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METHANE OXIDATION AND DEGRADATION OF HALOGENATED ORGANIC COMPOUNDS IN  
LANDFILL GAS AFFECTED SOIL

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**ABSTRACT:** In an investigation of the oxidation of methane and halogenated organic compounds in landfill gas affected soil all the chlorinated ethylenes were shown to be degraded in presence of oxygen and methane. The degradation followed zero-order kinetics and occurred in parallel with the oxidation of methane. In general, the degradation rates of the chlorinated ethylenes were inversely related to the chlorine/carbon ratios. While HCFC-21 and HCFC-22 were shown to be degradable, CFC-11 and CFC-12 were not degradable under methane-oxidizing conditions. The oxidation of methane and halogenated organic compounds was very dependent on temperature, showing optimum rates at 30°C. However, oxidation occurred at temperatures as low as 2°C. Batches with soil moisture contents between 17 and 33 %w/w produced maximum oxidation rates for methane, HCFC-21 and HCFC-22. High oxidation potentials were found in batch experiments conducted with soil collected from 5 to 40 cm depth and maximum rates were obtained with soil from 20-25 cm depth.

**Keywords:** landfill gas, methane oxidation, co-oxidation, halogenated organic compounds, freon, methanotrophic bacteria, soil moisture content, depth distribution.

## 1. INTRODUCTION

Waste deposited in a landfill will undergo anaerobic decomposition resulting in generation of landfill gas, which is transported through soil top covers causing emission of gas into the atmosphere. Besides methane (55-60 % v/v) and carbon dioxide (40-45 % v/v) landfill gas also contains numerous trace compounds (up to 5 % v/v) (Brosseau & Heitz, 1994). The trace compounds originate from hazardous materials deposited in the landfill or from biological/chemical degradation of materials deposited in the landfill.

Emission of methane from landfills accounts for between 7 and 20% of the global anthropogenic sources of methane emissions thus contributing to the global climate change (Thorneloe et al. 1991). Emission of trace compounds like benzene and vinyl chloride to the ambient air can be a threat to workers and local habitants, while other trace compounds like freons contribute to the depletion of the ozone layer (Christensen & Kjeldsen, 1995).

Microbial oxidation of methane in aerobic soils plays a significant role in reducing the emission of methane to the atmosphere. In landfill top covers methane and oxygen counter-gradients may appear due to emission of methane from the waste and diffusion of oxygen from ambient air. Oxidation of methane by methanotrophic bacteria in landfill top cover soil has been shown to reduce the amount of methane emitted to the atmosphere. A defining characteristic of the methanotrophic bacteria is the enzyme methane monooxygenase (MMO) which catalyze the oxidation of methane. MMO has very broad substrate specificity and is known to co-metabolize a variety of aliphatic compounds including some halogenated hydrocarbons (Hanson & Hanson, 1996).

The objective of this study was to investigate the potential of natural oxidation of methane and halogenated organic compounds (HOCs) in soil exposed to landfill gas. In addition, the impact of individual factors (soil moisture, soil temperature, and sampling depth) on methane oxidation and co-oxidation of selected trace compounds was studied. The investigations have been carried out through laboratory experiments. The chosen trace components included six chlorinated ethylenes (perchloroethylene (PCE), trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE), cis-1,2-dichloroethylene (c-1,2-DCE), trans-1,2-dichloroethylene (t-1,2-DCE), and vinyl chloride), and four freon compounds (trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), dichlorofluoromethane (HCFC-21) and chlorodifluoromethane (HCFC-22)).

## **2. MATERIAL AND METHODS**

### **2.1 Soil sampling**

Soil samples were collected at Skellingsted Landfill south of Holbæk, Western Sealand, Denmark. Prior to the soil sampling soil gas samples were taken to ensure that the soil was being exposed to landfill gas and thereby holding the potential of containing active methanotrophic bacteria. Soil samples were collected using a hand auger and kept cold and in darkness in closed containers prior to the laboratory experiments. The soil samples were kept in closed containers to avoid dehydration. The soil was sieved through a 4 mm mesh to increase homogeneity. The grain size distribution, pH, water and organic content of the soil were measured before conducting the experiments.

