



## Attenuation of methane and trace organics in landfill soil covers

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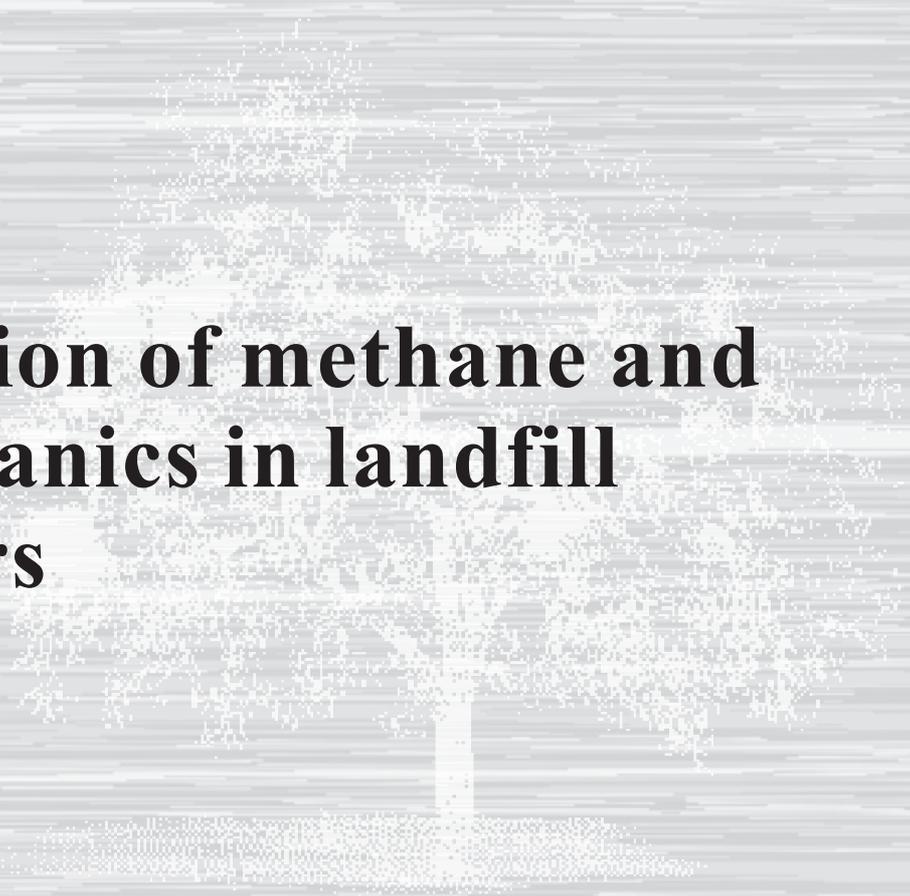
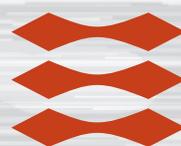
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Environment & Resources  
Technical University of Denmark

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# Attenuation of methane and trace organics in landfill soil covers

Charlotte Scheutz



**ATTENUATION OF METHANE AND TRACE  
ORGANICS IN LANDFILL SOIL COVERS**

**CHARLOTTE SCHEUTZ**

**Ph.D. Thesis  
September 2002**

**Environment & Resources DTU  
Technical University of Denmark**

**ATTENUATION OF METHANE AND TRACE ORGANICS IN LANDFILL  
SOIL COVERS**

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## FOREWORD

The present thesis has been submitted as part of the requirement for the Ph.D.-degree at the Technical University of Denmark. The study was carried out from August 1998 to August 2002 at Environment & Resources DTU, Technical University of Denmark, under the supervision of Associate Professor Peter Kjeldsen. The project was financed by the Technical University of Denmark.

The thesis consists of a summary on “Attenuation of landfill gas components in soil covers” and of the following updated papers:

- I. Scheutz, C., Mosbæk, H. and Kjeldsen, P. 2004. Attenuation of Methane and Volatile Organic Compounds in Landfill Soil Covers. *Journal of Environmental Quality*, 33:61-71.
- II. Scheutz, C., and Kjeldsen, P. 2004. Environmental Factors Influencing Attenuation of Methane and Hydrochlorofluorocarbons in Landfill Cover Soils. *Journal of Environmental Quality*, 33:72-79.
- III. Scheutz, C., and Kjeldsen, P. 2003. Capacity for Biodegradation of CFCs and HCFCs in a Methane Oxidative Counter-Gradient Laboratory System Simulating Landfill Soil Covers. *Environmental Science and Technology*, 37:5143-5149.
- IV. Scheutz, C., and Kjeldsen, P. 2005. Biodegradation of Trace Gasses in Simulated Landfill Soil Cover. *Journal of the Air & Waste Management Association*. 55:878-885.
- V. Scheutz, C., Bogner, J., Chanton, J., Blake, D., Morcet, M., Kjeldsen, P. 2003. Comparative Oxidation and Net Emissions of Methane and Selected Non-Methane Organic Compounds in Landfill Cover Soils. *Environmental Science and Technology*, 37:5150-5158.
- VI. Scheutz, C., Winther, K., and Kjeldsen, P., 2000. Removal of Halogenated Organic Compounds in Landfill Gas by Top Covers Containing Zero-Valent Iron. *Environmental Science & Technology*. 34:2557-2563.

The in-text references of these Papers are: Scheutz et al., I; Scheutz and Kjeldsen, II; Scheutz and Kjeldsen, III; Scheutz and Kjeldsen, IV; Scheutz et al., V; and Scheutz et al., VI.

I would like to thank Associate Professor Peter Kjeldsen for his inspirational and committed support throughout the study, and Mette Christophersen for good discussions and for comments on my manuscripts. Thanks also to my co-authors for a fruitful collaboration, and special thanks to Jean Bogner for the stimulating work together. The illustrations and figures in this report have been made by Birte Brejl and Torben Dolin, whom I gratefully thank, as I thank my colleagues at Environment and Resources DTU for the good working environment.

Charlotte Scheutz, September 2002



## **POSTSCRIPT**

At the time of the Ph.D.-defense, four of the included papers were submitted for publication, one paper had been published, and one paper was in preparation for submission. All papers were later accepted for publication with only minor revisions. For completeness the published papers have been included in this printed version of the thesis instead of the former preliminary versions.

Charlotte Scheutz, January 2006

The papers are not included in this www-version but may be obtained from the Library at the Environment & Resources DTU, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Kgs. Lyngby ([library@er.dtu.dk](mailto:library@er.dtu.dk))



## SUMMARY

Landfills release, in addition to methane, numerous volatile organic compounds (VOCs) including halogenated hydrocarbons and aromatics, of which many are toxic and/or contribute to the depletion of the ozone layer and global warming. Microbial oxidation by methanotrophic bacteria has been shown to play an important role in reducing methane emissions from landfills. The methanotrophic bacteria are known to co-metabolize a variety of compounds, including some halogenated hydrocarbons. It could therefore be expected that several VOCs should be co-oxidized during transportation through landfill top cover soils.

This thesis reports the results of an investigation into the potential for natural attenuation of VOCs in landfill top cover soil.

Methanotrophic active soil sampled at a Danish landfill at a location emitting methane showed a high capacity for co-oxidation of a number of VOCs. In total 26 VOCs were investigated, including chlorinated methanes, ethanes, ethenes, fluorinated hydrocarbons, and aromatic hydrocarbons. All lower chlorinated compounds were shown degradable and the degradation occurred in parallel with the oxidation of methane. In general, the degradation rates of the chlorinated aliphatics were inversely related to the chlorine/carbon ratios. Maximal oxidation rates for the halogenated aliphatic compounds varied between 0.7 and 41  $\mu\text{g g}^{-1} \text{d}^{-1}$ . Fully substituted hydrocarbons (such as tetrachloromethane, perchloroethylene, trichlorofluoromethane, dichlorodifluoromethane and 1,1,2-trichloro-1,2,2-trifluoroethane) were not degraded under oxidative conditions. Aromatic hydrocarbons were rapidly degraded giving high maximal oxidation rates (4.1 to 34  $\mu\text{g g}^{-1} \text{d}^{-1}$ ). Soil sampled at a French landfill also demonstrated the capability of co-oxidation of lower halogenated compounds, even though to a lesser extent than the soil from the Danish landfill. Maximal oxidation rates for the halogenated aliphatic compounds varied between 0.06 and 8.6  $\mu\text{g g soil}^{-1} \text{d}^{-1}$ . However, aromatic hydrocarbons were rapidly degraded with oxidation rates varying between 28 and 39  $\mu\text{g g soil}^{-1} \text{d}^{-1}$ .

The most important parameters controlling oxidation were found to be temperature, soil moisture, and methane/oxygen supply, all showing significant impact on the oxidation ratios. The capacity for methane oxidation in soil covers was related to the depth of oxygen penetration. The maximal oxidation activity occurred in rather narrow zones of approximately 20-30 cm, which had overlapping concentration gradients of methane and oxygen *in-situ*. Temperature had a strong influence on the methanotrophic activity giving high  $Q_{10}$  values of 3.4 to 4.1 when calculated for the oxidation over the temperature range of 2 to 25°C. Temperature optimum was around 30°C, however, oxidation occurred at temperatures as low as 2°C. A moisture content of 25%w/w yielded the maximum oxidation rate as it allowed good gas transport together with sufficient microbial activity. The optimum pH was around neutrality (pH 6.5 to 7.5) showing that the methane oxidizers were optimally adapted to the *in situ* pH. Copper showed no inhibitory effect when added in relatively high concentrations (up to 60  $\text{mg kg}^{-1}$ ), which most likely was due to sorption of copper ions to soil particles. At higher copper concentrations the oxidation rates decreased. The oxidation rates for methane, HCFC-21, and HCFC-22 were unaltered in ammonium-amended soil up to 14  $\text{mg kg}^{-1}$ . Higher ammonium concentrations inhibited the oxidation process.



