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Methane and nitrous oxide emissions from biomass waste stockpiles

Prepared for PCF*plus* Research by *Biomass Technology Group BV*

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Project No.	**1050**

Title

Methane and Nitrous Oxide Emissions from Biomass Waste Stockpiles – Final Report

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Methane and Nitrous Oxide Emissions from Biomass Waste Stockpiles - Final Report

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SUMMARY

Large wood residue stockpiles may represent a potential source of the greenhouse gases nitrous oxide (N_2O), and - if anaerobic digestion occurs inside the stockpiles - methane (CH_4). If these gases are indeed emitted, a project which would mitigate the generation and stockpiling of wood residues could be allowed to claim greenhouse gas emission reductions. At present not much is known about the extent of methane and nitrous oxide emissions from wood stockpiles. Therefore an assignment has been commissioned by The World Bank (PCF*plus* research) to build a general methodology for assessing methane and nitrous oxide emissions from wood residue stockpiles, and using it for assessing the likelihood of estimated methane emissions in one such project in Bulgaria.

The assignment consists of a literature survey on methane and nitrous oxide emissions from wood stockpiles, followed by field methane emission measurements on wood stockpiles in Bulgaria, and the development of a spreadsheet model for predicting future methane emissions.

Literature survey

As expected only a few articles about methane emissions from wood residue stockpiles were found. Therefore also literature on methane emissions from landfills was included in the survey, of which a large number of publications exists. Methane emissions from landfills show a large temporal and spatial variability, implying that methane emissions at different spots on one landfill can vary up to a factor 1000, and that emissions can vary significantly dependent on the time of day, the season, barometric pressure and precipitation. Seasonal variation is caused by biological oxidation of methane in the top layer of a landfill, and is more pronounced at higher ambient temperatures. It is expected that the same mechanisms and variations in methane emissions from landfills will also take place in wood stockpiles.

Nine possible methods for measuring methane emissions from wood stockpiles were identified. As most appropriate methods were selected:

Table S.1 Applicable methods for measuring methane emissions from wood stockpiles

Method	Description
static and dynamic closed chambers	An enclosed volume is placed on the stockpile and methane concentrations are measured. With static closed chambers methane accumulation is measured, while with dynamic closed chambers methane concentrations in a controlled airflow are measured.
mass-balance method	Measurement of methane and carbon dioxide concentrations at fixed positions at different heights around a stockpile.
sub-surface vertical gradient method	Determination of methane emissions by measuring methane concentration gradients inside a stockpile using probes, which was the originally planned method.

Inception mission

Three sites in Bulgaria were visited during the inception mission. At these sites large wood stockpiles had been accumulating: Svishtov, Razlog and Stamboliynski. The site in Stamboliynski was unsuitable for measurements, because of pollution with municipal solid waste. The Svishtov and Razlog sites were considered suitable for the methane emission measurements.

Measurement method selection

The mass-balance method was deemed unsuitable for measuring methane emissions on the Svishtov and Razlog sites, since other waste stockpiles that also might emit methane were located next to both. Since the mass-balance method cannot make a distinction between methane emissions from adjectant sources, the results would be unreliable.

The two other methods show the same low resolution regarding spatial and temporal variance. Both measure methane in a small area (maximum several m^2), and at a single point in time. By executing a large number of measurements the spatial resolution can be increased. Advantages of the sub-surface gradient method are the low costs, and the fact that it is possible to follow the processes inside a stockpile. However, the sub-surface vertical gradient method suffers the drawback of not being able to measure the methane emissions directly, and neglects convective transport. From literature sources it is clear that methane transport through convection can sometimes be substantial. Chamber methods have the advantage of extensive experience with landfills and the possibility to measure the methane flux directly. Considering these arguments, the dynamic chamber method was selected to measure the methane flux on both wood stockpiles in Bulgaria.

Modeling

Several models exist for predicting methane emissions from anaerobic digestion in landfills, namely first order, second order and zero order models. The models can be further detailed to account for different phases in the waste, after which these are called multiphase models. Three requirements were applied in the model selection with respect to this project:

- The model should be able to predict methane emissions as a function of time for wood stockpiles;
- The model should only require easily obtainable input parameters;
- The model should be applicable for a variety of locations, and be able to incorporate wood waste of various ages and types.

Based on these requirements a multi-phase model, based on first order kinetics was selected. Zero order models cannot predict emissions as a function of time, the simple first order model fails to estimate emissions when wood is dumped during several years, and the second order model is considered to lack a physical basis.

For the specific case of wood stockpiles, the general multiphase model was adapted as follows:

$$Q_m = V_m(za\sum_{j=0}^{n}(A_j - A_{ox,j})kC_{0,j}\,rv_0e^{-k(t-j)})*(1-z_{ox})$$

This model describes the methane emission Q_m (m^3/year) in one wood stockpile in which wood is dumped for a number of years n (year). This model uses as input values the amount of wood waste dumped and under anaerobic conditions in each year j (A_j-$A_{ox,j}$). The initial (non-lignin) organic carbon fraction from waste of year j ($C_{0,j}\rho\upsilon_0$) is converted to the equivalent maximum gas quantity using the known conversion factor a, and the decomposition constant k (dependent on the half life $t_{½}$ of the waste). The resulting maximum gas formation is subsequently converted to methane emissions by applying factors for loss through oxidation ($1-\zeta_{ox}$) and the methane fraction in the gas (V_m). The generation factor (ζ) is an empirical factor which accounts for non-ideal circumstances for gas formation in the wood stockpile. This generation factor cannot be measured directly, but should follow from the other parameters.

The organic fraction which is converted follows an exponential decay pattern, following first order kinetics.

Measurement results

The measurements proved that in large parts of both stockpiles anaerobic conditions exist, because high concentrations of methane, and very low concentrations of oxygen were measured below 0.5 meter (Svishtov) and 1.5 meter (Razlog) inside both piles using a probe. Furthermore, methane emissions from both stockpiles were significant. Both for the Svishtov and the Razlog stockpiles methane emissions were measured with the dynamic chamber of respectively 6.4 and 5.7 liter/m^2/hr. An inherent problem with the chamber method is that, despite the large number of measurements, the 90% confidence interval remains large for both Svishtov (3.1 – 9.5 liter/m^2/hr) and Razlog (2.0 – 9.5 liter/m^2/hr).

Conditions for anaerobic digestion are favourable both in the Svishtov and in the Razlog stockpiles. Small particles, bruised in the debarking process are regularly compacted, in an environment with abundant water availability. From literature it is known that these factors accelerate methane formation. Although during measurements both piles were for a large part under water, it is expected that the water level will vary throughout the year, primarily caused by rainfall. Based on historic rainfall records, the measurement period was not considered to be exceptionally wet.

Modeling results

Based on the measurements and literature values, model parameters were selected. For the generation factor the IPCC default value (0.77) was taken, and for the half-life the minimum value quoted in literature for wood decomposition in landfills (15 years). The modeled methane emissions have values close to the lower end of the 90% confidence interval of the methane measurements for both Svishtov and Razlog, as is shown in Table S.1.

Table S.1 Modeling results for the measurement area of the Svishtov and Razlog sites, comparison with measurements

	Svishtov	**Razlog**
Yearly modeled methane emissions in 2002 (m^3/year)	153,000	94,300
Measurement area (m^2)	6,300	5,625
Specific modeled methane emissions (liter/m^2/hour)	2.8	1.9
Measured methane emissions (liter/m^2/hour)	6.4	5.7
Measured methane emissions – lower end of the 90% confidence interval (liter/m^2/hour)	3.1	2.0

Estimating future methane emissions

With the model it is possible to estimate future methane emissions both for the existing piles, as well as for newly dumped biomass. These estimations are commonly carried out for landfills using a similar IPCC model, which is well validated and calibrated. The estimated future methane emissions are considered a conservative estimation. Default IPCC parameter values for landfills are used, even though much better circumstances for anaerobic digestion exist in these stockpiles. This is also confirmed by the calculated emissions which were at the lower end of the 90% confidence interval of the measured methane emissions.

In Figure S.1 the estimated future methane emissions of both the Svishtov and the Razlog piles are given, for newly dumped wood waste, as well as from the existing piles.

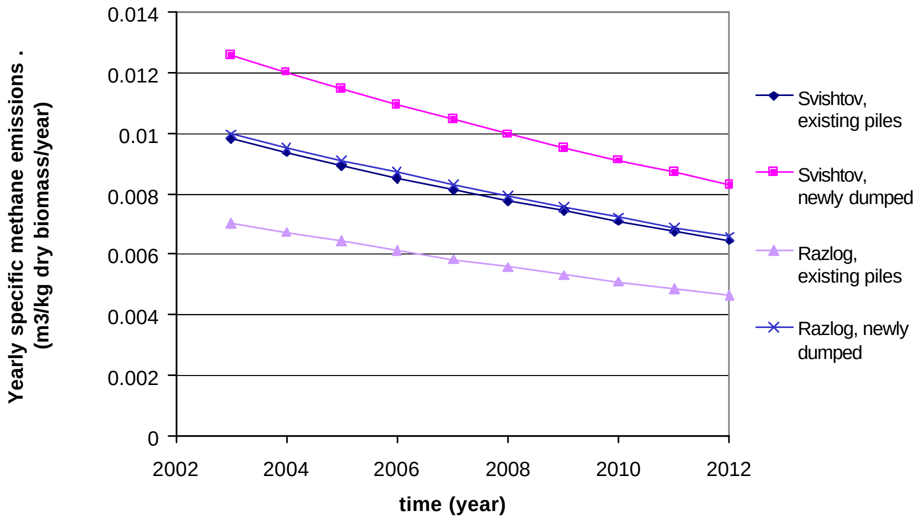

Figure S.1 Estimated future methane emissions for the Svishtov and the Razlog stockpile, for both newly dumped biomass and for the existing piles.

The pattern of decreasing methane emissions as a function of time is a logical consequence of the applied model, which predicts exponentially declining emissions. Methane emissions from newly dumped biomass are higher compared to existing biomass, because methane has already been emitted for some time from the existing piles.

Spreadsheet model

The model and the measurements have been combined into a spreadsheet model, that can be used by future project developers to estimate methane emissions from biomass stockpiles. To adapt the spreadsheet model to other biomass stockpiles, biomass- and site-specific parameters need to be replaced with literature values or measured data. The generation factor, oxidation layer thickness, and possibly the half-life for other piles and biomass types need to be established by field measurements.

It is recommended to collect and utilise data from subsequent methane emission measurements, carried out in the course of future projects, to be able to derive widely validated model parameters for the accurate prediction of methane emissions from a variety of biomass stockpiles.

N_2O emissions

Besides methane emissions, nitrous oxide emissions from biomass stockpiles may contribute significantly to the greenhouse effect. N_2O emission literature is primarily focussed on composting, and in a few cases on landfill sites. Data on emissions from wood stockpiles is not available. Emissions are often related to the amount of nitrogen present, of which in the case of compost piles generally 0.5% is converted to N_2O.

If N_2O emissions from biomass stockpiles are comparable to those from compost piles, 50,000 ton_w biomass (annual dumping in Svishtov) causes a nitrous oxide emission of 2.3 kton CO_2-equivalents, comparable with 6.4 kton CO_2-equivalents from methane emissions. In that case, N_2O emissions would contribute a significant share of 26% of the total GHG emissions. It is recommended to measure nitrous oxide emissions, and build a general methodology to quantify the possible GHG reductions which could be achieved.

ABBREVIATIONS AND DEFINITIONS

a	conversion factor from kg carbon to landfill gas quantity (equal to 1.87 m^3/kg carbon)
A	amount of biomass waste in place (tonne)
A	surface area (m^2)
$C_{o,j}$	amount of initial organic carbon in the waste in a specific year j (kg/m^3)
C	concentration (liter/m^3 or ppm)
db	dry basis (-)
GHG	greenhouse gas
GWP	greenhouse warming potential
J	methane flux (liter/m^2/hr)
k	decomposition rate constant ($year^{-1}$)
MC_{wb}	moisture content on a wet basis (-)
MSW	municipal solid waste
Q	landfill gas emissions in year t (m^3/year)
Q_m	methane emissions (m^3/year)
$Q_{m,sp}$	specific methane emissions (m^3/year/kg dry biomass)
t	time elapsed since the depositing of the waste (year)
TS	dry matter content (in mass$\%_{wb}$)
VS	organic matter content (in mass$\%_{TS}$)
V_m	methane fraction in landfill gas (-)
wb	wet basis (-)
a	landfill gas formation (m^3/year)
Φ_v	volume flow of air (m^3/hr)
υ_0	initial fraction (hemi-)cellulose (-)
ζ	generation factor (-)

1 INTRODUCTION

In Bulgaria large stockpiles of wood residues of all sorts from the pulp and paper industry have been accumulated. These stockpiles cause local nuisances but also represent a potential source of greenhouse gases (carbon dioxide and methane) due to anaerobic digestion. If methane (CH_4) and possibly nitrous oxide (N_2O) is emitted in sufficiently large amounts from wood stockpiles in the business-as-usual scenario, a project that would mitigate the generation and stockpiling of wood residues would be allowed to claim significant greenhouse gas emission reductions.

At present not much is known about the extent of methane emissions from wood stockpiles. Therefore an assignment has been commissioned by PCF*plus* research to build a general methodology for assessing methane emissions from wood residue stockpiles, and at using it for assessing the likelihood of estimated methane emissions reduction in two selected stockpiles in Bulgaria.

The assignment consists of three main parts:

- a literature survey;
- field measurements of methane emissions in selected Bulgarian wood stockpiles;
- construction, calibration and validation of a spreadsheet model for methane emissions from biomass stockpiles.

In Chapter 2 and 3 respectively, a literature survey concerning methane and nitrous oxide emissions from biomass piles is given. The measurement procedure, and the model choice regarding methane emissions from biomass stockpiles are presented respectively in Chapter 4 and 5. In Chapter 6 the results are presented, followed by the model parameter selection on Chapter 7. In Chapter 8 future methane emissions are estimated.

2 LITERATURE SURVEY FOR METHANE EMISSIONS

Hardly any literature is available concerning methane emissions form wood *stockpiles*. Therefore also a survey has been made of the main literature concerning methane emissions of waste dumped in *landfills.* Although many uncertainties still exist, methane emissions from landfills are a recognised fact and a large number of reports on this subject exist. One of the reasons is that in many countries landfill gas recovery has become a proven technology for generating energy, for which an accurate estimation of the possible gas recovery is necessary. Also in the light of the Kyoto Protocol attention has been paid to a reliable estimation of the GHG (greenhouse gas) emissions from landfills. For these reasons significant research efforts have been undertaken to measure, model and predict methane emissions from numerous landfills across the world.

This Chapter starts with a brief introduction of the anaerobic digestion process in which methane and carbon dioxide are produced. The produced methane can either be emitted in the air, or be recovered for energy generation, or be oxidised in the aerobic top layer of the landfill. In Paragraph 2.2 an overview is presented of the various measurement procedures for methane emissions, and the large variations that can occur when measuring within one landfill are discussed. The results that have been reported in literature concerning methane emissions from landfills and the oxidation of the methane are presented. Modeling of landfill gas emissions is finally discussed.

An overview of the rare literature concerning methane emissions from wood *stockpiles* is presented (Paragraph 2.3).

2.1 INTRODUCTION

Organic waste in a landfill starts to decompose as soon as the waste is dumped and compacted. Four phases can be distinguished in the process of the methane formation [Schepers and Van Zanten, 1994]:

- Aerobic degradation – the available oxygen in the landfill is used for the aerobic degradation of the organic bonds. This phase lasts relatively short (a few days to a few weeks), and ends when the available oxygen is depleted.
- Hydrolysis – under anaerobic circumstances the large organic molecules are broken down to smaller, soluble molecules, such as simple fatty acids and sugars.
- Acidification – the hydrolysed compounds are through anaerobic bacteriological activity further transformed into fatty acids, which lowers the pH.
- Methanogenesis – by anaerobic bacteria the fatty acids are transformed to mainly methane (CH_4) and carbon dioxide (CO_2).

The four phases are described in more detail in Annex A.

Pressure and concentration gradients force the methane out that is produced inside the landfill. Not all the methane that is produced is actually emitted into the air. Under certain circumstances part of the methane can be biologically oxidised into carbon dioxide and water in the top layer of a landfill. In a number of landfills methane is also recovered for energy generation. Therefore the following simplified formula is valid for landfills (see also Figure 2.1):

Methane emission = methane formation – methane recovery – methane oxidation

The process of oxidation occurs in the top layer of the landfill, since air and landfill gas are mixed there. Because of this, methanotropic bacteria can exists which cause a decrease in methane emissions due to oxidation [Boeckx et al., 1996].

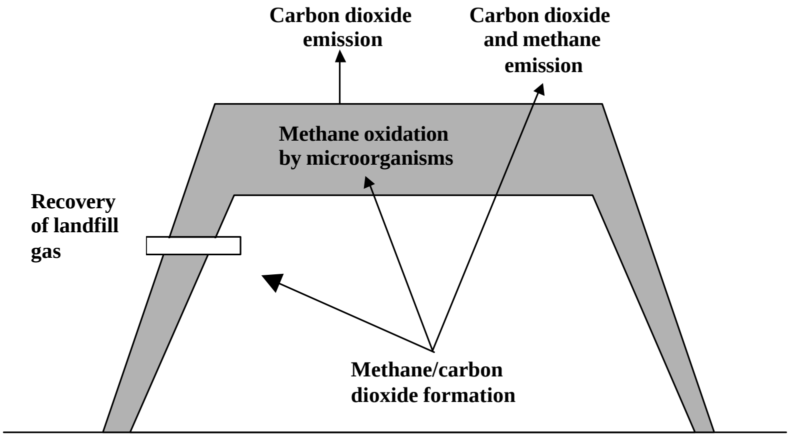

Figure 2.1 Methane emissions originating from a landfill

2.2 MEASUREMENT OF METHANE EMISSIONS FROM LANDFILLS

2.2.1 Measurement procedures

By [Scharff et al., 2000] an overview is presented of measurement procedures that can be used for measuring methane fluxes from landfills. The following nine methods, as well as a short description are listed below:

a) soil core measurements;
Soil samples are taken and incubated in a laboratory

b) static closed chambers;
An enclosed volume is placed on a landfill and methane concentrations are measured

c) dynamic closed chambers;
As with static closed chambers, but now an air flow is applied through to the chamber to avoid methane build-up

d) mass-balance method;
Measurement of methane and carbon dioxide at fixed positions at different heights around a landfill

e) micrometeorological methods;

Measuring gas flux densities above a landfill

f) mobile plume measurements;
Methane concentrations measured across a downwind transect screen

g) stationary plume measurements;
Collection of air samples at selected fixed locations around a landfill

h) isotope measurements (methane oxidation only);
Measuring the ratio of $^{12}C/^{13}C$ *isotopes to determine quantitatively methane oxidation*

i) sub-surface vertical gradient method.
Determination of methane emissions by measuring methane concentration gradients inside a landfill using probes

The methods are presented in more detail Paragraph 3.1 and in Annex C, where also the advantages and disadvantages of the methods are discussed.

2.2.2 Variability of methane emissions within one location

A significant number of methane emission measurements in landfills have been executed over the years. These measurements have in common that they show large variations in the measured emission levels, even when the measurements took place within one and the same landfill. The variations can occur due to a number of reasons, as discussed below.

Spatial variations

Spatial variations within one landfill with respect to methane emissions are well known and catalogued by several authors. These spatial variations are caused by the heterogeneity of the waste. In [Scharff et al., 2000] variations of a factor 1000 in the measured methane emission within one and the same landfill are reported. [Czepiel et al., 1996a] studied the spatial variation at two landfills in New England and found no correlation anymore between the emissions from two points of a landfill, when the distance was more than 7 meters.

Hourly and daily variations

Climatological phenomena are important. A correlation between changes in the atmospheric pressure and the methane emission has been observed. [Czepiel et al, 1996a] shows a change in the methane emissions of a factor 2 during a change in atmospheric pressure of 30 mbar over a five day period (see Figure 2.2). It is expected that variations in wind can have a similar effect, because of the associated pressure effect (through Bernoulli). Another factor influencing emissions is rainfall, since this reduces the permeability of the top layer.

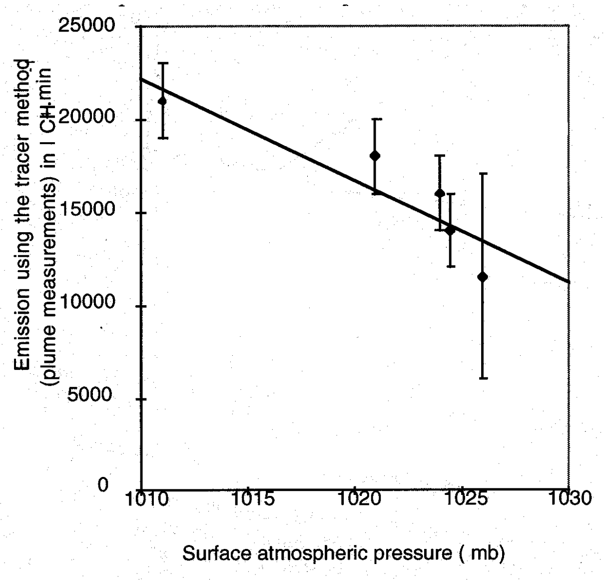

Figure 2.2 The methane emissions at a landfill in the USA, measured on 5 subsequent days. Higher emissions occur with a decrease in the atmospheric pressure (after [Czepiel et al, 1996b]).

Seasonal variations

It is expected that conditions in a landfill are subject to seasonal fluctuations. Changing temperature and humidity will have an effect on the biological activity in the landfill and hence on the methane formation and oxidation. There are indications that especially methane oxidation, which takes place in the top layer of a landfill, shows a seasonal variation. This is shown by [Boeckx et al., 1996], which measured the oxidation in the top layer during various seasons (Figure 2.3). Oxidation significantly decreases during November. It could however not be explained why the oxidation increased strongly during December, since it is unlikely that the temperature increased in that month.

