sampling rod attached to a mobile FID (Flame ionization detector. Type: Toxic Vapor Analyzer TVA1000, Thermo Scientific, detection limit 0.25 ppm) (Figure 11b). Values were taken after 15 seconds, which was the time for a complete exchange of the measuring device volume, given the pumping rate of approx. 2 L min⁻¹. The grid was placed exactly to the same position every time with the hotspot center in the middle. Six campaigns were performed from October 2009 until April 2010.



Figure 11a/b: Hotspot 13 survey scheme. a: Monitoring setup for surface screening and gas probe measurement on Hotspot 13. Central 8 × 8 grid was used for placement of the surface screening probe. Points indicate gas probes. N1,2,3...: gas probe IDs north of central probe "NULL" (W: west etc.). b: FID surface screening scheme.

4.2.2 Wieringermeer test field

From October 2013 until April 2014, surface screenings were conducted on the biocover test field on Wieringermeer landfill. The screening was performed for methane and carbon dioxide. Surface gas samples were collected with a sampling rod connected to a portable FID (Flame ionization detector. Type: Toxic Vapor Analyzer TVA1000, Thermo Scientific, detection limit 0.25 ppm). A part of the gas stream was diverted to a chamber built to contain the NDIR-Sensor (non-dispersive Infrared, IAQ-CALC, Model 7525, TSI, detection limit 1 pm) for analysis of carbon dioxide concentration (Figure 12 (scheme analog to Figure 14 with the chamber replaced by the sampling rod)). On each 17 m² grid field, four points were sampled, one in each quarter. On one occasion, nine points per grid field were sampled measuring only methane.



Figure 12 a/b: a: CO₂ probe and sampling chamber. b: CO₂ probe inserted into sampling chamber.

4.3 Soil gas concentration

The measurement of the soil gas concentration using gridded gas probes gives insight into the spatial distribution of the measured gas. By monitoring at several depths, the concentration shift with soil depth could be determined. Both was done on both sites while on Landfill K an area of about 9 m² was covered with 25 gas probes and on Wieringermeer test field 162 gas probes were installed to 54 positions in three depths each.

4.3.1 Soil gas probes and measurement

The probes consisted of aluminum tubes with an inner diameter of 7 mm. They were closed with butyl rubber stoppers and sampled by means of a 60 ml syringe. In the sampling procedure first the inner volume of the gas probe was extracted and discarded and then a 60 ml sample was taken and analyzed immediately with a biogas analyzer (BM 2000 "Biogas", Geotechnical Instruments (UK) Ltd.) for the content of methane, carbon dioxide and oxygen. The accuracy of the device was 0.1% v/v. Nitrogen content was calculated as balance to 100% as the landfill gas of both sites did not contain any other components important for this survey.

4.3.2 Gas probe setup at Landfill K

Gas probes were installed to monitor soil gas phase composition at the selected hotspot 13 on landfill K. 25 Probes were installed at the hotspot. One was installed directly into the hotspot center. Around that center three gas probes were installed into eight directions with 45° angle toward each other. The distance between the gas probes of one direction was 50 cm (scheme: Figure 11 a). Measurement took place on six dates from October 2009 to April 2010. At the first date, probes were installed to 20 cm. At the second date probes were measured, than brought to 40 cm and measured again. The next date probes were measured at 40 cm depth again, than brought to 60 cm depth and sampled again. At fourth through sixth occasion, measurement took place in 60 cm depth only.

4.3.3 Gas probe setup at Wieringermeer test field

In order to assess the spatial distribution of the gas load to the methane oxidation layer, the composition of the soil gas phase was monitored by means of 162 gas probes permanently installed to 54 sites marked out by the 4.25 m grid (Figure 6). The probes were installed to 25, 60 and 100 cm depth with the latter being the lower part of the methane oxidation layer.

Additionally four gas profiles (C1-4) were installed with gas probes in 5, 10, 15, 30, 50, 90, 120 and 145 cm depth.

Measurements were carried out on 23 occasions from June 2012 to February 2015.

4.4 Soil excavation and laboratory analyses of Landfill K

The hotspot 13 on landfill K was excavated. A first preliminary profile wall was excavated 30 cm away and parallel to the hotspot center section. The main profile wall was aligned through the hotspot center (photos and schematics: Figure 34 and Figure 35). Disturbed samples (DS) and undisturbed samples (US) were taken from both profile walls from hotspot and non-hotspot areas, which were differentiated according to the discoloration of the soil and their proximity to the hotspot center. Soil classification was performed according to *Bodenkundliche Kartieranleitung 5* (German Soil Classification) (Ad-hoc-AG Boden, 2005) and to *World Reference Base for Soil Resources* (WRB) (FAO, 2014). Total porosity, bulk density and water retention at pressure heads of 0.3, 2, 6 and 30 kPa were measured from the undisturbed samples. The disturbed samples were analyzed for grain size distribution, TOC (DIN ISO 10694, 1996) salinity (DIN ISO 11265, 1997), pH (DIN ISO 10390, 2005) and sulfate concentration.

4.5 Emission measurement - Large chamber

4.5.1 Design and operation of the large static chamber

The chamber used for emission measurement on Wieringermeer test field was a large-scale static accumulation chamber. Approach and results of the validation of the chamber and measurement setup are given in section 5.3.1.

The dimensions of the chamber were $4.2 \times 4.2 \text{ m}^2$ at a height of 0.5 m, thus its volume was 8.82 m^3 . The frame consisted of aluminum beams and the cover was made from aluminum coated plastic foil (Figure 13). Two fans ensured the mixing of the enclosed air volume. The sampling air was drawn from the chamber by 18 tubes of equal length with the endings dispersed evenly over the chamber area. The chamber was sealed to the ground with a weighted-down apron made of plastic sheet.

Gas analysis was done by an FID (Flame ionization detector. Type: Toxic Vapor Analyzer, Thermo Scientific, detection limit 0.25 ppm) for methane and a NDIR sensor (non-dispersive Infrared, IAQ-CALC, Model 7525, TSI, detection limit 1 pm) for carbon dioxide. A scheme of the setup is given in Figure 14. Retention time of the gas in the manifold was 20 seconds. The analysis data of the continuous sampling was logged every 15 seconds over the time of enclosure. Enclosure time was four to six minutes.

Slopes were calculated by linear regressions over (1) the total measurement time, (2) minute 1 to minute 2 (five data points) and (3) minute 1 to minute 4 (twelve data points). Resulting slopes were used for calculation if they were significant (level of significance 0.05).



Figure 13: Large chamber in operation.

Methane and carbon dioxide emission were calculated from the increase of the concentration in the chamber in relation to the volume of the chamber and covered area. Emission was computed as:

$$E = \frac{m * V}{A}$$
 Equation 8

with

E = Emission [m³ h⁻¹ m⁻²]

- m = slope of linear regression of concentration increase $[m^3 m^{-3} h^{-1}]$
- V = Chamber volume [m³]
- A = area covered by chamber $[m^2]$



Figure 14: Schematic of chamber and connected analysis instruments.

The regression analysis for flux calculation was performed over three different time intervals of the measurement. These were (1) minute zero to six, (2) one to two and (3) one to four. All intervals yielded very similar results (Figure 15). Hence, it was considered valid to assume a linear characteristic of the concentration increase under the emission chamber for the first minutes. To eliminate effects of the chamber placement, it was considered most valid to exclude the first four data points (first minute) from the measurement. This was done after visual inspection of the raw data. Emissions calculated over six minutes were 17% lower than calculated over the second minute in October 2012, but on average calculations over the whole time were 3% lower and over minute one to four 0.3% lower than calculated over the second minute only. Due to the lower number of valid regressions when using only one minute, it was decided to calculate emissions from the regression over minute one to four.



Figure 15: Comparison of methane emissions calculated from linear regression over different time intervals. Solid line: minute 1-2, dashed: minute 1-4; dotted: whole measurement interval (4 to 6 minutes).

4.5.2 Sampling strategy for emission measurement

Development of a reliable sampling strategy was a crucial task with respect to the abovementioned heterogeneities of the emission regime (section 2.1.2.5.2). The work of Röwer (2014) extensively explores different approaches of chamber measurements and extrapolation to whole site emissions for the Wieringermeer test field. The findings imply a good representation of the emissions when all sites with elevated surface concentration are measured with a large chamber. Previously to this study, extensive FID-surface screenings and emission measurements were performed, covering the entire test field area. Based on these data and on reference campaigns in which all grid fields and thus the entire surface area of the test field were measured (May 2012 and April 2014), the first monitoring scheme for this work was developed. The second scheme was developed after the reconstruction of the test field (described in section 3.2). Both schemes are being described in the following.

The first sampling scheme (Figure 16) was used from August 2012 to July 2013. It included 22 grid fields accounting for 90% of the total methane emissions of the reference campaign in May 2012. These grid fields were measured in each campaign (permanently monitored fields). One third of the remaining fields was measured each third campaign (13, 13 and 12 fields). Each campaign covered 58% of the test field area (35 out of 60 grid fields). Assuming a spatially stable emission pattern, each campaign captured 93% of the overall methane emissions. The value was than adjusted to 100%. A re-evaluation of this scheme based on a full area campaign in May 2013 showed that it was still valid and needed only minor adaptations (adding two fields to the permanently monitored group).

The reconstruction of the test field changed the conditions of the test field. To adjust the campaigning strategy to the new conditions a new sampling scheme (Figure 16) was

developed. It was in use from June 2014 to February 2015. The reference emission was the average of a campaign in April 2014, covering all grid fields and two campaigns in February and March 2014, covering 50% of the grid fields respectively. The scheme derived from this included 27 grid fields that accounted for 90% of the average emission of the reference emission. The remaining fields were grouped to three sets of 11 grid fields and were measured every third time.



Figure 16: Top view and sampling scheme of test field. A1 to F10: grid fields for emission measurement. 1st sampling scheme was in use from 08.2012 to 07.2013, 2nd scheme from 06.2014 to 10.2014. The grey fields were measured in each campaign. A third of the white field was measured every three campaign. Grey fields account for 90% of the total methane emissions of the reference campaign.

4.6 Calculation of the methane oxidation efficiency, oxidation rates and base fluxes

To calculate the efficiency of the investigated biocover test cell, the following two approaches were used:

(1) A **methane mass balance** was calculated by comparing the ingoing methane flux with the emitted methane flux. This approach is straightforward but can assess the test field performance only in total without showing spatial variability of oxidation efficiency.

(2) The **carbon shift approach** is based on the fact that the ratio of carbon dioxide to methane shifts to higher values as a result of the oxidation process while the total volume of carbon dioxide and methane remains constant as one mol of methane is converted into one mol of carbon dioxide (see Equation 7). Christophersen et al. (2001) and Gebert et al. (2011c) proposed that hence the oxidation efficiency along a path of interest can be derived

from the shift of the carbon dioxide - methane ratio when concentrations in the raw landfill gas and in a soil depth of interest or in the emitted gas are known (Equation 9). This approach is robust against dilution of soil gas components by diffusive air ingress from the surface because both components are diluted to the same extent.

$$Eff_{0x} = \frac{x}{CH_{4_LFG}} * 100$$
 Equation 9

with

$$\frac{\mathrm{CO}_{2_\mathrm{LFG}} + x}{\mathrm{CH}_{4_\mathrm{LFG}} - x} = \frac{\mathrm{CO}_{2_i}}{\mathrm{CH}_{4_i}} \iff x = \frac{\frac{\mathrm{CO}_{2_i}}{\mathrm{CH}_{4_i}} \times \mathrm{CH}_{4_\mathrm{LFG}} - \mathrm{CO}_{2_\mathrm{LFG}}}{1 + \frac{\mathrm{CO}_{2_i}}{\mathrm{CH}_{4_i}}}$$

with

EffOx = Oxidation efficiency (% of inlet methane) $CO_2_LFG = CO_2$ concentration in landfill gas (vol.%) $CH_4_LFG = CH_4$ concentration in landfill gas (vol.%) $CO_2_i = CO_2$ concentration in depth i (vol.%) $CH_4_i = CH_4$ concentration in depth i (vol.%) x = Share of oxidized methane (fraction of 1)

The approach assumes soil respiration to be negligible, gas migration to be vertical and the system to be in a steady state.

Using the carbon shift approach the efficiency for each grid field was calculated using the inlet gas concentrations and the volumetric emissive flux of carbon dioxide and methane at the surface derived from chamber measurements. Additionally, the oxidation accomplished in the gas distribution system was calculated by comparing the gas composition of the supplied gas and the gas composition in the depth of 1 m. The efficiency between 1 m depth and the surface was calculated as the difference between the total efficiency from inlet to surface and the efficiency from inlet to 1 m depth.

The calculation of the **methane oxidation rate** was done according to Equation 10.

Ox_rate = load to field * ox_efficiency / area of field	Equation 10
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The calculation of the **base flux** into each grid field is given in Equation 11.

Base flux = methane emission / (100 - oxidation efficiency) * 100 Equation 11

4.7 Introduction to the Methane Oxidation Tool (MOT)

The *Methane Oxidation Tool* (MOT) (Gebert et al., 2011d) is a simplified model approach to estimate methane oxidation potentials in landfill cover soils. It factorizes a standard oxidation potential of 17.1 g CH₄ m⁻² d⁻¹ (equivalent to 6.2 kg CH₄ m⁻² a⁻¹ or 1 L m⁻² h⁻¹) at 14% porosity, 20 °C and 6 kPa water potential. According to the prevailing conditions of temperature, air capacity and soil water potential, based on the known influence of these parameters on the process of methane oxidation, the standard oxidation potential is correcting it to a more realistic site specific factorized oxidation unit. The value for the

standard oxidation unit is an empirical assumption made by the authors of the model based on literature and own data. In the following, the factors are described briefly and the calculation for the factorized oxidation unit is given.

The temperature factor can vary from 0.25 to 2.78 (hence modifying the standard oxidation unit from 25% to 278%). For each 5°C step from 0°C to 50°C one factor is defined according to the known temperature - activity relationships (Figure 17). With increasing temperatures, oxidation rates increase. Above about 35 °C, rates decrease due to degeneration of methanotrophic bacteria.

Air capacity factor varies from 0.05 to 9.73 for porosities from 10 to 36% v/v. The relationship is based on the relation between porosity and diffusivity calculating the amount of oxygen that is able to diffuse into the soil. As two mol of oxygen are required to oxidize one mol of methane, the diffusive oxygen ingress defines the oxidation potential.

The factor for soil water potential covers the range of water potentials from pF 1.8 (6 kPa) to pF 4.2 (1500 kPa) and assigns factors from one to zero. At water potentials lower than pF 1.8 (6 kPa) the water cannot drain freely and the soil is water logged. At pF 1.8 (6 kPa) water supply for methanotrophic bacteria is optimal and air capacity pore space is fully available. At pF 4.2 (1500 kPa) it is too dry for methanotrophic bacteria so no oxidation will happen.



Figure 17: MOT factors for temperature, porosity and water potential. Adapted from (Gebert et al., 2011d).

After identifying the factors they are multiplied with the standard oxidation potential (SOP) to derive the factorized oxidation potential (FOP) according to Equation 12. This output is the expected site specific oxidation rate at the prevailing point in time for which the environmental conditions (temperature, air-filled porosity and water potential) are valid.

Equation 12

FOP	= factorized oxidation potential
SOP	= standardized oxidation potential
F_{temp}	= factor for influence of temperature
F_{por}	= factor for influence of porosity
F_{wp}	= factor for influence of water potential
	FOP SOP F _{temp} F _{por} F _{wp}

The model is available online in form of a spreadsheet and an explanatory document from http://www.afvalzorg.nl/EN/About-us/Publications/Methane-oxidation.aspx.

In the comment to the model it is proposed to use the input data on soil temperature, water potential and air capacity for the depth corresponding to the middle of the assumed oxidation horizon. As in the case of the investigated test field gas profiles indicate oxidation down to 1 m (see chapter 5.3.6), soil temperature and moisture data from the sensor set installed in 40 cm depth were chosen (details on sensors in section 3.2). Water potential was calculated by applying the data on volumetric water content measured by the FDR probes to the water retention curve analyzed for the subsoil material.

Direct emissions are considered in the MOT as a cover type dependent share of the load to the cover that bypasses the oxidation layer through macropores such as cracks and hence do not take part in the methane oxidation process. Correction factors of 0.1 (i.e. 10% direct emissions) for permanent covers >100 cm thickness with a gas distribution layer and a porosity of over 20% up to 0.9 (i.e. 90% direct emissions) for daily covers or uncovered landfills are proposed. The assumption on the share of direct emissions from each cover type is based on field data on methane oxidation in Dutch landfills from *The Netherlands Organisation of Applied Scientific Research* (TNO). Still, the database has to be broadened to derive a reliable relationship between cover type and share of direct emissions.

Instead of the air capacity, which is a material constant reflecting the air-filled porosity at field capacity water content (corresponding to a pressure head of 6 kPa), the actual air-filled pore volume was used here. It was derived subtracting the measured volumetric water content from the total porosity determined for the material.

4.8 Data processing and statistics

Data from gas probes as well as soil surface concentrations were interpolated for a better visualization of the data with spline interpolation. Interpolation analysis and visualization were performed with SAGA-GIS 2.1.4.

Descriptive statistical analyses were made with *OriginPro 9.1G* (OriginLab Corporation). For analysis of variance (ANOVA), PASW Statistics 18.0.3 (SPSS Inc.) was used. To do so first homogeneity of variance was confirmed with a Levene test. Normality was tested with a Shapiro Wilk test. If these two prerequisites for ANOVA were confirmed it was executed. If significant variance between groups was confirmed, a Tukey post hoc test was done to identify homogeneous groups.

5 Results

5.1 Gas diffusivity and permeability of landfill cover soils at low water tensions

This section presents the results from the laboratory experiments on diffusive and advective gas transport through undisturbed 100 cm³ soil cores retrieved from the Wieringermeer test field and from the recultivation layer at Eckerkoppel landfill. Gas transport investigations were carried out at pressure heads from 2 - 30 kPa while the water retention curve was determined down to 0.3 kPa. This range covers soil moisture conditions from very wet occurring only at hindered drainage or during rainfall events (< 6 kPa) up to a state were the narrow coarse pores are drained (30 kPa). Water in the coarse pores (equivalent diameter \geq 10 µm) is still subject to gravitational water movement. At 6 kPa, the pores with an equivalent diameter of \geq 50 µm are void. This state is defined as field capacity and the corresponding air-filled pore space is defined as air capacity (Ad-hoc-AG Boden, 2005). Diffusive and advective transport processes were studied individually followed by considerations on the ratio of the magnitude of both processes and an estimation of resulting fluxes for different concentration and pressure gradients in field settings.

5.1.1 Structures of pore space

The soil water retention characteristics define the relationship between the water content and the corresponding pressure head of a soil. Next to texture, this soil- and site-specific property is strongly impacted by the degree of compaction and soil structure. The total pore volume (given in section 4.1.1) is filled with different shares of water and air. A decrease in water content results in an identical increase of air-filled porosity. Every pressure head is related to an equivalent pore diameter that can still hold water against the applied suction. A large change of water content indicates a large volume of pores of the equivalent pore diameter. The water retention characteristics for topsoil and subsoil differed (Figure 18 a). Along with the water retention curves of the actual samples the water retention curves for the soil texture of the sites (KA5: Slu (Wieringermeer topsoil), St2 (Wieringermeer subsoil) and Su2 (Eckerkoppel)) are given according to Wessolek et al. (2009). At Wieringermeer, the topsoil air-filled porosities relating to the applied pressure heads at which diffusive and advective gas transport was determined ranging from 11.7 - 30.9% (2 - 30 kPa), the subsoil from 27.3 – 41.9%. Air-filled porosity of Eckerkoppel topsoil was 10.6 – 35.4% the subsoil airfilled porosities were 3.9 - 30.4% (Figure 18 b). The topsoil materials of Eckerkoppel had a higher air-filled porosity than the Wieringermeer topsoil. The difference between the subsoil samples is such that air-filled porosity of the Eckerkoppel subsoil at 30 kPa suction is about as high as the Wieringermeer subsoil at 2 kPa.



Figure 18 a/b: Water retention curve (a) and resulting air-filled porosity (b) of the material from Wieringermeer and Eckerkoppel. Symbol: average; bars: min/max; n=5. Typical water retention curves for the soil material of the sites are given in (a).

Not only the absolute porosity of the examined materials, but also the structure of the pore size distribution differs between the examined samples.

The pores space of both **Wieringermeer soils** increases relatively constant with increasing pressure heads albeit on different levels. Topsoil and subsoil exhibited an increase in air-filled porosity of 7.2% between 0.3 kPa and 2 kPa (980 μ m and 150 μ m equivalent diameter) followed by an increase of 7.3% and 10.3% from 2 kPa to 30 kPa (150 μ m to 10 μ m) (Table 2). In this range, the increase of air-filled porosity of the Wieringermeer topsoil material was from 17.2% to 24.5% and of the Wieringermeer subsoil material it was from 29.6% to 39.9%. The air-filled porosity at 0.3 kPa (hence with pores > 980 μ m being void) was 10% for the Wieringermeer topsoil and 22.4% for the suboil.

The pore size distribution of the **Eckerkoppel soils** is less homogeneous. Both topsoil and subsoil had very low air-filled porosities at 0.3 kPa of 3.7% and 6.2%. While the topsoil had only 2.5% pore space with an equivalent diameter of 70 μ m to 980 μ m, the subsoil had 13.8% pore volume in that range of pore diameters. Pores between 50 μ m and 70 μ m (3 kPa to 6 kPa) contribute 9.5% to the pore volume in the topsoil and 5.2% in the subsoil. From 50 μ m to 30 μ m (6 kPa to 10 kPa) the topsoil had a pore volume of 8.4% and the subsoil of 5.2%. Pores between 30 μ m (10 kPa) and 10 μ m (30 kPa) diameter added 3.6% (topsoil) and 4.2% (subsoil) to the air-filled porosity.

In comparison, the loamy Wieringermeer soils exhibit a homogeneous pore space distribution over the observed range of equivalent pore diameters while the pore volume is lower than the volume of the sandy Eckerkoppel soils. The pore space distribution of the latter is characterized by a larger share of pores > 50 μ m, hence wide coarse pores. The Eckerkoppel topsoil shows a peculiar pore size distribution: a substantial share of pore volume is between 70 μ m and 30 μ m equivalent diameter. Larger and smaller pores seem to be virtually absent.

To ascertain if the different pressure heads resulting in significantly different groups of airfilled porosity, an analysis of variance (ANOVA) with Tukey post-hoc test was performed. The 0.3 kPa, 8 kPa and 10 kPa data displayed in Figure 18 were not included in the analysis because no gas transport parameters were determined at these pressure heads.

For the **Wieringermeer topsoil** no significantly different groups could be determined (Table 2), meaning that variability of air-filled porosity resulting from the different pressure heads was not higher than the variability within the five parallels at any single pressure head. For the **Wieringermeer subsoil** samples three different groups of air-filled porosity were determined, one covering the pressure head of 2 kPa and one covering the 6 kPa heads and a third containing the 20 kPa and 30 kPa data. Porosities at 4 kPa were assigned to an intermediate group between the 2 kPa and 6 kPa groups. For the **Eckerkoppel topsoil** one group was formed by the 2 kPa porosities, a second group was formed by the 6 kPa porosities and a third group was formed by the 20 and 30 kPa data. An intermediate group was covered with the 4 kPa data. The **Eckerkoppel subsoil** divides into three groups. One is covered with the 2 and 4 kPa data, one with the 6 kPa data and one with the 20 and 30 kPa data.

It can be stated that the range of APF within each pressure head group is high and hence the small spatial variability within the set of five samples is considerable.

Table 2: Results of the Tukey HSD test performed on the values for air-filled porosity corresponding to the pressure heads of 2, 4, 6, 20 and 30 kPa. n=5. Superscripts indicating homogeneous groups are valid over the individual columns only. n.d.: no data: Wieringermeer topsoil 6 kPa value was excluded from further analysis because the samples did not drain to that water tension. Additionally porosity at 0.3 kPa and total porosity are given, both not included in the ANOVA.

	Mean air-filled porosity [%v/v ± SD]				
kPa / pore diameter [μm]	Wieringermeer topsoil	Wieringermeer subsoil	Eckerkoppel topsoil	Eckerkoppel subsoil	
0.3 / 980	9.97 ± 1.94	22.42 ± 3.41	6.18 ± 1.90	3.70 ± 1.26	
2 / 150	17.21 ^ª ± 4.23	29.62 ^a ± 2.52	15.78 ^ª ± 1.11	5.34 ^a ± 3.3	
4 / 70	18.17ª ± 4.34	31.13 ^{a,b} ± 2.13	19.96 ^{a,b} ± 1.09	6.21ª ± 3.25	
6 / 50	n.d.	33.63 ^b ± 2.06	25.17 ^b ± 2.24	15.68 ^b ± 2.85	
20 / 15	23.86 ^a ± 4.86	40.43 ^c ± 1.47	31.32 ^c ± 2.14	24.88 ^c ± 2.63	
30 / 10	24.50 ^a ± 4.68	39.89 ^c ± 1.36	32.66 ^c ± 2.70	27.63 ^c ± 2.67	
total porosity	59.35 ± 1.75	54.69 ± 1.02	47.45 ± 2.87	43.67 ± 0.50	

5.1.2 Variability of diffusive properties with changing moisture

According to the procedure described in section 4.1.2, the diffusion coefficients (D_{eff}) of the four sets of soil samples were determined in a diffusion chamber experiment in the laboratory. The water content of the samples governs the air-filled porosity. As gas fluxes

happen through the water free (i.e. air-filled) pore space the parameter *air-filled porosity* is used for the evaluation of the experiment albeit water content is the actual determining factor. The diffusion models presented in section 2.1.1.4 are applied to the data. The relationship between air-filled porosity and D_{eff} was examined first for the whole dataset followed by the four individual datasets. After that, it was analyzed if the D_{eff} values were significantly different between the examined water potentials using ANOVA.

