Investigation of emissions from the AV Miljø Landfill

1. Gas quantity, quality and attenuation properties

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Publication date:
2007

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Scheutz, C., Fredenslund, A. M., Lemming, G., & Kjeldsen, P. (2007). Investigation of emissions from the AV Miljø Landfill: 1. Gas quantity, quality and attenuation properties. Kgs. Lyngby: Institute of Environment & Resources, Technical University of Denmark.

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Authors: Scheutz, C., Fredenslund, A.M., Lemming, G., Kjeldsen, P.
Fonts: Times New Roman, Verdana, Arial
Graphics: Authors and Torben Dolin
Cover: Julie Camilla Middleton
ISBN: 978-87-91855-36-8

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March 2007

Foreword

This is the first report for the collaboration project between AV Miljø and Institute of Environment & Resources. The aim of the project was to evaluate the present and future emissions from the AV Miljø Landfill both with respect to gas and leachate. This report has been carried out in the period March to December 2006. We would like to thank Jonas Nedenskov, AV Miljø for his support in the project.

List of content

Dansk sammendrag

Institut for Miljø & Ressourcer DTU og AV Miljø indledte i 2004 et samarbejdsprojekt ”Udvikling af deponeringsanlægget AV-Miljø – Et dynamisk samarbejde mellem AV-Miljø og Miljø & Ressourcer DTU”. Samarbejdsprojektet har indbefattet to delprojekter omhandlende hhv. gasproduktion og -emission samt perkolatdannelse.

AV Miljø affaldsdeponiet modtager affald med et lavt indhold af organisk materiale. Erfaringerne med gassammensætning, produktion og emission fra sådanne affaldsdepoter er ret begrænsede. Et væsentligt tværgående element har været affaldstypen, shredderaffald, som modtages på AV Miljø i store mængder, og hvor viden i form af karakterisering, gas- og perkolatdannelse i dag ikke er til stede.

Nærværende rapport omhandler første del af projektet vedrørende gasproduktion og -emission. Projektet har haft til formål:

- at undersøge gassammensætning ved udtagning af gasprøver fra udvalgte deponienheder med henblik på analyse for hovedkomponeterne metan, kvælstof, kuldioxid samt udvalgte sporgasser
- at bestemme gasproduktionen ved hjælp af eksisterende gas produktionsmodeller samt ved laboratorieforsøg
- at måle emissionen af metan og sporgasemission fra udvalgte deponienheder
- at undersøge potentialet for nedbrydning af metan og sporstoffer i udvalgte deponienheder vha. gas profilmålinger samt nedbrydningsforsøg udført i laboratoriet
- at bestemme den totale gasemission fra AV Miljø vha. storskala sporstofforsøg

Affaldsdeponiet AV Miljø er beliggende på inddæmmet land i den nordlige del af Køge Bugt. Under affaldsdeponiet findes et oprindeligt lag af moræneler med en tykkelse på 7 meter. Herunder findes vandførende kalklag. AV Miljø deponiet er inddelt i flere forskellige celler med varierende affaldssammensætning. De tre udvalgte affaldsceller indeholder forskelligt affald: Celle 1.3 indeholder blandet affald med en overvægt af industriaffald og forbrændingsegnet affald.. Celle 2.2.2 har primært modtaget industriaffald og sand fra sandfang. Celle 1.5.1 har langt overvejende modtaget restaffald fra frakmenteringsanlæg for biler og andre metalholdige affaldselementer, i daglig tale kaldet shredder affald. Under frakmenteringsaffaldet er deponeret et lag af slamaske.

Målinger af gassammensætningen i de tre udvalgte celler viste, at der i alle tre celler dannes metangas. Gassammensætningen varierer dog mellem cellerne. For eksempel sås gassen dannet i celle 1.3 med blandet brændbart affald at bestå af hovedsageligt CH_4 (70%) and CO_2 (29%), mens gassen prøvetaget fra celle 1.5.1 med shredderaffald bestod af CH_4 (27%) and N_2 (71%) og kun spor af CO_2. De højeste koncentrationer af halogenerede flygtige organiske stoffer (VOCs) blev målt i cellen med shredderaffald (op til 27 $\mu g\ L^{-1}$), mens de højeste koncentrationer af aromatiske forbindelser (op til 50 $\mu g\ L^{-1}$ benzene og toluene) blev målt i cellen med ikke-brandbart affald. Tilstedeværelse af HCFC-21 og HCFC-31 indikerede, at der foregår anaerob dechlorering af CFC-11.

Gasprofiler samt laboratorieforsøg med materiale fra cellen med shredderaffald viste, at der foregår en væsentlig metanoxidation i den øverste aerobe zone på ca. 40 cm af shredderaffaldet. VOC-gasprofiler viste, at der i den anaerobe del af afaldet foregår anerob dechlorering af både CFC-11 og CFC-12, idet der ses nedbrydningsprodukter som HCFC-21, HCFC-31 and HCFC-22. Dette blev understøttet af resultaterne fra de udførte batchforsøg. Gasprofiler viste dog også, at der sker en væstenlig oxidation at de dannede nedbrydingsprodukter i den øvre oxidative zone, hvor der også ses methanoxidation. Gasprofilerne fra afdækningslagene på celle 1.3 og celle 2.2.2 viste en gassammensætning lignende atmosfærisk luft, hvilket indikerer at gas dannet i de to celler ikke emitteres gennem dæklagene enten pga. deres lave permeabilitet eller, fordi gassen oxideres i den nedre del af dæklagene. Oxidation i den nedre del af dæklagene er sandsynlig, da laboratorieforsøg viste en tendens til stigende oxidationsrate med dybden.

For at undersøge metanemissionen gennem overfladen på de tre celler blev der indledningsvis udført en række screeninger, hvor metankoncentrationen i luften lige over overfladen blev systematisk målt. Resultaterne viste, at overfladeemissionen fra alle tre celler er minimal og primært sker langs kanten af cellerne eller på skråninger. Vha. fluxkammermålinger blev overfladeemisssionen fra celle 1.5.1 med shredderaffald bestemt til mellem -1,9 and 78 g CH_4 m^{-2} d^{-1}, de højeste emissioner kun blev målt i enkelte hotspots. Emissionen af flygtige organiske forbindelser som CFC-11, HCFC-21, and HCFC-31 blev målt til mellem 0,002 og 0,006 g m^{-2} d^{-1}. Emissionen af metan og VOC fra de to afdækkede celler 1.3 og 2.2.2 var under detektionsgrænsen (for metan: 0,1 g CH_4 m^{-2} d^{-1}).

En indledende screening af metankoncentrationer tydede på, at der sker en væsentlig emission fra perkolatsystemet via perkolatbrøndene. Metanemissionen fra perkolatbrønde blev derefter målt vha. af en sporstofmetode. Den samlede emission fra hele perkolatsystemet blev fundet til 211 kg CH_4 d^{-1}.

Metanproduktionsrater og metanpotentialer for de tre testceller blev beregnet ud fra to modeller: GasSim og Afvalzorg Multi Phase Model. Metanproduktioner beregnet for 2006 var henholdsvis 86 til 100 kg CH_4 d^{-1} (celle 1.3), 27 til 83 kg CH_4 d^{-1} (celle 1.5.1) og 63 til 65 kg CH_4 d^{-1} (celle 2.2.2). Beregnede metanpotentialer var 1.210.000 kg CH_4 (celle 1.3), 394.000 kg CH_4 (celle 1.5.1) og 487.000 kg CH_4 (celle 2.2.2). Metanpotentialer var defineret som metan produktion fra start af deponering til 30 år efter afslutning af deponering i hver celle.

Metanproduktionsrater var desuden fundet eksperimentelt for de tre test celler, hvor produktion af metan var målt på affaldsprøver opbevaret i tætte stålbeholdere over 140 dage. Metanproduktioner omregnet til totale produktioner for hver celle blev fundet til 190 kg CH_4 d^{-1} (celle 1.3), 35 kg CH_4 d^{-1} (celle 1.5.1) og 21 kg CH_4 d^{-1} (celle 2.2.2). Der blev observeret VOC i disse prøver, men det var ikke muligt at udregne frigivelsesrater ved brug af disse data.

Frigivelse af VOC blev målt for prøver af shredderaffald udtaget fra celle 1.5.1. Raterne blev bestemt ved at måle koncentrationer af VOC 14 gange i løbet af 140 timer efter at stålbeholdere indeholdende 75 til 88 kg shredderaffald blev skyllet med ilt, for at sikre aerobe forhold i affaldet. Under forsøget blev luften i de forseglede beholdere kontinuert pumpet gennem affaldet for at sikre, at der ikke skete anaerob nedbrydning af frigivet VOC i dele af affaldsmassen. Der blev observeret frigivelse af

CFC-11, HCFC-21 og HCFC-31 ved dette forsøg, og frigivelsesrater blev målt til mellem 0,005 og 0,78 μg VOC kg affald^{-1} d^{-1}. Frigivelse af HCFC-21 og HCFC-31, hvilke er nedbrydningsprodukter af CFC-11, skyldtes sandsynligvis desorption, da disse stoffer måltes i relativt høje koncentrationer i gasprøver udtaget i celle 1.5.1.

Ved håndsortering af prøver af shredderaffald brugt til måling af VOC frigivelsesrater, blev indholdet af polyurethan (PUR) skum fundet. Det totale indhold af CFC-11 i PUR skum fra prøverne blev målt. Ved at sammenholde indhold af CFC-11 i PUR skum for hver af prøverne af shredderaffald med de observerede frigivelsesrater, blev det fundet, at mellem 0,070 % og 0,095 % af det totale indhold af CFC-11 blev frigivet per dag for prøverne.

AV Miljøs samlede metan emission måltes med sporstofmetode. Et sporstof blev (lattergas) kontinuerligt frigivet fra anlægget mens der blev målt metan og sporstof koncentrationer nedstrøms vindretningen. Ved at sammenholde koncentrationer af metan og sporstof målt ved brug af FTIR infrarød spektroskopi, med målte baggrundskoncentrationer, måltes anlæggets samlede metan emission til 33,1 ± 7,8 kg CH_4 h^{-1} (eller 793,3 ± 188 kg CH_4 d^{-1}). Cirka 20 % af emissionen kom fra anlæggets østlige del, 44 % fra den midterste del og de resterende 36 % fra anlæggets vestlige del.

Metanbalancer for de tre testceller viste, at en betydelig emission af metan (mellem 15 og 67 %) sker gennem perkolatdrænsystemet for cellerne 1.3 og 2.2.2, hvilket skyldes afdækning med en relativt lav permeabel jordtype. For celle 1.5.1 indeholdende shredderaffald var emissionen gennem perkolatdrænsystemet lav, grundet en høj permeabilitet af affaldet, og at cellen ikke var afdækket. Her blev der til gengæld målt emission af metan gennem overfladen af cellen adskillige steder. Produceret metan, der ikke emitteredes gennem perkolatdrænsystemet eller overfladen kunne potentielt være oxideret, da den målte oxidationskapacitet oversteg emissionsraten.

Den totale metanemission fra AV Miljø blev målt til 793 ± 188 kg CH_4 d^{-1}, mens den totale emission gennem perkolatdrænsystemet blev målt til 211 kg CH_4 d^{-1}. Dette viser, at ¼ af gasemissionen fra anlægget sker gennem perkolatdrænsystemet, som gør dette til en meget væsentlig kilde til gasemission. Emissionen gennem andre veje er mere usikre, men det vurderes sandsynligt, at en væsentlig emission fra ikke afdækkede celler, hvor der foregår deponering eller udgravning af midlertidigt deponeret affald finder sted. En væsentlig emission fra horisontale perkolatdrænrør placeret i tomme celler er ligeledes sandsynlig.

Summary

Emission and attenuation of methane and selected volatile organic compounds was studied at AV Miljø landfill. The objectives of this study were determination of composition of landfill gas in different types of disposal units, quantification of gas emissions from selected locations, study on methane oxidation in temporary soil covers, measurement of the total methane emission from AV Miljø, improvement of the environmental assessment at AV Miljø regarding gaseous emissions.

Measurement of landfill gas composition in the waste mass showed that landfill gas was produced in all study disposal cells at the site. The composition of the gas varied highly comparing samples from the three cells. The gas sampled from the cell containing mixed combustible waste consisted of mainly CH_4 (70%) and CO_2 (29%), whereas gas sampled from the cell containing shredder waste mainly consisted of CH_4 (27%) and N_2 (71%) and only traces of CO_2. All selected volatile organic compounds (VOCs) were detected. The highest concentrations of halogenated organic compounds were observed in the shredder waste (up to 27 $\mu g\ L^{-1}$), whereas the highest concentrations of aromatic compounds were seen in the cell with non-combustible waste (up to 50 $\mu g\ L^{-1}$). Presence of HCFC-21 and HCFC-31 indicated that anaerobic degradation of CFC-11 was occurring.

Gas profiles and incubation experiments from the cell with shredder waste showed an oxidation zone of 40 cm below the surface with significant methane oxidation. The VOC gas profiles showed that anaerobic dechlorination of both CFC-11 and CFC-12 led to generation of degradation products like HCFC-21, HCFC-31 and HCFC-22. Anaerobic dechlorination of CFC-11 was verified in batch incubation experiments with shredder waste. However, gas profiles of the lower chlorinated compounds like HCFC-21, HCFC-31 and HCFC-22 suggested oxidation in the upper oxic zone of the shredder waste. The gas profiles from cell 1.3 and 2.2.2 containing mixed waste showed a similar composition to atmospheric air indicating that landfill gas generated in the two cells is not emitted through the cover or is being oxidized in the lower part of the cover. Methane oxidation in the lower part of the covers is possible as methane incubation experiments showed a tendency to increasing oxidation rates with increasing cover depth.

Methane emission through the soil cover at the cells was screened by measuring concentration of methane near the soil surface on three study cells on a grid of measurement locations. Results suggested that the emission through the soil cover was minimal, and mostly occurring on edges and slopes of the soil cover. Using flux chambers, rates of methane emissions on the uncovered shredder cell where measured between -1.9 and 78 g $CH_4\ m^{-2}\ d^{-1}$. Flux rates of the volatile organic compounds CFC-11, HCFC-21, and HCFC-31 where measured at between 0.002 and 0.006 g $m^{-2}\ d^{-1}$. Methane flux measurements on the two covered cells 1.3 and 2.2.2 were all below detection limit (0.1 g $CH_4\ m^{-2}\ d^{-1}$).

Methane emission through the leachate wells was done by use of a continuous tracer release method. The emission rate through the entire leachate collection system at AV Miljø was found to be 211 kg $CH_4\ d^{-1}$.

Methane production and methane gas potential of the study cells were determined through use of the models GasSim model and Afvalzorg Multiphase Model. The calculated production rates for 2006 were 86 to 109 kg $CH_4\ d^{-1}$ (cell 1.3), 27 to 83 kg $CH_4\ d^{-1}$ (cell 1.5.1) and 63 to 65 kg $CH_4\ d^{-1}$ (cell 2.2.2). The calculated methane gas

potentials set to be the production from start of deposit to 30 years after end were 1,210,000 kg CH_4 (cell 1.3), 394,000 kg CH_4 (cell 1.5.1) and 487,000 kg CH_4 (cell 2.2.2).

Methane production rates were also determined experimentally using waste sampled at the cells 1.3, 1.5.1 and 2.2.2. Methane production of the sampled waste stored in closed steel drums was observed over a period of 140 days. The observed methane production rates were 190 kg CH_4 d^{-1} (cell 1.3), 35 kg CH_4 d^{-1} (cell 1.5.1) and 21 kg CH_4 d^{-1} (cell 2.2.2). VOCs were observed released from the waste materials, but it was not possible to calculate release rates.

Release rates and content of VOCs in shredder waste sampled from cell 1.5.1 were determined. Release rates were determined by keeping waste material (75 to 88 kg waste samples) aerobic in closed steel drums, which were flushed with O_2 and fitted with a system to circulate air through the waste material. 14 measurements of content of VOCs in the headspace of the steel drums over 140 hours showed steady continuous increasing concentrations of the VOCs CFC-11, HCFC-21 and HCFC-31. Release rates between 0.005 and 0.78 μg VOC kg $waste^{-1}$ d^{-1} were observed.

Contents of PUR foam and size distributions of PUR foam particles were established through hand sorting of the shredder waste used to measure release rates of VOCs. Contents of VOCs in the PUR foam were determined using a heating method to drive out VOCs from foam samples into the headspace of glass bottles which were analysed for VOCs. Normalizing the release rates measured of CFC-11 to the content of CFC-11 found in PUR foam in the shredder waste, it was established that between 0.07 and 0.095% of CFC-11 was released per day.

The whole methane emission from the disposal site was measured using a tracer technique, combining controlled tracer gas release (N_2O) from the landfill with time-resolved concentration measurements downwind the landfill using FTIR absorption spectroscopy. Traversing the plume on the road just north of the site showed methane concentrations up to 300 ppb above background level. The whole methane emission from the disposal site was measured to be 33 ± 7.8 kg CH_4 h^{-1} (or 793 ± 188 kg CH_4 d^{-1}). Dividing the methane and tracer plume into three parts, it was estimated that about 20 % of the methane emission originated from part A (east), 44 % from part B (mid) and the remaining 36 % from part C (west).

Setting up total methane mass balances from three individual cells showed that a significant part (between 15% to 67%) of the methane generated in cell 1.3 and 2.2.2 is emitted through leachate wells, as a result of the relatively impermeable covers in place at these two cells preventing gas vertical migration. At cell 1.5.1 the methane emission through the leachate system is low due to the high permeability of the shredder waste. Instead the gas is emitted through the waste resulting in some hotspot observations on the shredder surface with higher emission rates. The remaining gas that is not emitted through surfaces or the leachate collection system could potentially be oxidized as the measured oxidation capacity exceeds the emission rate.

The whole methane emission was from the disposal site was found to be 793 ± 188 kg CH_4 d^{-1}. The total emission rate through the leachate collection system at AV Miljø was found to be 211 kg CH_4 d^{-1}. This show that approximately ¼ of the emitted gas is emitted through the leachate collections system making the leachate collection system an important source controlling the overall gas migration from the site. The emission pathway for the remaining part of the gas is more uncertain, but emission from open cells where waste is being disposed of or being excavated for incineration, or from horizontal leachate drainage pipes placed in permeable gravel layers in the bottom of empty cells is likely.

1. Introduction and objective

The Institute of Environment & Resources (E&R) at the Technical University of Denmark and the waste disposal site AV Miljø started a partnership to investigate certain environmental impacts from disposal of different waste types at AV Miljø. The aims of this collaboration were:

- To examine gas emissions from AV Miljø
- To analyze the leachate quality from deposited waste
- To establish a large scale leachate testing facility, to asses leachate quality from incoming waste

This report describes methods and results from the first subject in the list regarding gaseous emissions. The following tasks were planned for in the original project proposal and carried out:

- Determination of composition of landfill gas in different types of disposal units
- Quantification of gas emissions from selected locations
- Study on methane oxidation in temporary soil covers
- Measurement of the total methane emission from AV Miljø
- Improvement of the environmental assessment at AV Miljø regarding gaseous emissions

Not listed in the project proposal, but performed in agreement with the management at AV Miljø, some additional related studies were performed. A study of degradability of selected volatile organic compounds (VOCs) in a batch experiment, using sampled cover soil and shredder waste was carried out under both aerobic and anaerobic conditions. A large scale batch experiment using sampled waste was performed to study methane production relative to waste mass. Of special interest was the emission from disposal units containing shredder waste, of which little is known regarding formation of landfill gas, and release of trace gasses such as VOCs. The large scale batch experimental setup was reused to measure content, release rates and attenuation of selected VOCs from this waste fraction.

Using two gas generation models, landfill gas generation was estimated for three disposal cells at AV Miljø containing three types of waste. The output of these models was produced in amount of landfill gas generated per year over a time frame of several decades. Methane potentials of different waste types at AV Miljø were also calculated using these models.

A method developed at E&R to determine methane potential of municipal solid waste, was applied in an effort to determine methane potentials of different waste types sampled at AV Miljø. This method involves adding crushed waste sample to an active inoculum from a biogas plant.

2. Site description

AV Miljø is a modern waste disposal site situated in Avedøre Holme, approximately 10 km south of Copenhagen, Denmark. The disposal site was established in 1989 and has a total disposal capacity of 2 million m^3. The landfill receives waste from approximately 1.2 million people and 80,000 larger and smaller enterprises. It is owned by the waste management companies I/S Vestforbrænding and I/S Amagerforbrænding, which in turn are owned by municipalities in the Copenhagen metropolitan area and northern Zealand.

AV Miljø was established on land reclaimed from Køge Bugt for the purpose of creating the waste disposal site. It is constructed on the original clay with no installed bottom liner. Contamination of ground water with leachate from the landfill is avoided by pumping away water collected in drainage pipes installed in a layer of sand between the waste and underlying clay. Since the drainage layer is situated below sea level, the vicinity of the sea (see figure 2.1) causes a net inflow of saline water into the site creating a hydraulic barrier preventing migrating of leachate from the site to the surroundings. The flow of water into the site through the bottom and the sides of the site is relatively low due to the low permeability of the clay.

Figure 2.1.Arial photograph of AV Miljø and its' neighbors Køge Bugt, Avedøreværket (a power plant), Avedøre Spildevandscenter (a waste water treatment facility), and various trade, manufacturing and transport companies.

The landfill is divided into disposal cells of varying size. When waste is received, it is weighed, and assigned to one of these cells. Weighing also takes place when transporting waste away from the site, or from one disposal cell to another. This has been done since the site was taken into use. Through the weigh-in records, an inventory on how much waste divided into waste types is available for each disposal cell. Figure 2.2 shows the layout of disposal cells.

Figure 2.2.Map of disposal cells at AV Miljø.

Leachate is as mentioned previously collected in the drainage pipes, which are situated in a layer of sand between the deposited waste and underlying clay. The network of drainage pipes covers all area intended for waste disposal. Figure 2.3 shows a section of the leachate collection system (cells 2.2.2 and 2.1.4).

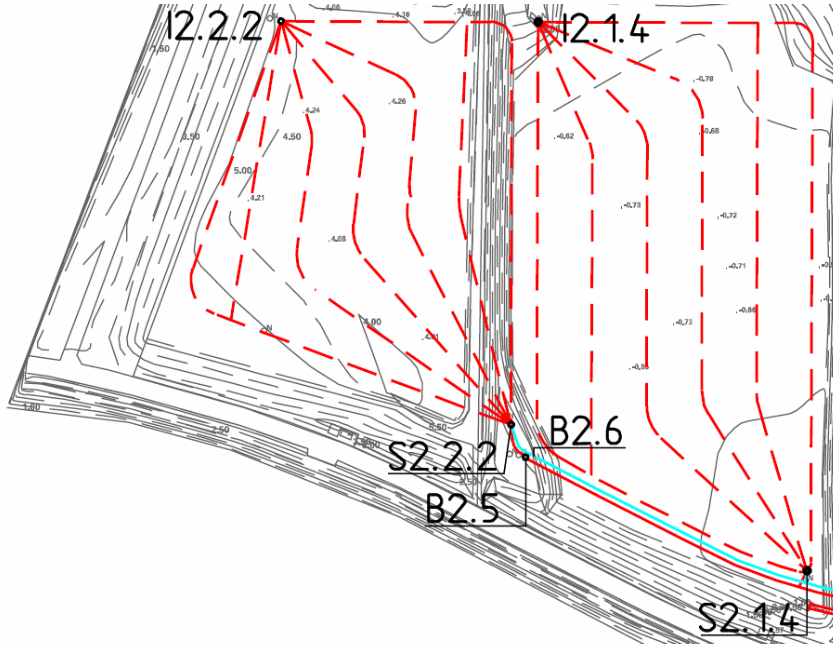

Figure 2.3. Section of the leachate collection system. Red dotted lines signify drainage pipes, and red solid lines signify transport pipes. Black dots represent inspection- and collection wells.

At each cell the network of drainage pipes are connected at two points. At these points so-called inspection wells and collection wells provide access to the leachate collection pipes. The inspection wells (called I (+ cell number)) are situated at the highest elevation of the drainage pipes, whereas the collection wells (called S (+ cell number)) are situated at the lowest point. In figure 2.3 two inspection wells are shown: I2.2.2 and I2.1.4. Water collected in the drainage pipes flows toward the collection wells (S2.2.2 and S2.1.4 in figure 2.3) from where water flows via transport pipes toward one of two underground pumping stations. Between the collection wells and the pumping stations there are other, similar wells. In figure 2.3 two of these are shown (B2.5 and B2.6). In all there are 74 leachate wells, which are concrete cylinders of circa 1.5 meters of diameter. In Appendix A, a technical map of the entire leachate collection system is shown.

Finally covering is done with a 20 cm layer of root blocking gravel and 100 cm of soil above the gravel layer. There is no gas collection system installed at AV Miljø.

The site both receives waste for final disposal as well as waste for temporary storage. The main waste type temporarily stored at AV Miljø is combustible waste, which is stored at the site before being utilized for energy production at waste incineration facilities. Main waste types finally disposed of at AV Miljø are: shredder waste, asbestos, street sweepings, contaminated soil not suitable for remediation, ashes from sludge incineration, slags, and fly ash. Various types of industrial waste, which are not recyclable or suitable for incineration, are landfilled. Disposal of fly ash ceased in 1999. Municipal solid waste is not landfilled at the site. From 1989, when AV Miljø was established, through 2005 a total of 2,406,010 tons of waste was received at AV Miljø, whereof 1,070,881 tons were landfilled.

Three disposal cells were selected, which were the focus of most of the activities of this project. Table 2.1 describes the cells. The three cells were filled to capacity. Only cell 1.3 and cell 2.2.2 were covered. The cover on cell 1.3 and cell 2.2.2 consisted of app. 100 cm clayey material on top of 20 cm coarse gravel. Only on cell 1.3 a final layer of top soil was applied.

Table 2.1. Description of the cells 1.3, 1.5.1, and 2.2.2.

Cell	Cell area (m^2)	Waste amount (tons)	Active period	Main waste types	Final top covering
1.3	24,000	94,000	1997-2001	• Industrial waste • Combustible waste • Construction waste	1997-2001
1.5.1	7,200	47, 000	1990-2000	• Shredder waste • Ash from sludge incineration*	
2.2.2	10,500	41,000	1992–2000 (Main period: 1998-2000)	• Industrial waste • Sand from sand traps	2003 (20 cm of top soil lacking)

* At time of reporting

* The bottom 30 cm of cell 1.5.1 consists of ash from sludge incineration, whereas the remaining volume consists of shredder waste

Figure 2.4 shows locations of gas probes for sampling of landfill gas, flux chambers to measure gas surface emissions etc. which have been installed during this project.

The deep gas probes where used to sample gas from the waste mass to determine landfill gas composition. The shallow gas probes were sets of six probes in different lengths at each marked location, from where gas was sampled to study attenuation processes in the near surface of the three disposal cells. Cell 1.5.1 was equipped with five permanently installed flux chambers to measure emission of gas through the surface. Two compost biofilters where installed at cell 2.2.2, to study the attenuation of methane in compost at a high load. The “grid points” shown in figure 2.4 are locations for screening of methane concentrations near the surface of the cells.

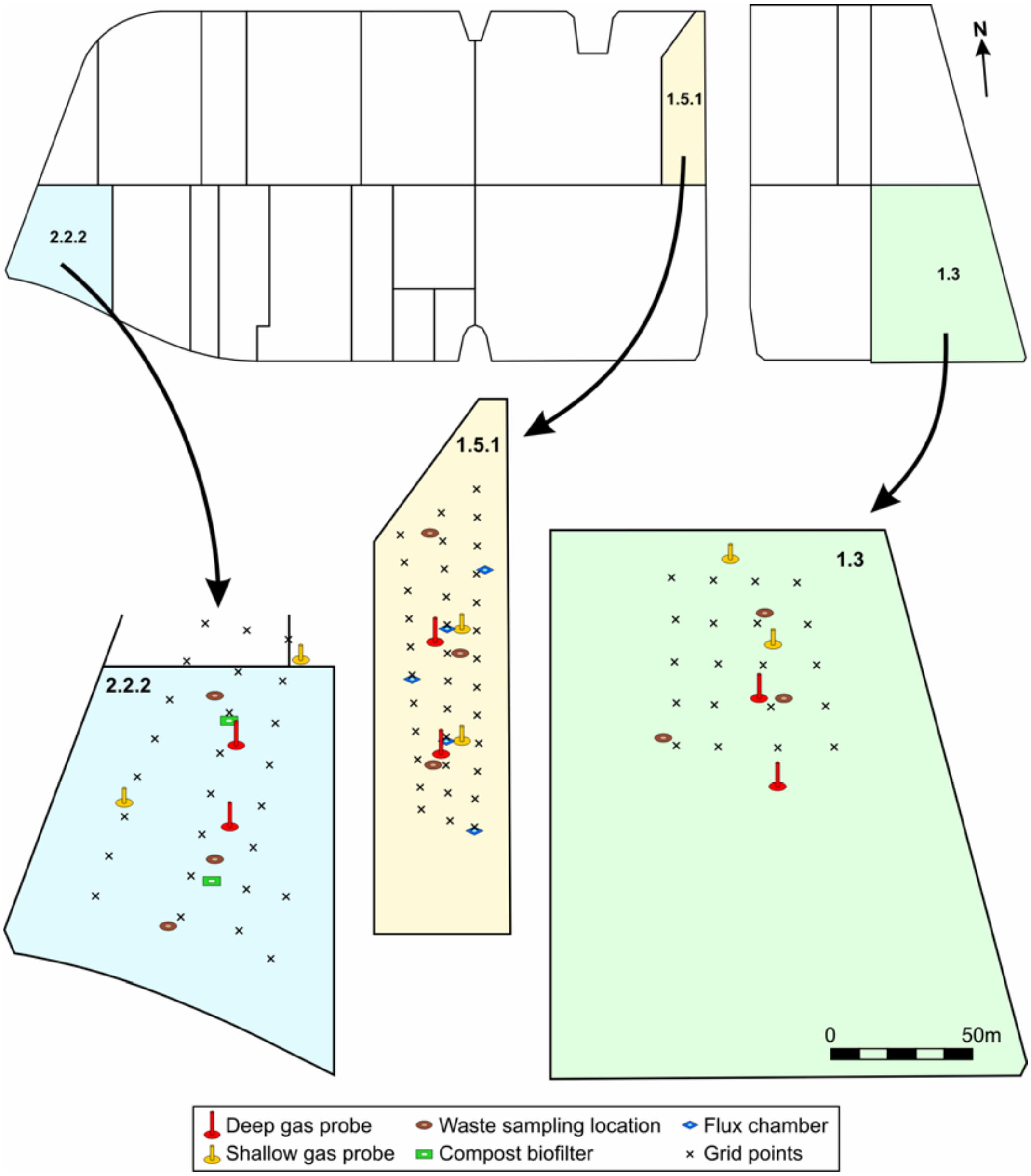

Figure 2.4. Placement of gas probes, flux chambers, compost biofilters, methane screening grid points and locations of sampling of waste.