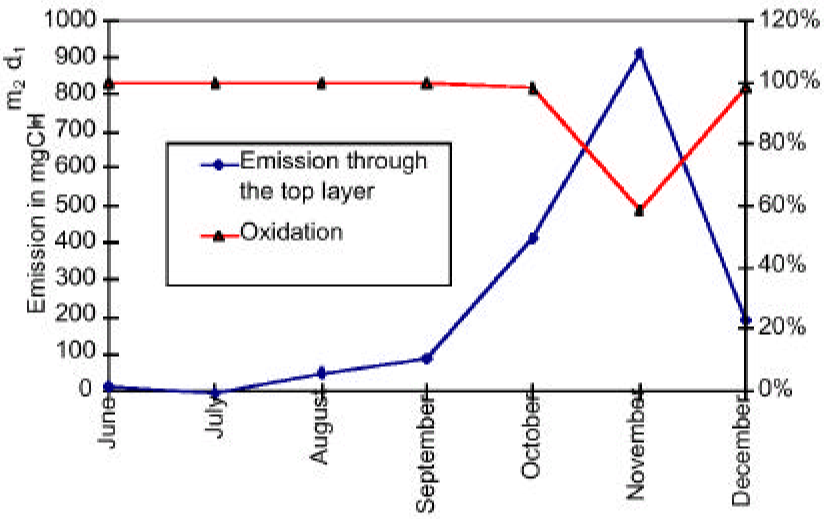

Figure 2.3 Methane emissions measured in different months at a landfill in Belgium indicate seasonal variation caused by a variation in the oxidation in 30 cm top soil layer [Boeckx et al., 1996].

The seasonal difference is more apparent in [Borjesson et al., 2001] who utilised the Carbon-13 to Carbon-12 isotope measurement to determine methane oxidation in two Swedish landfills in summer and in winter. In summer, methane oxidation was estimated between 41% and 50% for one landfill, and between 60% and 94% for the other one. In the winter, when the soil temperature was below zero, no difference between the isotopes was measured, indicating no soil oxidation. Methane emissions were measured in winter as well as in summer by using the static chamber method. This implies that the formation of methane is less influenced by seasonal ambient temperature variations, since the conditions (temperature, humidity) in the landfill most likely will not follow ambient conditions.

2.2.3 Results of measurements of methane emissions from landfills

A number of literature sources present data on measured methane emissions from landfills and data on the oxidation of the methane in the top layer of the landfill.

Measurement of methane emissions

[Bogner and Scott, 1997] have collected data of all methane emissions measured from landfills up to about 1995. The summarised data comprise twenty different emission measurement campaigns in the USA, the UK, The Netherlands, and Japan. For most measurements the static closed chamber method was used, but also other methods like the dynamic closed chamber, subsurface gradient, micrometeorological and SF6 tracer method were used. The measured values show a large variation from 0.0002 to 200 liter/m^2/day, which is partly explained by the following differences:

- The presence or absence of pumped gas recovery wells;
- The physical properties of the cover soils;
- The rates of methane oxidation.

When emission measurements from different sites are compared with more corresponding characteristics, the measured methane emissions show far less scatter, as shown in the results from [Oonk, 1995].

Oonk executed a measurement programme on number of Dutch landfills, were the methane and carbon dioxide emissions were measured using the mass balance method. These measurements were subsequently checked against the calculated emissions for those landfills. The calculation was carried out using a multi-phase model, using correction factors for oxidation, and for pumped gas recovery. As is shown in Figure 2.4, calculated and measured emissions show for some of the landfills a reasonably good correspondence, while for other landfills differences of up to a factor four occur.

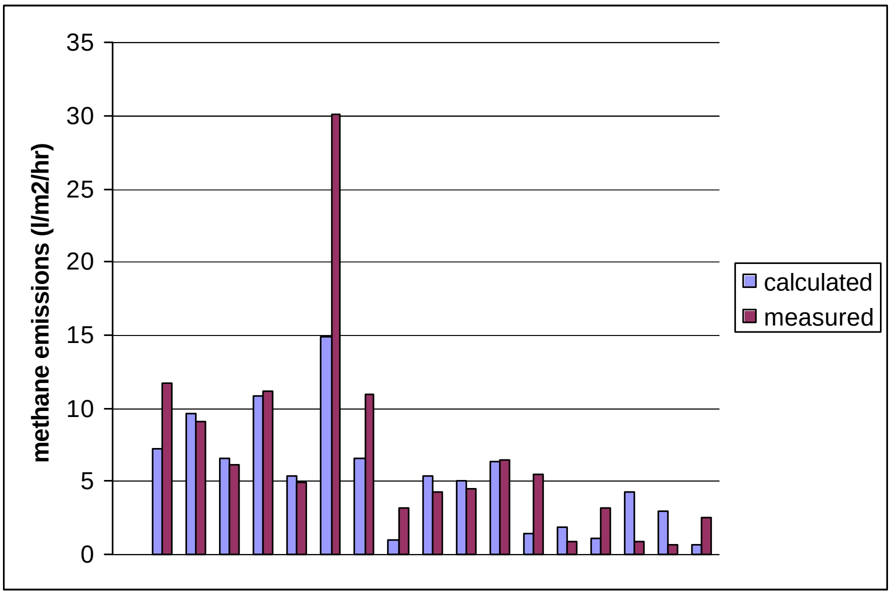

Figure 2.4 Calculated versus measured emissions for a number of Dutch landfill sites. [After Oonk, 1995].

Another typical example of methane emission measurements from landfills is [Czepiel et al., 1996a]. Methane emissions were measured at two locations on the Nashua, New Hampshire landfill, using the chamber measurement and the stationary plume method.

The Nashua landfill consist of 23.5 ha of MSW, and an adjectant 5.5 ha of C&D (construction and demolition) waste. 139 Chamber flux measurements were carried out on the MSW site and 48 on the C&D site, resulting in a whole-landfill flux of 15,800 liter methane/minute. Eleven stationary plume measurements were carried out, using an SF_6 tracer to calibrate. The resulting whole-landfill flux as measured with the stationary plume was 17,750 ± 22% liter methane/minute, showing good agreement with the chamber flux measurements.

The 139 chamber flux measurements were carried out during a five day period on both the MSW and the C&D locations. Emission measurements ranged from the detection limit (0.6 ml/m^2/hr) to 95 liter/m^2/hr, with a mean of 3.7 ± 326% liter/m^2/hr for the MSW location. For the C&D site measured emissions ranged from the detection limit to 9.2 liter /m^2/hr, with a mean of 0.19 ± 95% liter/m^2/hr.

This high uncertainty of 326% and 95% for the two locations is a consequence of the data set. In Figure 2.5 a cumulative probability plot of the data set is shown.

From this Figure it follows that the data distribution is skewed, implying that a lot of the chamber measurements yielded zero emissions, while a few measurements showed very high emissions. This high spatial variation is, as mentioned in Paragraph 2.2.2, uncorrelated beyond a range of 7 meters on the landfill. Because of the skewed data distribution, the mean methane flux is low compared to the maximum flux and consequently the standard deviation is very high.

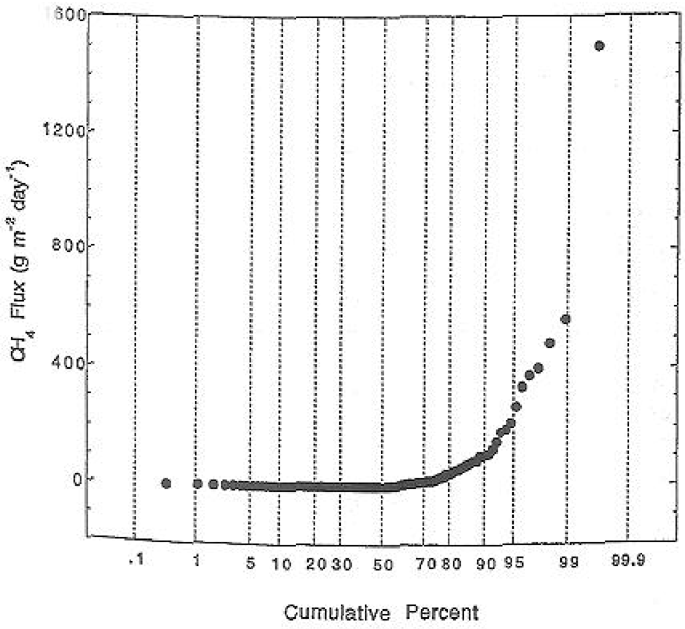

Figure 2.5 Cumulative probability plot of the methane emission measurements carried out with the chamber method by [Czepiel et al. 1996a]. The data distribution is skewed, implying in this case a large number of low values.

In their discussion Czepiel et al. point to other studies, showing similar spatial heterogeneity in the methane flux. A possible explanation for this large variation is that the heterogeneity of a typical landfill induces preferred subsurface pathways for gas transport, leading to limited areas with a very high methane emissions, as opposed to large areas with little or no emissions.

Measurement of methane oxidation

There is no unambiguous figure for the share of methane that is oxidised in the top layer of the landfill. According to default values of the IPCC [IPCC, 2000] a 10% reduction factor is assumed, but the scientific argumentation for this figure is superficial [Scharff et al., 2000].

Methane oxidation in landfill sites has been measured directly by several authors, such as [Borjesson et al., 2001] and [Boeckx et al., 1996]. As already mentioned in the previous Paragraph, [Borjesson et al., 2001] measured that 41% - 50% of the produced methane was oxidised in a landfill, respectively 60% to 94% in another. Using the same methodology as Borjesson (Carbon-13 to Carbon-12 isotope ratio) results are reported of around 10% methane oxidation in the North Eastern part of the USA, 25 to 35% in Florida, and 39 to 53% in Germany.

[Boeckx et al., 1996] used another method to determine the methane oxidation directly, namely soil incubation (the method also used by Borjesson in conjunction with the isotope method). In his article Boeckx focuses more on the circumstances controlling methane oxidation. It was found that microbial oxidation was controlled by several soil properties, such as soil moisture content, ammonium and nitrite content, temperature and nitrogen turnover.

[Czepiel et al, 1996b] has made a detailed study on the oxidation potential in landfill top layers. Czepiel also finds negligible oxidation when temperatures are below zero. Furthermore, he derives a semi-quantitative correlation between oxidation rate and temperature (Figure 2.6) and between the oxygen concentration and methane oxidation rates (Figure 2.7). Below 1% oxygen concentration, no methane oxidation occurs.

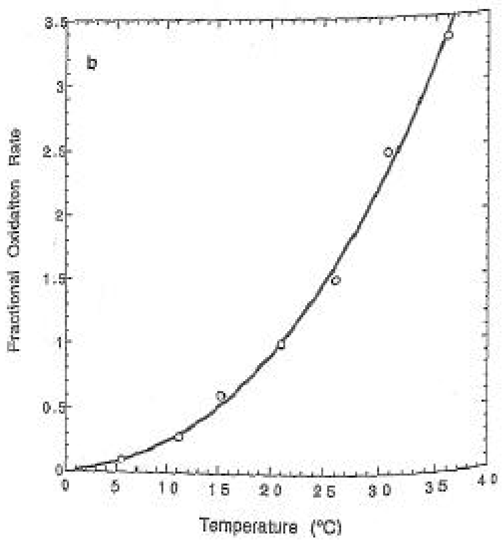

Figure 2.6 Semi-quantitative relation between temperature and methane oxidation rate in the top-layer of a landfill. From this figure it follows that methane oxidation is highly temperature dependent. Methane oxidation at 5°C is for example only 5% of methane oxidation at 30°C

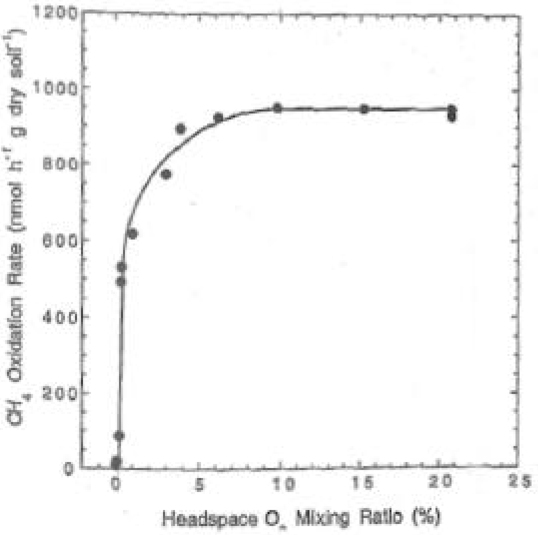

Figure 2.7 Oxygen-dependency of methane oxidation in the top-layer of a landfill, as measured by [Czepiel et al, 1996a]. Below 1% methane oxidation rates drop rapidly to zero.

2.3 METHANE EMISSIONS FROM WOOD STOCKPILES

Literature on the measurement of methane emissions from biomass stockpiles is very scarce. [Pier et al., 1995] measured the methane and carbon dioxide emissions from several sawdust stockpiles, located in the Tennessee valley in the USA. In this region the practise of storing wood waste in piles of over 10 m that are exposed to ambient conditions, provides an anaerobic environment for methane production in at least parts of the pile.

Pier used a combination of two methods: the probe sampling and the static chamber method. Measurements were carried out on eight wood waste piles of varying age. Probe samples were taken at three to four locations at depths of 1.5, 3.0, and 4.6 m for each location. Temperature and moisture content were also measured at these locations. Chamber sampling was done at four locations on each sawdust pile concurrent with the probe sampling.

Probe sampling results

The probe sampling yielded methane concentrations varying from 4 vol% to 63 vol%, with a mean of 20 vol%. This large variation occurs, despite the fact that these separate data points were each already the mean of twelve values measured at different spots in one pile.

Compared to landfill gas measurements, differences of an order of 3 within the same pile were observed when using the chamber method (see Paragraph 2.2.2). It is therefore realistic to assume a similar variation in methane concentration deeper in the stockpiles, such as measured with the probe method. Questions can however be posed regarding the number of data points used for the probe measurements by Pier. It is highly likely that overall methane emissions from the eight sawdust stockpiles would differ considerably, first of all because of their different age. Given this, and the normally observed spatial variation of an order three within the same pile, a data set of 12 points per pile is considered too small, except to show general trends.

Temperature measurement results

Temperatures in the sawdust pile showed at 1.5 meters a correlation (R = 51%) with ambient air temperatures. At 3.0 and 4.6 meters no effect on air temperature was observed, indicating that at these depths the pile temperature is independent of the ambient temperature, which was during measurements

Chamber measurement results

The chamber measurements yielded methane emissions in the range of 0.15 – 6.3 ml/m^2/hr, which is at the lower end of the range for landfills reported by [Bogner and Scott, 1997], and an order three lower than typical landfill values reported by [Czepiel et al., 1996a] and [Oonk, 1995]. The number of chamber measurements per pile was 4. The chamber measurements showed in all cases a significantly larger carbon dioxide emission compared to the measured methane emissions. The remark about the small number of sampling points that was made for the probe sampling results is even more valid in this case. Given the usually observed spatial variation of an order of three within the same location, a data set of four points per pile is considered too small, except to show general trends.

Compared to earlier mentioned landfill gas methane emission measurements, these low emission rates suggest that a large percentage of the methane produced was either oxidized or otherwise consumed before reaching the pile surface. Pier et al. state that the degree of methane oxidation as an explanation for low surface methane emissions cannot be determined with the data at hand. Since the methane oxidation was not measured directly in their study this conclusion seems right.

3 NITROUS OXIDE EMISSIONS

Regarding nitrous oxide emissions, data from wood stockpiles is non-existent, while even data from landfill emissions are rare. Since nitrous oxide emissions also related to aerobic activities, literature on emissions from compost piles is included here. In this Chapter nitrous oxide emissions mechanisms, measured emissions from landfills and compost piles and expected differences and similarities with wood stockpiles are discussed.

N_2O emissions are already at low values of importance because N_2O is a strong greenhouse gas. The IPCC [IPCC, 1996] recommends to assume that N_2O has a Greenhouse Warming Potential (GWP) of 310 based on a 100 year timeframe. This means that N_2O is 310 times more detrimental than CO_2 as a greenhouse gas. This is far higher than methane, which has a GWP of 21.

3.1 THE PROCESS OF N_2O FORMATION

Nitrous oxide is a stable gas which leaks from microbial cells during the complex processes of nitrification and denitrification. Because of these complex processes, increased N_2O emissions can be found under a combination of aerobic/anaerobic decomposition. Nitrification involves the oxidation of ammonium to nitrate. It is not clearly understood whether the N_2O is produced by nitrifying bacteria themselves, or if there is a nitrification/denitrification step. Denitrification involves the reduction of nitrate/nitrite to nitrogen gas, where facultative anaerobic bacteria utilise nitrate and nitrite as an electron acceptor when there is no oxygen present. Nitrous oxide is an intermediate product in the process. Figure gives a possible pathway of nitrification and denitrification in waste.

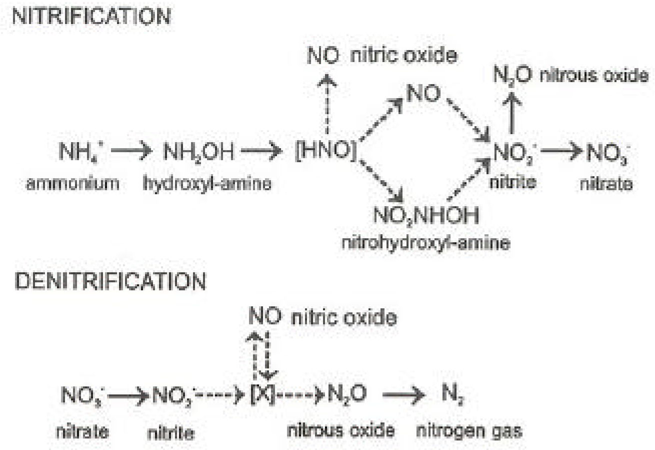

Figure 3.1 Possible pathways for nitrification and denitrification in waste [Barton et al., 2002]

N_2O formation in landfills is associated with the bacteria (methanotrophs) that consume methane in the oxidation layer of the landfill. This has been proven by field measurements and by soil incubation experiments. During these soil incubation experiments landfill soils were exposed to several methane concentrations and after a specific period the N_2O formation was measured. Beside the soil incubation experiments also stable isotopic analysis were executed with landfill soil. The researchers concluded after these two types of experiments that methanotrophs are important for the production and emissions of N_2O from landfill soils [Mandernack et al., 2000].

3.2 INFLUENCES OF MOISTURE ON N_2O EMISSIONS

In the United States monthly N_2O flux measurements were carried out on a landfill from July to December 1995. The N_2O fluxes were highest in early summer and decreased throughout the fall and early winter. The researchers assumed that the decrease in N_2O fluxes from July to December was due to lack of moisture and its effect on the soil microbial population, as there was virtually no rainfall [Mandernack et al., 2000].

By soil incubation experiments these assumptions were supported. For these soil incubation experiments soil was collected from one of the landfills in the USA. This soil had a moisture content of 7.2%. By increasing the moisture content of this soil sample to 13.1% the N_2O production rate increased about 20-fold over a period of 8 hours [Mandernack et al., 2000]. A Swedish research group confirmed the relation between moisture content and N_2O production [Börjesson et al., 2000].

Other evidence for the statement that moisture influences the N_2O emissions, can be found by executed measurements on grasslands in southern California. With these experiments it was concluded that N_2O formation in grasslands was primarily due to nitrification when the water content was below the water field capacity [Mandernack et al., 2000].

These experiments prove that desiccation suppresses nitrifying activities and associated N_2O production in the soil, resulting in lower N_2O emissions [Mandernack et al., 2000].

3.3 N_2O EMISSIONS FROM WASTE DISPOSAL IN LANDFILLS

Research papers regarding nitrous oxide emissions from landfills are very scarce. Only two papers were found addressing nitrous oxide emissions from landfills. Some papers were found dealing with soil incubation experiments.

[Barton et al., 2002] mentions the measurement of N_2O emissions from landfills. In this Japanese study of 1994 two landfills were examined: one active and the other one closed. In both landfills 10 Mton waste was dumped. Average N_2O emissions of 40.2 and 7.8 g/day for the active and closed landfill respectively, were observed in the landfill gas vent. These emissions mean that annually only 9.3 and 1.8 kg N is converted into N_2O, implying 0.019% (active landfill), and 0.004% (closed landfill) of the initial nitrogen [Barton et al., 2002].

Questions can be raised regarding this measurement method. Since N_2O emissions are associated with biological activity in the top-layer of a landfill, it is unknown how much N_2O is emitted via the landfill surface, and how much is emitted via the gas vent.

N_2O fluxes measured by Mandernack et al. [2000] in four landfills are shown in Table 3.1. The average fluxes of the four landfills are between 1.4 to 2.6 mg N/m^2/day[1] [Mandernack et al., 2000]. As shown in the table the ranges are very wide and the number of measurements are limited.

Table 3.1 N_2O emissions measured on landfills in the USA [Mandernack et al., 2000]

	Average flux (mg N m^{-2} day^{-1})	**Range** (mg N m^{-2} day^{-1})	**n**
Brea-Olinda (CA)	2.59	0.0-7.9	12
UCI (CA)	1.36	0.4-4.0	16
San Joaquin (CA)	1.81	0.4-4.0	5
Houghton (WA)	2.25	0.4-7.2	6

Monthly N_2O soil profile measurements were executed during the same period. Soil N_2O profiles at one location (UCI) indicated maximum concentrations were reached at a depth of 40 cm, which implies that N_2O production takes place near this depth. Soil N_2O concentrations at 40 cm declined from summer to early winter. This decline is in general agreement with the flux measurements which also declined over the same time interval. The researchers assumed that the decline in N_2O fluxes and soil concentrations from July to December was due to lack of moisture and its effect on the soil microbial population, as there was virtually no rainfall. Soil incubation experiments support this assumption [Mandernack et al., 2000].

3.4 N_2O EMISSIONS BY COMPOSTING

Research papers regarding nitrous oxide emissions from composting installations are mainly focussed on waste in combination with manure. These papers are beyond the scope of this literature review. In this Paragraph only papers regarding to composting of waste without mixing of manure are considered.

In 1993 three compost piles were made in Gaden near Freising in Germany. All piles consisted of 40% municipal solid waste (MSW) and 60% yard waste (brush, leaves and grass clipping). Each pile covered an area of about 20 m^2 (10 m x 2 m) and was initially about 0.8 m high. Concurrent with normal practices in composting these piles were turned regularly to improve the aerobic composting process. The three piles were turned in a daily, 3 days and a weekly turning rate for 52 days (main rot). After the main rot, the compost was cured for another 88 days (post rot) to produce more mature final compost.