In Figure 19, the derived diffusion coefficients D_{eff} for all samples are plotted against airfilled porosity. The accuracy of the determination was very high for most of the samples. The distribution of the D_{eff} clearly follows a power function. In Figure 19 the Buckingham (1904) model (Equation 3) and the Troeh et al. (1982) model (Equation 6) (with parameters u=0.045, v=1.9) is given over the range of all data. The root mean square error (RMSE) of the fitted Troeh model is smaller than the one of the Buckingham model (Table 3). Still, the scatter is quite high; hence, describing the entire dataset with a single function would lead to less accurate model predictions. The least diffusive material was the Eckerkoppel subsoil material, the highest diffusion coefficients were found for the Wieringermeer subsoil. The topsoil material from both sites was comparable albeit the Wieringermeer topsoil showed slightly higher D_{eff} . At the same air-filled porosity, samples with higher organic matter content (Table 1) yielded higher D_{eff} values except for the Wieringermeer subsoil samples which were almost always the most diffusion penetrable samples.



Figure 19: Diffusion coefficients (D_{eff}) of all four sample groups against air-filled porosity (AFP). Error bars: accuracy of determination.

In the following, particular functions for the four individual datasets were determined. The data for the **Wieringermeer top- and subsoil** show the best accordance with the Buckingham (1904) model that only considers air-filled porosity (Equation 3) as input parameter. The model fits better with the topsoil data than with the subsoil data. Root mean square errors for the applied models are given in Table 3. For the **Eckerkoppel top- and subsoil** the model proposed by Moldrup et al. (2005b) using a 10 kPa porosity form factor was most suitable. In all cases the non-predictive model from Troeh et al. (1982) (only shown in Figure 19) could be fitted to the data very well. Only for Eckerkoppel topsoil the Moldrup et al. (2005b) model was closer to the data. The Millington-Quirk model including only total porosity did not exceed the quality of the other models applied in any occasion.



Figure 20: Measured and modeled diffusion coefficients (D_{eff}) against air-filled porosity (AFP). Error bars: noise of measurement. Lines: models. Solid line: Buckingham (1904); dashed line: Millington and Quirk (1961), dotted line: Moldrup et al. (2005b).

After the examination of the correlation between air-filled porosity and effective diffusion coefficient it was analyzed if the variance of D_{eff} between the different pressure head groups was higher than the variance within the datasets for one pressure head (Figure 21). To this end, analysis of variance (ANOVA) with Tukey post-hoc test was made. In accordance with the description of the pore space distribution in chapter 5.1.1, groups could be identified most clearly when the pore volume of the associated pore sizes was high.

	Predictive models			Non-predictive model
		Millington-		
RMSE of Model	Buckingham	Quirk	Moldrup et al.	Troeh et al.
	(1904)	(1961)	(2005b)	(1982)
				u=0.045, v=1.9
All data	4.22×10 ⁻⁷	n.d.	n.d	4.04×10 ⁻⁷
Wieringermeer		ф=0.593	φ=0.593 ;ε ₁₀ =0.211	u=0.003; v=1.97
topsoil	2.34×10 ⁻⁷	5.91×10 ⁻⁷	3.72×10 ⁻⁷	2.34×10 ⁻⁷
Wieringermeer		φ=0.54	φ= 0.54 ; ε ₁₀ =0.333	0.045; v=1.8
subsoil	4.81×10 ⁻⁷	7.49×10 ⁻⁷	7.73×10 ⁻⁷	4.81×10 ⁻⁷
Eckerkoppel		φ=0.475	φ=0.475 ; ε ₁₀ =0.248	u=0.064;v=1.95
topsoil	4.32×10 ⁻⁷	4.10×10 ⁻⁷	2.63×10 ⁻⁷	2.63×10 ⁻⁷
Eckerkoppel		φ=0.437	φ= 0.437 ; ε ₁₀ =0.241	u=0.1; v=1.9
subsoil	4.92×10 ⁻⁷	4.12×10 ⁻⁷	2.71×10 ⁻⁷	1.68×10 ⁻⁷

Table 3: RMS errors of models applied to diffusion data. Bold number: best prediction. ϕ = total porosity; ε_{10} : air-filled porosity at 10 kPa; u,v: empiric parametrisation of Troeh model.

Except for the **Wieringermeer topsoil** ANOVA confirmed significantly different groups albeit not all pressure heads proved to be independent groups (Table 4). **Wieringermeer subsoil** data showed three groups. The first one was covered by the 2 and 6 kPa data, the second one by the 4, 6 and 20 kPa data and the third one by the 4, 20 and 30 kPa datasets. **Eckerkoppel soil** showed three groups for topsoil and subsoil as well. The first group of the topsoil data was covered by the 2, 4 and 6 kPa data, the second group contained only the 20 kPa data and the third group only the 30 kPa data. The first group of the subsoil data was covered by the 2 and 4 kPa data, the second group by the 4 and 6 kPa data and the third group by the 20 and 30 kPa data.


Figure 21: Diffusion coefficients (D_{eff}) of all four sample groups against water potential. Error bars: accuracy of determination.

As the scattering in the correlation between water potential and air-filled porosity already implied (5.1.1), the relationship between water potential and D_{eff} is weak too. Unlike for the air-filled porosity - D_{eff} relationship no model could be found for the water potential - D_{eff} relationship.

Table 4: D_{eff} means at the applied pressure heads and assignment to homogeneous groups identified by Tukey HSD test. n=5. Values in parenthesis: standard deviation. Subscripts indicating homogeneous groups are valid over the individual columns only.

	Mean D _{eff} [m ² s ⁻¹] (SD)												
	Wieringermeer	Wieringermeer	Eckerkoppel	Eckerkoppel									
кра	topsoil	subsoil	topsoil	subsoil									
2	6.29×10 ⁻⁷ a	1.58×10 ⁻⁶ a	3.41×10 ⁻⁷ a	4.08×10 ⁻⁸ a									
	(2.71×10 ⁻⁷)	(4.8×10 ⁻⁷)	(2.16×10 ⁻⁷)	(8.32×10 ⁻⁸)									
4	1.05×10 ⁻⁶ a	2.75×10 ⁻⁶ b,c	5.24×10 ⁻⁷ a,b	5.48×10 ⁻⁸ a									
4	(4.72×10 ⁻⁷)	(5.36×10 ⁻⁷)	(1.18×10 ⁻⁷)	(1.00×10⁻ ⁷)									
6	5.15×10 ⁻⁷ a	2.09×10 ⁻⁶ _{a,b}	7.63×10 ⁻⁷ b	5.78×10 ⁻⁸ a									
	(2.87×10⁻ ⁷)	(1.58×10 ⁻⁷)	(1.03×10 ⁻⁷)	(3.43×10⁻ ⁸)									
20	1.02×10 ⁻⁶ a	2.91×10 ⁻⁶ c	1.53×10 ⁻⁶ c	4.99×10 ⁻⁷ b									
20	(4.09×10 ⁻⁷)	(3.11×10 ⁻⁷)	(1.39×10 ⁻⁷)	(8.06×10⁻ ⁸)									
20	1.12×10 ⁻⁶ a	3.09×10 ⁻⁶ c	1.64×10 ⁻⁶ c	8.04×10 ⁻⁷ c									
50	(3.68×10 ⁻⁷)	(2.41×10 ⁻⁷)	(1.73×10 ⁻⁷)	(1.21×10 ⁻⁷)									

The coefficient of variation for air-filled porosity and D_{eff} was calculated and is shown in Figure 22. The coefficient of variation is a normalized measure for the relation of the standard deviation to the mean. Hence, the variation of datasets with different means is made comparable. The coefficient of variation of the air-filled porosity of the Wieringermeer topsoil was high over the whole range of water potentials. It was only exceeded by the Eckerkoppel subsoil variation for 0.3 to 4 kPa water potential and by Eckerkoppel topsoil at 0.3 kPa. The variation of the Wieringermeer subsoil and Eckerkoppel topsoil was comparably low and constant over the whole range of water potentials except for the 0.3 kPa saturation where both had a maximum. The coefficient of variation of the D_{eff} values was again constantly high for the Wieringermeer topsoil and again Eckerkoppel subsoil data was higher at 2 and 4 kPa (no diffusion data for 0.3 kPa). For this range of water potentials, an increase was found for Eckerkoppel topsoil and Wieringermeer subsoil as well. Hence, a constant variation within these samples over the range of the investigated air-filled porosities was accompanied with a higher variation of D_{eff} values for low water potentials for these samples.



Figure 22: Coefficient of variation of air-filled porosity and Deff.

5.1.3 Variability of advective properties with changing soil moisture

Gas permeability (k_{gas}) data is displayed in Figure 23. For higher values of k_{gas} the accuracy of determination was slightly lower than for the determination of the diffusion coefficients. The data could not be described by a single function over the four groups of pore size classes reflected by the applied pressure heads. Also, no describing functions could be found for the particular sites. The following description of the data sets for each site is illustrated in Figure 24. The **Wieringermeer topsoil** permeability was highly scattered with an insignificant positive trend over the range of air-filled porosity while the **Eckerkoppel topsoil** permeability increased slightly but significant with air-filled porosity. **Wieringermeer subsoil** permeability seemed to be within the same range over the observed range of air-filled porosity without any influence of the increasing air-filled porosity. **Eckerkoppel subsoil** was virtually impermeable until about 20% air-filled porosity. Above that value, permeability

increased without showing a significant trend. The topsoil data for both soils showed about the same range of air-filled porosity and k_{gas} , while the Eckerkoppel topsoil was more homogeneous than the Wieringermeer topsoil. The subsoils showed less heterogeneity than the topsoils but could be distinguished a lot between each other. The Wieringermeer subsoil samples had about one order of magnitude higher permeabilities than the Eckerkoppel subsoil samples while air-filled porosity of the Wieringermeer subsoil showed a smaller range at higher level than the Eckerkoppel subsoil samples.



Figure 23: Gas permeability coefficients (k_{gas}) of all four sample groups. Error bars: accuracy of determination.

To explore the variability of the permeability data over the water potentials (Figure 25), an analysis of variance (ANOVA) with Tukey post-hoc test was performed (Table 5). Grouping was less selective than for the D_{eff} values. ANOVA yielded only one significant subgroup for Wieringermeer topsoils. For Wieringermeer subsoil two groups were identified. One covering the 6 kPa data and the other covering the 4 kPa and 30 kPa data. 2 kPa and 20 kPa data were assigned to both groups. For both Eckerkoppel soils, three groups were identified. For the Eckerkoppel topsoil data, 2 kPa data were assigned to one group and 30 kPa data to a second group. The third group was covered with 4 kPa, 6 kPa and 20 kPa data which all belong to one of the other groups as well. For Eckerkoppel subsoil one group was formed by the 6 kPa data and one by the 20 kPa data. The third group was covered by 2 kPa, 4 kPa and 30 kPa data which all were assigned to one of the other assigned to one of the other groups as well.



Figure 24: Coefficient of gas permeability (k_{gas}) of the four sample sets of the range of air-filled porosity (AFP). Error bars: standard deviation.

Table 5: k_{gas} means at the applied pressure heads and assignment to homogeneous groups identified by Tukey HSD test. n=5. Values in parentheses: standard deviation. Subscripts indicating homogeneous groups are valid over the individual columns only.

	Mean k _{gas} [m s ⁻¹] (SD)												
L-D-	Wieringermeer	Wieringermeer	Eckerkoppel	Eckerkoppel									
кра	topsoil	subsoil	topsoil	subsoil									
2	2.55×10 ⁻² a	2.32×10 ⁻² _{a,b}	1.49×10 ⁻² a	1.68×10 ⁻³ _{a,b}									
2	(5.81×10 ⁻³)	(1.55×10 ⁻³)	(3.13×10 ⁻³)	(2.45×10 ⁻³)									
Л	2.48×10 ⁻² a	2.54×10 ⁻² b	2.11×10 ⁻² b,c	2.31×10 ⁻³ _{a,b}									
4	(4.18×10 ⁻³)	(1.66×10 ⁻³)	(4.35×10 ⁻³)	(8.16×10 ⁻⁴)									
G	1.52×10 ⁻² a	2.18×10 ⁻² a	2.00×10 ⁻² _{a,b}	1.65×10 ⁻³ a									
0	(6.91×10 ⁻³)	(1.30×10 ⁻³)	(2.04×10 ⁻³)	(4.63×10 ⁻⁴)									
20	1.79×10 ⁻² a	2.35×10 ⁻² _{a,b}	2.12×10 ⁻² b,c	6.77×10 ⁻³ c									
20	(6.75×10 ⁻³)	(1.46×10 ⁻³)	(1.11×10 ⁻³)	(3.25×10 ⁻³)									
20	1.97×10 ⁻² a	2.52×10 ⁻² b	2.56×10 ⁻² c	5.32×10 ⁻³ b,c									
50	(6.65×10 ⁻³)	(1.92×10 ⁻³)	(1.64×10 ⁻³)	(1.13×10 ⁻³)									

The ANOVA results propose that at Eckerkoppel topsoil, the measured gas permeability at 2 kPa and 30 kPa can be attributed to one of the water tensions while for the other pressure heads the variability within the data groups is higher than the variability between the groups. For Eckerkoppel subsoil measurement data from 6 kPa are homogeneous enough to be assigned to one group and data derived at 20 kPa could be assigned to another group. The measured variability of the permeability of the other groups could not be attributed to the different water tensions but to variance within the sample group. For Wieringermeer topsoil the variance of gas permeability within each pressure head is higher than the variance between the pressure heads thus from water tension gas permeability cannot be estimated. For Wieringermeer subsoil two groups, one for 6 kPa data and another for 30 kPa and 4 kPa data were identified yielding significantly different gas permeability while for the rest of the pressure heads it was not so obvious.

As it has been shown already for the AFP - k_{gas} relationship it was impossible to find a describing function for the k_{gas} – water potential relationship.



Figure 25: Coefficients of permeability of all four sample groups. Error bars: accuracy of determination. n = 5.

The coefficient of variation of k_{gas} values is shown in Figure 26. The coefficient of air-filled porosity is given above (Figure 22). Between 6 and 30 kPa all sample groups showed a constant coefficient of variation while again Wieringermeer topsoil and Eckerkoppel subsoil had the highest variation. At low water potentials the k_{gas} variation of the Eckerkoppel topsoil increased while the variation of the Wieringermeer topoil values decreased. Eckerkoppel subsoil variation was excessively high at 2 kPa as it was already found for air-filled porosity and D_{eff} .



Figure 26: Coefficient of variation of kgas. n=5.

5.1.4 Relation of diffusive and advective gas permeability

The change of the gas transport parameters with changing air-filled porosity was examined. The focus was to identify, if the two gas transport parameters under survey (D_{eff} and k_{gas}) changed differently over the range of air-filled porosity. To do so, their ratios were plotted (Figure 27). For all plots attempts of curve fitting for the $D_{eff} - k_{gas}$ ratio did not yield meaningful results (data not shown). The quality of all fits was quite poor and more or less equal for all tested functions. So no clear trend could be identified. In the following, the scatterplots are described by visual inspection.

The Wieringermeer topsoil showed a more or less linear correlation between diffusivity and conductivity. The Wieringermeer subsoil increased in diffusivity with only a minor increase of gas permeability. Eckerkoppel topsoil data visually seemed to follow a logarithmic distribution albeit a quadratic curve fitting gave a better coefficient of determination. First diffusivity and permeability increased until the permeability level ceased to increase while the diffusivity still did. The Eckerkoppel subsoil was virtually impermeable between 2 and 6 kPa (Figure 20 and Figure 24). At 20 and 30 kPa increasing diffusivity was paired with a low and more or less constant permeability.

The Wieringermeer samples showed generally a more or less linear relation between both parameters albeit the slope was about double for the topsoil. For the Eckerkoppel soils, it appeared to exist two regimes. Diffusive and advective transport parameters increased over the 2 and 4 kPa measurement while for the 6 kPa to 30 kPa measurement advective transport properties stayed at one level while diffusive properties increased.



Figure 27: Ratio of D_{eff} and k_{gas}.

5.1.5 Resulting fluxes

In this section, the effect of changes in water saturation on diffusive and advective fluxes will be reviewed. The considerations are made for a soil depth of one meter, which is the thickness of the methane oxidation layer of the Wieringermeer test field. As gradients forcing the diffusive flux a low, a medium and a high gradient of 1%, 10% and 40% methane concentration were assumed. These gradients were selected because the average concentration of the supplied gas in the Wieringermeer field trial was around 40 percent methane. The first quartile of the methane concentrations was often found to be around ten percent methane. The one percent gradient was chosen to explore flux height at small concentration gradients that were found to be the median value in some gas probes. As pressure gradients driving the advective flux small differences of 1 Pa, 5 Pa and 10 Pa are considered. These are in the order of magnitude that was found in a campaign where the pressure in the gas probes was mapped (data not displayed).

Diffusive flux is linearly connected with D_{eff} , the concentration gradient and the pathway. For each of the concentrations gradients a flux was calculated according to Equation 1 for each D_{eff} derived from the diffusion experiment. In all cases, a one meter soil column was

assumed. Calculations were done for each pressure head. The average and the minimum and maximum fluxes are plotted in Figure 28 and Figure 29 (left side).

Advective fluxes are linearly dependent on the pressure gradient, the length of the pathway and the coefficient of permeability (k_{gas}). The fluxes resulting from the abovementioned pressure gradients were calculated according to Equation 2 for each k_{gas} value derived from the experiment. Again, the flux over a one meter of soil column was considered and calculations were made for each pressure head. A concentration of 40% methane is assumed for the calculation of the methane mass flow. The average and the minimum and maximum fluxes are plotted in Figure 28 and Figure 29 (right side).



Figure 28: Comparison of resulting diffusive and advective fluxes for Wieringermeer top- and subsoil. Bars: min/max.



Figure 29: Comparison of resulting diffusive and advective fluxes for Eckerkoppel top- and subsoil. Bars: min/max.

The resulting fluxes for diffusive transport were in the range of the expected oxidation capacity of methane oxidation systems. The advective fluxes were far beyond the capacities even at pressure gradients as low as 5 Pa.

It was explored at which gradients the order of magnitude of the resulting fluxes from diffusive and advective transport was equal. For most sites, it was found that at a concentration gradient of 40% methane a pressure gradient of only 1 Pa was sufficient to cause fluxes in the same order of magnitude while a pressure gradient of 5 Pa caused fluxes of an order of magnitude above the diffusive fluxes. For the Eckerkoppel subsoil, a pressure gradient of 2 Pa was necessary to obtain advective fluxes in the same order of magnitude than the diffusive flux at a concentration gradient of 40%.

The effect of a change in air-filled porosity on the resulting fluxes was different for diffusive and advective fluxes. For diffusive fluxes, it was found that the same volumetric change of air-filled porosity results in a higher change of D_{eff} and hence higher fluxes the higher the air-filled porosity was. This means, at a constant volumetric change of air-filled porosity, the dryer the soil, the faster the increase of the resulting fluxes (Figure 30). For example, at a concentration gradient of 40% methane over one meter of soil depth and an air-filled

porosity of 10%, an increase of air-filled porosity by one percentage point would resulted in changes of diffusive flux of 0.1 - 0.9 g CH₄ m⁻² d⁻¹ (Eckerkoppel subsoil and Wieringermeer subsoil, respectively). At 45% air-filled porosity, the same increase of air-filled porosity would change diffusive fluxes by 4 - 4.3 g CH₄ m⁻² d⁻¹.

As no model could be derived for the gas permeability, advective fluxes were calculated for the actual air-filled porosity during the experiments. The effect of air-filled porosity on resulting advective fluxes did not show a significant correlation. Over the whole range of occurring values for air-filled porosity a slight increase of resulting fluxes with increasing air-filled porosities was found (Figure 31). The increase of resulting advective fluxes for an increase of air-filled porosity of 1% was between 0.6 and 3.5 g CH₄ m⁻² d⁻¹ per pascal pressure difference over the whole range of air-filled porosities according to the linear models derived for each site and depth from the pooled data from all measurements on all samples of the particular set. Models for individual soil cores were not developed.



Figure 30: Comparison of change of diffusive fluxes over air-filled porosity (AFP). Fluxes were calculated using the model of Troeh et al. (1982) (Equation 6) fitted to the respective soils. A 40% methane gradient and one meter of soil column was assumed.



Figure 31: Comparison of advective fluxes over air-filled porosity (AFP) and linear regression lines. Fluxes were calculated assuming a pressure gradient of five Pa and one meter of soil using the k_{gas} values from all individual measurements (n = 1).

5.2 Soil gas composition patterns, morphology and properties of a *Reduktosol* formed in a landfill soil cover due to preferential escape of gas¹

In the previous chapter 5.1, the small scale variability of gas transport parameters was explored in a laboratory experiment. In this chapter, the interdependence of soil properties and preferential gas flow is explored. On this behalf, the results of research work on a hotspot site on the abandoned landfill K (3.1) are presented. Emissions from the hotspot were as high as 4.4 mol d⁻¹ (70.5 g d⁻¹) (Rachor et al., 2013). More details on the emission pattern can be found in Rachor et al. (2013) and Röwer (2014) (the hotspot reference number is 13). After a short description of the surface gas concentration and soil gas concentration monitoring the results of the subsequent excavation are presented. Differences of soil physical and chemical properties between hotspot and non-hotspot material were focused in the excavation to reveal feedback effects between soil structure and preferential gas flow.

5.2.1 Methane surface concentration and soil gas phase

Monitoring of the methane surface concentrations and the soil gas phase over half a year was done to explore the spatial and temporal stability of the gas concentration pattern and hence of the soil gas path ways. The campaigns for methane surface screenings and soil gas measurements at the hotspot site took place at six dates from October 2009 to April 2010. Soil moisture and temperature data were recorded 20 m away from the hotspot in 5, 15, 40 and 80 cm depth.

The **campaigning dates and ambient conditions** likely to influence the gas dynamics at the hotspot site are provided in Figure 32. Over the first five campaigns, temperature was generally falling, showing temperatures below zero in the topsoil at the 5th campaign in end of January 2010. The interval between the last two campaigns was longer than the intervals between the other ones. At the 3rd and the 5th campaign air pressure was falling. At the other ones air pressure was rising.

Surface concentrations are a clue to the presence and activity of hotspots but cannot be used to quantify emissions (Rachor, 2012; Röwer et al., 2016b). The **temporal variability** of the surface concentration through the campaigns is displayed in Figure 32. Dates with falling air pressure (3rd and 5th campaign) showed higher methane surface concentrations (Figure 32). The effect was more visible in the median value than in the arithmetic mean. Dry conditions in 80 cm depth seemed to lead to slightly lower methane concentrations at the surface (1st and 4th campaign). The frozen ground (5th campaign) seemed to increase concentrations although effects could not be attributed to isolated ambient variables. Due

¹ Some of the data used in this chapter were presented in the diploma thesis of the same author (Geck (2011)). It was decided to integrate the material into the context of this study to broaden the interpretation and to supplement and explain the newly presented data.

to the small number of measurement dates, no statistical analysis could be done. Surface methane concentration data showed a stable **spatial pattern** with variations of intensity through all campaigns (Figure 33). Within 20 cm from center outwards methane concentrations decreased over up to four orders of magnitude in each campaign. The highest methane concentration found at the hotspot center accounted for >8% v/v CH₄ (upper detection limit of FID) on 27.11.2009. The lowest methane concentration found in the center was 0.23% v/v on 06.11.2009. Beyond 50 cm outside the center values were typically below 100 ppm CH₄ (0.01%).



Figure 32: Ambient environmental conditions and variability of corresponding soil surface methane concentrations for six measurement campaigns. Box: data within 25^{th} to 75^{th} percentile; bar: median; square: arithmetic mean; whiskers: 10^{th} and 90^{th} percentile; triangles: minimum, maximum; n = 64. dP = averaged change of pressure over the last three hours prior to each measurement. Adapted from Geck (2011).

Soil gas concentration and its **spatial pattern** are depicted along with the spatial distribution of the surface concentration in Figure 33. For the examined depth of 20 cm, 40 cm and 60 cm a stable spatial pattern was found for the two respectively four campaigns per depth. The gas probe in the hotspot center contained high methane concentrations in all depth and in all campaigns. With increasing depth, the area of elevated methane concentrations increases radially (Figure 33). This proposed the existence of a cone shaped zone of high methane concentrations with a wide base in 60 cm depth and a very narrow spatial

extension at 20 cm depth. The **temporal variability** is lower than the one found for the surface concentration. The two occasions of falling air pressure are not noticeably different from the other dates.



Figure 33: Methane surface concentration (top) and soil gas methane concentration (bottom) of hotspot 13. Sampling scheme of the gas probes is given next to the methane concentration legend. Each square represents one gas probe. The circle indicates the position of the colored diagrams. Sampling scheme of surface screening is provided (bottom left). The rectangle of the survey grid is indicated in the center of the interpolated gas probe data. Adapted from Geck (2011).

5.2.2 Soil properties

The excavation of the hotspot site was intended to answer the question if soil physical or chemical features were present that can explain the soil gas and surface gas concentration pattern. A special focus was set on the description of small-scale features that might get lost in a standardized excavation.

5.2.2.1 Field observations and soil classification

The excavation of the hotspot site was documented according to *Deutsche Bodenkundliche Kartieranleitung 5* (KA5) (Ad-hoc-AG Boden, 2005). The landfill cover soil was excavated in two steps in order to not destroy important features. First, a **preliminary profile wall** was excavated 30 cm away from the hotspot center but still cutting the zone of elevated surface concentrations. This first profile wall, reaching down to 60 cm below surface, was characterized by a 40 cm thick layer of sandy loam (Sl2) below which a layer of 20 cm of mainly clayey sand (St2) was found (detailed soil texture description see section 5.2.2.2).