### **2.2 Batch experiments**

Methane oxidation and degradation of trace components was examined in simple batch experiments. A fixed amount of soil (17 g) was added to a 117 mL batch container equipped with butyl rubber stoppers, which enable gas to be sampled or injected by a syringe. Fixed water content was obtained by adding water to the soil. To obtain methanogenic conditions, air was withdrawn from each container using a syringe and replaced with methane, which gave initial mixture of methane (15% v/v), oxygen (35% v/v) and nitrogen (50% v/v). Gas samples containing the test compound were removed from gaseous stock solutions by a gas tight glass syringe and injected into the batch containers. The initial concentrations were selected so as to be within the linear concentration range of gas chromatographic analysis. Gas samples withdrawn from headspace were sampled continuously and analyzed by gas chromatography. From the measured gas concentration the total amount ( $\mu\text{g}$ ) of test compound in the batch was determined by phase distribution calculations using Henry's Law. The kinetics of oxidation were examined by plotting the total concentration of the halogenated compound versus time.

In order to check if any disappearance could be due to non-microbial processes (abiotic degradation, sorption and volatilization) sodium azide (25mg/kg soil) was added to avoid microbial growth in control batches. To verify that the degradation of HOCs was not due to the presence of anaerobic bacteria in the soil, anoxic batch experiments flushed with methane or nitrogen were carried out. In addition to the sterilized control experiments, other experiments were carried out where acehylene (known to inhibit MMO) was added instead of sodium azide to batches containing HCFC-21 and HCFC-22.

## **3. ANALYSIS**

Soil moisture content was determined gravimetrically by oven drying at 105°C for 24 hours, and expressed as the mass ratio of water to dry soil. Soil organic matter content was determined by the loss of ignition method.

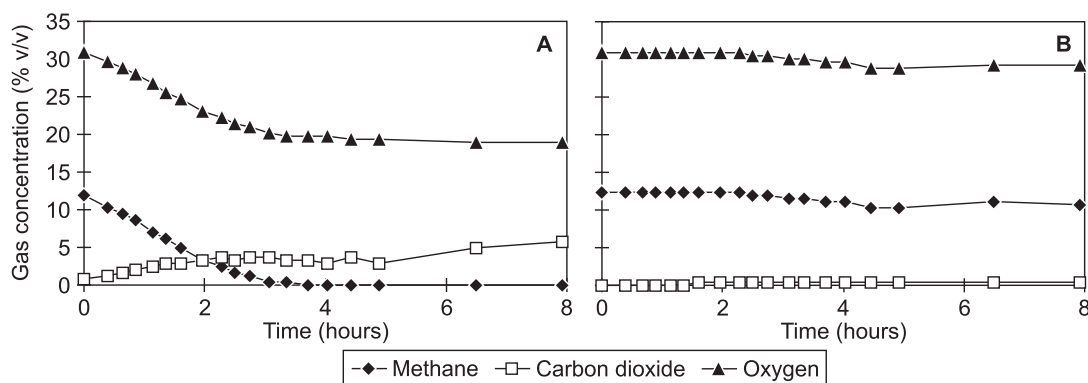
The degradation of the trace components was determined by periodic sampling of the gas phase and analysis by gas chromatography. For analysis, gas samples (10-500  $\mu\text{l}$ ) taken directly from the reaction bottles were injected manually via an on-column inlet to a gas chromatograph. The halogenated compounds were measured on Carlo Erba HRGC 5300 equipped with an electron capture detector and a WCOT fused silica capillar column (CP-Sil-19 CB) with nitrogen being the carrier gas. The freon compounds were analyzed with a isotherm column temperature of 40°C, while the chlorinate ethylenes were analyzed by running a temperature program with a start temperature of 40°C and raising the temperature to 80°C by a rate of 10°C /min. The main gas components were analyzed on a Chrompack Micro GC CP-2002P gas chromatograph equipped with a thermal conductivity detector and two columns. Oxygen and nitrogen were

quantified on a 4 m long Molsieve 5A and methane and carbon dioxide on a 10 m long Poraplot Q column. Carrier gas was helium and the column temperature was 40°C.