3. Landfill gas composition

Objective

AV-Miljø mainly receives non-combustible waste, i.e., waste with low organic content such as shredder waste, asbestos waste, contaminated soils, construction waste, street cleaning residues, slag, air-pollution-control ashes, and fly ashes from waste incineration. Due to a low organic content of these waste fractions very little gas generation is expected and therefore gas collection systems are often not considered necessary to install in landfills receiving these waste types. However, currently very little is known concerning the gas generation and composition in disposal sites receiving these non-combustible waste fractions, where gas generation and composition is expected to be a result of chemical processes rather than biological processes. An objective of the project was to determine the gas composition in three disposal cells at AV Miljø containing mixed combustible waste, shredder waste, and industrial waste.

Methodology

Installation of deep gas probes for analysis of the landfill gas composition

In order to analyze the composition of the gas generated within the three waste cells two deep gas probes were installed in the centre of the cells. At the cells with shredder waste (cell 1.5.1) each probe had two individual screens ranging from 2-3 m and 4-5 m below the surface. The gas probes used at the two other cells had only one 15 cm screen and were all inserted to a depth of app. 2 m below the surface. Placement of deep gas probes are shown in figure 2.4 in section 2.

Prior to gas sampling the probes were purged corresponding to three times the internal volume of the probes. Gas samples were redrawn through a gas tight fitting equipped with a septum using a syringe and injected into vacuumed sampling vials. Gas samples were collected 14 times approximately once a month between February 2005 and June 2006.

Gas analysis

Analysis of the VOCs was performed by gas chromatography (GC) on a Hewlett Packard 6890 gas chromatograph coupled with a Hewlett Packard 5973 mass spectrometer. The gas samples were injected manually as direct on-column injections on a CarbonPlot column (30m×0.32mm×1.50µm) with helium as carrier gas. All compounds were analyzed using the following temperature program: an initial temperature of 60°C (2 min hold), temperature ramp of 40°C/min until reaching 100°C (3 min hold), temperature ramp of 30°C/min until reaching 210°C (1 min hold), temperature ramp of 45°C/min until reaching a final temperature of 300°C (2.8 min hold). The carrier gas column flow was set at 1.9 ml/min, and a sample split of 1:3 was used. The gas chromatograph was operated in a SIM-mode. Injection volume of samples varied between 50 to 200 µL throughout the project period, and was done using VICI Precision Sampling Inc Pressure Lock gas syringes. Concentrations of the target compounds were calibrated by injection of gas standards (5 concentration levels) and constructing a standard curve. Calibration standards were made by adding a specific volume of a saturated pure gas at atmospheric pressure to a known volume of air. The standard curves were linear throughout the concentration range. Standard curves were made for each day of measurement. Table 3.1 shows the lists of VOCs analyzed for in the study.

The main gas components (CH_4, CO_2, O_2, and N_2) were analyzed on a Chrompack Micro GC CP-2002P gas chromatograph equipped with a thermal conductivity detector and two columns. Oxygen and nitrogen were quantified on a 4 m long Molsieve 5A column and methane and carbon dioxide on a 10 m long Poraplot Q column. Carrier gas was helium, and the column temperature was 40°C. Gas standards produced by MicroLab, Aarhus, Denmark ranging from 0.02 to 50 % v/v were used for calibration.

Methane in the low concentration range was analyzed using a portable Photovac MicroFID-gas analyzer. Specially produced gas mixtures were used for calibration (500 ppm) produced by Air Liquide, Calgaz, Cheshire, UK). The detection limit was 0.5 ppm.

Results

The average gas composition in three different waste cells is shown in table 3.1. The gas generated in the three individual waste cells showed differences in gas composition. The gas composition in waste cell 1.3 containing combustible waste consisted of almost 70% methane and 30% carbon dioxide resembling the composition of landfill gas often seen in municipal solid waste (MSW). The gas generated in the two other cells 1.5.1 and 2.2.2 also contained methane (27-64%) indicating that methanogenesis was occurring, but only low concentrations of carbon dioxide (<8%). This was most significant for cell 1.5.1 containing shredder waste, which showed a gas composition of 27% CH_4, 71% N_2, and only traces of CO_2 (Table 3.1). During anaerobic fermentation of organic material CO_2 is always formed together with CH_4. The lack of CO_2 in cell 1.5.1 and 2.2.2 in comparison with cell 1.3 could be due to dissolution of CO_2 in infiltrating water, precipitation of different carbonates or microbial methanogenesis by hydrogenophilic bacteria in combination with a low gas generation rate. Metals remaining in the shredder waste may corrode under anaerobic conditions resulting in hydrogen production. The hydrogen produced can be used for microbial methanogenesis (generation of CH_4) by hydrogenophilic bacteria (Belay and Daniels, 1990; Lorowitz et al., 1992).

Overall the gas analyses of the main components indicate that landfill gas containing methane is produced in all three cells investigated in this study.

In addition to the main components selected trace gasses were analyzed. VOCs were measured in concentrations up to 50 $\mu g\ L^{-1}$. In general the highest concentrations were seen in cell 1.5.1 containing shredder waste. An exception was the toluene where relatively high concentrations were found in all three waste cells. The higher level of halogenated VOCs in cell 1.5.1 is most likely a result of the waste composition consisting of shredded white goods like refrigerators, dishwashers etc. and shredded automobiles. Of the VOCs detected and quantified in the gas samples from cell 1.5.1 HCFC-21 and HCFC-31 came out in relatively high concentrations (up to 32 $\mu g\ L^{-1}$). CFC-11 is known to undergo sequential dechlorination to HCFC-21 and HCFC-31 under anaerobic conditions (Deipser and Stegmann, 1997; Ejlertson et al., 1996). The presence of HCFC-21 and HCFC-31 in landfill gas thus indicates that anaerobic degradation of CFC-11 is occurring since neither of these compounds have been produced for industrial applications. CFC-11 has been used as blowing agent in insulation foam in home appliances. Under anaerobic conditions the degradation rate of halogenated organic compounds decreases with decreasing number of halogen substituents (Vogel et al., 1987). Hence, HCFC-31, HFC-41, HCFC-22, and HFC-32 may accumulate during anaerobic dechlorination of CFC-11 and CFC-12. Anaerobic defluorination of HFC-32 and HFC-41 is probably unlikely due to the high bond energy between carbon and fluoride making these compounds very stable under anaerobic conditions (Key et al., 1997). The landfill gas samples only contained traces of CFC-12 and its corresponding anaerobic degradation products (<1 $\mu g\ L^{-1}$). CFC-12 has been used as coolants in refrigerators and freezers. In Denmark, CFC-12 in the refrigerant circuit is tapped of before shredding and disposal, and low concentration of CFC-12 is therefore expected. However, elevated concentrations of HCFC-22 (12 $\mu g\ L^{-1}$) were observed in cell 2.2.2. This could be due to dechlorination of CFC-12 or due to disposal of HCFC-containing waste materials. For the other halocarbons very low concentrations were obtained (<2 $\mu g\ L^{-1}$), only HFC-134a showed elevated concentrations (9 $\mu g\ L^{-1}$). HFC-134a is expected to be used extensively in the future as foam blowing agents as a substitute for CFC-11 and HCFC-141b.

Table 3.1. Average gas concentrations of selected landfill gas components in three different waste cells (1.3, 1.5.1, and 2.2.2) based on 14 samples sampled approximately once a month between February 2005 and June 2006.

Landfill gas components			**Measured gas concentrations**			**Gas concentrations corrected for dilution with atmospheric air**		
Chemical name	Chemical formula	Abbreviation	1.3	1.5.1	2.2.2	1.3	1.5.1	2.2.2
Main components			% v/v	% v/v	% v/v	% v/v	% v/v	% v/v
Methane	CH_4		70	27	64	73	51	81
Carbon dioxide	CO_2		29	0	8	30	0	10
Oxygen	O_2		1	1	3	1	2	5
Nitrogen	N_2		3	71	24	3	7	15
VOCs			µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Trichlorofluoromethane	CCl_3F	CFC-11	4	2	0	3	3	1
Dichlorofluoromethane	$CHCl_2F$	HCFC-21	3	27	2	3	45	2
Chlorofluoromethane	CH_2ClF	HCFC-31	8	20	5	8	33	5
Fluoromethane	CH_3F	HFC-41	0	1	0	0	2	0
Dichlorodifluoromethane	CCl_2F_2	CFC-12	1	1	1	1	2	1
Chlorodifluoromethane	$CHClF_2$	HCFC-22	3	2	12	3	3	14
Difluoromethane	CH_2F_2	HFC-32	0	0	0	0	0	0
1,1,1,2-tetrafluoroethane	CH_2FCF_3	HFC-134a	0	10	1	0	17	1
1,1-dichloro-1-fluoroethane	CCl_2FCH_3	HCFC-141b	0	2	0	0	4	0
Benzene	C_6H_6		3	1	1	3	2	1
Toluene	C_7H_8		50	22	23	50	37	29

In all three cells relatively high gas concentrations were obtained for toluene with concentrations ranging from 21 to 33 $\mu g\ L^{-1}$, whereas benzene was measured in much lower concentrations (<2 $\mu g\ L^{-1}$).

The high content of N_2 in both cell 1.5.1 and 2.2.2 indicated dilution with atmospheric air most likely due to a high porosity combined with a low gas production rate. This was especially significant for the shredder waste which also is un-covered, where the concentration of N_2 was about 71%. For comparison with gas concentrations measured in closed anaerobic systems like laboratory batch systems, gas concentrations were corrected for dilution with atmospheric air based on the N_2-content measured in the generated gas (c.f. table 3.1). However, in spite of dilution, the VOC concentrations in the gas generated in the three waste cells disposed at AV-Miljø tended to be lower than results reported by Allen et al. (1997) for seven co-disposal landfills in the UK and results compiled by Brosseau & Heitz (1994). The data are reasonably comparable to the results of Eklund et al. (1998) for the Fresh Kills Landfill receiving municipal solid-waste (Staten Island, New York, USA) and to results of Scheutz et al. (2003), for a French landfill receiving mixed waste.

Summary

Overall the gas analyses of the main components indicated that landfill gas containing methane was produced in all three cells investigated in this study. However, the gas generated in the investigated waste cells showed very different compositions, as the gas generated in the cell with mixed combustible waste consisted of mainly CH_4 (70%) and CO_2 (29%) in opposition to the composition of the gas generated within the shredder waste, which primarily consisted of CH_4 (27%) and N_2 (71%), containing no CO_2. All of the selected VOCs were detected and quantified in the gas. The VOCs were present in concentrations up to 50 µg/L. The highest concentrations of halogenated organic compounds were observed in the shredder waste (up to 27 $\mu g\ L^{-1}$), whereas the highest concentrations of aromatic compounds were seen in the cell with non-combustible waste (up to 50 $\mu g\ L^{-1}$). The presence of HCFC-21 and HCFC-31 indicated that anaerobic degradation of CFC-11 was occurring since neither of these compounds has been produced for industrial applications.

4. Attenuation of methane and VOCs in temporary covers

Objective

Today it is well known that landfill soil covers can develop a high capacity for methane oxidation reducing the amount of methane emitted to the atmosphere (Czepiel et al., 1996; Kightley et al., 1995; Liptay et al., 1998; Bogner et al., 1997; Christophersen et al., 2001). More recently, it was shown that VOCs present in landfill gas also can be degraded in both the anaerobic deeper part of a landfill cover or in the upper oxic part where methane oxidation is taken place (Scheutz & Kjeldsen, 2003; Scheutz et al., 2003;2004). Enhancing methane oxidation in landfill top covers may therefore also reduce the emission of VOCs to the surroundings. At AV Miljø the potential of attenuation of both methane and VOCs were investigated at three waste cells.

The investigation was carried out by installing shallow gas probes in the covers at cell 1.3 and cell 2.2.2. At cell 1.5.1 the gas probes were inserted in to the top of the shredder waste as the cell was not covered yet. Furthermore, laboratory batch experiment were conducted where cover soil or shredder residues were incubated under aerobic or anaerobic conditions to study the potential for methane oxidation and degradation of VOCs. The obtained results from the laboratory experiments could be used to verify the field observations.

Methodology

Installation of shallow gas probes

Gas profiles were determined by installing gas probes at different depths in the soil cover or in the top of the waste. The gas probes consisted of steel tubes, which were closed at the bottom and provided with slits over the lower 3 cm. The steel probes were hammered into the ground at different depths. In general, samples of the main components (CH_4, CO_2, O_2, and N_2) were taken at 10, 20, 30, 40, 60, 80, and 100-cm depth. Samples of 5 mL were withdrawn with a syringe and stored in vacuumed glass bottles. The probes were purged before sampling by redrawing three times the volume of the probes using a 250 mL syringe. Between sampling the probes were capped. Two sets of gas probes were installed on each cell. Placement of the gas probes on the three cells is shown in figure 2.4 in section 2.

Batch experiment and soil sampling

To verify observed degradation patterns indicated by the shallow gas profiles, simple batch experiments were conducted. Cover soil or shredder residue was incubated with trace components under both aerobic and anaerobic conditions. A fixed amount of soil or shredder material (20 g moist soil) was added to a 117 mL batch container equipped with Mininert (VICI AG, Schenkon, Switzerland) valves made of Teflon. The valves enabled gas to be sampled or injected by a hypodermic needle and a syringe. To simulate anaerobic conditions the gas phase in the batch containers was flushed with a 20/80% mixture of carbon dioxide and nitrogen. To obtain methane oxidation conditions, air was withdrawn from each container using a syringe and replaced with methane and oxygen, which gave an initial mixture of methane (15% v/v), oxygen (35% v/v) and nitrogen (50% v/v).

Gas samples containing the test compound were removed from gaseous stock solutions by a gas tight glass syringe and injected into the batch containers. The degradation of the VOCs was studied in single compound tests. The initial concentrations were generally selected so that they were in the range of typical trace gas concentrations in landfill gas (app. 200 mg m^{-3}). Gas samples withdrawn from headspace were sampled periodically and analyzed by gas chromatography. The gas chromatographic set-up and the procedure for data evaluation are described in section 2. The batch experiments were conducted at room temperature (22°C). All experiments were carried out in duplicate. The procedure for data evaluation is described in Scheutz et al. (2004).

In order to check if any disappearance could be due to non-microbial processes (abiotic degradation, sorption and volatilization) control batches with sterilized soil (autoclaving followed by addition of sodium azide (0.2 g kg^{-1})) were conducted.

The methane oxidation potential was studied by incubation of cover soil and shredder material sampled at 10-20 cm intervals from the surface to 100 cm depth. At the cell with shredder residue material was sampled in 10 cm intervals from the surface to 60 cm depth below the surface. The texture of the shredder waste prevented sampling at deeper depths than 50-60 cm. Samples were collected at two different locations at all three cells; a area with methane emissions below detection and a hotspot area, where higher emissions of methane previously had been measured (c.f. figure 2.4 in section 2)

To verify the degradation pattern of VOCs indicated by the gas profiles aerobic incubation experiments containing VOCs were conducted. The soil and shredder material used in the aerobic experiments were sampled at app. 20 cm depth. As the shallow gas profiles for the shredder waste indicated anaerobic conditions 60 cm below the surface anaerobic experiments with shredder residue were also conducted. The shredder residue for these batch experiments were sampled at app. 60 cm depth.

All soil and shredder samples were stored at 4ºC in darkness in closed plastic bags to avoid dehydration prior to the laboratory experiments.

Results

Gas profiles

Numerous biochemical, transport, and meteorological processes influence observed concentrations of soil gases: diffusion, advection, dilution, volatilization, sorption, biodegradation, and barometric pressure fluctuations. Although gas profiles are snapshots representing a single sampling episode, comparative profiles for several gases can provide information about vertical zonation of processes. Figure 4.1A show gas profiles for major gases and selected VOCs at a location on the shredder cell, which showed low or no methane emission. The gas profiles shown are average concentrations based on 14 measuring campaigns. At 60 cm below the surface, the waste is fully anaerobic (no O_2) consisting of CH_4 and N_2 similar to the gas composition measured in the deeper gas probes (c.f. section 3). The steep decrease in

CH_4 concentration and an increase in CO_2 concentration between 60 and 40 cm indicate CH_4 oxidation. The gas profiles of HCFC-21 show a steady decrease from 100 cm to 60 cm along with an increasing HCFC-31 concentration, indicating anaerobic dechlorination of HCFC-21 to HCFC-31. The concentration of HCFC-31 decreases steeply from 60 to 40 cm probably due to oxidation, as oxygen is present and as no HFC-41 is observed, which is the expected degradation product of HCFC-31 under anaerobic condition (Deipser and Stegmann, 1997; Scheutz et al., 2003). Also HCFC-21 is relatively rapidly degraded under oxic conditions. A similar degradation pattern was observed for CFC-12, which also is shown in figure 4.1A. Gas profiles indicate anaerobic dechlorination of CFC-12 to HCFC-22 and partly HFC-32. Both HCFC-22 and HFC-32 are oxidized in the aerobic part of the waste.

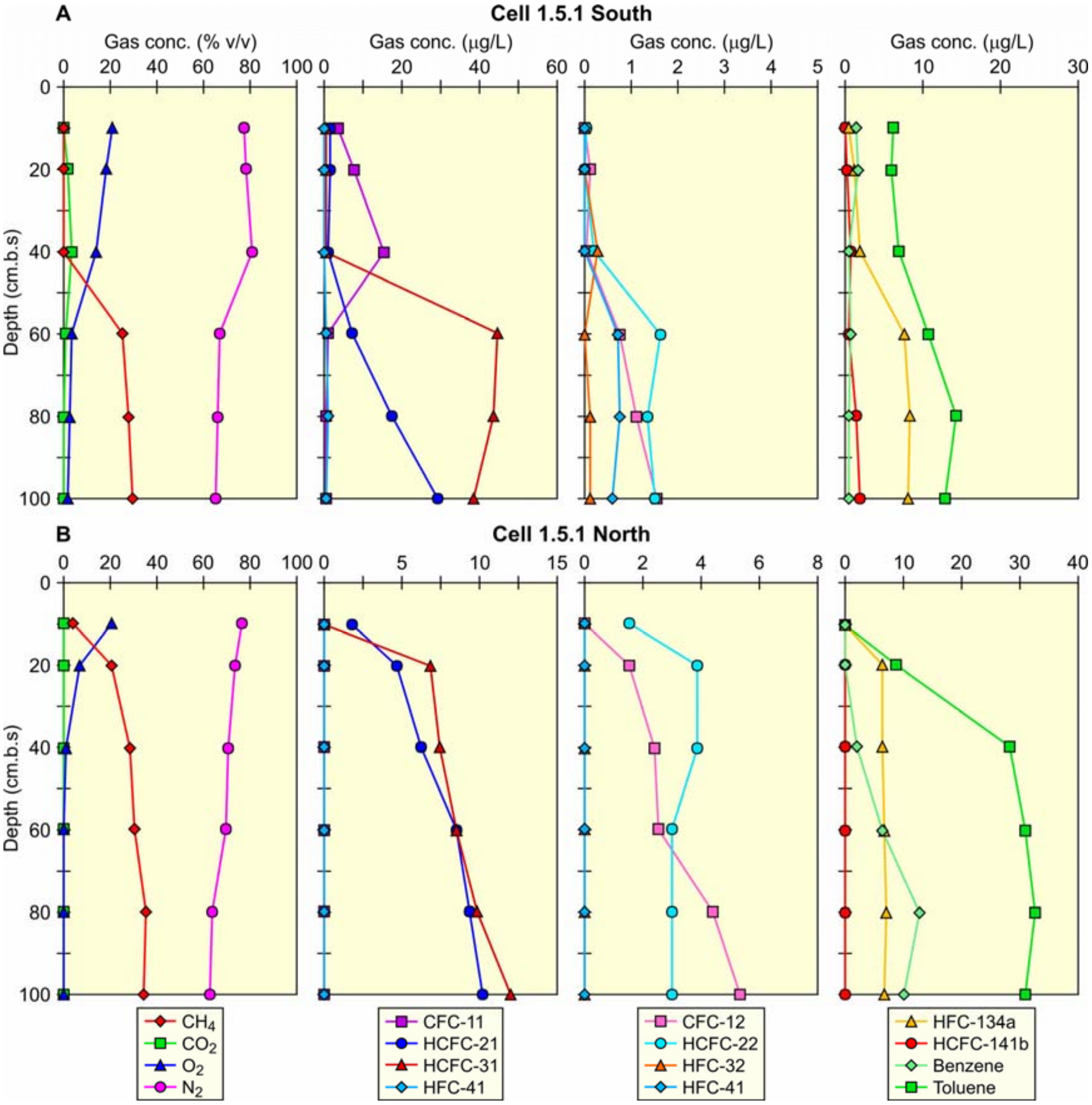

Figure 4.1. Vertical gas profiles of main components and selected VOCs *vs.* depth below surface at two locations with different gas emissions: Figure A represent an area with methane emissions below detection whereas Figure B represent a hot spot with high methane emissions (up to 78 g m^{-2} d^{-1}).

Figure 4.1B show the gas profiles for major gases and selected VOCs close to a flux chamber, which showed a very high methane emission representing a hot spot. Major components indicated dominance by landfill gas at 40-cm depth. At this depth, all VOCs were present in concentrations comparable to the samples from deeper gas probes representing the gas generated within the shredder waste. The shape of the concentration profiles and the overall decreasing concentrations of species from 40 cm to the surface suggest that emissions were mainly controlled by advective flow of landfill gas through the upper layer of the disposed waste. At this location, a higher emission of HCFC-21 and HCFC-31 was measured in comparison with the chamber measurements made close to the profile depictured in Figure 4.1A, where the emission was below detection, suggesting a removal of these compounds in the upper part of the waste.

Figure 4.2 and 4.3 shows gas profiles for the two soil covers at cell 1.3 and 2.2.2. Both cells are covered with clay, which made gas sampling difficult due to the low permeability of the cover material. During periods with high precipitation water tend to accumulate in small pools on the cover. Gas profiles of the main components taken during drier periods showed a similar composition to atmospheric air indicating that landfill gas generated in the two cells are not emitted through the cover or is being oxidized in the lower part of the cover. In general VOC concentrations were also very low (< 5 µg/L). At cell 1.3 gas concentrations profiles for HCFC-21 and HCFC-22 showed a decrease towards the surface due to dilution and oxidation. HCFC-21 and HCFC-22 are both anaerobic degradation products of CFC-11 and CFC-12 and were found in samples taken from the deeper gas probes installed at the cells (c.f. table 3.1 in section 3). The higher concentrations of toluene (up to 30 µg/L) observed at cell 1.3 and 2.2.2 are in coherence with the higher concentrations measured in the deeper part of the waste, where toluene was found in concentrations of up to 50 µg/L (c.f. table 3.1 in section 3). Both toluene and also benzene are known to be oxidized in aerobic soil environments rather rapidly and emissions of these compounds from landfill covers are therefore expected to be low due to oxidation in the oxic zone of the cover. Gas profiles of benzene and toluene at cell 2.2.2 indicates uptake from the atmospheric air which could be due to gas leakage from a close-by leachate collection well. Other sources to benzene and toluene are vehicle exhaust from trucks handling waste at the site.

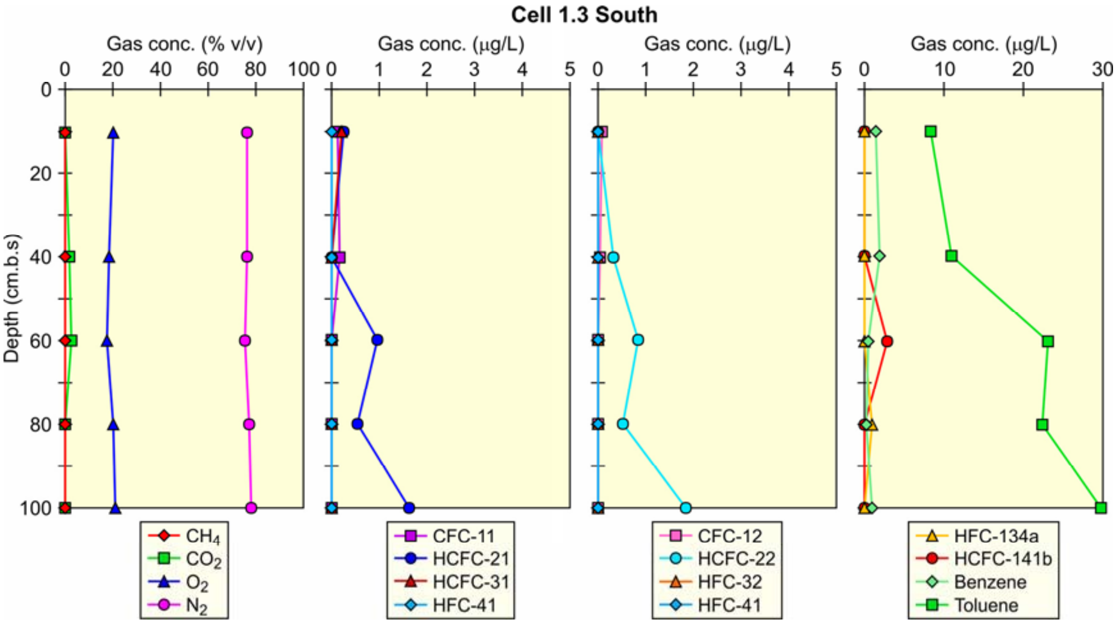

Figure 4.2. Vertical gas profiles of main components and selected VOCs *vs.* depth below surface at cell 1.3 containing mixed burnable waste.

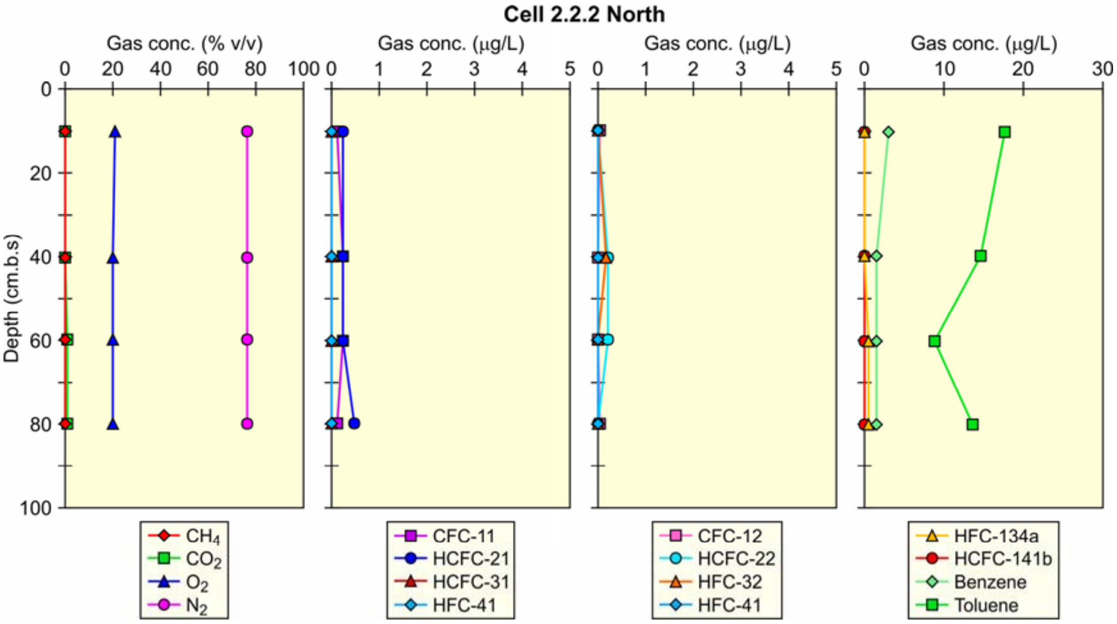

Figure 4.3. Vertical gas profiles of main components and selected VOCs *vs.* depth below surface at cell 1.3 containing mixed industrial waste.

Depth distribution of methane oxidation activity

The variation of methane oxidation potential of the shredder waste *vs.* depth was determined in microcosms containing cover soil or shredded waste incubated with methane. Maximal oxidation rates were calculated by applying zero-order kinetics to the data describing 90% of the mass transformation, which gave regression coefficients often higher than 0.90. In general, very good reproducibility was obtained and results from duplicate batches were almost identical.

The shredder waste place in cell 1.5.1 showed a relatively high capacity for methane oxidation with maximum oxidation rates up to 17 µg CH_4 g^{-1} h^{-1}, which are comparable to rates obtained for landfill cover soils (Figueroa, 1993; Scheutz et al., 2004). Figure 4.4A shows the CH_4, O_2 and carbon dioxide concentrations measured in headspace versus time, in a batch experiment containing shredder waste. CH_4 oxidation followed zero-order kinetics, indicating that the oxidation was not CH_4-limited. The oxidation was microbially mediated as seen from comparison with the sterilized control batch (Figure 4.4B). Maximal oxidation activity occurred at 40 cm below the surface, which corresponds to the depth with methane oxidation indicated by gas profiles (c.f. Figure 4.5A). The methane oxidation activity was significantly lower in the upper 20 cm of the profile and at 50 cm depth.

Incubation of shredder samples taken at the hot spot showed a different oxidation potential profile as the maximum oxidation capacity was found in the upper 30 cm of the profile and decreased significantly at 40 cm depth. However, this agrees well with the measured gas concentrations profiles showing a very shallow oxidation zone between 10 and 20 cm depth (c.f. Figure 4.5B).

The cover soil placed at cell 1.3 also showed a high capacity for methane oxidation with maximum oxidation rates up to 13 µg CH_4 g^{-1} h^{-1} (c.f. Figure 4.5A). The zone with the highest oxidation capacity was found between 80 to 100 cm.b.s., which is lower than the zone identified in the shredder profile. This is most likely a result of the low flux of methane through the cover due to its low gas permeability. The small flux of methane that is entering the lower part of the soil cover is relatively rapidly oxidized due to the aerobic conditions also in the deeper part of the cover. Thus the lower methane oxidation activity is a result of methane limitation and thereby a low number of methane oxidizing bacteria. The oxidation profile taken close to a methane leaking area shows a higher oxidation capacity in the upper profile as a result of a higher methane flux at this location (c.f. Figure 4.5B). Gas concentrations profiles taken at this location showed elevated methane concentrations and reduced oxygen concentrations in the lower part of the cover around 80 cm depth indicating methane oxidation (gas profiles are not shown).

The cover placed at cell 2.2.2 showed a relatively low capacity for methane oxidation throughout the whole profile (c.f. Figure 4.5A). This is coherent with the gas profiles showing and the flux measurements either indicating very low or no methane emission through the cover. Even the soil profile taken at a leaking area close to the border of cell 2.2.2 showed no methane oxidation capacity (c.f. Figure 4.5B).

The depth integrated methane oxidation rate, K_0 (g m^{-2} d^{-1}), was calculated using the formula below:

$$K_0 = k_0 \cdot d_a \cdot \rho_b$$

where k_0 is the methane oxidation rate (µg g^{-1} d^{-1}) obtained from the incubation experiments, d_a is the oxidation zone (m) and ρ_b is the soil bulk density (metric tons m^{-3}). Table 4.1 lists the calculated methane oxidation rates. The highest methane oxidation capacity was found for cell 1.3 and 1.5.1, which gave a depth integrated methane oxidation capacity of 108 and 101 g m^{-2} d^{-1} respectively. In comparison the capacity for cell 2.2.2 was much lower; 10 g m^{-2} d^{-1}.