Within the second layer, a concrete block was found. Above the block, some degraded blue plastic material was found. Around that material, the soil appeared greyish (Figure 34).



Figure 34: Preliminary profile wall 30 cm away from hotspot center. Top: Photo of profile wall. Bottom: Location of samples within the profile wall of landfill K.DS: disturbed sample; US: undisturbed sample. NULL, NW1 and NW2 are gas probes. Samples next to the gas probe NULL (hotspot center) were considered representative for the hotspot, the rest was considered to represent non-hotspot material. Geck (2011).





Figure 35: Main profile wall of hotspot excavation on landfill K. Top: Photo of profile wall. Bottom: Location of samples within the main profile wall of landfill K. Grey color: reduced soil colors/hotspot area. DS: disturbed sample; US: undisturbed sample. NULL, NW1 and NW2 are gas probes. Samples within the gray area were considered representative for the hotspot, the rest was considered to represent non-hotspot material.

The **main profile wall** through the center of the hotspot revealed a two layer soil profile (Figure 36 top). The upper 55-65 cm consisted of homogeneous loamy sand (Sl2) with a low bulk density (Ld 2). Many earthworms were found, especially in the transition area to the lower layer. The worms were classified as *Dendrobaena hortensis* (U. Graefe, personal information, 2010). The lower layer was a loamy sand (Sl3) with a high bulk density (Ld 4). The lower layer appeared brindled with oxidized and reduced spots, especially in its upper area. Around the center of the hotspot, a cone-shaped bluish black and grayish black area was found. The cone was surrounded by bulked soil material with many earthworm burrows (Figure 36 left). The contact zone between the reduced black area and the surrounding oxic milieu showed an area of a dense worm population. In this worm-influenced area, material of jelly like consistency was found, very likely due to the accumulation of exopolysaccharides (EPS), especially intense in the upper most decimeter. The soil showed a purple color here. At the base of the preliminary profile under the now removed concrete block, a crack of about 7 cm length was found. Its inner walls were covered with iron oxide (Figure 36 right).



Figure 36: Details of hotspot soil profile. Left: bulky sponge like material from hotspot center. Earthworm burrows are visible and covered with orange oxic colors on its walls. Right: the walls of a crack in the base of the profile were coated with oxidized material. Adapted from Geck (2011).

In order to classify the soil profile according to the German soil classification system (Ad-hoc-AG Boden, 2005) the horizons were identified as follows: The topsoil (0-15 cm b.s.) was classified as *humic topsoil horizon* (Ah). In the hotspot center a reduced horizon (Yr) followed below beginning at 15 cm below surface. Some decimeters beside the topsoil was followed by an oxic subsoil horizon from 15-50 cm below surface (Yo). Beginning at a depth of 50 cm, a reduced subsoil horizon (Yr) was found. Thus, the horizon sequence from top to bottom in the very hotspot center was Ah/Yr classifying the profile as *"Fahlreduktosol (XXu)"* while outside the center the sequence Ah/Yo/Yr classified the soil type as *"Normreduktosol (XXn)"*.

The World Reference Base for Soil Resources (WRB) (FAO, 2014) defines the reference group Gleysols as soils having" (...) a layer \geq 25 cm thick, and starting \leq 40 cm from the mineral soil surface, that has (a) gleyic properties throughout; and (b) reducing conditions in some parts

of every sublayer." *Gleyic properties* are found where reducing conditions occur which can be due to upmoving gases such as methane (FAO, 2014). This is a novelty to the WRB 2006 where the influence of reducing conditions due to gas was not mentioned. The diagnostic criteria for gleyic properties are a layer with "95% (exposed area) having colors considered to be reductimorphic, that have a Munsell colour hue of N, 10Y, GY, G, BG, B, PB, moist (...)" (FAO, 2014). No detailed Munsell colors classification was done in the excavation but black and grey were the dominant colors matching the Munsell hue of 10Y and N.

Since the landfill cover soil material was brought to the site when the landfill was closed the material could be additionally qualified as *transportic (tn)* (FAO, 2014) but according to the WRB classification the qualifier *transportic* cannot be combined with the reference group of Gleysols. The profile meets the criteria for the qualifier *reductic (rd)* because in more of 25% of the fine earth fraction within 100 cm of the soil surface prevail reducing conditions caused by gaseous emissions. Thus, the excavated profile could be classified on the second level as a *Reductic Gleysol*.

5.2.2.2 Soil physical properties

Disturbed and undisturbed samples were taken from both profile walls. The samples were distinguished in hotspot and non-hotspot samples according to their position in the profile. Samples close to the hotspot center and soil material of the cone shaped reductimorphic area were defined as hotspot samples (for sample location see Figure 34).

The texture of the disturbed samples was analyzed in the laboratory. The highest sand content was found in sample DS1 (DS: disturbed sample) which was from the topsoil of the center of the first profile wall close to the inner center of the hotspot (Figure 37). DS 6, 3 and 7 follow behind, all of which are hotspot samples (location of samples see Figure 35). DS1 is classified as sand (WRB: S/KA5: Ss), DS 6, 3 and 7 consisted of clayey sand (WRB: LS/KA5: St2). All other samples were loamy sand (WRB: SL/KA5: Sl2 – Sl4).

From the undisturbed soil samples, the water retention curve and thereby the pore size distribution was determined (Figure 38). Total porosity and water-free porosity at pressure heads of 0.3, 2, 6 and 30 kPa were determined (Table 6). These pressure heads were chosen because they represent the coarse pores (> 10 μ m) which are of particular importance for the gas transport (see also chapter 5.1.1).

The pore space distribution of the samples from the **preliminary profile** wall did not show a pronounced difference between hotspot and non-hotspot samples. All samples from 10 cm depth were very similar over the whole range of observed water tensions while the hotspot samples from 40 cm depth had slightly lower air-filled pore space at low water tensions compared to the non-hotspot samples. The subsoil (40 cm) had a larger air-filled pore space than the topsoil (10 cm) over the whole range of water tensions. For the topsoil samples no pore space with an equivalent diameter between 150 μ m (2 kPa) and 980 μ m (0.3 kPa) was detected while the subsoil exhibited about 5% of porosity over the same range. Above 2 kPa

the air-filled pore space of all samples increased evenly indicating a similar porosity for pore diameters between 2 kPa (150 μ m) and 30 kPa (10 μ m).



Figure 37: Grain size distribution of the cover soil. DSx: Disturbed sample ID.HS/NHS: Hotspot/Nonhotspot. Pre: sample from preliminary profile wall (see 5.2.2.1). Letters in columns: soil texture according to KA5/WRB. Adapted from Geck (2011).

The subsoil samples (90 cm b.s.) from the **final profile** wall were similar for hotspot and nonhotspot material. The air-filled pore space increased by six to nine percentage points over the observed water range of tension. The non-hotspot topsoil had a comparable pore space to the subsoil up to 2 kPa water tension. From there on air-filled porosity increased until at 30 kPa it was about as much as the air-filled porosity of the hotspot sample (24%). The set of samples from the hotspot center (US1, hotspot, 10 cm depth) showed the highest values for air-filled porosity for each water tension. In comparison to the non-hotspot reference samples (US6, non-hotspot, 10 cm depth) air-filled porosity was larger while the difference was highest (8.5%) at 2 kPa and declined with increasing water tension until being alike the non-hotspot sample at 30 kPa (26.5%). The share of coarse pores bigger than 980 μ m (difference at 0.3 kPa) and below 30 kPa (10 μ m) was higher in the hotspot topsoil. The coefficient of variance of the air-filled porosity is displayed in Figure 39. The main differences were found at the lower water potentials. The topsoil sample sets did have the highest coefficient of variation especially at 2 and 0.3 kPa. Table 6: Pore size distribution and bulk density each with standard deviation of the undisturbed samples (US) from hotspot 13. Samples with very low bulk density and high total porosity stemming from hotspot topsoil are highlighted. US1-4 were take from the preliminary profile wall 30 cm away from the very center of the hotspot while samples US5-10 were take from the profile wall through the hotspot center. n = 5. B.s. = below surface.

Sample	(N on) Hot S pot	Depth b.s. [cm]	Total porosity [% v/v]	Pore space at 0.3 kPa [%v/v]	Pore space at 2 kPa [%v/v]	Pore space at 6 kPa [%v/v]	ore space Pore space t 6 kPa at 30 kPa %v/v] [%v/v]	
US 1	HS	10	62.4±0.6	3.0±0.6	4.0±0.5	11.6±0.7	21.4±0.8	0.79±0.01
US 2	NHS	10	55.9±0.4	3.7±0.4	3.2±0.3	10.7±0.4	21.4±0.5	1.02±0.01
US 3	HS	40	56.0±0.2	2.9±0.2	9.1±0.5	17.4±0.6	25.04±0.4	1.13±0.04
US 4	NHS	40	52.2±0.4	5.7±0.4	11.0±0.7	17.8±0.8	26.7±0.8	1.29±0.02
US 5	HS	10	74.2±1.1	8.4±1.1	15.7±1.2	21.2±1.1	26.5±1.1	0.63±0.01
US 6	NHS	10	54.9±1.0	2.8±1.0	7.2±1.4	14.9±1.3	23.9±1.4	1.07±0.01
US 9	HS	90	33.5±0.3	4.0±0.3	5.0±0.4	7.3±0.5	14.3±0.5	1.76±0.01
US 10	NHS	90	32.4±0.5	5.1±0.5	5.7±0.5	7.3±0.6	11.8±0.6	1.83±0.02



Figure 38: Air-filled pore space at different pressure heads of hotspot and non-hotspot samples. Numbers in line signature indicate depth of sampling location in dm. Grey areas indicate standard deviation. n = 5. Adapted from Geck (2011).



Figure 39: Coefficient of variation of the air-filled porosity of the K samples. n=5. Red: hotspot, black: non-hotspot. Numbers in line signature indicate depth of sampling location in dm.

5.2.2.3 Soil chemical properties

Soil chemical properties were analyzed for the disturbed samples from hotspot and nonhotspot material from both profile walls. Inorganic carbon, nitrogen content, salinity and sulfate concentration were analyzed.

Inorganic carbon concentrations ranged around 0.31% and were not dependent on depth, i.e. they were equally distributed within the soil profile (data not shown). There was no difference between the hotspot site and the non-hotspot site. However, for organic carbon content a difference of mean concentrations of 1.9% w/w between hotspot and non-hotspot samples was found with higher concentrations in the hotspot samples and a linear depth dependency (Figure 40). From the five samples of 10 - 20 cm depth the samples DS1, 6 and 7, (DS: disturbed samples) stemming from hotspot material, had a higher C_{org} concentration than DS2 from non-hotspot material and DS5 from hotspot material. The highest C_{org} content of all samples (8.18%w/w) was found in the topsoil of the hotspot, 20 cm below surface (sample DS7). No non-hotspot material was sampled below 30 cm depth.



Figure 40: C_{org} content dependency on depth for hotspot and non-hotspot soil material of both profile walls. Linear regression is given for hotspot and non-hotspot samples showing a similar decrease with depth and an offset around 3% for C_{org} in hotspot material against non-hotspot material. HS: hotspot; NHS: non-hotspot; DSx: Disturbed sample ID.

With respect to the total nitrogen content, the research resulted in the same picture. The soil at the hotspot site in all depths contained approximately 0.2% w/w total nitrogen more than the non-hotspot samples. At both locations, the nitrogen content declined with depth. Again, sample DS7 yielded the highest content of 0.79% w/w.

Albeit the absolute levels of carbon and nitrogen were highest in the hotspot samples, the resulting carbon to nitrogen ratios were not systematically higher for the hotspot samples (Figure 43). The highest ratio of 16.8 was found in sample DS9, which is from the hotspot subsoil, while the lowest ratio of 7.2 was found in the sample DS12, which was next to DS9.

A similar pattern was found for the salinity data (Figure 42). Salinity decreased with depth and the hotspot samples showed an average salinity of about 111.3 μ S cm⁻¹ higher than the non-hotspot samples.

Our analysis of sulfate revealed an elevated sulfate concentration of 530 mg kg_{dw}⁻¹ in sample DS5, which was taken in 20 cm depth in the hotspot center. Sample DS8 from 30 cm depth had a sulfate concentration of 136 mg kg_{dw}⁻¹, sample DS9 from 50 cm depth of 81 mg kg_{dw}⁻¹ both stemming from the hotspot center. The average of all other samples was 19.3 mg kg_{dw}⁻¹.



Figure 41: Total nitrogen content declining with depth in hotspot and non-hotspot material of both profile walls. HS: hotspot; NHS: non-hotspot; DSx: Disturbed sample ID.



Figure 42: Electric conductivity dependence on depth for hotspot and non-hotspot material of both profile walls. Linear regression is given for hotspot and non-hotspot samples. HS: hotspot; NHS: non-hotspot; DSx: Disturbed sample ID.



Figure 43: C - N ratios of hotspot (HS) and non-hotspot (NHS) material. DSx: Disturbed sample ID.

To widen the scope, soil physical data were set into relation to organic carbon content. To do so the disturbed and undisturbed samples were matched according to Table 7. It was found that high organic carbon contents were related with low bulk densities (Figure 44) but high total porosity (Figure 45) and high air capacity (**Figure** 46). Field capacity and organic carbon did not relate (Figure 47). The two hotspot topsoil samples covered the extreme positions in each relation.

Undisturbed sample	Disturbed sample
US 1	DS1
US 2	DS2
US 3	DS3
US 4	DS4
US 5	DS6
US 6	DS10
US 9	
US 10	DS13

Tahlo	7· N	A atching	undisturbed	and	disturbed	samn	عما
lable	7 : N	natching	unaisturbea	anu	uistuibeu	samp	ies.



Figure 44: Relation between organic carbon and bulk density of undisturbed samples from hotspot (HS) and non-hotspot (NHS) site. USx: Undisturbed sample ID.



Figure 45: Relation between organic carbon and total porosity of undisturbed samples from hotspot (HS) and non-hotspot (NHS) site. USx: Undisturbed sample ID.



Figure 46: Relation between organic carbon and air capacity of undisturbed samples from hotspot (HS) and non-hotspot (NHS) site. USx: Undisturbed sample ID.



Figure 47: Relation between organic carbon and field capacity of undisturbed samples from hotspot (HS) and non-hotspot (NHS) site. USx: Undisturbed sample ID.

5.3 Spatial and temporal variability of methane emissions, oxidation efficiencies and oxidation rates of a methane oxidation cover test field

A biocover test field of 1060 m² on Wieringermeer landfill in The Netherlands was subject to in-depth exploration of methane oxidation performance with a special focus on spatial and temporal heterogeneity of methane emissions, methane oxidation efficiencies and methane oxidation rates. Spatial and temporal variability of the soil gas phase composition and of surface methane concentrations were analyzed. The variability of the soil gas composition in a period without landfill gas supply was compared to that of a natural soil in a park. This was done to ensure that under natural conditions, the soil gas phase concentration is homogenous and hence heterogeneity of the soil gas phase composition can be attributed to gas distribution within the test field. Emission and soil gas concentration measurements were performed over a period of 30 months covering summer and winter conditions. Oxidation efficiencies were calculated by constructing a methane mass balance over the whole test field and subscale efficiencies were calculated using the carbon shift method. The measurements are related to predictions of the MOT model (see chapter 4.7).

Before the actual results from the biocover test field will be presented, the validation process of the employed large static chamber will be outlined in the following section.

5.3.1 Evaluation of the large chamber method

For the Wieringermeer test field survey, a novel static emission chamber, covering a base area of 17.64 m^2 , was developed and employed. In this section, the validation of the measurement setup is described.

5.3.1.1 Chamber validation setup

To validate the measurement setup defined fluxes of a methane and carbon dioxide mixture (60%/40%) were applied to the chamber. The application was done by a tube with four endings placed evenly distributed on a plastic ground sheet covering the chambers footprint. The ground sheet was used to eliminate interactions with the soil. In a first step, it was tested that no gas entered the chamber. To do so the chamber was placed on the plastic ground sheet and monitored for six minutes. After that, a flux was applied until the methane concentration in the chamber was about 160 ppm. The concentration was monitored for about six minutes to prove if a concentration drop would occur indicating an exchange with the surrounding air. Both tests were carried out in a similar way by Röwer (2014). After that several fluxes were applied. Inlet gas flux was controlled by a gas flow controller and a rotameter. The rotameter was calibrated beforehand with the used test gas.

During one test run, five samples were taken in intervals of one minute to be analyzed in the gas chromatograph in the laboratory.

On a prior test without proper flux control, it was examined if differences occur when injection was realized by only one of the four tubes at a time, which was meant to represent one single point source. One test run was done without the fans to see if mixing of the air was necessary.

5.3.1.2 Results of chamber validation

The first run proved that neither methane nor carbon dioxide accumulated or depleted within the chamber. The average methane level over the test run was 2.12 ppm (SD 0.21), the average carbon dioxide level was 478 ppm (SD 2.33) during the six minutes of enclosure. In the second run, test gas was applied and left within the chamber to proof if it was sealed up against the ambient. During this test, the methane level was on average 162.9 ppm (SD 0.96) and carbon dioxide level 600.9 ppm (SD 1.31) over seven and a half minutes (Figure 48).



Figure 48: Course of methane and carbon dioxide concentrations during and after injection of gas.

After that defined fluxes were applied. Over the performed experiments good correlation was found between aplied and measured fluxes. Fluxes calculated from the detected methane fluxes using the flame ionisation detector (FID) were most accurate. The slope of linear regression over the mean values of two respectively three repetitions versus applied fluxes was 1.03 (Figure 49). The linear regression over fluxes calculated with the carbon dioxide data from the NDIR measurement versus the applied fluxes had a slope of 1.12 hence overpredicting the flux by approximately 11%.



Figure 49: Validation of large chamber flux measurement. Terms of linear regression are given.

The five gas samples taken during one test run were analyzed by gas chromatography in the laboratory. The laboratory data yielded the same slope for methane than detected by in the field measurement (data not shown).

In the previous experiment without proper flux contol it could be shown that it did not matter if the gas supply was realized by only one of the inlets nor by its position (data not shown). However it could be shown that mixing of the chamber volume with the fans was necessary to receive constant slopes (Figure 50).



Figure 50: CH₄ slope captured with the large chamber without fans and with fans. Fans were activated on after six minutes.

5.3.2 Environmental conditions over the study time

The performance of the biocover test field using the abovementioned methods was assessed over a period from May 2010 to October 2014. The air temperature, air pressure, soil temperature and soil moisture from August 2012 to October 2014 are listed in Table 8. Data from temperature and moisture probes installed in 40 cm depth were used (see section 4.7) averaged over three sites (up-, mid-, and downslope). In this period air temperature ranged between 0.1 °C and 27.3 °C, soil temperature between 5°C and 22.8°C and soil moisture between 16.4% v/v and 25.5% v/v. The resulting air-filled porosity ranged between 25.6% and 35.3%. Air pressure ranged between 997.6 hPa and 1023.2 hPa. The time course of soil temperature and moisture in an upslope, midslope and downslope position in 40 cm depth is shown in Figure 51 and Figure 52. Air temperature and pressure is shown in Figure A - 7 (Appendix). Temperature amplitude for the up-, mid- and downslope sensors was different with a higher amplitude upslope. The course was similar; hence, for correlation analysis the average could be used. Signals from the soil moisture sensors differed between the three positions without an apparent relation to the slope position. A soil moisture mapping campaign (see 5.3.3.5.2) did not show a moisture gradient over the slope. As soil moisture sensors are sensible to their directly surrounding soil material, it was considered most robust to average the sensor output of the three sites.

Table 8: Air temperature, air pressure, soil temperature, soil moisture and air-filled porosity of the
test field. Temperature and moisture data collected from the three (up- mid- and downslope
sensor were averaged. b.s. = below surface.

	Air	Air pressure	Soil temperature	Soil moisture	Air-filled		
Data	temperature		(40 cm b.s.)	(40 cm b.s.)	porosity		
Date		[hPa]	[°C]	[vol.%]	[%]		
	[°C]						
Aug 2012	24.2	1013.1	20.34	21.9	29.8		
Sept 2012	14.8	1010.5	18.1	20.6	31.1		
Oct 2012	n.d.	n.d.	14.6	25.5	26.2		
Nov 2012	8.4	1002.0	10.9	25.5	26.2		
April 2013	7.4	1001.2	5.3	24.8	26.9		
May 2013	13.6	997.6	12.5	22.5	28.9		
June 2013	24.9	1012.5	18	18.8	32.9		
July 2013 27.3		1012.1	22.9	16.4	35.3		
		Reconstructio	on of the test field				
Feb 2014	n.d.	n.d.	5	23.8	27.9		
Mar 2014	11.6	1012.4	9.9	22.4	29.3		
April 2014	10.3	1023.2	10.9	22.3	29.4		
May 2014	n.d.	n.d.	17.2	18.1	33.6		
June 2014	n.d.	n.d.	20.4	22.7	29.0		
Aug 2014	n.d.	n.d.	21.4	20.2	31.5		
Sept 2014	18.2	1017.4	22.8	16.5	35.2		
Oct 2014	14.7	1002.9	20.9	18.6	33.1		
Jan 2015	0.1	1009.4	6	26.1	25.6		
Feb 2015	2.2	1019.8	4.9	25.2	26.5		



Figure 51: Soil temperature of Wieringermeer test field in 40 cm depth.



Figure 52: Soil moisture of Wieringermeer test field in 40cm depth.

5.3.3 Soil gas phase

5.3.3.1 Temporal variability

The soil gas survey of the gas phase in 25, 60 and 100 cm depth by means of gas probes gave an insight into the gas distribution within the test field area during the survey. As methane is removed by the oxidation process, the absence of methane at one point in the soil gas phase can indicate that no methane did reach that point or that it had been completely oxidized. Nitrogen is inert in the oxidation process. While oxygen is consumed, nitrogen accumulates at locations where atmospheric air penetrates the soil and oxidation occurs. Thus, nitrogen was used as an indicator for aeration. As the landfill gas fed into the field contained around 30-40% nitrogen, all nitrogen levels above that were attributed to aeration. As oxygen is consumed in the process, its concentration does not give information about aeration. Carbon dioxide is produced within the oxidation process and by soil respiration. Both sources could not be separated. This is why in the following, only methane and nitrogen data are displayed. Carbon dioxide and oxygen data are given in the appendix (Figure A - 5 and Figure A - 6).

Soil gas composition was examined with respect to its temporal variability within four distinct time periods. The first period was June 2012 to July 2013, which was before the reconstruction works and with a load to the test field of $32.9 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. The second period was from October 2013 to January 2014. It was after the reconstruction. The load to the field was 29.2 g CH₄ m⁻² d⁻¹. The third period was after the reconstruction, too and lasted from February 2014 to June 2014. The load to the field was 13.5 g CH₄ m⁻² d⁻¹. The fourth and final period was August 2014 to February 2015 at a load of 38.6 g CH₄ m⁻² d⁻¹. The survey was performed in the depth of 25, 60 and 100 cm at an interval of about one month.

The maximum possible methane concentrations are predetermined by the methane concentration of the supplied landfill gas. From February 2014 until September 2014 the gas showed methane concentration of around 32% while at all other times the methane concentration usually was around 40%.

In the first period, **methane concentrations** in 100 cm depth varied showing lowest concentrations in spring and summer and maxima in late autumn (Figure 53). In the first period after reconstruction, mean concentrations were the highest of the total observation time and the scattering was decreasing over the three campaigns. In the second period after the reconstruction, the mean concentrations were generally higher while the scattering was lower. From autumn to summer the mean concentration was falling. In the fourth period, after a strong increase of the load, the scattering increased again. The last two winter campaigns showed the highest means of this period. In 25 and 60 cm depth, a very similar pattern was found compared to the one in 100 cm depth. Concentrations in the summer months were lower than in the winter months. During the reconstruction shutdown, no methane was detected at any sampling location.

The **nitrogen concentrations** followed the methane concentration pattern inversely (Figure 54). With increasing depth the nitrogen concentration decreased, indicating declining levels of aeration with increasing depth. In 100 cm depth, after reconstruction concentrations ranged around the nitrogen level of the supplied gas while before reconstruction average levels were higher as was the scattering. In 25 cm depth, the nitrogen concentration in many probes was by far lower than atmospheric levels. This corresponds to the high methane concentrations in some of the 25 cm probes. The concentrations in 60 cm depth were intermediate between the concentrations in 25 cm and 100 cm depth. During the reconstruction shutdown, nitrogen levels in all probes and depth were almost at atmospheric level.



Figure 53: Methane concentrations 25, 60 and 100 cm below surface over time.

The effect of the parameters air temperature, air pressure, air-filled porosity and soil temperature on the methane and nitrogen soil gas concentration was explored for each of the four abovementioned periods. Mean concentration, standard deviation and coefficient of variation as indicator for homogeneity for each campaign over all gas probes were used for the examination. It was found that in the first period air-filled porosity was negatively correlated with the level of methane concentration in all depths while the coefficient of variation was positively correlated (Table 9). Rising air pressure had a negative effect on the concentrations in 25 and 60 cm while the coefficient of variation increased and air temperature had a negative effect on the concentrations in 60 cm depth. No correlation was

found as far as the change of air pressure six hours and twelve hours before the measurements is concerned. In the second period an influence of air-filled porosity on 60 cm and 100 cm depth was found and a correlation between soil temperature and the concentration in 25 cm depth. Higher air temperature resulted in higher heterogeneity while the mean concentration was affected only in 60 cm depth. In the third period, concentrations in 25 cm and 60 cm depth were correlated to soil temperature. In the fourth period, a correlation between air temperature and soil temperature with the concentrations in 60 and 100 cm depth was found. Air-filled porosity had an effect in 60 cm depth; soil temperature was correlated to mean concentrations in 100 cm depth.