During main and post rot the N_2O emissions were respectively 2.19 and 2.18 g/(t_0.day). Taking into account the number of composting days and a moisture content of 50%$_w$, this results in a N_2O emission of 150 g N_2O/t_{50}. These figures do not take into consideration the initial N content and the N losses of the compost. During the main rot experiments also the initial N content and the N losses during the first 52 days was measured. These experiments showed that during the main rot 0.5% of the initial N in the compost was converted into N_2O [Hellman, 1995], [Hellman et al., 1997].

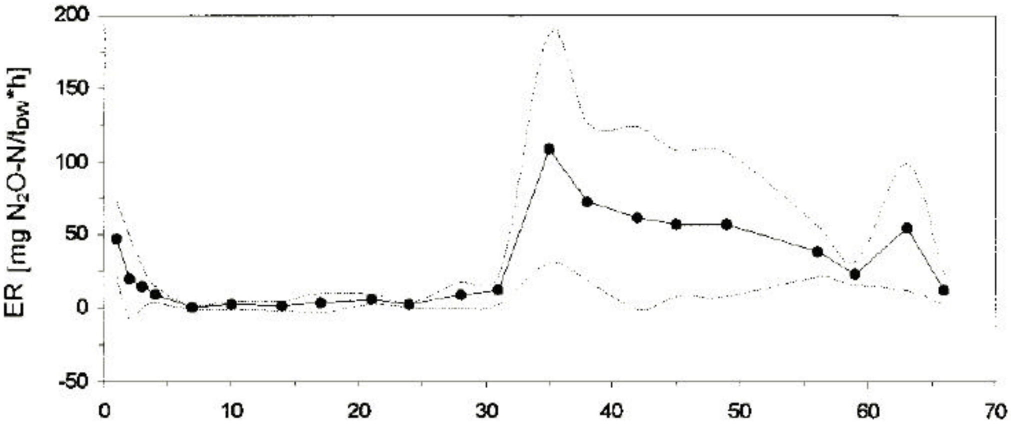

Figure 3.2 Emission rates (ER)of N_2O, measured over the course of maturation of a compost windrow, corresponding to tons (dry weight, t_{dw}) per hour over a period of 70 days [Hellman et al., 1997].

In Potsdam, German researchers investigated in 1996 the influence of aeration on the emission of trace gases by field-scale and laboratory scale experiments. During these experiments compost heaps (grass cuttings from land maintenance on bare soil) were equipped with measuring tubes to analyse the trace gases. These analysis showed a large variety of nitrous oxide emissions over a period of 3 months. In combination with the nitrogen analysis of the composting material it was concluded that 0.5% of the initial nitrogen was converted into nitrous oxide [Hellebrand, 1998].

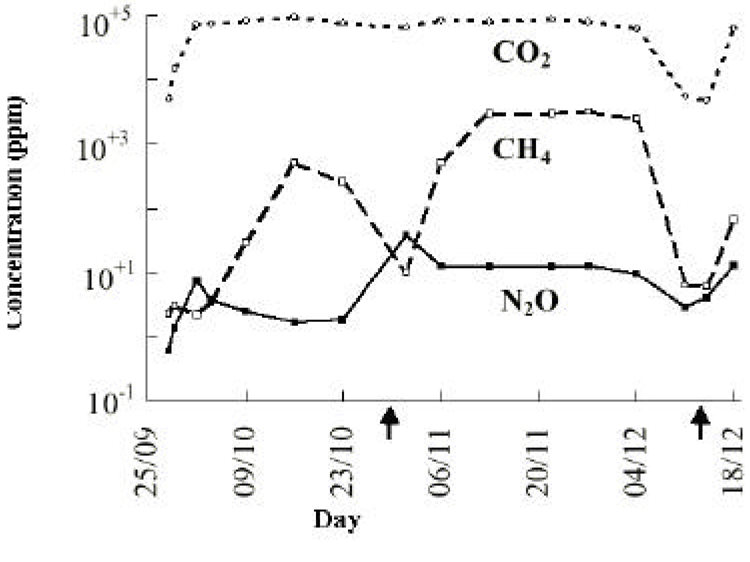

Figure 3.3 Average CO_2, CH_4 and N_2O concentration in compost air during composting. Arrows: turning piles. Source: [Hellebrand, 1999]

In other papers researchers have observed that between 0.2 to 1.2% of the initial total N content are emitted as N_2O. Table 3.2 gives an overview of the results of other research papers [Barton et al., 2002].

Table 3.2 Review of nitrous oxide emissions from composting [Barton et al., 2002], [Paul et al., 2000]. N_2O-N data represent the loss of initial N in the material that is converted into N_2O.

Compost and method	N_2O-N loss	Source
Yard waste-turned windrow	0.5%	[Hellebrand, 1998]
Food and yard waste-tunnel and static pile	0.2-0.4%	[Schenk et al., 1997]
Yard waste-turned windrow	1.2%	[Ballestero et al., 1996]
MSW (40%) and yard waste (60%) Windrow	0.5-0.8%	[Hellman, 1995] [Hellebrand, 1998]

Besides the high reported N_2O emissions during composting, there is also one research paper that reports the opposite of the earlier mentioned results. In this paper a Japanese research group investigated in 1999 N_2O emissions of a standard mixture of Japanese MSW in 18 liter reactors. According to the results of these experiments nitrous oxide was mainly generated at the beginning of composting and peaked during the first day. After two days, N_2O emission decreased near about the background level in the atmosphere [He et al., 2000].

3.5 DIFFERENCES IN EMISSIONS BETWEEN PROCESSES

Many nitrous oxide emission measurements have been carried out for composting installations, which is in sharp contrast to the limited data that were found for landfills. For wood stockpiles, no data were found. Therefore it is useful to examine the expected differences between these cases. These differences are especially important for the modeling of nitrous oxide emissions from wood stockpiles.

The most distinct difference is of course the type of waste. Wood stockpiles are far less heterogeneous than landfills and composting piles. Landfills can contain a large variety of materials, like garden waste, textiles, leather, plastics, wood and practically all other materials. Composting heaps can contain a large variety of organic materials, like garden waste, wood, grass and practically all other biomass materials. The Bulgarian wood stockpiles contain mainly wet bark and wood. This has consequences for the moisture content and the nitrogen content of the material.

The analysis of the moisture content of the Bulgarian biomass stockpiles showed a moisture content of 50 weight% (wet basis). This moisture content is much higher than the moisture content as reported for landfills in which N_2O emission were limited. With this fact it is likely that the moisture content is not a limiting factor for N_2O generation.

As far as known the nitrogen content of landfills, composting heaps and biomass stockpiles are in the same order of magnitude. Therefore, differences caused by this effect can be neglected.

A uniform parameter by which N_2O emissions can be characterised, is the conversion of initial nitrogen into nitrous oxide. As presented before, researchers demonstrated that 0.02% of the initial nitrogen in landfill waste is converted into N_2O. On the other hand emission experiments of composting heaps showed that 0.2 – 1.2% of the initial nitrogen in the heap is converted into N_2O.

As written in Chapter 3.1, N_2O formation in landfills is associated with the bacteria (methanotrophs) that consume methane in the oxidation layer of the landfill. In the biomass stockpiles under study methane oxidation has been proven by field measurements. With this argument it is likely that N_2O is formed is the biomass stockpiles.

4 MEASUREMENT PROCEDURE

Based on the findings of an inception mission, the most suitable measurement procedure for measuring methane emissions from the specific wood stockpiles in Bulgaria has been selected.

4.1 INCEPTION MISSION RESULTS

An inception mission was carried out in the framework of this project in January 2002. During this inception mission three locations have been visited:

A) Razlog;
B) Svishtov;
C) Stamboliynski

In Figure 4.1 the location of the three wood stockpiles is indicated

In the next Paragraphs the stockpiles are described briefly. In Annex B the locations are described in more detail.

Figure 4.1 Geographical location of both measurement locations (A: Razlog, B: Svishtov, C: Stamboliynski)

4.1.1 Razlog

The Razlog site consists of a ravine, in which the biomass is dumped. This dump has a maximum height of about 10 meter and a size of 50 by 300 meter. It is polluted with large stones. It contains mainly soft wood bark (spruce, etc). It is a small dump, located next to a landfill dump. Because of self-ignition, some areas of the dump have been burned.

4.1.2 Svishtov

In Svishtov three wood waste piles are located. One dump is in operation since 1994. It has a surface of ca. 28.000 m^2 and a size of approximately 400 by 70 meter. The pile looks like a slope starting at the gate at ground level and reaches a maximum height of about 8 meter at the end of the pile. It contains mainly hard wood bark (oak, acacia, etc). In the neighbourhood of this pile two other older piles are located. Because of self-ignition, some areas of the dump have been burned. The dump is located in an area with industrial activities. One of the older piles (the 1985-1994 pile) is contaminated with municipal waste, making it less suitable for measurement.

4.1.3 Stamboliynski

This dump has a maximum height of about 6 meter and a size of 300 by 500 meter. It contains mainly soft wood bark (spruce, etc). It is a large dump that is polluted at some points with municipal waste (especially the older parts of the dump).

4.1.4 Conclusions inception mission

The most suitable locations for methane flux measurement are Razlog and Svishtov (the 1994-now pile), because:

- at these locations information is available about the history, composition, etc.;
- the piles are homogenous (hard wood bark and sawdust in Svishtov and softwood in Razlog);
- the piles are not polluted by other waste streams like municipal waste;
- in one of the piles at Svishtov a relatively good separation of waste from different years is possible.

However, self-ignition at Razlog may hamper certain measurements (e.g. organic matter analysis). Furthermore, at Razlog a distinction with respect to the waste of different years is more difficult.

4.2 SELECTION OF METHANE EMISSIONS MEASUREMENT METHOD

The measurement of the methane emissions of the wood stockpiles should result in quantitative and representative results that can be used as input for the methane emission model, developed in the course of this project.

Nine possible methods to measure methane emissions and/or methane oxidation from wood stockpiles are encountered (see Annex C). Each of this methods has its advantages and drawbacks, which have to be carefully assessed, taking into account the project specific conditions and the needed input for the spreadsheet model.

4.2.1 Project-specific conditions

The specific requirements and boundary conditions for this project are:

- The location and time of the field measurements. The wood stockpiles are located in Bulgaria, and measurements will take place during early spring, when ambient temperatures will most likely be low. This means that methane oxidation will be low or absent.

- The surrounding of the wood stockpiles. Both the Razlog and the Svishtov pile are located next to other sources that emit methane, limiting the use of several measurement methods.

- The shape and appearance of the wood stockpiles. The surface of the Razlog and Svishtov piles is not flat, which hampers the use of some methods

4.2.2 Applicability of measurement methods

In this Paragraph the applicability of the various methods, described in Annex C, to measure methane emissions and/or methane oxidation for the specific wood piles is discussed.

Two of the nine methods listed in Annex C can be classified as supporting, namely *isotope measurements* and s*oil core measurements.*

Isotope measurements can be useful in determining the amount of methane oxidation, which is only a part of the overall system. The method can thus play a supportive role to methods that are used for measuring the methane flux.

Soil core measurements can be used to study two important aspects of the system, namely diffusion and oxidation. Convection is not taken into account. Because emissions are measured indirectly, and because only an impression of emission and oxidation on a small spot on a single moment is given, this method is considered supportive to other methods which can measure emissions directly.

Static and dynamic closed chambers can both be used for measuring methane emissions in a wood stockpile. Obvious advantages are the extensive experience that has been developed world-wide with this method, other methane sources nearby cannot disturb the measurements, and methane emissions are measured directly. Since the spatial resolution is very limited, a large number of measurements are required to obtain representative values. If vegetation occurs, the method is not useable. With respect to the type of measurement (static or dynamic chambers) dynamic chambers are preferred, since problems with pressure differences inside the chambers are avoided. The duration of one single measurement is however limited to a maximum of several hours.

The mass balance method can be used to measure methane emissions directly. Automated measurements can be carried out, allowing a good insight in the temporal variation in the methane emissions. Since variations in methane emissions will be far less once the methane has left the surface, spatial variation in the wood stockpile emission measurement will be limited. The geometry of the wood stockpiles, as well as the proximity of nearby methane sources can limit the applicability. A drawback of this method is that it is not widely applied.

The static and mobile plume method are both in principle suitable for measuring the methane emissions. The mobile plume method allows for a direct measurement and easy interpretation, especially when an SF_6 tracer is used. A measurement transect should be available downwind of the site, while other methane sources in the proximity may limit applicability. A drawback of this method is that it is new and needs evaluation. The mobile plume method has the disadvantage of being expensive and requiring significant manpower. The methods account well for spatial variability, but temporal variability is not accounted for, since the method is not executed automatically. Taking all these issues into account the static and mobile plume measurement methods are considered less suitable compared to the mass balance method, since they have about the same advantages, while having the additional drawback of a low temporal resolution.

Micrometeorological methods are not suitable in the framework of this assignment, because of the requirement of a large flat surface, which severely limits applicability to other sites, should a flat wood stockpile even be found.

The sub-surface vertical gradient method cannot be used to measure the methane emissions directly. Methane emissions are measured indirectly, using Fick’s law for diffusion. Convective transport is not directly accounted for, only as a correction factor to the diffusion coefficient. This is an approximation which is only valid if there is indeed at least some diffusion, since pressure differences without diffusion would result in a measured flux of zero, while in reality convective transport could cause an unspecified methane flux. The method suffers from the same low spatial and temporal resolution as the chamber methods. Important advantages however are the low costs, and the fact that it is possible to follow the processes inside the wood stockpile.

4.2.3 Methane emission measurement method selection

From the overview in the previous Paragraph, the following methods are considered possibly useful:

- Mass-balance method
- Static or dynamic closed chambers
- Sub-surface vertical gradient method (probe sampling)

The *mass-balance method* will result in a reliable figure (±25%) for the methane flux of an entire dump. Based on the results of the inception mission, it is however concluded that this method is not suitable for this project. because:

- At both the Razlog and the Svishtov sites, there are other waste stockpiles located nearby. Since distinction between CH_4 emissions from adjectant sources is not possible with this method, an error of unknown magnitude is introduced in measurement, rendering the results unreliable.
- In one site (Svishtov), distinction between methane emissions from wood waste of different ages could possibly be made. The mass balance method measures these methane emissions not separately, so no distinction can be made

The two other methods (*static or dynamic closed chambers and the sub-surface vertical gradient method*) show the same low resolution regarding spatial and temporal variation: Both measure methane in a small area (maximum several m^2), and at a single point in time. By executing a large number of measurements the spatial resolution can be increased. The sub-surface vertical gradient method suffers the additional drawbacks of not being able to measure the methane emissions directly, and that convective transport is neglected. From literature sources it is clear that methane transport through convection can sometimes be substantial. Advantages are the low costs, and the fact that it is possible to follow the processes inside a stockpile. Chamber methods have the advantage of extensive experience and the possibility to measure the methane flux directly. Since it has been determined that vegetation is not present on the selected stockpiles in a quantity sufficient to disturb measurements, this drawback is not applicable in the scope of this project.

Considering these arguments, the chamber method has been selected as best suited to measure the methane flux in the framework of this project.

4.3 MEASUREMENT PROCEDURE

Besides measuring the methane flux from the wood stockpiles, additional data are needed for the model that predicts the methane emissions. Necessary measurements include:

- The organic carbon content of the wood waste, to be able to compare the measurement results to the spreadsheet model;
- The thickness of the oxidation layer, to determine which part of the pile is under anaerobic conditions;
- Temperature, barometric pressure and wind speed, to be able to compare the results to other wood stockpiles.

In the next Paragraph the full measurement procedure, with all supportive measurements is discussed.

Methane emission measurements

For the methane flux measurements a dynamic chamber was used. The principle according to which this chamber operates is that a controlled amount of air (retrieved from two meter above ground level) is inserted into the chamber, to generate an air flow at the chamber outlet. In Figure 4.2 this principle is illustrated. For accurate measurement this flow should be as low as possible, without causing methane accumulation inside the chamber. The methane concentration at the entrance and the exit of the chamber is measured in triplo, by collecting the inlet and outlet gas in sample bags, and measuring the methane concentrations with a gas chromatograph (GC).

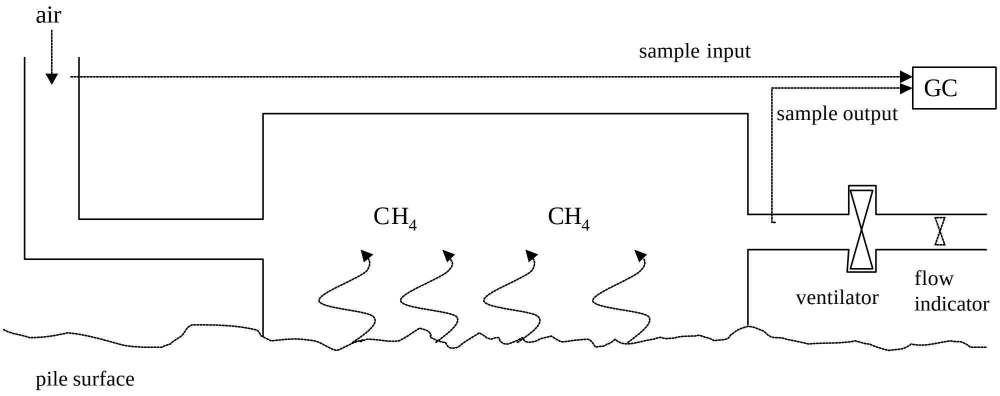

Figure 4.2 Methane flux measurement method. Methane, emitted from the pile surface, is mixed with a known air flow, and the resulting concentration difference is measured with a gas chromatograph.

The methane flux is calculated according to the following formula:

$$J = \frac{\Phi_v \cdot \Delta C}{A}$$

Where J is the methane flux (liter/m^2/hr), Φ_v is the volume flow of air (m^3/hr), ΔC is the methane concentration difference between the chamber inlet and outlet (in liter methane/m^3) and A is the surface area of the chamber (m^2). The methane concentration was measured with a Chrompack micro gas chromatograph model CP-2002 P. This is a portable gas chromatograph with an accuracy of 1 ppm.

The **thickness of the oxidation layer** can be measured through measuring the concentration of oxygen in the top layer. It has been derived in literature that below an oxygen concentration of 1% practically no methane oxidation takes place [Czepiel et al., 1996b]. The oxygen content in the top layer can be measured via:

- Probe sampling;
- Soil incubation methods to determine the oxidation potential of the top layer, which can subsequently be used as a measure for the oxygen content.

However, since the methane oxidation and the oxygen content of the top layer are not automatically coupled (f.e. when top layer temperatures are below zero, and no methane oxidation takes place), the first method is preferred. It is assumed that the thickness of the oxidation layer is not constant in one pile, so several measurements will be necessary.

The **organic carbon content of the fresh material**. This parameter can be measured by analysis of the dry matter fraction and the organic carbon content of fresh wood waste. An important aspect is sampling. Since any biological material shows a variation in composition, an averaged sample must be extracted. This involves taking several samples and thoroughly mixing these.

The **hemicellulose and cellulose content of the fresh material (u_0)** This parameter can be measured by measuring the acid-insoluble residue in biomass. Since biomass consists generally of:

- cellulose, a polymer of glucose;
- hemicellulose: a shorter polymer consisting also of carbohydrates;
- lignin, a complex, cross-linked molecule, which gives biological material its mechanical strength.

It is known that lignin in biomass will not decompose under anaerobic conditions which implies that it should be excluded from emission models. Because lignin is also acid-insoluble, determining the acid-insoluble fraction of the fresh biomass also gives the lignin fraction. This measurement is standardised in ASTM E1721/E1757. The sampling of the fresh biomass should also receive considerable attention.

The **CH_4 concentration inside the stockpile** can serve as a useful check to determine whether or not anaerobic conditions occur inside a stockpile. This way methane formation can be determined independent of oxidation. The CH_4 concentration inside a stockpile can be measured through probe sampling.

Temperature, (barometric) pressure and wind speed must be measured because of their known influence on methane emissions. Temperature measurement inside the top layer can be used to estimate the oxidation potential. Pressure and wind speed are not explicitly accounted for in the model, but must be measured to be able to compare with later measurements on the same stockpile, emission measurements on other stockpiles, and to be able to assess measurement conditions.

5 MODEL CHOICE

Generally a first order model is used for the modelling of anaerobic decomposition of organic waste. But also other models exist like zero and second order models. The models are discussed in the Paragraphs below.

5.1 FIRST ORDER MODEL

When a first order approach is used for the modelling of anaerobic decomposition of organic waste, the rate of decomposition is taken proportional to the available organic material:

$$\frac{dC(t)}{dt} = -kC(t)$$

C(t) is the concentration of available organic carbon (in kg per ton of waste) that can be transformed into gas at the time t. The rate constant *k* can be calculated by:

$$k = \frac{-\ln(0.5)}{t_{1/2}}$$

The factor $t_{1/2}$ (year) is the 'half-life', which is the time when half of the carbon is converted. Since the half-life is generally known for most types of refuse, the rate constant can be determined for each type of refuse. In table 5.1 decomposition data for some common waste materials is shown [Van Zanten and Schepers, 1997]:

Table 5.1 Decomposition data for a number of domestic waste materials.

Decomposition rate	$t_{1/2}$(y)	k(y^{-1})	$t_{1/2}$(y)	k(y^{-1})
1. fast (bread, green waste)	2	0.347	3	0.231
2. moderate (paper)	7	0.099	10	0.069
3. slow (textile, leather, wood)	15	0.046	30	0.023

The half-life for a typical landfill can therefore be determined when the average composition of the waste is known. The rate of methane formation α (in m^3 per ton per year) can be determined using a recalculation factor thereby expressing the quantity of decomposed carbon into the corresponding quantity of gas. This factor is 1.87 m^3 per kg carbon, as shown in the calculation in Annex D. The rate of formation is thus:

$$a = -a\frac{dC(t)}{dt} = akC_0e^{-kt}$$

The above mentioned model assumes that methane formation starts immediately after emplacement, and reaches its maximum rate immediately. In the real situation methane formation starts after decomposition and gradually increases until a maximum is reached. This is sometimes incorporated in a modified first order model.