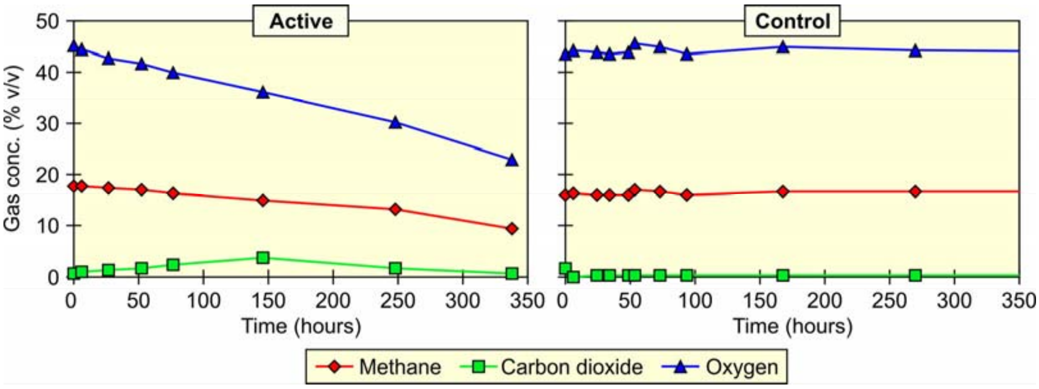

Figure 4.4. Headspace concentration of methane, oxygen and carbon dioxide as function of time, showing methane oxidation in a batch experiment containing 20 g shredder residue sampled at 20 cm below the soil surface. A. Active batch experiment. B. Control experiment.

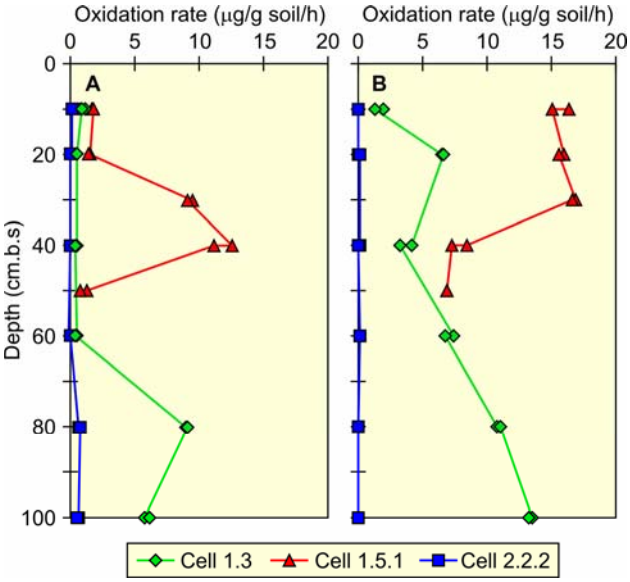

Figure 4.5. Methane oxidation rates *vs.* sampling depth below surface at two locations with different gas emissions: Figure A represents an area with methane emissions below detection whereas B represents a hot spot with higher methane emissions.

Table 4.1. Depth integrated methane oxidation capacity at cell 1.3, 1.5.1, and 2.2.2.

1.3 Cover depth 100 cm			**1.5.1 Cover depth 50 cm**			**2.2.2 Cover depth 100 cm**		
Depth interval (d_a)	k_0	K_0	Depth interval (d_a)	k_0	K_0	Depth interval (d_a)	k_0	K_0
cm.b.s.	$\mu g\ g^{-1}\ d^{-1}$	$g\ m^{-2}\ d^{-1}$	cm.b.s.	$\mu g\ g^{-1}\ d^{-1}$	$g\ m^{-2}\ d^{-1}$	cm.b.s.	$\mu g\ g^{-1}\ d^{-1}$	$g\ m^{-2}\ d^{-1}$
0-15	24	6	0-15	42	10	0-15	6	1
15-30	11	3	15-25	38	6	15-30	2	0
30-50	11	3	25-35	223	36	30-50	1	0
50-70	11	4	35-45	284	46	50-70	0	0
70-90	218	70	45-55	24	4	70-90	18	6
90-100	144	23				90-100	15	2
Total		**108**	**Total**		**101**	**Total**		**10**

Aerobic VOC oxidation potential in cover materials

The attenuation capacity of VOCs in the cover material at cell 1.3 and 2.2.2 and in the oxic part of the shredder waste (cell 1.5.1) was studied in batch experiments incubated under aerobic conditions. Table 4.2 lists maximal oxidation rates obtained from batch experiments conducted with cover soil (cell 1.3 and 2.2.2) and shredder waste (cell 1.5.1) incubated with methane, oxygen, and selected VOCs.

Figure 4.6 shows the concentrations of trace components measured in headspace versus time in batch experiments containing 20 g moist shredder waste. In experiments with shredder residues all lower chlorinated compounds were degradable under aerobic conditions with maximal oxidation rates varying between 0.003 and 0.067 $\mu g\ g^{-1}\ d^{-1}$. The highest rates were observed for the lower chlorinated compounds like HCFC-31, HFC-41 and the aromatic hydrocarbons; benzene and toluene. The degradation occurred in parallel with the oxidation of CH_4. Highly substituted carbons like CFC-11, CFC-12, HCFC-141b, and HFC-134a were not degraded in presence of CH_4 and O_2.

Similar results were obtained in experiments with cover material from cell 1.3. However, the cover material on cell 1.3 showed a much higher oxidation potential for the lower chlorinated compounds and the aromatic hydrocarbons with oxidation rates varying between 0.087and 2.598 $\mu g\ g^{-1}\ d^{-1}$.

The cover material in place at cell 2.2.2 showed a very low potential for oxidation of VOCs as only HFC-41, benzene and toluene were observed to be degraded in the experiments. Also the rates were low; 0.006 and 0.123 $\mu g\ g^{-1}\ d^{-1}$.

The highest VOC-oxidation capacity was observed for the cover material at cell 1.3 and for the shredder residue. This is coherent with the results form the methane oxidation experiments with also showed the highest oxidation capacity at cell 1.3 and 1.5.1, whereas the oxidation potential at cell 2.2.2 was very limited. It is possible that the oxidation in the experiments with shredder material was oxygen limited during some periods of the experiments as it was necessary to re-inject oxygen to the batches due to the high methane oxidation potential of the shredder material. Oxygen limitation could limit the oxidation of the VOCs and thereby underestimate the observed oxidation rates. However, the results confirm the field observations where gas profiles indicate oxidation of several VOCs in the cover materials and in the upper oxic part of the shredder waste.

In general the rates are lower compared to results obtained by Scheutz et al. (2004), who report oxidation rates for a number of halogenated compounds in the range of 0.72 and 41 µg g^{-1} d^{-1}. However, these oxidation rates were obtained in experiments with landfill fill cover soil, which for years had been exposed to high concentrations of landfill gas. The gas profiles taken at cell 1.3 and cell 2.2.2 clearly show very low methane concentrations indicating a very low flux of landfill gas to the two covers.

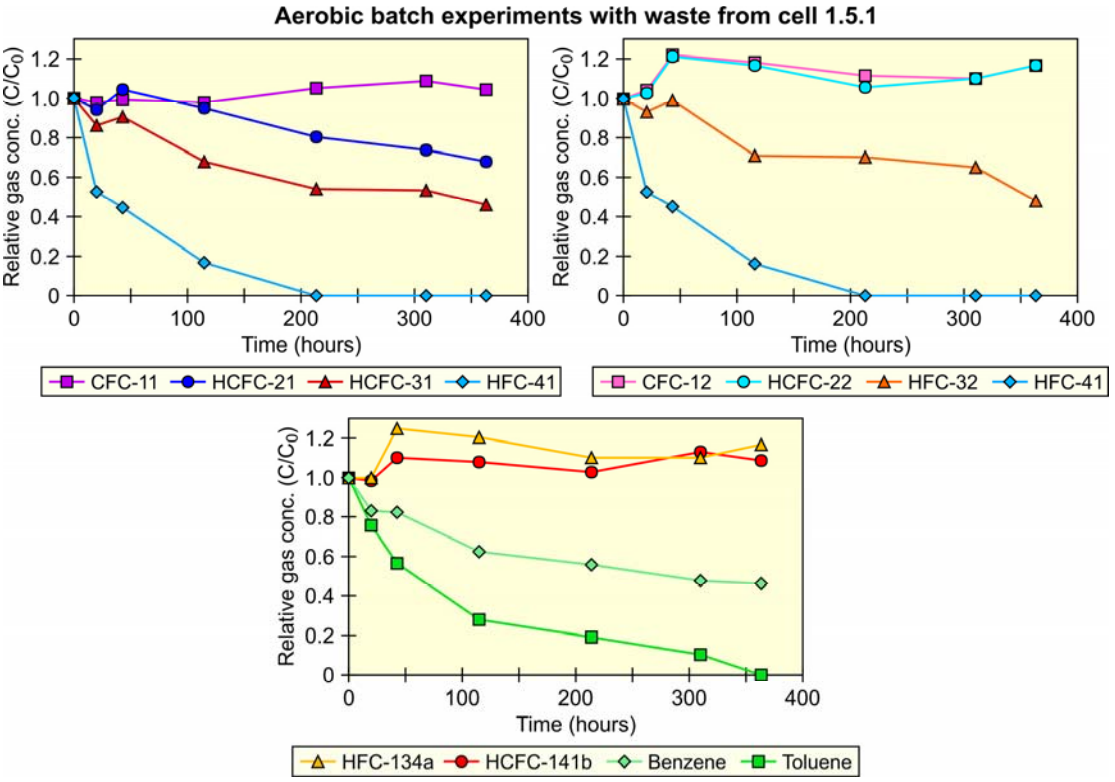

Figure 4.6. Relative headspace concentration of selected VOCs as a function of time in aerobic batch experiments, containing 20 g shredder residue pre-exposed to landfill gas. A. CFC-11, HCFC-21, HCFC-31, and HFC-41. B. CFC-12, HCFC-22, HFC-32, and HFC-41. C. HFC-134a, HCFC-141b, benzene, and toluene.

Table 4.2. Maximal oxidation rates obtained from batch experiments conducted with cover soil (cell 1.3 and 2.2.2) or shredder waste (cell 1.5.1) incubated with methane, oxygen, and selected VOCs. Average oxidation rates are calculated from two replicates. Regression coefficient (R^2) obtained from fitting the experimental data to a zero-order oxidation process. The batches held moisture content of 20%w/w and were conducted at room temperature.

Chemical name	**Abbreviation**	**1.3**		**1.5.1**		**2.2.2**	
		Rate µg/g/d	R^2	Rate µg/g/d	R^2	Rate µg/g/d	R^2
Trichlorofluoromethane	CFC-11	n.d.	-			n.d.	-
Dichlorofluoromethane	HCFC-21	-0.764	> 0.96	-0.007	> 0.92	n.d.	-
Chlorofluoromethane	HCFC-31	-2.598	> 0.94	-0.006	> 0.91	n.d.	-
Fluoromethane	HFC-41	-1.989	> 0.97	-0.067	> 0.84	-0.006	> 0.80
Dichlorodifluoromethane	CFC-12	n.d.	-	n.d.	-	n.d.	-
Chlorodifluoromethane	HCFC-22	-0.049	> 0.74	n.d.	-	n.d.	-
Difluoromethane	HFC-32	-0.230	> 0.99	-0.005	> 0.82		
1,1,1,2-tetra-fluoroethane	HFC-134a	n.d.	-	n.d.	-	n.d.	-
1,1-dichloro-1-fluoroethane	HCFC-141b	n.d.	-	n.d.	-	n.d.	-
Benzene		-0.087	> 0.98	-0.003	> 0.84	-0.013	> 0.92
Toluene		-0.248	> 0.85	-0.062	> 0.30	-0.123	> 0.80

n.d.: no degradation observed

Anaerobic VOC degradation potential in cover materials

In order to verify the observed degradation pattern indicated by the shallow gas profiles anaerobic incubation experiments with VOCs were conducted. Experiments were only conducted with shredder waste as the gas profiles for the soil covers on cell 1.3 and 2.2.2 both showed aerobic conditions throughout the covers.

In batch experiments with shredder waste incubated under anaerobic conditions degradation of CFC-11, CFC-12, HCFC-21, HCFC-22, HCFC-31, HCFC-141b was observed (Figure 4.7). Table 4.3 shows the maximum degradation rates as well as the regression coefficient from fitting the experimental data with a zero-order model equation. No degradation was found for HFC-134a, HFC-32 and HFC-41.

Virtually all of the amended CFC-11 was degraded within 5-10 days. In batch experiments were CFC-11 was added as a single component, CFC-11 was degraded to HCFC-21, HCFC-31, and HFC-41 (results not shown). However, the degradation pattern did not indicate sequential dechlorination but rather a simultaneous production of HCFC-21, HCFC-31, and HFC-41. Furthermore, the production of degradation products did not correlate with a stoichiometric removal of CFC-11 indicating that other degradation products were produced. HCFC-21 and HCFC-31 were further degraded whereas no further degradation of HFC-41 was observed. A similar degradation pattern has been observed in anaerobic experiments containing waste and sludge (Scheutz et al., 2003). No transformation of CFC-11 or its potential anaerobic degradation products occurred in the sterilized control experiments.

Figure 4.7A shows the anaerobic degradation of CFC-11, HCFC-21, HCFC-31, and HFC-41 in batch experiments with shredder waste. The degradation rate was directly correlated with the number of chloride atoms attached to the carbon as the highest degradation rate was obtained for CFC-11, the lowest for HCFC-31, whereas no degradation of HFC-41 was observed (no difference between sterilized controls and active batch experiments – results not shown). The degradation of CFC-11 occurred approximately 13 times as fast as the degradation of HCFC-21, which occurred three times as fast as the degradation of HCFC-31 (Table 4.3). In experiments with HCFC-21 and HCFC-31, production of their respective lower chlorinated compounds was observed, however, never in amounts corresponding to a stoichiometric release (results not shown).

Also CFC-12 and HCFC-22 were degraded in experiments added shredder waste. In general, the degradation of CFC-12 was much slower compared to CFC-11 giving degradation rates of 0.21 and 3.40 μg/g/d respectively (c.f. Figure 4.7B).

HCFC-141b was also degraded with rates comparable to HCFC-22 and HCFC-31. The degradation pathway of HCFC-141b was not investigated. Balsiger et al. (2005) observed degradation of HCFC-141b in microcosms inoculated with contaminated sediment whereas no transformation was observed in microcosms inoculated with sewage sludge. In the experiments reported by Balsiger et al. (2005) the rate of degradation of HCFC-141b was slower than CFC-12, which also is the case in our experiments.

Anaerobic degradation of HFC-134a was not observed in any of the experiments within a run time of up to 20 days. Defluorination (i.e. rupture of the carbon-fluorine bond) has only rarely been observed, and seems to require extreme reducing conditions (Key et al., 1997). Also Balsiger et al. (2005) did not see any degradation of HFC-134a in microcosms inoculated with sludge or sediment.

Of the aromatic hydrocarbons benzene was rapidly degraded whereas no significant decline in toluene concentrations was observed within the time frame of the experiment. In comparison with the other VOCs benzene was rater rapidly degraded (c.f. Figure 4.7C).

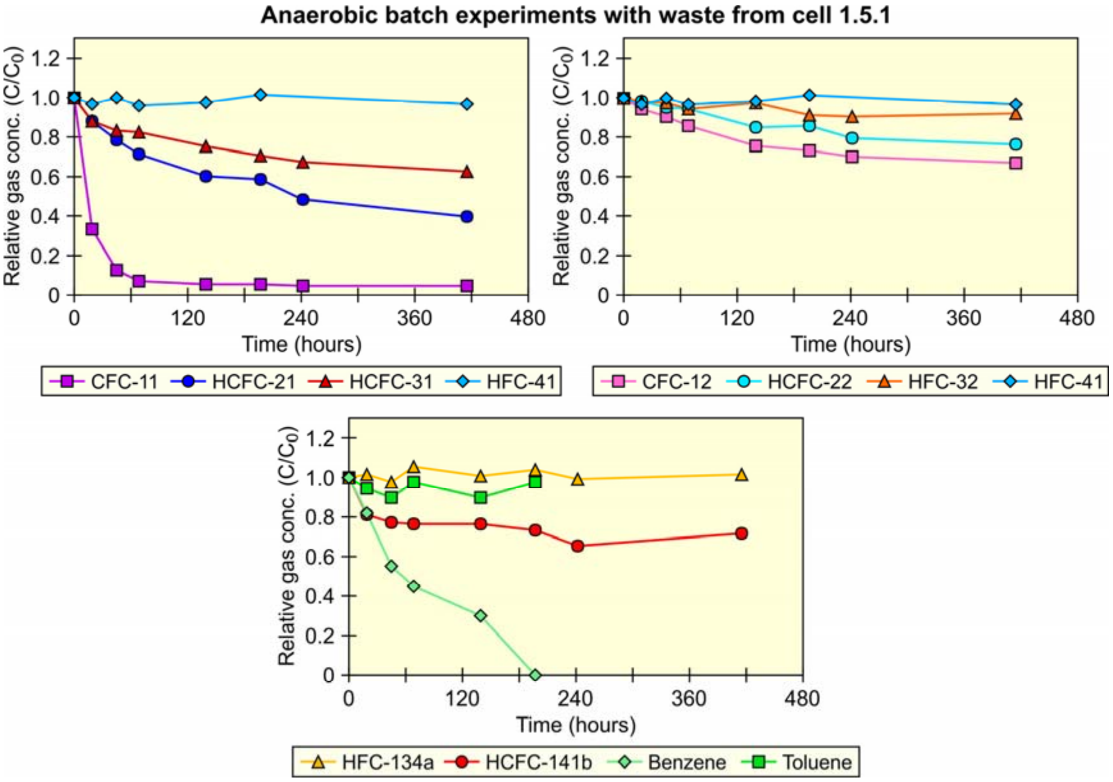

Figure 4.7. Relative headspace concentration of selected VOCs as a function of time in anaerobic batch experiments, containing 20 g shredder residue pre-exposed to landfill gas. A. CFC-11, HCFC-21, HCFC-31, and HFC-41. B. CFC-12, HCFC-22, HFC-32, and HFC-41. C. HFC-134a, HCFC-141b, benzene, and toluene.

Table 4.3. Maximal degradation rates obtained from batch experiments conducted with shredder waste from cell 1.5.1 incubated under anaerobic conditions. Average oxidation rates are calculated from two replicates. Regression coefficient (R^2) obtained from fitting the experimental data to a zero-order oxidation process. The batches held moisture content of 20%w/w and were conducted at room temperature.

Chemical name	**Abbreviation**	**Rate** $\mu g\ g^{-1}\ d^{-1}$	$\mathbf{R^2}$
Trichlorofluoromethane	CFC-11	-3,40	> 0.78
Dichlorofluoromethane	HCFC-21	-0,26	> 0.81
Chlorofluoromethane	HCFC-31	-0,09	> 0.73
Fluoromethane	HFC-41	-	-
Dichlorodifluoromethane	CFC-12	-0,21	> 0.74
Chlorodifluoromethane	HCFC-22	-0,10	> 0.77
Difluoromethane	HFC-32	-0,02	> 0.60
1,1,1,2-tetra-fluoroethane	HFC-134a	-	-
1,1-dichloro-1-fluoroethane	HCFC-141b	-0,11	> 0.54
Benzene		-0,46	> 0.93
Toluene		-	-

n.d.: no degradation observed

Summary

Gas profiles from the cell with shredder waste showed an oxidation zone of 40 cm below the surface with significant methane oxidation. This was supported by incubation experiments with shredder material, which showed a high potential of methane oxidation in the upper 40 cm of the shredder waste. The gas composition in the deeper part of the profile (below 60 cm depth) resembled the gas composition based on the deeper gas probes placed 2.5 m into the waste. The VOC gas profiles showed that anaerobic dechlorination of both CFC-11 and CFC-12 led to generation of degradation products like HCFC-21, HCFC-31 and HCFC-22. Anaerobic dechlorination of CFC-11 was verified in batch incubation experiments with shredder waste. Degradation of CFC-11 to HCFC-21 and HCFC-31 could be problematic as these two compounds are toxic (*24*). However, gas profiles of the lower chlorinated compounds like HCFC-21, HCFC-31 and HCFC-22 suggested oxidation in the upper oxic zone of the shredder waste. With the exception of CFC-11, CFC-12, HCFC-141b and HFC-134a all other VOCs were degraded in aerobic batch experiments incubated with methane and oxygen. Gas profiles taken at a hot spot were high methane emission were measured showed a smaller oxic zone limiting the oxidation at this location.

The gas profiles from cell 1.3 and 2.2.2 showed a similar composition to atmospheric air indicating that landfill gas generated in the two cells is not emitted through the cover or is being oxidized in the lower part of the cover. Methane oxidation in the lower part of the covers are possible as methane incubation experiments showed a tendency to increasing oxidation rates with increasing cover depth. This was especially the case at cell 1.3. In general VOC concentrations were also lower in comparison with the concentrations measured at the shredder cell.

In general, a high potential for attenuation of both methane and VOCs were seen in the upper part of the shredder waste disposed at cell 1.5.1. The high oxidation capacity is thought to be a result of the high porosity of the shredder material enhancing oxygen transportation into the waste. These finding correlates wells with the surface emission measurements, which showed that the surface emission with the exception from a few hot spots were below detection. At cell 1.3 and 2.2.2 the low surface emission is more likely to be due to the very low permeability of the cover soil forcing the gas to be emitted through leachate wells etc.

5. Local gas emissions

The overall objective was to map emission pathways and to quantify emissions of methane through the soil cover and leachate collection system at AV Miljø. A qualitative survey of was done by performing concentration screenings near the surface of the soil cover and in the leachate inspection and collection wells. Emission rates were determined using flux box measurements of emission through the soil cover and a tracer release method to determine flow rates of methane from the leachate collection system.

5.1 Methane concentration screenings

Objective

The main objective of the surface methane concentration screenings was to obtain a qualitative overview of methane emission pathways of the site. Main focus was on the three cells 1.3, 1.5.1, and 2.2.2, where concentrations of methane near the surface of the covers were measured.

Initial screenings suggested that an important source of methane emitting from the site were through wells, which are part of the leachate collection system. Since it was not possible to measure emission rates from all wells due to time constraints, repeated screenings of concentrations of methane inside the wells were used. This was to categorize these wells, so that emission rate measurement of wells of each category could be used for an assessment of the amount of methane emitting through the leachate collection system as a whole.

Method

Field equipment

To conduct field measurements of concentrations of methane a Photovac MicroFID portable flame ionization detector (FID) was used. The lower detection limit of this instrument was 0.5 ppmv methane. Accuracy of the instrument was specified to be +/- 0.5 ppmv or +/- 10% of actual methane concentration (0.5 to 2000 ppmv range). Concentrations were measured every second with concentrations displayed in real time on the instrument, and it was possible to log data. The FID draws in 600 mL of air per minute under operation.

A Trimble 5700 RTK GPS with TSC1 controller was used to establish locations. Locations were measured with accuracy depending on weather conditions and other factors between less than 1 cm and 2 cm.

A La Crosse weather station measuring and logging data of atmospheric pressure, temperature, wind speed and direction, and rainfall was used to monitor weather conditions.

Surface screenings

To provide basis for a qualitative analysis on the spatial variability of methane emission through the soil cover, a grid of locations for measurements of methane concentrations were planned. Surface screenings were performed on the disposal cells 1.3, 1.5.1, and 2.2.2. The number of grid points and the average grid spacing was chosen adopting a strategy described in “Guidance for Monitoring Landfill Gas Surface Emissions” by the UK Environment Agency. In this report a statistical method for determination of the minimum number of measurement locations for flux box measurements is described. For zones larger than 5000 m^2 the minimum number of measurement locations can be calculated by the following equation:

$$n = 6 + 0.15\sqrt{Z}$$

Where n is the number of locations, and Z is the area of the zone in square meters. Table 5.1 lists areas of the three cells, average grid spacing and number of grid points.

On cell 1.3 a large part of the area had to be disregarded since it was used for temporary storage of soil intended for soil covering.

Table 5.1. Areas of disposal units, and average grid spacing.

Disposal cell	Area (m^2)	Average grid spacing (m)	Number of grid points
1.3	28400	15	19
1.5.1	8700	10	36
2.2.2	12200	15	26

After marking the grid of point locations for measurement, each location was measured for methane concentration just above ground level in four screening campaigns. Concentrations were measured on the grid points and hot spots using the FID coupled with a 10cm diameter funnel.

Each measurement location was marked at the site using labeled poles and measured for precise location using the GPS. The measurement locations are shown in figure 2.4. This was done to repeat measurements at the exact same locations. Screenings were also performed along the edges of each of the three cells while recording the position of each measurement using the GPS.

Three screening campaigns on the grid points were performed. Two of the campaigns were performed under decreasing atmospheric pressure; one was done when the pressure was increasing. From 12 hours before the first campaign and until end of the campaign, the atmospheric pressure dropped from 997 hPa to 995 hPa. In the period 12 hours before until end of measurement of the second campaign, the pressure went up from 1010 hPa to 1013 hPa. From 12 hours before the third campaign and until end of the campaign, the atmospheric pressure dropped from 1016 hPa to 1007 hPa.

Screening of leachate wells

Methane concentrations inside the approximately 70 leachate wells were measured at six campaigns. Measurements were performed using the FID sampling air from 1 meter of depth below the top lid inside each well. Air was withdrawn through plastic tubing using the FID's internal pump.

Two screening campaigns took place under rising atmospheric pressure. The pressure was rising from 1016 12 hours before to 1018 hPa at the end of the first campaign and from 1004 to 1010 hPa for the other campaign. One campaign took place under decreasing atmospheric pressure (falling from 1016 to 1007 hPa) . Three campaigns took place, when there was not a clear rising or falling tendency with regard to atmospheric pressure. Atmospheric pressure ranges and tendencies recorded in the period from 12h before and during measurement campaigns are listed in Appendix B.

Results

Surface screenings

At cell 1.5.1 methane concentration higher than background level (1.7 ppmv) was measured at one grid point at one of the three campaigns. The observed concentration was 7.5 ppmv. No difference was seen comparing the measurements at decreasing atmospheric pressure to the measurement at increasing pressure. On the cells 1.3 and 2.2.2 all methane concentrations observed on the grid points were at background level (1.7 ppmv), but the screening performed along the edges of these cells did show concentrations significantly higher at some locations. Highest concentration observed was 1600 ppmv. Appendix C shows results of the surface screenings along the edges of the three cells.

Based on the surface screenings the emission through the soil cover was found to be minimal. This was probably due to a low gas permeability of the soil cover at the two covered cells (1.3 and 2.2.2) in combination with a relatively low methane production, whereas methane oxidation can explain the low concentrations observed on the shredder cell. Some landfill gas is emitting at slopes and edges of the soil cover and close to installations such as leachate collection wells.

Screening of leachate wells

Concentrations in the leachate wells were measured on five campaigns over a period of six months. Concentrations measured at the screenings are listed in Appendix D. Based on these measurements the following categorization was chosen:

- Category A: Concentrations measured were above 3000 ppmv, and concentrations of methane above background level (1.7 ppmv) could be detected in a distance larger than one meter away from the well using the FID
- Category B: Concentrations were most often above 1000 ppmv
- Category C: Concentrations were most often between 10 ppmv and 1000 ppmv
- Category D: Concentrations were most often lower than 10 ppmv

Each well at AV Miljø was assigned to one of these categories in table 5.2.

Table 5.2. Leachate wells assigned to categories according to methane concentrations observed. "I" indicates inspection wells, whereas "S" and "B" indicates collection wells. A description of the leachate collection system is given in section 2.

Category	Leachate collection- and inspection wells	Number of wells in category
A	S1.3; S1.4; S1.6; I2.1.2.3; I2.1.4	5
B	I1.2.1; I1.3; S1.5; I1.6; I2.1.3; B2.1.2.3; S2.2.2; I2.3; S2.3; I2.4; S2.4; B2.5; S2.5; I2.6; B2.9; B2.11	16
C	B1.2.1; S1.5.1; I1.5.4; S2.1.4; I2.2.2; S2.6; B2.7	7
D	S1.1; I1.1.1; S1.1.1; S1.2; I1.2.2; B1.3.1; I1.4; I1.5.1; I 1.5.2; I1.5.3; I2.1; S2.1; I2.1.1; S 2.1.1; I2.1.2.2; S2.1.3; I2.2; S 2.2; S2.2.1; B2.3; B2.4; I2.5; B2.6; I2.7; S2.7; B 2.8; B2.10; B2.12; B2.13; B2.14; B 2.15; B2.16; B2.17; B2.18; B2.19; B 2.20; B 2.21; B2.22; B2.23; B 2.24	41

In the majority of the wells, the methane concentration was measured to be below 10 ppmv (category D). Many of these wells were connected to drainage pipes under vacant disposal cells, so low emissions of methane from these locations were expected. The leachate wells in categories A and B were mostly at cells covered at the time of measurement and containing mixed waste and temporarily stored combustible waste (Fredenslund, 2004). Wells I2.1.4 and I2.1.3, assigned to categories A and B respectively, were located at cells containing shredder waste.

Variations in concentrations of methane between the campaigns suggest that the emission rates vary over time. Since the screenings were performed over a period of eight months, some variation was expected caused by activities at the site such as removal of temporarily stored combustible waste. Measurements were performed under both rising and falling barometric pressures as well as oscillating barometric pressure. Atmospheric pressures and tendencies are listed in Appendix B, and methane concentrations measured in the wells in the six screening campaigns are listed in Appendix D. Comparing methane concentrations measured to tendencies of barometric pressure at time of measurement does not show any apparent connection. It was expected that concentrations would be higher during decreasing barometric pressure, but this was not observed.

5.2 Surface emission rates

Objective

The objective was to measure gas emission rates through the soil cover or other surfaces at the cells 1.3, 1.5.1, and 2.2.2 at AV Miljø. Methane emissions were measured on all cells, and emissions of selected volatile organic compounds were measured on cell 1.5.1 containing shredder waste.

Method

Flux chambers

Emission rates of methane and selected VOCs were determined using two types of static flux chambers: a stationary type and a mobile type

The stationary type was constructed using the top of a steel drum, which was pushed 3.5 cm into the ground. The removable top of the chamber was equipped with several sampling ports and a battery powered fan, which secures that the air inside the chamber, was totally mixed during sampling. The bases of the flux chambers were sealed with bentonite. When installed the flux chamber had a height of app. 20 cm and an inner diameter of 57 cm, so that the total chamber volume was 51,035 cm^3 over an enclosed surface area of 2552 cm^2. The volume/area ratio ($cm^3 \cdot cm^{-2}$) was 20. This type of flux chamber is referred to as a stationary chamber, as the frame was permanently installed at the cells. When performing the flux measurement, the lid was put in place on top of the chamber frame.

The other mobile type, which is pictured in figure 5.1, was equipped with a manual fan, and had a height of 20.5 cm and covers an area of 755 cm^2, and the volume was thereby 15,478 cm^3. The volume/area ratio of the second type was 20.5.

Figure 5.1 Mobile flux chamber coupled with a portable flame ionization detector (FID) for measurement of methane flux.