The nitrogen concentration of all depths was positively correlated to air-filled porosity in the first period. (Table 10) Air pressure had an influence on the 25 cm and 100 cm depth nitrogen concentration and air temperature on the 25 cm depth concentrations. An increase of each parameter resulted in a more homogeneous nitrogen concentration. In the second period, the concentration in 100 cm depth correlated with the air temperature. In the third period, only the soil temperature was correlated to the concentrations in 25 cm and 60 cm depth while in the fourth period air-filled porosity and air temperature were correlated to concentrations in 60 cm depth.

Summing up the interrelation between the average level of gas concentration of each campaign and the examined parameters, the height of concentration was found to correlate most with air temperature and air-filled porosity. The influence was most notable in the first period which was before the reconstruction. Higher mean methane concentrations were related to lower standard deviations while higher nitrogen concentrations were related to lower standard deviations. Hence, in the less compacted field higher air temperatures and higher air-filled porosity (i.e. dryer conditions) caused lower methane concentrations with less homogeneity and higher and more homogeneous nitrogen concentrations. The effect of temperature and air-filled porosity (or inversely: moisture) could not be separated because the parameters were auto-correlated.

Table 9: Coefficients of correlation between ambient parameters and methane soil gas concentrations. Mean methane concentration, standard deviation and coefficient of correlation for 25, 60 and 100 cm depth below surface (b.s.) (upper part of the table) and correlation coefficients of the correlation between air temperature, air pressure, air-filled porosity (AFP) and soil temperature and methane concentrations for four time periods (lower part of the table). Level of significance: p < 0.05. Mean, standard deviation (SD) and coefficient of variation were determined for each measurement date over all gas probes of the test field (n = 54). The number of measurements in each of the four time periods was n = 3 to 8. n.d.: no data; for the third period no available. air temperature and air pressure data was b.s.: below surface.

					•												
2015		0.80	0.57	0.59	Coefficient of Variation												
14 - 02/	[4 - 02/	7.37	7.45	7.29	DS					98							
08/20	n=5	13.0	24.1	25.8	nsəM		-1.0	97					98				97
014		0.76	0.40	0.24	Coefficient of Variation												
4 - 06/2		7.74	5.33	4.01	DS										97		
2/201/	n=5	14.2	20.6	25.0	nsəM	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.				96	92	
/2014		0.27	0.23	0.21	Coefficient of Variation	1.0	1.0	1.0									1.0
13-01		3.37	3.51	3.52	DS	1.0	1.0									1.0	1.0
10/20	n=3	30.0	32.5	33.6	nsəM		-1.0						94	94	-1.0		
/2013		1.71	1.39	0.80	Coefficient of Variation	90			.84	.74		.86	89.	68.			
12-07		6.03	8.06	8.75	DS	84	81		90	82		89	84				
06/20	n=8	5.9	10.5	16.9	nsəM		72		83	80		85	86	89			
		25	60	100	.s.d dtq9D	25	60	100	25	60	100	25	60	100	25	60	100
		CH₄ concehtr. [%]		[%]	Significant correlation coefficients (p < 0.05)	Air temp			Air	pressure		AFP			Soil temp		



Figure 54: Nitrogen concentrations 25, 60 and 100 cm below surface over time.

After the examination of the temporal variability of the whole test field, the focus lay on the temporal variability and response on external factors of three individual gas profiles. One up-, mid-, and downslope profile was chosen each (D2, C6 and B8) (Figure 55). In a correlation analysis it was found that the methane concentration in the upslope soil profile (D2) correlated positively with the methane load (in 100 cm depth) and to the methane concentrations of the supplied gas (25 cm and 100 cm depth) (p < 0.05). Air pressure had an influence on the concentrations in 25 cm and 100 cm depth. Mid- and downslope profiles were not affected by these parameters. The methane concentration in all profiles was influenced by soil temperature (D2: 25 cm; C6: all depth; B8: 25 and 100 cm) and partly by air-filled porosity (D2: 25 cm; C6: 60 cm; B8: 100 cm). Air temperature correlated with the 25 cm depth concentrations of the upslope profile and the 100 cm depth concentrations of the midslope profile. In 100 cm depth in the upslope profile (D2) the methane concentration was constantly high except for the reconstruction shutdown in August 2013. In summer, concentrations in 60 cm and 25 cm depth decreased below the level of 100 cm depth. Especially after the reconstruction, there was hardly any difference between concentrations in 60 cm and 100 cm depth. After the reconstruction, the midslope profile (C6) showed very similar concentrations compared to the upslope profile albeit the maximum concentrations showed a higher variation. Before reconstruction, concentrations were a lot lower in the midslope. No methane came up to 25 cm depth. At the downslope position (B8),
Table 10: Coefficients of correlation between ambient parameters and nitrogen soil gas concentrations. Mean nitrogen concentration, standard deviation and coefficient of correlation for 25, 60 and 100 cm depth below surface (b.s.) (upper part of the table) and correlation coefficients of the correlation between air temperature, air pressure, air-filled porosity (AFP) and soil temperature and nitrogen concentrations for four time periods (lower part of the table). Level of significance: p < 0.05. Mean, standard deviation (SD) and coefficient of variation were determined for each measurement date over all gas probes of the test field (n = 54). The number of measurements in each of the four time periods was n = 3 to 8. n.d.: no data; for the third period no air temperature and air pressure data was available. b.s.: below surface.

08/2014 -		n=5	0.16	0.20	0.09	Coefficient of Variation						83		92	89		89	
	02/2015		8.53	8.60	4.68	DS					96							
			64.9	50.6	49.8	nsəM		66.						.95				.89
2/2014 – 06/2014 n=5			0.15	0.10	0.10	Coefficient of Variation										99		
			8.87	5.55	4.06	DS										98		
	n=5		63.8	55.1	42.5	nsəM										96.	.91	
			0.09	0.10	0.19	Coefficient of Variation											1.0	
13 -	01/2014		4.03	4.08	10.8	DS		1.0									1.0	
10/20		n=3	47.3	43.8	59.8	nsəM			1.0									
06/2012 -	07/2013		0.13	0.18	0.20	Coefficient of Variation	81		77	87		79	87	82	81			
			7.97	10.2	8.94	DS	84		78	90			89	80				
		n=8	72.9	66.8	47.3	nsəM	.82			.87		.72	.88	.85	06.			
			25	60	100	.s.d dtq9D	25	60	100	25	60	100	25	60	100	25	60	100
			N ₂ concehtr. [%] Significant correlation coefficients (p < 0.05)		Air temp			Air pressure			AFP	40 cm b.s.		Soil temp	40 cm b.s.			

concentrations were still lower than at the midslope position. Between 100 cm and 60 cm depth, concentrations did not change much. In 25 cm depth, no methane remained in the soil gas phase hence the highest change happened in the upper part of the soil.



Figure 55: Gas profiles from test field. Profile D2: upslope, C6 midslope, B8 downslope. AFP:air-filled porosity.

5.3.3.2 Spatial variability

The methane concentration in the soil gas phase was examined with respect to its spatial variability within the four time periods mentioned in section 5.3.3.1. A spline interpolation of the average concentration of the respective period is given in Figure 56. The variability of the methane concentration at each location is expressed as a coefficient of variation. It is displayed as interpolation (spline) over the test field area in Figure 57. It can be seen as the spatial distribution of temporal variability. A boxplot graphing for each sampling location is given in Figure A - 1 to Figure A - 4 in the appendix. In general, it was found that the upslope gas probes showed higher methane concentrations than the downslope ones. This was found in all three depths through all four periods. The gas probes of column F were the only ones outside the catchment. Methane concentrations were lower there.



Figure 56: Mean CH₄ concentration in the depth of 25, 60 and 100 cm below surface. Average methane load to the test field and the time intervals are given at the top. Lower margin of the image is upslope. Grey line: catchment. Yellow dots: gas probes.



Figure 57: Mean coefficient of variation in the depth of 25, 60 and 100 cm below surface. Average methane load to the test field and the time intervals are given at the top. Lower margin of the image is upslope. Grey line: catchment. Yellow dots: gas probes.

The mean methane concentration of the first period (elevated base load, before reconstruction) was most heterogeneous. In 100 cm depth, the height of the methane concentration varies over the whole field with maxima upslope and on some downslope locations as A9 and F9. Concentrations decrease strongly from row one to row five. The sampling locations close to the inlet ports (B2/D2/B4/D4/B7/D7) except the two lowest ones showed elevated methane concentrations. In 60 cm depth, the pattern from below stays similar with an overall decrease of concentrations. In 25 cm depth, mean concentration is still lower. In the center, the highest methane concentrations occurred upslope. The coefficient of variance was highest at sites with low (but > 0) average concentrations.

The second period (high load, after reconstruction) showed a more homogeneous methane distribution in 100 cm depth than in the period before the reconstruction. The methane concentrations outside the catchment (row 9) were the lowest. The border of the catchment was situated between row 7 and 8. The closer the gas probe of row 7 and 8 were situated towards column E, the further they were inside the catchment. This is depicted by the methane concentrations in row 7 and 8 that show transient conditions with high concentrations within the catchment to low concentrations outside the catchment. The pattern found in 100 cm depth was repeated in 60 cm and 25 cm depth. Coefficient of variation was low over the whole test field and all depth. Some elevated coefficients were found at the border of the test field outside the catchment.

In the third period (low load, after reconstruction) mean soil gas concentrations were as homogeneous as in the second period while the concentration was lower. This was attributed to the lower methane content of the supplied gas (see above). Again, variation was very low. Highest coefficients of variance occurred in 25 cm at the border of the test field.

The fourth period (high load, after reconstruction) was characterized by high methane concentration in 100 cm depth within the catchment and no methane in the lower border of the test field and the downslope half of column F. The concentrations within the catchment were less homogeneous than in period two and three. Concentrations downslope in the catchment (row six and seven and in column E) were lower than the concentrations upslope. In 60 cm depth heterogeneity increased compared to 100 cm depth. In 25 cm depth, the concentration pattern was irregular. Coefficients of variation were elevated in 60 and 100 cm depth at the bottom of the test field and in column F and in 25 cm depth especially at the border of the catchment.

In summary, homogeneity of gas distribution was increased due to the reconstruction work. The load to the field was reflected in the level of concentration in all depth. Especially the concentration in 25 cm depth was sensible to the height of the load. After reconstruction, the temporal heterogeneity was highest at the border of the test field. Before reconstruction, temporal variability occurred at most sites. It increased with decreasing depth.

5.3.3.3 Distribution of supplied gas within the test field

The catchment area (510 m²) within the test field (1060 m²) was meant to contain the injected gas and release it upwards to the methane oxidation layer at a spatially uniform load. Emission measurements and soil gas composition measurements showed that the gas did not stay within the catchment but spread out over the whole test field. For each campaign it was analyzed which share of the test field area actually received landfill gas. To do, so the actual soil gas composition was compared with a reference soil gas composition. Based on the assumption that the soil gas composition of the test field after a prolonged

shutdown in May 2012 was not influenced by injected landfill gas, it was defined as reference soil gas composition. The soil gas composition of each grid field from every other campaign was compared to that "natural" background. Grid fields with no methane and less than the average carbon dioxide (15.8%) and nitrogen (75%) concentrations found in the reference measurement were counted as not being loaded. Grid field concentrations were calculated by averaging the gas probes at the corners.

It could be shown (Figure 58) that the upslope area (row 1 - 3) was loaded to its full spatial extent throughout the whole experiment. The midslope (row 4 -7) and downslope (8 - 10) area did not receive gas to their full extent where the downslope area showed the highest unloaded shares. The differentiation into border and catchment area shows that the catchment is loaded to its full extent at all times after the reconstruction (August 2013). Before reconstruction, some time with an incomplete loading was observed. The loading of the border region was more variable over the whole period. The total area was loaded to 90.3% (10.9 SD) over the whole time (excluding the shutdown in September 2013). Lowest loaded area was 64% June 2013.



Figure 58: Cumulative share of loaded area. Left: separated in up-, mid-, and downslope and right: in catchment and border. Shares of total area: left: upslope: 34%, midslope: 34%, downslope: 32%; right: border: 42%, catchment: 58%.

5.3.3.4 Variability of surface methane an carbon dioxide concentrations

From October 2013 until May 2014, surface concentration screenings of methane and carbon dioxide were conducted. The resulting pattern is displayed in Figure 59. It can be seen that the highest methane concentrations occurred on the upper slope and at the border of the test field. The resulting pattern is very similar to the one before reconstruction. Although it could be shown in chapter 5.3.3.2, that the gas distribution was more homogenous in 1 m depth after reconstruction, the heterogeneity at the surface is still high. In April 2014 an intensified surface screening was carried out covering nine points per grid field instead of four points (Figure 59 g). It can be seen that the general pattern is the

same between the intense (nine points per grid field) and normal (four points per grid field) campaign which was conducted the day before (Figure 59 f). Some noise may stem from the temporal variability from one day to the next.

As carbon dioxide concentrations were also recorded in the surface screening campaigns (except for the nine-point per grid field campaign), carbon dioxide – methane ratios could be computed. The ratio is an indicator for oxidation. The higher the ratio the more oxidation occurred. A low carbon dioxide – methane ratio in combination with a high methane surface concentration implies direct emissions. Zones of elevated methane concentrations were located on the upper slope and the borders of the test field. The pattern of high methane concentrations and low carbon dioxide – methane ratio (table in Figure 60) could be observed over the campaigns although they took place over the winter month. Oxidation efficiencies were calculated using the ratios from the surface screening and the ratio recorded at the injector station. The resulting oxidation efficiencies were higher than the ones calculated by the mass balance or the carbon shift method using the ratios from the emission measurements (see Table 12).



g) 15.04.2014

Surface CH₄ concentration [ppm]



Figure 59 a-g: CH₄ surface concentration on the test field. Each grid cell was measured at four locations except on 15.04.2014 where 9 point per grid cell were measured. Black line: border of test field catchment. Upper margin: upslope.

F F E E D D 1 1 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 3 1 1 1 1 1 4 1 1 1 1 1 5 1 1 1 1 1 6 1 1 1 1 1 7 1 1 1 1 1 9 1 1 1 1 1 9 1 1 1 1 1 9 1 1 1 1 1 9 1 1 1 1 1 9 1 1 1 1 1 9 1 1 1 1 1 10 1 1 1 1 1		F F E E D D C C B B A A 1	F F E E D D C C B B A A 1
a) 21.1	10.2013	b) 19.11.2013	c) 20.01.2014
P P E E D 1 1 1 1 1 2 1 1 1 1 3 1 1 1 1 4 1 1 1 1 5 1 1 1 1 6 1 1 1 1 7 1 1 1 1 8 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 1 9 1 1 1 <td></td> <td>F F E E D D C C B D A A 1</td> <td>1 F F E D D C C B B A A 1 A</td>		F F E E D D C C B D A A 1	1 F F E D D C C B B A A 1 A
d) 18.0	02.2014	e) 18.03.2014	f) 14.04.2014
Date	Mean CO ₂ -	Mean Oxidation	CO ₂ -CH ₄ -Ratio [-]

Date	Mean CO ₂ -	Mean Oxidation	CO ₂ -CH ₄ -Ratio [-]
	CH ₄ ratio	efficiency [%]	0-1
21.10.2013	62.3	86.4	1-5
19.11.2013	75.9	81.2	5-10
			10-20
20.01.2014	27.1	78.1	20-50
18.02.2014	106.1	86.7	50-100
			- 100-200
18.03.2014	172.5	91.2	200-500
14.04.2014	245.6	95.3	>500

Figure 60 a-f: Spatial distribution of CO_2 -CH₄ ratio from surface screening and mean CO_2 -CH₄ ratios and oxidation efficiencies for the survey dates (table). Ratio of injected landfill gas: approx. 0.8. Efficiencies were calculated using the CO_2 -CH₄ ratio from the injector station as initial ratio. Black line: catchment.

5.3.3.5 Comparison of the variability of carbon dioxide soil gas concentrations and soil water content between a homogeneous landfill cover and a natural soil

Initially, it was assumed that variations of soil gas concentration in Wieringermeer test field were based upon different gas supply intensities and not on the variability of soil properties. To test this hypothesis, the variability of the soil gas composition in the test field was compared to that of a non-engineered, i.e. non-constructed, reference site without gas supply. It was assumed that if the evenness of carbon dioxide soil gas concentration distribution in a situation without gas injection was the same as under natural conditions. This could be taken as an indicator to assign heterogeneity within the gas phase to heterogeneity of the gas supply and oxidation and emission processes. Soil moisture was measured along with the gas concentrations to be sure that gas concentration differences in soil moisture.

5.3.3.5.1 Carbon dioxide survey

During the shutdown of the Wieringermeer test field in May 2012 the carbon dioxide levels were lower than during operation but still at about 16.7% in 100 cm depth (Figure 61). The reference site Amsinckpark showed considerably lower carbon dioxide concentrations of only 0.9% in 100 cm depth. Still the coefficient of variation was comparably low. At Wieringermeer, it was 0.20 and at Amsinckpark it was 0.18. Nitrogen levels were very similar between the two sites with 76.6% (SD 11.5) at Wieringermeer and 79.9% (SD 0.4) at Amsinckpark with coefficients of variation of 0.01 and 0.15 respectively. Oxygen levels were very different: Wieringermeer had an average level of 3.0% (SD 2.3) and Amsinckpark of 19.2% (SD 0.5). The coefficients were 0.77 for the former and 0.2 for the latter. For normalized (normalized to the highest concentration per depth) data, the difference of the variance of the concentrations between the two sites was statistically not significant (p < 0.05).



Figure 61: Soil gas concentration in natural (Amsinckpark, left) and landfill cover soil (Wieringermeer, right) without gas supply. Note different y-axis for the two sites. For both sites: n = 54.

5.3.3.5.2 Soil moisture survey

The soil moisture surveys were done under summer conditions in a dry period. Both sites were covered with grass. While the grass at Wieringermeer was mowed bevor the campaign, the grass at Amsinckpark was not.

In a soil moisture survey on Wieringermeer test field in August 2013, gravimetric soil water content was measured with 20 cm resolution down to 80 cm depth on the 54 grid points (Figure 62). The moisture content did not show a dependency on slope position. A very small trend indicating dryer conditions with decreasing relative height on the slope was not statistically significant. The variance within each depth was quite similar. The water content over all samples was 12% w/w (SD 3.1). The difference between highest and lowest water content was as much as 16.3 percentage points in the 20-40 cm depth. On the average, the range of soil moisture in each depth was 14 percentage points (SD 2.3). Coefficients of variation for the observed depth were 0.18 (0-20 cm), 0.28 (20-40 cm), 0.28 (40-60 cm) and 0.30 (60-80 cm). Albeit the distribution of soil moisture content over all samples indicate slightly dryer conditions from the surface down to 60 cm followed by a small increase in moisture down to 80 cm no spatial pattern and no depth dependency of moisture content could be confirmed. For the soil type of the site (KA5: Sl4) a water content of 13% v/v indicates a suction close to the permanent wilting point (1500 kPa / pF 4.2). At 1.35 g m^{-3} , this is 9.6% w/w. There was no statistically significant difference (p < 0.05) between the variance of the different depth, irrespective of previous normalization to 0/1.

The reference site Amsinckpark was sampled in July 2014. On the average, the soil moisture content was 4.8% w/w. The highest water content was found in 20 cm depth and did not exceed 10.9% w/w. The average water content in 20 cm depth was 8.5% w/w (SD 1.2). In 60 cm depth it was 2.5% w/w (SD 0.7) and in 100 cm depth 3.3%w/w (SD 0.9). Again, between the depths no significant correlation was found. The range within each depth was much smaller at the Amsinckpark site. The highest range was 5.8 percentage points in 20 cm depth. The lowest range of 2.7 percentage points was found in 60 cm depth. Coefficient of variation was 0.14, 0.27 and 0.28 for 20, 60 and 100 cm depth. For a loamy sand (KA5: SI2) with a density of 1.6 g m⁻³ the permanent wilting point is reached at 8% v/v water content which is 5% w/w. The variance of the different depth was significantly different (p < 0.05) analyzing the not normalized data and not different when testing the data previously normalized to 0/1.

The variances of the corresponding depth of both sites were not significantly different between the sites if previously normalized to 1/0 but not normalized variances were significantly different.



Figure 62: Soil moisture content in the Wieringermeer test field (left, n=60), from drilling at the gridded gas probes before reconstruction and soil moisture content of Amsinckpark (right, n = 54).

5.3.4 Methane emissions, oxidation efficiencies and rates from methane mass balance and carbon shift method for the whole test field

The **methane emission** of the test field is shown in Figure 63 (see also Table 12) for each campaign along with the carbon dioxide emissions. During the measurements after the reconstruction (2014 - 2015) the mean and median values of the methane emission data are closer together than before. This indicates a more homogeneous distribution of the magnitude of emission within the whole test field during each campaign. The carbon dioxide – methane ratio is an indicator for oxidation. Based on a fixed initial ratio, an increase of the ratio indicates oxidation because methane converts into carbon dioxide and hence the ratio increases. Campaigns with comparably low oxidation efficiencies like October 2012, November 2012, January 2015 and February 2015 (see Figure 64) showed a notably smaller ratio of carbon dioxide to methane. During summer month campaigns showed lower methane emissions and higher carbon dioxide emissions. In the winter months, the ratio was

smaller under all loads before and after the reconstruction. This is in accordance with the findings on the test field oxidation efficiency (following section).



Figure 63: Distribution of CH₄ (red) and CO₂ (black) emissions from test field C. Box: $25^{th} - 75^{th}$ percentile, line in box: median, square: average, whisker: $10^{th} - 90^{th}$ percentile, triangles: minimum / maximum. Number of measurements (n): 2012: Aug = 38, Sept = 24, Oct = 34, Nov = 34, 2013: Apr = 35, May = 58, June = 34, July = 36. 2014: Feb = 30, Mar = 30, April = 60, May = 38, June = 27, Aug = 38, Sept = 54, Oct = 35. 2015: Jan = 38, Feb = 36.

The **oxidation efficiency** for the whole test field was determined in two different ways. First, by making up a methane mass balance for the whole field and secondly, by averaging the efficiencies calculated for each grid field with the carbon shift method. Results from both approaches are described in this section.

For the determination of the whole-site efficiency, methane emission measurements were performed with the large 17.6 m^2 chamber described in chapters 4.5 and section 5.3.1. From

the known load to the field, measured in the gas supply system (chapter 3.2) and the cumulated emissions, the oxidation efficiency could be determined. Table 12 provides the methane load to the test field, the methane and carbon dioxide emissions and the oxidation efficiencies of the test field for each of the 18 campaigns.

The oxidation efficiency over time is displayed in Figure 64. From the methane mass balance method over the considered period, an average oxidation efficiency of 84.0% (SD 17.5) was obtained. The mean oxidation efficiency was 83.6% (SD 18.9) before and 84.4% (SD 16.2) after reconstruction (August 2013). The maximum efficiency observed was 100% in June 2014 and the lowest performance was 48.1% in October 2012.

The mean oxidation efficiencies derived from the carbon shift method were slightly lower than those obtained by the methane mass balance approach. Mean oxidation efficiency was 72.6% (SD 26.1) before and 79.5% (SD 18.4) after reconstruction while the maximum was 99.6% in June 14 and the minimum 24.5% in February 2015 (Figure 64). If correcting for the linear term found in the chamber validation setup, overall efficiencies would increase by 3.7 percentage points for the February 2015 campaign and by 0.1 percentage points for the September 2014 campaign.

The **oxidation rates** can be obtained if the amount of methane removed is related to an area. The oxidation rates given in Figure 64 are calculated based on the total area of 1060 m^2 . For the determination of the rates oxidation efficiency data from methane mass balance were used. Minimum rates were 8.5 g CH₄ m⁻²d⁻¹ in March 2014 and maximum rates were 39.6 g CH₄ m⁻²d⁻¹ in October 2014. The load to the field ranged between 10.6 g CH₄ m⁻²d⁻¹ (March 2014) and 42.5 g CH₄ m⁻²d⁻¹ (October 2014).

Over the whole period, a clear **seasonality** was visible. Oxidation efficiency was high in summer and low in winter. The seasonal variation of the oxidation efficiency seems to be hardly influenced by the load to the field but by seasonal conditions. At favorable summer conditions, oxidation efficiencies were close to 100%. It has to be considered, that oxidation rates cannot exceed the load to the field. As the oxidation rates are most of the time close to the load, their seasonality cannot be seen as an independent reaction to the environmental conditions but are dependent on the loading of the field. This implies that the system was operated below its capacity for most of the time (for system capacity, see section 5.3.7).



Figure 64: Time course of load to field, oxidation efficiency from mass balance and carbon shift method as well as oxidation rate. Load to field and oxidation rate are related to the total test field (1060 m²).

5.3.5 Spatial and temporal variability of methane emissions, oxidation efficiencies and rates on grid field scale

The methane oxidation system was considered quite homogeneous in its setup as the same soil material was used over the entire area and the construction was carefully monitored. However, a large spatial heterogeneity of emissions, oxidation efficiency and oxidation rate was found over the entire course of the study.

Through all campaigns, oxidation efficiency and the level of emission were negatively correlated, as were oxidation efficiency and oxidation rate for most campaigns (Table 11). Oxidation rate and level of emission were correlated predominantly positive (p < 0.05). The relative grid field position on the slope (upslope – downslope) had a significant influence in many campaigns as follows: the higher the relative position (more upslope), the lower was the efficiency. This was most pronounced for the time after reconstruction at the elevated load of 38.6 g CH₄ m⁻² d⁻¹. Emissions were found to increase with the relative height as well as the rate.