The attenuation of eleven VOCs was also investigated in a dynamic methane and oxygen counter gradient system simulating a landfill soil cover. All the VOCs examined were degraded in soil columns, but the mechanisms in play were different for higher and lower chlorinated compounds. Indeed, the lower chlorinated compounds such as HCFCs, vinyl chloride and dichloromethane were oxidized in the upper part of the column in the zone with high methanotrophic activity, whereas the higher chlorinated compounds such as CFCs and tetrachloromethane were found degradable in the anaerobic zone. Under anaerobic conditions, which exist within the waste and in surrounding soils, fully halogenated hydrocarbons such as perchloroethylene, CFC-11, and CFC-12 may undergo reductive dehalogenation leading to accumulation of lower chlorinated compounds like vinyl chloride, HCFC-21 and HCFC-22, which are more toxic than the prime compound. However, this study demonstrates that these lower halogenated compounds might thereafter be rapidly degraded in the oxidative zone in the surface layers of soil due to the activity of methanotrophic bacteria.

The surface emission of VOCs was determined at two different areas at a French landfill: a permanently covered and fully vegetated area (40 cm coarse sand + 80 cm of loam) and a temporarily covered area (40 cm of coarse sand). The VOC fluxes from the permanently covered zone were all very small with both positive and negative fluxes in the order of  $10^{-7}$  to  $10^{-5}$  g m<sup>-2</sup> d<sup>-1</sup>. Higher and mainly positive VOC fluxes in the order of  $10^{-5}$  to  $10^{-4}$  g m<sup>-2</sup> d<sup>-1</sup> were obtained from the temporarily covered zone. The lower emission from the permanently covered and fully vegetated cell was attributable to the thicker soil layer, which functions as microbial habitat for methanotrophic bacteria. Interestingly, the inverse phenomenon to emission, i.e., uptake by the soil of VOCs from the air, was observed for easily aerobically degradable compounds such as, e.g., aromatics, vinyl chloride, methylene chloride, and methylchloride. This study demonstrates that landfill soil covers show a significant potential for co-oxidation of VOCs. Under certain conditions, landfills may even function as sinks of not only CH<sub>4</sub> but also selected VOCs, like aromatic hydrocarbons and lower chlorinated compounds.

*Keywords:* landfill gas, methane oxidation, co-oxidation, chlorinated solvents, chlorofluorocarbons, aromatic hydrocarbons, methanotrophic bacteria, soil microcosms, soil columns, gas emission, flux measurements.

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# ATTENUATION OF LANDFILL GAS COMPONENTS IN SOIL COVERS

## 1 INTRODUCTION

Organic material disposed in landfills will undergo anaerobic decomposition resulting in generation of landfill gas, which consists of approximately 55-60%v/v methane and 40-45%v/v carbon dioxide. In addition to methane and carbon dioxide, landfill gas often contains a high number of different volatile organic components (VOCs) including C<sub>1</sub>-C<sub>5</sub> hydrocarbons, sulphur and oxygen-containing compounds, halogenated hydrocarbons and aromatic hydrocarbons (Rettenberger & Stegmann, 1996; Allen et al., 1997). The trace components originate from hazardous materials deposited in the landfill or from biological/chemical degradation of materials disposed in the landfill. Although the VOCs account for only a few volume percentages, gas emission into the atmosphere can have an adverse effect on the environment due to their physical/chemical properties. Chlorofluorocarbons will, due to their high stability in the atmosphere, reach the stratosphere where they contribute to ozone depletion and global warming (Wallington et al., 1994). Compounds like benzene, vinyl chloride, carbontetrachloride are proven to be carcinogenic (Eikmann, 1996) and thus are of concern to workers at the landfill and to local inhabitants.

Currently, focus has been on methane emission from landfills, since methane absorbs terrestrial radiation in the atmosphere and causes global warming. Compared to carbon dioxide, methane is contributing about 26 times more (per mole) to the global climate change (Lelieveld et al., 1993). Landfills are estimated to release to the atmosphere between 9 and 70 Tg of CH<sub>4</sub> per year, out of an estimated annual global emission of 600 Tg (Bogner et al., 1997b; Lelieveld et al., 1998). It is important to note that these projections are based on estimated rates of methane production applied to national statistics for landfilled refuse, and not on field emission measurements. The net annual increase in atmospheric methane concentrations is estimated at 40 Tg per year (Hanson & Hanson, 1996), and thus a 10-15% reduction in emissions of methane may stabilize its current concentration in the atmosphere. Microbial oxidation of methane plays a significant role in reducing the emission of methane to the atmosphere (Lelieveld et al., 1998; Oremland & Cumberson, 1992). 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 the subject of several studies. Estimates of the methane amount oxidized in landfill soils range from 10 to 50% based on laboratory studies (Czepiel et al., 1996; Whalen et al., 1990; De Visscher et al., 1999). However, field studies have shown methane oxidation of up to a 100% at some landfills (Bergamaschi, 1998; Christophersen et al., 2001). Furthermore, methane flux emission measurements have showed negative fluxes indicating uptake of atmospheric methane showing that in some cases landfill cover soils may even serve as sink of atmospheric methane (Bogner et al., 1995; Bogner et al., 1997a,b; Boeckx et al., 1996).

A defining characteristic of the methanotrophic bacteria is the enzyme methane monooxygenase (MMO), which facilitates the conversion of methane to methanol – the first step on the pathway for methane utilization. MMO is non-specific and will facilitate transformation of a number of compounds including halogenated hydrocarbons; thus the potential exists for attenuation of not only methane but also trace components in landfill soil covers. However, research in this area has only recently been initiated.



## 2. RESEARCH OBJECTIVES

The overall goal of this research project was to investigate the potential of attenuation of volatile organic compounds in landfill soil covers and determine its governing factors, in order to optimize the degradation processes in landfill covers.

Several aspects were investigated:

- Potential for attenuation of different VOCs
- Influence of environmental factors (temperature, soil moisture, acidity, ammonium, copper and presence of trace components competing for enzyme) on the attenuation potential
- Attenuation mechanisms in soil covers for different VOCs

Several methods were used in the investigation:

- Batch experiments with landfill soil exposed under various conditions to the VOCs studied
- Column experiments with landfill soil exposed to a dynamic methane and oxygen counter gradient, and to the VOCs studied
- Flux chamber measurement of VOC release, on-site at an active landfill

**Table 1.** Concentrations of trace components in landfill gas ( $\text{mg m}^{-3}$ )

	Emerson, 1999*	Retten- berger, 1986	Allen et al., 1997	Brookes & Young, 1983	Young & Heasman, 1985	Arendt, 1985	Dent et al., 1986	Schilling & Hinze, 1987	Laugwitz et al., 1988
Tetrachloroethylene	1694	0.1-142	<0.1-255	250	0.3-110	10-100	<0.1-110	6.9-104	0-10
Trichloroethylene	1520	0-182	<0.1-152	10	1.2-116	3-150	0.07-116	26-312	0-14
dichloroethylene		0-294					0.07-28		
1,2-dichloroethylene		2-100	1-182	68	0.07-28	1		0.4	
1,1-dichloroethylene			<0.1-6						
Vinylchloride	281	0-264	<0.1-87	16	0.03-3	1-30	0.03-8.3	0-43	0-22
Carbontetrachloride	13		<0.1-21						
Trichloromethane	28	0-2		<1	<0.2-1	1-50			0-3
Dichloromethane	833	0-6	1-85	140	7.7-490	1-100	0.1-397	36-684	0-51
1,1,2,2-tetrachloroethane									
1,1,2-trichloroethane	1309	0.5-4	<0.1-18	29	<0.1-3.7				
1,1,1-trichloroethane			<0.1-62		<0.5-21				
1,1-dichloroethane	782								
1,2-dichloroethane									
Trichlorofluoromethane		1-74	<0.1-74	20	0.4-185	1-500	<0.1-185	11-56	0-220
Dichlorodifluoromethane		4-119	28-231	10	6-602	5-700	<0.1-486	99-149	4-145
1,1,2-trichloro-1,2,2- trifluoroethane			<0.5-6						
Dichlorofluoromethane		5	<0.5-114	4	<2-276		0.1-602		0.4-14
Chlorodifluoromethane			<0.5-404	5			<0.1-276		3-28
Benzene	163		<0.1-7	15	0.6-12				
Toluene			10-287	34	18-197				
Xylenes			36-440	14	7.9-139				
Ethylbenzene			5-156		3.6-49				

\*Maximum concentrations

### 3. LANDFILL GAS COMPONENTS

Landfill gas is produced by the microbial degradation of the organic components in municipal waste under anaerobic conditions. The organic material in waste includes paper, animal and vegetable matter and garden waste. The main components in landfill gas are methane (55-60%v/v) and carbon dioxide (40-45%v/v). The production of the principal landfill gas components occurs through three initial sequential phases followed by a phase characterized by stable methane and carbon dioxide production (Christensen et al., 1996). The production of landfill gas will continue until the majority of the organic material in the waste has been degraded, which can take up to 20-30 years. Due to pressure and concentration gradients the landfill gas will migrate through the surrounding soil of landfills causing emission of landfill gas into the atmosphere.

