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ATTENUATION OF ALTERNATIVE BLOWING AGENTS IN LANDFILLS

Charlotte Scheutz
Anders M. Fredenslund
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Report for The Appliance Research Consortium

FOREWORD

Many home refrigerators are shredded after the end of their useful life. When this occurs, the insulating foam is reduced to fragments that may be incinerated, or disposed of in a landfill or, in a minority of cases, further processed for re-use. In the USA most of this is disposed of directly in landfills and very little is incinerated or otherwise processed. The foam contains fluorocarbon compounds (blowing agents) such as CFCs, HCFCs or HFCs, which are strong greenhouse gases that contribute to global warming and/or, where chlorinated, also contribute to ozone depletion if released into the atmosphere. During decommissioning of refrigerators a proportion of the blowing agent is released while the remaining amount may be released very slowly after disposal of the foam waste in landfills. Relatively little information is available concerning the fate of blowing agents in landfill environments. However, CFCs such as CFC-11, CFC-12, and CFC-113 are known to undergo reductive dechlorination in a variety of anaerobic ecosystems. Methanotrophic bacteria in landfill soil covers have been shown to play an important role in mitigating the emission of methane from landfills. Methanotrophic bacteria facilitate transformation of a number of chlorinated hydrocarbons compounds including some fluorinated hydrocarbons; thus the potential exists for attenuation of blowing agents both within the disposed waste as in landfill soil covers.

AHAM (Association of Home Appliance Manufacturers) is interested in data based on research in this area because many environmental assessments of household refrigerators assume that the entire blowing agent is released into the atmosphere when a product is shredded at end of its useful life. Furthermore, attenuation processes that might occur in landfills are not assessed.

The Appliance Research Consortium (ARC), which is an independent entity operated by AHAM, has solicited bids on a research initiative, resulting in this research project.

Charlotte Scheutz, Anders M. Fredenslund, and Peter Kjeldsen from Environment and Resources DTU, Technical University of Denmark, have carried out the project in the period May 1st, 2002 to February 31st, 2003.

SUMMARY

The blowing agent (BA) for insulating foam used in appliances such as refrigerators and freezers is frequently a fluorocarbon. Many appliances are shredded after the end of their useful life. When this occurs, the insulating foam is reduced to pieces that often are disposed of in landfills. The escaped blowing agent may contribute to ozone depletion in the atmosphere or to the greenhouse gas effect. Relatively little information is available regarding the degradability of blowing agent in landfill environments. The objective of this project was to evaluate the potential for degradation of alternative foam blowing agents in landfills and landfill soil covers, and to develop a landfill model which could simulate the fate of foam blowing agents in landfills using the laboratory determined degradation rates. The investigation was performed by batch and column studies using soil collected from a landfill soil cover and organic household waste or refuse excavated from a landfill. The blowing agents studied were CFC-11, HCFC-141b, HFC-134a, and HFC-245fa. As the rate of anaerobic, reductive dechlorination of CFC-11 has been previously reported, this compound was mainly used as a reference to evaluate the overall reactivity of the soil and waste samples. The landfill model was developed as a spreadsheet model with possibilities of simulating the dynamic behavior and fate of the foam released blowing agents.

The potential of anaerobic bacteria to degrade blowing agents under landfill conditions was tested in presence of three types of waste material, which mainly differed in age. The waste sources included fresh organic waste collected from Danish households, older pre-disposed waste from an American landfill, and waste from a laboratory experimental digester simulating landfill conditions. The batches were inoculated with sludge from a mesophilic biogas reactor to insure anaerobic microbial activity. Confirming the earlier work, CFC-11 was rapidly degraded in all experiments regardless of the type of waste. CFC-11 was degraded close to 100% under present conditions within 10-14 days. HCFC-141b was also degraded and, as with CFC-11, followed first order degradation kinetics. The degradation of HCFC-141b occurred at a slower rate compared to CFC-11 giving approximate half-lifes of 50 days and 2 days respectively. Anaerobic degradation of HFC-134a and HFC-245fa was not observed in any of the experiments within a run time of up to 210 days. Methane was produced in all bottles indicating active methanogenic bacteria. CFC-11 was degraded to HCFC-21, HCFC-31, and HFC-41. The degradation pattern indicated a simultaneous production of HCFC-21, HCFC-31, and HFC-41 rather than sequential dechlorination. HCFC-21 and HCFC-31 were further degraded whereas no further degradation of HFC-41 was observed. This was confirmed in batch experiments with high initial concentrations of HCFC-21, HCFC-31, and HFC-41. The degradation rate was directly correlated with the number of chlorine atoms attached to the carbon, as the highest degradation rates were obtained for CFC-11, the lowest for HCFC-31, whereas no degradation of HFC-41 was observed. A degradation of CFC-11 to HFC-41 would overall lead to emission of a compound from landfills with zero ozone depletion potential (ODP) and much lower global warming potential (GWP).