Sampling and analysis

Stationary flux chambers (cell 1.5.1)

In total five stationary flux chambers were permanently installed on the shredder cell, covering two hot spots identified during the initial surface screening and three areas representing the average conditions of the cell (c.f. figure 2.4 in section 2). Surface emission rates of methane and selected VOCs were measured by taking a time series of gas samples from the chambers. A minimum of seven gas samples of 5 mL were withdrawn using gas-tight syringes and stored in Labco Exetainer 5 mL evacuated soda glass vials fitted with pierceable rubber septa pre-evacuated glass bottles. 14 campaigns were measured over a period of 14 months at the cell 1.5.1. At 13 of these campaigns, methane fluxes were measured, and at three campaigns fluxes of VOCs were measured.

To conduct laboratory measurements of methane concentrations, a Shimadzu GC-14A gas chromatograph with a flame ionization detector was used. Five gas standards ranging from 100 ppmv to 10,000 ppmv were used for calibration. A calibration was performed for each day of analysis. Considering an instrument detection limit of 5 ppmv, the detection limit of the methane flux measurements using stationary flux chambers was estimated to be 0.1 g $m^{-2}d^{-1}$. Concentrations of VOCs were measured using GC/MS as described in section 3. The detection limit of flux measurements of VOCs was estimated at 0.001 g $m^{-2}d^{-1}$.

In general, the methane concentration *vs.* time curves showed good linear fits (r^2>0.9) without any change in slope for the final sampling times. Fluxes were calculated from the product of the change in concentration over time (dc/dt) and the [chamber volume/chamber area] ratio.

Mobile flux chambers (cells 1.3 and 2.2.2)

At the cells 1.3 and 2.2.2, the smaller type flux chamber was used coupled with the FID. Measurements of methane flux were performed where methane concentrations higher than background level were seen during the methane concentration screenings (see section 2.1) as well as on other places of the soil cover (c.f. figure 2.4 in section 2). Two campaigns were performed at cells 1.3 and 2.2.2.

The detection limit of the methane flux measurements using the mobile chamber coupled with the FID was estimated to be 0.1 g $m^{-2}d^{-1}$. This was calculated considering the accuracy of the FID specified at 0.5 ppmv, a sampling period of 5 minutes per flux measurement.

Results

Stationary flux chambers (cell 1.5.1)

At the hot spots on cell 1.5.1 observed methane flux rates were seen to vary over time. At one measurement a negative flux was observed, suggesting a net uptake of methane from the atmosphere due to methane oxidation in the waste. The observed flux rates from the random location on the cell were very small, as seen in table 5.3. In most cases no flux was observed, and the maximum flux rates were low.

Table 5.3. Measured methane flux rates at the five locations at cell 1.5.1. Values listed are minimum flux rates, average flux rates and maximum flux rates measured during the 13 campaigns. B.d.L.: Below detection limit.

Location	Minimum flux (g m^{-2} d^{-1})	Average flux (g m^{-2} d^{-1})	Maximum flux (g m^{-2} d^{-1})
Hot spot 1	-1.9	17	78
Hot spot 2	b.d.l.	6,6	23
Random 1	b.d.l.	*	0.2
Random 2	b.d.l.	*	b.d.l.
Random 3	b.d.l.	*	0.3

* The methane average flux could not be calculated since most measurements showed flux rates below the detection limit of this method (< 0.1 g m^{-2} d^{-1}).

Flux rates of VOCs above detection limit (> 0.001 g m^{-2} d^{-1}) were exclusively observed at hot spot 1. On one of the three flux measurements, flux of CFC-11 was measured to be 0.002 g m^{-2} d^{-1}, whereas emissions of the other VOCs included in this study were below detection limit. At another campaign, emissions of HCFC-21 and

HCFC-31 were 0.005 and 0.006 g m^{-2} d^{-1}, respectively at hot spot 1. The emissions of the other VOCs included in this study were all below the detection limit (< 0.001 g m^{-2} d^{-1}).

Mobile flux chambers (cells 1.3 and 2.2.2)

At all locations on cell 1.3, and 2.2.2 methane emissions was below detection limit (0.1 g m^{-2} d^{-1}). Since flux measurements were performed at locations where emissions where expected based on the concentration screenings, the emission through the soil cover at these cells is considered to be minimal. It was not possible to analyze for VOCs due to the low concentrations.

5.3 Methane emission through leachate collection system

Objective

As described in section 6.1, screenings of methane concentrations in the leachate inspection and collection wells indicated that a significant amount of methane was emitted through the leachate collection system at AV Miljø. The objective of this part of the project was to quantify this emission.

Changes in atmospheric pressure are known to have a generally important impact on landfill gas emissions from landfills (Christophersen & Kjeldsen, 2001). To avoid as best as possible impacts of dramatic changes in atmospheric pressure, times of measurements were chosen where the weather conditions were stable. The development of atmospheric pressure 12 hours before emission measurements and during measurements where determined using a weather station recording pressures at the site.

Method

To measure methane emission rates from the leachate system, a continuous tracer release method was adapted for use on leachate wells and pumping stations at AV Miljø. Tracer release measurements to measure gaseous emissions from landfills have been used by others (Galle et al., 2001; Samuelsson et al., 2005; Mosher et al., 1999). The principle of this method was to continuously release a gaseous tracer at a known rate near the source of the methane emission, and subsequently measure the concentrations of tracer and methane downwind after background concentrations of tracer and methane were determined. The basic equation for calculating emission rates through these measurements of concentrations was derived from the assumption that the ratio between flow rates of methane and tracer was equal to the ratio between observed concentrations measured downwind:

$$\frac{Q_{CH_4}}{Q_{CO}} = \frac{C_{CH_4}}{C_{CO}} \Leftrightarrow Q_{CH_4} = Q_{CO} * \frac{C_{CH_4}}{C_{CO}} \qquad (1)$$

Q_{CH4} was the flow rate of methane (L/min), Q_{CO} was the flow rate of carbon monoxide tracer, C_{CH4} was the concentration down wind of methane (ppmv), C_{CO} was the concentration of carbon monoxide tracer (ppmv).

This relationship assumes perfect mixing of LFG and carbon monoxide tracer, and that background levels of methane and carbon monoxide were negligible. To take background levels into account, an approximate compensation was introduced, so that

$$Q_{CH_4} = Q_{CO} * \frac{C_{CH_4,t} - C_{CH_4,background}}{C_{CO},t - C_{CO,background}} \qquad (2)$$

Carbon monoxide was chosen as tracer gas since a highly reliable method for measurement of this gas was available. The tracer release system consisted of a CO-gas bottle fitted with a two stage gas regulator and a flow meter.

To measure the methane concentrations the FID used for methane screenings and flux measurements was chosen as detector. The measurement frequency of this instrument was 1 Hz.

To measure CO concentrations, an Innova Photoacoustic Field Gas-Monitor 1312 was used. This instrument was set to perform one measurement every 34 seconds, which was the maximum measurement frequency possible at the setup of the instrument. Besides carbon monoxide, water vapor and carbon dioxide concentrations were measured using the photoacoustic detector. Measured concentrations on both instruments were displayed in real time.

When measuring methane emissions from leachate wells, carbon monoxide was added through 4 mm diameter tubing in a depth of 4 meters below the top of the wells at a rate of 2.7 L/min. The point of measurement (distance from the well where air was sampled) was evaluated in each case, but was generally approximately one meter. Measurements were done continuously over a period of four hours after start of tracer release. Figure 5.2 illustrates the setup of methane emission measurements of the leachate wells.

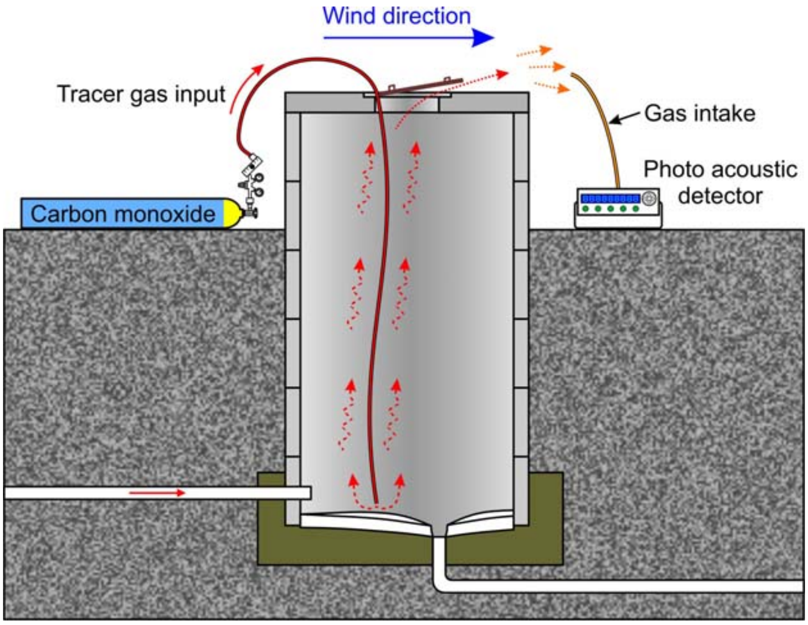

Figure 5.2. Tracer release measurement of methane emission at a leachate collection well. Only one detector is shown on the illustration.

When measuring methane emissions from the two leachate pumping stations, tracer gas was released at a rate of 2.7 L/min. in the air ventilation intakes, from where tracer gas was led to the ambient air inside of the pumping stations. Concentrations of methane and tracer were measured at the entrances to the pumping stations. Figure 5.3 shows the setup of these measurements.

Figure 5.3. Tracer release measurement of methane emission from a leachate pumping station.

Results

Figure 5.4 shows concentrations of methane and carbon monoxide as a function of time after start of tracer release of one of the emission measurements of a leachate well.

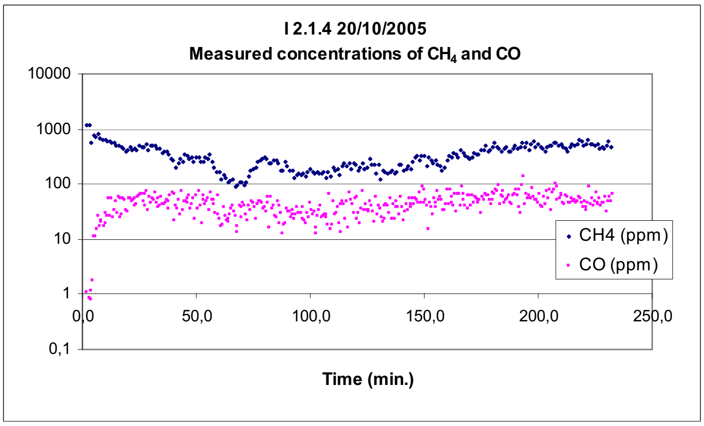

Figure 5.4. Example of data from methane emission measurement at a leachate well. Time was indicated in minutes after start of the release of carbon monoxide tracer.

The fluctuation of concentrations was most likely caused by changes in wind speed and direction during measurement. Fluctuation of methane concentration was seemingly lower than that of carbon monoxide concentration. This was due to the higher measurement frequency of the detector used to measure methane (1 Hz).

Methane concentrations plotted in figure 5.3 are each average values of 60 measurements.

The concentration of carbon monoxide tracer was observed to be below 2 ppmv until six minutes after start of the release. After approximately 20 minutes breakthrough of tracer gas was observed in this case, and the concentration of carbon monoxide was 45 ppmv on average after 20 minutes. Observing the methane to carbon dioxide ratio shown in figure 5.5, it is seen that the ratio was increasing after 160 minutes of tracer release. This suggests that the methane emission rate was not constant during the measurement period.

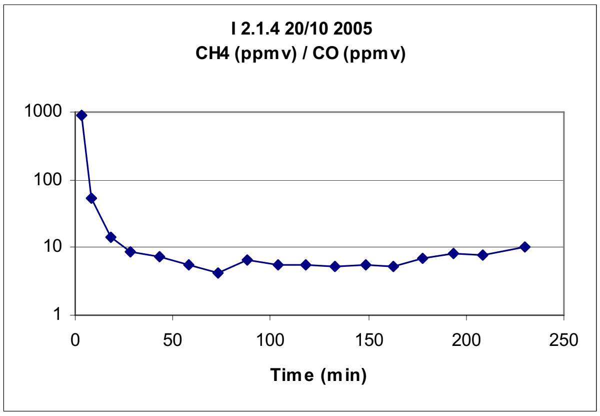

Figure 5.5. Methane to carbon monoxide ratio is plotted in ten minute intervals, so that each point was average values of ten minutes of measurement. Ratios were compensated for background concentrations in accordance to equation 2.

To calculate the methane emission rate the average concentrations of methane and carbon monoxide after breakthrough of tracer were used in equation 2 as well as background concentrations. This means that average values of emissions were given in each case, even though dynamics with regards to emission rates some times were observed as in the example. Methane emissions from ten leachate collection wells and the two pumping stations were measured twice on each location. The leachate wells measured were chosen so that all four categories as explained in section 6.1 were represented.

Table 5.5. Measured methane emission rates leachate wells and pumping stations. The tendency of the atmospheric pressure at time of each measurement is listed.

Location	Well category	Methane emission – 1st measurement (kg CH_4 d^{-1})	Pressure tendency	Methane emission – 2nd measurement (kg CH_4 d^{-1})	Pressure tendency
S 1.3	A	14.6	Oscillating	34.9	Oscillating
S 1.6	A	10.7	Rising	14.4	Oscillating
I 2.1.4	A	20.7	Falling	32.0	Oscillating
I 1.3	B	2.6	Oscillating	20.2	Oscillating
S 2.2.2	B	7.8	Falling	3 .1	Falling
S 2.4	B	0.51	Oscillating	2.7	Falling
S 1.5.1	C	0.19	Oscillating	b.d.l.	Oscillating
I 2.2.2	C	0.14	Falling	b.d.l.	Oscillating
I 1.5.1	D	0.06	Oscillating	0.39	Oscillating
I 2.7	D	0.03	Rising	b.d.l.	Rising
Pumping station south (P1)		0.07	Oscillating	0.74	Falling
Pumping station north (P2)		0.17	Oscillating	0.13	Falling

As seen in table 5.5 emission rates correlate well to the categorization based on methane concentration screenings. Emission rates observed from wells in category A were several orders of magnitude higher than emission rates from wells in categories C and D.

Difference between measurements on the same location was in some cases high. Notable differences were seen for well I1.3, which was in category B and I1.5.1, which was in category D. The first measured emission rate of I.3 was 2.6 kg CH_4/d, but the second measured rate was 20.2 kg CH_4/d, which by far was the highest rate seen of category B wells. The first measured rate of well I1.5.1 was 0.063 kg CH_4/d, and the second was 0.39 kg CH_4/d. In both cases the atmospheric pressure was not clearly either increasing or decreasing. The relatively high emission rate observed of I1.5.1 causes the average emission of category D wells to be higher than that of category C wells. If the value was to be disregarded, the average rate of category D wells will be 0.03 kg CH_4/d.

Well S1.3, which is in category A, was furthermore measured after a period of rising atmospheric pressure. The pressure went up steadily from app. 1004 hPa 12 hours before measurement to 1016 hPa during measurement. The rising pressure seemed in this case to have a strong effect on the emission rate of methane since the observed emission rate this time was 0.024 kg CH_4/d compared to an average emission at more stable conditions at 24.7 kg CH_4/d. A clear relationship between rise or fall of atmospheric pressure and emission rates cannot be established based on the measurements listed in table 5.5. To study the impact of pressure gradients, continuous measurement of the emission rates at one well over a longer period is necessary. However, the preliminary measurements made at well SI3 suggest that the emission from the leachate system may be highly dynamic and influenced by changes in atmospheric pressure.

Emission from the leachate pumping stations was measured to be low compared to the wells of categories A and B. The total emission of methane from each category is estimated by multiplying the average emission rates of the wells measured with the number of wells or leachate pumping stations assigned to each category.

Table 5.6. Attributing methane emissions to categories of leachate wells and to pumping stations.

Category	**Average emission per location (kg CH_4 d^{-1})**	**Number of locations in category**	**Total average emission from category (kg CH_4 d^{-1})**
A	21.2	5	106
B	6.2	16	99
C	0.05	7	0.4
D	0.12	41	4.9
Pumping stations	0.28	2	0.6
Total		**71**	**211**

Due to the large span of emission rates seen, nearly all of the methane emission occurs through category A and B wells even though they are outnumbered by wells of the remaining two categories. If the relatively high emission rate seen on one occasion of well I1.5.1 is disregarded as an outlier, the total emission through category D wells will be estimated at 1.4 kg CH_4/d. In all cases, the emissions through the category C and D wells were negligible.

Summary

Methane emission through the soil cover at the cells was screened by use of a portable FID measuring concentration of methane near the soil surface on the cells 1.3, 1.5.1 and 2.2.2. Results of the surface screening suggested that the emission through the soil cover was minimal, and mostly occurring on edges and slopes of the soil cover. Quantification of methane flux through the soil was done by use of two types of stationary flux chambers. Flux rates seen on the uncovered shredder cell where between -1.9 and 78 g CH_4 m^{-2} d^{-1}. Flux rates of the volatile organic compounds CFC-11, HCFC-21, and HCFC-31 where measured at between 0.002 and 0.006 g m^{-2} d^{-1}. Methane flux measurements as well as VOC-flux measurements on the two covered cells 1.3 and 2.2.2 where all below detection limit (< 0.1 g CH_4 m^{-2} d^{-1} and < 0.001 g VOC m^{-2} d^{-1}).

Methane emission through the leachate wells was done by use of a continuous tracer release method. Carbon monoxide was used as tracer gas, and measurements of tracer and methane were done using a photoacoustic detector and FID to measure CO and CH_4 respectively. The total emission rate through the leachate collection system at AV Miljø was found to be 211 kg CH_4 d^{-1}.

6. Gas production

To determine production of landfill gas both modeling and experimental methods were used. Methane production rates were needed in order to set up methane balances for the three cells 1.3, 1.5.1, and 2.2.2. Modeling was used to calculate methane production rates and methane potentials for the cells. Two bench scale laboratory experiments using waste samples from the cells were conducted to establish methane production rates and methane potentials respectively.

6.1 Modeling of gas production

Objective

Two gas production models were applied to estimate the production of landfill gas at the three cells 1.3, 1.5.1, and 2.2.2 at AV Miljø landfill in terms of production rates, and methane potentials. These were:

- GasSim version 1.52 by UK Environment Agency and Golder Associates (2004)
- Afvalzorg multi phase model by the Dutch waste management company Afvalzorg (1998)

Both models describe the waste degradation using first order kinetics and require waste input data on an annual basis. They are so-called multiphase models that operate with three grades of degradability of the biodegradable waste (slow, moderate and fast). Further details and comparison of the models can be found in Jacobs & Scharff (2005).

Input to gas production models

In order to use the two gas production models GasSim and Afvalzorg, the compositions of the accepted waste must be specified. The landfilled waste at AV Miljø Landfill falls within 43 categories as specified by the landfill management. Each of these categories must be "translated" to the waste categories used in the two gas production models.

The applied parameter values for the first order degradation rates were adopted from the default values in the two models as presented in Table 6.1 and were within the same range.

Table 6.1. Default first order decay rates and corresponding half lives in GasSim and Afvalzorg for slowly, moderately and rapidly biodegradable waste fractions. In GasSim the degradation rates varies within the stated range dependent on the water content of the fraction.

Decay rates	GasSim	Afvalzorg
Slow (k_1)	0.013-0.076 year^{-1} ($t_{\frac{1}{2}}$ = 9-53 years)	0.03 year^{-1} ($t_{\frac{1}{2}}$ = 23 years)
Moderate (k_2)	0.046-0.116 year^{-1} ($t_{\frac{1}{2}}$ = 6-15 years)	0.1 year^{-1} ($t_{\frac{1}{2}}$ = 7 years)
Rapid (k_3)	0.076-0.694 year^{-1} ($t_{\frac{1}{2}}$ = 1-9 years)	0.23 year^{-1} ($t_{\frac{1}{2}}$ = 3 years)

Waste amounts

The annual quantities of landfilled waste at cell 1.3, 1.5.1 and 2.2.2 is presented in Figure 6.1. These waste amounts neglects intermediately stored waste. Cell 1.3 and cell 2.2.2 received the main part of the waste within a 3-year-period, whereas cell 1.5.1 the waste was received over a longer period, with lower quantities each year. Detailed waste data for each cell can be seen in Appendix E.

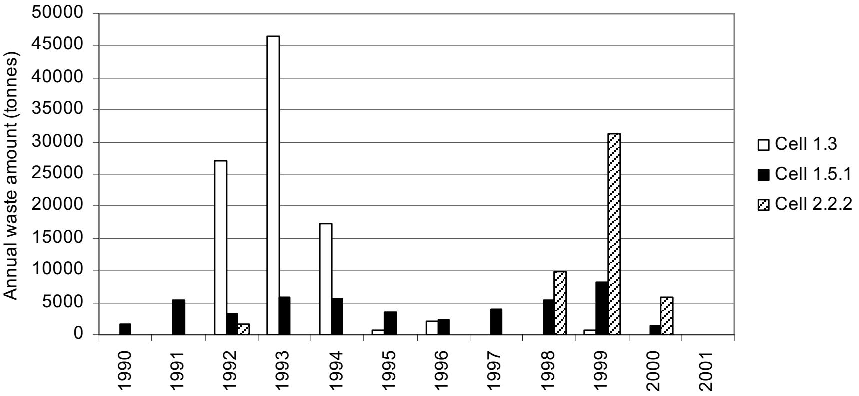

Figure 6.1. Annual waste amounts landfilled at cell 1.3, 1.5.1 and 2.2.2 at AV Miljø.

GasSim

In the GasSim simulations, the waste is divided into the following categories:

- Municipal solid waste (MSW)
- Sewage sludge
- Incinerator ash
- Combustible waste
- Shredder waste
- Inert waste

For each of these waste categories a division into waste fractions (paper, card, textiles, putrescibles, garden waste etc.) must be defined. Default compositions were available for the categories municipal solid waste, sewage sludge and incinerator ash, whereas the composition of the categories combustible waste and shredder waste needed to be defined. Furthermore, instead of using the predefined composition of MSW, a composition of Danish household waste from Christensen (1998) was applied.

The compositions of the six categories specified in content of the fractions paper/card, textiles, putrescibles etc. are presented in Table 6.2. Table 6.3 lists the default properties regarding water content and degradability of each fraction type as applied by the GasSim model.

Table 6.2. Fractionation of waste categories used in GasSim.

Waste fraction		**Composition of GasSim categories**					
		Household refuse [1]	Sewage sludge	Incinerator ash	Com-bustible [2]	Shredder waste[3]	Inert
		%	%	%		%	%
Paper/Card	Newspapers	7					
	Magazines	7					
	Other paper	10			5	2.7	
	Liquid cartons						
	Card	6					
	Other Card				5		
Textiles	Textiles				5	4.6	
Mis-cellaneous	Disposable	6					
	Other misc.						
Putrescible	Garden waste	4					
	Other	39			5		
Fines	10mm fines					25	
Sewage sludge	Sewage sludge		100				
	composted incinerator ash			100			
Non-degradable		24			80	67.7	100

1 Composition of household refuse was based on data from Danish household waste composition from Christensen (1998)

2 Composition of combustibles was estimated.

3 Compostion based on analysis of shredder waste composition from AV Miljø (2003).

Table 6.3. Default values for waste fractions in GasSim (UK Environment Agency and Golder Associates, GasSim manual).

Waste fraction		**Degrada-bility**	**Water content** %	**Cellulose content** %	**Hemicellu-lose content** %	**Decompo-sition[1]** %
Paper/Card	Newspapers	Slow	30	48.5	9	35
	Magazines	¼ Moderate ¾ Slow	30	42.3	9.4	46
	Other paper	¼ Moderate ¾ Slow	30	87.4	8.4	98
	Liquid cartons	¼ Moderate ¾ Slow	30	57.3	9.9	64
	Card	¼ Moderate ¾ Slow	30	57.3	9.9	64
	Other Card	¼ Moderate ¾ Slow	30	57.3	9.9	64
Textiles	Textiles	Slow	25	20	20	50
Miscellaneous	Disposable	Moderate	20	25	25	50
	Other misc.	Moderate	20	25	25	50
Putrescible	Garden waste	Rapid	65	25.7	13	62
	Other	Rapid	65	55.4	7.2	76
Fines	10mm fines	Rapid	40	25	25	50
Sewage sludge	Sewage sludge	Rapid	70	14	14	75
	Composted	Moderate	30	7.47	7.47	57
	incinerator ash	Rapid	30	0.5	0.5	57
Non-degradable	Non	-	0	0	0	0

1 Describes the dissimilable fraction of the cellulose+hemicellulose content.

Afvalzorg multi phase model

The Afvalzorg multi phase model includes 8 waste categories:

- Soil and decontaminating residues
- Construction and demolition waste
- Commercial waste
- Shredder waste
- Street cleansing
- MSW coarse
- Sludge and composting waste
- MSW

The existing categories were found adequate for description of the waste at AV Miljø; however it was not directly possible to define further waste categories for the Afvalzorg model. Table 6.4 presents the default composition of the Afvalzorg waste categories.

Table 6.4. Default composition of waste categories in Afvalzorg Multi Phase Model. The calculations were carried out using a minimum and a maximum value as represented by the given interval.

Waste category	Fast	Moderate	Slow	Inert	Organic matter content
		%	%	%	kg/tonne wet waste
Soil and soil decontaminating residues	0	4-6	14-18	76-82	40-42
Construction and demolition waste	0	14-18	28-34	48-58	44-46
Commercial waste	5-7	20	40	33-35	260-270
Shredder	0	10-15	30-35	50-60	60-70
Street cleansing waste	7-12	20-22	30-40	26-40	90-100
MSW coarse	5-7	15-18	40	35-40	260-270
Sludge and decomposting waste	5-7	25-28	30	35-40	150-160
MSW	20-22	25-28	15	35-40	300-320

Waste categories

The translation of the AV Miljø waste categories into GasSim and Afvalzorg categories respectively is in Appendix F. Some of the categories used at AV Miljø correspond well to the categories of the two models, whereas others were difficult to categorize. An example of this was industrial waste, since the composition of this waste type depends on the type of industry. Thus, the models do not have predefined compositions for this type of waste. Below, some comments on the categorization of the waste types were given:

Storaffald ("Bulky waste")

This category covers combustible waste. Due to a lower sorting efficiency earlier on, the landfill company expects that some household waste was contained in this waste type in the beginning of the 90s (AV Miljø, 2006). In GasSim, "Bulky waste" was represented by the waste category Combustible and in Afvalzorg, the category MSW coarse was used. A content of 10% household waste was assumed for the period 1992-1994.

Industrial waste

Three categories of industrial waste were found in the waste data from AV Miljø. The largest fraction of the industrial waste was of unspecified origin ("Industrial waste") and smaller quantities originate from "Past and rubber industry" and "Paper and graphical industry". The industrial waste was suspected to be a mixture of waste with a highly biodegradable content and of waste with a very low biodegradable content. Therefore it was placed in the category combustible in GasSim and divided equally between commercial waste and construction waste in Afvalzorg.

Shredder waste

The dominating waste type for cell 1.5.1 was automotive shredder residue. In GasSim the composition of this waste type was defined based on a composition analysis of shredder waste accepted at AV Miljø in 2003. In Afvalzorg, the predefined Shredder waste category was used.

Street sweepings

In Afvalzorg the existing Street sweepings category was used, whereas in GasSim street sweepings were assumed to consists of 50% combustible waste and 50% inert waste.

Harperest ("Screening residue")

This category covers a mixture of partly decomposed combustible waste and soil (AV Miljø, 2006). Thus, in GasSim 2/3 was assumed inert and 1/3 as combustible waste. In Afvalzorg 2/3 was categorized as soil and decontamination residues and 1/3 as MSW coarse.

Inert waste types

A number of waste types were not expected to contribute notably to the production of landfill gas and were categorized as inert:

- Sand from sandblowing
- Sand, industrial
- Fly ash from incineration plants and Residues from other incineration products (in GasSim, however, the category Incineration ash was used)
- Slag from incineration plants
- Other slag products
- Residues from dry/semidry cleaning processes
- Outsorted waste at recycling stations
- Contaminated soil (in Afvalzorg, however, the category Soil and decontaminating residues was used)
- Asphalt
- Construction waste (in Afvalzorg, however, the category Construction and demolition waste was used)
- Contaminated stones and bricks
- Landfill filling material (in Afvalzorg, however, the category Soil and decontaminating residues was used)
- Clay

Results

The production of landfill gas (LFG) was simulated using the gas production models GasSim and Afvalzorg. The resulting gas production at cell 1.3, 1.5.1 and 2.2.2 respectively in m^3 LFG per year is illustrated in figure 6.2.

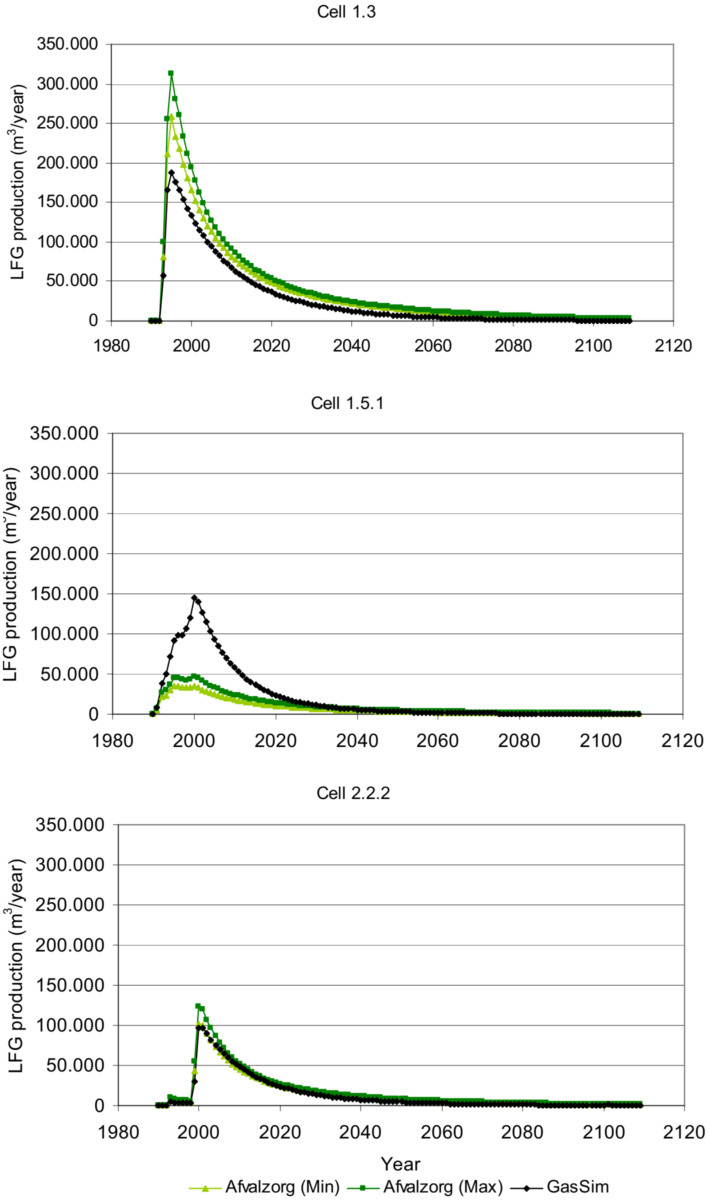

Figure 6.2. Model simulated production of landfill gas at cells 1.3, 1.5.1 and 2.2.2 at AV Miljø Landfill.