Besides methane and carbon dioxide landfill gas also contains numerous trace compounds representing a maximum of a few volume percentages (Brosseau and Heitz, 1994). The trace gasses arise from volatilization of compounds contained within hazardous materials deposited in the landfill or from biological/chemical degradation of materials deposited in the landfill. The trace components in landfill gas include hydrocarbons, aromatics, halogenated hydrocarbons, organic compounds containing oxygen and sulfur, and inorganic compounds. Oxygen-containing compounds such as alcohols, esters and fatty acids are generated during decomposition of organic waste components and appear only early in the phase of gas generation (Rettenberger and Stegmann, 1996; Young and Heasman, 1985). The sulphur components are mainly responsible for the odour of the gas and are generated in all phases of landfill gas production (especially hydrogen sulphide). However some sulphur components such as mercaptans occur mainly during the operation phase of the landfill (Rettenberger and Stegmann, 1996). The hydrocarbons may be naturally generated in the landfill or deposited with the waste. However, predominance of hydrocarbons in landfill gas is usually associated with older refuse (Young & Parker, 1983).

Aromatic and chlorinated hydrocarbons are considered anthropogenic compounds and their concentration in landfill gas is therefore mainly governed by waste composition. Aromatic and chlorinated hydrocarbons are widely used in the industry as for example solvents, and degreasing agents and as a result very detected in landfill gas. Typical gas concentrations are in the range of 10-250 mg m<sup>-3</sup> (table 1). Landfills receiving industrial wastes might expect to have a high content of these compounds. However, investigations of landfills, which in principle only have received household waste, often show high contents of aromatic and chlorinated hydrocarbons. Brosseau and Heitz (1994) refer to an investigation of 23 American landfills only receiving household waste: in 85% of these landfills benzene and vinyl chloride were found. Biodegradation of aromatic hydrocarbons in the landfill environment is probably limited and most of the aromatic hydrocarbons will persist in the landfill. Emission of aromatic hydrocarbons from landfills is of special concern due to the possible exposure of humans working on the disposal site or living nearby. Benzene, for instance, is proven carcinogenic (Eikman, 1996).

Due to physical/chemical properties such as high volatility, high stability, and non-toxicity the chlorofluorocarbons (CFCs) have been used in a number of industrial processes and products like refrigerating aggregates, foaming agents, solvents, propellants etc. Chlorofluorocarbons are thus often found in landfill gas in relatively high concentrations because of their wide-spread use, their high volatility, and high persistence. In landfill gasses sampled at seven disposal sites in the UK the chlorofluorocarbons accounted for up to 95% of the total chlorine content (Allen et al., 1997). The fluorinated halocarbons most frequently



occurring in waste are: CFC-11, CFC-12, HCFC-21, HCFC-22, CFC-113, and CFC-114 (Deipser et al., 1996). The emission of CFCs can continue for long periods after waste disposal if the compounds are released slowly from their sources within the waste. For example, the release from insulation foam is governed by closed cell diffusion and it has been estimated that it can take 9-300 years before 50% of the residual CFC is released from insulation foam that is shredded into 2-cm sized pieces (Kjeldsen and Jensen, 2001). If refrigerator cabinets and cooling circuits are kept intact after disposal the release will continue for an even longer period. As an example, high levels of CFC-12 and HCFC-22 (between 111-404 mg m<sup>-3</sup>) have been found in more than 20 years old waste (Allen et al., 1997).

Polychlorinated aliphatic compounds may undergo biodegradation under methanogenic conditions by reductive dehalogenation. Under anaerobic conditions the degradation rate of halogenated compounds decreases with increasing number of halogen substituents. Hence, dichloroethylene and vinyl chloride may accumulate during anaerobic degradation of tetrachloroethylene (Vogel et al., 1987). CFC-11 and CFC-12 may be reductively dechlorinated resulting in generation of the far more toxic HCFC-21 and HCFC-22 under landfilling conditions (Ejlertson et al. 1996, Deipser & Stegmann, 1994).

The presence of chlorinated compounds in landfill gas is critical when landfill gas is utilized in electricity generation, as the chloride reacts with oxygen and water during the combustion process forming HCl, which corrode the surface of the combustion chamber and significantly lowers the operational time. Emission of CFCs to the atmosphere is a threat to the global environment. CFCs are considered as greenhouse gasses, absorbing long wave radiation emitted from the earth and thereby contributing to global warming. In addition, CFCs react with ozone, causing depletion of the ozone layer, which is the mechanism shielding the earth from ultra-violet solar radiation (Wallington et al., 1994; Rowland, 1974). Due to increasing concern about the global environment, production of CFCs has been intensively regulated through international conventions. Many governments signed the Montreal protocol on substances that deplete the ozone layer, which stated a ban on production and use of most CFCs from 1996 on. Although the production of CFCs is decreasing, an increase in the atmospheric concentration will continue for years to come. Moreover, due to the CFCs long lifetimes in the atmosphere they can be expected to be active in atmospheric chemistry for hundreds of years.

**Table 2.** Characteristics of type I, type II and type X methanotrophs (Hanson and Hanson, 1996)

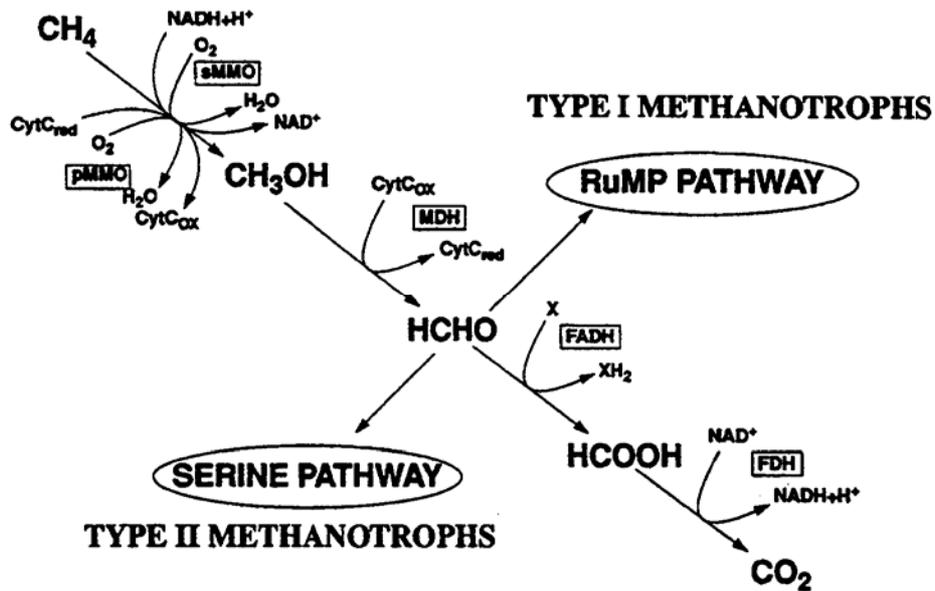
<b>Characteristic</b>	<b>Type I</b>	<b>Type II</b>	<b>Type X</b>
Cell morphology	Short rods, usually occur singly; some cocci or ellipsoids	Crescent-shaped rods, rods, pear-shaped cells, sometimes occur in rosettes	Cocci, often found as pairs
Growth at 45°C	No	No	Yes
G+C content of DNA (mol%)	49-60	62-67	59-65
Membrane arrangement			
Bundles of vesicular discs	Yes	No	Yes
Paired membranes aligned to periphery of cells	No	Yes	No
Nitrogen fixation	No	Yes	Yes
Resting stages formed			
Exospores	No	Some strains	No
Cysts	Some strains	Some strains	Some strains
RuMP pathway present	Yes	No	Yes
Serine pathway present	No	Yes	Sometimes
Ribulose-1,5 biphosphste carboxylase present	No	No	Yes
Proteobacterial subdivision	Gamma	Alpha	Gamma

#### 4. METHANOTROPHIC BACTERIA

Methanotrophic bacteria (or methanotrophs) are a subset of a physiological group of bacteria known as methylotrophs and are unique in their ability to utilize methane as a carbon and energy source. The use of enzyme methane monooxygenases (MMO) to catalyze the oxidation of methane to methanol is a defining characteristic of methanotrophs. Whittenbury et al. (1970) established the basis of the current classification of the methanotrophs based on morphology, types of resting stages, and the fine structures of intracytoplasmic membranes. More recently Bowman et al. (1993b;1995) made some revisions in this classification, based on a more thorough analysis including DNA-DNA-hybridization, and phospholipid fatty acid composition analysis. More than 136 methane-utilizing bacteria have been isolated and characterized (Bowman et al., 1993b;1995). The methane-utilizing bacteria can be divided into six genera: *Methylomonas*, *Methylobacter*, *Methylococcus*, *Methylocystis*, *Methylosinus*, and *Methylomicrobium*. Methane-oxidizing bacteria are classified into three types: I, II, and X, on the basis of intracytoplasmic membrane fine structure, phospholipid fatty acid content, DNA base composition, carbon assimilation pathways utilized, and other characteristics. Table 2 shows the characteristics of type I, type II, and type X methanotrophs. Methane-oxidizing bacteria classified as type I include *Methylomonas*, *Methylobacter*, and *Methylomicrobium*. Type I methanotrophs assimilate formaldehyde through the ribulose monophosphate pathway (RuMP); most of them form cyst and are incapable of fixing N<sub>2</sub>. Type II methanotrophs include the genera *Methylocystis* and *Methylosinus*, which assimilate formaldehyde via the serine pathway. *Methylosinus* form exospores and *Methylocystis* form cysts, and both can fix N<sub>2</sub>. Type X consists of the genus *Methylococcus* that like type I methanotrophs utilized the RuMP as the primary pathway for formaldehyde assimilation. Type X methanotrophs were distinguished from type I methanotrophs because they also processed low levels of enzymes in the serine pathway - a characteristic of type II methanotrophs (Hanson & Hanson, 1996). However, more and more researchers classify the type X methanotrophs together with the type I methanotrophs as the family *Methylococcaceae*. The most striking feature of type X methanotrophs is their moderately thermophilic nature.