Descriptive statistics reveal the pattern of spatial and temporal heterogeneity of methane emissions from the grid fields. In the boxplot graph Figure 66, the difference of emissions between the grid fields illustrates the **spatial variability**. The two upslope rows (1 and 2) were most emissive (for location of grid fields see Figure 6). The columns outside the catchment (A and F) area did have high emissions but not as high median values as the columns within the catchment (B-E). Another but smaller maximum was found around row 6-9 which is the lower margin of the catchment. The level of emission correlated positively

(p < 0.05) with the relative position on the slope (1 = topslope; 0.1 = downslope) in October 2012, November 2012, April 2013, February 2014, April 2014, August 2014, October 2014, January 2015 and February 2015, nearly all of which are in the winter half of the year (Table 11). The same connection was found for the parameters oxidation rate and with negative prefix for oxidation efficiency.

Table 11: Correlation coefficients between parameters emission height, oxidation efficiency, oxidation rate and relative altitude over the study time. p < 0.05. Relative altitude: highest position on the slope (row 1) was assigned 1, lowest (row 9) position 0.1.

Correlation	Emission	Emission	Efficiency	Rel. altitude	Rel. altitude	Rel. altitude
coefficients	vs.	vs.	vs.	vs.	vs.	vs.
(P < 0.05)	Efficiency	Rate	Rate	Efficiency	Emissions	Rate
August 2012	-0.88	0.82	-0.67			
September 2012	-0.94	0.74	-0.69			
October 2012	-0.79	-0.72		-0.80	0.59	
November 2012	-0.74	-0.61	0.46	-0.48	0.65	
April 2013	-0.73	0.48	-0.41		0.50	0.59
May 2013	-0.86	0.45				0.45
June 2013	-0.91	0.58				
July 2013	-0.79	0.74				
February 2014	-0.73			-0.90	0.62	0.43
March 2014	-0.83					
April 2014	-0.88	0.73	-0.57	-0.56	0.39	0.43
May 2014	-0.95	0.54	-0.43			
June 2014	-0.68					
August 2014	-0.70	0.40		-0.60	0.43	0.44
September 2014	-0.94	0.60	-0.42	-0.32		
October 2014	-0.94	0.46	-0.48	-0.66	0.49	0.57
January 2015	-0.55			-0.76	0.55	
February 2015	-0.58		0.57	-0.68	0.48	0.52

To depict the spatial dimension of the base flux and emission pattern, maps of three campaigns are given in Figure 65 (October 2012, February 2014 and September 2014). The October 2012 campaign was a campaign with a low overall oxidation efficiency of 51.5% at a load of 31.7 g CH₄ m⁻² d⁻¹. High emissions were correlated with low efficiencies and low oxidation rates. Emissions occurred predominantly upslope (Table 11). In February 2014, the efficiency was 63.7% at a load of only 14.1 g CH₄ m⁻² d⁻¹. Again emissions occurred predominantly upslope and high emissions were correlated with low efficiencies but not with low rates. The rates increased with the relative altitude. In September 2014, efficiency was at 99.5% at a load of 34.0 g CH₄ m⁻² d⁻¹. At grid fields of high emissions, the efficiencies were low but the rates were high. The correlation between relative altitude and height of emission was the weakest of the three campaigns.



Figure 65: Spatial pattern of base flux and methane emission. White fields: no data. Black line: border of catchment.

In the range of emissions from each grid field, **temporal variability** was visible (Figure 66). At almost each upslope location (left: upslope, right: downslope), the arithmetic mean value

was much higher than the median indicating a high temporal heterogeneity. This means that the upslope area reacts most strongly on changing seasonal conditions.

With a correlation analysis it was explored if the parameters air temperature, soil temperature, air pressure and air-filled porosity had an effect on the level of emission, oxidation rate or oxidation efficiency and if there was a spatial pattern of that influence.

The input parameters air temperature and soil temperature were correlated. Air-filled porosity (and hence soil moisture content) was correlated with air and soil temperature and air pressure.

August 2012 - February 2015 upslope --- downslope | upslope downslope upslope --- downslope upslope --- downslope upslope --- downslope upslope --- downslope 200 Emission 150 [g CH₄ m⁻² d⁻¹1 100 40 30 20 10 0 80 Oxidation rate [g CH₄ m⁻² d⁻¹] 60 40 20 Ьþ ę 自由甲草同自 0 120 Oxidation efficiency 100 80 60 % 40 20 A10_1_ B10 C1⁻J-C10_D1 - 68 Ë .96 έ - <u>-</u> 2 . 6Ш Ŀ Ľ B3 B5 S C5 8 D2 60 В БЧ <u>۳</u> Å B7 5 6 Ξ D10 <u>-</u> A8 B2 B6 B8 B8 C 2 2 0 8 D6 D6 D8 Ч Е2 Е4 Е6 Е8 F6 F4

The correlating grid fields were displayed in a map of the test field (Figure 67).

Figure 66: Distribution of emissions from the individual grid fields over the entire measurement period. Box: $25^{th}/75^{th}$ percentile, line in box: median, square: average, whisker: $10^{th}/90^{th}$ percentile, small lines: minimum / maximum. $n_{avg} = 8.0$ (SD 3.6) $n_{min} = 2$, $n_{max} = 16$.

Soil temperature had the highest effect on oxidation efficiency (positive) followed by oxidation rate (positive). Both processes were affected most in the catchment region and its upslope surrounding. The level of emission was less affected (negative). Only grid fields adjacent to the catchment border were influenced. Spatial pattern of soil and air temperature influence were very similar, hence only soil temperature is shown.

The effect of air-filled porosity could be seen upslope and within the catchment. Especially the oxidation efficiency correlated with the level of air-filled porosity (positive) almost only

in the upper half of the test field. Emission levels correlated especially upslope and the border of the catchment between column E and F (negative).

Air pressure had a far less extensive effect. Except for very few grid fields in the downslope region of the test field, a correlation was found exclusively upslope, mainly within the catchment (on efficiency and rate: positive, on emissions: negative).

Additionally to the boxplot graph (Figure 66), the time course of emissions from two upslope and downslope grid fields each was displayed (Figure 68). The grid fields were selected because they are situated at the up and downslope margin of the catchment area and emission data were available for most of the time. The general course of the two upslopeand downslope grid field emission pattern was similar, respectively. The upslope fields showed high emissions especially under high loads (2012 and August 2014 until end; see also Figure 55). Maximum emissions were highest before reconstruction. Downslope emissions were generally low. As shown above (Figure 67) the emission of the upslope fields were significantly influenced by air pressure while one of the downslope fields was significantly influenced by soil temperature (B8).



Figure 67: Spatial distribution of significant correlations between the indicated parameters over time. (p < 0.05). Green: positive correlation; red: negative correlation. Soil temperature: average of up-, mid- and downslope sensors 40 cm below surface. Air-filled porosity: derived from the soil moisture data averaged from up-, mid- and downslope sensors 40 cm below surface.



Figure 68: Methane emissions from two upslope (C2, E2) and two downslope (B8, E8) grid fields.

5.3.6 Oxidation efficiencies for different soil depths

To explore the depth distribution of the oxidation process in the soil, efficiency for various depths was calculated from the shift in the soil methane and carbon dioxide concentrations along the upward path of gas migration through the soil (method given in chapter 4.6). The concentrations were measured at 54 points using gas probes (see chapter 4.3.1 and 4.3.3). For 18 campaigns, the mean efficiency was determined for the gas distribution layer and the methane oxidation layer. For two campaigns a more detailed survey was performed to show the spatial variability of each layer. Temporal variability of oxidation profiles is shown using oxidation efficiencies calculated from the concentrations at the standard gas profiles (see chapter 4.3.1 and 4.3.3).

By means of the carbon shift method, oxidation efficiencies were calculated for the part between the blower station and the probes in 100 cm depth (Table 12). It was assumed that the gas composition at the blower station was the same as at the inlet ports at the test field base. The difference between the overall efficiencies (from shift between blower station and surface) and the efficiencies between blower station and 100 cm depth was attributed to **oxidation within the methane oxidation layer**. The results suggest that on an average 19.9% of the methane was oxidized already in the gas distribution layer. The share of oxidation assumedly taken place in the gas distribution layer was 27.8% before and 13.5% after the reconstruction. This matches the finding of higher nitrogen concentrations in 100 cm depth before the reconstruction, indicating a deeper aeration (Figure 54). Table 12: Methane load to test field methane and carbon dioxide emissions, oxidation efficiencies from methane mass balance and carbon shift method. The initial carbon dioxide – methane ratio for the carbon shift method is derived from the concentration data at the injector station. The surface ratio is derived from the chamber measurement data. The ratio in 100 cm depth is derived from the corresponding soil gas concentration data.

	CH₄ Load	CH4 CH4 CO2 Load Emissions Emiss		Total oxidation	Total oxidation	Oxidation efficiency	Oxidation efficiency
				efficiency	efficiency	below	Surface to
	[kg d ⁻¹]	[kg d ⁻¹]	[kg d ⁻¹]			100cm	100 cm
Date				Methane mass balance [%]	Carbo	on shift meth	od [%]
Aug 12	36.21	1.05	71.47	97.10	97.17	11.41	85.75
Sept 12	34.45	3.90	70.82	88.68	88.61	28.63	59.97
Oct 12	33.68	17.48	47.61	48.11	64.95	20.78	44.16
Nov 12	39.92	18.05	42.80	54.79	41.93	14.76	27.17
April 13	32.03	3.34	26.31	89.57	67.30	23.42	43.88
May 13	31.79	0.73	45.17	97.70	84.21	27.68	56.53
June 13	38.43	1.76	76.76	95.42	95.64	46.11	49.53
July 13	32.07	0.86	46.71	97.32	95.84	49.29	46.54
			Reconstructio	on of test fiel	d		
Feb 14	14.91	4.95	15.99	66.82	60.69	16.08	44.61
March 14	11.22	1.99	28.66	82.27	71.72	9.88	61.84
April 14	11.88	0.56	36.32	95.27	92.80	7.32	85.48
May 14	11.84	0.20	58.20	98.34	98.04	-4.55	102.59
June 14	21.87	0.00	46.37	100.01	99.86	17.54	82.32
Aug 14	42.80	2.93	39.58	93.16	71.20	23.94	47.26
Sept 14	36.00	0.16	100.90	99.55	99.23	17.26	81.98
Oct 14	45.10	3.67	42.16	91.86	77.75	21.92	55.83
Jan 15	39.99	14.87	33.53	62.82	30.19	16.59	13.60
Feb 15	40.46	18.70	45.69	53.78	24.47	9.42	15.05
Mean				84.03	75.64	19.86	55.78

Spatial variability

In addition to the permanently installed gas probes in 25, 60 and 100 cm depth, gas concentration was measured in 10 cm depth using a mobile gas probe in September 2014. Oxidation efficiencies were calculated with the carbon shift method (Figure 69). The reference depth was always the concentration in 100 cm depth. In 60 cm depth, the spatial heterogeneity of soil gas composition was high. At some locations, 100% oxidation was achieved already in 60 cm depth. The mean oxidation efficiency was around 30% while the median value was below 10%. In 25 cm depth, no oxidation was found at some locations, however, the mean oxidation efficiency was around

90%. In 10 cm depth, hardly any point with efficiencies below 50% was found. The mean value was about 90% oxidation efficiency and the median value was 99.9%. At the surface, the mean oxidation efficiency over all gas probes was above 99%.

In January 2015, when the overall efficiency was considerably lower than in September 2014, the depth dependency of efficiency was different. In 60 cm depth, hardly any oxidation was observed. In 25 cm b.s., the range was high with some points reaching 100% oxidation while the mean was 18% and the median was close to zero. For the surface, a mean value of 26% and a median of 19% were calculated. Surface concentration data (0 cm) were derived from the emission chamber data, not from the gas probes. The different sensitivity of the employed measurement devices of each method (chapter 4.3 and 4.5) might explain the decrease of the 90% whisker line from 25 cm depth to the surface for the measurement in January 2015. In September 2014, the effect of the different methods was not notable because the methane surface concentrations were very low.



Figure 69: Oxidation efficiency from carbon shift method over depth below surface for September 2014 (left) and January 2015 (right). The efficiency was calculated from the shift of the ratio from the 100 cm gas probe to the indicated depth. n = 54. Triangles: min / max.

Temporal variability

The changing depth of the oxidation horizon in the course of time was explored by calculating and graphing the oxidation efficiencies at the standard gas profiles C1 - C4 (Figure 70). Profile C1 was situated upslope, C2 midslope and C3 downslope. Profile C4 was situated between Profile C1 and C2. Profile C1, C2 and C3 were situated close to gas inlet points, while profile C4 was further away from them. At all four sites the oxidation horizon extended to greater depth in the warmer and dryer summer month (Figure 55). Oxidation took place in greater depth before the reconstruction in August 2013. At the downslope position (C3) and at the site afar from the gas inlet point (C4), oxidation efficiencies were higher and extending to greater depth than at the up- and midslope positions. After reconstruction, the efficiency increased much steeper with the highest increase within the upper 20 cm in winter times, still reaching 100% at the surface of site C3 and C4. After reconstruction, the zone of complete oxidation reached down to 50 cm in summer conditions.



Figure 70: Methane oxidation horizon at gas profiles C1-4. %: share of methane oxidized. Hatched area: no data. b.s.: below surface.

5.3.7 Oxidation rates as predicted by the MOT

The Methane Oxidation Tool (MOT) was applied to estimate potential oxidation rates. The temporal variability of the input parameters for the MOT (air-filled porosity, soil temperature and water potential) and the resulting factors are displayed in Figure 71. A typical seasonal pattern can be seen for the temperature and moisture course with warm temperatures and dryer conditions in summer and moister and colder winters. The derived factors and the resulting factorized oxidation potential (FOP) are displayed along with the input factors. The variability of air-filled porosity had the highest influence on the factorized oxidation potential, followed by the temperature. Thus, the water content of the soil was the crucial parameter. The model predicts oxidation potentials (FOP) ranging from 20.6 to 92.7 g CH₄ m⁻² d⁻¹ with a mean of 44.7 (SD 20.6) g CH₄ m⁻² d⁻¹ over the time of the study.



Figure 71: Methane Oxidation Tool (MOT) input parameters (top), factors (bottom, left y-axis) and resulting estimation of factorized oxidation potential (FOP) (bottom, right y-axis). Temp: Temperature; AFP: air-filled porosity; pF: logarithmic value of water tension in the unit hPa.

5.3.8 Model predictions and measurements - resolving the test field to grid field scale

Achieving a spatially even distribution of the base load is a primary goal of any methane oxidation system design as spatial heterogeneity of base fluxes may lead to some areas being overloaded while others are loaded below their methane oxidation capacity. Hence, it was of interest to spatially resolve the base flux to the methane oxidation layer. As the chamber measurements were used as input parameter, the resulting scale was the grid field scale (4.2 m \times 4.2 m). From grid field scale data on emission and oxidation efficiencies derived from the carbon shift method the flux into the base of each grid field was calculated

(see Equation 11 in chapter 4.6). From the resulting individual loads for each grid field and the respective emissions, oxidation rates could be computed for each grid field and could be related to the MOT model predictions (chapter 4.7 and section 5.3.7).

Before the reconstruction of the test field in August 2013, the scattering of the base fluxes was a lot higher than after the reconstruction (Figure 72, box plots). This indicates a more homogeneous distribution of the load as a result of the reconstruction measure leading to a higher degree of compaction (see chapter 3.2). As a base flux could be calculated only for emissive fields, loads to grid fields with 100% oxidation are lacking in the graph. The 90th percentiles of the base fluxes of each campaign were higher bevor the reconstruction while the peak fluxes were comparable. Emissions occurred in autumn/winter 2012, spring 2013, late winter 2014 and autumn/winter 2014/2015 (hatched area in Figure 72). The average load exceeded the oxidation potential predicted by the model (FOP, factorized oxidation potential) only in November 2012, April 2013 and January and February 2015 while base fluxes higher than the FOP occurred in most cases before the reconstruction and the first and two last campaigns after reconstruction. To account for changes of the total pore volume due to settlement of the soil material over time and for uncertainties in the soil moisture measurement, the FOP is calculated with a factor for air-filled porosity for ± 5% water content. This accounted for the moisture sensor accuracy given by the manufacturer and the experience of Röwer (2014), working with the same setup. Except for the month August 2012 and June 2013 base fluxes higher than the FOP resulted in emissions.



Figure 72: MOT predictions for factorized oxidation potential (FOP) (grey area). Measured loads (solid line) oxidation rates (dashed line, for the whole test field from methane mass balance data), resulting emissions (hatched area) and calculated base flux at 1 m depth (boxplot) (Box: $25^{th} - 75^{th}$ percentile, square: arithmetic mean, whiskers: $10^{th} - 90^{th}$ percentile, triangles: minimum / maximum). Load and oxidation rates refer to test fields total area of 1060 m². For the FOP the effect of ± 5% moisture content is indicated.

The MOT estimates a share of the load to bypass the MOS as direct emission. The height of the share is stated to depend on the cover type. However, the data clearly show that no fixed share of the load emits always.

5.3.8.1 Exemplary campaigns exploring relations between base flux and oxidation rate

The relationship between base flux and oxidation rate was examined in-depth for six exemplary campaigns. The data is plotted in Figure 73. Each circle represents one grid field that was emissive in the relevant campaign.

Base loads were found to range from close to zero up to 150 g CH_4 m⁻² d⁻¹. The variation was high in each campaign. Individual grid fields were loaded below and beyond the load to the test field in the respective campaign. Except for September 2014 and April 2014 there were grid fields loaded at rates higher than the predicted oxidation potential. Generally, with increasing base fluxes the oxidation rates increased as well but deviated ever more from the 100%-line the more the base flux increased. Especially when the base flux exceeded the oxidation potential, the scattering increased strongly. In September 2014, all the measurements showed a base flux – oxidation rate - ratio close to one. In this state, the system was loaded below its potential. In most cases, it was observed that already at loads below the factorized oxidation potential, not all of the methane was oxidized.

Comparing the base fluxes with the oxidation rates on grid field scale revealed different scenarios depending on seasonal conditions. The achieved top oxidation rates were up to 10 g $CH_4 \text{ m}^{-2} \text{ d}^{-1}$ in the winter and up to 40 g $CH_4 \text{ m}^{-2} \text{ d}^{-1}$ in summer. In contrast to the unique relation between base flux and oxidation rate close to the 100% isoline in September 2014, on all other occasions in different grid fields a different share of similar base fluxes was oxidized under similar environmental conditions.

From the known water retention curves it could be calculated that the soil water tension ranged from pF 3.7 (July 2013) to 2.17 (January 2015) (equaling 501 kPa to 14.8 kPa). Hence, in dry conditions pores > 0.6 μ m were available for gas transport while in moist conditions gas transport was restricted to pores > 20 μ m. Under moist winter conditions this indicated a blockage of the middle pores (0.2 – 10 μ m diameter (Ad-hoc-AG Boden, 2005)) leaving only a part of the coarse pores (> 20 μ m diameter (pores > 10 μ m are defined as coarse pores (Ad-hoc-AG Boden, 2005)) available for gas transport while under summer conditions also most of the middle pores were water-free too.



Figure 73: Relationship between base flux, oxidation rate and oxidation efficiency on grid field scale. Isolines for 10, 25, 50 and 100% oxidation are given. Dashed isoline: efficiency from mass balance; dotted isoline: efficiency from carbon shift method. Solid vertical line: average load to test field; dashed vertical line: factorized oxidation potential (FOP). Note the different x and y axis.

6 Discussion

In the discussion section, the related hypotheses from chapter 1 are stated for each section. Some paragraphs are introduced with guiding questions related to the field covered by the hypothesis.

6.1 Relevance of pore size distribution for gas transport in differently saturated soil samples at low water tensions

6.1.1 Influence of changing air-filled pore space on gas transport

Hypothesis corresponding with this section: 1 a: At a higher degree of water saturation, the change of gas transport parameters for diffusion (D_{eff}) and advection (k_{gas}) with available water-free pore volume is highest and nonlinear.

Was the examined range of water tensions in a relevant range for field situations?

Aim of the laboratory study on diffusion and advection resistance of the soil over a range of water contents was to assess the influence of soil moisture on the gas transport processes. In this study, measurements of gas permeability were conducted for water tensions between 2 kPa and 30 kPa. The average water tension over all depths and slope positions was around 23 kPa (pF 2.3), indicating on water saturation of middle-sized pores (< 10 μ m equivalent diameter) and hence restriction of gas transport to coarse pores. In dry summer times, water tension occasionally rose above 300 kPa (pF 3.4). Except for rare occasions, the water tensions never fell below 2 kPa (pF 1.3). Hence, the examined range was the relevant range of field water potentials over all measurement campaigns on Wieringermeer test field.

Was the water retention curve typical for the material texture and compaction?

As the sample material from Wieringermeer and Eckerkoppel was taken from constructed soil layers, the water retention curves were compared to the standard retention curves for natural soil material to confirm if the pores space distribution was alike. This should be the case to select soil material for construction according to empirical data from natural soil material. The water retention curves given in Wessolek et al. (2009) are averaged for the texture class, hence deviations according to the actual grain size distribution, density and organic carbon content of the examined soil are to be expected.

The water retention curve for the material from the topsoil of the test field at Wieringermeer landfill differed from the standard curve for loamy silty sand (Slu, (Ad-hoc-AG Boden, 2005)) at the given soil bulk density. The topsoil material was ab about 10% points wetter and the subsoil material was about 10% points dryer. The deviation of the topsoil can be attributed to the very high organic content of 7.7% w/w and the low bulk density of 1.07 g m⁻³ (for soil properties see Table 1). The density of the reference curve soil was 1.54 g m⁻³ and its organic content was < 1%.

The water retention curve for the slightly clayey sand from the Wieringermeer subsoil (methane oxidation layer) (St2, (Ad-hoc-AG Boden, 2005)) was in good accordance with the standard curve.

The retention characteristic of the sandy material from Eckerkoppel was corresponding to the standard water retention curve for slightly silty sand material (Ad-hoc-AG Boden (2005): Su2) at water potentials above 10 kPa. At lower water tensions some difference was found with the topsoil about 5% points wetter and the subsoil about 10% points wetter. The shape of the subsoil retention curve was different from the standard retention curve. Nearly all dewatering happened between 4 and 10 kPa. Both soil layers were slightly less compacted than the soil material of the reference curve (1.62 g m⁻³).

The resulting air-filled porosities ranged from about 5% for the Eckerkoppel subsoil at 2 kPa up to about 40% at 30 kPa for the Wieringermeer subsoil. The Eckerkoppel subsoil had the highest air-filled porosity over all water tensions while the other soils were close together with Eckerkoppel topsoil at the top of the range. Under wet conditions, Eckerkoppel subsoil had an extremely low air-filled porosity.

The water retention curves of the constructed layers were at large in accordance with the retention curves from natural soils. The shape of the retention curve for the Eckerkoppel subsoil deviated at low water tensions towards higher water contents and the Wieringermeer topsoil was wetter than expected from the standard curve.

Why is it important to know the air-filled porosity scattering at any one water tension?

The difference in air-filled porosity at the same water tension within the five samples taken as parallels at one spot points to heterogeneity of the soil pore space that was not integrated at the sampling scale with the method applied. Consequently, the scattering of values for D_{eff} was much higher when compared to water tension than to air-filled porosity. The same was found for kgas values albeit the relation between air-filled porosity and kgas was not very clear anyways. The air-filled porosity of the groups of different water tensions in many cases was not different statistically. This means that albeit the mean value of air-filled porosity for each water tension group increased with increasing water tensions, the deviation was such that many of the observed values of air-filled porosity and therefore the values of D_{eff} or k_{gas} could occur in various water tension groups. Hence, the overall trend indicated a positive relationship between water tension and air-filled porosity while the scatter of the corresponding values for air-filled porosity introduced a large factor of uncertainty. The clumpy soil structure was considered a source of small-scale heterogeneity (< 100 cm²). Lange et al. (2009) found that small samples (about 100 cm²) do not represent the structural variability of soil, hence larger samples would yield a smaller variability of diffusion coefficients while Werner et al. (2004) reviewed comparative studies of in situ and laboratory measurements of diffusion coefficients and found a good correlation between both. The latter worked with sandy soils and found a larger scattering for field methods investigating small soil volumes. This indicates an influence of spatial variability on field measurements. All of this emphasizes the importance of keeping the scale in mind when planning measurements or interpreting results. The results from this study confirm a high variability within a set of small samples. Yet small samples are advantageous for the study of small-scale variability of gas transport parameters that would be integrated and hence invisible using larger samples. The small scale variability was described for water migration through soils by various authors showing that preferential flow is not an exception but the rule for all soil textures (Flury et al., 1994; Vogel et al., 2010; Weiler and Flühler, 2004). Delahaye and Alonso (2002) suppose that for both wetting and desaturation processes in soils, preferential pathways control the advancing of the wetting or desaturation front. Heterogeneous wetting and drying would create a pattern of air-filled porosity changing over space and time. Rachor et al. (2013) found that soil moisture was the predominant factor influencing emissions from a landfill at water tensions between 6 kPa and 30 kPa. The water tension governs the minimum drained pore diameter. Deepagoda et al. (2012) examined the relationship between pF value (log of water tension in hPa) and tortuosity of soils. They found that the larger pores drained at lower pF values (higher water saturation) have a lower probability of interconnection and the smaller but more abundant pores available to gas transport at higher pF values are more likely to be interconnected and connecting the large pores promoting gas diffusion. Summed up, it can be said that in a soil at one water tension according to variations in texture, pore space geometry and density the water free pore space varies as well as the resulting D_{eff} and k_{gas} values. The scale of the variability has to be considered. In this study differences were found even between samples of 100 cm³. Consequently spatial variability of gas fluxes has to be expected already on that spatial scale.