Not all carbon is converted into landfill gas. Part of the organic carbon cannot be decomposed by the enzymes and bacteria, while in parts of the landfill no anaerobic digestion can take place due to a hostile environment for the bacteria. This factor, the generation factor ζ(-), is amongst other things dependent on the composition of the waste, temperature and moisture. In The Netherlands this factor is generally assumed to be in the range of 0.5 to 0.6 [Van Zanten and Schepers, 1997].

5.2 OTHER MODELS

Besides the first order model, other models are possible. For global methane emissions for example, a zero order model is used, which assumes a steady state methane generation of the degradable organic carbon content of the landfill. This model can be used when the formation of landfill gas is entirely dependent on moisture transport.

Another possibility mentioned by [Van Zanten and Schepers, 1997] is a second order model, which accounts for presumed deficits in the first order model. These presumed deficits relate to the prediction of the methane emissions at the beginning and at the end of the landfill lifetime. In the beginning gas production is usually higher than predicted by a first order model, due to the higher than average temperature combined with the availability of easily degradable waste. At the end of a landfill lifetime, the rate of decomposition is more and more determined by the moisture content, and the first order model predicts too high methane emissions. In a second order model, the relation between decomposition and organic content is quadratic, resulting in a high gas production at the beginning and a low gas production at the end of a landfill's lifetime. The physical basis for the second order model is however not clear. Apart from this, questions can be raised by the approach. Used for the end of a landfill lifetime, a mass-transfer limited process is thus approximated by changing reaction kinetics.

As described in an overview relating to the measurements and modelling of methane fluxes by [Smith and Bogner, 1997], of the three modelling methods which are currently used, two are based on a first order approach. The third is the current IPCC zero-order approach. First order models are also at the heart of more rigorous modelling efforts, such as by [Manna et al., 1998].

To distinguish between several types of refuse, the first order model can also be detailed into a multi-phase model. The multi-phase model is essentially a superposition of a number of first-order kinetic terms, one for each type of refuse. The multiphase model is expressed mathematically as follows:

$$Q(t) = \zeta a \sum_{j=0}^{n} \sum_{i=1}^{m} A_j k_i C_{0,,i,j} v_0 e^{-k(t-j)}$$

In this model the following variables are used:

Q(t)	(m^3/year) the annual landfill gas generation
ζ	(-) generation factor
a	(m^3/kg carbon) recalculation factor

k_i	(year^{-1}) decomposition rate constant for a waste of type i
A_j	(tonne) amount of waste in tonnes, dumped in year j
$C_{0,i,j}$	(kg/tonne) the amount of initial organic carbon in waste of type i, dumped during year j
t	time in years elapsed since the depositing of the waste
m	(-) number of separate waste types
n	(year) number of years during which waste is dumped

The amount of initial organic carbon is determined according to the following formula

$$C_{0,i,j} = \frac{\sum_{c=1}^{m} A_{c,j} d_i o_i c_i}{A_j} \cdot 1000$$

Here the following symbols are introduced:

$A_{c,j}$	(tonne) amount of waste in tonnes of category c, dumped in year j
c	(-) number of separate waste categories
d_i	(-) dry matter content of waste type i
o_i	(-) organic matter content of waste type i
c_i	(-) carbon content of waste type i (dry basis)
m	(-) number of separate waste categories.

None of these models take methane oxidation explicitly into account. In the approach of [Oonk, 1995] a deduction factor is assumed for the amount of methane formed that is oxidised. In the case of Oonk this factor is estimated at 10-15%.

5.3 MODEL CHOICE

In this Paragraph a selection is made of the most appropriate model for the estimation of methane emissions from wood stockpiles. The selection was made on the basis of the requirements of the model that were mentioned in the assignment. These requirements include that with the spreadsheet model it should be possible to estimate methane emissions from wood stockpiles as a function of time and relevant variables. The spreadsheet model is intended to be used by future project developers, which need to be instructed on how to use the model, and how to assess methane emissions with a sampling protocol. Based on these requirements the following demands are made on the model:

- The model should predict methane emissions as a function of time for wood stockpiles, using methane emission measurements at a specific time as a possible input. This means that a zero order model is not appropriate, since an exponential decline of methane emissions from wood stockpiles is expected, similar to landfills.

- The model should preferably only require input parameters that are relatively easy to obtain by the project developer.
- The model should be applicable for a variety of locations, and be able to incorporate wood waste of various ages and types. The model should also be able to incorporate the effects of wood that will be dumped in the future.

Based on these requirements a multi-phase model, as described in an earlier Paragraph, is the most suitable. The multi-phase model uses a superposition of first order kinetic models, one for each type of waste, and takes also waste dumping over a number of years into account. In the specific case of wood stockpiles, the model can be modified in such a way, that one first order kinetic model is used for wood waste of a particular year. With respect to methane oxidation a correction factor can be applied to the resulting methane emission.

Two alternatives, the simple first order kinetic model and the second order model are not suitable for this specific application. The simple model fails namely in estimating methane emissions in a wood stockpile if wood is dumped over a number of years, which will most often be the case. The second order model is considered not suitable because it lacks a physical basis, as described earlier.

More rigorous modelling exercises, such as described in [Manna et al., 1998] can potentially result in a better estimations of the methane emissions, by taking temperature variations in time and depth into account. Such models have however not been generally accepted, and are for the specific application in this project considered too complicated.

The resulting methane emission has to be corrected for methane oxidation. For landfills the part of methane that is oxidised can be substantial, as was discussed in Paragraph 2.2.3. As for wood stockpiles accurate data are lacking, initially a reduction factor of 10% (the IPCC default value for landfills) will be assumed, although the scientific base for this figure is poor.

5.4 WOOD STOCKPILE METHANE EMISSION MODEL

For the specific case of wood stockpiles, the general multiphase model is adapted as follows:

$$Q_m = V_m(za\sum_{j=0}^{n}(A_j - A_{ox,j})kC_{0,j}\,rv_0 e^{-k(t-j)})*(1-z_{ox})$$

This model describes the landfill methane emission Q_m (m^3/year) in one wood stockpile in which wood is dumped for a number of years n (year). In this model several factors are known beforehand:

A_j (m^3) The volume of wood which is dumped during year j. In this model it is assumed that for all values of j (0..m) the accurate volume is known, for example through records on wood dumpings through the years.

a	The conversion factor from available organic carbon for decomposition (in kg) to cubic meters of biogas (m^3). This factor is equal to 1.87 m^3/kg carbon.

There are a number of unknown parameters, which need to be measured or – if necessary – estimated:

$Q(t)$	(m^3/year) The total landfill gas flux of a specific wood stockpile can be measured by an “entire landfill method” or a “specific pile method”. According to the model the total landfill gas flux is a superposition of the landfill gas fluxes of the biomass dumped every year.
$A_{ox,j}$	(m^3) Volume of the wood stockpile in which no anaerobic digestion takes place. This volume can be determined by multiplying the thickness of the oxidation layer with the geometrical dimensions (length and with) of the wood dumped in year j. Measurement of the thickness of the oxidation layer can be carried out by probe sampling or soil incubation measurements.
k	($year^{-1}$) The decomposition constant k is calculated using the half-life ($t_{½}$) of wood. This decomposition constant is assumed to be constant for one specific biomass stockpile.
$C_{0,j}\ \rho$	(kg/m^3) The initial organic carbon content of the dumped wood waste in a given year j. In this contraction ρ is the bulk density of the material in kg/m^3, while $C_{0,j}$ is the carbon fraction of the wood on a wet basis. This parameter can be measured by analysing the dry matter fraction and the carbon content of a sample fresh wood waste. This parameter can be replaced by the carbon fraction, measured on a dry basis, through the following: $C_{0,j,wb} = C_{0,j,db} \times (1 – MC_{wb})$.
υ_0	(-) fraction of the initial organic carbon content ($C_{0,j}$) which is hemicellulose and cellulose. The reason for this is that it is known that the lignin in the $C_{0,j}$ will not decompose [Micales et al., 1997]. The υ_0 fraction can be measured by acid solubility measurement of a fresh wood waste sample.
ζ	(-) the generation factor is an empirical factor which is included to account for the fact that the decompostion of organic carbon to methane is not taking place under ideal circumstances. In this case, this generation factor also accounts for the fact that not only methane is formed, but also carbon dioxide. This generation factor cannot be measured directly, but should follow from the other parameters.
V_m	(-) The methane fraction in the emitted landfill gas. It is assumed that landfill gas in the case of wood stockpiles in Bulgaria consists for 60% of methane.
ζ_{ox}	(-) methane oxidation factor represents the amount of methane which is oxidised in the top-layer through biological activity. This factor can be measured by isotope measurement or by soil incubation. Literature values of oxidation in landfill top soils are available. There are also methane oxidation rates as a function of temperature available from literature [Czepiel, 1996b].

6 RESULTS

6.1 MEASUREMENT RESULTS SVISHTOV STOCKPILE

6.1.1 Description of the Svishtov pile

In Figure 6.1 a schematic representation of the Svishtov pile and the part on which methane emission measurements were carried out are shown. The Eastern part of the pile (marked red in Figure 6.1) was on fire during the measurements. Measurements were executed on the remaining part of the pile which was not on fire.

In Figure 6.2 a top-down view of the unburned part of the Svishtov pile is shown. On this part measurements were carried out. It is an area of 150 meters by 50 meters, on which both new and old wood waste is present. The gate area is excluded, since in this part almost no wood waste is present. In this drawing a grid, representing 10 x 10 meters per cell is defined. The grid identifiers range from A0 to P50. 46 Chamber measurements have been carried out in triplo each in a different grid cell.

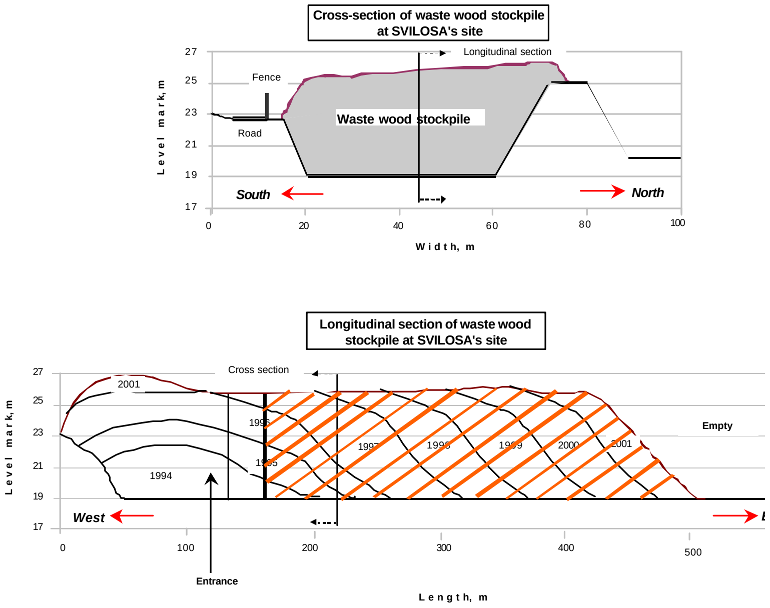

Figure 6.1 Schematic representation of the Svishtov pile. The area on fire is marked red.

Flux measurements were always carried out in the middle of a cell. Probe measurements were also carried out in the middle of a cell, with the exception of some measurements on the edge of the pile. The height of the wood pile is roughly 8 meters. Water was consistently encountered at three meters depth, so 5/8 of the pile is below this water level during measurements.

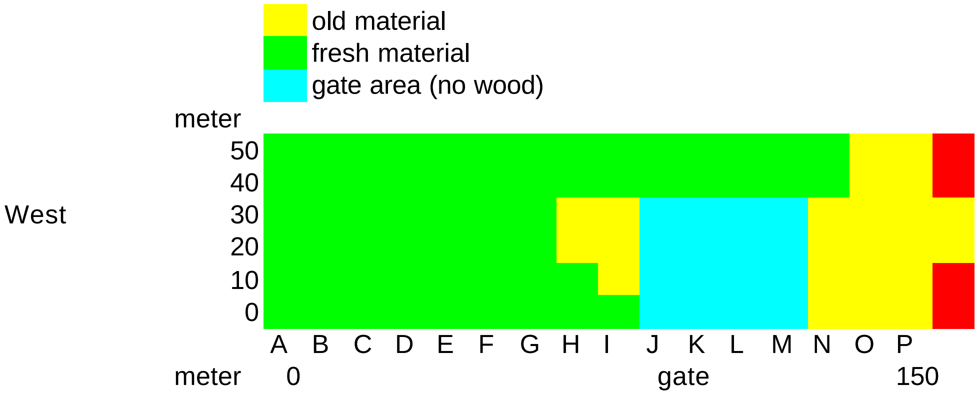

Figure 6.2 Top-down view of the part of the Svishtov pile on which measurements were carried out.

6.1.2 Measured methane fluxes

Measurements were carried out during week 13 and 14 of 2002. The weather was usually sunny, with one day of light rain. Ambient temperatures were ca. 10°C. Barometric pressures were also fairly constant, ranging from 1020 to 1025 mbar. Wind speeds were negligible during measurements. The methane fluxes measured are presented in Figure 6.3. In Annex E the results are presented in tabulated form.

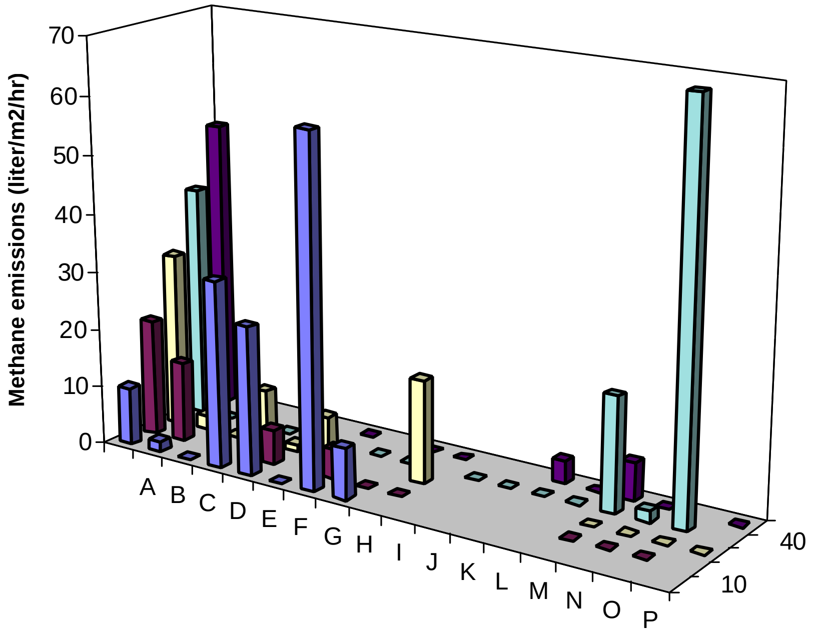

Figure 6.3 Measured methane fluxes on the Svishtov pile. In the cells without entry no measurements were carried out.

Measurements were carried out in triplo, and the averaged values were used to compute the resulting fluxes. Standard deviations were roughly 10%. Some flux measurements were carried out near the entrance, with the expected result of no methane emissions. These measurements are excluded from further calculations.

The pattern of methane fluxes is according to expectations. On a number of spots no methane was measured, on a number of spots some methane was measured, and on some spots (for example F10 and O40) methane emissions were very high. On these spots measurements were repeated, giving similar results.

Based on the results shown in Figure 6.3 it can be concluded that the methane emissions are not related to the fire in the other parts of the pile. Should this be the case, a methane emission gradient would have been observed, with higher emissions near the fire (Sections M, N, O, and P). The observed pattern does however appear to be random.

The average methane flux from this section of the Svishtov pile is 6.4 liter/m^2/hr. Regarding the accuracy of the measurements, reference is made to Annex F. From the analysis shown there it is clear that measurement errors are small, especially when compared to the large confidence interval mentioned below.

6.1.3 Statistical considerations

The results from the flux measurements as depicted in Figure 6.3 show a wide scatter, which is in line with the results of others, for example [Czepiel et al. 1996a]. Similar to the measurements of Czepiel, the distribution of methane flux quantities is not a normal distribution, with most measurements centred around a mean, but a skewed one. Most of the data points are zero's, and a few data points show a very high methane flux. Therefore, the average flux is low compared to the maximum measured flux.

Because of the large number of data points (n = 46), it is possible to determine a standard deviation and a confidence interval. Generally speaking, when the number of sample points is higher than 40, it is possible to determine a standard deviation and a confidence interval, irrespective of the underlying distribution [Devore, 2000]. In Table 6.1 some important statistical parameters are given.

Table 6.1 Main statistical parameters of the Svishtov methane flux measurements.

Average methane flux (liter/m^2/hr)	6.4
Standard deviation (liter/m^2/hr)	13.6
90% confidence interval (liter/m^2/hr)	3.1 – 9.5
95% confidence interval (liter/m^2/hr)	2.5 – 10.4

A 90% confidence interval implies that there is a 90% chance that the actual methane emissions of the Svilosa pile lie within the given interval. From this table it is clear that the data set shows a large confidence interval and a large standard deviation. A reason for this is the average flux, which is low compared to some of the highest flux measurements. This is also in line with the results from Czepiel, who reported for two landfills methane fluxes standard deviations of 326% and 95%.

6.1.4 Probe measurement results

Probe measurements were carried out in sections C and F in the middle of the pile and also near the edges of the pile. Probe measurements were hampered by the occurrence of stones, which limited the amount of measurements.

Table 6.2 Oxygen concentrations (volume percentage) inside the Svishtov pile, as measured with a probe. In the cells without entry no measurements were carried out.

Cell	1	3	10	20	30	40	50
C – 1 m	15.4		1.0	1.4	1.7	1.1	
C – 2 m	5.9		1.0	1.2	0.7	0.8	
C – 3 m	0.8		1.3	0.7	0.7	0.7	
F – 1 m	6.0	2.9	0.6				
F – 2 m	5.9	1.3	0.7				
F – 3 m	8.8	1.2	water				

From this table it follows that already at 1 meter depth the oxygen percentage has dropped from 20% (ambient oxygen concentration) to 2% or less, indicating an aerobic layer depth of less than 1 meter. Water was encountered consistently at ca. 3 meters in the pile.

From the measurements near the edges of the pile, designated as cell 1 and 3 to indicate a distance of respectively 1 and 3 meters from the edge of the pile, it is clear that the oxygen concentration gradients follow the same pattern as on top of the pile. Near the edge the concentration is still relatively high, but further from the edge the oxygen percentage drops rapidly.

Table 6.3 Methane concentrations (volume percentage) inside the Svishtov pile, as measured with a probe. In the cells without entry no measurements were carried out.

Cell	1	3	10	20	30	40	50
C – 1 m	0.6		27.9	30.3	11.2	14.5	
C – 2 m	7.3		28.0	29.4	20.6	18.8	
C – 3 m	17.9		29.0	29.8	20.4	19.4	
F – 1 m	0.1	2.1	47.4				
F – 2 m	0.1	3.4	43.7				
F – 3 m	0.0	2.7	water				

Methane concentrations inside the pile show a variation from 10% to 50%. Given the significant methane emissions as shown in Figure 6.3, it is no surprise that the methane concentration is also significant inside the pile. When comparing the methane concentrations inside the pile with the measured methane emissions, a relationship between the measured methane flux and the concentrations inside the pile is not straight-forward. In C10 and C20 a significant methane flux is measured (see Figure 6.3), while in C40 no methane flux is measured, despite significant methane concentrations inside the pile. This implies that methane is indeed emitted erratically from the pile surface, probably because of “channelling”.

The oxygen percentage and the methane concentration are not directly linked. One of the reasons may be that methane is flowing vertically through the pile to the surface. This implies the possibility of no anaerobic digestion in the top layer, while there is still a significant methane concentration present. The low methane concentrations near the edge of the pile show that it is likely that at these locations little or no methane is flowing sideways out of the pile.

From Table 6.4 it follows that temperatures are significantly above ambient inside the pile, with temperatures as high as 53°C in location C30. Also the water, which was encountered at F10, shows a higher than ambient temperature. Temperatures ranging from 30°C to 50°C substantially improve gas production, which could be one of the explanations for the high methane emissions.

Table 6.4 Temperatures (°C) inside the Svishtov pile, as measured with a probe. In the cells without entry no measurements were carried out.

Cell	1	3	10	20	30	40	50
C – 1 m	64		44.0	34.0	37.0	38.0	
C – 2 m	66		41.0	37.0	35.0	35.0	
C – 3 m	54		37.0	53.0	36.5	35.0	
F – 1 m	60	60	30.0				
F – 2 m	40	50	29.0				
F – 3 m	32		water				

The high temperatures inside the pile might be caused by the initial aerobic conversion, which is an exothermic process. The heat generated this way will only slowly leak away, because of the low heat transfer rates inside a pile. This phenomenon is also observed in landfills [Van Zanten and Schepers, 1996]. Near the edge of the pile temperatures are even higher, indicating aerobic activity there. Further evidence of aerobic activity near the edges of the pile was the smoke coming from the edges of the piles.

6.1.5 Analysis results

In Table 6.5 the analysis results of the fresh wood samples taken from the Svishtov pile are presented. The results are according to expectations. The measured moisture content is lower than the 65% (wet basis) as reported by Svishtov (see inception report). The carbon and ash content of the bark is roughly half of the dry sample, which is in line with literature data for beech, oak and poplar bark, as shown in several databases.

Table 6.5 Analysis results of the fresh mixed samples from the Svishtov pile

Sample	Method	Result (mass %, wet basis)
Svishtov – 1		
- Moisture (wet basis)	Gravimetric	49.5
- Ash (wet basis)	ASTM D 5291	2.86
- Carbon (wet basis)	ASTM D 482mod.	26.7
Svishtov – 2		
- Moisture (wet basis)	Gravimetric	42.6
- Ash (wet basis)	ASTM D 5291	4.21
- Carbon (wet basis)	ASTM D 482mod.	26.9

6.1.6 Water level

During the measurements, it was observed that the water level at the Svishtov pile was higher than the Danube river. Furthermore, next to the pile there was a lower area, to be used for future wood waste, which was dry during the measurements. These observations could lead to the assumption that the water level inside the pile is independent of the Danube river level.

However, according to Mr. Vitkov of the Svilosa company, the Danube river and the underground water levels of the entire site are linked, with a delay of ca. 2 days. The dry area next to the Svishtov pile is under water during the time the Danube river is at it's highest level (May-June). This implies that during the other parts of the year, the pile water level is not directly influenced by the Danube water level, and that the high water level inside the pile during measurements is probably caused by rainfall.