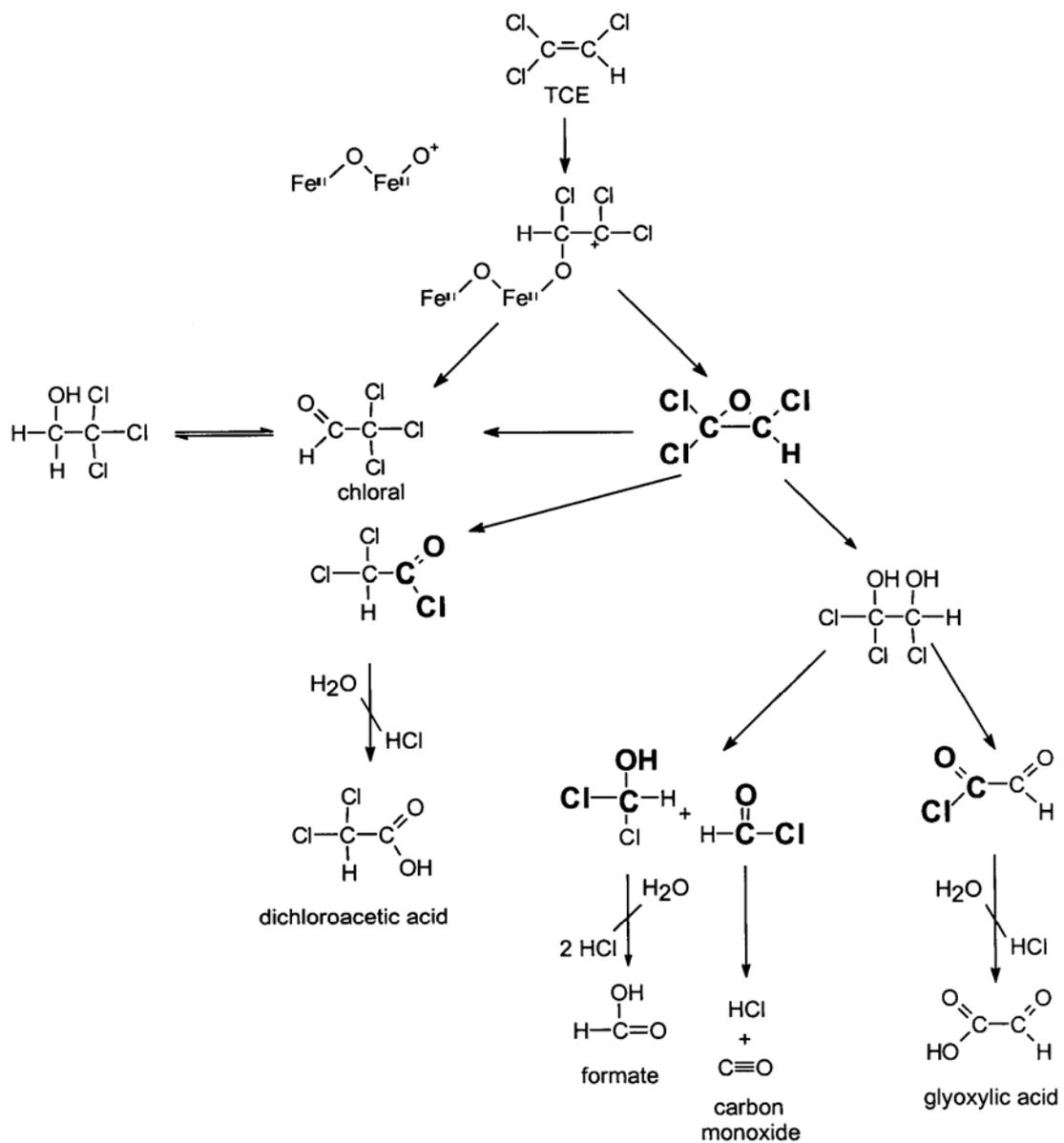
Oxidation of methane by aerobic methanotrophs is initiated by the MMO enzymes. MMOs utilize two reducing equivalents to split the O-O bond in O<sub>2</sub>. One of the oxygen atoms is reduced to form H<sub>2</sub>O, while the other is incorporated into methane to form methanol (CH<sub>3</sub>OH). Figure 1 shows the pathway for the oxidation of methane and assimilation of formaldehyde by methanotrophs. Two forms of the enzyme MMO have been found in methanotrophs on the basis of their intracellular localization (Dalton, 1991; Dalton, 1992). All methanotrophs are capable of forming a particulate or membrane-bound MMO (pMMO) when grown in the presence of copper. Methanotrophs classified as types II and X have been shown to synthesize a soluble MMO (sMMO) under copper limiting growth (Stanley et al., 1983; Hanson & Hanson, 1996). Cells of methanotrophs that contain pMMO have higher growth yields on methane than cells that contain sMMO (Jørgensen and Degn, 1987). The synthesis of sMMO by some methanotrophs may be a survival mechanism in the many environments where copper limits the growth of methanotrophs capable of synthesizing only pMMO (Hanson & Hanson, 1996).

Methanol is oxidized to formaldehyde by a periplasmic methanol dehydrogenase (MDH) (figure 1). Most of the reducing power required for the metabolism of methane is produced by oxidation of formaldehyde via formate to carbon dioxide. There are multiple enzyme systems for the oxidation of formaldehyde to formate in methylotrophs. An example is the



**Figure 1.** The pathway for the oxidation of methane and assimilation of formaldehyde by methanotrophs. Abbreviations: CytC, cytochrome c; FADH, Formaldehyde dehydrogenase; FDH, formate dehydrogenase (Hanson and Hanson, 1996)

NAD(P)-linked aldehyde dehydrogenase. Formate is oxidized to carbon dioxide by an NAD-dependent formate dehydrogenase in most if not in all methanotrophs. Formaldehyde produced from the oxidation of methane and methanol by methanotrophs is assimilated to form intermediates of the central metabolic routes that are subsequently used for biosynthesis of cell material. Two pathways for synthesis of cell materials from formaldehyde are known: the serine and the ribulose monophosphate (RuMP) pathway. In the RuMP pathway (used by Type I methanotrophs) one ATP is used in the formation of one glyceraldehyde-3-P from three formaldehyde molecules whereas in the serine pathway (used by type II methanotrophs) three ATP and two NADH are needed to assimilate two formaldehyde and one CO<sub>2</sub>. A 100% conversion of methane to biomass is not possible since assimilatory pathways lead to a net production of at least 12% carbon dioxide (Gommers et al., 1988).



**Figure 2.** Molybdenum mediated conversion of TCE. For those products that have been identified the names are given; very reactive structures are given bold-faced (Fox et al., 1990; Little et al., 1988)

## 5. CO-OXIDATION OF HALOGENATED HYDROCARBONS BY METHANOTROPHIC BACTERIA

Methanotrophs are capable of performing oxidative conversions of a very large number of compounds, including halogenated hydrocarbons, due to the lack for substrate specificity of MMO (Oldenhuis et al. 1989; Higgins et al., 1980). The conversion of halogenated hydrocarbons is the result of a process referred to as co-metabolism. Co-metabolism is the transformation of a compound by organisms that do not obtain energy or carbon for cell growth from the transformation and hence require an alternative source of carbon and energy (Alvarez-Cohen & McCarty, 1991a).