Related to air-filled porosity, diffusion follows a power function but different models describe different sample sets best. What is the reason?

Allaire et al. (2008) concluded from a literature review on diffusion experiments that a suitable model for gas diffusion cannot be chosen before at least some measurements, not a priori. In this study the Wieringermeer material is described best by the Buckingham (1904) model while the Moldrup et al. (2005b) model describes the Eckerkoppel soil best. In both cases, the topsoil data fit better although the difference between topsoil and subsoil is smaller for the Wieringermeer material. The RMSE values found in this study were in the same range as reported in Moldrup et al. (2013). The Millington-Quirk (1961) model was least accurate in all cases which was also found by Ungureanu and Statescu (2010). One reason for the better performance of the Moldrup et al. (2005b) model on the Eckerkoppel soil data could be a faster dewatering characteristic between 0.3 and 10 kPa in comparison to the Wieringermeer soil (see chapter 5.1.1). The Buckingham (1904) model does not account for any form of shape factor but uses only air-filled porosity while the Moldrup et al. (2005b) model integrates total porosity and porosity at 10 kPa water tension. The 10 kPa reference point approximates the function to the real value of the Eckerkoppel soil. The sandy material from Eckerkoppel landfill was highly compacted and not aggregated in any way, hence, it could be seen as "repacked material". Moldrup et al. (2013) found the Buckingham (1904) model to underestimate data from repacked soils. They introduced a media complexity factor which was higher for undisturbed than for repacked soil samples. A higher complexity factor reduced their predictions. In this study an overestimation of the Eckerkoppel data was found with the Buckingham (1904) model. This is in accordance with the findings of Moldrup et al. (2013) where pore space complexity of repacked soils was lower than from natural soil. The overestimation can be interpreted as a tortuous or unconnected pore network within the Eckerkoppel samples resulting in lower diffusion coefficients. This assumption is supported by the data that showed diffusion to only begin at about 20% air-filled porosity. Hence, the pores are not connected at lower air-filled porosities. This was not expected for a sandy soil material. A grain size spectrum would be of interest to explore if the finer particles could have blocked the pore space between the larger particles. In combination with high water saturation resulting in further pore space blockage by water menisci pore geometry might become highly tortuous or even disconnected.

What model proved best for which type of soil in other studies and what influences the shape of the curve fit for diffusivity versus porosity?

The Millington and Quirk (1961) (Equation 4) model yielded higher RMSE for the Wieringermeer soil than for the Eckerkoppel soil. Hamamoto et al. (2012) found that the Millington-Quirk model was not able to express diffusion through soils with bimodal pore structure featuring large inner-aggregate pores and small intra-aggregate pores. As the Wieringermeer soil was of a finer texture than the Eckerkoppel soil and it showed a much more aggregates, the larger error for the former can be attributed to the aggregation. More complex pore geometry resulting in higher tortuosity were mentioned as a reason for lower diffusivities with increasing organic matter content in soils (Hamamoto et al., 2012). The organic content of the examined soils ranged from 0-85% w/w. Higher initial threshold values for soil with higher organic matter content could not be confirmed in this research. In this study it was shown that samples with higher organic content were more penetrable for diffusive fluxes and showed lower initial threshold values. Organic matter usually increases the aggregation of soils which might result in more macropores. Higher organic matter content can be associated with an increased abundance of soil organisms, which contribute to macroporosity as well. The range of organic material in the studied soils was 0.7 to 7.7% w/w. It is likely that the D_{eff} of the soils used in this study increased due to higher organic content due to the aforementioned reasons, while the mentioned tortuosity effect of organic matter only becomes important for soils higher in organic matter. Research on soil structure and pore geometry using non-invasive methods like tomographic imaging (e.g. Schlüter et al.) combined with diffusion and permeability experiments could be useful to broaden the understanding of the influence of organic matter and clay content on pore space geometry and gas transport.

The fitted model by Troeh et al. (1982) (Equation 6) suggests initial thresholds of 0.03 - 10% air-filled porosity (Wieringermeer topsoil/Eckerkoppel subsoil) for diffusion to start. A threshold of 10% air-filled porosity as minimum pore space for diffusion was also found by

Gebert et al. (2011a). Although the Troeh et al. (1982) model indicated a 10% air-filled porosity threshold for the Eckerkoppel subsoil apparently diffusion started at air-filled porosity over 20%. The same was found for air permeability. This suggests a discontinuity of the pore space below 20% air-filled porosity. This was not expected for the sandy material. Maybe the space between the sand grains was filled with the smaller grains. Water menisci could have formed between the finer grains blocking the pore continuity and rendering the pore space continuity into the one of a finer texture. A sudden increase of air permeability around pF 3 was found by Moldrup et al. (2003) for an Andisol soil. The effect was found only for air permeability, not for diffusivity. As gas permeability is more dependent on soil structure than diffusivity (Kühne et al., 2012; Wickramarachchi et al., 2011), this effect was attributed to different pore geometries below and above pF 3. In this study, both parameters change, indicating a transition from unconnected to connected pore space at 20% air-filled porosity, which was achieved at pF 2.

Summed up it would be of interest to investigate gas transport through soil materials with known grain size spectra and different clay and organic matter contents. Bimodality of grain size and pore size distribution as well as pore geometry might play an important role in understanding gas transport through soils.

Could there be errors influencing the measurement of diffusion coefficients?

Possible errors associated with diffusion chamber measurements are (1) drying of the sample, (2) advective flow, (3) reaction of gas with or within the sample or chamber parts and (4) diffusion through chamber parts (Klute et al., 1994). All four sources of errors are addressed in the following section. The samples were weighed before and after each measurement. On average 1.3 g (SD 0.35) of water evaporated during measurements (data not shown) reducing air-filled porosity by 1.3%. Using the determined Troeh et al. (1982) model (Table 3 in section 5.1.2), it was calculated how great the change of D_{eff} resulting from a change of 1.3% water content would be. The result was that in no case the error for the resulting Deff would have exceeded 1%. The flush gas was given some time to adjust to the temperature in the laboratory. Hence, no temperature-driven volume change of the gas volume within the diffusion chamber during the course of the experiment was expected. No fans were used in the diffusion chamber. Advective fluxes could only have occurred due to changes of barometric pressure. However, in the oxygen saturation curves, no inconsistencies were found pointing to the occurrence of advective fluxes. The flush gas was argon, which is considered inert. Therefore, the flush gas could not have caused a change in advective fluxes by reacting with a component within the soil. As the samples were not sterilized in any way, oxygen could be consumed within the soil sample due to soil respiration, which could be a source of error. Schjønning et al. (2013) compared measurements on soil cores with measurements on inert material and could not find an effect of oxygen consumption. They quantified the error of oxygen consumption as a maximum underestimation of 2% for mineral soils. A maximum error of 1.5% was reported from Moldrup et al. (2000) for soils with up to 1.3%w/w organic matter content. Röwer (2014) determined respiration rates of the Wieringermeer topsoil of $0.3 - 3.1 \mu g C g_{dw}^{-1} h^{-1}$. If the oxygen concentration in the chamber increases up to 15% over on hour of measurement, which was a typical range in the experiments of this study, the error due to soil respiration would range between 0.3 and 5.2%. Diffusion through chamber parts was excluded by monitoring the closed chambers for ten minutes before each measurement without finding a significant change of concentration.

How could the data on advective transport be described?

Advective gas transport could not be described with any statistically significant function for the analyzed range of water potential (2 - 30 kPa). Hence, the development of a predictive model for k_{gas} was not possible from data on pore structure or water retention characteristics, but was also not part of this study. In contrast to diffusion, advective transport does not only rely on the absolute share of air-filled porosity but, according to Hagen Poiseuille's law, is influenced to the power of four by the pore radius (Kühne et al., 2012). This means for advective transport that the largest pores are most important for the process and that a pore size distribution with a large share of coarse pores is more effective than the same volume of pores with a smaller diameter. This does not account for the effect that usually smaller pores have a higher tortuosity, albeit Moldrup et al. (2001) found diffusivity not being affected by soil structure. In Klute et al. (1994), the prediction of air permeability from air-filled porosity is reviewed. The authors report typical uncertainties for proposed models of one order of magnitude. As the measurement of kgas is comparably easy, it is proposed to measure it instead of predicting it from the soil properties. As source of uncertainty, the effect of soil structure on k_{gas} is named. It was found that not only total available pore space influences the advective gas transport but also tortuosity.

The (not significant) relationships between air-filled porosity and k_{gas} found in this study were linear and different for each set of samples (Figure 31). The difference of the models was attributed to the variability of soil pore space. The soil texture difference between the sites resulted in different models between the sites, and the structural differences between the individual soil cores, which was resulting in the scattering of the data which was too high to derive a significant model. An extensive variation of k_{gas} values was also described in Wickramarachchi et al. (2011) . It was attributed to soil structure, especially the pore size distribution and the continuity of larger air-filled macropores, as an integral of soil moisture, compaction and texture. Such effects are considered to be the reason for the large scattering within the sample sets of the five soil cores each of this study, too.

Linear relationships between air-filled porosity and air permeability for natural soil cores of 1200 cm^3 with less than 20% clay were found also by McCarthy and Brown (1992). They found individual functions for each soil as well and attributed that to soil texture and structure. Structured soils exhibited greater permeability than poorly structured ones. This was proposed to be due to the higher inter-aggregate flow channels. Also in this study the highly aggregated Wieringermeer subsoil had considerably higher k_{gas} values than the unstructured Eckerkoppel subsoil.

If soils were poorly structured, it was found that the finer the texture, the lower the permeability. For a sandy loam, Gebert and Gröngröft (2010) found a log-linear relationship between k_{gas} and air-filled porosity where increasing compaction at the same water potential was the determining factor for air-filled porosity at a given texture. An increasing compaction changes the pore structure eliminating the coarse pores. The resulting log linear relationship is a hint that the coarser pores contribute exponentially more to advective transport. Hence, when the macropores are not being successively destroyed by compaction but remain air-filled over all measurements as for the Wieringermeer topsoil samples in this study, the remaining reaction is governed only by the change of the share of finer air-filled pores. If no macropores exist the same small reaction on a lower level is expected which was found for the Eckerkoppel subsoil samples (Figure 31).

In this study, it was observed that the range of the scattering of k_{gas} over air-filled porosity increased with total carbon content of the soil. As soil organic material is a major factor for the aggregation of soil, it is assumed that the scattering can be attributed to increasing structure of the soil and hence larger heterogeneity on a spatial scale that is not covered with a single sample but appears as the variability between the parallel samples. It is assumed that due to the aggregated clumpy structure of the Wieringermeer subsoil, a large share of macropores was present there. These pores are especially important for advective transport while pores with increasingly smaller radii have exponentially less ability to mediate advective gas fluxes (see above). It is likely that the clumps developed either by swelling and shrinking of the loamy material or during construction of the Wieringermeer test field. A clumpy structure can form in loamy material when it is handled in a too dry or too wet state (Scheffer et al., 2010). During reconstruction the material was excavated in a dry state. The previously more coherent loamy material soil broke down to clumps that were refilled to the test field.

6.1.2 Influence of water content on emissive fluxes

Hypothesis corresponding with this section: 1 b: The ratio of diffusion to advection decreases with increasing degrees of water saturation.

It was hypothesized that with increasing water saturation advective transport potentially becomes more dominant than diffusive transport. This could not be confirmed generally. The ratio of the coefficients describing these two processes did not have a significant trend in relation to air-filled porosity. Still, there seemed to exist an upper limit of the gas permeability coefficient of about 2.5×10^{-2} m s⁻¹ that was reached between 20% and 30% air-filled porosity while the diffusivity increased with air-filled porosity over the whole observed range of porosities. The increase of diffusivity leveled off at about 30% air-filled porosity, which was also found in the data of Deepagoda et al. (2013) and McCarthy and Brown (1992).

Advection is more dependent on pore geometry (Klute et al., 1994; Kühne et al., 2012) and pore structure (Moldrup et al., 2001) than diffusivity. At high water saturation, both processes are restricted to the remaining coarse pores which are less tortuous than the finer

pores. At dryer conditions, both processes can occur through the finer pores as well while permeability is hindered more by the increasingly complex pore geometry of the finer share of the pore network. Moldrup et al. (2001) found decreasing permeability with increasing air content. That could be attributed to the sample preparation: the material was mixed with increasing amounts of water. More water led to higher aggregate formation in the mixing process hence the effect of increasing air content was overridden by the effect of decreasing aggregation. To quantify the effectivity of a pore network for diffusive gas transport, Perdok et al. (2002) introduced an effectivity factor. Assuming a linear relationship for the restriction of the diffusion process by the share of air-filled porosity between diffusion in air (D_0) at 100% air-filled porosity and no diffusion at 0% air-filled porosity, the effectivity factor gives the deviation from the linear assumption, resulting from pore structure effects as tortuosity and connectivity. It ranges from 0 to 1. They found a linear increase ($R^2 > 0.9$) of the effectivity factor with air-filled porosity between 6 and 25% from about zero up to approx. 0.25. For the diffusion data of this study, the linear regression of the effectivity factor showed a higher variation ($R^2 > 0.5$) (data not shown). If the 2 kPa and 4 kPa were excluded the relationship improved ($R^2 > 0.7$). The data of Perdok et al. (2002) as well as the data of this study suggest that the effectivity factor and hence the restriction of the pore system due to tortuosity and discontinuity deviate especially from a 1:1 relationship with airfilled porosity at values below about 15 - 20%. This is in accordance with the thresholds discussed in section 6.1.1.

Both fluxes, advective and diffusive, were considered separately in this study and the potential fluxes according to the physical soil properties were explored and compared. In reality, both processes are not independent from each other. Advective flux could transport gas of high methane concentration to the surface, thereby shortening the pathway of diffusion and hence increasing the concentration gradient. While diffusion is affected far less by pore structure, it is expected to occur in a spatially more homogeneous manner while the magnitude of advective fluxes depends more on pore geometry. This is assumed to cause a flux and emission pattern that appears random in flux monitoring but is related to soil properties and pressure conditions in the soil pore system.

In this study, anisotropy of the pore system was not considered. As vertical flow paths show better pore connectivity than horizontal ones (Peng and Horn, 2008), it might be important for the understanding of preferential flow. These are often well connected biopores or cracks from drying or settlement, hence random biotic activity or soil movement paired with a critical soil moisture status might influence the dynamic of the occurrence of preferential flow.

Hypothesis corresponding with this section: 1 c: Small differences in soil water content convert equal concentration or pressure gradients into considerably different diffusive and advective fluxes depending on the initial saturation of the soil.

The models describing diffusive flux for the examined soils were used to calculate the change of flux resulting from a change of air-filled porosity. The resulting change of the flux
per one percent of air-filled porosity changed between 0.1 and 4.3 g $CH_4 \text{ m}^{-2} \text{ d}^{-1}$ in the range of 5 to 45% AFP for a 40% concentration gradient over one meter of soil.

For advective fluxes, no model could be applied. Over the range of observed air-filled porosity, a general increase of resulting fluxes between 0.6 and $3.5g \text{ CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ per pascal pressure loss over one meter of soil was found. Still the scattering was too high to predict a flux change from a change in air-filled porosity with any significance.

In soil gas concentration surveys it was found on landfill cover soils that the range of methane concentration in the soil is often in the range of some tens of percent. Pressure differences between soil and atmosphere did not build up or were equilibrated instantly (Schack-Kirchner, 2002), indicating the occurrence of advective fluxes.

The influence of given change of air-filled porosity on the resulting fluxes was found to increase for diffusive fluxes with increasing absolute soil water content while the influence was more or less constant for the advective fluxes. Other than hypothesized there was no pronounced increase of advective flux potential for a small increases of air-filled porosity at low water potentials, probably because either all macropores were air-filled already (Wieringermeer subsoil) or because there were no macropores (Eckerkoppel subsoil) that could open up at a threshold water potential. Changes of the process drivers (pressure and concentration gradient) were found to be of higher importance for the resulting potential fluxes. Hence, for both transport processes it was very likely that the heterogeneous flow patterns were measured as well on Wieringermeer landfill as on landfill K were to a large extend caused by heterogeneous concentration and pressure gradients and only to a smaller extent by the range of air-filled porosities occurring at one water potential. In both cases the methane emission and surface concentration patterns are in accordance with the soil gas methane concentration patterns.

In practice, the rate of gas generation in a landfill body limits the possible flux of landfill gas through the cover per time unit. Assuming a 200.000 m² landfill receiving 200.000 Mg y⁻¹ of waste with an organic carbon content of 105 kg C Mg⁻¹ over 19 years, Gebert et al. (2011d) calculated a maximum advective flux of 65.5 g CH₄ m⁻² h⁻¹ 20 years after the commencement of deposition. In this example, advective flux declined to below 10 g CH₄ m⁻² h⁻¹ in year 38 (MOT spreadsheet, worksheet "Diffusive flux"). Even if the consideration is an estimation, it shows that the gas generation will limit the advective fluxes to amounts far below what could be potentially transported. With this limitation of the advective flux in mind the potential diffusive flux gains a higher relative importance. It was calculated that the potential diffusive flux through the examined landfill soils was up to 70 g CH₄ m⁻² d⁻¹ at field capacity (6 kPa) and a concentration gradient of 40% methane over one meter of soil (Figure 28).

6.2 Emission hotspots – Prerequisites for hotspot formation and response of soil to methane point sources on an old landfill

Hypothesis corresponding with this section: 2 a: The spatial soil gas and surface concentration pattern of hotspots is caused by small-scale differences in pore size distribution of the cover soil.

How big is the influence of differing pore size distribution on potential diffusive flux?

It was hypothesized that the spatial variability of soil gas and surface concentrations at the hotspots are caused by small-scale differences of the soil pore space distribution. The analysis of the samples from the hotspot site H13 revealed about 7% points higher air-filled porosity in the upper 10 cm for the hotspot site (sample US5) than for the non-hotspot site (sample US6, see chapter 5.2.2.2) used as reference if the coarse pores > 50 μ m were air-filled (at water tensions up to 6 kPa). Flux estimations using the diffusion coefficients from the laboratory experiment on diffusion (chapter 5.1.2) were carried out for that 7% points difference of air-filled porosity at a concentration gradient of 40% methane over one meter of soil, a gradient frequently incurred in landfill covers. A change from 13% air-filled porosity (non-hotspot site) to 20% air-filled porosity (hotspot site) would change the potential diffusive methane flux from 2.7 g CH₄ m⁻² d⁻¹ to 10.9 g CH₄ m⁻² d⁻¹ for the least (Eckerkoppel topsoil) and from 8.1 g CH₄ m⁻² d⁻¹ to 19.2 g CH₄ m⁻² d⁻¹ for the most diffusive material (Wieringermeer topsoil).

Maximum emissive fluxes of 70.6 g CH₄ d⁻¹ (4.4 mol⁻¹)were reported by Rachor et al. (2013) for the hotspot site. In the mentioned study, a chamber with a base area of 0.12 m² was used. As the flux was assumed to stem only from the hotspot, the exact spatial extension was not known and hence, the flux data were given without a relation to an area. To compare the emission from the hotspot to the calculated maximum diffusive potential, the flux was related to one square meter, resulting in a flux of 588 g CH₄ m⁻² d⁻¹. According to the calculated maximum diffusive potential of about 80 g CH₄ m⁻² d⁻¹ (Figure 28), it is highly likely that the emissive gas transport was realized with a major advective component.

How big is the influence of differing pore size distribution on potential advective flux?

The methane concentration profile in the soil showed a continuous zone of elevated concentrations from 60 cm depth up to the surface, which suggests a zone of increased gas transport compared with the surroundings (chapter 5.2.1). The water retention curve indicated a share of pores > 980 μ m (0.3 kPa) of 8.4% for the soil at the immediate hotspot and of only 2.8% for the soil next to it (non-hotspot sample). The air-filled porosities of the samples used for the gas flux experiment were in the same range (5.1.1) and hence, the results from these soils (Wieringermeer topsoil and Eckerkoppel subsoil) are used for the following consideration. For the material with 10% pores > 980 μ m, potential advective fluxes of 50 g CH₄ m⁻² d⁻¹ per Pascale pressure difference were identified. For the material with 3.7% it was only 5 g CH₄ m⁻² d⁻¹ per Pascale (in both cases assuming a methane concentration of 40%). Assuming that the main emissions from the hotspot stem from only

one tenth of a square meter, it was calculated that about 14 Pa pressure difference would be required to force the maximum emissive flux of 588 g CH₄ d⁻¹ through the soil with the higher porosity, i.e. in the hotspot center topsoil. In contrast, 140 Pa would be needed for the non-hotspot topsoil with the lower permeability. From these data it can be concluded that the difference in pore space distribution with the 7% higher share of pores > 980 μ m (0.3 kPa) in the hotspot topsoil compared to the adjacent area, is an explanation for the small scale pattern of soil gas concentrations, methane surface concentrations and emission. As a consequence it seems likely that the structure of the topmost decimeter of soil has a very high influence on the emissive gas fluxes. For a deeper insight, flux measurement data with a high spatial resolution would be useful for a further understanding of small scale flux dynamics.

Hypothesis 2 b: The preferential gas flow through the soil, leading to prolonged exposure of soil to reducing gas, influences the soil's physical and chemical properties.

The spatial soil gas composition pattern of the *Reduktosol* area was stable during the time of this study. Based on this it was assumed that the causal soil structure remained stable over the period of investigation, such that the gradients driving fluxes (concentration, pressure) continuously resulted in preferential gas flow. This is supported by other findings that preferential flow paths can be stable over decades (Hagedorn and Bundt, 2002). The authors analyzed the age of preferential flow paths for water, identified by dye tracer application, in a fine-loamy forest soil using radionuclides. As the landfill under study is known to have stopped operations in the 1980s, the *Reduktosol* features cannot be older than that. Anthropogenic *Reduktosol* soils over waste are considered soils of comparatively short existence, disappearing again when the methane generation in the waste body declines considerably (Blume, 2002). When the subsoil is reduced, metal sulfides of grey and black color will form and can migrate to the oxic topsoil or from the inside of aggregates to their outward surfaces with the soil water by capillary forces. In these regions, they precipitate after contact with atmospheric oxygen (Blume, 2002). The formation of metal sulfides might be favored by the presence of hydrogen sulfide, which is a common trace component in landfill gas. At the study site, thick iron oxide coatings were found on the walls of the cracks in the subsoil of the *Reduktosol*, indicating at least a part time aeration of the crack.

How can the oxic features in the subsoil be explained?

Influx of atmospheric air into a passively vented landfill by "barometric pumping" was described by Gebert and Gröngröft (2006a). Others authors also found strong inverse correlations between landfill gas emissions and barometric pressure (Czepiel et al., 2003; Xu et al., 2014), implying the ingress of air in times of rising barometric pressure. Effects of changing atmospheric pressure are also reported for natural ecosystems like tundra or peatland (Sachs et al., 2008; Tokida et al., 2007). The soil matrix around the crack was grey, indicating reducing conditions. The crack in the subsoil was hypothesized to be the source of methane from the waste body to the soil above. That means a very punctual load to the cover soil with probably changing intensity due air pressure variations and thus methane emission. Gebert (2004) and Xu et al. (2014) found emission and atmospheric influx to

alternate with barometric pressure on a daily to weekly time scale. In the study of Gebert (2004) the landfill gas was routed through highly permeable sand drainage layers to an equally permeable biofilter, a setup that instantly could facilitate the equilibration of pressure differences. As in in the aforementioned biofilter, the crack at the hotspot sites' subsoil in combination with the overlying bulked topsoil material functioned as a path of least resistance compared to the surrounding. The influence of changes in atmospheric pressure on the soil methane concentrations of the site was examined in Geck (2011). No significant correlation between the rate of pressure change and the height of methane concentration in the soil gas phase was found. It was estimated that even a 30 hPa pressure drop within 24 h would not result in a pressure build-up because the potential convective flux was two orders of magnitude higher, indicating rapid equilibration of pressure between the landfill body and the atmosphere. As discussed in the previous section, the potential advective flux through the hotspot soil was in the same order of magnitude as the emission from the site found by Rachor et al. (2013). For rising barometric pressure, an equivalent influx of atmospheric air can be expected.

How could the hotspot have evolved?

The crack in the subsoil was considered a point source, channeling the gas from the waste body towards the soil cover. From here, further gas transport through the soil would follow the path of the least resistance, i.e. highest permeability (gas conductivity and/or gas diffusivity). In the first place, this could have been a root channel, a crack or a burrow of animals. Further, it is assumed that the high methane load stimulated the growth of the methanotrophic community, which was supplied with an excess of methane due to the small contact zone in connection with high fluxes. As a reaction to excess carbon supply, the bacteria started producing exopolysaccharides (EPS), which also moderate the variability of water and nutrient supply (Or et al., 2007). EPS production in landfill cover soils has been described by various authors (Hilger et al., 2000; Streese et al., 2001; Wilshusen et al., 2004). On the one hand, these substances changed the pore space geometry of the soil as pores are clogged (Morales et al., 2010), on the other hand it is assumed that they attracted the lumbricides, which were found in great abundance in the soil (identified as *Eisenia foetida*). These fed on the EPS but, being an aerobic species only in the outer, still partially aerated zone. They tolerate carbon dioxide up to 6.5% in the gas phase albeit their respiration is increasingly inhibited (Moment and Hobermann, 1978). The grubbing activity of the lumbricides bulked the soil locally, leading to an increased gas transport potential through the created macropores for landfill gas emissions and atmospheric air immisions. A wellstructured chimney of secondary pores formed on the outside of the region with high methane concentrations (for position see Figure 33). The region of high methane concentrations narrows from bottom to top of the profile resulting in the cone-shaped structure of the soil region that appeared reduced (grey colors). The continuous decrease of the reduced area from bottom to top could be caused by the depletion of methane along the flow path due to successive oxidation from the oxic surrounding towards the center or by channeling along preferential pathways or a combination of both.