In Annex H the rainfall pattern in Razgrad, located 120 km from Svishtov, is shown. From these graphs it is clear that rainfall just before the measurement period (week 13 and 14 of 2002) was more than average, but not exceptional. According to these graphs, rainfall is rather regular throughout the year.

From these comments it is therefore considered likely that the water level inside the Svishtov pile will vary, because of rainfall and sometimes because of the water level in the Danube river. Given the fact of reasonably regular precipitation, the water level measured is expected to be in line with the yearly averaged water level.

6.2 MEASUREMENT RESULTS RAZLOG STOCKPILE

6.2.1 Description of the Razlog pile

In Figure 6.4 a schematic representation of the Razlog pile and the part on which methane emission measurements were carried out are shown. About 75% of the pile surface is polluted with municipal waste. Measurements were taken on the unpolluted part,

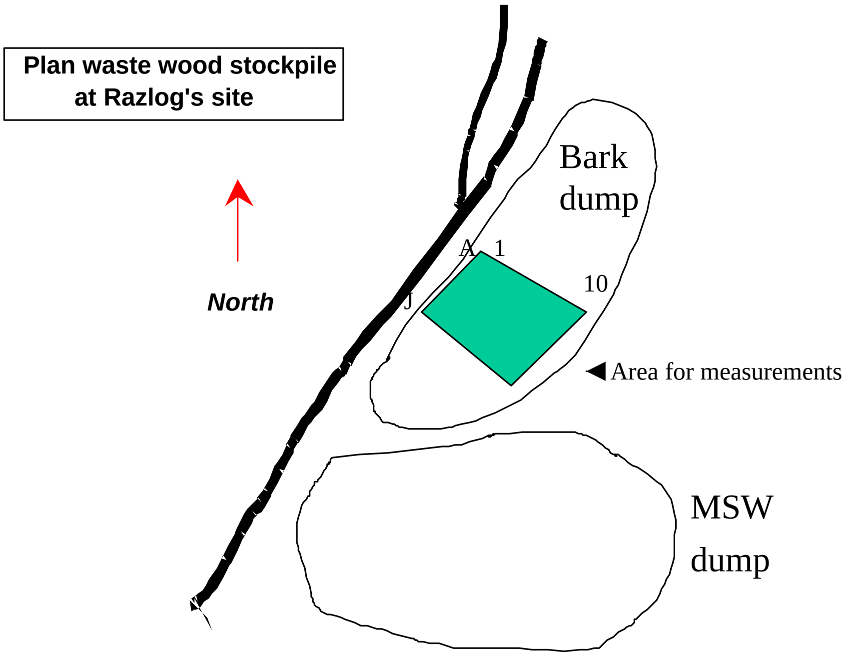

Figure 6.4 Schematic representation of the Razlog pile. The measurement area is marked green.

which is the area marked green. It is an area of 75 meters by 75 meters were both new and old wood waste is present. A grid, representing 7.5 x 7.5 meters per cell was defined.

The grid identifiers range from A0 to J10. In Figure 6.4 the grid orientation is shown. 87 Chamber measurements have been carried out in triplo each in a different grid cell.

Flux measurements were always carried out in the middle of a cell. Probe measurements were also carried out in the middle of a cell, with the exception of some measurements on the edge of the pile. The height of the wood pile is roughly 8 meters. Water was consistently encountered at 1.5 meters depth, so 6.5/8 of the pile is below the water level. There is no river or other body of water in the proximity of the Razlog pile.

6.2.2 Measured methane fluxes

Measurements were carried out during week 14 and 15 of 2002. During that time there was light rain. Ambient temperatures were about 5°C. Barometric pressures were fairly constant, ranging from 905 to 910 mbar. This low barometric pressure is caused by the high altitude on which the Razlog pile is situated. It is not expected that this will have a very large influence on the methane emissions as the pressure is relatively low all the time. Wind speeds were negligible during measurements. The measured methane fluxes are presented in Figure 6.5.

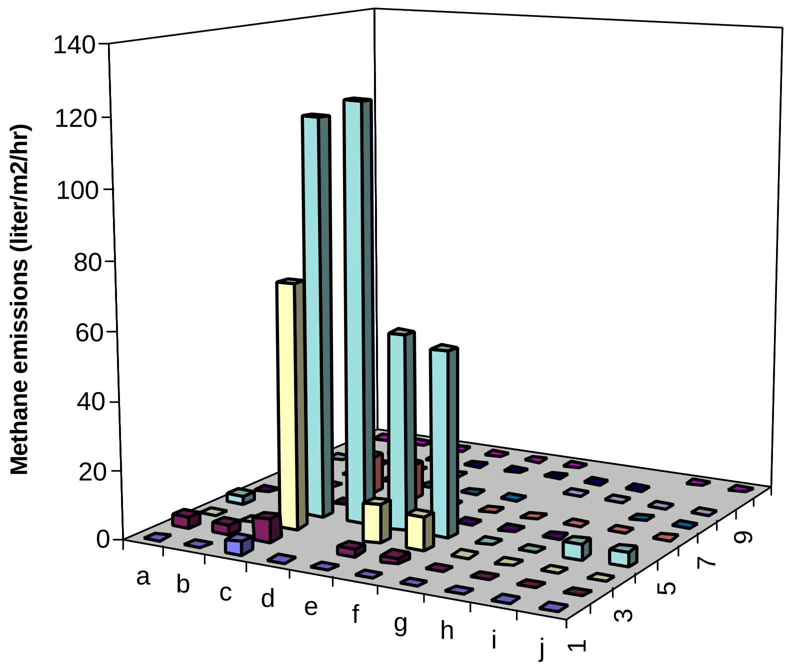

Figure 6.5 Measured methane fluxes on the Razlog pile. In the cells without entry no measurements were carried out.

Measurements were carried out in triplo, of which the averaged values were used to compute the resulting fluxes. Standard deviations were roughly 10%.

The pattern of methane fluxes is according to expectations. On a number of spots no methane was measured, on a number of spots some methane was measured, and on some locations (for example C4 and D4) methane emissions were very high. Compared to the Svishtov measurements, emissions appear to be more localised. The number of zero methane emission measurements is higher compared to Svishtov, and the highest measured methane emissions are twice as high as in Svishtov. A possible explanation for this phenomenon could be the different structure of the top layers of Svishtov and Razlog, but no quantitative data are available to substantiate this.

The average methane flux from this section of the Razlog pile is 5.7 liter/m^2/hr, which is comparable to the measured methane emissions from the Svishtov site. Regarding the accuracy of the measurements, reference is again made to Annex F. From that Annex it follows that uncertainties are small, compared to the confidence interval.

6.2.3 Statistical considerations

The results from the flux measurements depicted in Figure 6.5 show a wide scatter, which is in line with the results of others, such as Czepiel et al. [1996a], and in line with the

Svishtov measurements. Also in Svishtov, the averaged methane flux is far lower than some of the higher flux values.

Because of the large number of data points (n = 87), it is also for the Razlog measurements possible to determine a standard deviation and a confidence interval. In Table 6.6 some important statistical parameters are given.

Table 6.6 Main statistical parameters of the methane flux measurements in Razlog.

Average methane flux (liter/m^2/hr)	5.7
Standard deviation (liter/m^2/hr)	21.0
90% confidence interval (liter/m^2/hr)	2.0 – 9.5
95% confidence interval (liter/m^2/hr)	1.3 – 10.4

Compared to the Svishtov results the standard deviation is higher, pointing to a more uneven distribution of the methane flux measurements.

6.2.4 Probe measurement results

Probe measurements were carried out in sections C and G in the middle of the cells. Probe measurements were hampered by the occurrence of stones, which limited the amount of measurements.

Table 6.7 Results of the probe measurements inside the Razlog pile. In this table oxygen concentrations (as volume percentage) are shown. In the cells without entry no measurements were carried out.

Cell	1	3	5	7	9
G - 1 m	0.7	2.3	5.5	10.1	
G - 1.5 m	water	1,4			
G - 2 m		water	water	stones	
C - 0.5 m	10.2				
C - 1 m	10.8	4.6	5.2	5.3	
C - 2 m	water	water			

From this table it follows that at 1 meter depth the oxygen percentage has dropped to 1% - 10%. At one point on 1.5 meters depth the oxygen percentage has dropped to 1-2%. Because of this, and because of the oxygen percentage being already substantially lower than ambient, the aerobic layer is estimated to be 1.5 meters. Water was encountered consistently at ca. 2 meters in the pile. Compared to the Svishtov pile the oxidation layer is thicker, which is likely caused by the larger particle size in Razlog. Because of this, the porosity inside the pile is likely higher, resulting in more oxygen penetration.

Table 6.8 gives an overview of the methane percentages measured inside the Razlog pile. These methane percentages range between 30% to 50%. In the Svishtov pile these percentages were in the range of 20% to 30%.

Table 6.8 Methane concentrations (as volume percentages) measured in the Razlog pile. In the cells without entry no measurements were carried out.

Cell	1	3	5	7	9
G - 1 m	58.3	45.5	45.7	31.7	
G - 1.5 m	water	43.9			
G - 2 m		water	water	stones	
C - 0.5 m	31.8				
C - 1 m	30.3	48.3	36.9	36.8	
C - 2 m	water	water			

Just as with the Svishtov pile, a relation between methane flux and methane concentrations inside the pile is not apparent. In sections G1-G7 measured methane emissions were zero, while methane concentrations inside the pile were high, which points to "channelling" of the methane. Table 6.9 gives an overview of the temperature in the Razlog pile. Almost all locations showed a temperature of around 10ºC. In the Svishtov pile these temperatures were in the range of 30ºC to 60ºC.

Table 6.9 Results of the probe measurements inside the Razlog pile. In this table temperatures (°C) inside the pile are shown. In the cells without entry no measurements were carried out.

Cell	1	3	5	7	9
G - 1 m	10.0	10.0	9.0	9.0	
G - 1.5 m		10.0			
G - 2 m					
C - 0.5 m	8.0				
C - 1 m	10.0	9.0	10.0	10.0	10.0
C - 2 m				9.0	18.0

These low temperatures are remarkably different from those in Svishtov. This is probably caused by the lower aerobic activities near the edges of the pile. In Razlog, opposed to Svishtov, no smoke was observed near the pile edges, indicating less aerobic activities. It would be expected that low temperatures would inhibit the digestion process. However, this appears not to be the case.

6.2.5 Analysis results

In Table 6.10 the analysis results of the samples taken from the Razlog pile are presented. The results are according to expectations. The (fresh) carbon and ash content of the bark is roughly half of the dry sample. Compared to Svishtov, the carbon content is slightly less.

Table 6.10 Analysis results of the fresh mixed samples from the Razlog pile

Sample	Method	Result (mass %, wet basis)
Razlog – 1		
- Moisture (wet basis)	Gravimetric	55.3
- Ash (wet basis)	ASTM D 5291	2.47
- Carbon (wet basis)	ASTM D 482mod.	21.0
Razlog – 2		
- Moisture (wet basis)	Gravimetric	49.8
- Ash (wet basis)	ASTM D 5291	1.40
- Carbon (wet basis)	ASTM D 482mod.	23.1

6.3 DISCUSSION

From the previous Paragraphs it is clear that the methane emissions from both the Svishtov and the Razlog piles are significant.

The significant methane emissions show that anaerobic conditions exits in large parts of both piles. Probe measurements indicate that anaerobic conditions also exist in parts of the piles which are above the water level, as it is determined that below 0.5 meters (Svishtov) and 1.5 meters (Razlog) anaerobic conditions exist, while the water level was determined to start at 3 meters depth (Svishtov) or 2 meters depth (Razlog).

It is furthermore clear that conditions inside the piles are favourable for anaerobic digestion. The presence of water might be an important factor in accelerated decomposition and an increased proportion of the material actually decomposing. From landfills it is known that water plays a pivotal role in the first phase of anaerobic digestion (hydrolysis), and has further positive effects on the transport of nutrients. Since anaerobic digestion is a slow process, it is not expected that the changing water level will have an instantaneous effect on the methane production, which implies that the measured methane emissions were not exceptionally high just because the water level was high during measurements.

The biomass is well-suited for anaerobic digestion. The wood bark has been bruised by the debarking process, and has undergone size reduction. Furthermore, both the Svishtov and the Razlog piles are regularly compacted by bulldozers. In the transformation of landfills to bio-reactors, which is a conversion carried out to accelerate decompostion, these are precisely the actions which are taken (size reduction, increasing moisture, and compression) [Yuen et al., 2001], [Warith, 2001]. It appears that these favourable conditions are present in both the Svishtov and the Razlog pile.

Regarding the representativity of the measured methane flux for the yearly methane emissions from the Svishtov and the Razlog piles, caution should be observed. As discussed extensively in the literature survey (Chapter 2), methane emissions from landfills show large temporal variations, and are influenced by precipitation, day-night rhythm, barometric pressure and the occurrence of methane oxidation, although the influence of this last factor will be low, because of the relatively low ambient temperatures (ca. 10°C for Svishtov and 5°C for Razlog). Apart from these variations, the large confidence interval of the measurements also implies uncertainty regarding the representativity of the measurements.

7 MODELING

The model presented earlier will be validated using the measured methane emissions from Razlog and Svishtov. The following model was presented in Paragraph 5.4:

$$Q_m = V_m(za\sum_{j=0}^{n}(A_j - A_{ox,j})kC_{0,j}\,rv_0e^{-k(t-j)})*(1-z_{ox})$$

In this Chapter, first the theoretical quantity of methane emissions from both piles is calculated, using literature values, and the measured parameters from the previous Chapter (such as geometrical dimensions, values for the organic carbon content, etc.) in the model.

The next step is to compare these theoretically calculated methane emissions with the actually measured methane emissions, firstly by using IPCC values for the generation factor and the half-life in the case of landfills, and secondly by calibration of the model by varying the half-life.

7.1 PARAMETERS USED IN THE MODELING

Methane content of the landfill gas V_m

For the methane content of the landfill gas (V_m), a literature value of 0.6 is used [Oonk and Boom, 1995]. Oonk and Boom measured sometimes lower concentrations of methane, which are according to them attributable to methane oxidation. Since methane oxidation is separately accounted for in the model, it is not included in this factor.

Generation factor z

In the IPCC guidelines [IPCC, 2000], a default value of 0.77 is given for the generation factor in landfills, with the remark that this value may be too high, and that it should only be used when lignin is excluded from the generation factor. In the model used here, lignin is indeed excluded. Furthermore, the favourable circumstances for anaerobic digestion inside the piles, such as:

- small particles,
- presence of water, and
- regular compaction

will likely result in degradation of a large part of the available carbon. Therefore the high IPCC default value of 0.77 for the generation factor is considered conservative in this case.

Wood volume A_j

The actual wood volume which is dumped over the years on the Svishtov and Razlog piles (measurement area only) is estimated using measurements of the geometrical dimensions of the piles, as shown in Paragraph 6.1.1., with the results for Svishtov and Razlog listed in Table 7.1.

Table 7.1 Volumes of wood waste in Svishtov and Razlog measurement areas (A_j)

Svishtov		**Razlog**	
Wood dumped in (year)	**Volume (m^3)**	**Wood dumped in (year)**	**Volume (m^3)**
- 1994	15,120	- 1987 – 2001	2,285 each year
- 1995	15,120		
- 1995	15,120		
- 2001	5,040		

Wood volume under aerobic conditions $A_{ox,j}$

The wood volume which is under aerobic conditions is calculated using the probe measurements listed in Chapter 6. From these measurements, the oxidation layer was for Svishtov estimated tot have a thickness of 0.5 meters, and for Razlog 1.5 meters. Using the geometrical data from the measurement areas, the wood volume under aerobic conditions can be determined. An assumption is made that from every yearly wood dumping A_j, the same ratio is under aerobic conditions. In table 7.2 the actual volumes are listed.

Table 7.2 Volumes of wood waste in Svishtov and Razlog measurement areas under aerobic conditions ($A_{ox,j}$)

Svishtov			**Razlog**		
Wood dumped in (year)	**Fraction under aerobic conditions(-)**	**Volume (m^3)**	**Wood dumped in (year)**	**Fraction under aerobic conditions(-)**	**Volume (m^3)**
- 1994	0.5/8	945	- 1987 – 2001	1.5/8	429 each year
- 1995	0.5/8	945			
- 1995	0.5/8	945			
- 2001	0.5/8	315			

Decomposition rate constant k

The decomposition rate constant is directly related to the half-life. For the modeling of both the Svishtov and Razlog sites, the lowest reported half-life for wood decomposition in landfills is used, namely 15 years [Micales et al., 1997]. Reasons for using the lowest reported half-life are that conditions for rapid digestion are favourable inside the pile. It was already mentioned that small particles, bruised in the debarking process, with abundant presence of water, and regularly compacted, would likely result in fast decomposition. The k-value corresponding to a half-life of 15 years is $k = \ln 2 / t_{½} = 0.046$ year^{-1}.

Initial organic carbon content $C_{0,j}$

The initial organic carbon content for Svishtov and Razlog is based on the measurements listed in Chapter 6. The average initial organic carbon content (wet basis) of Svishtov is 0.268, and for Razlog (wet basis) 0.221. Both figures are below the IPCC default value of 0.3 (also on a wet basis) [IPCC, 1996]. It is assumed that the initial organic carbon content remains the same during the years in which wood waste was dumped.

Bulk density ρ

ρ is the bulk density of the material in kg/m^3, and assumed to be 600 kg/m^3. This value is high compared to literature values for bulk densities of wood particles, but since the wood waste is regularly compacted, the density will probably be high.

Non-lignin fraction u_0

The fraction of the initial organic carbon content ($C_{0,j}$) which is hemicellulose and cellulose is taken from literature. A normal lignin fraction in wood bark is 0.25, so for the non-lignin fraction a value of 0.75 is taken. It is assumed that this fraction remains the same for the fresh dumped wood during the years in which wood waste was dumped.

Oxidation factor z_{ox}

The oxidation factor is taken to be 0.1, which is the default IPCC value for well-managed landfills. This fraction is considered justified for the Svishtov and Razlog piles, because the wood waste is regularly compacted. For unmanaged waste sites, it is known that most of the methane is emitted through cracks and channels, therefore this fraction should be zero according to IPCC guidelines [IPCC, 2000].

7.2 MODELING RESULTS

With the parameters as described in Paragraph 7.1, The yearly methane emissions from the measurement areas of Svishtov and Razlog can be computed. The results are listed in Table 7.3.

Table 7.3 Modeling results for the measurement area of the Svishtov and Razlog sites

	Svishtov	**Razlog**
Modeled yearly methane emissions in 2002 (m^3/year)	153,000	94,300
Measurement area (m^2)	6,300	5,625
Specific modeled methane emissions (liter/m^2/hour)	2.8	1.9

In the calculation shown above, the specific methane emissions are derived by subdividing the total emissions by the total measurement area, followed by recalculation to an hourly basis.

7.3 COMPARISON OF MODEL VALUES WITH MEASUREMENTS

The modeled emission are compared with the measurements, as shown in Table 7.4:

Table 7.4 Comparison between measurements and modeling results for the measurement area of the Svishtov and Razlog sites.

	Svishtov	**Razlog**
Average methane flux measured (liter/m^2/hour)	6.4	5.7
Methane flux – lower end of the 90% confidence interval (liter/m^2/hour)	3.1	2.0
Modeled methane flux (liter/m^2/hour)	2.8	1.9

This table shows that the modeled methane flux is far lower than the average measured methane flux. This can mean two things:

1) The model prediction is too low, implying that parameters should be adapted
2) At the time of measurement the emissions were higher that the yearly average

With respect to possibility 1), it was already mentioned that conservative literature values for landfills have been chosen for the model, given the favourable circumstances for anaerobic digestion inside the wood piles. Therefore the model is also calibrated through the adaptation of the half-life. In table 7.5 the modeling results are presented for the case that the half-life of the wood waste is such that the modeled methane emissions are comparable to the average measurements.

Table 7.5 Calibration of the emission model based on the average of the methane emissions measured. The generation factor is fixed, while the half-life is allowed to vary

	Svishtov	**Razlog**
Average methane flux measured (liter/m^2/hour)	6.4	5.7
Modeled half-life (years)	3.8	0.9
Modeled methane flux (liter/m^2/hour)	4.9	5.2

Some difference between model and measured values remains, even though the half-lifes are now considerably lower that before.

Regarding possibility 2), it is considered that the measurement period was only two weeks, while temporal variations in methane emissions are known to happen. Another point is the large confidence interval of the measurements, which implies that it is indeed possible that the actual methane emissions from the stockpiles were significantly lower than the averages reported in Chapter 6. It is therefore considered that for making a conservative estimation of the methane emissions, the conservative model parameters can best be used.

7.4 SENSITIVITY ANALYSIS

The sensitivity for the modeled methane emissions for the Svishtov case for the chosen parameters are given in table 7.6. Influences of changing parameters on the Razlog case are of the same order.

Table 7.6 Results of a sensitivity analysis for the Svishtov pile. Relative changes with respect to the base case are shown.

Parameter	**Original value**	**Literature range**	**Changed value**	**Resulting modeled methane emissions (liter/m^2/hour)**	**Relative change (%)**
Oxidation factor ζ_{ox} (-)	0.1	0.0 – 0.1	0	3.1	10%
Initial organic carbon content wood $C_{o,i}$ on dry basis (-)	0.496	ca 0.4 – 0.6	0.6	3.4	17%
Non-lignin fraction υ_0 (-)	0.75	0.5 – 0.8	0.8	3.0	6%
Bulk density ρ (kg/m^3)	600	250 – 800	800	3.7	25%

In this table the initial organic carbon on a dry basis is used, because the carbon content on a wet basis can range from zero to 0.6 due to changes in the moisture content. From this table it follows that changes in these parameters do not result in very significant changes in the modeled methane emissions.

7.5 DISCUSSION AND CONCLUSIONS

From the previous Paragraphs it follows that the measured methane emissions are far higher than the modeling results. Because of the large variation in the results for both Svishtov and Razlog, it is nevertheless possible that methane emissions are in reality indeed far lower than measured. Both for Svishtov and Razlog, the lower end of the 90% confidence interval is about the same as the modeled methane emission. This means that there is a 90% chance that the ‘real’ methane emissions are actually higher, and a 10% chance that these are lower.