## 4. RESULTS AND DISCUSSION

### 4.1 Methane oxidation and degradation of trace components in landfill gas

The degradation of different trace components often found in landfill gas was studied under methane oxidizing conditions. Figure 1a shows the measured methane and carbon dioxide concentrations in headspace versus time in a batch experiment containing CFC-11. Lag phases was never observed which indicate that the bacteria were well adapted to oxidize methane. The figure also shows that the oxygen concentration never was below 18% v/v and methane oxidation was therefore not limited by low oxygen concentration. The oxidation of methane followed zero order kinetics. In table 1 the methane oxidation rates observed in the different batch experiments are listed. The soil showed a high capacity for methane oxidation resulting in very high oxidation rates between 25 and 163  $\mu\text{g CH}_4/\text{g dry soil per hour}$ . Increasing concentrations of the HOC seem to result in decreased methane oxidation rates, which is a combination of inhibition due to toxicity of the halogenated compounds and increased competition between methane and the halogenated compounds for the enzyme methane monooxygenase (which induces the oxidation). The methane oxidation rates are very high compared to those reported by Whalen et al. (1990) and Jones & Nedwell (1993), and are closer to the results obtained by Figueroa (1993) (between 40 and 86  $\mu\text{g CH}_4/\text{g dry soil per hour}$ ). The sterilised control experiments showed no decrease in the methane concentration, which indicates that microbial oxidation is the only explanation for the decrease in the active experiments. Figure 1b shows the results of the control experiment corresponding to figure 1a.



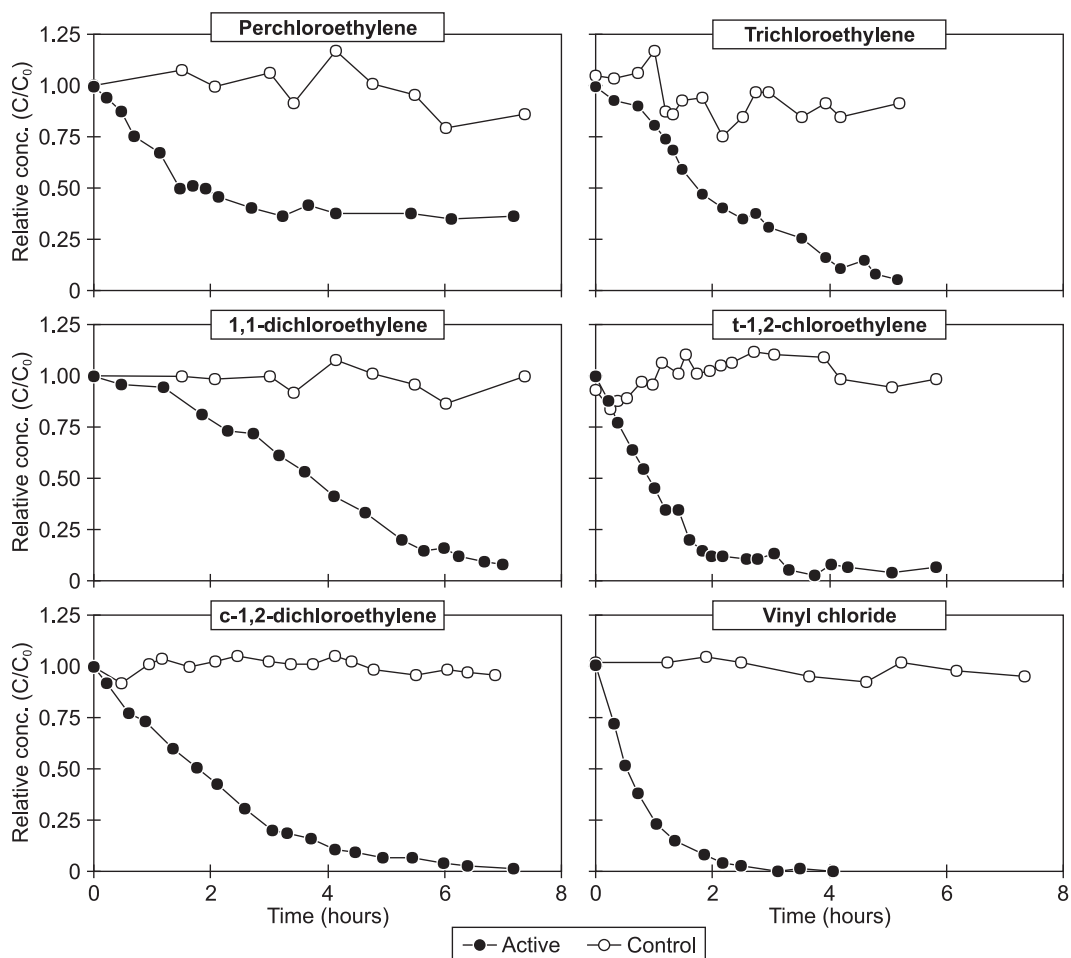
**Figure 1. a.** Headspace concentration of methane, oxygen and carbon dioxide as function of time showing methane oxidation in a batch experiment containing 17 g soil pre-exposed to landfill gas. **b.** Control experiment.