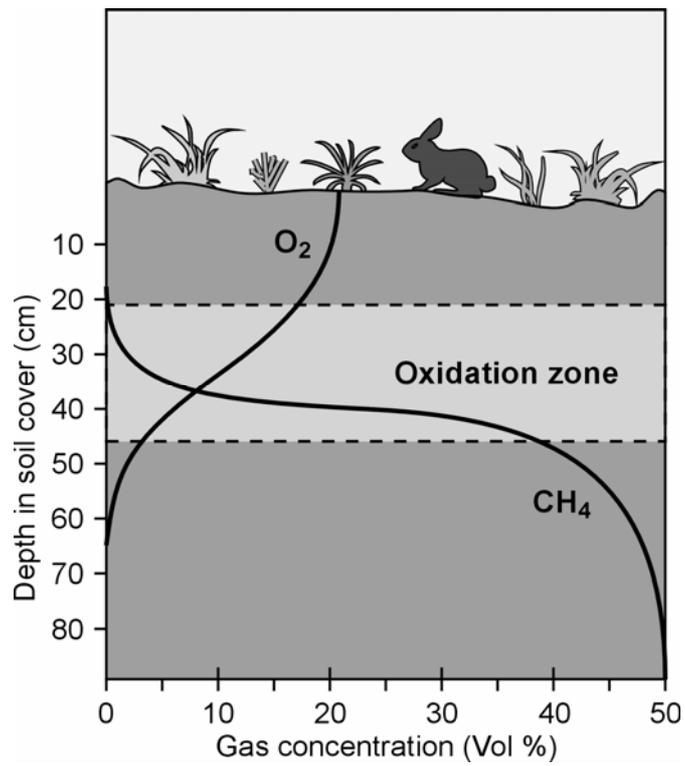
Wilson and Wilson (1985) first reported that trichloroethylene (TCE) was aerobically degraded to carbon dioxide and chloride in an unsaturated soil column exposed to natural gas in air (0.6 vol.%). Without exposure to natural gas TCE was not degraded and the authors suggested that methanotrophic bacteria were responsible for the destruction. Several subsequent studies have shown that methanotrophs are capable of transforming a variety of halogenated aliphatic compounds. Fogel et al. (1986), Janssen et al. (1987), and Henson et al. (1989) have shown that mixed cultures enriched by growth on methane degraded several chlorinated derivatives of methanes, ethanes, and ethylenes. Vinyl chloride was degraded more rapidly than dichloroethylene and TCE, while dichloromethane was oxidized faster than trichloromethane. Methanotrophs have also been shown to transform fluorinated hydrocarbons such as HCFCs and HFCs (De Flaun et al., 1992; Chang and Criddle, 1995; Oremland et al., 1996; Matheson et al., 1997; Streger et al., 1999; Scheutz et al., I, III, V). The order of reactivity was found to be HCFC-22>HCFC-142b>HFC-134a>HCFC-123 (Chang and Criddle, 1995). Further compounds reported to be bio-transformed by methanotrophs are HCFC-21, HCFC-141b, and HCFC-143 (Streger et al., 1999; Scheutz et al., I). HCFC-124, HFC-134, and HFC-245fa were not degradable by methanotrophs (Streger et al., 1999; Scheutz et al., I). The rates and extent of aerobic degradation of chlorinated compounds for any series (methanes, ethanes, ethylenes, and haloforms) are inversely related to the chlorine/carbon ratios (Chang and Alvarez-Cohen, 1995). Highly chlorinated hydrocarbons including perchloroethylene, tetrachloroethane, carbontetrachloride, and CFCs are not degraded by methanotrophs (Montgomery et al., 1994; Sylvestre et al., 1997).

Methanotrophs exhibiting sMMO activity seem to be responsible for the degradation of halogenated hydrocarbons under copper limited conditions, due to the broader substrate range of soluble MMO compared to particulate MMO (Alvarez-Cohen et al., 1992; Tsien et al. 1992; Bowman et al., 1993a). However, pMMO can catalyze the oxidation of a number of alternative substrates including TCE, although the substrate range is more limited compared to sMMO (DiSpirito, 1992). Furthermore, the oxidation rate constants are generally lower for pMMO co-metabolism (Lohtoh and Semrau, 1998; DiSpirito, 1992). Rate constants in the order of 0.1-1% of the maximum values measured for *Methylosinus trichosporium* OB3b are typical (Alvarez-Cohen and Speitel, 2001). However, sMMO is only produced in the wild type organism at very low copper concentrations and it is not known how often the Cu-deficient conditions required for production of this enzyme actually occur in nature (Arp et al., 2001).

The reaction of chlorinated aliphatics with MMO generates chlorinated oxidation products that may react with cellular macromolecules or may be hydrolyzed spontaneously into carbon dioxide, chloride, or other non-volatile products that are easily mineralized by microorganisms (Alvarez-Cohen and Speitel, 2001). The first step in the oxidative pathway of chlorinated ethylenes is the formation of the corresponding epoxides, which are highly



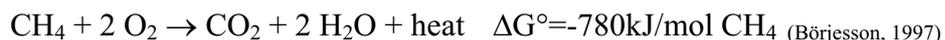
reactive molecules and thus have short lifetimes (Fox et al., 1990; Vlieg et al., 1996; Alvarez-Cohen and McCarty 1991b). The metabolic pathways have been fully elucidated for trichloroethylene and involve both biological and abiotic processes. The proposed pathways are illustrated in figure 2. The first step in the TCE degradation pathway is the reaction between TCE and the enzyme MMO resulting in the production of TCE epoxide. TCE epoxide is unstable and decomposes non-enzymatically to glyoxylate, formate, dichloroacetate, and CO as the major products (Fox et al., 1990). Soluble MMO generates a small quantity of trichloroacetaldehyde (chloral), which is converted to 2,2,2-trichloroethanol and trichloroacetic acid by whole cells of methane-oxidizing bacteria (Newmann and Wackett, 1991). Alvarez-Cohen and McCarty (1991b) studied the degradation of TCE by a mixed methanotrophic culture and report that 93% of the C<sup>14</sup> was detected in transformation products, 58% as non-volatile compounds and 35% as CO<sub>2</sub>; 5% of the C<sup>14</sup> was not recovered, possibly due to incorporation into cell materials. Fogel et al. (1986) also examined the transformation of TCE by a mixed methane-utilizing culture and found that 23% of the C<sup>14</sup> appeared in the CO<sub>2</sub> fraction, 34 % was associated with the bacteria, and 43% remained in solution as a nonvolatile or non-chlorinated species. In addition, these authors concluded that vinyl chloride and vinylidene chloride could be degraded to products that are not volatile chlorinated substances and therefore likely to be further degraded to CO<sub>2</sub>. Complete transformation of TCE is believed only to be possible with mixed cultures, where both methanotrophic and heterotrophic bacteria are present (Uchiyama et al., 1992; Little et al., 1988).



**Figure 3.** Oxidation zone in a landfill soil cover.

## 6. METHANE OXIDATION IN LANDFILL TOP COVER SOILS

Methane oxidation is a microbial process that occurs in the biosphere wherever methane and oxygen are present at the same time. 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, thus providing living conditions for the methanotrophic bacteria. Aerobic methane oxidation proceeds according to the overall reaction



Most methanotrophic bacteria are obligate methanotrophs and strict aerobes (Hanson & Hanson, 1996). Their activity depends on the presence of sufficiently high concentrations of both methane and oxygen, and thus they tend to be confined to fairly narrow horizontal bands within their habitat, limited in their distribution by the downward diffusion of atmospheric oxygen and the upward diffusion of methane (figure 3). In simulated landfill soil covers the greatest methane potential was found around 20 cm below the surface in zones where vertical profiles of methane and oxygen overlap (Scheutz et al., III, IV; De Visscher et al., 1999; Kightley et al., 1995). In general, the methanotrophic active zone is located in the upper 30-40 cm of the soil profile with maximal oxidation activity in a zone between 15-20 cm below the surface (Czepiel et al., 1996; Scheutz et al., I; Jones and Nedwell, 1993). At greater depth the methanotrophic activity is limited by low oxygen concentrations. However, at sites with low methane emission due to, e.g., installation of gas extraction system, the oxidative zone may occur at a greater depth (Scheutz et al., V). Since methane oxidation requires simultaneous supply of methane and oxygen, limitation on physical gas transport thus becomes an important control in methane oxidation in soil covers.

Previous laboratory studies of methane oxidation kinetics in non-landfill and landfill soils suggest that at least two groups of methanotrophs are active in methane oxidation in soils (Bender and Conrad, 1993,1995; Bogner et al. 1997a). The first group of methanotrophs, which has a high methane affinity, favours low CH<sub>4</sub>/high O<sub>2</sub> setting near atmospheric concentrations, with low oxidation rates limited by available methane. The second group, which has low methane affinity but high oxidation rates, favours higher methane concentrations and lower oxygen concentrations. The second group is probably limited by oxygen in presence of abundant methane.

Type I and type II methanotrophs seem to adapt for survival under different growth conditions. Amaral & Knowles (1995) examined the growth of methanotrophs in methane and oxygen counter gradients and found that a feature, which distinguishes types I and II methanotrophs is efficiency of growth under different CH<sub>4</sub> conditions. They concluded that type I appear to be best adapted to grow in low CH<sub>4</sub> concentrations while type II dominates under high CH<sub>4</sub> concentrations. Their hypothesis has been supported by observations that a type I methanotroph (*Methylomonas albus* BG8) out-competed a type II methanotroph (*Methylosinus trichosporium* OB3b) in continuous cultures under methane-limiting conditions (Graham et al. 1993). Furthermore, they found that the growth of some type II methanotrophs was favored when combined nitrogen and oxygen levels were low, and when copper was substantially depleted in the growth media. This suggests that in a landfill cover system with opposite methane and oxygen gradients, type II methanotrophs will dominate in deeper zones with sub-ambient oxygen levels and a continuous supply of methane providing the methanotrophs with high CH<sub>4</sub> concentrations. In the shallow soil with low methane concentration near atmospheric level (1.7 ppmv) type I will dominate with high methane

**Table 3.** Summary of maximal methane oxidation rates for landfill cover soils obtained from batch studies

Reference	Soil texture	Maximum CH <sub>4</sub> oxidation rate µg CH <sub>4</sub> g <sup>-1</sup> h <sup>-1</sup>	Depth integrated CH <sub>4</sub> oxidation rate <sup>a</sup> g CH <sub>4</sub> m <sup>2</sup> d <sup>-1</sup>	Initial CH <sub>4</sub> concentration %v/v	Investigated temperature range °C	Optimum temperature °C	Q <sub>10</sub>	Investigated soil moisture range %w/w	Optimum soil moisture content %w/w
Stein & Hettiaratchi, 2001	Loam	16	92	2.5	4-40	30		0-27	15
Kightley et al., 1995	Coarse sand	37	207	5	20				
Hilger et al., 2000a	Sandy loam	2.3	13	8	22			15	
De Visscher et al., 1999	Sandy loam	26	150	0.5					
Scheutz et al., II	Loam	118	680	15	2-50	30	3.4 (2-25°C)	5-50	25
Figuerola, 1993	Humic soil	86.4	487	10	20	30		0-50	21
	Till	40	230	10	10-40	30		0-23	12
Jones and Nedwell, 1993		0.2	7.2 <sup>b</sup>	12.5	22				
Whalen et al., 1990	Sandy mixed with clay	2.7	45 <sup>c</sup>	7.7	5-46	31	1.9 (5-26°C)	5-71	11
Boeckx and Van Cleemput, 1996	Sandy loamy soil	0.0024	0.014	0.001	12-35	25-30		5-35	15
Czepiel et al., 1996	Sand-clay loam	41.6	240	2	5-45	36	2.4 (20-30°C)	0-40	16
Boeckx et al., 1996	Sandy/loamy/loamy soil	0.01	0.06	0.001	5-30	20-30	1.9 (10-20°C)	5-30	16-19
Börjesson, 1997	Sandy loam	48	276	5	25	38	5.2 (2-25°C)	15-50	35
Christophersen et al., 1999	Sandy loam	19	109	18	2-15	15	4.1-7.3 (2-15°C)	5-35	11-32
Bender and Conrad, 1994	Loamy clay	0.0096	0.06	5		25			22