However, conditions in both the Svishtov and the Razlog pile are pointing towards higher methane emissions. As mentioned in Chapter 6 and in this Chapter, the presence of water during the measurements, compaction, and the fact that the wood particles are small, is likely to accelerate digestion. Quantitative data regarding this effect are however not yet available.

Because of these two reasons:

- measured methane emissions are 90% likely to be higher than modeled methane emissions, and
- conditions in the Svishtov and Razlog piles are favourable to anaerobic digestion,

the selection of the relatively high default value for the generation factor (0.77) and the relatively low value for the half-life (15) is considered conservative, especially when considering that these default IPPC values have been derived for landfills, in which conditions are generally not as favourable as in the Svishtov and the Razlog pile.

Changes in other parameters (the oxidation factor, initial organic carbon content, non-lignin fraction, and the density) have only a moderate impact on the modeled methane emissions, and cannot explain the difference between the average of the measured methane emissions and the modeled methane emissions.

8 MODELING FUTURE METHANE EMISSIONS

8.1 EXTRAPOLATION OF THE METHANE EMISSION MODEL

In this Chapter the future methane emissions for the Svishtov and Razlog pile are estimated, based on the developed model.

Since the model is a modification of the IPCC First Order Decay model for landfills, the model is considered to be suitable for year-round extrapolation, and for estimating future methane emissions. The IPCC FOD model for landfills is commonly used for such extrapolations, and has been validated and calibrated extensively.

Since a measurement period of one week cannot be used for extrapolation due toe temporal variations in the methane emissions, the model is used for extrapolation and future estimations. With the choice of the model parameters, a conservative approach has been applied, since measurements showed a high likelihood of higher methane emissions, and the conditions for anaerobic digestion are favourable for methane generation. Therefore it is considered justified to use the model parameters for estimating future methane emissions.

8.2 MODELING METHANE EMISSIONS FROM SVISHTOV AND RAZLOG

Two types of methane emissions are presented:

1. Methane emissions that will occur during the coming years when ***new biomass*** is dumped on the piles;
2. Methane emissions for the ***existing biomass*** in the piles that will occur during the coming years when the biomass is not otherwise utilised.

For the existing biomass in the pile, the future methane emissions are (per kg dry material) lower than for the fresh biomass. This is because part of the initially present (hemi)cellulose has already been converted into methane. As can be derived from the model, for a particular volume of biomass the produced amount of methane will decrease with time.

In the following Paragraphs future methane emissions during the coming years for new dumped biomass, respectively the existing biomass in the piles, are estimated. Also the maximum possible methane emissions, in case of infinite time, is presented.

NOTE: it is important to realise that calculations for the methane emissions during the coming years is based on the total Svishtov and Razlog piles, NOT taking into account eventualities like fires, pollution, etc. Corrections for this kind of uncertainties should be made in the Base Line Studies for the project.

8.2.1 Case 1: methane emissions from newly dumped biomass

The maximum amount of methane that would be emitted when new biomass is dumped on the piles, can be calculated from the model, by filling in the infinite time for the number of years:

$$Q_m = V_m z a C_0 r v_0 \sum_{j=0}^{n} (A_j - A_{ox,j}) * (1 - z_{ox})$$

To determine the specific methane emission $Q_{m,sp}$ (in m^3/kg dry biomass) the methane emission is divided by the total quantity of dry biomass present:

$$Q_{m,sp} = \frac{V_m z a C_0 r v_0 \sum_{j=0}^{n} (A_j - A_{ox,j}) * (1 - z_{ox})}{r(1 - MC_{wb}) \sum_{j=0}^{n} A_j}$$

In Table 8.1 the specific methane emissions are presented for the parameters that were discussed in Chapter 7. In this calculation the half-life is unimportant, since all available carbon is eventually converted. These calculations are based on the assumptions that the relevant parameters remain constant throughout the years. This implies that the generation factor, the oxidation factor, the moisture content, but also the thickness of the oxidation layer remain constant.

Table 8.1 Maximum methane emissions for newly dumped biomass.

Parameter	z **(-)**	**Svishtov (m^3 methane/kg dry biomass)**	**Razlog (m^3 methane/kg dry biomass)**
$Q_{m,sp}$	0.77	0.27	0.22

Since the amount of methane emissions is not constant throughout the years, in Table 8.2 the yearly methane emissions for Svishtov and Razlog are shown. A timeframe of 10 years is selected because of the commitment period of 2008 – 2012.

Table 8.2 Yearly specific methane emissions for newly dumped material on the Svishtov and Razlog piles, based on the entire pile area.

	Newly dumped biomass methane emissions (m^3 methane/kg dry biomass/year)	
	Svishtov pile	**Razlog pile**
Year	**z = 0.77,** **$t_{1/2}$ =15 years**	**z = 0.77,** **$t_{1/2}$ =15 years**
year 1	0.0125	0.0100
year 2	0.0120	0.0095
year 3	0.0114	0.0091
year 4	0.0109	0.0087
year 5	0.0104	0.0083
year 6	0.0100	0.0079
year 7	0.0095	0.0075
year 8	0.0091	0.0072
year 9	0.0087	0.0069
year 10	0.0083	0.0066
Total	**0.1028**	**0.0816**

8.2.2 Case 2: Methane emissions from existing biomass

When computing the future methane emissions of the Svishtov and the Razlog piles, it is assumed that all parameters remain constant, implying a constant shape and size of the pile, a constant oxidation layer, etc. in Table 8.3 the yearly methane emissions for the existing piles are shown.

In Figure 8.1 data from Table 8.2 and 8.3 is graphically depicted. When using biomass from the existing piles, figures from the table above are used. Regarding newly dumped biomass, it is postulated that these are dumped starting in the beginning of 2003, to be comparable with Table 8.3. The future emitted methane is significantly higher for the case of newly dumped biomass.

Table 8.3 Yearly methane emissions for the existing biomass on the Svishtov and Razlog piles, based on the entire pile area.

	Svishtov pile (z = 0.77, $t_{½}$ =15 years)		**Razlog pile (z = 0.77, $t_{½}$ =15 years)**	
Year	**(m^3 methane/kg dry biomass/year)**	**(m^3 methane/year)**	**(m^3 methane/kg dry biomass/year)**	**(m^3 methane/year)**
2003	0.0098	477,000	0.0070	360,000
2004	0.0093	455,000	0.0067	344,000
2005	0.0089	434,000	0.0064	328,000
2006	0.0085	415,000	0.0061	313,000
2007	0.0081	396,000	0.0058	299,000
2008	0.0078	378,000	0.0056	286,000
2009	0.0074	361,000	0.0053	273,000
2010	0.0071	345,000	0.0051	261,000
2011	0.0068	329,000	0.0049	249,000
2012	0.0065	314,000	0.0046	238,000
Total	**0.0802**	**3,904,000**	**0.0576**	**2,951,000**

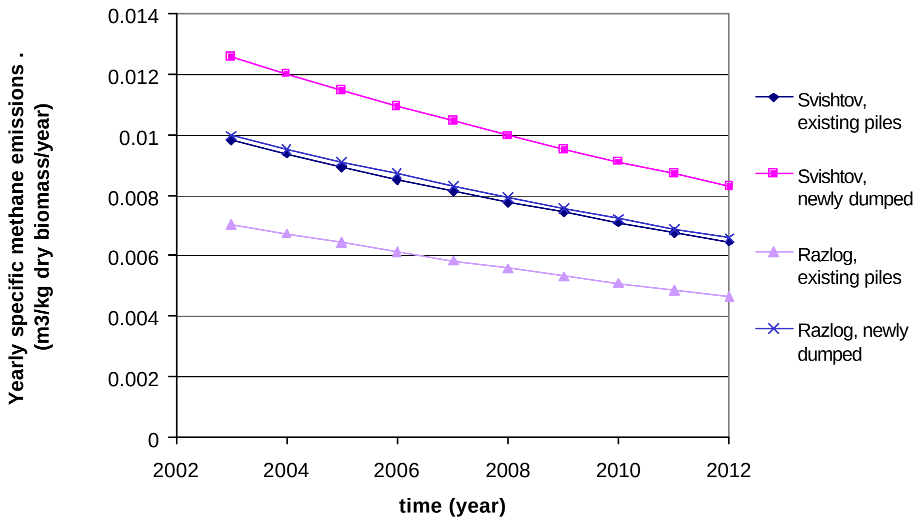

Figure 8.1 Estimated future methane emissions for the Svishtov and the Razlog stockpile, for both newly dumped biomass and using the existing piles.

8.3 SPREADSHEET MODEL

Based on the methane emission model presented in Chapter 5, a spreadsheet model is developed to assist project developers in their first assessment regarding the amount of methane emission reduction achievable through their project. An example of the use of the spreadsheet model is given in Annex G.

The model meets the following requirements:

- Relatively simple and transparent
- Flexible and multi-purpose

Project developers are able to compute the avoided methane emissions for biomass utilisation from existing piles. By adding and removing rows in the spreadsheet model, flexibility regarding the period, the amount and age of waste types is assured. The user is expected to be able to fill in a number of project specific parameters, such as:

- The carbon content of the biomass
- The part of the biomass stockpile in which aerobic conditions occur

If no values are available, values are given that can be used as a first estimate. Based on the uncertainties regarding the generation factor and the half-life, as discussed in Chapter 6, it is necessary to complement the spreadsheet calculations with field measurements regarding the methane emissions. These field measurements are needed for the adaptation of the generation factor, the half-life of the biomass waste, and the thickness of the oxidation layer. Without adequate field measurements, the results should be regarded as indicative only.

Obviously the spreadsheet model does only calculate the avoided methane emissions which are associated with methane emissions resulting from anaerobic degradation of the waste. Further GHG emissions (or reductions) associated with the use of the biomass, for example as a fuel, are not taken into account. Project specific issues like these should be included in the project Base Line study.

8.4 WIDER APPLICABILITY

Wider applicability of the spreadsheet model to other biomass piles, biomass types, climatic regions, etc., concerns two points:

- Applicability of the model;
- Applicability of the parameters.

The *model* can be readily used for other biomass piles, types, etc. The model is derived from a landfill gas formation model, which can be considered a generalisation of the specific case for biomass stockpiles. Since the first order multiphase model for landfill gas formation is widely used and thoroughly tested, it is expected that the model developed in the framework of this project will also prove to be applicable to other biomass stockpiles.

Applicability of the *parameters* is dependent on the type of application. For other biomass piles a number of parameters can be found in literature, such as lignin content, amount of carbon, the half-life, etc. If not available from literature, field measurements or estimations are needed. With respect to the generation factor and the half-life, the model has been calibrated for two specific piles (the Svishtov and the Razlog piles). These piles are not expected to be representative of a lot of other biomass stockpiles, among other things because of the high water level inside the piles. Because of this, the generation factor, and possibly the half-life of other biomass types need to be established by field measurements. In the future, when more data on different biomass stockpile methane emissions becomes available, the need for additional field measurements will diminish.

9 CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSIONS

Literature on methane (CH_4) emissions from wood stockpiles is scarce, as opposed to the large body of literature on methane emissions from landfills. One publication on methane emissions from wood stockpiles revealed methane presence inside the stockpiles, but hardly any emissions.

Measurements of methane emissions from landfills, which can be considered comparable regarding methane emissions, show large spatial and temporal variations. Methane emissions vary orders of magnitudes dependent on the location on the landfills site, and are influenced by day-night rhythm, barometric pressure, moisture content and precipitation. Biological methane oxidation is furthermore causing seasonal variations in observed methane emissions.

For the measurement of methane emissions from landfills, a number of methods are available, both new and proven. Taking into account the specific circumstances of the wood residue stockpiles selected in Bulgaria (the Svishtov and the Razlog pile) the dynamic chamber method was selected as the preferred method for measuring the methane emissions.

High concentrations of methane, and very low concentrations of oxygen were measured below 0.5 meter (Svishtov) and 1.5 meter (Razlog) inside both piles using a probe. Together with the high methane emissions measured, this confirms that anaerobic conditions exist in large parts of both piles. In both piles favourable conditions for methane generation exist: particles are small and bruised by the debarking process, large parts of the piles are under water, and the piles are regularly compacted.

Both for the Svishtov and the Razlog wood stockpiles significant amounts of methane emissions, of respectively 6.4 and 5.7 liter/m^2/hr were measured with the dynamic chamber method. An inherent problem with the chamber method is that, despite the large number of measurements, the 90% confidence interval remains large for both Svishtov (3.1 – 9.5 liter/m^2/hr) and Razlog (2.0 – 9.5 liter/m^2/hr). In addition to this, the observed spatial and temporal variation of the methane emissions from landfills are probably similar for wood stockpiles.

A model has been developed to predict methane emissions from biomass stockpiles:

$$Q_m = V_m (za \sum_{j=0}^{n} (A_j - A_{ox,j}) k C_{0,j} r v_0 e^{-k(t-j)}) * (1 - z_{ox})$$

This model was adapted from existing landfill gas formation models, and predicts an exponential decline of methane emissions dependent on the amount and age of the biomass waste. The developed model distinguishes between different types of biomass with respect to carbon content, half-life, lignine content, moisture content and ash content.

The model parameters have been selected using measurement data and literature values. For the generation factor the IPCC default value (0.77) has been taken, and for the half-life the minimum value for wood decomposition in landfills (15 years). The modeled methane emissions have values close to the lower end of the 90% confidence interval for both Svishtov and Razlog.

With the validated model it is possible to estimate future methane emissions both for the existing piles, as well as for newly dumped biomass. In Tables 8.2 and 8.3 these estimations are listed. From the existing piles it is estimated that Svishtov will emit in the next 10 years a total of 3.9 million m^3 of methane, with 3.0 million m^3 of methane for Razlog. This is considered a conservative estimation. Default IPCC values for landfills are used, even though much better circumstances for anaerobic digestion exist in these stockpiles. This is also confirmed by the calculated emissions which were at the lower end of the 90% confidence interval of the measured methane emissions.

The model and the measurements are combined in a spreadsheet model, which can be used by future project developers to estimate methane emissions from biomass stockpiles. To use the spreadsheet model for other biomass stockpiles, biomass- and site-specific parameters need to be replaced with literature values or measured data. The generation factor, and possibly the half-life for other piles and biomass types need to be established by field measurements.

Besides methane emissions, nitrous oxide emissions from biomass stockpiles may contribute significantly to the greenhouse effect. The high GWP of N_2O of 310, as opposed to the GWP of methane of 21, would results in a substantial GHG contribution, even at low emission levels. N_2O emission literature is primarily focussed on composting, and in a few cases on landfill sites. Data on emissions from wood stockpiles is not available. Emissions are often related to the amount of nitrogen present, of which in the case of compost piles generally 0.5% is converted to N_2O.

9.2 RECOMMENDATIONS

The possibility to reduce methane emissions by diminishing biomass stockpiling is apparent. A methane emission model, which is applicable to a wide variety of biomass stockpiles, has been validated for the specific case of wood stockpiles in Bulgaria. For other stockpiles specific parameters have to be measured, in the course of future projects. It is recommended to collect these data from subsequent measurements and make them generally available, so that in the future less measurements are necessary, because future project developers can use a database to estimate emissions beforehand.

N_2O emissions from biomass stockpiles may contribute significantly to the total GHG emission from these piles. Currently literature data is scarce, and the extent of possible emissions is unknown. If N_2O emissions from biomass stockpiles are comparable to those from compost piles, 50,000 ton_w biomass (annual dumping in Svishtov) causes a nitrous oxide emission of 2.3 kton CO_2-equivalents, comparable with 6.4 kton CO_2-equivalents from methane emissions. In that case, N_2O emissions would contribute a significant share of 26% of the total GHG emissions. To be able to determine the extend to which nitrous oxide emissions from biomass stockpiles are relevant, it is recommended to measure nitrous oxide emissions, and build a general methodology to quantify the possible GHG reductions which could be achieved.

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A. STEPS IN ANAEROBIC DECOMPOSITION

Source: IEA Caddet, *International Perspective on Energy Recovery from Landfill Gas*, IEA CADDET Centre for Renewable Energy, Oxfordshire, United Kingdom, 2000.

Biomass stockpiles contains energy and nutrient, which can be used by micro-organisms. Initially, aerobic degradation processes will dominate, but when the oxygen in the pile has been consumed, anaerobic degradation processes will dominate. Anaerobic degradation proceeds in several steps, as presented in Figure AA1.

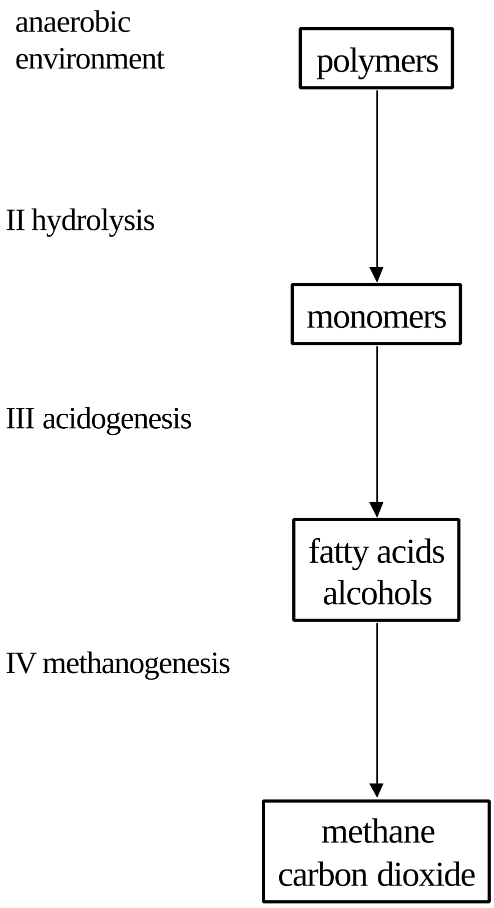

Figure A1 Major steps in anaerobic decomposition [IEA CADDET, 2000]

-*hydrolysis*

Large organic molecules are converted into smaller, soluble molecules such as short chain fatty acids, simple sugars and amino acids.

- *acidogenesis*

The hydrolysed compounds are converted by bacteria into organic acids and alcohol's. These are further degraded to smaller compounds. As a result, pH decreases. Gas formed in this stage contains a small amount of hydrogen (H_2), the rest is mainly carbon dioxide (CO_2).

- *methanogenesis*

Organic acids, formed in the acidogenic stage, are converted into CH_4 and CO_2. An important intermediate is acetate, since methanogens can only consume 1-2 carbon compounds. Methane generation may start within a few months, but in other cases it may take several years. Methanogens are more sensitive to sudden changes in their environment than the acidogens, e.g. oxygen may poison methanogens.

Aerobic and anaerobic degradation have different end-points. In aerobic decomposition oxygen is used as an oxidant, as in incineration, and carbon dioxide, water and new cells are generated as organic material is degraded. New cells are formed corresponding to about 40% of mass of degraded material and substantial amounts of energy are liberated as heat during the degradation. For example, the aerobic decomposition of glucose will liberate about 10 MJ of heat per kg of substrate degraded.

The end products of anaerobic degradation are methane, carbon dioxide, water and cells. Under anaerobic degradation a much smaller portion of the available energy is liberated as heat, about a tenth of that liberated under aerobic conditions. Most of the energy available in substrates will be preserved as methane and only a minor part of the substrate energy will be available for cell synthesis. Consequently the mass of cells formed per mass of degraded substrate will only be about a tenth of that formed under aerobic conditions.

B. INCEPTION REPORT

B1: INCEPTION REPORT RAZLOG

Mission participants:
Berry Meuleman (BTG)
Martin Cmiral (BTG CZ)
Miroslav Platenik (DPB)
Radan Novotny (DPB)
Kamen Simeonov (EnEffect)

Local representatives:
Todor Stoyanchev (Vice Mayor Razlog)
Krassimir Mitzin (Board member Pirinhart PLC)

Description of the process

Bark and saw dust are residues of the local paper pulp process. Within this process pine logs with a length of 2-4 meter are debarked. After debarking the logs are chipped and processed into pulp for the paper production. The bark and sawdust are collected and transported together to the dump.

Description of the biomass

The bark and sawdust originate from soft woods, like spruce

Quantities

According to the plant owners about 1,500 tonnes of biomass (bark 80%; sawdust 20%) is dumped by the plant annually. About 45,000 tonnes of biomass is dumped at the location in the last 15 years.

Location of the dump

The location of the dump is about 1 km uphill in a valley. On the other side of the road municipal solid waste is dumped.

Description of the dump

The dump is located near the top of a hill next to a road. On the left side of the road municipal waste is dumped and on the right side the bark and sawdust are dumped. According to the plant owners about 45,000 tonnes material is dumped at the location in the last 15 years. The bark/sawdust dump is a ravine. This means that there are no piles with a defined age, but layers piled upon layers. At the bottom of the ravine near the road the oldest material can be found and on the top of the dump the fresh material is spread out. Standard procedure is that the trucks with bark and sawdust dump their load in the ravine after which a shovel spreads out the material.

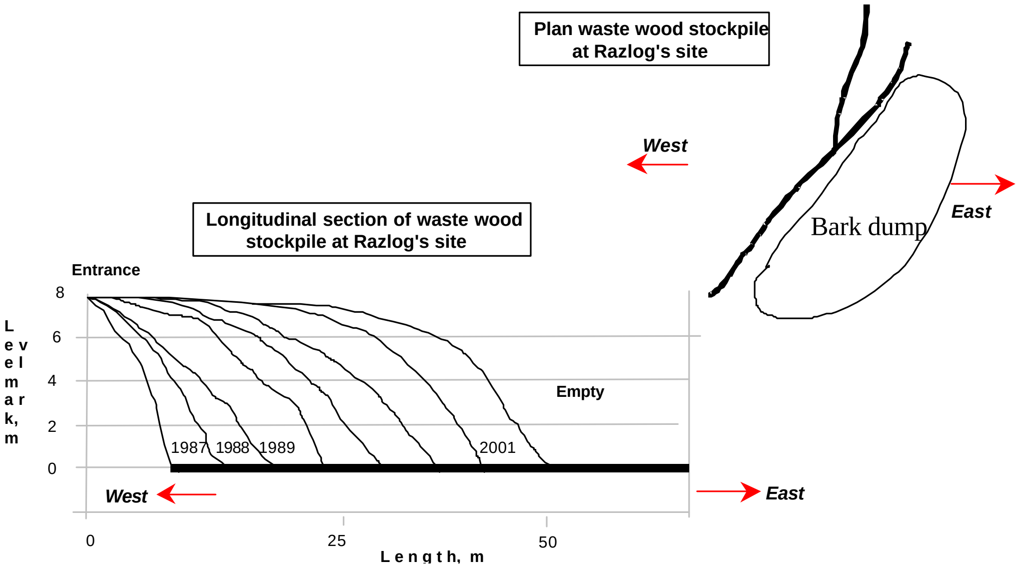

Figure B.1 Map of the situation in Razlog. Near the biomass stockpile with bark and sawdust a municipal waste dump is situated across the road. The biomass stockpile is situated in a shallow of approximately 10 meter deep.