Figure 2 shows the degradation of the chlorinated ethylenes. All the chlorinated ethylenes were shown to be degraded in presence of oxygen and methane, and the degradation occurred in parallel with the oxidation of methane. However, total transformation of perchloroethylene was not observed. In general, the degradation rates of the chlorinated ethylenes were inversely related to the chlorine/carbon ratios. The lower degradation rate obtained for vinyl chloride compared to *c*-1,2,-DCE and *t*-1,2,-DCE is thought to be a result of the vinyl chlorides high toxicity since methane oxidation was also reduced. Kjeldsen et al. (1997) carried out similar experiments also with soil from Skellingsted Landfill and found much lower oxidation rates for both methane and TCE (3.75 and 0.00125  $\mu\text{g/g soil}\cdot\text{h}$  respectively). This can be explained by a combination of several factors: Kjeldsen et al. (1997) collected soil from other sampling sites and had less

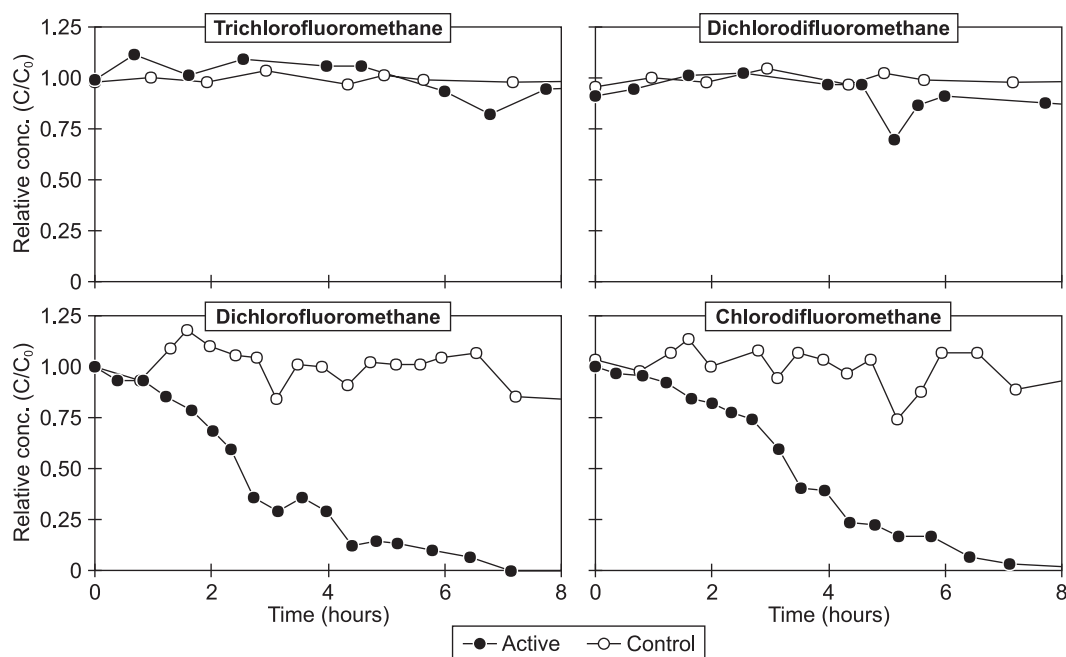
favourable experimental conditions, i.e., lower temperatures (10°C), deeper sampling depths (50-60 cm b.s.) and exposure of soil samples to dehydration during storage.