The results show, that the highest gas production was expected at cell 1.3. Overall, the agreement between the results obtained using the GasSim and the Afvalzorg model was fair. However, the result for cell 1.5.1 was an exception, since the GasSim result here was significantly higher than the Afvalzorg result.

Assuming a methane content of 50% (vol./vol.) the simulated gas production for 2005 and 2006 was converted to kg CH_4 produced per day. Results are listed in table 6.5.

Table 6.5. LFG production (m^3/year) and methane generation (kg/day) in 2005 and 2006. The Afvalzorg values are average values.

	LFG production (m^3 LFG/year)		**Methane generation (kg CH_4/day)**	
	Afvalzorg	GasSim	Afvalzorg	GasSim
Cell 1.3				
2005	120 000	94 000	117	92
2006	112 000	88 000	109	86
Cell 1.5.1				
2005	29 000	94 000	28	92
2006	27 000	85 000	27	84
Cell 2.2.2				
2005	73 000	70 000	71	69
2006	67 000	65 000	65	63

Another output of the models is methane potential, which is amount of methane expected to be produced from decomposition of the waste over a large timeframe. These are listed in table 6.6.

Table 6.6. Methane potentials, from start of deposit to 30 years after end of deposit, determined through use of the GasSim and Afvalzorg Multi Phase models.

Cell	**Methane potential GasSim** kg CH_4	**Methane potential Afvalzorg MIN** kg CH_4	**Methane potential Afvalzorg MAX** kg CH_4	**Average** kg CH_4
1.3	968 000	1 238 000	1 424 000	1210 000
1.5.1	592 000	256 000	334 000	394 000
2.2.2	457 000	466 000	538 000	487 000

6.2 Landfill gas production from sampled waste

Objective

The primary objective of this action was to measure methane production rates relative to amount of waste in a simulated landfill environment using waste sampled at AV Miljø. The production of landfill gas was studied over five months. A secondary objective was to study release and attenuation of VOCs. Waste sampled from the cells 1.3, 1.5.1, and 2.2.2 was used for the experiment.

Method

Waste sampling and experimental setup

Waste from three locations on each of the disposal cells were dug out yielding nine samples in all. These were stored in 218 L steel drums with airtight lids closed upon sampling. Samples were named “north”, “middle”, and “south” according to the relative location from where they were taken. Lids were fitted with sampling ports with Teflon covered septa for gas sampling and fittings for attachment of bags for collection of produced gas. Waste material was sampled from a depth between 1 and 1.5 meters below surface where anaerobic conditions before excavation were assumed. Large samples (75 to 188 kg) were taken in an effort to reduce sampling error caused by heterogeneity of the waste.

The samples were then transported to the laboratory and each drum was flushed with 0.5 m^3 nitrogen and sealed to reestablish anaerobic conditions in the waste material. Transportation to the laboratory and flushing with nitrogen was done the same day as sampling at AV Miljø. Figure 6.3 shows waste sampling at cell 1.5.1 and the experimental setup.

Figure 6.3. The top picture shows excavation of waste at cell 1.5.1 containing shredder waste AV Miljø. The bottom picture shows the experimental setup.

Gas sampling and analysis for production determination

The sealed drums were kept in the laboratory for a period of 140 days while monitoring gas production. Excess gas from the drums was collected in 5 liter or 20 liter SKC Tedlar sample bags. Gas samples were taken using a 5 mL syringe extracting gas from the headspace of each drum and injecting the gas into Labco Exetainer 5.9 mL evacuated glass vials fitted with pierceable rubber septa, which subsequently were measured for concentrations of main components (O_2, N_2, CH_4, and CO_2) on the MicroGC (see section 3) and VOCs on the GCMS (see section 3). Volume of excess gas from the drums were determined by timing the emptying of gas sample bags using a Fluid Metering Inc. laboratory pump set and tested at a constant flow rate of 0.5 L/min. The flow rate of the pump was tested approximately ten times during the experiment. Gas sampling was done 27 times in the period of the experiment, while measurements of excess volume were done 14 times. The first measurement of excess gas volume was done after the experiment had run 45 days due to an initial low production of gas, and since larger gas collection gas had been used initially. After 45 days gas volume was measured each time gas samples were taken.

Total amount gas produced or released start to end of the experiment (or any other period) was the amount of gas accumulated in the drums plus the gas removed when emptying the gas collection bags:

$$P = (C_{end} - C_{start}) \cdot V_d + \sum_{t=0}^{t} C_t \cdot V_{b,t} \qquad (3)$$

Where P is the production or release of the gas (L), C_{start} and C_{end} are concentrations of gas measured at the start and end of the experiment respectively (vol. %), V_d is the volume of headspace in the drum plus the air-filled pore volume in the sampled waste (L), C_t is the concentration at time t of each sampling (vol. %), and $V_{b,t}$ is the volume of excess gas removed from the system when sampling at time t (L).

V_d was calculated using measurements of concentrations of nitrogen, which was considered to be a conservative compound, and was thus not produced or consumed in the drums (P_{N2}=0). The amount of nitrogen lost from each drum can thereby be assumed to be equal to the amount removed when emptying the gas collection bags:

$$\begin{gathered} V_d \cdot \left(C_{N_2,start} - C_{N_2,end}\right) = \sum_{t=0}^{t} C_{N_2,t} \cdot V_{b,t} \\ \Updownarrow \\ V_d = \frac{\sum_{t=0}^{t} C_{N_2,t} \cdot V_{b,t}}{\left(C_{N_2,start} - C_{N_2,end}\right)} \end{gathered} \qquad (4)$$

Where $C_{N2,start}$ and $C_{N2,end}$ are nitrogen concentrations measured at the start and end of the experiment respectively (vol. %) and $C_{N2,t}$ is the concentration of nitrogen at the time of each sampling.

The mass of sample material was determined by weighing each drum containing sample and subtracting the weight of an empty drum. Table 6.7 lists mass of waste samples and calculated headspace and pore volumes in each drum (V_d).

Table 6.7. Waste mass and calculated headspace volume + pore volume (V_d) in each drum.

Waste sample	Waste mass (kg)	Gas volume - V_d (L)
1.3 south	188.0	105.8
1.3 middle	171.2	147.7
1.3 north	157.0	30.2
1.5.1 south	87.6	70.9
1.5.1 middle	82.0	59.7
1.5.1 north	75.1	102.0
2.2.2 south	149.5	47.2
2.2.2 middle	183.8	123.1
2.2.2 north	167.8	39.8

The relatively low masses of waste from cell 1.5.1 were due to the low density of this waste type.

Results

In all waste samples a lag phase was observed between start of the experiment until start of methane production. Methane concentrations were measured four times during the first ten days. On the tenth day methane production was observed in some of the waste samples. After the initial lag phase of low or no methane production, relatively constant production rates were seen.

As mentioned in the previous section, the procedure for measuring excess gas was changed after the experiment had run 45 days. This did seem to have an impact on the accuracy of the production measurements. Because of this, and to avoid any error caused by the initial lag phase of methane production, all production rates were calculated using data measured after 45 days. Accumulated methane productions observed are shown in figure 6.4.

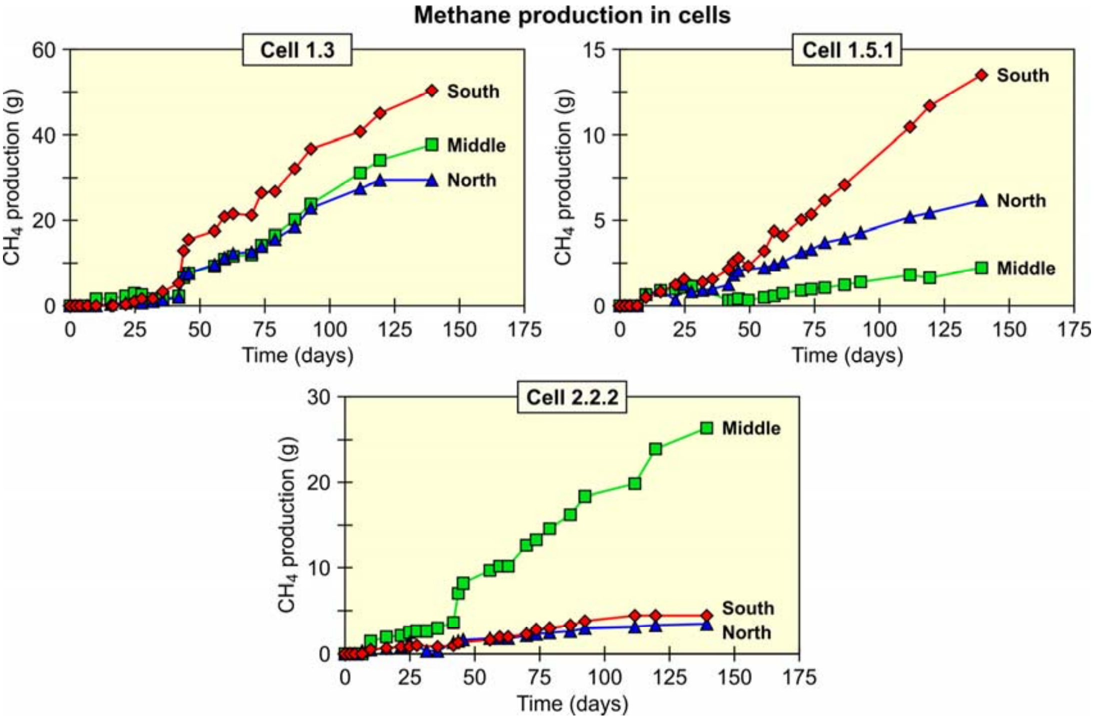

Figure 6.4. Accumulated methane productions measured of sampled waste from AV Miljø. Some outliers were discarded.

Using equation 3 and measurements of methane concentrations and excess gas volumes, methane production rates are calculated for each sample, and the rates are divided with the mass of each sample. This yields methane production rates relative to waste mass:

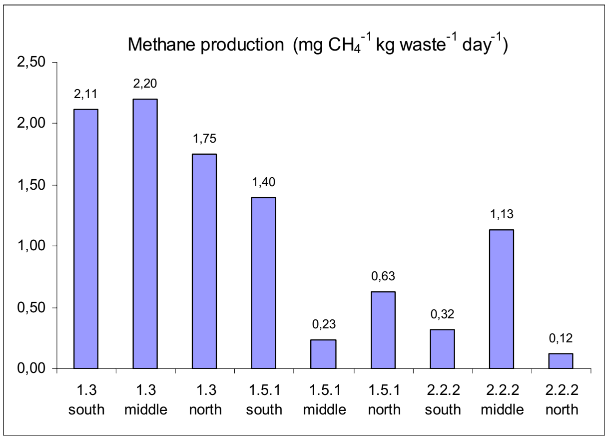

Figure 6.5. Observed methane production rates related to sample mass.

Compared to landfilled municipal solid waste, of which a production rate between 0.7 and 9.5 mg CH_4 kg waste^{-1} day^{-1} can be expected (El-Fadel et al., 1997), the production rates measured are low. As expected, the more inorganic waste types deposited in cells 1.5.1 and 2.2.2 produced less methane than waste from cell 1.3. The production rates relative to waste mass shown in figure 6.5 were seen to vary between samples taken at different locations at the same cells. This was likely due to heterogeneity of the waste deposited in the three cells with regards to content of degradable organic matter.

By multiplying average methane production rates with the total waste amount deposited known from records of waste deposited at the landfill, total methane production rates were estimated. These rates are listed in table 6.8. Waste amounts, and types of waste deposited in each cell are listed in Appendix E.

Table 6.8. Estimated methane production rates for the cells 1.3, 1.5.1, and 2.2.2.

Cell	**Average observed methane production rate (mg CH_4 kg waste^{-1} day^{-1})**	**Total amount of waste deposited (ton waste)**	**Total methane production rate (kg CH4 d^{-1})**
1.3	2.02	94 000	190
1.5.1	0.75	47 000	35
2.2.2	0.52	41 000	21

The results showed a much higher methane production of the mixed waste containing organic waste (cell 1.3). It was expected that the methane production in cell 1.3 was significantly higher than the methane production rates of the two other cells, due to a larger content of degradable organic matter.

The experimentally determined total methane production rates for the three test cells shown in table 6.8 can be compared to results of methane production modeling (table 6.5). For the cell containing shredder waste (1.5.1), the average experimentally determined total methane production (35 kg CH_4 d^{-1}) was seen to be much closer to the results of the Afvalzorg model (28 kg CH_4 d^{-1}) than the GasSim model (92 kg CH_4 d^{-1}). The average experimentally determined total methane production for cell 1.3 (190 kg CH_4 d^{-1}) was much higher than results from both models (92 to 117 kg CH_4 d^{-1}), whereas the measured production rate for cell 2.2.2 (21 kg CH_4 d^{-1}) was lower than the model results (69 to 71 kg CH_4 d^{-1}). These discrepancies can be explained by error caused by the "translation" of waste data into the models as described in section 6.1, and by heterogeneity of the waste causing average production rates measured from the sampled waste to differ from the average production at the three test cells.

Volatile organic compounds were seen in all samples. For CFC-12, HCFC-22, HFC-32, HFC-134a, HCFC-141b, HFC-41, and benzene the observed concentrations were in general low. High concentrations of toluene were seen in some cases. In one of the nine samples, concentration of toluene was measured at 400 μg/L at one point. The concentrations of toluene fluctuate so that the data cannot be used to calculate a release rate using equation 4. Higher concentrations of CFC-11 and its degradation products HCFC-21, and HCFC-31 were seen in samples from cell 1.5.1 containing shredder waste and from cell 2.2.2 containing mixed industrial waste

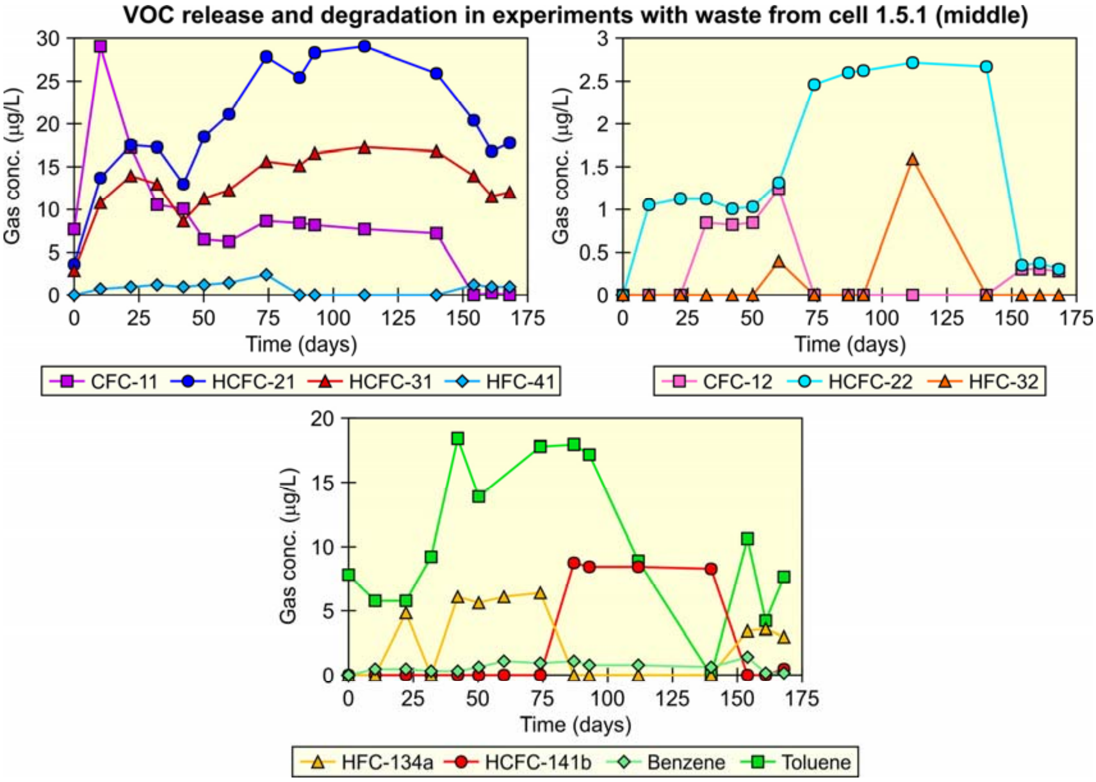

Figure 6.6. Concentrations of VOCs over time in the headspace of one of the drums with shredder waste (cell 1.5.1)

Generally the concentrations of CFC-11 were highest during the beginning of the experiment. In the example in figure 6.6 the concentration of CFC-11 was below detection limit after app. 70 days, which can be explained by anaerobic degradation of this compound (Scheutz & Kjeldsen, 2003). The presence of the compounds HCFC-21 and HCFC-31 was observed. They were likely to be produced by degradation of CFC-11, but were possibly degraded as well, which data plotted in figure 6.6 also suggest. It was also possible that sorbed HCFC-21 and HCFC-31 was released. Similar concentration levels were observed in the two other drums containing shredder waste. It was not possible to calculate production rates of any of the compounds, since removal of the compounds were observed.

VOCs were observed in drums containing other waste types. Figure 6.7 shows concentration of VOCs in the headspace over time of one of the drums containing waste from cell 2.2.2.

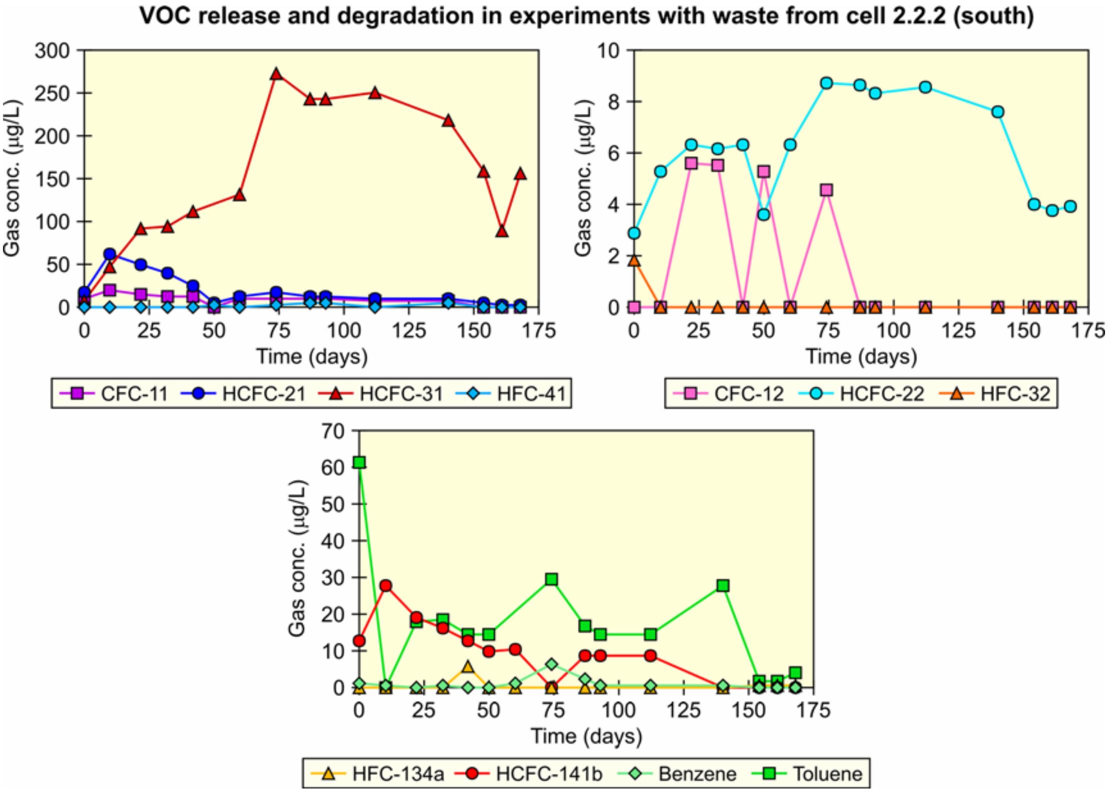

Figure 6.7. Concentrations of VOCs over time in the headspace of one of the drums containing waste material from cell 2.2.2.

As shown in figure 6.7, remarkable high concentrations of HCFC-31 were measured in this drum. Concentrations were much higher of HCFC-31 in this case than the rest of the samples from cell 1.3 and 2.2.2, where concentrations of CFC-11 and its degradation products HCFC-21, HCFC-31 and HFC-41 were in all cases below 20 µg/L, and most often below 10 µg/L. The decline of concentration of HCFC-31 after app. 100 days in 2.2.2 south suggests degradation of this compound. The seemingly high significance of degradation or other removal processes of the compounds made it impossible to calculate release rates directly using equation 3. The concentration of the compounds CFC-12, HCFC-22 and HFC-32 were in all drums from all cells always below 10 µg/L.

To measure release rates of CFC-11, a similar experiment was made where aerobic conditions were ensured to avoid degradation, which was also measured more frequently and over a shorter time period. This activity is described in section 8.1.

6.3 Methane gas potential

Objective

Methane potentials (i.e. how much methane will be produced in total), as well as production rates, were determined using modeling. Methane production rates were measured experimentally as described in section 4.1. To determine the methane *potentials* experimentally, a method described in Hansen et al. (2004) was applied using waste sampled from the cells 1.3, 1.5.1, and 2.2.2.

Method

The principle of this method to determine the methane potential is adding homogenized waste material to closed flasks containing biologically active biomass (inoculum) and an anaerobic headspace consisting of 80% nitrogen and 20% carbon dioxide. Methane formation over time is determined by extracting gas samples from the headspace of the flasks, and measuring the methane concentrations on a gas chromatograph.

Sampling and preparation of waste material

Waste material was sampled from nine locations at approximately one meter below surface. Sampling was done on the same day and at the locations as in the experiment described in section 7.2. Sample amounts of each of the nine samples were between 3.4 kg and 10.8 kg. Until measurement of methane potentials, the samples were stored in air tight containers at 4°C.

It was necessary to measure moisture content of the samples. This was done by drying sample material in aluminum trays in an oven set at 80 °C for 48 hours. Samples were weighed before and after drying. To reduce heterogeneity of the samples, the dried samples were crushed in a Retsch SM2000 cutter mill with a 2 mm sieve. The setup caused the particle size of all matter to be reduced to 2 mm or smaller. Prior to crushing, some material from each sample was removed. This was mainly stones, pieces of metal, wire. The removed material was considered inorganic, and not contributing to methane production.

Table 6.9 lists dry mass of waste samples, Moisture content of raw samples and the fraction of removed inorganic material.

Table 6.9. Dry mass, moisture content, and mass of removed inorganic material expressed in percent of dry mass of sample.

Cell	Dry mass (g)	Moisture content of raw sample (% w/w)	Removed inorganic material (% of dry mass)
1.3 total	17606	30.8	14.6
1.5.1 total	8058	31.6	4.3
2.2.2 total	18312	20.7	8.4

In one of the waste samples taken from cell 2.2.2, some tar-like material was removed, to be measured for methane potential separately, since this material caused operational problems when crushing the sample in the cutter mill. 1272 g tar-like material was removed from waste material from cell 2.2.2 out of a total dry mass of 18,312 g.

To produce one sample representing waste from each of the three cells 1.3, 1.5.1, and 2.2.2, 100 grams of crushed sample material from each of the “north”, “middle”, and “south” samples from each cells were mixed using a kitchen type hand mixer.

The end result of the sampling and sample preparation was three dry, crushed samples, each containing waste equally distributed between three sampling locations from AV Miljø. A separate sample containing the tar-like material from one of the locations at cell 2.2.2 was also to be used, leaving four samples in all to be measured for methane potential.

Experimental setup

An active inoculum from a thermophilic biogas plant primarily treating manure and running at 55 °C was used. Prior to use for the measurement, the inoculum was readapted by storing it in an oven set at 55 °C for three days. Two batches of inoculum from the same shipment were used.

For each of the four samples three sample amounts were used. This was done since if the sample amount was too high, there was a risk of inhibition of the inoculum caused by chemicals in the waste material. Conversely, if the sample amount was too low, it would not be possible to distinguish the methane production in the flasks containing inoculum only, which was necessary in order to calculate methane potential. All samples were prepared in triplicates. To evaluate the quality of inoculum, three flasks were prepared where 1.5 grams of cellulose was added, to test utilization of easily degradable matter by the inoculum.

Table 6.10. Overview of batch experiment. In all 45 flasks containing either inoculum and waste, inoculum only, or inoculum with cellulose and Avicel added were prepared.

	No sample	**1.5 g sample**	**5 g sample**	**15 g sample**	**Total**
Cell 1.3		3	3	3	9
Cell 1.5.1		3	3	3	9
Cell 2.2.2		3	3	3	9
"tar"		3	3	3	9
Inoculum only (batch A)	3				3
Inoculum only (batch B)	3				3
Inoculum and cellulose/Avicel mix	3				3
Total	9	12	12	12	45

Each 330 mL glass flask was prepared by adding 60 mL inoculum from a continually stirred container, which was constantly flushed with a mix of 80 vol. % nitrogen and 20 vol. % carbon dioxide. While flushing the flask with nitrogen and carbon dioxide, a weighed amount of sample was added plus 20 mL of demineralized water. Flushing with nitrogen and carbon dioxide was continued for approximately five minutes, before closing the flask with a rubber septum, and aluminum screw cap.

Measurements were done by first extracting 0.5 mL gas from the headspace using a glass syringe with a pressure lock. The pressure lock was closed before withdrawing the syringe from the headspace of the flasks, thereby taking a fixed volume of the sample at the pressure in the headspace at time of sampling. In this way the methane content in the headspace could be determined without measurement of gas pressure.

Measurement of methane content was performed using a Shimadzu GC 14A gas chromatograph with a thermal FID detector. Five gas standards with methane concentrations ranging from 100 ppmv to 100 vol. % methane were used to produce linear standard curves. For each analytical series, a 30 vol. % methane gas standard was measured.

In some of the flasks, excess pressure was relieved by inserting a hospital syringe needle through the rubber septa. This was done two times in some cases. Methane when relieving pressure was accounted for by measuring methane concentration in the headspace of the flasks before and after relieving pressure.

Results

To calculate methane potentials, methane production in flasks containing waste were to be compared to methane production in controls. This was done by measuring methane concentrations in the headspace of the flasks were done over 36 days, until the methane production had ceased. Figure 6.8 shows methane formation observed in the two sets of controls. A good correlation between triplicates was observed.

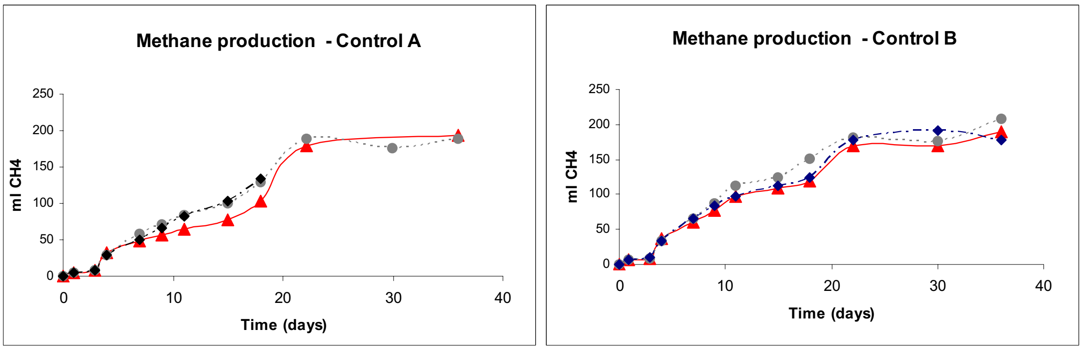

Figure 6.8. Methane production measured in the two sets of controls.

To calculate methane potentials, the surplus amount of methane produced in samples containing waste compared to samples containing inoculum only is considered. As mentioned, three amounts of waste material were added to the flasks. Figure 6.9 shows methane concentrations over time for the samples containing waste compared to the controls.

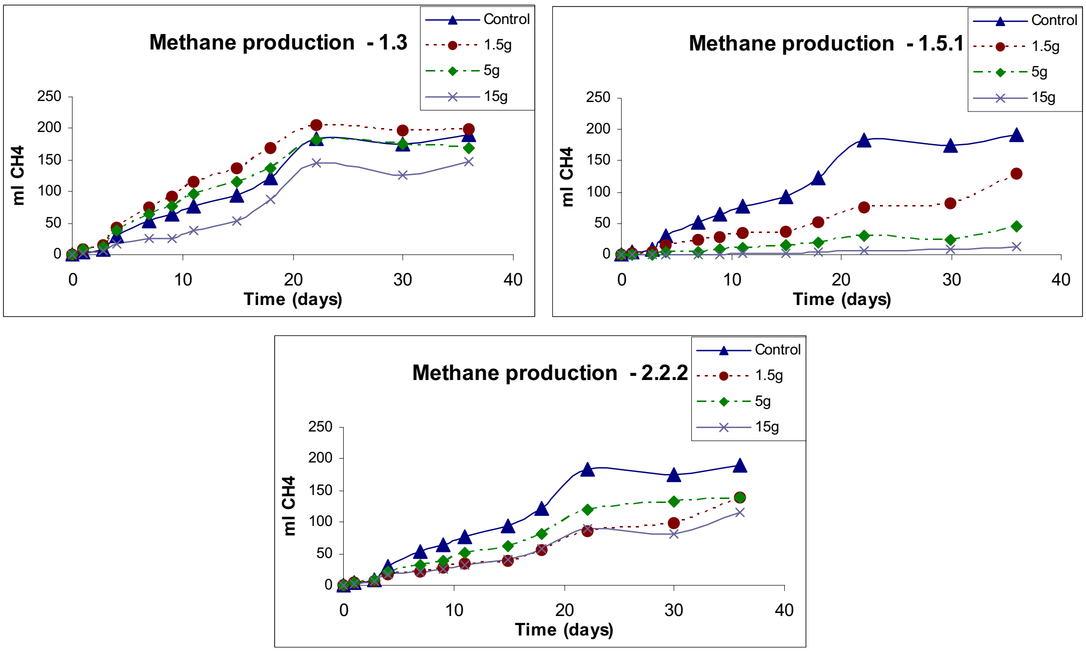

Figure 6.9. Methane production observed from waste samples. Each point is an average of triplicates. Three waste amounts were used.

Results plotted in figure 6.9 show that inhibition of the inoculum had occurred in nearly all samples, since the produced amount of methane is higher in the controls compared to the flasks containing waste samples. Inhibition is most clearly seen in the flasks containing shredder waste (cell 1.5.1), were the methane production decreases significantly with increasing waste mass added. Therefore it is concluded that this method could not be used to determine methane potentials of waste from cells 1.3, 1.5.1, and 2.2.2 experimentally.

Summary

Methane production and methane gas potential of the three cells 1.3, 1.5.1 and 2.2.2 were determined through use of the models GasSim model and Afvalzorg Multiphase Model. The calculated production rates for 2006 were 86 to 109 kg CH_4 d^{-1} (cell 1.3), 27 to 83 kg CH_4 d^{-1} (cell 1.5.1) and 63 to 65 kg CH_4 d^{-1} (cell 2.2.2). The calculated methane gas potentials set to be the production from start of deposit to 30 years after end were 1,210,000 kg CH_4 (cell 1.3), 394,000 kg CH_4 (cell 1.5.1) and 487,000 kg CH_4 (cell 2.2.2).