Size of the dump

The dump has a maximum height of about 8 meter and a size of 50 by 300 meter. It is polluted with large stones.

Biological activities

During the visit smoke was coming out of the dump at several locations. This probably implies that aerobic digestion occurs in the dump. According to the plant owners it happens frequently during the summer that self-ignition occurs at the dump. This was also noticeable by the burned bark/sawdust at the location.

Figure B.2 Smoking biomass stockpile in Razlog

Figure B.3 Cross-section biomass stockpile Razlog

Additional information

Hydrolysed lignin: 15 years ago the factory ended a fermentation process in which wood residues were used to make animal fodder. The residues of this process were dumped at an enormous pile, with a height of about 30 meter and a size of 200 by 400 meter. According to the plant owners that pile contains about 300 ktonnes (another source mentioned 500 ktonnes) of biomass residue (called hydrolysed lignin) with a very low pH (2.5). The pile is polluted with large stones and during the visit smoke was coming out of the pile at several locations. This could imply that after 15 years aerobic digestion is still taking place.

There are no plans to restart this process (so no new waste is to be produced) and there are no plans to use the existing material for energy purposes. From that follows that measuring methane emission from this pile is not relevant in the framework of the current project.

B2: INCEPTION REPORT SVISHTOV

Mission participants:
Berry Meuleman (BTG)
Martin Cmiral (BTG CZ)
Miroslav Platenik (DPB)
Radan Novotny (DPB)
Kamen Simeonov (EnEffect)

Local representatives:
Rumen Vitkov (Svilosa Company, New Technology Department)

Description of the process

Svilosa Company was established in 1973 and produces beechwood pulp, poplar wood pulp, filament yarn and carboxymethyl cellulose. For the pulp production hardwood (beech, poplar, acacia, oak) logs with a length of 2-4 meter are debarked. After debarking the logs are chipped and processed into pulp. This product is sold to the paper industry. The bark and sawdust (a small quantity) are collected and transported together to the dump. These waste streams are dumped on the territory of the company. Since 1999 the company produces wood briquettes out of the sawdust waste stream.

Table B.2 Wood species, used for pulp production by Svilosa (Source: Svilosa company)

Year	Wood, total t_w/y	Species, %		
		beech	oak	poplar
1995	140 362	36.8	37.9	25.3
1996	171 817	20.4	59.1	20.5
1997	211 130	25.0	59.9	15.1
1998	184 399	13.7	66.6	19.7
1999	213 512	9.2	77.5	13.3
2000	228 725	8.7	79.5	11.8

There are three locations (see map) with biomass next to each other on the domain of the company:

(a) 1973-1985 dump: This dump was in operation during the period 1973-1985. It has a surface of 47.600 m^2. This pile has suffered from self-ignition in 1998-1999 and is out of function now.

(b) 1985-1994 dump: This dump was in operation during the period 1985-1994. It has a surface of 22.924 m^2. This pile burned out in 1999-2000 and is out of function now. The pile is polluted by municipal waste.

(c) 1994-now dump: This dump is in operation since 1994. It has a surface of 28,000 m^2 and a size of approximately 400 by 70 meter. There is an open space for another

7,041 m^2 dump. The pile looks like a slope starting at the gate at ground level and reaches a maximum height of about 8 meter at the end of the pile. The whole pile is situated in a shallow with a depth of approximately 3 meter. According to Mr. Vitkov the pile consists of 400,000 tonnes of material with a moisture content of 65% (wet basis).

The pile growths annually with 50,000 tonnes$_w$ bark. The last two years less sawdust is dumped because this material is used for briquette production. It seems to be possible to divide the pile in several sections so that each section represents 1-2 years. This division can only be approximate, because it is possible that bulldozers mixed up several layers.

Table B.2 Analyses for moisture content and heat value determination of the waste bark on the pile have been carried out on 16 October 2001 (warm and sunny day) (source: Svilosa Company).

Sample #	Layer's depth	Moisture content	Heat value
1.1	5	17.6	3036
2.1	5	26.17	2963
3.1	5	50.15	1512
Average value		**31.3**	**2503**
1.2	15	61.12	1119
2.2	15	51.86	1694
3.2	15	52.62	1615
Average value		**55.2**	**1476**
1.3	30	50.19	1031
2.3	30	53.10	1650
3.3	30	50.81	1543
Average value		**51.4**	**1408**
1.4	60	53.09	1711
2.4	60	58.41	1296
3.4	60	51.15	1471
Average value		**54.2**	**1493**

Biological activities

During the inception mission the dump was smoking at a few locations near the edge. The smoke quantity was less compared to the Razlog pile. It is however likely that aerobic digestion occurs also in this dump.

Additional information

Weather conditions (source: Svilosa Company)

The typical climatic conditions for this region are:

During the winter:

- Lowest temperature in January: – 29 ^{0}C.
- Average temperature in January: –10 ^{0}C at average humidity approx. 88%.

During the summer:

- Max. temperature in July: +43 ^{0}C
- Average temperature in July: + 26.6 ^{0}C at average humidity approx. 66%.

During the entire year the winds are mostly in the direction east – west. The annual average speed of the wind is 1.7 m/sec. The underground waters are hydraulically linked with Danube River and the level fluctuations come with 20 days delaying due to the river's level.

Conclusion

This pile is suitable for measurements in the framework of this project. It is not possible to use any technique other than the chamber method or probe sampling because other nearby sources of methane (two old piles) will influence the results. Compared to the Razlog pile this pile seems to be more suitable for measurements.

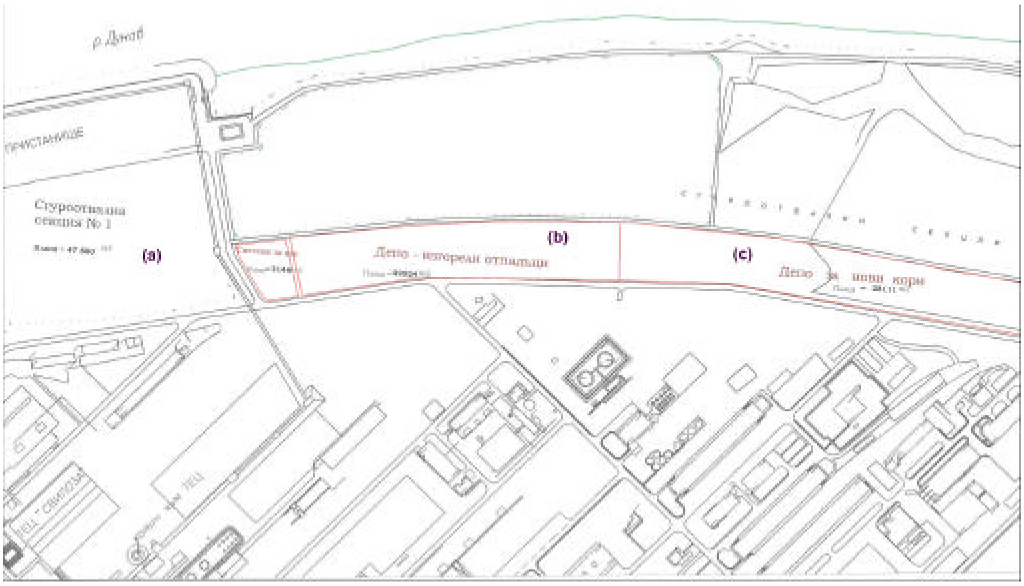

Figure B.4 Map Svilosa Company. (a) oldest dump; (b) old dump; (c) operational dump. The plants are situated in the south of the dumps. The Donau river is situated north of the dumps.

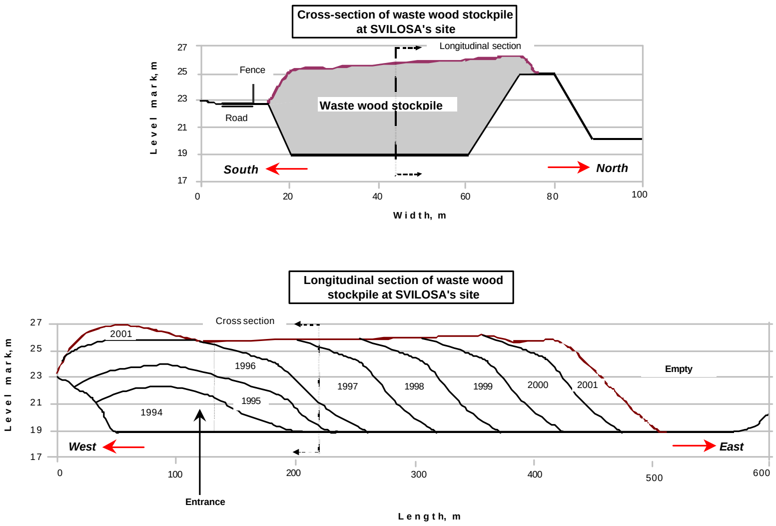

Figure B.5 Drawing of the cross-section of the biomass stockpile (c) in Svilosa.

Figure B.6 Biomass stockpile Svilosa. At the background the older dump (b) polluted with municipal waste is shown.

Figure B.7 Biomass stockpile Svilosa at the end of the dump (~10 meter high). At the background the bulldozer of above-mentioned Figure 6 is shown.

B3 INCEPTION REPORT STAMBOLIYNSKI

Mission participants:
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Martin Cmiral (BTG CZ)
Miroslav Platenik (DPB)
Radan Novotny (DPB)
Kamen Simeonov (EnEffect)

Local representatives:
Ivan Ivanov (municipality Stamboliyski)

To compare the methane measurements of hard wood storage at Svilosa with a similar soft wood storage, the inception team searched for other locations. The most suitable location could be found in Stamboliyski. In this village a pulp plant is located and the waste streams are dumped in piles.

Location Stamboliyski

The city is located besides the highway A1 125 km from Sofia.

Description of the process

Bark and sawdust are the residue of the paper pulp process. This process was out of order during the last 4 months. Within this process pine logs with a length of 2-4 meter are debarked. After debarking the logs are chipped and processed into pulp for paper production. The bark and sawdust are collected and jointly transported to the dump.

Description biomass

The bark and sawdust originate from soft wood, like spruce.

Quantities

According to Mr. Ivanov about 40,000 tonnes of bark/sawdust is dumped by the plant annually. About 600,000 tonnes of biomass has been dumped at the location in the last 37 years.

Location of the dump

The location of the dump is besides a railway. On the other side of the railway the pulp plant is located.

Description of the dump

In contrast to Razlog and Svilosa this dump is situated on level ground and has a surface of 24.500 m^2. The dump is not well organised and it is hard to say were what kind of waste is dumped.

Size of the dump

The dump has a maximum height of about 6 meter and a size of 300 by 500 meter. It is polluted with municipal waste.

Biological activities

During the visit the dump was smoking at the locations in which recently bark/sawdust was dumped. Most smoke was emitted near the edges of the pile. This signals aerobic digestion in the dump. Craters with burned biomass were located at the places were recently bark/saw dust was dumped implying that self-ignition occurs at the dump. Because of this, it is dangerous to walk over the dump.

About ¼ of the surface of the dump was covered with relatively fresh smoking bark/saw dust. The rest of the surface was polluted with municipal waste or covered with vegetation like grass. The pollution with municipal waste makes the site unsuitable to conduct measurements in the framework of this project, since it is not possible to separate the methane emitted by the municipal waste from the methane emitted by the bark/sawdust.

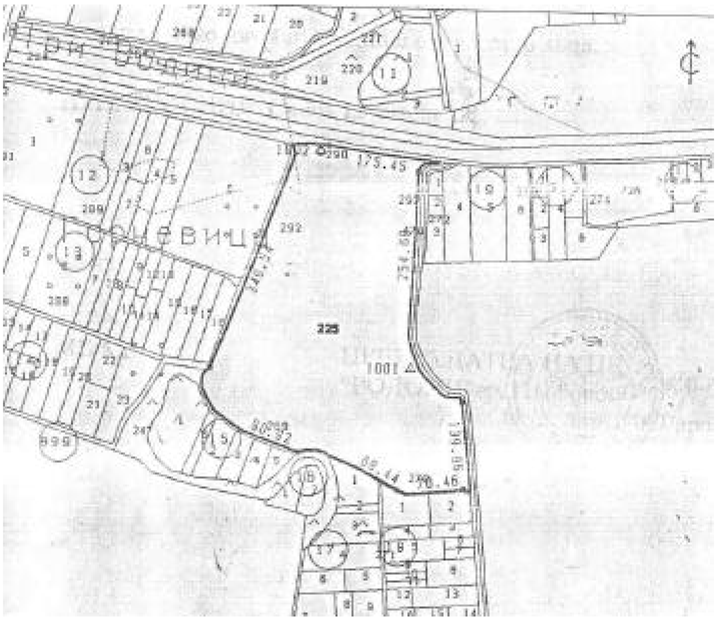


Figure B.8 Location of the biomass stockpile in Stamboliyski. The plant is located to the north of the railway line.

Figure B.9 The biomass stockpile in Stamboliyski. The plant is located at the background.

C. METHODS FOR DETERMINING THE METHANE FLUX

This Annex gives an overview of existing methods for measuring methane fluxes, namely:

a) soil core measurements;
b) static closed chambers;
c) dynamic closed chambers;
d) mass-balance method;
e) micrometeorological methods;
f) mobile plume measurements;
g) stationary plume measurements;
j) isotope measurements (methane oxidation only);
k) sub-surface vertical gradient method/probe sampling.

This section has been adapted from [Scharff et al., 2000].

a) Soil core measurements.

Measurements in the top-layer may give useful mechanistic information about the fundamental steps leading to methane emissions: diffusion and oxidation. Methane and concentration gradients in the soil may give an indication of methane and carbon dioxide diffusion through the layer [Bogner et al., 1997]; landfill soil cores may be collected and transported to the lab for determining bacteriological activity of methanotrophes. The latter is done by exposing the soil sample to a high concentration of CH_4 and measure the decrease of the CH_4 concentration in time, thus giving an indication of the oxidation capacity of the soil. These experiments may be carried out at different temperatures or soil moisture levels etc. to study oxidation process further.

The advantage of soil-core measurements is that it gives insight in the fundamental steps leading to emissions. The method however also has some disadvantages: it is does not take into account emissions caused by convection and its spatial and temporal resolution are low (one gets an impression of emission and oxidation of a very small spot on a single moment). Besides, the methodology is quite costly.

b) Static closed chambers

Static closed chambers are the most simple method to measure fluxes through a surface and are most frequently used in literature. A sampling device consists of a box with a surface area of around 1 m^2 in which the increase in concentration of methane in time is measured. Methane fluxes through the surface are directly obtained from the rate in increase of concentrations. Advantages of this closed chamber method are:

- it is simple, easy understandable and often applied;
- although the sample area is small (see disadvantages below, a number of literature references mention good agreement with other methods, provided that sufficient measurements are conducted on the landfill [Czepiel et al., 1996a];
- since it is often applied, the method is a good candidate for international acceptance;
- e.g., in the UK plans exist to base the British estimate of methane emissions from landfills on measurements using these closed chambers [Scharff et al., 2000].

Disadvantages are:

- small sampling area (in most cases less than 1 m^2) so less appropriate to measure inhomogeneous emissions and landfills prove to be very inhomogeneous. Czepiel et al. [1996a] conclude that there is no correlation between emissions from two sampling points located further than 6 meters apart.
- in order to get this good correlation, a large number of measurements are required, namely more than 20-30 on a typical landfill according to Czepiel et al. [1996a];
- Because of the large number of samples to be taken, the method is costly;
- upon measurement, concentrations in the chamber are being increased. Assuming diffusion to be the prime mechanism of methane transport, this build-up of concentration influences fluxes again, thus limiting the duration of a single measurement. To overcome this problem, correction methods are sometimes proposed;
- on surfaces with vegetation, CO_2 -emissions can not be measured, since the closed chamber influences assimilation-dissimulation patterns of the vegetation.

c) Dynamic closed chambers

Dynamic closed chambers resemble static closed chambers, except for one aspect: in a dynamic chamber a continuous air-flow is maintained through the box, thus avoiding the build-up of concentrations and the influence of fluxes. In dynamic closed chambers, fluxes are obtained from the air-flow through the chamber, the inlet and outlet concentrations. Upon performing closed chamber measurements, maintaining the pressure in the chamber at comparable levels as ambient pressures is of utmost importance [Scharff et al., 2000].

Dynamic chambers have in general the same advantages and disadvantages as static closed chambers.

d) Mass-balance method

In the mass-balance method, methane and carbon dioxide emissions can be obtained from an interpretation of wind velocity and the methane concentrations at different heights over the landfill surface. At each level the product of concentration and wind velocity provides the horizontal flux and is subsequently related to the landfill area upwind of the sampling point. If the measurements are performed to a sufficient height over the landfill the whole methane plume is sampled and the emission flux is obtained. At varying wind directions, emissions from all part of the landfill are sampled, so this method also provides some spatial information about high and low emission areas. With this method is automated, continuous measurement is possible. Experience with this method exists in the Netherlands at almost 30 landfills e.g., [Oonk, 1995].

Advantages of the mass balance method:

- gives representative emission levels for large parts of the landfill;
- continuous measurements over a longer period are feasible;
- the interpretation is straightforward;

- CO_2 -emissions can be measured as well. The combination of methane emission and carbon dioxide emissions give a better indication of landfill gas formation and methane oxidation, since formation can be obtained from the sum of methane and carbon dioxide emissions and methane oxidation from the ratio of methane and carbon dioxide emissions, compared to the ratio in extracted landfill gas. Formation of exopolymers might however be a problem here [Scharff et al., 2000];
- compared to the box method only a few measurement locations are needed.

Disadvantages:

- the geometry of the landfill can limit applicability of the method: at larger landfills problems might occur, since the upper sample points have to be mounted at impractical heights on a pylon;
- the method shows a combination of spatial and temporal variation in the signal;
- upscaling to obtain the emission level for the whole site is in some cases still needed.

e) Micrometeorological methods

Micrometeorological methods are often proposed to measure emissions from larger surfaces. In these measurements concentration gradients are measured and recalculated as vertical fluxes using information about air transport and mixing at the scale of a few m^3 (this explains the name micrometeorology). These techniques however can only be applied on terrain that is rather flat over a large distance (several hundreds of meters), and where emissions occur in a rather homogeneous way. There are almost no landfills that are entirely flat and where the distance to the slope is in excess of 200-300 m. besides the slope itself will be a major source of emissions. This severely limits emission measurement with these techniques [Oonk et al., 1995] and further discussions about advantages and disadvantages superfluous.

f) Mobile plume measurements

In the mobile plume method, emissions from the landfill are obtained from the difference in the methane fluxes through a transect screen downwind and upwind from the landfill. Using a fast response methane monitor (TDL) the concentration upwind of the landfill is determined. Downwind of the landfill a methane plume is found that originates from the landfill. In this plume the methane concentrations are higher than the background level.

Using a dispersion model the concentration pattern can be used to estimate the emission level of the landfill. Simultaneous release of a tracer (SF_6 or N_2O for example) at the landfill can be used to either calibrate the dispersion model, or to, directly, calculate the methane emission level by comparison of the plumes obtained from the landfill and the tracer. This type of measurement provides an integrated estimate of the emission of the whole landfill. The spatial differences of the emission level on the landfill automatically taken into account. The method was used in the US by Czepiel et al [1996a]. Also in Europe experiments were performed in France and in The Netherlands [Scharff et al., 2000].

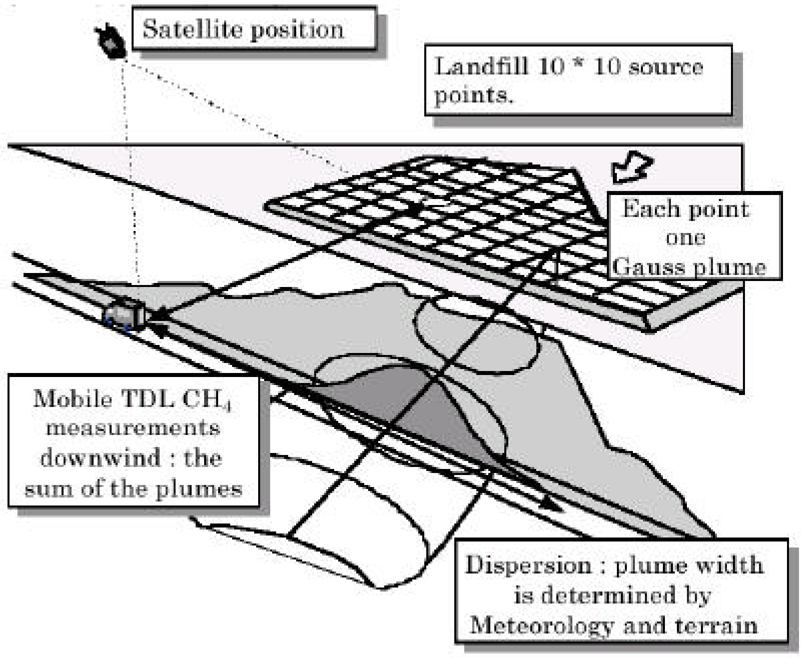


Figure C1 Schematic representation of the plume measurement

Advantages of plume measurements:

- an emission estimate for the whole landfill is obtained, spatial inhomogenity of the source is accounted for;
- especially when using a tracer with a known source strength the interpretation of the data is straightforward.