Figure 3 shows the results of the experiments containing freon compounds: HCFC-21 and HCFC-22 were also shown to be degradable, however CFC-11 and CFC-12 did not seem to be degradable within the duration of the experiment. In all cases the degradation process was best described by zero-order kinetics, however, in some of the experiments the degradation declined at the end of the experiment, which could be a result of substrate limitation or intoxication due to accumulation of degradation products. In table 1 the degradation rates for the studied compounds are listed together with the regression coefficients obtained from fitting the data with a zero-order equation.

The sterilised control experiments showed no decrease in the HOC concentration, which indicates that microbial oxidation is the only explanation for the decrease in the active experiments. In anoxic batch experiments containing HCFC-21, HCFC-22 and atmosphere consisting of pure methane or nitrogen no degradation occurred within the duration of the experiment (8 hours) (results not shown), which indicates that oxygen is needed for the oxidation to take place. In batch containing approximately 10 % v/v acetylene in headspace methane oxidation and degradation of HCFC-21 and HCFC-22 was totally inhibited, as a result of the binding of acetylene to the MMO (results not shown). This indicates that the oxidation of methane and HOCs observed in the active batches is due to the activity of methanotrophic bacteria.



**Figure 2.** Headspace concentration of chlorinated ethylenes as a function of time in a batch experiment containing 17 g soil pre-exposed to landfill gas.



**Figure 3.** Headspace concentration of freon compounds as a function of time in a batch experiment containing 17 g soil pre-exposed to landfill gas.

**Table 1.** Methane oxidation and degradation rates obtained from batch experiments containing methane and HOCs. Regression coefficients ( $r^2$ ) obtained from fitting the experimental data to a zero-order oxidation process. The batches held soil water content of 25 %w/w and were conducted at room temperature.

Compound studied	Initial gas conc. $\mu\text{g/l}$	Methane oxidation rate $\mu\text{g/g soil}\cdot\text{h}$	Degradation rate $\mu\text{g/g soil}\cdot\text{h}$	$r^2$ -values for methane oxidation	$r^2$ -values for degradation of HOCs
PCE	7	132	0.025	0.991	0.935
TCE	30	141	0.094	0.992	0.945
1,1-DCE	80	132	0.114	0.987	0.990
c-1,2-DCE	400	87	1.381	0.977	0.982
t-1,2-DCE	700	135	3.244	0.990	0.981
Vinyl chloride	120	25	0.509	0.982	0.0911
CFC-11	20	163	No degrad.	0.982	No degrad.
CFC-12	35	159	No degrad.	0.995	No degrad.
HCFC-21	300	93	0.403	0.945	0.860
HCFC-22	300	93	0.307	0.945	0.912