Methane production rates were also determined experimentally using waste sampled at the cells 1.3, 1.5.1 and 2.2.2. Methane production of the sampled waste stored in closed steel drums was observed over a period of 140 days. The observed methane production rates were 190 kg CH_4 d^{-1} (cell 1.3), 35 kg CH_4 d^{-1} (cell 1.5.1) and 21 kg CH_4 d^{-1} (cell 2.2.2). Discrepancy between methane production rates calculated using models to experimentally determined rates were likely due to error caused by the "translation" of waste data into the models as described in section 6.1, and by heterogeneity of the waste causing average production rates measured from the sampled waste to differ from the average production at the three test cells. VOCs were observed released from the waste materials, but it was not possible to calculate release rates.

A method to measure methane potentials experimentally using waste samples was applied, but it was found that the method could not be used successfully in this case.

7. Release and content of volatile organic compounds in shredder waste

Shredder waste deposited at AV Miljø contains polyurethane foam, which in turn potentially contains so-called blowing agents including chloroflourocarbons (CFCs). Analysis of gas sampled from cell 1.5.1 containing shredder waste did show presence of these compounds. The amount of foam materials from where these compounds originate, and the content and release rates of the VOCs were also not known. To determine release and content of volatile organic compounds in shredder waste, the three large samples of shredder waste used to measure gas production described in section 7.2 were reused. A note on polyurethane foam, its content of blowing agents, and disposal can be found in Appendix G.

7.1 Release of volatile organic compounds in shredder waste

Objective

The objective was to observe release rates of the volatile organic compounds (VOCs) CFC-11, HCFC-21, HCFC-31, HFC-41, CFC-12, HCFC-22, HFC-32, HFC-134a, HCFC-141b, benzene, and toluene. A slow continuous release of CFC-11 from polyurethane foam in the shredder waste was expected, which in turn for a large part is subject to anaerobic dechlorination in deposited waste as discussed in section 3.

Method

In the gas production experiment, CFC-11 was observed, but since this experiment was performed with the sample material stored in an anaerobic environment, release rates of CFC-11 could not be quantified due to anaerobic degradation of the compound. Scheutz et al. (2003) and the anaerobic VOC degradation batch experiments conducted during this project suggested that stoichiometric conversion of CFC-11 to the degradation products (HCFC-21, HCFC-31, and HFC-41) was not to be expected. A calculation of the release rate of CFC-11 using the observed production rates of the degradation products would thereby be highly uncertain. Therefore a similar experiment as described in section 7.2 was performed but modified to ensure aerobic conditions in the waste materials. When oxygen is present, degradation of CFC-11 is negligible in a relatively short timeframe (Scheutz et al., 2003).

After completing the gas production experiment, lids from the drums were removed allowing atmospheric air to diffuse into the waste material for more than a month. When initiating the aerobic experiment, waste sample was removed from each drum, and placed on a sheet of plastic for approximately two hours. Each drum was then fitted with a system to circulate air through the sample mass. Watson-Marlow peristaltic pumps were mounted on top of each lid with the pump axle penetrating through the lid. The gaps between each axle and the lid were less than 1 mm, and each gap was sealed using Glisseal^{TM} lubricating grease. Under each lid, two pump heads were attached to the pump axles and fitted with Watson Marlow silicone tubing with an internal diameter of 6.4 mm. The lids were fitted with Teflon covered silicone septa to for use to withdraw gas samples from the headspace. In the bottom of each drum, a 5 cm layer of gravel (2 cm) was placed to ensure a homogenous gas distribution. The waste material was replaced in the drums, and two stainless steel pipes (internal diameter = 6 mm, length = 71.5 cm) were inserted through the waste to the gravel layer, and the silicone tubes were connected to the steel pipes. Air from the headspace of each drum was thereby circulated through the waste material by pumping it to the gravel layer at the bottom. Upon initiating the experiment each drum were flushed with 1.75 m^3 of oxygen through the stainless steel pipes, and the lids were sealed, creating closed systems.

The gas circulation flow was measured at 0.35 L/min for each pump head. Since the gas volume of the drums varied, the retention times of the gas were 1.3, 1.7, and 2.4 hours for the samples labeled south, middle, and north respectively.

Gas samples from the headspace of each of the three drums were taken using a normal 5 mL syringe into 5 mL Exetainer^{TM} evacuated glass vials. Gas samples were taken immediately after sealing of each drum, and labeled with sample name (south, middle, or north) and date/time of sampling. Sampling was done four times each of the following three days and once on the fifth and sixth day after the drums had been sealed.

VOC concentrations were measured using the GC/MS analysis as described in section 3, and analysis for main components (O_2, N_2, CO_2, CH_4) was done using the MicroGC also described in section 3.

Results

When evaluating measurement data of the experiment a few assumptions were made: First it was assumed that the concentration of each gas component was even in the entire gas phase of each drum. Since gas was circulated through the waste with a relatively high flow rate, and the shredder waste has a high porosity, this is believed to be a viable assumption.

It was assumed that released CFC-11 was not degraded or lost from the systems. Degradation was unlikely to be significant, since CFC-11 is very stable in aerobic environments, which results of the aerobic batch experiments using shredder waste (see section 4) also show. Loss of CFC-11 from the system was evaluated by observing the development of N_2 concentration in the headspace. A significant increase of N_2, which was a conservative gas in this system, would indicate a leak and thereby exchange of gas to the outside of the system.

Release of VOC per kg of waste is calculated by the equation:

$$M_{VOC,t} = \frac{C_{VOC,t} * V_d}{M_{waste}} \qquad (5)$$

Where $M_{VOC,t}$ is the released amount of VOC at the time of sampling (µg), $C_{VOC,t}$ is the measured concentration of VOC measured in the headspace (µg/L), V_d is the measured air volume in the drum (L), and M_{waste} is the mass of the shredder waste in the drum (kg).

The release rate is evaluated by plotting released amount of VOC ($M_{VOC,t}$) as a function of time after start of the experiment.

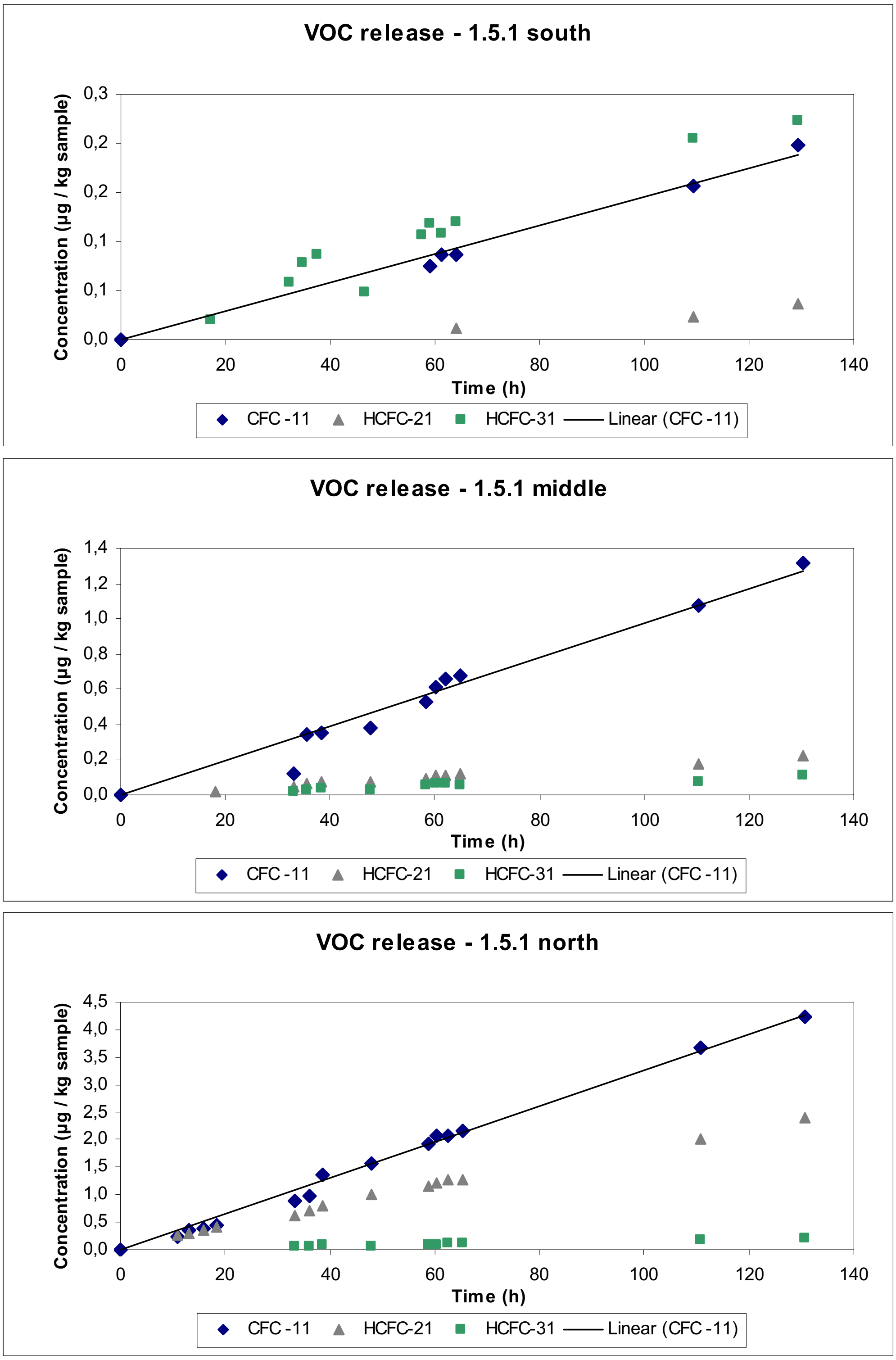

Figure 7.1. Development of measured VOC concentrations related to gas volume, and waste sample mass of each drum. Results of some measurements are omitted, where the concentration of VOC was below detection limit.

Results illustrated in figure 7.1 clearly show a steady and continuous release of the VOCs CFC-11, HCFC-21, and HCFC-31 from the shredder waste to the ambient air inside the drums within the sampling period. Using linear regression, release rates of the VOCs from the three waste samples were calculated. These are listed in table 7.1.

Table 7.1. Observed release rates of VOCs from the three drums containing shredder waste.

Sample label	**Observed release rate of CFC-11 μg CFC-11·kg waste^{-1} ·d^{-1}**	**Observed release rate of HCFC-21 μg CFC-11·kg waste^{-1} ·d^{-1}**	**Observed release rate of HCFC-31 μg CFC-11·kg waste^{-1} ·d^{-1}**
South	0.04	0.005	0.04
Middle	0.24	0.04	0.02
North	0.78	0.46	0.04
Average	0.35	0.17	0.03

Of the other VOCs analyzed for, benzene and toluene was observed at some measurements. Concentrations of benzene and toluene were not steadily increasing, and therefore release rates for these compounds could not be calculated. Release of the compounds HCFC-21 and HCFC-31 is probably attributed to sorption of the gasses in the waste mass prior to the experiment followed by release during the experiment, since the presence of these compounds, as described in section 3, is believed to be due to anaerobic degradation of CFC-11.

The observed release rates of CFC-11 related to waste mass in the samples are seen to vary. This could be due to varying amounts of CFC-11 in the foam, and varying mass fractions of foam in the samples.

The following section describes characterization of these samples, where content of PUR foam and VOC in the foam was done.

7.2 Content of polyurethane foam and volatile organic compounds in shredder waste

Objective

The main objectives were to determine the content of polyurethane (PUR) foam in shredder waste, and the content of the VOCs in the foam fraction. The size distribution of the foam particles was to be established as well as the content of VOCs in the different particle size fractions.

Method

Waste composition

The sampled shredder waste from each location was sorted by hand in order to quantify the content of PUR foam in each sample. Initially the waste was sieved through a 4 cm screen. A representative portion of the fine waste fraction (< 4 cm) was taken out using a sample divider device, which splits a waste stream into two "identical" waste streams of which one was kept and the other discarded. The kept waste stream was sent through the sample divider device again and this was repeated until the remaining waste amount was appropriate for hand sorting (2 - 5 kg).

The two fractions, "> 4 cm" and "< 4 cm" respectively were hand sorted into the waste types 1) PUR foam, 2) metal & wires and 3) other waste. PUR foam particles were distinguished from other materials by judgment of the color, structure and density. The waste fractions were then weighed. The PUR foam was left to dry for a week and brushed in order to remove the dirt on the surface of the particles before being weighed.

The out sorted PUR foam was subsequently screened through a set of screens with mesh sizes 32 mm, 16 mm and 8 mm in order to determine the size distribution of the foam particles.

Content of VOCs in the PUR foam

The content of CFC-11 and CFC-12 and the degradation products HCFC-21, HCFC-31, HFC-41, HCFC-22 and HFC-32 as well as HCFC-141b and HFC-134a in PUR foam from each site was determined using triplicates of samples from each size fraction. This was done using a heating method, which requires that the foam samples have a maximum thickness of 1 cm. Thus, before heating the foam, the 16R and 32R samples were cut up with a knife inside a glove box. The released amount of VOC during shredding was determined based on the increased air concentration within the glove box, which was monitored by taking air samples before and after shredding of the foam samples.

Three samples of 0.7-1.3 g was taken from each PUR fraction (4 size fractions from each site, giving a total of 36 samples) and transferred to 1125 mL glass bottles. The samples were heated in an oven for 48 hours at 140°C and cooled to room temperature before gas was withdrawn from the headspace and analyzed using gas chromatography (see section 1). Afterwards the bottles were flushed with atmospheric air and subjected to a second 48 hour heating step with subsequent analysis using gas chromatography. See further description of the heating method in Scheutz & Kjeldsen (2002).

Sample purity

Since the PUR foam was stained with dirt it was necessary to determine the purity of the samples in order to calculate the content of VOCs per mass of foam. This was done by determining the density of the samples and relating this to the density of pure PUR foam, which was found to be 27.6 g/L in Fredenslund et al. (2005). The density was determined for the exact same samples as was previously heated and analyzed for release of VOCs. The density was determined using a simple method as described in Fredenslund et al. (2005).

Results

Content of PUR foam in waste samples

The result of the hand sorting of the waste samples is shown in Table 7.2. Waste from the site 1.5.1 North contains the largest fraction of PUR foam (0.12% by weight), whereas the sample 1.5.1 Mid contains 0.06% PUR foam and 1.5.1 South contains 0.02% of PUR foam. The fraction of metal + wires ranges from 1.3% to 3.2% and is largest for 1.5.1 South.

Table 7.2. Content of PUR foam and metal & wires in the 3 waste samples. The purity of the PUR samples has been included in calculations. For the fine waste fraction (< 4 cm) the composition of the representative sample has been scaled up to apply for the total fine fraction.

	Weight of fraction (kg)			**Distribution (%)**		
	1.5.1 South	1.5.1 Mid	1.5.1 North	1.5.1 South	1.5.1 Mid	1.5.1 North
PUR foam	0.013	0.049	0.090	0.02	0.06	0.12
Metal & wires	2.84	1.03	1.44	3.2	1.3	1.9
Other waste	84.7	80.9	73.6	96.7	98.7	98.0
Total sample weight	*87.6*	*82.0*	*75.1*			

Size distribution and purity of foam samples

As expected, the purity of the foam samples increases with increasing particle size; i.e. the smallest size fraction (< 8 mm) only consists of 21-35 % PUR, whereas the largest fraction (> 32 mm) was found to consist of 53-69 % PUR. The adjusted size distribution of PUR particles from each sampling site shows very similar size distribution for 1.5.1 Mid and 1.5.1 North. With 16-32 mm and 8-16 mm being the dominating size fractions followed by < 8 mm and > 32 mm. For 1.5.1 South particles > 32 mm are the most frequent. Compared to the size distributions of shredded foam presented in Fredenslund et al. (2005) with 82-94% of the foam mass being larger than 16 mm, the foam particles in the present shredder waste are significantly smaller (only 47-50% of the foam mass is larger than 16mm). Table 7.3 lists the size distribution and measured purity of foam samples.

Table 7.3. Average purity of foam fractions and adjusted size distribution based on the purity of the fractions. The standard deviation (St. dev.) between the purity of the 3 samples from the same size fraction has been calculated.

1.5.1 "South"	**Size distribution (%)**	**Average purity of foam in fraction** (w(foam)/w(sample))	**St. dev.**	**Adjusted size distribution (%)**
>32 mm	24.0	0.53	0.11	35.1
16 - 32 mm	14.7	0.38	0.12	15.3
8 - 16 mm	32.6	0.37	0.04	33.4
< 8 mm	28.7	0.21	0.02	16.2
1.5.1 "Mid"				
>32 mm	5.7	0.62	0.09	7.7
16 - 32 mm	29.7	0.60	0.11	39.0
8 - 16 mm	35.4	0.48	0.02	36.8
< 8 mm	29.3	0.26	0.03	16.4
1.5.1. "North"				
>32 mm	7.2	0.69	0.07	10.3
16 - 32 mm	28.1	0.63	0.02	36.8
8 - 16 mm	40.2	0.42	0.12	35.0
< 8 mm	24.5	0.35	0.02	17.9
Average				
>32 mm		0.61		17.7
16 - 32 mm		0.54		30.4
8 - 16 mm		0.42		35.1
< 8 mm		0.27		16.9

Content of CFC-11 and other VOCs in PUR foams

The CFC-11 content was largest in the PUR particles from the sampling site “North” and was found to increase with increasing particle size. This was, however, not the case for the sampling site “South” where the largest particles (> 32 mm) only had very low CFC-contents. The results of the content of the other VOCs showed that significant amounts of HCFC-141b and HFC-134a were contained in some of the PUR fractions. This suggested that some of the foam particles had been expanded using not only CFC-11, but also HCFC-141b and HFC-134a.

The content of VOCs in each size fraction was measured on three different samples. The calculated standard deviations between the content of VOCs in these 3 replicates is quite high as seen in Appendix G. This inhomogeneity further suggests that shredder waste contained PUR foam with different blowing agents.

Only low concentrations of the degradation products HCFC-21 and HCFC-31 from dechlorination of CFC-11 were measured in the samples. The highest concentrations of these degradation products were generally found in samples with high CFC-11 content.

Besides the VOCs included in table 7.4, HFC-41, HCFC-22 and HFC-32 were also included in the analysis, but were not detected in the foam samples. The latter two are degradation products from the degradation of CFC-12, which was only detected in very low concentrations in the samples. The absence of HFC-41 in the foam samples indicates that no further dechlorination of the HCFCs has taken place. Appendix G lists the content of selected VOCs included in the analysis.

Table 7.4 summarizes the average VOC contents of PUR foam from the 3 sampling locations assuming that the results from the 3 sample replicates are representative for the total PUR content. The average CFC-11 content ranged from 0.4-1.2 g/kg foam with an average of 0.7 g/kg foam. This result was very low compared to the CFC-content of 150 g/kg foam in pre-shredded foam and 110 g/kg foam in post-shredded foam from refrigerators and freezers as reported by Fredenslund et al. (2005).

Table 7.4. Calculated average content of VOCs in shredder waste from the 3 sites 1.5.1 South, 1.5.1 Middle and 1.5.1 North based on the size distribution of foam for each site and the VOC content of each size fraction.

	Average content of CFC-11	**Average content of CFC-12**	**Average content of HCFC-21**	**Average content of HCFC-31**	**Average content of HCFC-141b**	**Average content of HFC-134a**
	(g/kg foam)	(g/kg foam)	(g/kg foam)	(g/kg foam)	(g/kg foam)	(g/kg foam)
1.5.1 "South"	0.36	0.0002	0.002	0.0004	0.2308	0.057
1.5.1 "Middle"	0.51	0.001	0.003	0	0.0001	0.006
1.5.1. "North"	1.23	0.00	0.004	0	0.0093	0.281
Average	0.70	0.0004	0.003	0.0002	0.080	0.115

The sampled shredder waste from cell 1.5.1 at the solid waste disposal site AV Miljø was assessed to be disposed of in 1999. Rigid PUR foam were identified and sorted from the shredder waste. The content of PUR foam in shredder waste sampled from 3 locations in the cell ranged from 0.02-0.12 % by weight. The source of PUR foam was most likely to be foam panels contained in shredded cars and caravans. The estimated life-time of these products is 15 years in average; therefore the majority of the auto waste discarded in 1999 was produced prior to the ban of CFC-11 from 1995. Due to large deviations in the CFC-11 content between foam samples of equal particle size and significant contents of the blowing agents HCFC-141b and HFC-134a it is possible that the PUR foam contained in the shredder waste had not solely been expanded using CFC-11.

The CFC-11 content in the PUR foam was found to be very low (0.4 to 1.2 g CFC-11/kg foam) compared to the content of 150 g CFC-11/kg foam found in refrigerator/freezer PUR foam panels prior to shredding. The results show a very significant loss of blowing agent from the foam. Whether the loss of blowing agent is mainly due to the shredding process or to the waste management at the landfill e.g. compaction of the waste, is unclear. The particle size distribution of the PUR particles contained in the waste reveals that a high portion of the particles is smaller than 16 mm. This indicates that loss of BA has occurred during the shredding process. It is furthermore possible, that a portion of the CFC-11 has been lost as a consequence of biological degradation taking place in the landfill. However, only low concentrations of the degradation products HCFC-21 and HCFC-31 from dechlorination of CFC-11 was detected in the foam.

The experiment described in section 7.1 yielded release rates in CFC-11 related to total mass of shredder waste in each of the three samples from cell 1.5.1. If the observed release rates were related to foam content *and* CFC-11 content measured in the foam, results were much more similar. In table 7.5 release rates of CFC-11 are converted into percent release of CFC-11 of the total content in the PUR foam in each sample per day.

Table 7.5. Observed release rates of CFC-11 from the three drums containing shredder waste, mass of PUR foam in each sample, average content of CFC-11 in the foam of each sample, and percentage of CFC-11 content in the foam sample emitted daily at the present rate.

Sample label	**Observed release rate of CFC-11 (µg CFC-11·kg waste^{-1} ·d^{-1})**	**Mass of foam in sample (kg foam·kg waste^{-1})**	**Observed release rate of CFC-11 (µg CFC-11·kg foam^{-1} ·d^{-1})**	**Average content of CFC-11 (g CFC-11·kg foam^{-1})**	**Percent of CFC-11 emitted per day**
South	0.04	0.132	0.27	0.36	0.076%
Middle	0.24	0.489	0.49	0.51	0.095%
North	0.78	0.903	0.87	1.23	0.070%
Average					0.080%

Since the release of CFC-11 given in terms of percentage of content emitted were quite similar, it is concluded that varying release rates in relation to waste mass seen were due to varying foam content (kg foam/kg shredder waste) and varying CFC-11 content in the foam (g CFC-11/kg foam).

Summary

Release rates and content of VOCs in shredder waste sampled from cell 1.5.1 were determined. Release rates were determined by keeping waste material (75 to 88 kg waste samples) aerobic in closed steel drums, which were flushed with O_2 and fitted with a system to circulate air through the waste material. 14 measurements of content of VOCs in the headspace of the steel drums over 140 hours using GC/MS showed steady continuous increasing concentrations of the VOCs; CFC-11, HCFC-21 and HCFC-31. Release rates between 0.005 and 0.78 µg kg waste^{-1} d^{-1} were observed.

Contents of PUR foam and size distributions of PUR foam particles were established through hand sorting of the shredder waste used to measure release rates of VOCs. Contents of VOCs in the PUR foam were determined using a heating method to drive out VOCs from foam samples into the headspace of glass bottles which were analysed for VOCs. Normalizing the release rates measured of CFC-11 to the content of CFC-11 found in PUR foam in the shredder waste, it was established that between 0.07 and 0.095% of CFC-11 is released per day.

8. Whole methane emission measurements with FTIR

Objective

An important part of the project was to quantify the whole methane emission from the disposal site. The very inhomogeneous surface gas emission from the site combined with several significant individual emission sources like the leachate collection system prevented using traditional flux chambers for emission measurements. Instead the whole methane emission from the disposal site was measured using a tracer technique, combining controlled tracer gas release from the landfill with time-resolved concentration measurements downwind the landfill using FTIR absorption spectroscopy (Galle et al., 2001; Samuelsson et al., 2005). A secondary objective was to estimate the emissions from different sections of the landfill.

Methodology

For quantification of the whole methane emission from the disposal site dynamic plume measurements were conducted in combination with a tracer-release. Knowing the tracer release rate, and measuring concentrations of methane and tracer downwind the site, the methane emission rate can be calculated. The method is illustrated in figure 8.1.

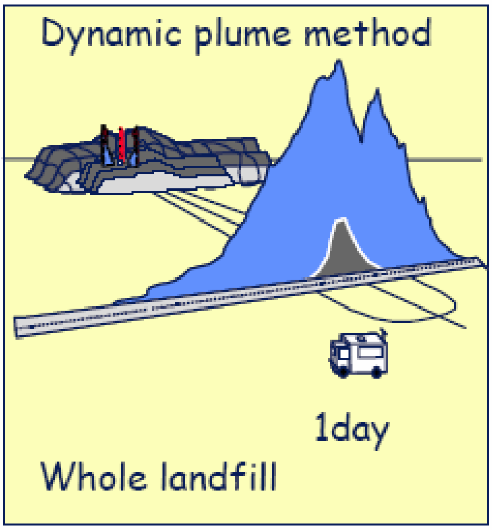

Figure 8.1. The dynamic plume method. Concentrations measurements of methane and tracer is conducted in the downwind plume along a transect perpendicular to the wind direction. By releasing a tracer on the landfill, meteorological measurements and modeling can be omitted increasing the accuracy of the method.

Concentration measurements of CH_4 and N_2O were made with a mobile FTIR instrument, operating with a time resolution of 21 seconds (Galle 2001, Samuelsson 2005). Initially the instrument was driven around the site to identify potential leak sources. In order to quantify the emission, tracer gas was released from the emitting areas, and the concentration ratio of the different gases relative to the emitted tracer was determined downwind the landfill. N_2O was used as tracer, pin-pointing different source areas. The release rate of the tracer was determined setting the tracer flow rate from each bottle with a two-stage regulator, clocking the release time, measuring the total weight of gas released with a precision scale, and also by integrating the number of liters released, as a backup. Figure 8.2a shows one of the N_2O tracer release units. As a result of the shape of the disposal site (long and relatively narrow), the wind direction and the emission pattern N_2O tracer was released from three points at the site. As the wind was coming from the south this approach would not only aloud quantification of the whole site methane emission, since the emission from individual waste sections could be differentiated as well.

Figure 8.2a.
N_2O tracer release unit, including gas bottle, two-stage regulator and volume integrator.

Figure 8.2b.
The mobile FTIR instrumentation.

Figure 8.2b shows the measuring van with the FTIR built in, sampling air continuously from the roof. The position of the van was logged with GPS.

On a high plateau in the centre of the landfill wind speed, wind direction, air and soil temperature were measured with a meteorological unit. Barometric pressure was measured in the van. The Field campaign was performed on the 9th of October 2006.

General leak search at the AV Miljø landfill

Initially to the release experiment a general leak search at the AV Miljø landfill was conducted with the main purpose to identify high emission areas for placement of the N_2O-tracer release bottles.

Figure 8.3 displays the result of a methane leak search over the AV Miljø landfill area on the 9th of October 2006. Presented values are the average concentration of methane in ppb during 21 seconds. Roughly, each plotted concentration dot represents the average concentration of the plume in the area halfway from the dot before, up to halfway to the next dot. The size and colour of the dot is related to the concentration, going from blue (clean) to red (max), as indicated by the colour scale. The lines emerging from the colour dots points up in the wind towards potential leak areas. Figure 8.4 displays an overview of the different cells at the landfill.

Three main source areas of methane were identified: Leachate collection well S1.3 at the southern part of cell 1.3, the area around cell 2.2.1, 2.1.1 and 2.2

(potentially partly from some leachate wells there), and finally area 2.1.4 and 2.2.2 (potentially partly from some leachate wells there).

Figure 8.3. Leak search of methane at the AV Miljø landfill area. Color scale and dot size indicate concentration of methane in ppb, sampled 2 m above ground. The scale is linear from 0 to 3417 ppb. The colored lines are pointing up in the wind, and thus indicate potential leak source area. The yellow hexagons indicate positions for the three tracer sources used in the emission quantification.

Figure 8.4. Map of the different cell areas at the AV Miljø landfill area. In the emission quantification, cell 1.1+1.1.1+1.2+1.3+1.4 are referred to as part A, cell 1.5+1.5.1+1.6+2.3+2.1.1+2.1+2.2+2.2.1 are referred to as part B, and the remaining cells 2.1.2A+B+C and 2.1.3+2.1.4+2.2.2+2.4+2.5+2.6+2.7 are clumped into part C.

Methane emission measurement results

Tracer experiment with N_2O-release from 3 point sources was conducted between 11:30 and 14:15 on the 9th of October. During the experiment the wind velocity was on average 4.9 m/s coming from the SSE (166˚). The weather was cloudy, and the air temperature was 17˚C. A small increase in atmospheric pressure (15 hPa) was measured during a 48 hour prior to the field campaign. An increase in atmospheric pressure would normally tend to lower the emission as atmospheric air is pushed into the cover soil of top of the waste. However, the small pressure increase observed before the field trial is not expected to influence the measured emission rates significantly.

One tracer was located near the leachate collection well at the southern border of cell 1.3, another tracer was put at the southeast corner of cell 2.1.1, and the third tracer was located centrally in cell 2.1.4 (c.f. figure 8.3). The overall tracer release rate was 6.1 kg N_2O per hour. The methane and tracer plume was traversed repeatedly on the road just north of the landfill, and also at about 500 m distance further north. Traversing the plume on the road just north of the site showed methane concentrations up to 300 ppb above background level. Both approaches gave similar results. Table 8.1 shows the resulting methane emission from each individual traverse. The derived methane emission was 33.1±7.8 kg h^{-1} corresponding to 793.3± 88 kg CH_4 d^{-1}.

Table 8.1. Methane emission measurement at AV Miljø.

Time (at centre of plume)	**CH_4 emission ($kg\ h^{-1}$)**	**CH_4 emission ($kg\ d^{-1}$)**
11:56	27.3	655.2
12:14	22.2	532.8
12:42	28.4	681.6
12:52	48.3	1159.2
13:02	37.5	900.0
13:37	29.5	708.0
13:46	30.9	741.6
13:53	43.4	1041.6
Average, close by measurement	*33.4*	*802.5*
STD	*8.9*	*212.3*
STD / Average	*26 %*	*26%*
12:03	37.6	902.4
13:10	32.0	768.0
13:27	26.5	636.0
Average, distant measurement	*32.0*	*768.8*
STD	*5.6*	*133.2*
STD / Average	*17%*	*17%*
Average, over all	***33.1***	***793.3***
STD	*7.8*	*188.0*
STD / Average	*24 %*	*24 %*

Dividing the methane and tracer plume into three parts, see Figure 8.4 and 8.5, it was estimated that about 20 % of the methane emission originated from part A (east), 44 % from part B (mid) and the remaining 36 % from part C (west). Figure 8.5 shows one of the plume traverses in the emission measurement, mapped onto an aerial photo of the landfill.