It is hypothesized that the ecological niche of high methane concentrations in a very confined area with a steep gradient to the surrounding aerated soil formed an extreme habitat that was self-stabilizing via the positive feedback of the lumbricide burrows. The burrows channeled gas transport and the methanotrophs delivering the EPS to the lumbricides, which could thrive in the region of reduced oxygen concentrations. The gas is assumed to not have dispersed to a wider area due to the high (macro-) porosity (lumbricide channels and inter-aggregate macropores) and thus the low flow resistance in vertical direction at the hotspot site (Geck et al., 2012; Gröngröft and Gebert, 2012).

An impact on microbial community by elevated methane soil gas concentrations was shown by Gebert and Perner (2015). They found a less diverse, but more specialized population at methane point sources in the cover soils of the same landfill as investigated in this study. Morales et al. (2010) stated that only resilient microorganisms can survive in soil prone to preferential flow because of the strongly varying conditions. The strong variations are constituted by the temporal influence of temperature, precipitation and changing barometric pressure that is mediated through the preferential flow paths, hence the change between dry and moist, high and low oxygen content and warm and cold is more pronounced than in the soil matrix. The highly variable soil gas regime was found as well in this study. Gebert and Perner (2015) found elevated C - N ratios at point sources compared to the surrounding soil material not affected by preferential gas flow. That was attributed to the EPS material, also found in their study, which typically increases the C - N ratio compared to other biomass like soil organic matter (Costerton et al., 1978). The C - N ratios from this study could not confirm that finding. For above or below-average C - N ratios no explanation was found. However, most of the samples from Gebert and Perner (2015) were taken at a depth above seven centimeters b.s. and in a spatial resolution on the centimeter scale, purposely separating samples according to visible features such as EPS presence and soil discoloration. In contrast, the samples of this study were bulk samples at much lower spatial resolution. The hotspot topsoil sample from the main profile showed purple discoloration as well. It is likely that due to the preferential pathway pattern within a few centimeters environmental conditions within the soil change drastically and that the disturbed samples taken for this study were too big to resolve the shift of the C - N ratio from hotspot to non-hotspot conditions.

How can the difference in pore size distribution between the soil at the preferential pathway and the adjacent soil be explained?

The two soils directly at the principal preferential pathway for gas (indicated by peaking surface methane concentrations, sample US5) and in the adjacent area (sample US1) were where both low in bulk density but differed regarding their pore space distribution. Adjacent to the main preferential pathway, the air-filled porosity was lower at all water tensions below 30 kPa (pores >10 μ m). Total porosity, however, was equally high. The organic carbon content in the sample from the adjacent soil was about double than in sample from the preferential pathway. The high organic carbon content was assumed to stem from the EPS, and hence high microbial biomass and activity. Morales et al. (2010) found that microbes

tend to concentrate along preferential flow paths and less within the aggregates. This could lead to clogging of the pores by an abundant production of EPS. It is assumed that EPS skew the pore size distribution towards finer pores in comparison to sample from the preferential pathway.

6.3 Spatial and temporal variability of methane emissions, oxidation efficiencies, oxidation rates and soil gas concentrations of a methane oxidation cover test field

This section discusses the findings from the field survey on methane fluxes to, through and from a large-scale methane oxidation cover test field (chapter 5.3). Oxidation efficiency and rate are assessed and the spatial and temporal pattern of base flux, methane oxidation, methane emission and soil gas concentrations are being discussed. Influence of constructional features and measures are being considered. A special focus is set to temporal and spatial pattern.

6.3.1 Consideration of methodological errors

How reliable was the emission monitoring scheme?

Based on the results of an emission measurement campaign covering the total area of the test field and on complementary FID screenings, the campaigning strategy (section 4.5.2) for the flux chamber measurements was derived. The respective grid fields were chosen in such a way that each campaign would capture 93% of the total emissions. The sum was then adjusted to 100%. Uncertainties might result from gas escaping the test field through lateral migration or strong emissions from grid fields other than those identified as being highly emissive. However, when re-evaluating the chosen sampling scheme in a later campaign, again covering all available grid fields, it was found that the spatial emission pattern had remained constant and that hence also the measurement scheme remained valid over the year of its employment. The assumption that during the investigation period the level of coverage of emissions was close to 100% was, therefore, considered valid. Further, the results imply that the factors resulting in the observed pattern remained effective during the whole observation period.

What effect of changing barometric pressure was expected?

In emission monitoring, barometric pressure usually is a crucial parameter (Czepiel et al., 2003; Gebert and Gröngröft, 2006a; Xu et al., 2014), determining the temporal variability of emissions, especially in passively vented landfills. In this study, however, the effect of barometric pressure was not pronounced because the gas supply to the test field was realized by a flow controller absorbing possible effects of barometric pressure on the underlying waste body. Furthermore, the air column within the soil could not respond to changing barometric pressure with high fluxes due to its limited depth of 1.4 m. It was calculated that even a strong pressure drop of 20 hPa over ten hours would expand the soil column by only 3 cm. For an air-filled porosity of 30% and a methane concentration of 20%

in the soil gas phase (in the topmost 3 cm) this would result in an emission of $1.5 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ during the falling pressure conditions at a methane concentration of 5% it would be only $0.3 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (for comparison: average emissive fluxes from grid fields ranged around $5 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. It must be considered that the higher topsoil methane concentrations occurred in winter when average methane emissions from the grid fields was up to $17.6 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$). It was shown that the barometric pressure was negatively correlated to soil methane concentrations (5.3.3.2) while no correlation was found to the change of air pressure six and twelve hours previous to the measurements. Due to the low expected fluxes, barometric pressure was considered a minor factor of influence for the magnitude of emissions on this specific site.

What errors were associated with the determination of the oxidation efficiency?

For the determination of the oxidation efficiency (1) using the methane mass balance method the methane influx data recorded at the gas supply station and the methane emission data from the large chamber emission measurements and (2) using the carbon shift method gas concentration data recorded at the gas supply station and during emission measurement below the chamber were used.

The oxidation efficiencies derived by the carbon shift method were somewhat lower than if calculated by methane mass balance. The carbon shift method relies on carbon dioxide measurements unbiased by soil respiration, dissolution of carbon dioxide in soil water or precipitation of carbon dioxide. For grassland, a soil respiration rate of 442 g C m⁻² a⁻¹ was reported from Raich and Schlesinger (1992). In contrast to the lower efficiencies resulting from the carbon shift method in this study, Röwer et al. (2016a) found for the same study site that neglecting soil respiration in using the carbon shift method might result in an overestimation of oxidation efficiencies of about 10% points. According to these authors, carbon dioxide fluxes from plant respiration and photosynthesis were negligible and from dissolution and release of carbon dioxide in and from soil water were small in relation to the inlet fluxes. As illustrated by the validation of the emission measurement method involving the novel large chamber (5.3.1.2), carbon dioxide emissions were overestimated by about 11%. This would increase the corrected resulting efficiencies as calculated from the carbonshift-method by up to 3.7 percentage points in winter conditions while leaving the obtained values nearly unaltered in the summer months when efficiencies were high anyways. This error is considered of minor importance as the measured efficiencies ranged from 24.5% to 100%.

6.3.2 Assessment of oxidation efficiency and rates

How was the system performance compared to other field trials?

The survey of the large-scale test field performance confirmed an average methane **oxidation efficiency** of 84% (SD 17.5) at loads from 10.6 - 42.5 g CH₄ m⁻² d⁻¹. The findings on the magnitude of the oxidation efficiency are in accordance with other studies (Capanema and Cabral, 2012; Scheutz et al., 2014), albeit the former was achieved at loads up to 290

and 818 g CH₄ m⁻² d⁻¹ and the latter at loads around 27 g CH₄ m⁻² d⁻¹. Other studies found a somewhat lower oxidation efficiency of about 50% (Dever et al., 2011) at loads from 48 to 83 g CH₄ m⁻² d⁻¹, hence comparable to the loads in this study.

The **oxidation rates** obtained in this study ranged from 8.5 to 39.6 g CH_4 m⁻² d⁻¹. They were comparable to findings of other studies (Sadasivam and Reddy, 2014; Scheutz et al., 2009). Average rates for a biowindow of 20.4 g CH_4 m⁻² d⁻¹ were reported by Scheutz et al. (2011a). Mei et al. (2015) found oxidation rate of 140 - 200 g $CH_4 m^{-2} d^{-1}$ in a green waste biocover. Extremely high rates up to 818 g CH₄ m⁻² d⁻¹ are reported from Capanema and Cabral (2012) for a sand and compost biofilter. In contrast to the presented study the aforementioned methane oxidation systems used compost material as filter substrate. Huber-Humer et al. (2011) showed that mature compost is a more effective filter bed material than mineral soil. The advantage of mineral soil material is its mechanical long term stability which is not given for compost material (Jugnia et al., 2008). The achievable oxidation rate of a system depends not only on the used material setup and environmental conditions but also on the exposure to methane. Röwer et al. (2011) found a positive correlation between methane concentration in the soil of an old landfill and its methane oxidation capacity. They assumed that even a low-level exposure to methane builds the potential for rapid population growth when the soil is exposed to higher loads. Gebert et al. (2003) showed that prolonged methane exposition of a biofilter increased its methane oxidation rates. In batch tests, Gebert (2013) showed that repeated cycles of methane incubation and oxidation increased the soils methane oxidation rates. The final rates (0.5 - 45 μ g CH₄ g_{dw}⁻¹ h⁻¹) were dependent on the incubation temperature while the asymptotic shape of the curve over the cycles was similar for all incubation temperatures (4 °C to 37 °C). Findings from laboratory column studies often indicate higher rates which can be explained by higher applied loads and optimal conditions of substrate supply as well as favorable temperatures (overview in Scheutz et al., 2009). Measurement data from landfills in The Netherlands indicate that the oxidation rate increases with the load but deviating ever more from a 1:1 relationship until reaching a maximum at about 24 g CH₄ m⁻² d⁻¹ (Oonk and Boom, 1995). The results from this study show that higher maximum rates can be obtained in optimized systems. It has to be considered that oxidation rates in this study have been restricted over most of the time by the applied load, hence, the potential of the cover was not challenged.

Is the system performance suitable for landfill aftercare?

The minimum load to the test field was $13.7 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. The application of methane oxidation systems is proposed for the treatment of low activity aftercare. An upper load of 8.5 g CH₄ m⁻² d⁻¹ to the recultivation layer is proposed for changing gas management from active to passive aftercare (Stegmann et al., 2006). In this study, it was shown that optimized methane oxidation covers are capable to treat loads up to 46 g CH₄ m⁻² d⁻¹ under favorable conditions. Some emissions occurred even at low loads (see below). It might be indicated to calculate a safety margin, especially in dimensioning biowindows where the size is a matter of planning and not only dependent on the size of the landfill. The obtained methane oxidation efficiencies of 84% on average argue for the application of methane oxidation

systems in the passive landfill gas aftercare. It is expected that the oxidation capacity of the soil cover remains at a stable level, given a constant supply of methane. A constant oxidation capacity in combination with a decreasing load would result in a decrease of emissions and an increase of the efficiency. In terms of the avoidance of greenhouse gas emissions, possible emissions from a passive system have to be weighed against the additional emissions due to the operation of a technical system.

6.3.3 Effect of MOS constructional features on gas fluxes

Hypothesis corresponding with this section: 3 a: Spatial patterns of soil moisture on sloped areas lead to gas emission patterns with predominant emission in the upslope area.

How did the capillary barrier affect the gas flux pattern?

It could be shown that oxidation efficiency, rate and emission were heterogeneous on a spatial scale of several meters (grid fields). In all campaigns, some grid fields showed oxidation efficiencies of around 100%. The lowest oxidation efficiencies were always found on the upper slope and the lateral limits of the catchment. If percolation water is discharged into the capillary barrier, a saturated water seam forms at the interface between the capillary block and the capillary layer, reducing the permeability to gas. As water accumulated along the path length, i.e. in the downslope direction, this effect became more pronounced in downslope positions and especially in the moister seasons. Vice versa, it is likely that the capillary seam forming in the capillary layer just above the capillary block was less continuous the more upslope it was located. This effect was also observed by Tétrault and Cabral (2013). Thus, the gas that spread out in the capillary block / gas distribution layer could enter the methane oxidation layer passing the capillary layer more easily in the upslope area. The result was an uneven load to the methane oxidation layer with peak loads upslope that could be seen in the pattern of the base fluxes (Figure 65). Consequently, the upslope area received a load that was higher than the nominal load derived from the relation of the bulk base flux to the base area. This lead to an overload of the upslope area while some parts downslope received less than they could oxidize and thus could not exploit their full oxidation potential. This could be observed for example in October 14 and January 15 where the upslope third of the test field accounted for 82%, respectively 89% of the emission from the total test field. This is especially critical if wet and cold conditions prevail in combination, as in the winter month at the study site. As a result of these temporal conditions, increased loads coincide with reduced oxidation capacities, resulting in emissions predominantly upslope (Figure 65). The problems arising from the combination of gas distribution system and capillary barrier were confirmed by Wawra and Holfelder (2003) who found a reduction of gas conductivity along a hill slope of two orders of magnitude as a result of capillary effects.

How did the reconstruction affect the gas flux pattern?

Hypothesis corresponding with this section: 3 c: Compaction of topsoil resulted in a more homogeneous distribution of the soil gas phase.

The test field was initially built with a high effort not to compact the soil material. The effort was exceeding a realistic application scenario. Later, a reconstruction of the test field was carried out, primarily to assess the field performance when built with conventional machinery yielding a higher compaction. Besides the observation of performance before and after the reconstruction, the gas distribution within the field was an objective of investigation. The reconstruction was meant to increase the resistance, of the methane oxidation layer without changing the gas distribution layer.

The reconstruction work was performed under dry weather conditions. Aggregates of the dry soil material were stable and were probably not destroyed during the work. It is suspected that after refilling, the material inter-aggregate pore space remained. The main impact of the work might have been the destruction of continuous macropores with the result of a higher vertical flow resistance which especially affects the advective component of the gas flux (Kühne et al., 2012).

The spatial distribution of the soil gas phase before reconstruction was much more heterogeneous than thereafter. Upslope concentrations were higher and the gas inlet ports could be seen in the soil gas concentration measurements as concentration peaks. After reconstruction, the gas concentrations within the catchment area were much more homogeneous. A clear catchment – non catchment gradient was found. As the layers of the test field soil material stretched beyond the catchment area but the high concentration areas did not, it is likely that the gas migrated until the boundary of the catchment. There it was forced upwards out of the gas distribution layer into the less permeable material of the methane oxidation layer. There, a further lateral spreading was limited because the flow resistance within the methane oxidation layer was least in vertical direction due to the steepest concentration and pressure gradients towards the atmosphere.

The heterogeneous emission pattern was found before and after the reconstruction works. However, the heterogeneity was less pronounced after the reconstruction. This was attributed to the increased compaction (changing bulk density from 1.34 to 1.39 g cm⁻³) of the methane oxidation layer that was realized during the reconstruction, yielding a higher difference of gas conductivities between gas distribution layer and the methane oxidation layer. This led to a more homogeneous distribution of the gas within the gas distribution system (capillary block layer). The effect was corroborated by gas composition measurements using gas probes in 1 m depth on grid field scale resolution (Figure 56, see also section 5.3.3). This points to the importance of carefully balanced porosities of the individual layers of the methane oxidation system in order to obtain a maximum spatial evenness of gas flow as recommended in German guidelines (LAGA Ad-hoc AG "Deponietechnik", 2011c). For methane oxidation systems, it is emphasized that the difference in permeability between gas distribution layer and methane oxidation layer

should be at least two orders of magnitude while on the other hand a capillary barrier effect should be avoided.

It was found that the depth of aeration decreased after reconstruction, which was attributed to the effect of compaction already mentioned above, limiting the diffusive oxygen ingress into the soil. The oxidation horizon shifted upwards to the upper soil layers, which were more affected by changing soil moisture and temperature (higher moisture and temperature amplitudes in shallower soil depth, data not shown). The negative effect on especially the share of wide coarse pores was described in Gebhardt et al. (2009). The finer the texture, the higher was the impact on compaction. The effect of compaction on gas diffusivity was examined by Gebert et al. (2011a). As in the study mentioned before, it was found that especially the coarse pores were affected.

After reconstruction, the share of oxidation already taking place within the gas distribution layer and hence indicating a very deep aeration of the test field, was only 13.5% compared to 27.8% observed before reconstruction. However, in spite of the decreased diffusivity, the average oxidation efficiency of the test field increased slightly. The enhanced spatial distribution of the gas, resulting from increasing the permeability between the gas distribution system and the methane oxidation layer, seemed to compensate the effect of reduced aeration depth.

How did the distribution of soil moisture influence the gas diffusivity of the soil?

In the methane oxidation layer, no topologically dependent moisture pattern was found (section 5.3.3.5.2). The random soil moisture pattern could not explain the elevated emissions in the upslope and border regions. This lead to the conclusion that the moisture distribution within the capillary barrier was the controlling parameter. Still, the spatial variability of soil moisture content would have been high enough to influence the magnitude of diffusive gas transport through the soil cover. A spatial variability of soil moisture content for the methane oxidation layer of $\pm 7\%$ w/w_{DW} points was found with all sampling points and depths while the mean soil moisture content was 12% w/w_{DW} (chapter 5.3.3.5.2). As shown in chapter 5.1.5, the change potential of diffusive flux caused by a change in air-filled porosity of one percentage point range from 0.8 - 0.9 g CH₄ m⁻² d⁻¹ at 10% air-filled porosity to 4.1 - 4.2 g CH₄ m⁻² d⁻¹ at 45% air-filled porosity. The observed range of field soil moisture from 5% to 19% w/w_{DW} was not covered by the gas flux experiments. The lowest water content at which gas flux experiments were performed was 14.7%w/w_{DW} which was equivalent to 39.8% air-filled porosity at the given bulk density. From the models derived from the laboratory data the change of diffusive flux resulting from that change of soil moisture content (5% to 19% w/w_{DW} or 30.1% v/v to 44.1% v/v air-filled porosity) could be determined as from 43.3 - 92.5 g CH₄ m⁻² d⁻¹ (an increase of 46.2 g CH₄ m⁻² d⁻¹) for Wieringermeer topsoil and from 43.7 – 95.8 g CH₄ m⁻² d⁻¹ (an increase of 52.1 g CH₄ m⁻² d⁻¹) for Wieringermeer subsoil. Hence, the observed field soil moisture distribution can be expected to influence the variation of diffusive emissive fluxes by the factor of two. As stated above, this effect is assumed to have been overridden by the effect of moisture distribution along the slope length in the capillary barrier.

6.3.4 Temporal and spatial pattern of methane concentrations and fluxes

Hypothesis corresponding with this section: 3 b: Spatial emission patterns are constant but vary over time as a result of changing environmental conditions affecting physical gas transport and biological oxidation processes.

How can temporal and spatial variability of concentrations and fluxes be explained?

The soil gas concentration showed a clear seasonal pattern with higher concentrations in winter and lower concentrations in summer across all depths. The influence of the factors air-filled porosity (inversely related with soil moisture), temperature (soil and air) and air-pressure was examined. Air pressure had a significant influence only before the reconstruction. The influence of the factor air-filled porosity was highest before the reconstruction, which was attributed to the higher permeability of the soil (see 6.3.3). The factor temperature was had an influence over most of the time. The most significant factor of influence on the average methane concentration was the air-filled porosity, followed by temperature (Table 9). All factors were inversely correlated with the mean methane concentration.

Air-filled porosity was identified to be the factor with a correlation in the most cases. Higher air-filled porosity is associated with a lower soil moisture content. During the study it was never dry enough to substantially decrease the oxidation potential of the soil (see 5.3.8). Hence, the more important influence is the one on gas exchange which is favored by increasing air-filled porosity. As a result aeration of the soil reaches deeper layer and oxidation residues can be expelled from the soil faster.

Higher temperature accelerates up the oxidation process. Thus it is obvious that higher temperatures result in lower methane concentrations. Before the reconstruction soil temperature did not correlate. This was attributed to the more homogeneous gas concentration pattern that might have covered the influence of this single factor probably due the higher influence of the air-filled porosity.

Air pressure was found to be of influence only before reconstruction. Air pressure changes can induce advective fluxes. Rising air pressure can push air into the landfill cover increasing aeration while falling air pressure can cause an increase of landfill gas emissions. The effect was found only before reconstruction because the soil permeability was higher at that time. After the reconstruction the reduced aeration resulted in an oxidation horizon in a shallower depth (Figure 70) while the soil gas phase was more homogeneous with higher methane concentrations. These conditions were more robust against the influence of air pressure.

After reconstruction, gas distribution was more homogeneous over the whole test field. The distribution of the base fluxes to the single grid fields was more even too after reconstruction. The aim to force the gas into the area within the gas distribution layer by increasing compaction and reducing permeability of the methane oxidation layer was obviously met. However, a gradient of methane fluxes (emissions and base fluxes) and

concentrations over the slope of the test field remained, with increasing concentrations and fluxes towards the upslope section. This was supported also in the determination of the areas loaded with landfill gas (Figure 58). After reconstruction, only in the downslope and border region about 15 to 20% of the area were unloaded (or a load was not detectable) before reconstruction, the load to the catchment was variable, too. When focusing not on the aggregated test field but on individual grid fields, it was found that before the reconstruction the gas rose higher to the surface in midslope and downslope position. After reconstruction the methane concentrations were almost identically high in 100 cm and 60 cm depth b.s. most of the time while at the downslope position the absolute concentrations was lower than above. At all three sites, between October and April, methane concentrations in 25 cm depth were as high as in 60 and 100 cm depth. This showed that the gas could rise up higher in these times because soil aeration and hence oxygen supply was reduced due to high soil moisture, and oxidation rates were reduced due to low temperatures. These periods were associated with temperatures around 5-10 °C and air-filled porosities of below 28%. The highest change of methane concentrations occurred above 25 cm b.s., which is also the zone of the highest influence of climatic factors. Amplitudes of temperature and moisture are highest in the topmost soil layers rendering the conditions for methane oxidation highly variable. This variability was reflected in the analysis of the coefficient of variation of the methane concentrations: the variation was highest within the topsoil.

Another zone of high variability was the area outside of the catchment, especially at the upslope position. This implies an influence of the catchment border on gas distribution. The plastic bevel framing the catchment seems to deflect the horizontal distribution of the gas within the gas distribution layer into a vertical direction. In combination with the finding discussed in section 6.3.3 that the capillary barrier emphasizes upslope emissions, this could explain that emissions occurred predominantly upslope and along the catchment border. This was the region where effects of air pressure on the magnitude of emissions height were found. It was considered likely that the elevated supply of landfill gas to the upslope region caused advective fluxes. As these are pressure-driven, they can be influenced by changes of air pressure. Another evidence for advection at the upslope region of the test field are the high methane surface concentrations and the low carbon dioxide - methane ratios found in surface screenings especially upslope of the catchment (section 5.3.3.4), indicating lower methane oxidation efficiencies. Seasonal variability of environmental parameters had more impact on the performance of the upslope region than on other areas of the test field. This was due to the preferential routing of gas to the upslope area, which was most pronounced under cold and wet winter conditions, thus creating the coincidence of higher methane loads and less favorable conditions for methanotrophic activity.

Still, there was evidence for an all-year round effect of the capillary barrier on gas distribution. The base fluxes were heterogeneous under summer conditions too, albeit less pronounced. A moisture gradient over the length of the capillary barrier might persist the whole year through.

The landfill gas hat a temperature of about 30 °C in the injector station. The soil temperature in 40 cm depth had the highest amplitude at the upslope sensor position (3 $^{\circ}$ – 6 $^{\circ}$ C higher than up- and midslope position, Figure 51). While all slope positions showed about the same temperature in winter, the maximum values in summer were highest upslope. The elevated upslope temperatures were recorded during dry summer conditions under high methane loads. The observed offset beginning in April 2013 was not found in April 2014, though. It started to appear in July 2014 which was the time when the gas supply was increased from 13.7 to 46.4 g CH₄ m⁻² d⁻¹. The relative change of soil moisture between summer and winter conditions was around 10% v/v. The excessive warming of the topslope position was attributed to the warm landfill gas that was injected into the relatively dry soil. It is suspected that the warming could be detected only in the summer because the heat capacity of the moist soil in winter was elevated and hence the temperature increase caused by the same energetic input was lower. Heat capacity of soils increases about linearly with increasing water content (Bachmann, 2014). It would be of interest to run a model of the soils energy balance accounting for the water and energy from methane oxidation, to prove the contribution of the injected gas temperature and the oxidation process to soil temperature. As shown in chapter 5.3.5 the gas entered the test field predominantly upslope (base fluxes, see Figure 65), hence under dry summer conditions at high levels of gas load the gas flux resulted in an additionally warming of the soil. As no moisture gradient was found in the soil moisture mapping of the methane oxidation layer (section 5.3.3.5.2) the gas redistribution must have happened below in the gas distribution layer.