<sup>a</sup> calculated for a methanotrophic active zone of 15 cm and a soil bulk density of 1.6 g·cm<sup>-3</sup>

<sup>b</sup> methanotrophic active zone of 36 cm

<sup>c</sup> methanotrophic active zone of 12 cm

affinities and capacity to atmospheric uptake. However, the composition of methanotrophic communities and distribution of the methanotrophic bacteria in landfill soil covers are only sparsely investigated. Mandernack et al. (2000) investigated landfill cover soils from California and Washington and found that the phospholipid fatty acids extracted from these soils were representative of type II methanotrophs. This was confirmed by a study of the isotope signature of the organic N and the organic C in the microbially most active soil layer. In a comprehensive study Wise et al. (1999) found both type I and type II methanotrophs in a landfill cover soil. Börjesson (1997) found mainly type I methanotrophs in a sewage sludge landfill cover, probably due to the high nutrient content, and mainly type II methanotrophs in a mineral landfill cover soil. Svenning et al. (2002) found that type II methanotrophs were dominating in the cover soil (20-25 cm.b.s) of a Danish landfill: 15 isolates of type II (where of 10 carried the genes for sMMO) were identified and only one type I. It is interesting and perhaps fortunate if the conditions that exist in landfill soil covers favor the growth of type II methanotrophs and the synthesis sMMO that is essential for the rapid degradation of low-molecular-halogenated hydrocarbons.

Landfill cover soils can develop a high capacity for methane oxidation by selection of methanotrophic bacteria. Very high rates of methane oxidation (up to  $680 \text{ g m}^{-2} \text{ d}^{-1}$ ) in landfill top cover soils have been reported by several authors (table 3 and table 4). These rates are the highest rates of methane oxidation observed in natural soils (Hanson and Hanson, 1996). However, reported methane oxidation rates in landfill cover soils range over six orders of magnitude, from  $0.0002$  to  $680 \text{ g m}^{-2} \text{ d}^{-1}$  (Bogner et al., 1997b, Scheutz et al., I). Czepiel et al., 1996 estimated the total annual methane oxidation at a northeastern USA landfill to 10-20% based on modeling combined with emission measurements. Whalen et al., 1990 estimated that methane oxidation consumed approximately 50% of methane production in landfills in the United States. Quantification of methane oxidation in landfill covers using isotope techniques showed annual methane oxidation between 12-26% (Chanton and Liptay, 2000; Chanton et al. 1999). A higher value was found by Bergamaschi et al. (1998), who report a range of 80-97% oxidation of methane in landfill cover soils. Christophersen et al. (2001) found an annual methane oxidation of 89% in a field study at a Danish landfill using static flux chambers. Furthermore, no emission occurred during summer due to methane oxidation, while the lowest percentage of methane oxidation was 60%, measured during winter. Negative  $\text{CH}_4$  fluxes have been reported in by several researchers (Bogner et al., 1997a; Bogner, et al., 1995; Boeckx, et al., 1996; Scheutz et al., V). In such cases the methanotrophs in the cover soil are oxidizing all of the methane transported upward from landfill sources and additionally are oxidizing methane from the atmosphere, resulting in the cover soil functioning as a sink for atmospheric methane. Quantification of the methane oxidation in landfill soil covers is complicated by the natural variability in methane emissions spanning more than seven orders of magnitude from less than  $0.0004$  to more than  $4000 \text{ g m}^{-2} \text{ d}^{-1}$  (Bogner et al., 1997b). Even within the same landfill high spatial variability is observed (Czepiel, 1996; Scheutz et al., V). This wide range reflects the net emissions resulting from gas production, gaseous transport processes, and consumption due to methane oxidation.

Methane oxidation is controlled by a number of environmental factors: soil texture, temperature, soil moisture content, methane and oxygen supply, nutrients, etc. Thus, the climatic conditions are of importance for the actual methane oxidation rate. In landfill soil covers temperature and soil moisture are very important parameters controlling methane oxidation.

Temperature has a profound effect on methane oxidation activity. Most methanotrophs available in pure cultures are mesophiles (Hanson & Hanson, 1996). Optimum temperatures

**Table 4.** Summary of methane oxidation rates obtained in soil column experiments simulating landfill soil covers

Reference	Soil texture	Inlet gas	CH <sub>4</sub> Load g CH <sub>4</sub> m <sup>-2</sup> d <sup>-1</sup>	Steady state oxidation g CH <sub>4</sub> m <sup>-2</sup> d <sup>-1</sup>	Peak oxidation %	Duration Days
Stein & Hettiaratchi, 2001	Loam	99% CH <sub>4</sub>	Low: 186 High: 319	93 102-120	32-38 50	260 183
Kightley et al., 1995	Coarse sand Clay topsoil Fine sand	99% CH <sub>4</sub>	266	166 109 110	61 40 41	
Hilger et al., 2000a	Sandy loam	50% CH <sub>4</sub> :50% CO <sub>2</sub>	281	50	18	37
De Visscher et al., 1999	Sandy loam	50% CH <sub>4</sub> :50% CO <sub>2</sub>	368	240	65	79
Humer and Lechner, 1999	Topsoil	99% CH <sub>4</sub>	150	55	37	47
Scheutz et al., III, IV	Loam	50% CH <sub>4</sub> :50% CO <sub>2</sub>	250	210	81	30

are around 25-35°C for methane oxidation in soil environments (table 3 and the references cited therein), although methane oxidation occurred down to 1-2°C (Primé and Christensen, 1997; Christophersen et al., 2000). Omel'chenko et al. (1993) isolated methanotrophs from acid soils in a bog hollow in the Arctic that had optimum growth at temperatures of 10°C or lower indicating that some populations of methanotrophs can adapt to lower temperatures in nature. In cold areas or during winter season with temperatures below 10°C the methane oxidation might be significantly reduced or even come to standstill. Börjesson & Svensson (1997) investigated the seasonal as well as the diurnal variation in methane emissions from a small Swedish landfill and found temperature to be the controlling factor. Methane emissions were negatively correlated with soil temperature, indicating that microbial oxidation was an important regulating factor. Christophersen et al. (2001) also found higher methane emissions during winter, while no methane was emitted during summer at Skellingsted landfill in Denmark, which was attributed to temperature.

Although methanotrophs require wet conditions to grow, when the soil moisture content increases, the methane oxidation may decrease due to limited methane and oxygen diffusion in the soil. At optimum soil moisture content there is both rapid gas phase molecular diffusion and a sufficient soil moisture content to achieve microbial activity to oxidize the delivered methane. Soil moisture optimum for landfill cover soils ranges between 10-20% w/w (table 3 and the references cited therein). However, in some cases higher soil moisture optimums are observed (Scheutz and Kjeldsen, II; Börjesson, 1997; Christophersen et al., 2000). The oxidation activity is significantly reduced when soil moisture content decreases below 5% (Czepiel et al., 1996; Whalen et al., 1990; Stein & Hettiaratchi, 2001; Scheutz and Kjeldsen, II). In a field experiment conducted at a small landfill in Belgium Boeckx et al. (1996) found that methane emission was controlled by soil moisture content. Likewise, Jones & Nedwell (1990) measured the highest methane emissions from a landfill in England during the driest periods. In arid areas or during periods with very low precipitation, moisture content can be a critical factor in limiting the oxidation capacity in landfill soil covers.

**Table 5.** Summary of maximal VOC oxidation rates for landfill cover soils obtained from batch studies conducted at room temperature (22°C)

Compound studied	Abbreviation	Kjeldsen et al.,	Scheutz et al.,I	Scheutz et al., V
		1997		
		$\mu\text{g g}^{-1} \text{d}^{-1}$	$\mu\text{g g}^{-1} \text{d}^{-1}$	$\mu\text{g g}^{-1} \text{d}^{-1}$
<b>Methane</b>	CH <sub>4</sub>	250	2688	35
<b>Methanes</b>				
Dichloromethane	DCM		16.5	0.9
Trichloromethane	TCM		0.7	0.1
Tetrachloromethane	TeCM		No degra.	No degra.
<b>Ethanes</b>				
1,1-dichloroethane	1,1-DCA		4.1	1.7
1,2-dichloroethane	1,2-DCA		41.2	2.8
Trichloroethane	1,1,1-TCA	0.03*	No degra.	No degra.
<b>Ethylenes</b>				
Vinyl chloride	VC		34.9	8.6
c-1,2-dichlorethylene	c-1,2-DCE		7.6	4.1
t-1,2-dichlorethylene	t-1,2-DCE		26.9	1.8
Trichloroethylene	TCE	0.03*	1.4	0.1
Perchloroethylene	PCE		No degra.	No degra.
<b>Halocarbons</b>				
Trichlorofluoromethane	CFC-11		No degra.	No degra.
Dichlorodifluoromethane	CFC-12		No degra.	No degra.
1,1,2-trichloro-1,2,2-rifluoroethane	CFC-113		No degra.	No degra.
Dichlorofluoromethane	HCFC-21		12.2	0.2
Chlorodifluoromethane	HCFC-22		8.2	0.1
<b>Aromatics</b>				
Benzene	Benzene	8.0	20.2	27.9
Toluene	Toluene	8.0	33.4	38.7

\* conducted at 10°C

## 7. ATTENUATION OF TRACE GASSES IN LANDFILL SOIL COVERS

The fortunate capability of methanotrophs to co-oxidize a number of compounds including some halogenated hydrocarbons offers a potential for natural attenuation of selected trace gases in landfill soil covers. Recent research confirms that a high number of halogenated compounds can be co-oxidized in landfill cover soils (Scheutz et al., I-V; Kjeldsen et al., 1997).