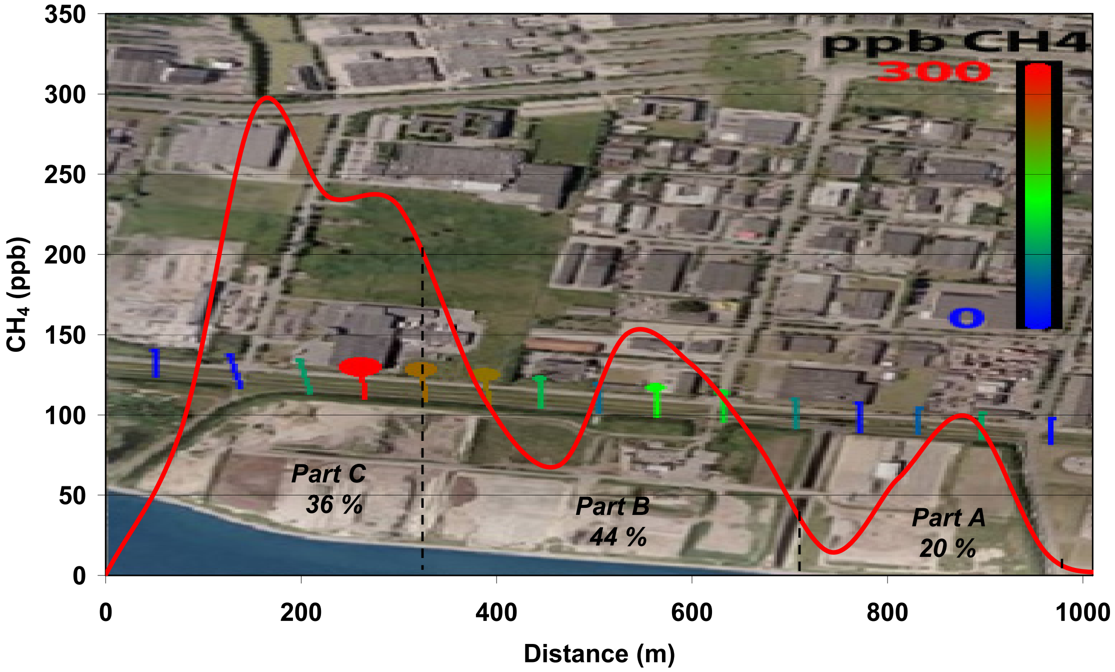

Figure 8.5. Methane plume traverse at the AV Miljø landfill 9th October 2006. Dot color scale and dot size indicate concentration of methane in ppb, sampled 2 m above ground. The scale is linear from 0 to 300 ppb. The colored lines originating from the dots are pointing up in the wind, and thus indicate potential leak source area. The red solid line corresponds to the left axis, and shows the plume cross section. The contributions from three different parts are indicated.

Summary

The whole methane emission from the disposal site was measured using a tracer technique, combining controlled tracer gas release (N_2O) from the landfill with time-resolved concentration measurements downwind the landfill using FTIR absorption spectroscopy. Initially to the release experiment a general leak search at the AV Miljø landfill was conducted with the main purpose to identify high emission areas fore placement of the N_2O-tracer release bottles. During this test three main source areas of methane were identified wherefrom tracer later was released. The overall tracer release rate was 6.1 kg N_2O per hour. Traversing the plume on the road just north of the site showed methane concentrations up to 300 ppb above background level. The whole methane emission was from the disposal site was measured to be 33.1 ± 7.8 kg CH_4 h^{-1}. Dividing the methane and tracer plume into three parts, it was estimated that about 20 % of the methane emission originated from part A (east), 44 % from part B (mid) and the remaining 36 % from part C (west).

9. Overall discussion; methane mass balances for the three individual cells; 1.3, 1.5.1, and 2.2.2 and the whole site

Objective

The following section will discuss and combine the results from the different investigations by setting up a methane mass balance for the three cells studied and the whole landfill. The following results are included in the discussion:

- gas composition and generation
- emission through surface and leachate collection system
- attenuation in top covers
- total methane emission from the disposal site

The total mass balance for the individual cells at AV Miljø is:

CH_4 Production = CH_4 Recovered + CH_4 Emitted through surfaces + CH_4 Emitted through leachate collection wells + CH_4 Oxidized + ΔCH_4 Storage (all units = mass t^{-1})

The production of methane depends on several factors: the landfilled waste volume, content of organic waste fractions and the degradability of these fractions, waste age and environmental factors (temperature, water content, nutrients, inhibiting compounds etc.). The LFG generation for the three individual cells has modelled using two different gas models based on information on waste volumes, ages and compositions often based on first order gas generation equations. Furthermore, the current gas production rate has been determined based on laboratory experiments.

Often methane is recovered from landfills by installing a gas extraction system in the landfill and utilizing the gas for energy purpose in a gas engine. However, at AV Miljø there is no gas extraction system, as the gas generation is expected to be relatively low. Surface screenings and field flux measurements have shown that a significant part of the generated gas is emitted through leachate extraction wells installed in the cells, whereas the surface emission is relatively low especially at the covered cells. The amount of methane oxidized in covers is difficult to quantify. Laboratory test as well as field data from AV Miljø indicates that a significant part of the methane might be oxidized at cell 1.5.1 containing shredder waste. Also at the two other cells the cover soil showed some capacity for methane oxidation.

Due to seasonal changes of cover permeability due to changes in water content, the gas pressure within the landfilled waste building up as a result of LFG production may vary. This result in temporary storage of methane in the landfill during permeability decrease, and may result in temporary higher emissions during permeability decrease. Changes in barometric pressure may lead to similar processes on a much shorter time frame. Since the filling height is only 7 m and as a significant part of the methane is emitted through the leachate collection system pressure build up and thereby methane storage is expected to be insignificant on a longer time frame in the three investigated cells at AV Miljø. On a shorter time frame changes in barometric pressure can have an impact on the gas emission through the leachate collections system.

Results

The gas generated in the investigated waste cells showed very different compositions, as the gas generated in the cell with mixed combustible waste consisted of mainly CH_4 (70%) and CO_2 (29%) in opposition to the composition of the gas generated within the shredder waste, which primarily consisted of CH_4 (27%) and N_2 (71%), containing no CO_2. However, the results indicate that methane is produced within the waste in all three cells. Quantification of the gas production in the three individual cells was determined by modelling and by laboratory experiments (c.f. section 6.1 and 6.2). Table 9.1 shows the obtained gas production rates based on laboratory experiments whereas table 9.2 shows the production rates modeled for 2006 using two different gas generation models.

Table 9.1. Methane production rates for the cells 1.3, 1.5.1, and 2.2.2 determined experimentally.

Cell	**Average observed methane production rate**	**Total amount of waste deposited**	**Total methane production rate**	
	mg CH_4 kg waste^{-1} day^{-1}	tons waste	g CH_4 d^{-1}	kg CH_4 d^{-1}
1.3	2.02	94 000	190034	190
1.5.1	0.75	47 000	35432	35
2.2.2	0.52	41 000	21484	21

Table 9.2. Calculated methane production rates for the cells 1.3, 1.5.1, and 2.2.2 using models.

Cell	**Methane generation (kg CH_4/day)**	
	Afvalzorg	GasSim
1.3	109	86
1.5.1	27	83
2.2.2	65	63

An initial screening showed that all surface methane concentrations were below 1.7 ppm except for a few hotspots primarily along fences and on slopes. This was confirmed by flux chamber measurements, which showed that the surface emission in general was below detection (< 0.1 g m^{-2} d^{-1}) and limited to a few hot spots exhibiting high methane fluxes (up to 78 g m^{-2} d^{-1}). At covered cells, the low surface emission is due to the very low gas permeability of the cover material, whereas at the un-covered cells with shredder waste a significant part of the methane is oxidized in the top layer of the waste before being emitted into the atmosphere, which is most likely due to the high gas diffusivity of the shredder waste allowing oxygen transportation into the shredder material and thus supports methane oxidation. To estimate the emission through the surface of the three cells it is assumed that hot spots with high emission take up 1% of the surface area at cell 1.3 and cell 2.2.2. At the cell with shredder waste hot spots are assumed to make up 5% of the area, mainly a result of that the cell is uncovered. Table 9.3 shows the estimated amount of methane emitted through the surface of the cells.

Table 9.3. Estimation of the total amount of methane emitted through cell surfaces.

Cell	**Total area**	**Estimated hotspot area**	**Estimated hotspot area**	**Maximum measured surface emission rate**	**Total amount of methane emitted through cell surfaces**
		%	m^2	g CH_4 m^2 d^{-1}	g CH_4 d^{-1}
1.3	28420	1%	284	0.01	3
1.5.1	8748	5%	437	23.00	10060
2.2.2	12227	1%	122	0.04	5

The initial surface screening of leachate collection wells showed very high methane concentrations (up to 26,000 ppm) indicating that a part of the generated gas migrates through the leachate collection system and emits through the leachate collection/inspection wells. The emission from the leachate collecting wells at the three cells was determined by using a continuous tracer release method. Table 9.4 list the amount of methane emitted from the leachate collection wells in connection with the three cells. The estimated emission is based on average rates measured from the individual wells (c.f. section 5.3). The total amount of methane emitted from the two leachate wells at cell 2.2.2 is measured to be 2.41 kg CH_4/d.

Table 9.4. Estimation of the total amount of methane emitted through leachate collection wells at the three cells.

Cell	**Wells**	**Well category**	**Average methane emission from each well**	**Total amount of methane emission from each cell**
			kg CH_4/d	kg CH_4/d
1.3	S1.3	A	21.2	27.57
	I1.3	B	6.2	
	B1.31	D	0.12	
1.5.1	S1.5.1	C	0.05	0.22
	I1.5.1	D	0.12	
	B1.2.1	C	0.05	
2.2.2	S2.2.2	B	6.2	12.45
	I2.2.2	C	0.05	
	B2.5	B	6.2	

The total methane mass balances from each individual cell are shown in table 9.5. The highest methane production rate is seen in cell 1.3, which is also expected as the cell contains combustible waste with a higher organic content in comparison with the other two cells. At cell 1.3 and 2.2.2, between 15% to 67% of the methane generated is emitted through the leachate wells, which most likely is due to the relatively impermeable covers in place at these two cells preventing gas migration through the soil covers. Instead the gas is migrating through the leachate drainage systems and collection wells. At cell 1.5.1 the methane emission through the leachate system is low due to the high permeability of the shredder waste. Instead the gas is emitted through the waste resulting in some hotspot observations on the shredder surface with higher emission rates.

For each cell the amount of methane that is not accounted for in the investigations is calculated. This amount of methane can potentially be oxidized in the cover soils or in the top of the shredder waste. In order to compare whether this is likely, the depth integrated methane oxidation rate for the three cells are shown in table 9.5. The highest methane oxidation capacity was found for cell 1.3 and 1.5.1, which gave a depth integrated methane oxidation capacity of 108 and 101 g m^{-2} d^{-1} respectively. In comparison the capacity for cell 2.2.2 was much lower; 10 g m^{-2} d^{-1}. The oxidation capacity is significant larger (factor 10-30) than the amount of methane that is not accounted for, suggesting that the methane that is not emitted through leachate collection and water drainage wells or cracks in the cover could be oxidized before emitted to the atmosphere. Even if the highest methane production based on the gas generation models are used this does not change the results. If the methane is not oxidized in cover layers, it is possible that the gas is transported through the leachate collection system to other cells where is it then emitted from collections wells or drainage pipes placed in permeable gravel layers in the bottom of the cells.

Table 9.5. Total methane mass balances from each individual cell. Last column lists the depth integrated methane oxidation rate based on batch experiments (c.f. section 4).

	Production	**Emitted**			**Potentially oxidized**		
Cell	**Total methane production rate**	**Through wells**	**Through cover**	**Through water drainage wells**	**Amount of methane that is not accounted for**		**Depth integrated methane oxidation rate**
	kg CH_4 d^{-1}	kg CH_4 d^{-1}	kg CH_4 d^{-1}	kg CH_4 d^{-1}	kg CH_4 d^{-1}	g m^2 d^{-2}	g m^2 d^{-2}
1.3	190	28	0	0	163	6	108
1.5.1	35	0	10	0	25	3	101
2.2.2	21	12	0	2	7	1	10

It is not possible to make a methane mass balance for the whole site as modeling of the gas production for the various cells was not included in the project and therefore is unknown. Due to the very variable activities at the sites; were waste is often is moved around on site or going out of the site due to excavation of temporary storages, measurements of surface emissions using flux chambers would not be possible.

The whole methane emission from the site was measured using dynamic plume measurements combined with a tracer release. The whole methane emission was from the disposal site was found to be 793 ± 188 kg CH_4 d^{-1}. Dividing the methane and tracer plume into three parts, it was estimated that about 20 % of the methane emission originated from part A (east), 44 % from part B (mid) and the remaining 36 % from part C (west). In comparison AV Miljø has in their green accounting estimated the total methane emission for 2006 to 96495 m^3 CH_4 corresponding to 182 kg CH_4 d^{-1}, which is only approximately ¼ of the amount of methane emitted from the site determined by the tracer method. During the October 9th, the day the whole methane emission was measured; a sludge pit located in cell 1.6 in the center of the disposal site was emptied and the sludge was stored in a windrow close to the sludge pit. It is possible that a part of the methane emission measured this day originates from emptying the sludge pit. Subtracting the methane emission from part B of the disposal site (44%) results in a whole methane emission of 444 kg CH_4 d^{-1}, which is twice the amount of methane emission listed in AV Miljø's green accounting.

The total emission rate through the leachate collection system at AV Miljø was found to be 211 kg CH_4 d^{-1}. This show that approximately ¼ of the gas is emitted through the leachate collections system making the leachate collection system an important source controlling the overall gas emission from the site. At cells covered with an impermeable cover as on cell 1.3 and 2.2.2, the gas emission through the leachate collection system might be even more important. The emission pathway for the remaining part of the gas is more uncertain. It is most likely that the gas is emitted from open cells where waste is being disposed of or being excavated for incineration. Also from an open sludge pit on site, a significant gas production end emission could be expected. It is also possible that gas generated within specific waste filled cells migrates through the leachate system and emits through the horizontal leachate drainage pipes placed in permeable gravel layers in the bottom of other cells without waste. If the later is the case, the surface from where gas can be emitted can be rather large.

Summary

Setting up total methane mass balances from three individual cells showed that a significant part (between 15% to 67%) of the methane generated in cell 1.3 and 2.2.2 is emitted through leachate wells, as a result of the relatively impermeable covers in place at these two cells preventing vertical migration of the gas. At cell 1.5.1, the methane emission through the leachate system is low due to the high permeability of the shredder waste. Instead the gas is emitted through the waste resulting in some hotspot observations on the shredder surface with higher emission rates. The remaining gas that is not emitted through surfaces or the leachate collection system could potentially be oxidized as the measured oxidation capacity exceeds the emission rate.

The whole methane emission was from the disposal site was found to be 793 ± 188 kg CH_4 d^{-1}. The total emission rate through the leachate collection system at AV Miljø was found to be 211 kg CH_4 d^{-1}. This show that approximately ¼ of the emitted gas is emitted through the leachate collections system making the leachate collection system an important source controlling the overall gas migration from the site. The emission pathway for the remaining part of the gas is more uncertain, but emission from open cells where waste is being disposed of or being excavated for incineration, or from horizontal leachate drainage pipes placed in permeable gravel layers in the bottom of empty is likely.

10. Conclusion

Based on the results obtained in the project the following overall conclusions can be made:

- Overall the gas analyses of the main components indicate that landfill gas containing methane is produced in all three cells investigated in this study. However, the gas generated in the investigated waste cells showed very different compositions, as the gas generated in the cell with mixed combustible waste consisted of mainly CH_4 (70%) and CO_2 (29%) in opposition to the composition of the gas generated within the shredder waste, which primarily consisted of CH_4 (27%) and N_2 (71%), containing no CO_2. The results indicate that the gas composition in the shredder waste is governed by chemical reactions rather than microbial reactions.
- The gas generated contained different VOCs in concentrations up to 50 μg/L. The presence of HCFC-21 and HCFC-31 indicated that anaerobic degradation of CFC-11 is occurring, since neither of these compounds has been produced for industrial applications.
- Gas profiles from the cell with shredder waste showed an oxidation zone of 40 cm below the surface with significant methane oxidation. This was supported by incubation experiments with shredder material, which showed a high potential of methane oxidation in the upper 40 cm of the shredder waste. The gas composition in the deeper part of the profile (below 60 cm depth) resembled the gas composition based on the deeper gas probes placed 2.5 m into the waste. The VOC gas profiles showed that anaerobic dechlorination of both CFC-11 and CFC-12 led to generation of degradation products like HCFC-21, HCFC-31 and HCFC-22. The gas profiles from cell 1.3 and 2.2.2 showed a similar composition to atmospheric air indicating that landfill gas generated in the two cells is not emitted through the cover or is being oxidized in the lower part of the cover. Methane and VOC oxidation in the lower part of the covers are possible as methane incubation experiments showed a tendency to increasing oxidation rates with increasing cover depth.
- The surface methane and VOC emission from all three cells was very low and limited to a few hot spots on slopes, edges, and around leachate collection wells. The low emission was due to placement of a low permeable clay cover at two of the cells. At the cell with shredder waste, the waste showed a very high methane and VOC oxidation capacity reducing the surface emission from the cell.
- However, a significant amount of the gas was emitted through the leachate collection system. Mass balances for the two covered cells 1.3 and 2.2.2 indicate that up to 67% of the generated gas is emitted through leachate collection wells.
- Methane production and methane gas potential of the three cells 1.3, 1.5.1 and 2.2.2 were determined through use of the models GasSim model and Afvalzorg Multiphase Model. The calculated production rates for 2006 were 86 to 109 kg $CH_4\ d^{-1}$ (cell 1.3), 27 to 83 kg $CH_4\ d^{-1}$ (cell 1.5.1) and 63 to 65 kg $CH_4\ d^{-1}$ (cell 2.2.2). The calculated methane gas potentials set to be the

production from start of deposit to 30 years after end were 1,210,000 kg CH_4 (cell 1.3), 394,000 kg CH_4 (cell 1.5.1) and 487,000 kg CH_4 (cell 2.2.2).

- Methane production rates were also determined experimentally using waste sampled at the cells 1.3, 1.5.1 and 2.2.2. The observed methane production rates were 2.02 kg CH_4 kg waste^{-1} d^{-1} (cell 1.3), 0.75 kg CH_4 kg waste^{-1} d^{-1} (cell 1.5.1), and 0.52 kg CH_4 kg waste^{-1} d^{-1} (cell 2.2.2). By multiplying average methane production rates with the total waste amount deposited known from records of waste deposited at the landfill, total methane production rates were estimated to190 kg CH_4 d^{-1} (cell 1.3), 35 kg CH_4 d^{-1} (cell 1.5.1) and 21 kg CH_4 d^{-1} (cell 2.2.2).
- The whole methane emission was from the disposal site was found to be 793 ± 188 kg CH_4 d^{-1}. The total emission rate through the leachate collection system at AV Miljø was found to be 211 kg CH_4 d^{-1}. This show that approximately ¼ of the emitted gas is emitted through the leachate collections system making the leachate collection system an important source controlling the overall gas migration from the site. The emission pathway for the remaining part of the gas is more uncertain, but emission from open cells where waste is being disposed of or being excavated for incineration, or from horizontal leachate drainage pipes placed in permeable gravel layers in the bottom of empty is likely.

11. Perspectives and further research needs

The presented studies have revealed that gaseous emissions from the AV Miljø landfill occur both including methane and other VOCs. Especially the methane emission seems to be significant while the VOC emissions are of minor importance. Overall, there is a need for further detailed studies of the methane emission and the spatial patterns as well as means of mitigating the emitted methane. It would be worth while considering the following possible future investigations:

- *Whole methane emission measurements.* The presented tracer method for measuring the total methane emission from the whole landfill site was successful, but was only performed once. Measurement campaigns – about four in total - could be carried out at different seasons using the tracer method. The campaigns should be performed at stable weather conditions to ensure representative conditions.

- *Spatial methane emission patterns.* The studies showed that methane emission through the leachate wells was a significant route, while emission through the cover soil was insignificant due to low gas permeability of the used cover soil. A comparison of the estimated gas production on the studied landfill cells with the amount released through leachate wells located at the cell, indicates that a considerable fraction of the gas produced may be redistributed to other cells through the inter-connected leachate collection system. In open cells gas may easily escape the leachate collection drains which are only covered by a thin layer of gravel. Methane emission measurements on the open cells have, however, not been included in the reported studies. Besides, the methane generation in cells containing temporary landfilled combustible waste has neither been evaluated. Information on the spatial methane emission patterns is crucial if methane emission mitigation is to be performed at the AV Miljø landfill.

- *Methane emission mitigation.* The performed study indicates that the landfill produces significant volumes of landfill gas, which are emitted to the atmosphere. If the emission patterns are fully understood the uncontrolled emission can be avoided by closing the uncontrolled emission routes and construct permeable biowindows in the cover soils where the produced landfill gas will escape instead. By replacing the low permeable cover soil in the biowindow areas with mature compost, passive biofilters are created where the methane will be oxidized to carbon dioxide.

- *Landfill gas production processes in shredder waste*. Shredder waste constitutes a significant fraction of waste received at the AV Miljø landfill. The gas produced at the shredder waste cells contains no carbon dioxide. It is hypothesized that coupled chemical/microbial processes are the reason for the unexpected gas composition, where the metal content of the shredder waste plays an important role. However, research investigating the hypothesis has not been carried out.

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13. List of appendices

Appendix A Leachate drainage system

Appendix B Atmospheric pressures at field campaigns

Appendix C Surface screening of methane concentrations

Appendix D Methane concentration in leachate wells

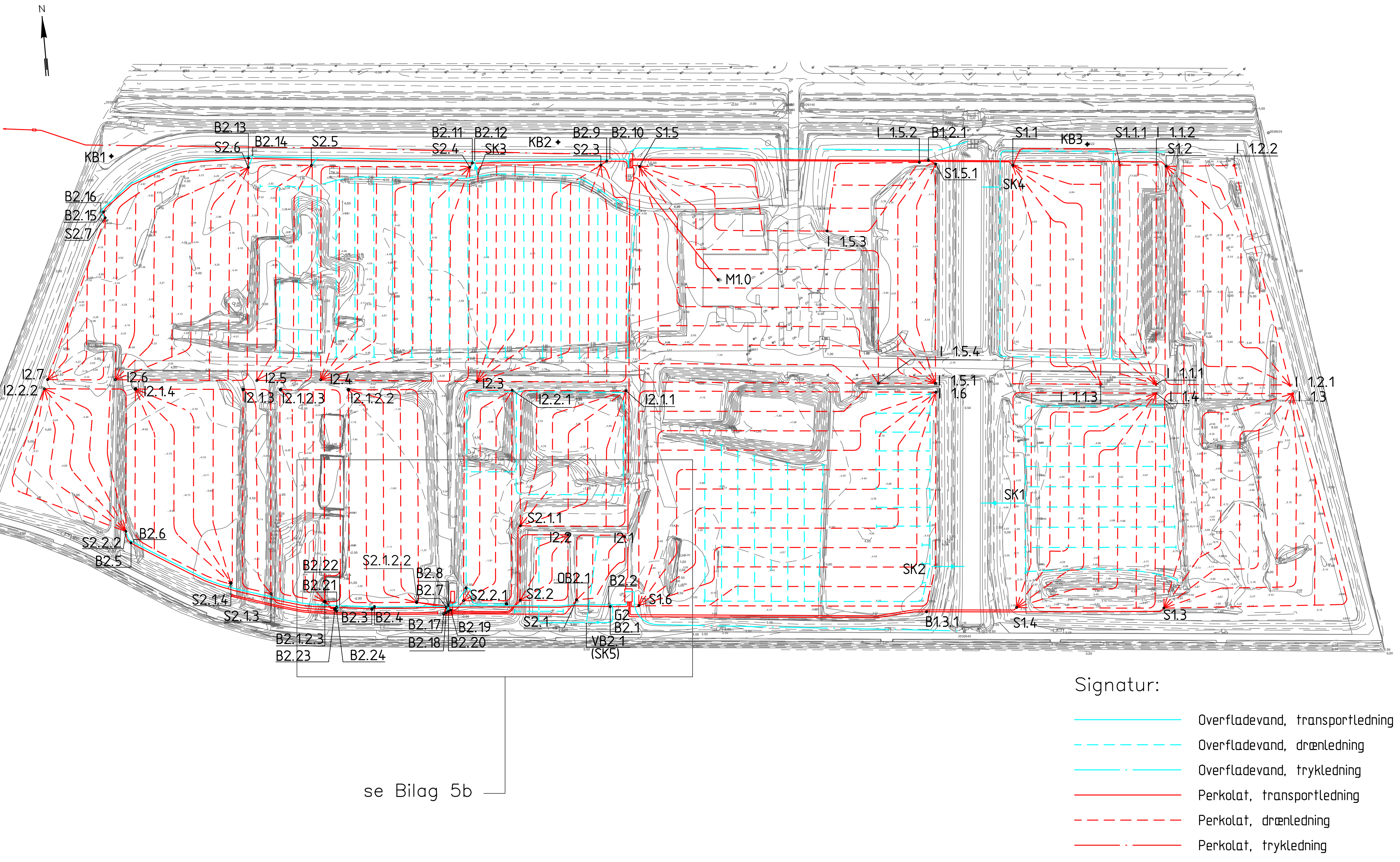
Appendix E Waste data

Appendix F Waste categories

Appendix G Note on polyurethane foam and its content of blowing agents

Appendix H Content of VOCs in foam from sampled shredder waste

Appendix A



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Appendix B

Atmospheric pressures at field campaigns.

Ranges of absolute atmospheric pressures measured during methane concentration screenings and during methane emission measurements on leachate wells and pumping stations. Pressures were measured on site using a portable weather station logging pressures hourly.

Tendencies of the pressure over time from 12 hours before measurement of methane concentrations/emissions through the period of measurement are listed categorized as falling, rising or oscillating.

Screenings of methane surface concentrations

	Date	**Range of absolute atmospheric pressure – 12h period (hPa)**	**Tendency**
Screening 1	Sep. 22 2004	995 – 997	Falling
Screening 2	Sep. 30 2004	1010 – 1013	Rising
Screening 3	Jul. 15 2005	1007 – 1016	Falling

Screenings of methane concentrations in leachate wells

	Date	**Range of absolute atmospheric pressure – 12h period (hPa)**	**Tendency**
Screening 1	Nov. 9 2004	1019 – 1023	Oscillating
Screening 2	Nov. 11 2004	1016 – 1018	Rising
Screening 3	Dec. 7 2004	1016 – 1020	Oscillating
Screening 4	Apr. 29 2005	1022 – 1024	Oscillating
Screening 5	May 10 2005	1004 – 1010	Rising
Screening 6	Jul. 15 2005	1007 – 1016	Falling

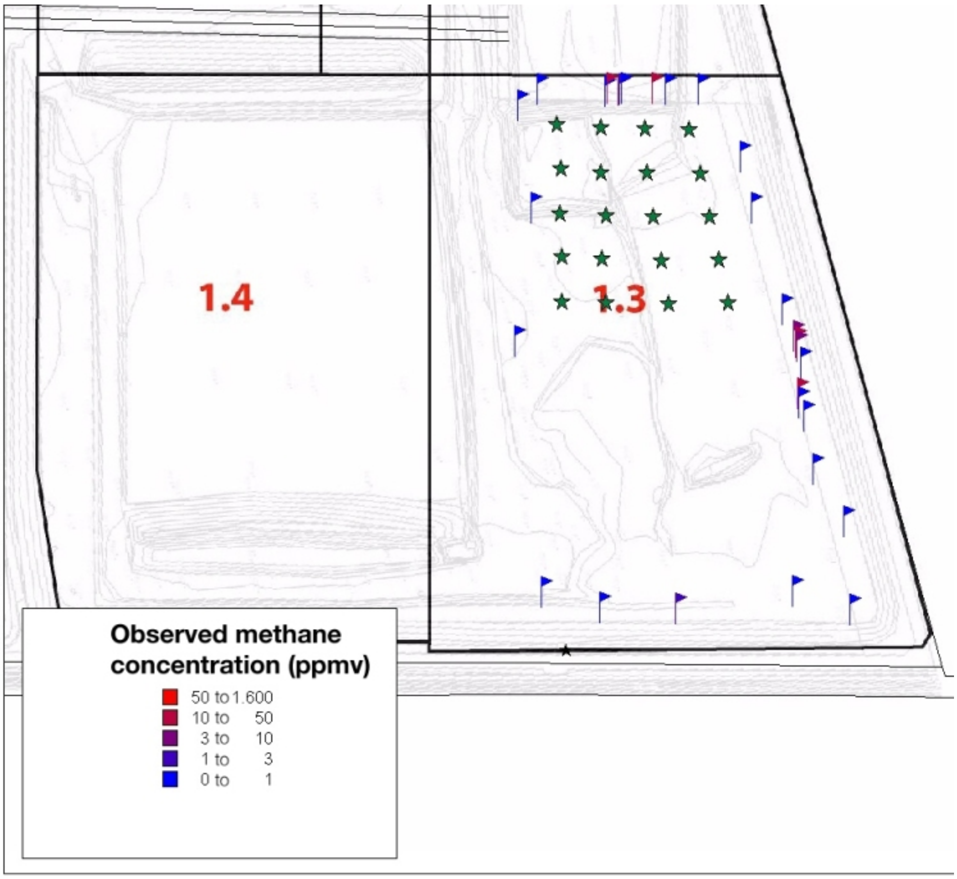
Measurement of methane emissions through leachate wells and pumping stations

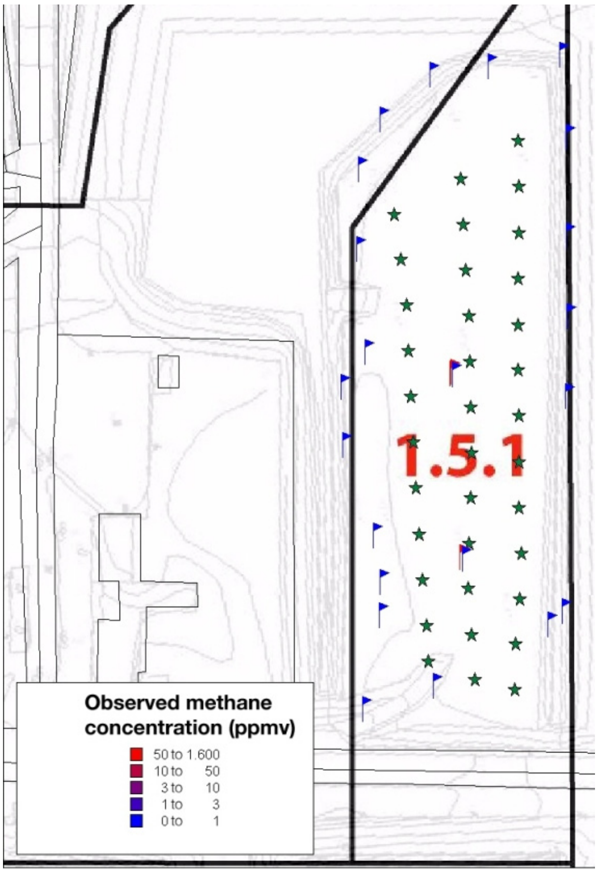
Location	Date	Range of absolute atmospheric pressure – 12h period (hPa)	Tendency
S 1.3	Oct. 11 2005	1019 – 1025	Oscillating
S 1.3	Nov. 9 2005	1018 – 1022	Oscillating
S 1.6	Oct. 24 2005	1011 – 1016	Rising
S 1.6	Nov. 10 2005	1022 – 1026	Oscillating
I 2.1.4	Oct. 20 2005	1008 – 1019	Falling
I 2.1.4	Nov. 2 2005	1009 – 1015	Oscillating
I 1.3	Aug. 16 2005	1018 – 1019	Oscillating
I 1.3	Oct. 11 2005	1023 – 1025	Oscillating
S 2.2.2	Oct. 19 2005	1019 – 1029	Falling
S 2.2.2	Nov. 9 2005	1018 – 1022	Falling
S 2.4	Oct. 21 2005	1003 – 1006	Oscillating
S 2.4	Nov. 1 2005	1011 – 1014	Falling
S 1.5.1	Oct. 18 2005	1027 – 1031	Oscillating
S 1.5.1	Nov. 7 2005	1017 – 1020	Oscillating
I 2.2.2	Oct. 19 2005	1022 – 1029	Falling
I 2.2.2	Nov. 9 2005	1018 – 1021	Oscillating
I 1.5.1	Oct. 18 2005	1028 – 1032	Oscillating
I 1.5.1	Nov. 7 2005	1017 – 1019	Oscillating
I 2.7	Oct. 26 2005	995 – 1004	Rising
I 2.7	Nov. 2 2005	1013 – 1016	Rising
P1	Nov. 8 2005	1022 – 1025	Oscillating
P1	Nov. 11 2005	1021 – 1019	Falling
P2	Nov. 8 2005	1020 – 1024	Oscillating
P2	Nov. 11 2005	1009 – 1021	Falling

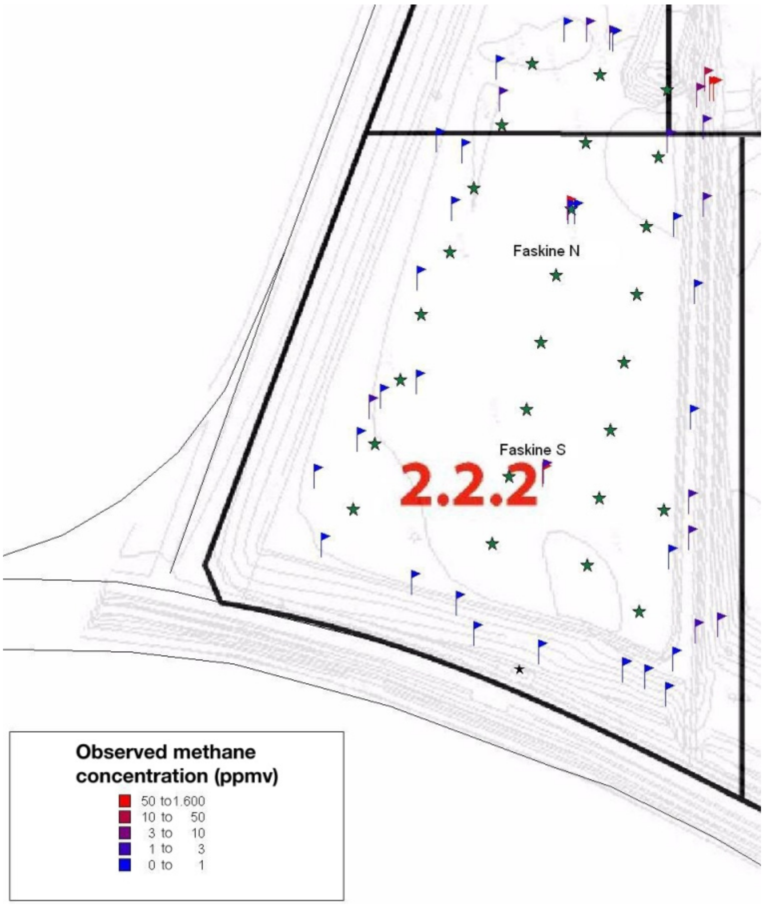
Appendix C

Surface screening of methane concentrations

The maps shows measured locations of grid points marked as green stars. The results of a near surface screening of methane concentrations at slopes and other features of the soil cover are displayed as flags. The color of the flags show the range of concentration of methane observed.