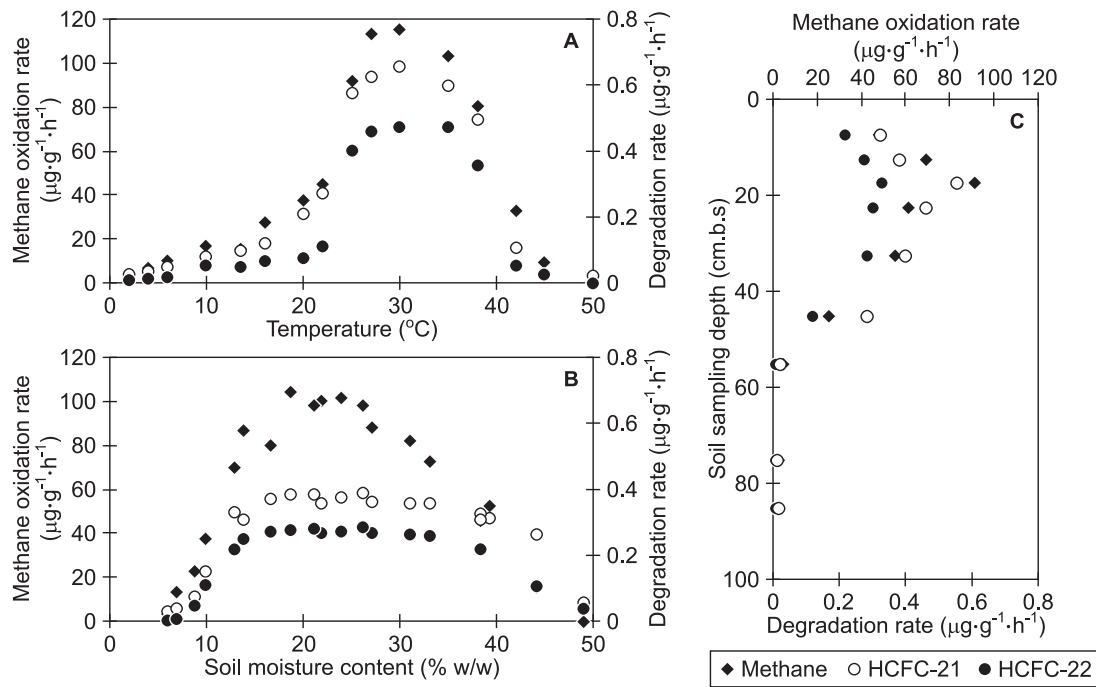
## 4. 2 Impact of temperature, soil water content and sampling depth on the oxidation process

**Temperature.** The influence of temperature on microbial oxidation was studied in batch experiments containing methane, HCFC-21 and HCFC-22 in a temperature range of 2-50°C. Figure 4a shows the zero-order oxidation rates in relation to temperature. Temperature had a profound influence on the methanotrophic activity in oxidizing methane, HCFC-21 and HCFC-22. The oxidation rates increased exponentially ( $r^2 > 0,91$ ) from 2°C up to 25°C reaching maximum rates around 30°C. Optimum temperature for methane oxidation around 30°C have also been reported by Whalen et al. (1990). A further increase in temperature to 40°C resulted in a steep decline in oxidation rates and at 50°C the activity of the microorganisms was totally

inhibited. However even at 2°C bacteria were active oxidizing methane and HCFCs, which implies that even during winter some methanotrophic activity might be expected and thereby reducing the emission of methane and trace compounds from landfills.