Kjeldsen et al. (1997) first investigated the oxidation of methane and the aromatic hydrocarbons benzene and toluene, and the co-oxidation of the chlorinated solvents trichloroethylene (TCE), and 1,1,1-trichloroethane (TCA) in soil affected by landfill gas. High methane oxidation potentials and high degradation rates for benzene and toluene were found (up to  $8 \mu\text{g g}^{-1} \text{d}^{-1}$  - cf. table 5). In addition, slow co-metabolic degradation of TCE and TCA was observed in the presence of methane. The oxidation rates for both TCE and TCA were  $0.03 \mu\text{g g}^{-1} \text{d}^{-1}$  (table 5). The authors concluded that degradation processes might have a significant effect on mitigating the emission of the studied compounds from landfill covers.

More recently, Scheutz and co-workers (I) studied the potential of natural attenuation of a high number of volatile organic compounds (VOCs) in soil microcosms incubated with methane and atmospheric air, simulating the gas composition in landfill soil covers. In total, 26 VOCs were investigated including chlorinated methanes, ethanes, ethenes, fluorinated hydrocarbons, and aromatics. Soil sampled at a Danish landfill at a location emitting methane showed a high capacity for not only methane oxidation but also co-oxidation of VOCs. All lower chlorinated compounds were shown degradable and the degradation occurred in parallel with the oxidation of methane. In general, the degradation rates of the chlorinated aliphatics were inversely related to the chlorine/carbon ratios. For example, in batch experiments with chlorinated ethylenes, the highest rate was observed for vinyl chloride, and lowest rate for TCE, while PCE were not degraded. Maximal oxidation rates for the halogenated aliphatic compounds varied between  $0.7$  and  $41 \mu\text{g g}^{-1} \text{d}^{-1}$  (table 5). Fully substituted hydrocarbons (TeCM, PCE, CFC-11, CFC-12 and CFC-113) were not degraded in presence of methane and oxygen. Aromatic hydrocarbons were rapidly degraded giving high maximal oxidation rates ( $20$  to  $34 \mu\text{g g}^{-1} \text{d}^{-1}$ ). Soil sampled at a French landfill also presented the capability of co-oxidation of lower halogenated compounds, even though the capacity was significantly lower (Scheutz et al., V). At this site, maximal oxidation rates for the halogenated aliphatic compounds varied between  $0.1$  and  $8.6 \mu\text{g g}^{-1} \text{d}^{-1}$ . However, benzene and toluene were rapidly degraded at the French site giving very high maximal oxidation rates ( $28$  and  $39 \mu\text{g g}^{-1} \text{d}^{-1}$ ) comparable to rates obtained by Scheutz et al. (I) (table 5).

The oxidation of trace gasses in soil covers occurs in zones with methanotrophic activity and is thus controlled by the supply of methane and oxygen. Incubation experiments with soil sampled at successive depths at Skellingsted landfill showed that methanotrophic bacteria were active in oxidizing methane and selected trace components down to a depth of  $50$  cm below the surface (Scheutz et al., I). Maximal oxidation activity occurred in a zone between  $15$ - $20$  cm below the surface. A similar study carried out at a French landfill showed a deeper oxidation profile as maximum oxidation activity was observed at  $50$  cm depth (Scheutz et al. V). However in both cases the methanotrophic active zone corresponded to soil layers which had overlapping concentration gradients of methane and oxygen *in-situ*.

Anaerobic bacteria in the deeper soil layers may play an important role in reducing the emission of trace gases into the atmosphere. This has been demonstrated in dynamic soil

**Table 6.** Methane oxidation and degradation rates obtained from soil column experiments permeated with artificial landfill gas (50% vol. CH<sub>4</sub> and 50% vol. CO<sub>2</sub>) containing volatile organic compounds (Scheutz et al., III, IV).

Volatile organic compound		Methane oxidation		Degradation of VOCs	
		Efficiency %	Capacity g m <sup>-2</sup> d <sup>-1</sup>	Efficiency %	Capacity g m <sup>-2</sup> d <sup>-1</sup>
Trichlorofluoromethane	CFC-11	81±3	210	90±6	1.0·10 <sup>-02</sup>
Dichlorodifluoromethane	CFC-12	81±3	210	30±3	5.8·10 <sup>-03</sup>
Dichlorofluoromethane	HCFC-21	74±4	185	61±5	1.1·10 <sup>-01</sup>
Chlorodifluoromethane	HCFC-22	74±4	185	41±3	7.6·10 <sup>-02</sup>
Tetrachloromethane	TeCM	60±4	146	88±5	3.6·10 <sup>-02</sup>
Trichloromethane	TCM	60±4	146	61±4	2.3·10 <sup>-02</sup>
Dichloromethane	DCM	57±5	126	75±4	7.3·10 <sup>-01</sup>
Trichloroethylene	TCE	35±3	85	57±5	4.1·10 <sup>-02</sup>
Vinyl chloride	VC	35±3	85	74±6	1.8·10 <sup>-01</sup>
Benzene	Benzene	77±6	184	26±4	1.8·10 <sup>-01</sup>
Toluene	Toluene	77±6	184	44±8	1.2·10 <sup>-01</sup>

columns with a counter gradient flow of methane and oxygen simulating a landfill soil cover system (Scheutz et al., III, IV). Fully halogenated compounds such as TeCM, PCE, CFC-11, and CFC-12 were degraded in the anaerobic zone while lower chlorinated compounds such as dichloromethane, and vinyl chloride were degraded in the upper oxic part of the column, which showed high methanotrophic activity. The soil columns had a high degradation capacity with removal efficiencies up to 88% (table 6). As for the chlorinated hydrocarbons, lower removal efficiencies were obtained for the medium chlorinated hydrocarbons (TCM, TCE, and HCFC-22), since their standard potentials are neither high nor low, implying that neither anaerobic nor aerobic mechanisms will be optimal. The slower degradation of medium halogenated carbons should therefore be taken into account as a constraint, when practically dimensioning managed landfill soil covers.

Changes in atmospheric pressure are an important parameter controlling gas migration and emission from landfills (Kjeldsen and Fischer, 1995; Christophersen et al., 2001; Williams and Aitkenhead, 1991). A drop in atmospheric pressure will increase the pressure gradient between the landfill and the atmosphere leading to a higher gas emission. The impact of such an event on degradation of trace gases was simulated in column studies by increasing the inlet flow (Scheutz and Kjeldsen, III). When increasing the column inlet flow the oxidation zone was moved upwards in the column and the removal efficiency of both methane and HCFCs decreased. The removal of CFCs, which were only anaerobically degraded, was however less affected since the anaerobic zone expanded with increasing inlet flow rates and apparently mitigated the effect of a lower retention time.

The methanotrophs use MMO to oxidize both methane and VOCs. The presence of trace components is thus expected to have a negative impact on methane oxidation due to competitive inhibition. Competitive inhibition has been the subject of significant interest, especially in the perspective of the treatment of polluted water. However, the effect of VOCs in landfill gas on the microbial activity in soil covers is only sparsely studied. The inhibition of methane oxidation by HCFCs was studied in soil microcosms and increasing concentrations of HCFCs lead to decreasing methane oxidation rates (Scheutz and Kjeldsen, II). In comparison with typical values for trace components in landfill gas ( $<250 \mu\text{g L}^{-1}$ ) relatively high concentrations ( $1600 \mu\text{g L}^{-1}$ ) were needed to observe a significant effect. In soil covers the trace gas concentration will be even lower due to dilution in the upper soil with atmospheric air, mitigating the inhibitory effect on methane oxidation. However, landfill gas contains a mixture of different trace gasses, where other compounds, like vinyl chloride, could have a more severe effect on the methanotrophic bacteria. In soil columns permeated with artificial landfill gas the presence of vinyl chloride and TCE inhibited the methanotrophic bacteria, resulting in reduced methane oxidation rates (table 6 - Scheutz and Kjeldsen, III). The inhibition of HCFC oxidation by methane was more pronounced, as the oxidation rate decreased by 90% when the methane concentration increased from zero to 23%v/v (Scheutz and Kjeldsen, II). Maximum HCFC oxidation is expected in soil layers with maximal methanotrophic activity. However, these results indicate that zones with lower methane concentrations might favour oxidation of trace components. Resting methanotrophs in the upper part of the soil profile, which are only periodically exposed to higher methane concentrations may also perform rapid oxidation of trace gasses.