1.5.1
Observed methane concentration (ppmv)
50 to 1.600
10 to 50
3 to 10
1 to 3
0 to 1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Faskine S
2.2.2
Observed methane concentration (ppmv)
50 to 1.600
10 to 50
3 to 10
1 to 3
0 to 1

Appendix D

Methane concentrations in leachate wells

This appendix lists results of screenings of methane concentrations inside leachate wells using a portable flame ionization detector. Unit of concentrations is ppmv. Grey background indicates that the well was inaccessible at the time of measurement.

Well	09-11-2004	11-11-2004	07-12-2004	29-04-2005	10-05-2005	15-07-2005
S 1.5	over 3000	over 3000	over 3000	2123	1056	2117
S 2.3	over 3000	over 3000	over 3000	1900	over 3000	16
B 2.10	110	<2	113	<2	10.1	13
B 2.9	over 3000	over 3000	over 3000	11.2	333	17
S 2.4	over 3000	over 3000	over 3000	over 3000	over 3000	11
B 2.11	over 3000	over 3000	over 3000	over 3000	over 3000	15
B 2.12	<2	2.7	<2	<2	<2	<2
S 2.5	over 3000	over 3000	61	over 3000	2092	206.9
S 2.6	over 3000	279	1.9	4.9	194	6.5
B 2.13	<2	<2	720	228	<2	<2
B 2.14	over 3000	1970		<2	50	309
S 1.5.1	101	120	186	158	211	0
B 1.2.1	305	149	147	143	258	228
I 1.5.2	12	<2	<2	<2	<2	<2
I 1.5.3	30	<2		<2	<2	<2
S 1.1	<2	<2	<2	<2	<2	<2
S 1.1.1	17	6.1	<2	<2	<2	<2
I 1.1.2						
S 1.2	3.7	<2	<2	2.2	3.7	<2
I 1.2.2	19	<2	<2	6.2	8.0	6.2
I 1.2.1	over 3000	41	75	41	7.4	1976
I 1.3	over 3000	796	420	1675	92	over 3000
S 1.3	over 3000	over 3000	over 3000	over 3000	over 3000	over 3000
S 1.4		<2	over 3000	over 3000	over 3000	<2
B 2.4	<2	<2	<2	<2	<2	<2
B 2.3	<2	<2	<2	<2	<2	<2
B 2.24	2	15	<2	<2	24	<2
B 2.23	150	4.5	<2	<2	<2	<2
B 2.22	<2	20	<2	<2	<2	65
B 2.21	<2	<2	3.5	9.9	2.3	128
B 2.1.2.3	200	4.4	2000	over 3000	2541	128
S 2.1.3	6.8	60	350	37	36	46
S 2.1.4	over 3000	75	over 3000	87	119	42
B 2.5	164	2200	1900	71	722	126
B 2.6	<2	<2	<2	<2	<2	<2

Well	09-11-2004	11-11-2004	07-12-2004	29-04-2005	10-05-2005	15-07-2005
S 2.2.2	over 3000	over 3000	over 3000	1080	over 3000	over 3000
B 2.16	430	185	620	62	152	24
B 2.15	<2	<2	<2	<2	<2	<2
S 2.7	<2	<2	<2	<2	<2	<2
I 2.7	566	109	330	208	71.4	69
I 2.2.2	330	209	over 3000	<2	6.0	<2
I 2.6	over 3000	1480	156	over 3000	3.2	455
I 2.1.4	over 3000	over 3000	0	over 3000	over 3000	over 3000
I 2.1.3	over 3000	over 3000	1550	35.1	1320	over 3000
I 2.5	over 3000	305	210	<2	<2	<2
I 2.1.2.3	2.9	over 3000	over 3000	over 3000	over 3000	over 3000
I 2.4	over 3000	over 3000	over 3000	2105	189	34
I 2.1.2.2	40	4		32	<2	<2
B 2.8	<2	<2		<2	<2	<2
B 2.7	138	1100		25	1538	over 3000
B 2.17	2	85		<2	19	294
B 2.18	13	128		<2	1616	over 3000
B 2.20	79	2.5		<2	430	over 3000
B 2.19	7	<2		7.4	706	over 3000
S 2.1.2.2						
S 2.2.1	6.5	<2		<2	<2	over 3000
S 2.1.1	<2	<2			<2	<2
I 2.3	over 3000	<2		over 3000	over 3000	54
I 2.2.1						
I 2.1.1	<2	<2				
I 2.2	<2	<2			<2	
S 2.2					<2	
S 2.1	<2	<2			<2	
B 2.1						
B 2.2	15	3				
I 2.1	<2	<2			<2	
S 1.6	over 3000	over 3000	over 3000	over 3000	over 3000	over 3000
B 1.3.1		25	1180	40	165	8.5
I 1.6		over 3000	160	over 3000	212	486
I 1.5.4		over 3000	165	363	31	18
I 1.5.1		15	<2	2.2	<2	<2
I 1.1.3						
I 1.1.1	<2	<2		<2	<2	<2
I 1.4	235	24		85	25	426

Appendix E Waste data

Cell 1.3

Deposited waste – cell 1.3 (kg)		Continues on following page					
Type	**Name**	1992	1993	1994	1995	1996	1997
18	Storaffald	1 272 175	1 705 080	452 570	12 340	90 290	
21	Genbrugsstation, brændbart (tidligere: "Genbrugsstation")		4 141 894		64 515		
71	Plast og gummiindustri	90 510	1 900				
74	Auto, jern- og metalaffald	126 320	18 690	4 070	2 260		
75	Papir og grafisk industri	2 340					
77	Sand fra sandblæsning	91 700	53 660				
78	Sand, industri	293 980	105 460	8 840	15 280	7 500	
79	Industriaffald (tidligere "Industri, andet")	7 405 757	21 295 287	4 236 745	330 660	780 125	
85	PVC	29 820	3 660				700
86	Trykimprægneret træ		940		5 240		
89	Bygningsaffald (tidligere: "Bygningsaffald, andet")	4 463 155	3 751 280	858 090	4 670	38 380	
211	Flyveaske fra forbrændningsanlæg		5 580				
217	Restprodukt fra andre forbrændningsprocesser	46 680	189 560				
218	Restprodukt fra tør/semitør renseprocess (til og med 1992: "Restprodukt fra kompost")	79 420					
221	Slamaske	106 060	3 462 430	984 770			
222	Sand fra spildevandsrensning (til og med 1991: "Sand fra vejbrønde")	880 040	2 920 390	2 311 140	5 040	14 680	14 060
224	Afvandet stabiliseret slam	23 320	545 820	22 840			
233	Frasorteret, genbrugsstationer	238 990	394 430	535 640	66 725	207 750	
241	Olieforurenet jord (max 2%)	412 220	2 205 870	270 760	23 220	14 240	
242	Tungmetalforurenet jord	1 012 190	307 300	5 548 902		198 280	
243	Mekanisk forurenet jord (tidligere "Tungmetal/olie/tjæreforurenet jord")	349 160	4 610				
249	Forurenet jord i øvrigt		182 160			8 500	
251	Gadefej (tidligere: "Oprenset vejaffald")	1 401 470	1 956 880	1 202 670	66 050	263 410	
252	Asfalt	34 330	42 480	2 320	7 820	7 240	
253	Sand fra sandfang og vejbrønde	417 510	840 380	963 450	21 670	25 380	
280	Lossepladsfyld (tidligere: "Gammelt lossepladsfyld")					329 320	
291	Sand fra sandblæsning	11 000					
292	Omdirigeret affald fra Vestforbrænding	8 360 387	544 740			2 740	
293	Omdirigeret affald fra Amagerforbrænding (tidligere: "Omdirigeret affald fra Amagerforbrænding (affaldstype 2)")		1 917 500				
454	Tilført harperest						
Total deposited		27 150 526	46 599 974	17 404 801	627 485	1 989 831	16 757

Deposited waste – cell 1.3 (kg)			Continued from previous page					
Type	1998	1999	2000	2001	2002	2003	2004	Sum
18								3 532 455
21								4 206 409
71								92 410
74								151 340
75								2 340
77								145 360
78								431 060
79								34 048 574
85								34 180
86								6 180
89								9 115 575
211								5 580
217								236 240
218								79 420
221								4 553 260
222								6 145 350
224								591 980
233								1 443 535
241								2 926 310
242								7 066 672
243								353 770
249								190 660
251								4 890 480
252								94 190
253								2 268 390
280								329 320
291								11 000
292								8 907 867
293								1 917 500
454		794 600						794 600
Total deposited	1 998	796 599	0	0	0	0	0	94 597 981

Cell 1.5.1

Deposited waste – cell 1.5.1 (kg)		Continues on following page					
Type	Name	1990	1991	1992	1993	1994	1995
72	Fint skrotaffald				14 580		1 940
74	Auto, jern- og metalaffald	43 110	167 740	47 930			
76	Skrotaffald			2 280 800	4 106 400	3 555 560	3 045 580
221	Slamaske	1 558 900	5 123 440	986 320	1 657 000	1 963 860	525 830
	Total deposited	1 602 010	5 291 180	3 315 050	5 777 980	5 519 420	3 573 350

Cell 2.2.2

Deposited waste – cell 2.2.2 (kg)		Continues on following page					
Type	Name	1992	1993	1994	1995	1996	1997
10	Storaffald						
18	Storaffald						
21	Genbrugsstation, brændbart (tidligere: "Genbrugsstation")	6 440					
77	Sand fra sandblæsning						
78	Sand, industri						
79	Industriaffald (tidligere "Industri, andet")						
85	PVC						
86	Trykimprægneret træ						
89	Bygningsaffald (tidligere: "Bygningsaffald, andet")						
211	Flyveaske fra forbrændningsanlæg						
213	Slagger fra forbrændningsanlæg						
214	Slagger i øvrigt						
222	Sand fra spildevandsrensning (til og med 1991: "Sand fra vejbrønde")						
233	Frasorteret, genbrugsstationer						
241	Olieforurenet jord (max 2%)						
244	Mekanisk forurenet jord						
249	Forurenet jord i øvrigt						
251	Gadefej (tidligere: "Oprenset vejaffald")						
252	Asfalt						
253	Sand fra sandfang og vejbrønde						
278	Forurenede sten og brokker						
280	Lossepladsfyld (tidligere: "Gammelt lossepladsfyld")						
292	Omdirigeret affald fra Vestforbrænding	1 546 052					
293	Omdirigeret affald fra Amagerforbrænding (tidligere: "Omdirigeret affald fra Amagerforbrænding (affaldstype 2)")						
294	Omdirigeret affald fra Amagerforbrænding (affaldstype 3)						
295	Stort brændbart Amagerforbrænding						
299	Sortering						
451	Tilført fra sortering						
454	Tilført harperest						
455	Tilført brændbart						
456	Tilført sand fra sandfang						
460	Tilført ler						
Total deposited		1 552 492	0	0	0	0	0

Deposited waste – cell 1.5.1 (kg) Continued from previous page

Type	1996	1997	1998	1999	2000	2001	2002	2003	2004	Sum
72		395 040								**411 560**
74	6 640									**265 420**
76	2 333 100	3 659 980	5 468 280	8 183 370	1 403 140					**34 036 210**
221	10 680									**11 826 030**
Total	2 350 420	4 055 020	5 468 280	8 183 370	1 403 140	0	0	0	0	**46 539 220**

Deposited waste – cell 2.2.2 (kg) Continued from previous page

Type	1998	1999	2000	2001	2002	2003	2004	Sum
10		3 860						3 860
18	2 490	51 830	11 630					65 950
21	2 409 330	152 625						2 568 395
77		103 640	17 320					120 960
78	12 280	45 160	28 760					86 200
79	1 610 859	9 312 730	2 111 315					13 034 904
85	7 210	61 320	16 080					84 610
86	5 250	37 520	14 915					57 685
89	207 400	1 042 345	211 350	680				1 461 775
211		9 480						9 480
213		1 268 920	1 121 240					2 390 160
214		80 560	18 120					98 680
222		18 960	17 940					36 900
233	346 815	3 789 390	914 300					5 050 505
241	33 600		10 960					44 560
244			6 300					6 300
249	35 260	307 340						342 600
251	260 650	1 715 250	913 080					2 888 980
252		18 440						18 440
253	941 000	179 070	49 980					1 170 050
278	21 120	509 760	295 730					826 610
280		12 460						12 460
292	0	0						1 546 052
293	3 862 387	0						3 862 387
294	2 950	238 300						241 250
295	93 080	93 820						186 900
299			710					710
451		2 924 910	57 500					2 982 410
454		3 168 320						3 168 320
455		9 680						9 680
456		6 194 100						6 194 100
460							6 120	6 120
Total deposited	9 851 681	31 349 790	5 817 230	680	0	0	6 120	48 577 993

Appendix F

Waste categories

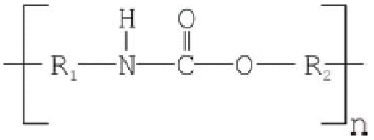
Waste No.	Waste name (Danish)	Afvalzorg category	GasSim category
10	Storaffald	MSW coarse	Combustible
18	Storaffald	1992-94: 10% MSW, 90% MSW coarse. 1995-1999: MSW coarse	1992-94: 10% MSW, 90% combustible. 1995-1999: combustible
21	Genbrugsstation, brændbart (tidligere: "Genbrugsstation")	MSW coarse	Combustible
71	Plast og gummiindustri	50%: Commercial, 50%:Construction	Combustible
72	Fint skrotaffald	Shredder	Shredder
74	Auto, jern- og metalaffald	Shredder	Shredder
75	Papir og grafisk industri	50%: Commercial, 50%:Construction	Combustible
76	Skrotaffald	Shredder	Shredder
77	Sand fra sandblæsning	Inert	Inert
78	Sand, industri	Inert	Inert
79	Industriaffald (tidligere "Industri, andet")	50%: Commercial, 50%:Construction	Combustible
85	PVC	Construction and demolition	Combustible
86	Trykimprægneret træ	Construction and demolition	Combustible
89	Bygningsaffald (tidligere: "Bygningsaffald, andet")	Construction and demolition	Inert
211	Flyveaske fra forbrændningsanlæg	Inert	Incinerator ash
213	Slagger fra forbrændningsanlæg	Inert	Inert
214	Slagger i øvrigt	Inert	Inert
217	Restprodukt fra andre forbrændningsprocesser	Inert	Incinerator ash
218	Restprodukt fra tør/semitør renseprocess (til og med 1992: "Restprodukt fra kompost")	Inert	Inert
221	Slamaske	Sludge and composting waste	Incinerator ash
222	Sand fra spildevandsrensning (til og med 1991: "Sand fra vejbrønde")	Sludge and composting waste	sewage sludge
224	Afvandet stabiliseret slam	Sludge and composting waste	sewage sludge
233	Frasorteret, genbrugsstationer	Inert	Inert
241	Olieforurenet jord (max 2%)	Soil and soil decontaminating residues	Inert
242	Tungmetalforurenet jord	Soil and soil decontaminating residues	Inert
243	Mekanisk forurenet jord (tidligere "Tungmetal/olie/tjæreforurenet jord")	Soil and soil decontaminating residues	Inert
244	Mekanisk forurenet jord	Soil and soil decontaminating residues	Inert
249	Forurenet jord i øvrigt	Soil and soil decontaminating residues	Inert
251	Gadefej (tidligere: "Oprenset vejaffald")	Street cleansing	50% inert, 50% combustible
252	Asfalt	Inert	Inert
253	Sand fra sandfang og vejbrønde	Sludge and composting waste	sewage sludge
278	Forurenede sten og brokker	Inert	Inert
280	Lossepladsfyld (tidligere: "Gammelt lossepladsfyld")	Soil and soil decontaminating residues	Inert

Waste No.	Waste name (Danish)	Afvalzorg category	GasSim category
291	Sand fra sandblæsning	Inert	Inert
292	Omdirigeret affald fra Vestforbrænding	MSW coarse	Combustible
293	Omdirigeret affald fra Amagerforbrænding (tidligere: "Omdirigeret affald fra Amagerforbrænding (affaldstype 2)")	MSW coarse	Combustible
294	Omdirigeret affald fra Amagerforbrænding (affaldstype 3)	MSW coarse	Combustible
295	Stort brændbart Amagerforbrænding	MSW coarse	Combustible
299	Sortering	Inert	Inert
451	Tilført fra sortering	Inert	Inert
454	Tilført harperest	2/3 soil and decont., 1/3 MWW coarse	2/3 inert, 1/3 Combustible
455	Tilført brændbart	MSW coarse	Combustible
456	Tilført sand fra sandfang	Sludge and composting waste	sewage sludge
460	Tilført ler	Inert	Inert

Appendix G

Note on polyurethane foam and its content of blowing agents

Polyurethane (in short PUR) is a group of polymer materials typically produced by a reaction between a di-isocyanate and a polyol in the presence of a catalyst. The resulting polymer (see figure) contains a urethane bond; thus the name polyurethane.



General structure of polyurethane

Polyurethane can be produced with different densities and hardnesses depending on the materials and process used for the production and both solid and foamed types are produced (www.plast.dk).

Polyurethane foam is polyurethane expanded by the use of a blowing agent (BA) in order to increase the volume of the material. The PUR foam can be divided into 2 main types: rigid PUR foam and soft PUR foam.

The rigid PUR foam is for instance used as insulation in refrigerators, freezers and district heating pipes and for panels in cars and buildings. The soft PUR foam is contained in products such as foam rubber/sponge rubber, textiles, cushions, (car seats) etc. Because of the open structure of soft PUR foam, the blowing agent is lost from the material during the expansion process or immediately after (Poulsen et al., 2006). Therefore, only rigid PUR foam will be of concern in this context.

Use of blowing agents in polyurethane foam

Traditionally, trichlorofluorocarbon (CFC-11), which is an ozone depleting substance as well as a greenhouse gas, has been used as a BA in rigid polyurethane foam. In 1987, the adverse effects of CFC-11 were specifically addressed in the Montreal Protocol, which obliged UN countries to phase out the production and use of CFC-11. The use of CFC-11 as a blowing agent has been prohibited in Denmark since January 1st 1994 and in the EU since 1995.

For a transition period, hydrochlorofluorocarbons (mainly HCFC-141b) were used as BA in insulation foam. HCFCs are, however, too, ozone depleting substances and was banned in Denmark from 2002 and under phase-out in EU (Pedersen, 1998).

The next generation of blowing agents were hydrofluorocarbons (mainly HFC-134a). These are not potential ozone depleting substances, but are still green house gasses, some of them with very substantial warming potential. HFCs are included in the list of green house gasses to be reduced according to the Kyoto Protocol from 1997 (Pedersen, 1998).

Following the ban of CFC-11 a transition towards using hydrocarbons, such as cyclopentane, as a BA has taken place. The largest Danish producer of refrigerators and freezers shifted to cyclopentane as BA in 1993/1994 and so did many of the largest producers in Europe. The smaller producers continued using HCFCs or HFCs for economic reasons. In 1998, 241 tonnes of HFC-134a was used in Denmark for blowing of PUR foam (Pedersen, 2001). The introduction of an environmental fee on the use of HFC in 2001, however, induced a shift towards replacing HFC with cyclopentane (Pedersen, 2001). As of today, all insulation foam for domestic refrigerators and freezers produced in Denmark is expanded with cyclopentane (Pedersen, 2006), as is the majority of domestic appliances available at the Danish market, which for instance includes imported freezers and refrigerators from Germany, Italy and Sweden (Pedersen, 2001).

As for blowing agents used for expansion of polyurethane for other purposes than insulation foam (e.g. construction foam used for panels in cars and caravans), CFC-11 has also been the dominant BA until the ban in 1995 (Poulsen et al., 2006).

Overview of blowing agents used historically in polyurethane foam. Ozone depletion potential (ODP) and global warming potential (GWP) integrated for a period of 100 years from Danish EPA (1995).

Blowing agent Group	Main compound	ODP	GWP	Use
Chlorofluorocarbons, CFCs	CFC-11	1.0	4000	Phase out initiated by the Montreal Protocol from 1987. Prohibited in EU from 1995.
Hydrochlorofluorocarbons, HCFCs	HCFC-141b	0.11	630	Replaced CFCs as BA as an interim solution. Subjected to regulations and phase-out in the EU.
Hydrofluorocarbons, HFCs	HFC-134a	0	1300	Replaced CFCs/HCFCs. Included in the Kyoto Protocol (1997) of green house gasses to be reduced. Environmental fee introduced in Denmark March 2001.
Hydrocarbons, HCs	Cyclopentane	0	(10)	Main BA used in Denmark today and main BA in refrigerators and freezers marketed in Denmark.
Carbon dioxide	CO_2	0	1	Potential future BA

Waste products and end-of-life treatment

Rigid PUR foam has been used in a range of products either for insulation purposes for example in refrigerators and freezers (r/f), insulation panels and district heating pipes or for construction purposes e.g. panels in cars.

A summary of the main product types containing rigid PUR foam and an estimated life-time is given in the table. The end-of-life treatment of these products includes both disposal of PUR waste in landfills and incineration.

Waste products containing rigid PUR foam. The product life times are estimated by Poulsen et al., 2006.

Product	Life time	End-of-life treatment
Domestic refrigerators and freezers	12 years (average) 20 years (maximum)	Draining of refrigerant followed by shredding in closed environment, where CFC is recovered from the air. The PUR foam is incinerated [3,4]
Refrigerators and freezers for retail commerce	20 years (average)	Do.
District heating pipes	20-60 years Average: 30 years	Shredding with subsequent incineration of the foam or disposal at solid waste disposal sites [1,2]
Building insulation and insulation panels for cold stores in industry and retail commerce	25-30 years (average)	The insulation foam is treated as demolition waste and mainly disposed of at solid waste disposal sites [1]
Construction foam (Panels in cars, caravans and sailing ships etc.)	10-20 years Average: 15 years	Cars and caravans are treated in shredder facilities with recovery of metals. The shredder residue containing the foam is disposed of at solid waste disposal sites. [1,2]

[1] Poulsen et al., 2006
[2] Hallam et al., 2005
[3] Ministry of Environment, 2005
[4] Jacobsen & Hansen, 1999

As opposed to the other PUR containing waste fractions, r/f-waste is the only waste type subjected to specific requirements regarding recovery of the CFC-content in the PUR foam. Since 1997 it has been imposed on the Danish municipalities to establish collection facilities for discarded CFC-containing refrigerators and freezers. This regulative aims at obtaining an environmental safe disposal and reuse of CFC. A minimum collection efficiency of 80% of the CFC-11 in isolation foam is a requirement (Ministry of Environment and Energy, 1996).
The end-of-life treatment consists of a pre-treatment step with draining of CFC-11 from the refrigeration system and draining of compressor oil. Movable elements and mercury contacts are disassembled. The final treatment step involves handling of CFC in the insulation foam. The applied treatment method varies between different treatment facilities in Denmark, but most methods involve shredding with subsequent incineration of the plastic and PUR fraction and reuse of the metal fraction (Jacobsen & Hansen, 1999). However, according to Danish EPA (1999) landfilling of the shredder residue from shredding of refrigerators has also been practised.

The procedures for treatment of r/f-waste has recently been tightened requiring that shredding takes place in a closed environment allowing recovery of CFCs as well as green house gasses with a GWP>10 released to the surrounding air during shredding (Ministry of Environment, 2005).
The EU WEEE directive (Directive 2002/96/EC on waste electrical and electronic equipment) came into force in Denmark in April 2006. This means that the producers of electrical appliances have now inherited the responsibility for financing the collection, treatment and disposal of their products (Ministry of Environment, 2005).

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Appendix 5.1 Content of VOCs in foam from sampled shredder waste

Average content of CFC-11, CFC-12, HCFC-21, HCFC-31, HCFC-141b and HFC-134a in g/kg foam. The standard deviation (St. dev.) is calculated based on results from analysis of 3 sample replicates from each size fraction.

		CFC-11		CFC-12		HCFC-21	
	Size distribution of foam (%)	Average content (g/kg foam)	St. dev. (g/kg foam)	Average content (g/kg foam)	St. dev. (g/kg foam)	Average content (g/kg foam)	St. dev. (g/kg foam)
1.5.1 "South"							
>32 mm	35.1	0.02	0.0	0.001	0.001	0.003	0.002
16 - 32 mm	15.3	1.41	1.3	0	0	0.004	0.002
8 - 16 mm	33.4	0.38	0.2	0	0	0	0
< 8 mm	16.2	0.02	0.0	0	0	0.002	0.002
1.5.1 "Mid"							
>32 mm	7.7	5.45	4.4	0.007	0.010	0.039	0.033
16 - 32 mm	39.0	0.21	0.3	0	0	0.001	0.001
8 - 16 mm	36.8	0.01	0.0	0	0	0	0
< 8 mm	16.4	0.05	0.0	0.003	0.005	0.001	0.000
1.5.1. "North"							
>32 mm	10.3	7.95	7.0	0	0	0.009	0.006
16 - 32 mm	36.8	0.74	0.5	0	0	0.003	0.001
8 - 16 mm	35.0	0.30	0.2	0	0	0.004	0.002
< 8 mm	17.9	0.21	0.2	0	0	0.003	0.003
Average							
>32 mm	17.7	4.48		0.002		0.017	
16 - 32 mm	30.4	0.79		0		0.002	
8 - 16 mm	35.1	0.23		0		0.001	
< 8 mm	16.9	0.09		0.001		0.002	

	Size distribution of foam (%)	HCFC-31		HCFC-141b		HFC-134a	
		Average content (g/kg foam)	St. dev. (g/kg foam)	Average content (g/kg foam)	St. dev. (g/kg foam)	Average content (g/kg foam)	St. dev. (g/kg foam)
1.5.1 "South"							
>32 mm	35.1	0.001	0.001	0.00	0.01	0.16	0.24
16 - 32 mm	15.3	0	0	0.68	0.94	0	0
8 - 16 mm	33.4	0	0	0.38	0.65	0	0
< 8 mm	16.2	0.000	0.001	0	0	0	0
1.5.1 "Mid"							
>32 mm	7.7	0	0	0.002	0.003	0.008	0.001
16 - 32 mm	39.0	0	0	0	0	0.014	0.024
8 - 16 mm	36.8	0	0	0	0	0	0
< 8 mm	16.4	0	0	0	0	0	0
1.5.1. "North"							
>32 mm	10.3	0	0	0.04	0.01	1.99	0.73
16 - 32 mm	36.8	0	0	0.01	0.00	0.21	0.17
8 - 16 mm	35.0	0	0	0	0	0	0
< 8 mm	17.9	0	0	0	0	0	0
Average							
>32 mm	17.7	0		0.02		0.72	
16 - 32 mm	30.4	0		0.230		0.074	
8 - 16 mm	35.1	0		0.126		0	
< 8 mm	16.9	0.001	0.001	0		0	

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ISBN 978-87-91855-36-8