In winter, methane maximum oxidation rates were around 10 g CH₄ m⁻² d⁻¹ while in summer they were up to 40 g CH_4 m⁻² d⁻¹, while the calculated base fluxes to the individual grid fields were up to 115 g CH₄ m⁻² d⁻¹ in winter and up to 45 g CH₄ m⁻² d⁻¹ in summer (Figure 73). The level of base fluxes was dependent on the gas supply rate. The spatial heterogeneity of the fluxes was attributed to the abovementioned effect of the capillary barrier (chapter 6.3.2). The range of base fluxes was higher in moist and cold winter conditions, which is in accordance with the finding that the influence of the capillary barrier on methane flux distribution is higher under moist conditions. Especially in situations with low overall oxidation efficiencies, the individual grid fields performed differently, i.e. similar base fluxes were oxidized to different shares (see Figure 73). The oxidation layer is situated above the capillary barrier/gas distribution layer; hence, it should be influenced by the moisture state of the latter only in receiving a heterogeneous load. If a similar load is oxidized to a different share in different grid fields, this must be a result of different conditions between the grid fields. Soil temperature was found to be homogeneous within the test field, especially in winter, which makes temperature an unlikely factor to explain spatial variability (Figure 51). The most likely reason is a difference in soil moisture content and resulting airfilled porosity. As was shown above (section 6.3.3) soil moisture variations (± 7% points) within the test field can be responsible for the variability of diffusive fluxes by the factor two. The diffusive influx of oxygen into the soil is of major importance for the oxidation process which is reflected in the MOT factorization where air-filled porosity is the most important factor (Gebert et al., 2011d). Increased methane emissions with increased soil water content were also observed by Rachor et al. (2013). The effect was attributed to the reduced diffusion of oxygen into the moister soil as well. Other authors found a relevant relationship of air-filled porosity to permeability as well (Gebert and Gröngröft, 2010; McCarthy and Brown, 1992). Hence, air-filled porosity is considered the major factor for spatial variability.

The difference in soil moisture between summer and winter conditions created differences in air-filled porosity of about 10% points v/v in 40 cm depth(Figure 52), with maxima of about 35% v/v in summer and minima of about 26% v/v in winter. The resulting potential diffusive fluxes, methane emission as well as oxygen influx, would double if the functions derived from the diffusion experiment were employed.

In 40 cm depth, the temperature difference between summer and winter was about 15 K. The increase of the maximum oxidation rate from 10 to 40 g $CH_4 \text{ m}^{-2} \text{ d}^{-1}$ can be explained by the reported Q_{10} values of 1.7 to 4.1 (Scheutz et al., 2009). This shows that temperature is an important factor for the temporal variability of the systems oxidation rate if the system is not limited by a lack of oxygen influx due to high soil moisture. A separated consideration of these factors temperature and air-filled porosity could not be done in this study because they were auto correlated.

Under winter conditions, water saturation of the middle pores (0.2 - 10 μ m diameter (Adhoc-AG Boden, 2005)) was found, leaving only the coarse pores > 20 μ m diameter (pores > 10 μ m are defined as coarse pores (Ad-hoc-AG Boden, 2005)) available for gas transport while under summer conditions also most of the middle pores were water-free (> 0.6 μ m). If only the coarser pores including secondary pores like cracks, root channels and animal burrows are available, gas transport becomes less homogeneous (Allaire et al., 2008; Giani et al., 2002) because the flux concentrates in the erratically organized secondary pore network (Scheffer et al., 2010). If the same volume of gas per time unit flows through a smaller share of available water-free pore space, the specific area-related methane load in the corresponding soil compartments is increased. This results in lower turnover rates and hence higher emissions due to (1) the specific load exceeding the methane oxidation capacity and (2) impeded ingress of oxygen caused by increased, possibly advective, flow rates (Dever et al., 2011). The latter restricts the oxidation process to the upper soil layers (Gebert et al., 2011b; Rachor et al., 2011) or impedes it completely, leading to direct emissions.

For most of the grid fields, no correlation between barometric pressure and oxidation rate, efficiency and emissions could be found. However, in the very upslope area of the catchment a statistically significant inverse relationship was found between the parameters air pressure and efficiency and a positive relationship between air pressure and efficiency. At the study site, atmospheric low-pressure systems are usually associated with precipitations. In the previous section, it was discussed that a water seam forms above the gas distribution layer that is less continuous upslope. The gas transport through this path of least resistance is most prone to pressure differences and hence advective transport. This is why there is a correlation only between barometric pressure and emission was observed.

6.3.5 Comparison of the variability of the landfill sites and natural soils

The examination of the coefficient of variation made possible a comparison of the variability between the two sampled landfill covers (sections 5.1.2 and 5.1.3). The coefficient of variation of the air-filled porosity of the Wieringermeer topsoil samples was constant and highest over the range of observed water potentials. This means a high variability between the samples from the site. A constant trend was found between 2 and 30 kPa for the Wieringermeer subsoil and Eckerkoppel topsoil samples too, both with lower coefficients than those of the Wieringermeer topsoil. At a water potential of 0.3 kPa the coefficients were elevated indicating a higher variability within the sample set at near water saturation, a moisture state that would usually not occur except during strong precipitation. Coefficients were highest for Eckerkoppel subsoil material at high water saturations. This was attributed to the low air-filled porosity mean values with relatively high standard deviation that result in high coefficient of variation. Between 6 and 30 kPa the variability was higher than the one of the Eckerkoppel topsoil samples but lower than the Wieringermeer topsoil variability. The coefficient of variation of the D_{eff} values of the Wieringermeer topsoil samples was constantly high too while the Wieringermeer subsoil and Eckerkoppel topsoil had decreasing values between 2 and 6 kPa. This indicates an increase of variability with increasing soil moisture. This increase was found also in air-filled porosity variation at water potentials below 2 kPa, a range where no gas flux experiments were done. The relative variation could not explain the absolute height of obtained D_{eff} values and hence the disposition of hotspot formation. The sample sets with the largest pore space at 0.3 kPa water saturation were the ones where the highest gas fluxes occurred. This was also found at the samples from landfill K. These samples showed a high change of the coefficient of variation of the air-filled porosity for the low water potentials too. Especially the topsoil samples had high coefficients of variation. No flux measurements were done at these samples but the finding supports the assumption that hotspots are a result of small-scale differences of soil pore space with a dominant importance of coarse macropores. Both highly permeable materials, the Wieringermeer subsoil and the hotspot center material from landfill K showed secondary macropores. The Wieringermeer samples had cracks and the hotspot samples were interspersed with worm burrows.

Gröngröft and Gebert (2012) found that the coefficient of variation of the total porosity of natural soils is not statistically different from "artificial" built up soil (like landfill covers). The variability of the topsoil was higher in both cases, which was explained with the higher biotic activity of the topsoil. They found the coefficient of variation to be highest for the wide coarse pores (air capacity). The higher variability of the topsoil could be confirmed with the data from this study except for the Eckerkoppel soil for the abovementioned effect of small mean values and relatively high standard deviations. The second finding regarding the highest variation of the pore space at air capacity could be confirmed and rendered more precisely: The data from this study showed an increasing variance with increasing soil

moisture up to a water potential of 0.3 kPa which emphasizes the importance of the widest pores > 1000 μ m.

For the test field, this implies that in addition to the general pattern of gas distribution resulting from constructional features (6.3.3) the small scale variability of the soil pore space governs the further redistribution within the methane oxidation layer: It was shown that the magnitude of the driving gradients were of a higher importance for the resulting fluxes than the variability of the air-filled porosity. Still the soil moisture distribution and hence air-filled porosity is expected to influence the diffusive emission by the factor two (6.3.3). High macroporosity (> 1000 μ m) has a major influence on diffusion because even at a high water saturation pore space is available for diffusion and on advection because usually macropores are well connected and often vertical. This makes them especially important for advective transport. It was shown that the advective transport potential did not evolve a lot with increasing air-filled porosity but was almost fully established once the macropores were drained.

6.3.6 Applicability of the MOT

Hypothesis corresponding with this section: 3 e: Using a simple model, oxidation potential of methane oxidation systems can be predicted.

The predictions for the achievable oxidation rate using the methane oxidation tool (MOT) seemed promising to predict methane oxidation system performance. Predicted trends, for example the seasonality of the bulk field oxidation rate were also reflected by the actual measurements. However, the average load to the test field was lower than its predicted oxidation potential most of the time, rendering a comparison of observed and predicted rates impossible. From soil gas concentration measurements at the base of the test field it was known that gas distribution within the test field was heterogeneous, hence the average bulk load to the field did not represent the local load for each grid field. Therefore, the loads to the individual grid fields were calculated from emission and oxidation efficiency data. The resulting data set of grid-field related methane loads (base fluxes) was compared to the methane oxidation potential predicted from soil temperature, air-filled porosity and water tension. As already suggested by the distribution of soil gas concentrations this assessment showed that indeed on grid field scale the base fluxes were subject to significant spatial heterogeneity. Emissions from the test field occurred only in times where base fluxes exceeded the predicted oxidation potential of the test field (Figure 72), as for example in October 2012 where a oxidation potential of about 40 g CH₄ m⁻² d⁻¹ was predicted and the 90^{th} percentile of the base fluxes was at 150 g CH₄ m⁻² d⁻¹. The efficiency was down to 48 %. Soil temperature was at 14.9 °C and air-filled porosity was 26.2 % v/v. The comparison of base fluxes and oxidation rates on grid field scale did show the trend of decreasing oxidation efficiencies when the predicted factorized oxidation potential was exceeded. Still, this was not a clear relationship with the factorized oxidation potential acting as a threshold for the efficiency to decrease. The empirical approach of the model is not and was never meant to capture the variability of soil properties in detail. While the general trends are represented well the precision of the prediction for individual grid fields is defective. The variability of soil moisture that was shown to affect diffusive fluxes by the factor two (section 6.3.3) is not accounted for in the model as these data were not recorded with the required spatial resolution. If the diffusive ingress of oxygen is restricted due to reduced air-filled porosity (compaction, soil moisture), it can become the limiting factor for oxidation. Despite the fact that physical heterogeneities are not considered in the MOT the data suggest that the MOT factors derived from their empirically determined influence on methane oxidation (chapter 4.7) were suitable for application in large scale systems and that average soil data are suitable for average efficiency estimation. The MOT predictions for "high potential times", i.e. for dryer and warmer conditions could not be challenged because neither the load to the bulk test field nor the load to any individual grid field reached the predicted rate of 71 g CH₄ m⁻² d⁻¹ (September 14) for these times during the investigation period.

Are direct emissions addressed correctly in the MOT model?

In order to account for the fact of preferential pathways and hence hotspot formation, the MOT suggests a share of the methane load to bypass the methane oxidation system as direct emissions through cracks, fissures, animal burrows etc. These fluxes would then not be modulated by the methane oxidation process and should therefore show a similar composition than the landfill gas. The magnitude of this share is estimated depending on the cover. For final covers (> 100 cm, gas distribution layer, porosity > 20%), 10% are assumed (Gebert et al., 2011d). In this study, an annual average of 16% of the injected methane could not be oxidized in the test field. The test field porosity was about 20%. This is in accordance with the range proposed by the MOT. Bergamaschi et al. (1998) attributed 70% of the methane transport from a non-optimized landfill cover into the atmosphere to direct emissions. However, from the data in this study, no fixed share of direct emissions could be derived. Surface screenings of methane and carbon dioxide concentrations did show spots with a carbon dioxide- methane ratio similar to the supplied landfill gas, indicating the existence of direct emission pathways. Based on the fact that locations of direct emissions, characterized by a carbon dioxide - methane ratio similar to the landfill gas, were not permanent it was assumed that the share of direct emissions via bypasses is likely to be smaller than suggested by the MOT, confirming the conservative assumptions of the model. For this study it could not be shown to which extent direct emissions happened. Rachor (2012) and Röwer et al. (2016b) showed that surface concentration data cannot be used to calculate emissive fluxes. No flux data was acquired for the identified spots, making a quantification of the emission through these spots and hence the assessment of the share of direct emissions impossible. A part of the detected methane emissions are more likely explained by a sporadic overloading of the test field. Still, it is considered important to integrate direct emissions into the model. Further research should refine the estimations and maybe establishing an empiric relationship for the direct emission estimation.

6.4 Relating findings from laboratory and field data

The three parts of this study consider different aspects of the temporal and spatial pattern of gas transport through landfill cover soils. The influence of soil properties on gas transport were investigated as well as the effects of methane fluxes on soil properties. Effects of design features on the application of methane oxidation covers as mitigation technology were examined too.

(1) In the laboratory, the diffusivity and conductivity of differently textured soils (KA5: Slu, St2, Su2) under different conditions of water saturation (2 - 30 kPa) was determined, alongside with the heterogeneity of the permeability features covering a spatial scale of less than a square meter (chapter 5.1). (2) In the hotspot case study, the influence of a methane point source, channeling the landfill gas flux from the waste body to the soil cover, on the soil gas composition and the soil properties was explored on a small scale of one square meter on an old landfill. Hotspots can be considered an extreme situation or failure of a methane oxidation system (chapter 5.2). (3) The biocover test field monitoring was performed to explore the applicability of methane oxidation as an emission mitigation technology on a large scale. The smallest emission observation unit was 17 m² integrating all real point sources while still resolving the 1060 m² area of the test field sufficiently to derive general information on spatial aspects of emission and efficiency (chapter 5.3).

Hypothesis corresponding with this section: 3 d: In situ the advective transport is most dominant at high water saturations.

Based on the assumption that advective fluxes are more prone to cause emissions and the observation that under wet and cold autumn to spring conditions the highest emissions occurred, it was assumed that the share of advective transport was highest under these conditions. For the winter month lower carbon dioxide - methane ratios were found in surface screenings proposing low oxidation efficiencies at these points of measurement (see chapter 5.3.3.4). Up to 7.5% of the measurement points (18 out of 240 in Jan. 2014) had a carbon dioxide - methane ratio in the range of the landfill gas which is an indicator but not a proof for direct emission. The surface coverage of low ratios is in the same range as reported from Czepiel et al. (1996a) for hotspots on a landfill. From the laboratory data on diffusivity and permeability of the Wieringermeer soil it could be taken that diffusive transport increased with drying of the soil while the advective gas transport was approximately of the same height over the whole range of soil moisture (section 5.1.5). Diffusion depends mostly on available pore space while advection additionally depends on pore geometry (Kühne et al., 2012). If the soil is wet, both processes can take place only in the water free coarse pores. As shown in section 5.1.5 the occurrence of any pressure gradient as small as one Pascale resulted in fluxes comparably high as diffusive fluxes driven by a methane concentration gradient of 40%. If gas moves through the remaining pore space of a wet soil by advection the diffusive transport becomes irrelevant for the vertical transport. As the emission measurements integrated an area of 17 m², it could not be distinguished between direct emissions from point sources and other emissions. From the presented data it is still highly likely that the share of advective transport is highest in times of higher soil water saturation and that it contributes to the overall emission to a larger extent compared to dryer conditions with diffusive transport through the soil matrix. It has to be considered that in real application, the advective emissive gas flux will be limited not by restriction through the soil pore system but by the amount of gas produced within the landfill. In this study it was not considered to which extend the volume reduction during the methane oxidation process influenced the aeration of the soil. As three mol of gas are converted into one mol on oxidation negative pressure would build up. According to the findings of this study, it will equilibrate instantly drawing atmospheric air into the soil. The immediate equilibration of pressure gradients was also shown by Schack-Kirchner (2002). It is most likely that the equilibration takes place along preferential flow paths (chapter 6.2). This may contribute to the deep aeration necessary for sustaining the oxidation process in deeper soil layers that was shown for the gas distribution layer in this study (section 5.3.6). Allaire et al. (2008) suppose preferential flow to be crucial for live forms in the depth of the soil, especially for wet, frozen or compacted soils.

Why did a hotspot evolve on landfill K but not on Wieringermeer test field?

The heterogeneous spatial pattern of the soil gas composition and the methane surface concentration at the hotspot on the old landfill K was persistent in time (spatial variability) and oscillating in its intensity (temporal variability). The formation of the hotspot was attributed to the difference in pore space between the hotspot and the surrounding nonhotspot site (section 5.2.2.2). The intra-sample variability of landfill K hotspot topsoil material (sample US 6) was more homogeneous (coefficient of variation at 2 kPa: 0.08) than the intra-sample variability at Wieringermeer test field topsoil (coefficient of variation at 2 kPa: 0.25). The Wieringermeer biocover test field also showed a spatially heterogeneous pattern of oxidation and emission which was constant over time with changes of the magnitude (temporal heterogeneity) (section 5.3.5). Spatial heterogeneity of gas fluxes prevailed in spite of the fact that the test field was constructed with the goal to achieve homogeneous distribution of soil properties. Gas diffusivity and permeability measured in the laboratory on Wieringermeer soil samples showed a considerable variability of the parameters among the five samples taken at the same location, i.e. on the scale of a few decimeters, indicating small-scale variability of soil pore space geometry that was highest at high soil moisture contents (section 5.1.2 and 5.1.3). So both landfill covers, the old one that was covered with available soil material and the engineered system built with selected material were heterogeneous to a certain degree. At landfill K the locally elevated pore space in combination with the lack of a gas distribution system was probably the reason why the point source in the subsoil could evolve into a permanent hotspot that stabilized itself (chapter 6.2) while at Wieringermeer test field the load was mediated by the gas distribution layer (albeit not rendering it completely homogeneous). The spatial heterogeneity was effective on an even smaller scale than the one that was found on landfill K avoiding the permanent concentration of the gas flux to distinct pores while passing the methane oxidation layers.

7 Conclusions

While engineered methane oxidation systems have proved to achieve high removal efficiencies and rates (section 5.3.4), spatial and temporal heterogeneity of soil properties and methane fluxes is an element of such systems (section 5.3.5). A part of the heterogeneity was shown to stem from constructional features like the use of the capillary barrier as gas distribution and an insufficient gradient of gas permeability between the gas distribution layer and the methane oxidation layer (section 6.3.3). Another part of the heterogeneity is influencing the flux and concentration pattern as the gas passes the methane oxidation layer. This heterogeneity is mainly governed by small-scale differences in pore size distribution and moisture (section 6.1.2). Diffusive fluxes can be affected by soil moisture variability by a factor of about two in the material used in the Wieringermeer biocover test field (loamy sand; 6.3.3). The influence of the variation in concentration gradients driving the diffusive transport was found to be of higher influence than the soil moisture variability for the magnitude of the resulting gas fluxes (section 5.1.5). The most unpredictable process spatially as well as temporally, might be advective transport. It was shown that even small pressure gradients would cause advective fluxes that outperform diffusive transport by far (section 5.1.5). However, a high advective efflux can occur over an extended period only if enough landfill gas is delivered from the landfill waste material (section 6.1.2). This is usually not the case for landfills with gas generation rates considered suitable for passive aftercare. Yet, processes like barometric pressure fluctuations or soil gas volume reduction due to methane oxidation will cause advective fluxes that will equilibrate predominantly through coarse vertical pores (chapter 6.2). Albeit the effects were not considered in this study, using a simple modelling approach could estimate bulk system performance and provide adequate guidance for the expectable oxidation capacity of engineered systems (section 6.3.6).

From the results of the three work packages the following conclusions could be drawn.

Gas transport in soils at low water tensions

For landfill cover soils, the hotspot phenomenon has been described by many authors. Often hotspot emissions occur only or pronounced in winter conditions or at falling barometric pressure. It is likely that the driver of hotspot emissions is advection. They are the least predictable component of landfill gas emissions. The laboratory experiment performed in this study focused on the question of how diffusive and advective transport properties change at low water tensions. The main findings are:

- The advective flux induced by an even minor pressure gradient outperforms the diffusive transport if gas supply is not limiting.
- Advective transport properties are especially related to coarse pore and macropore structure. Advective transport will dominate over diffusion if pressure gradients occur.

• D_{eff} can vary due to spatial heterogeneity by a factor of about two already at a sampling scale of 100 cm³.

Interaction between Reduktosol soil formation and preferential flow

A hotspot site was observed on an old landfill. Persistent soil gas and surface concentration patterns were documented over half a year. Cracks or other preferential pathways can initiate *Reduktosol* formation and persist for several decades. Soil features were altered due to the presence of the microbial community and macrofauna that was probably attracted by its products. Central finding of this part of the study are:

- Hotspot sites can result from point sources in the subsoil.
- Exposure to high loads of methane alter and/or pronounce soil structure via the soil biota.
- Point sources of methane form extreme habitats for bacteria and other soil organisms.
- Biologic activity induced by high methane fluxes can alter soil chemical and soil physical properties.
- Hotspots are spatially stable over years, which makes them susceptible for remediation.

Spatial and temporal pattern of test field performance

In two and a half years of monitoring, the efficiency of and gas distribution in a large-scale methane oxidation cover test field (1060 m²) was assessed. A special focus was set to spatial and temporal variations of the system that to the author's knowledge was the largest existing test field at the time of the study. The following points could be concluded from the survey:

- Heterogeneity of diffusive and advective permeability within a few decimeters is too high to consider soil homogeneous in terms of gas migration, even in systems built with the goal of homogeneity.
- Methane oxidation efficiency was 84% on average over a period of two and a half years at loads to the cover of up to 42.5 g CH₄ m⁻² d⁻¹. Flaring is possible down to 10 m³ CH₄ h⁻¹ (7156 g CH₄ h⁻¹) with a methane concentration of at least 10%. Based on the assumption of a one hectare landfill, this would be 17 g CH₄ m⁻² d⁻¹, hence methane oxidation can be employed as mitigation technology long before flaring becomes impossible. As a result the change from active to passive aftercare can be accomplished while flaring would still be possible.
- 13.5 27.8% of the oxidation process occurred within the gas distribution layer (> 1 m b.s.), indicating a deep aeration of the cover.

- The capillary barrier coined the principal pattern of gas distribution, the compaction level and pore structure of the methane oxidation layer and topsoil influenced the distribution on a secondary level.
- Preferential upslope emissions were attributed to the moisture distribution within the capillary barrier. Hence, methane oxidation systems have to be designed with the asymmetric gas load in mind that resulted in upslope loads of up to three times of the average load.
- Gas diffusivity can vary by the factor of two over the area due to differences in soil moisture, adding to the spatial heterogeneity induced by other constructional features.
- Direct emissions through preferential pathways could not be separated from emissions due to partial oxidation. A pronounced seasonal dynamic was found with maxima under unfavorable wet and cold conditions and usually no or very low emissions under dry and warm conditions. Hence, direct emissions are associated with emissions form partial oxidation, both of which occur under unfavorable conditions.
- The employed model (MOT) seems promising for the prediction of a system's oxidation potential at given temperature and moisture conditions.

Summing up, it could be shown in this study that methane oxidation systems can be used in landfill aftercare with high effectivity. Still, at field scale local emissions may occur. Constructional details can influence the gas distribution significantly which has to be considered in the planning process. Additional spatial heterogeneity due to heterogeneous soil moisture pattern will be a feature of all landfill covers and should be considered in the planning process as well. Hotspots are usually associated with macropores forming preferential pathways. Especially advective gas fluxes along preferential pathways add a random element to the gas flux dynamics of a landfill cover soil. However, the importance of advective gas fluxes should decline with the age of the landfill and hence the declining load to its cover.

Publication list

Peer-reviewed publications

- **Geck**, C., Scharff, H., Pfeiffer, E.-M., Gebert, J., 2016. Validation of a simple model to predict the performance of methane oxidation systems, using field data from a large scale biocover test field. Waste management (New York, N.Y.) 56, 280–289. 10.1016/j.wasman.2016.06.006.
- Oonk, Hans; Koopmans, Jan; **Geck**, Christoph; Peters, Bas; van Bergen, Jan (2015): Methane emission reduction from storage of manure and digestate-slurry. In: *Journal of Integrative Environmental Sciences*, S. 1–17. DOI: 10.1080/1943815X.2015.1096796.
- Röwer, Inga Ute; Geck, Christoph; Gebert, Julia; Pfeiffer, Eva-Maria (2011): Spatial variability of soil gas concentration and methane oxidation capacity in landfill covers. In: *Waste Management* 31 (5), S. 926–934. DOI: 10.1016/j.wasman.2010.09.013.

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- **Geck**, C. (2011): Räumliche und zeitliche Variabilität von Methangehalten in der Abdeckschicht einer Altdeponie. Diplomarbeit. Universität Hamburg, Hamburg. Institut für Bodenkunde.
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- **Geck**, Christoph; Scharff, Heijo; Pfeiffer, E.-M.; Gebert, Julia (2015): Validation of a simple model to predict efficiencies of methane oxidation systems. In: *Proceeding Sardinia, Fivetenth International Waste Management and Landfill Symposium*.
- **Geck**, Christoph; Röwer, Inga Ute; Kleinschmidt, Volker; Scharff, Heijo; Gebert, Julia (2016): Design, validation and implementation of a novel accumulation chamber system for the quantification of CH4 and CO2 emissions from landfills. Technical report.

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Appendix 25 cm b.s; 13.06.2012-22.07.2013; n=9 . CH4 [% v/v] Gas probe ID 60 cm b.s; 13.06.2012-22.07.2013; n=9 CH, [% v/v]



Figure A - 1: Distribution of the methane concentration in the gas probes before reconstruction at $32.9 \text{ g m}^{-2} \text{ d}^{-1}$. The gas probes with the ID number one is upslope, number nine is downslope (Figure 6)). The letters indicate the column of the probes location. Letter A indicates the position at the outer border of the test field but still at the border of the catchment while the column with the letter F is situated four meters away from the inner border of the catchment.



Figure A - 2: Distribution of the methane concentration in the gas probes after reconstruction at 29.2 g m⁻² d⁻¹.



Figure A - 3: Distribution of the methane concentration in the gas probes after reconstruction at 13.5 g m⁻² d⁻¹.



Figure A - 4: Distribution of the methane concentration in the gas probes after reconstruction at $38.6 \text{ g m}^{-2} \text{ d}^{-1}$.



Figure A - 5: Carbon dioxide concentrations in gas probes.



Figure A - 6: Oxygen concentrations in gas probes.



Figure A - 7: Air pressure and temperature