**Soil moisture.** The effect of soil moisture content on methane oxidation and co-oxidation of HCFC-21 and HCFC-22 was determined in a range of 6 to 50% w/w. Water was added the soil the day before start up in order to ensure a homogenous distribution of the water. To obtain soil moisture contents of less than 15% the soil was air-dried. All incubation batches showed a linear decrease in headspace concentration of methane, HCFC-21 and HCFC-22 indicating zero-order kinetics. Figure 4b shows the oxidation rates as a function of soil moisture content. Batches with soil moisture contents between 18 and 24 %w/w produced maximum methane oxidation rates. The response of soil moisture to degradation of HCFC-21 and HCFC-22 was similar but gave a broader optimum range compared to methane (17 til 33 %w/w). A decrease in moisture content reduced the oxidation rates significantly due to microbial water stress resulting in desiccation and reduced activity. In experiments with air-dried soil it also seemed to be difficult to recover the oxidation activity of the bacteria when re-wetting the soil, implying that after very dry periods with low methanotrophic activity a lag period could be expected for the methanotrophs to reproduce or regain their activity. An increase in soil moisture resulted in reduced oxidation rates. At a soil moisture content higher than 35 %w/w the soil will be water logged resulting in transport limitation due to the much lower molecular diffusion in water compared to air ( $10^4$ -fold less rapid). The broader optimum range observed for HCFC-21 and HCFC-22 could be explained by the higher water solubility and lower Henry's law constants for HCFC-21 and HCFC-22 compared to methane.

**Sampling depth.** Soil samples were collected from different depths to determine the distribution of methane oxidation and co-oxidation of HOCs. The soil was sampled in 5-cm intervals from the surface to 30 cm depth and in 10-cm intervals from 30 to 90 cm below the surface. The soil samples were incubated with methane and HCFC-21 and HCFC-22. Again the oxidation process followed zero-order kinetics. Figure 4c shows the depth distribution of methane oxidation and co-oxidation of HCFC-21 and HCFC-22. The form of the oxidation curves was similar for methane and HCFC-21 and HCFC-22. The methanotrophic bacteria were very active in oxidizing methane and degrading HCFC-21 and HCFC-22 down to a depth of 50 cm below the surface. Maximum rates was obtained with soil from 20-25 cm, which is consistent with results reported by Kightley et al. (1995), who observed peak oxidation in incubated landfill soil cores at a depth of 20 cm. Christophersen & Kjeldsen (2000) carried out an extensive field study at Skellingsted landfill, in which vertical soil profiles measured every second week during a one year period showed that both methane and oxygen often were present between 20 and 40 cm depth. This corresponds with the results from this study since the maximum oxidation zone is expected to form in a soil layer of overlapping O<sub>2</sub> and CH<sub>4</sub> gradients. The oxidation rates decreased dramatically at 50 cm depth as a result of O<sub>2</sub> limitation which is supported by soil air measurements conducted at 60 cm depth showing a gas composition of mainly methane and carbon dioxide and very low or no oxygen presence.



**Figure 4.** Methane oxidation and degradation rates for batch experiments containing HCFC-21 and HCFC-22 as a function of : **a.** soil water content. **b.** temperature. **c.** soil sampling depth.

## 5. PERSPECTIVES

The batch experiment showed very high rates of methane oxidation and degradation of the lower halogenated ethylenes and HCFCs. Lower rates were obtained for PCE, TCE and vinyl chloride. All the oxidation curves followed zero-order kinetics. In order to evaluate the potential of oxidizing methane and degrading trace components in landfill top covers some simple calculations based on the obtained oxidation rates were made. Assuming the zero-order rate constant to be valid for an active zone in a soil profile, the degradation rate integrated over the depth,  $K_0$  ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ), can be calculated as:

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

where  $k_0$  is the zero-order degradation rate ( $\mu\text{g}\cdot\text{g soil}^{-1}\cdot\text{h}^{-1}$ ),  $d_a$  is the oxidation zone (m) and  $\rho_b$  is the soil bulk density (metric tons $\cdot\text{m}^{-3}$ ). The maximal concentration,  $C_{\text{max}}$  ( $\text{mg}\cdot\text{m}^{-3}$ ) of the LFG compound that can be degraded while passing through the oxidative zone is:

$$C_{\text{max}} = \frac{K_0}{J_{LFG}}$$

where  $J_{LFG}$  is the total flux of LFG through the soil profile ( $\text{m}^3 \text{LFG}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) (Kjeldsen et al., 1997). Assuming a total LFG-flux of  $0.25 \text{ m}^3 \text{LFG}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  an oxidative zone of 40 cm, and typical values for bulk density and soil water content of  $1.6 \text{ tons}\cdot\text{m}^{-3}$  and 25 %w/w respectively the maximal degraded concentrations given in table 2 are obtained. For comparison maximum concentrations of HOCs measured in landfill gas reported in Christensen & Kjeldsen, 1995 are also listed in table 2.