Whereas methane oxidation has been observed in the field in several research projects, the attenuating effect of soil covers on trace gas emissions from landfills in-situ is only sparsely analyzed. Field measurement of trace gas emission is challenged by the extreme low concentrations (due to dilution with atmospheric air) which require high analytical performance and by high spatial variation in gas emission which entails a high number of measurements. Bogner et al. (1997c) measured emissions of selected VOC species at a



northeastern Illinois landfill using a static chamber method. Preliminary results indicated very low emissions for the species studied ( $10^{-6}$  to  $10^{-4}$  g m<sup>-2</sup> d<sup>-1</sup>) under “worst case” conditions (thin interim soil cover over recently landfilled waste). Moreover, in a comparison between the sum of measured emissions and calculated emissions using a conservative U.S. Environmental Protection Agency (EPA) regulatory model for total VOC emissions, results indicated that the EPA model overestimated emissions by more than 2 orders of magnitude.

Scheutz and co-workers investigated the surface emission of VOCs at a French landfill (Scheutz et al. V). The surface emission was determined at two different areas at this landfill: a permanently covered and fully vegetated area (40 cm coarse sand + 80 cm of loam) and a temporarily covered area (40 cm of coarse sand). The VOC fluxes from the permanently covered zone were all very small, in the order of  $10^{-7}$  to  $10^{-5}$  g m<sup>-2</sup> d<sup>-1</sup>. A very interesting finding was that for several VOCs negative fluxes were obtained, indicating that these compounds were taken up by the soil cover and not emitted. Higher and mainly positive VOC fluxes in the order of  $10^{-5}$  to  $10^{-4}$  g m<sup>-2</sup> d<sup>-1</sup> were obtained from the temporarily covered zone. These fluxes are comparable to the fluxes reported by Bogner et al. (1997c) measured at a landfill with only a thin soil cover. The lower emission from the permanently covered cell was attributable to the thicker soil layer, which functioned as microbial habitat for methanotrophic bacteria. Based on the emission measurements and the batch experiments conducted, a general coherence was seen between emission and biodegradability of various VOCs. In general, the emission mainly consisted of compounds that were not aerobically degradable or slowly degradable, while an uptake of easily degradable compounds was registered. As an example, perchloroethylene, trichloromethane, CFC-11 and CFC-12 were emitted, while negative emission rates were obtained for the aromatic hydrocarbons, and lower chlorinated hydrocarbons like vinylchloride, methylene chloride, and methylchloride.



## 8. OPTIMIZATION OF ATTENUATION OF LANDFILL GASSES IN SOIL COVERS

Manipulation of landfill cover soils to maximize their methane oxidation potential might provide a complementary strategy for controlling emissions, particularly at older sites where the methane production is too low for energy recovery or flaring. However, at present, landfill caps are not designed with methane oxidation in mind. In some developed and developing countries, landfills have little or no cover soil, or cover soil of very poor quality. At such landfills desiccation cracks may form during dry periods, unless the landfill is irrigated or tilled, and methane venting through such cracks and fissures will not reside in the cover long enough to be oxidized. In these cases a significant attenuation benefit could be achieved with relatively simple design and/or manipulation of the top-soil cover. For example, attenuation can be considerably improved thanks to better soil porosity allowing better through-flow of methane and oxygen. This can be for instance achieved by mixing compost to the soil. The possibilities of optimizing methane oxidation through soil amendment with organic materials have been studied in several projects. Stein & Hettiaratchi, 2001 observed comparable oxidation rates in landfill loam and peat (max. 55% removal at low methane flow rates) in column experiments. Kightley et al. 1995 found that amendment of coarse sand with sewage sludge enhanced methane oxidation capacity by 26%. De Visscher et al. 1999 studied the influence of organic residue addition on methane oxidation in an agricultural soil. Mixing sugar beet leaves with soil lead to a temporary stimulation of the methane oxidation rate, whereas wheat straw amendment lead to permanent stimulation. The difference was attributed to the higher nitrogen content of the sugar beets, which inhibited the methane oxidation. The highest methane up-take was observed in landfill cover soil, but the amendment of this soil with organic residues was not studied (De Visscher et al. 1999).

Humer and Lechner obtain by far the most convincing and well-documented results on the stimulating effect of bio-covers on methane oxidation (Humer and Lechner, 2002; Humer and Lechner, 2001; Humer and Lechner 1999). Humer and Lechner (2002, 2001) measured the methane emission from landfill test cells covered with sewage sludge compost or municipal solid waste compost during a three-year period. For both type of bio-covers a removal of 90-100% was obtained and no methane emission could be detected at the surface during the whole measuring period. This high performance was obtained when a layer of coarse gravel was installed beneath the compost layer, which facilitated a homogeneous gas distribution. For compost or sewage sludge to give optimal performance the organic matter must be ripe and stable and the nitrogen should be bound in stable compounds such as humic-substances, and above all the ammonium concentration must be below 350 ppm (Humer and Lechner, 2002, 1999).

Hilger et al. 2000 found that soil columns with grass vegetation on top produced a higher methane peak up-take (47%) than bare columns (37%) even though the steady-state oxidation rates were similar (18%). However vegetation was shown to mitigate the inhibitory effect of ammonia observed in bare soil columns. Hilger et al. suggest that application of lime could offer an inexpensive way to reduce methane emissions from landfills as lime addition to soil columns consistently enhanced methane oxidation. However this remains to be tested in field studies.

Recent results demonstrate that methane oxidation can be enhanced by forced aeration of the top layer of the waste and the covering material. Field emission measurements showed a reduction of approximately 40% after implementation of a forced aeration system (Scharff et al., 2001).



Scheutz et al. (VI) observed transformation of gaseous  $\text{CCl}_3\text{F}$  and  $\text{CCl}_4$  by reaction with zero-order iron under anaerobic conditions and suggested that zero-valent iron could be a technology to reduce gaseous emission of high-chlorinated compounds from old landfills. Emplacement of metallic iron in the anaerobic zone in landfill covers could work well with natural biological processes as degradation products produced from the reaction with iron might be rapidly oxidized in the upper oxic soil layers.

However, these investigations are at an early stage, and the stability of the oxidation stimulation techniques needs to be tested over a longer timeframe. Furthermore, the efficiency of these methods with regard to also removing trace gasses remains to be examined.



## 9. CONCLUSION

This study shows that not only methane but also volatile organic trace components can be attenuated in landfill soil covers. It also shows that landfill top covers are complex systems with counter gradient gas flows, resulting in different redox zones where both anaerobic and aerobic bacteria may play an important role in reducing the emission of trace components into the atmosphere.

A broad array of experimental approaches have been used in this study in order to examine the mechanisms and potentials for natural VOC attenuation, involving both static (batch) and dynamic (column) laboratory experiences, as well as in-situ measures and experiences. To our knowledge, it is the first time all these methods are combined coherently in one study, and their combination has enabled to enrich our understanding of VOC behavior in landfill covers.

The main conclusions that can be drawn from this study are:

- Methanotrophic bacteria in landfill cover soils are capable of co-oxidizing a large number of VOCs, such as, e.g., chlorinated methanes, ethanes, and ethylenes. Based on average VOC concentrations usually found in landfill gas, the degradation rates measured in optimal conditions appear to be sufficient to attenuate many of the VOCs totally. This is for instance the case for compounds such as vinyl chloride, dichloroethylene, and dichloromethane. Moreover, negative fluxes of the more easily degradable VOCs were measured at a landfill, indicating up-take from the atmosphere and showing that landfills under some conditions may function as sinks of VOCs.
- The degradation mechanisms in landfill covers can be quite complex, involving both anaerobic and aerobic degradation. Fully halogenated compounds were found to be degraded in the anaerobic zone, while lower halogenated compounds were degraded in the upper oxidative zone. Fully halogenated compounds such as CFC-11 or CFC-12 are transformed under anaerobic conditions into HCFC-21 and HCFC-22, which both were degraded in the aerobic zone of simulated landfill soil covers. Thus both aerobic and anaerobic bacteria can intervene in the total degradation of a compound.
- The degradation process is highly dependent on physical and chemical parameters at the landfill site. Indeed, while degradation might be total for many VOCs in optimal conditions, changes in weather, temperature, etc. can slow processes down significantly. The main influencing factor was found to be temperature, showing an optimum at 30°C, but allowing the oxidation to take place until as low as 2°C. Soil moisture content proved to be another important factor, with 25%w/w moisture yielding maximum oxidation due to a good gas transport combined with sufficient microbial activity. Other factors, such as pH, copper and ammonium concentrations had comparatively less influence, when within the natural value ranges; when reaching extreme values, these factors also inhibited the oxidation. Ambient conditions are thus very important when calculating the attenuation potential of a landfill cover.

It can be concluded based on this study that passive methods based on soil cover management can actually be efficient in reducing landfill gas emissions, including VOCs, which is important in the light of continued disposal of waste in landfills, especially in developing countries.



## 10. FUTURE WORK

The results obtained in this study point towards areas for future research:

- Field measurements of trace gas emission from landfills, focusing on controlling factors such as changes in barometric pressure, temperature, precipitation;
- Investigation of the microbial community in landfill soil covers and their response to shift in environmental conditions;
- Investigation of degradation products from co-oxidation of VOCs by methanotrophs and their implication on methane oxidation in landfill soil covers, as well as the potential for total mineralization in mixed bacterial communities;
- Models for estimation of trace gas emissions from landfills which take into account microbial processes and climatic parameters;
- Optimization of landfill covers in view of reducing the emission of trace gasses; more specifically the performance of bio-covers with regards to trace gasses needs to be investigated;
- Investigation of the potential for anaerobic degradation of halogenated compounds in waste.



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