Disadvantages of plume measurements:

- the method can only be applied when a measurement transect is available downwind of the site;
- mobile plume measurements cannot be performed continuously (like for example the mass balance or box measurements);
- since mobile measurement need manpower continuously this type of experiments is relatively expensive.

g) Stationary plume measurements

In stead of mobile plume measurements stationary plume measurements can be also be performed. Air samples are collected in canisters downwind of the landfill during a period of time. Experiments in the USA have shown a good agreement between these plume measurements and mobile measurements [Czepiel, 1996a]. In the Netherlands this method was used to evaluate the emission of NH_3 from manure plots. Here also mobile plume measurements and stationary plume measurements were performed. A dispersion model is used to obtain the concentration variation versus time at the location of measurement. This modelled time series is averaged over the period in which sampling takes place. Comparison of the modelled and measured concentration levels provide the estimate of the source strength that causes the plume. The method was tested for NH_3

using an artificial source and the emission estimates compared well with the amount of NH_3 released.

Advantages of stationary plume measurements:

- an emission estimate for the whole landfill is obtained, spatial inhomogenity of the source is accounted for;
- the method does not need attendance while sampling, so a monitoring system based on this method will be relatively low-cost.

Disadvantages of stationary plume measurements:

- the method is new and needs evaluation;
- sampling locations outside the landfill are needed, permission to use these locations is required.

h) Isotope measurements (methane oxidation only)

Isotope measurements of CH_4 give insight in the fraction of methane that is oxidised in the top-layer. Methane that is formed inside a landfill has a specific isotope contribution ($^{12}C/^{13}C$) which is different from ambient air. When this methane passes the top-layer of the soil part of the methane is oxidised. In this process again the ($^{12}C/^{13}C$) ratio changes. This change is determined by the preference for ^{12}C of the oxidising bacteria. The emitted CH_4 is enriched with ^{13}C. When the latter effect is determined (for example in the lab using cores-samples) the oxidation fraction can be obtained using the isotope composition measurements. The isotope composition measurement of the landfill gas itself is relatively easy to determine. More difficult is to determine the average isotope composition of the gas that is actually emitted into the atmosphere. This is done by filling gas-flasks downwind of the landfill different mixtures of background air and emitted gas are obtained. From these samples the isotope composition of the emitted gas is calculated.

Since this method also uses samples downwind of the landfill, the average of the oxidation over the whole site is obtained. The major drawback of the method is the cost for the sample preparations.

Advantages of isotope measurements:

- an oxidation level for the whole landfill is obtained, spatial inhomogenity of the source is accounted for.

Disadvantages of isotope measurements:

- the sample preparation is expensive.

i) Sub-surface vertical gradient method (or probe sampling) [IEA Caddet, 2000]

This method is quite simple and inexpensive. A probe is put into the landfill top-soil and gas samples are taken at different depths. From the concentration gradient over the depth, a diffusive transport can be calculated using Fick’s law:

$$J = \left(\frac{n}{T}\right)(D)\left(\frac{dC}{dZ}\right)$$

where: J = flux ($g.cm^{-2}.sec^{-1}$)

n = gas filled porosity (fraction)

T = tortuosity: dimensionless coefficient to describe the actual path of gas movement with respect to straight-line distance

D = bulk (free-air) diffusion coefficient for methane in air or carbon dioxide ($cm^2.s^{-1}$)

dC/dZ = vertical concentration gradient for methane ($g.cm^{-3}.cm^{-1}$)

With respect to D, the bulk diffusion coefficient, values taken from literature for methane, carbon dioxide, oxygen and nitrogen involved in two component diffusion vary over a small range from about 0.15 to 0.22 cm^2sec^{-1}. The diffusion coefficient can be modified for pressure and temperature at probe depth according to the following relationship:

$$D(at\ T, P) = D_0 (T / T_0)^n P_0 / P$$

where: D = bulk (free-air) diffusion coefficient

T = Temperature (K)

P = Pressure (Pa)

n = empirical coefficient, typically 1.70-2.00

Only diffusive transport is considered in these equations, with differential soil gas pressures only introduced as a correction factor to a diffusion coefficient. Potentially, small differential pressures in the shallow subsurface at the top of the landfill may also be important driving forces for convective flux and hence emissions.

As for the flux box techniques, the sub-surface vertical methane gradient method only covers a small part of the landfill surface, and variations in top-soil permeability affect the measurements. Therefore, a series of measurements should be performed at various locations over the landfill surface. Moving probes probably takes more time than moving flux box, but leaving the probes gives an opportunity for repeated measurements at exactly the same spot at various times of the year and changing weather conditions. Also, the results from this method are sensitive to variations in barometric pressure.

The soil properties controlling the gas permeability have to be estimated. Unfortunately these properties may vary over time. For example, the water content of the pores, which may have a large influence on gas movements, can change from one day to another. If only the methane gradient is measured, oxidation in the surface will result in a stepper gradient and an over-estimate of the flux [Lagerkvist, 1997].

D. RECALCULATION KG C TO CUBIC METER LANDFILL GAS

	Unit		Source
Mol. weight C	g/mol	12	[Perry, 1984]
1 kg C	mol C	83.3	Calculated
83.3 mol C = 83.3 mol CO_2/CH_4			
Specific volume gas at STP	m^3/mol	0.0224	[Perry, 1984]
Recalculation factor	m^3/kg carbon	1.87	Calculated

E. MEASUREMENTS FROM THE SVISHTOV AND RAZLOG PILE

In this Annex the exact measurement data regarding the methane emissions in Svishtov and Razlog is given.

Table E.1 Results of the methane flux measurements on the Svishtov pile in liter/m^2/hr. In the cells with no entry no measurements were carried out.

Cell	10	20	30	40	50
A	1.7	13.8	2.4	0.0	2.1
B	0.0		0.0		
C	32.0		9.5	0.0	0.0
D	25.5	5.9	1.3		
E	0.0		7.5		0.0
F	59.8	5.1		0.0	
G	8.8	0.0		0.0	0.0
H		0.0	17.7		0.0
I				0.0	
J				0.0	
K				0.0	3.9
L				0.0	0.0
M		0.0	0.0	19.6	6.5
N		0.0	0.0	1.9	0.0
O		0.0	0.0	69.3	
P			0.0		0.0

Table E.2 Results of the methane flux measurements on the Razlog pile in liter/m^2/hr. In the cells with no entry no measurements were carried out.

Cell	a	b	c	d	e	f	g	h	i	j
1	0.0	0.0	3.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	3.2	3.0	6.6		2.1	1.8	0.0	0.0	0.0	0.0
3	0.0	0.0	71.7		11.3	9.6	0.0	0.0	0.0	0.0
4	2.5		117.3	122.7	57.4	54.3	0.0	0.0	4.6	4.3
5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
6	0.0	0.0	11.3	10.6	0.0	0.0	0.0	0.0	0.0	0.0
7	0.0	0.0	0.0	0.0	0.0	0.0			0.0	0.0
8	0.0	0.0	0.0	0.0			0.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
10	0.0	0.0	0.0	0.0	0.0	0.0			0.0	0.0

F. POSSIBLE SOURCES OF FLUX MEASUREMENT ERRORS

Three possible errors can be identified regarding the accuracy of the flux measurements:

- Errors regarding the measurement procedure errors
- Dynamic errors of the gas chromatograph
- Systematic errors of the gas chromatograph

Measurement procedure errors

Measurement procedure errors are inaccuracies caused by the set-up of the measurement procedure. The question here is what are the possible errors, for a given flux on a patch of the pile, if measured with an ideal gas chromatograph. Possible errors are:

- *The actual size of the chambers.* Since these have been measured as accurately as possible (measurement accuracy 1 mm), this would only imply an error of less than 0.2%.
- *The volume flow measurements.* Volume flow was measured several times with a flow meter. These measurements were accurate to 0.05 m/s implying an accuracy in the volume flow measurements of less than 2.5%.
- *Variations in the volume flow.* The ventilator could be the source of unwanted variations in the volume flow, these were however not detected during several volume flow measurements.
- *Possible leakage along the side of the chambers.* Precautions were made so that air could not leak in from the outside of the chamber. Furthermore, the air inlet tube had a diameter of ca. 20 centimeter, resulting in a very low pressure drop inside this tube. Because of this the possible error resulting from air leakage along the side of the chamber is considered minimal.
- *Possible extra air input through the ventilator.* The ventilators which provides for the air flow through the chambers did also suffer for surplus air input through the side of the ventilator. This implied that the airflow measurement had to be corrected for this extra air flow. This correction has been made, so the resulting error is estimated to be minimal.
- *Pressure changes or concentration build-up inside the chamber*. Because the chamber measurement is carried out with a dynamic chamber, concentration build-up is not reasonably expected. Because of the ventilator, the chamber pressure is below ambient pressure, which could in theory have some influence on the methane emissions. However, because of the large diameter of the inlet tube and the low volume flow, the pressure drop is lower than 1 Pa, which is far lower than ambient variations, which are easily a few millibar.
- *Concentration gradients inside the chamber.* The sample point is located in the exit tube of the chamber. Because of the relatively high Reynolds number the air can be considered well-mixed at that point, implying no difficulties regarding this point.

Gas chromatograph calibration

The gas chromatograph is has been calibrated using several known methane concentration with the result as listed in Figure A.1:

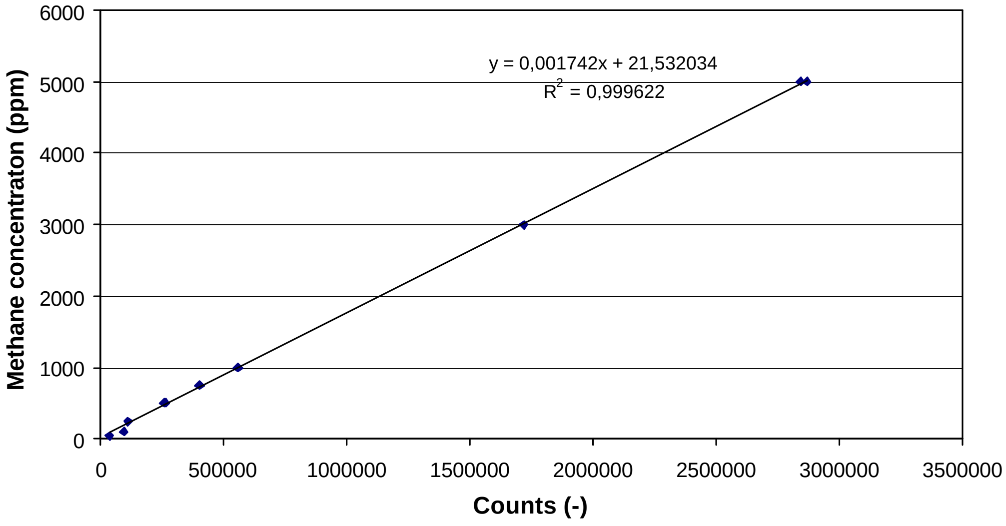
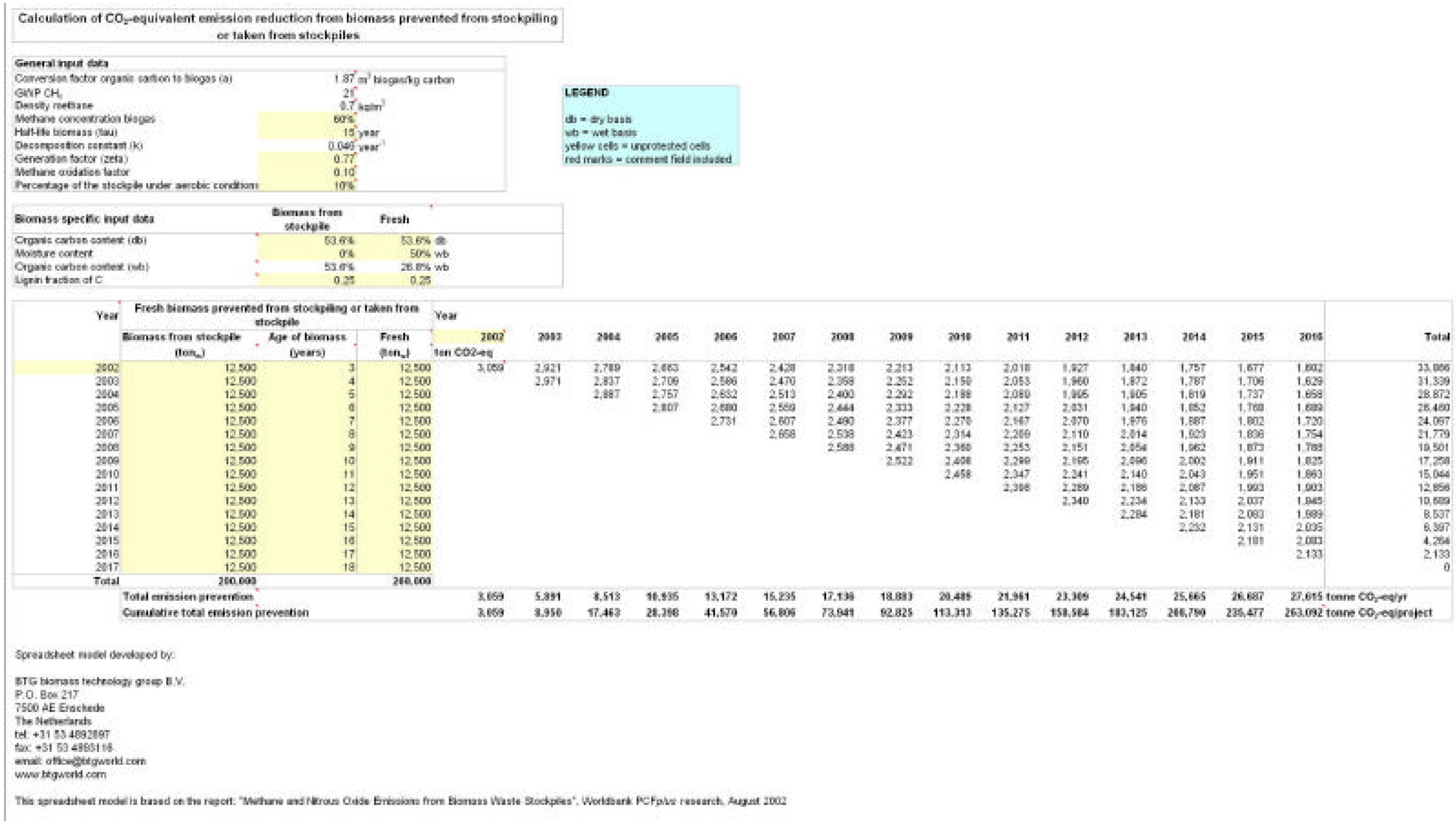


Figure F.1 Calibration of the gas chromatograph with known methane concentrations

From this calibration curve it follows that the threshold value, below which the gas chromatograph does not give any reading, is 21.5 ppm. This implies that at any point were the methane flux was measured to be zero, there could have actually been methane present. It is however not likely that this would consistently be the case, because of the skewed methane flux distribution.

From the calibration it follows that the dynamic accuracy is quite sufficient.

G. SPREADSHEET MODEL



Calculation of CO$_2$-equivalent emission reduction from biomass prevented from stockpiling or taken from stockpiles

General input data		
Conversion factor organic carbon to biogas (a)	1.87	m^3 biogas/kg carbon
GWP CH$_4$	21	
Density methane	0.7	kg/m^3
Methane concentration biogas	60%	
Half-life biomass (tau)	15	year
Decomposition constant (k)	0.046	year^{-1}
Generation factor (zeta)	0.77	
Methane oxidation factor	0.10	
Percentage of the stockpile under aerobic conditions	10%	

LEGEND

db = dry basis
wb = wet basis
yellow cells = unprotected cells
red marks = comment field included

Biomass specific input data	Biomass from stockpile	Fresh	
Organic carbon content (db)	53.6%	53.6%	db
Moisture content	0%	50%	wb
Organic carbon content (wb)	53.6%	26.8%	wb
Lignin fraction of C	0.25	0.25	

Year	Fresh biomass prevented from stockpiling or taken from stockpile			Year															
	Biomass from stockpile (ton$_{wb}$)	Age of biomass (years)	Fresh (ton$_{wb}$)	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	Total
				ton CO2-eq															
2002	12,500	3	12,500	3,059	2,921	2,789	2,663	2,542	2,428	2,318	2,213	2,113	2,018	1,927	1,840	1,757	1,677	1,602	33,086
2003	12,500	4	12,500		2,971	2,837	2,709	2,586	2,470	2,358	2,252	2,150	2,053	1,960	1,872	1,787	1,706	1,629	31,339
2004	12,500	5	12,500			2,887	2,757	2,632	2,513	2,400	2,292	2,188	2,089	1,995	1,905	1,819	1,737	1,658	28,872
2005	12,500	6	12,500				2,807	2,680	2,559	2,444	2,333	2,228	2,127	2,031	1,940	1,852	1,768	1,688	26,460
2006	12,500	7	12,500					2,731	2,607	2,490	2,377	2,270	2,167	2,070	1,976	1,887	1,802	1,720	24,097
2007	12,500	8	12,500						2,658	2,538	2,423	2,314	2,209	2,110	2,014	1,923	1,836	1,754	21,779
2008	12,500	9	12,500							2,588	2,471	2,360	2,253	2,151	2,054	1,962	1,873	1,788	19,501
2009	12,500	10	12,500								2,522	2,408	2,299	2,195	2,096	2,002	1,911	1,825	17,258
2010	12,500	11	12,500									2,458	2,347	2,241	2,140	2,043	1,951	1,863	15,044
2011	12,500	12	12,500										2,398	2,289	2,186	2,087	1,993	1,903	12,856
2012	12,500	13	12,500											2,340	2,234	2,133	2,037	1,945	10,689
2013	12,500	14	12,500												2,284	2,181	2,083	1,989	8,537
2014	12,500	15	12,500													2,232	2,131	2,035	6,397
2015	12,500	16	12,500														2,181	2,083	4,264
2016	12,500	17	12,500															2,133	2,133
2017	12,500	18	12,500																0
Total	200,000		200,000																
	Total emission prevention			3,059	5,891	8,513	10,935	13,172	15,235	17,136	18,883	20,489	21,961	23,309	24,541	25,665	26,687	27,615	tonne CO$_2$-eq/yr
	Cumulative total emission prevention			3,059	8,950	17,463	28,398	41,570	56,806	73,941	92,825	113,313	135,275	158,584	183,125	208,790	235,477	263,092	tonne CO$_2$-eq/project

Spreadsheet model developed by:

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This spreadsheet model is based on the report: "Methane and Nitrous Oxide Emissions from Biomass Waste Stockpiles", Worldbank PCFplus research, August 2002

H. HISTORIC DATA ON RAINFALL NEAR THE SVISHTOV SITE

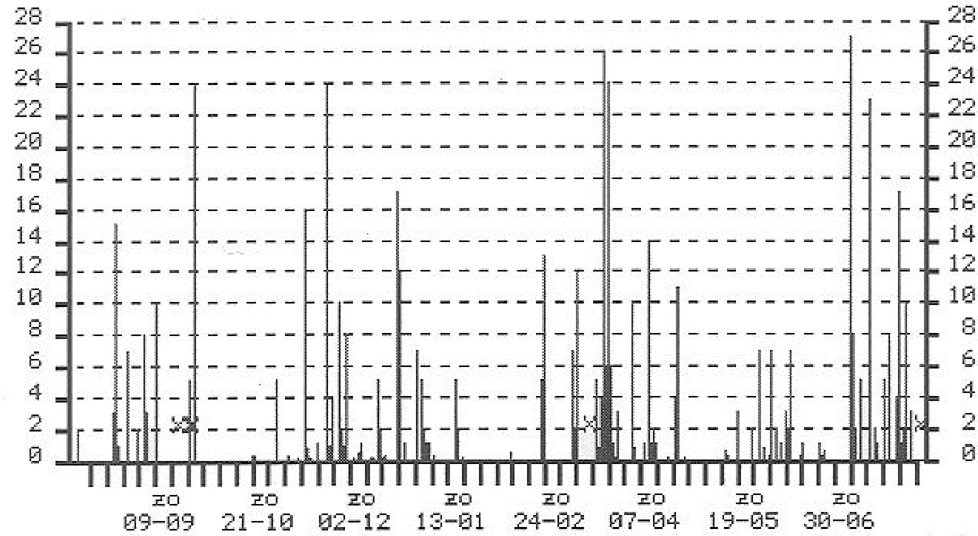

Figure H.1 Daily rainfall in Razgrad (120 km from Svishtov) in the last year. Svishtov methane emission measurements were conducted in week 13 and 14 of 2002 (25 March - 5 April). On the vertical axis rainfall is given in mm.

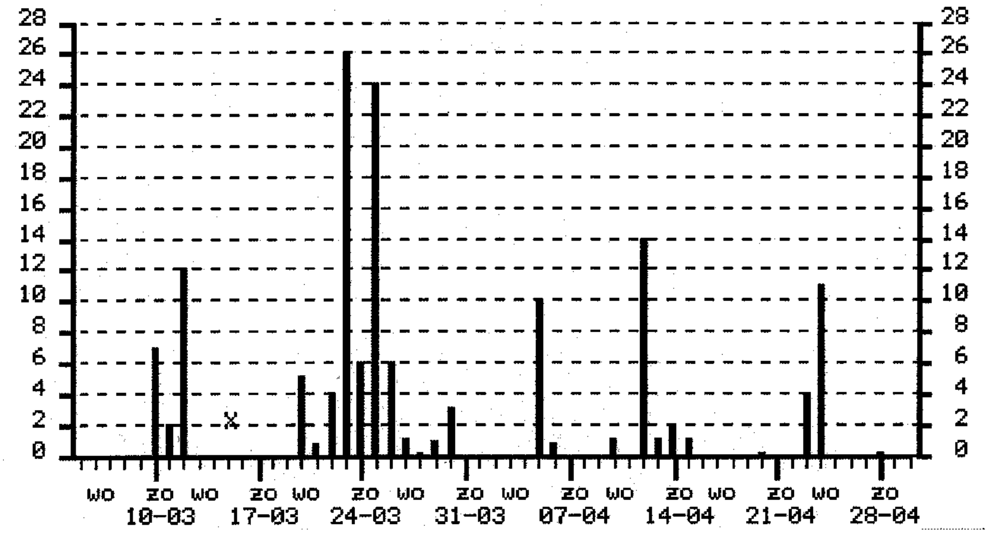

Figure H.2 Daily rainfall in Razgrad (120 km from Svishtov) from March to April 2002. Svishtov methane emission measurements were conducted in week 13 and 14 of 2002 (25 March - 5 April). On the vertical axis rainfall is given in mm.