**Table 2.** Calculated maximal oxidation concentrations based on zero-order methane oxidation and degradation rates obtained from batch experiments (table 1) and the equations and constants given in the text. The methane oxidation rate ( $132 \mu\text{g}\cdot\text{g soil}^{-1}\cdot\text{h}^{-1}$ ) obtained in batch containing PCE is used for calculation of the maximal degradable methane concentration.

Compound studied	Depth intergrated degradation rate $K_{0,\text{trace}}$ $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$	Maximal degradable concentration $C_{\text{max,trace}}$ $\text{mg}\cdot\text{m}^{-3}$	Maximal measured LFG concentration $C_{\text{max,meas}}$ $\text{mg}\cdot\text{m}^{-3}$
Methane	84,480	8,110,080	400,000
PCE	16	1536	250
TCE	60	5775	312
1,1-DCE	73	7004	134
c-1,2-DCE	884	84,849	100
t-1,2-DCE	2076	199,311	294
Vinyl chloride	326	31,273	264
CFC-11	No degrad.	No degrad.	500
CFC-12	No degrad.	No degrad.	700
HCFC-21	258	24,760	14
HCFC-22	196	18,862	276

Calculations based on the obtained methane oxidation rates show that all the methane in LFG can be totally oxidized under optimal conditions (temperature of  $25\text{ }^{\circ}\text{C}$  and water content of  $25\text{ \%w/w}$ ). Moreover, due to relatively high oxidation rates observed at  $10^{\circ}\text{C}$  and  $5^{\circ}\text{C}$ , total oxidation of methane is also possible for these lower temperatures.

For the chlorinated ethylenes, HCFC-21 and HCFC-22 the maximal degradable concentrations by far exceed the maximal measured concentrations in LFG, which indicates that these compounds also may be totally degraded in the top soil cover. The degradation rates are lower for the compounds with high chlorine substitution, thus resulting in smaller maximal degradable concentrations for these compounds. These concentrations are nevertheless high enough to indicate a potentially total degradation.

Degradation of CFC-11 and CFC-12 in the oxidative zone is limited, but these compounds have been found degradable under anaerobic conditions (Ejlertsson et al. 1996). Under methanogenic conditions which exist within the waste CFC-11 and CFC-12 may undergo reductive dehalogenation leading to accumulation of lesser chlorinated compounds like products HCFC-21 and HCFC-22, which then might be degraded in the oxidative zone in the surrounding soil. The same could be valid for other highly halogenated organic compounds, which are resistant to degradation or slowly degradable in the aerobic zone, like trichloroethanes, carbon tetrachloride etc.

The above evaluation is based on high oxidation rates obtained under optimal conditions and assuming a homogeneous soil layer with an intergranular flow of LFG (i.e., no macro pore flow due to cracks, root channels, worm holes etc.). However, landfill top covers are highly dynamic systems influenced by atmospheric pressure, temperature, precipitation etc. During cold periods with low temperatures and increased precipitation the emission will increase due to diffusion limitations in water saturated soil and lower microbial activity. Decreasing barometric pressure also causes higher emissions by enhancing the advective gas flow and thus shrinking the oxic zone. In order to simulate a more dynamic system the oxidation process is currently under investigation in a methane and oxygen counter-gradient column experiment.

However this study demonstrates that landfill gas affected soil shows a significant potential for methane oxidation and co-oxidation of HOCs. At old landfills with lower gas production methane oxidation and co-oxidation of HOCs in top soils may play a very important role in reducing the emission of both methane and trace components into the atmosphere.

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