Degradation of CFC-11 was also observed in un-inoculated batch experiments only amended with pre-disposed waste. However, the degradation rate was almost 10 times slower compared to the observed rate in the inoculated experiments. The highest degradation rates were obtained in bottles containing 10g waste material, whereas almost no degradation was observed in bottles containing only 1g waste. In experiments with fresh household waste no

degradation of CFC-11 was observed regardless of the amount of waste. The potential of the pre-disposed waste to facilitate degradation is probably a result of the fact that the micro-organisms have been earlier exposed to halocarbons and therefore are adapted to degradation these components. In un-inoculated experiments, with added HCFC-141b, no significant degradation was observed due to the slow degradation rate of HCFC-141b and the relatively short experimental run time.

The potential of anaerobic bacteria to mitigate the release of blowing agents from foam sources in landfilled waste was investigated in batch experiments containing organic waste mixed with pieces of insulation foam. In general, similar release patterns showing high initial release, which subsequently decreased were observed in bottles containing only foam pieces and bottles containing foam pieces and sterilized waste material. For all foam types most of the BA loss happed during the first 120 to 240 hours, and decreased afterwards. In experiments with active waste and inoculum, the microbial bacteria degrading CFC-11 significantly mitigated the release of CFC-11. In experiments with HCFC-141b no tendency toward a microbial removal was observed, which was due to the almost 30 times slower degradation rate of HCFC-141b compared to CFC-11 implying that the microbial removal of HCFC-141b under these conditions is insignificant compared to the release rate. In experiments with HFC-134a and HFC-245fa no difference between microbially active and sterile bottles was observed.

The potential for aerobic degradation of blowing agents was investigated in soil microcosms incubated with methane and atmospheric air, simulating the gas composition in landfill soil covers. Even though the soil showed a high capacity for methane oxidation resulting in very high oxidation rates of up to $132\ \mu g\ CH_4\ g^{-1}\ h^{-1}$ none of the four blowing agents were degraded. In anaerobic soil microcosms both CFC-11 and HCFC-141b were degraded, whereas no degradation of HFC-134a and HFC-245fa was observed within the run time of the experiment. The degradation of CFC-11 occurred almost twice as fast as the degradation of HCFC-141b giving degradation rates of 0.02 and 0.01 $\mu g\ g\ soil^{-1}\ d^{-1}$ respectively. For both CFC-11 and HCFC-141b degradation occurred after a lag phase of 40 days.

The potential of degradation of the four blowing agents was studied in a dynamic column set-up simulating a landfill top cover soil matrix through which gas is transported. The soil columns showed a high capacity of methane oxidation giving maximal methane oxidation rates up to $240\ g\ m^{-2}\ d^{-1}$ corresponding to a reduction of 93%. CFC-11 and HCFC-141b were degraded in the active soil columns with increasing removal rates over time. The average degradation capacities for CFC-11 and HCFC-141b after a four month-period were 0.07 and 0.05 $g\ m^{-2}\ d^{-1}$ corresponding to a removal efficiency of 75% and 42% respectively. No degradation of HFC-134a and HCFC-245fa was observed within the duration of the experiment.

The integrated evaluation of the fate of halocarbons contained in foam waste disposed in a landfill was carried out by extending a model for fate of organic compounds in landfills (the MOCLA model) to include a compartment (i.e. foam) continuously releasing blowing agent to the pore air space of the landfilled waste. The new model, MOCLA-FOAM, takes into account the time-dependent release patterns of blowing agent from foam. The extended model can estimate the fate route of the mass of blowing agent released from the foam waste over a specified period. The model specifies the fraction of the released blowing agent which is degraded, emitted with landfill gas or leachate, or contained in the three landfill phases (pore gas, pore water or sorbed to waste). Setting up the model for a landfill reactor scenario, where biodegradable waste and foam is mixed, and using the laboratory determined degradation

rates for CFC-11 and HCFC-141b, it is shown that a strong reduction of the emission of CFC-11 is observed, due to microbial degradation. This observation is a plausible explanation for at least some of the discrepancy between the predicted and the observed atmospheric concentration of CFC-11. Also for HCFC-141b, the microbial degradation seems significant leading to low emission of HCFC-141b. The model is set up using certain assumptions, which realization has not been fully investigated under full-scale landfill conditions.

Based on the conducted project, it can be concluded that there exists a very large potential for degradation of the originally used blowing agent, CFC-11, in landfill environments. Especially the anaerobic conditions within the waste layers are especially favorable for degradation. Of the alternative blowing agents only HCFC-141b showed similar behavior to that of CFC-11 but with much lower degradation rates. For the HFC blowing agents, HFC-134a and HFC-245fa, there was no indication that these two compounds are degradable in landfill environments (including anaerobic waste and cover soils under active methanotrophic conditions). However it should be pointed out that microbes in landfill environments have had 50-70 years to get accustomed to CFCs. Thus it is possible that in the future landfills may also adapt to new anthropogenic compounds, such as HFCs. This research, coupled with previous work done by the authors regarding the amount of blowing agent released during shredding, provides a plausible explanation for at least some of the discrepancy between the predicted and the observed atmospheric concentrations of CFCs noted by others.

CONTENTS

1. INTRODUCTION

The blowing agent (BA) for insulating foam used in appliances (e.g. refrigerators and freezers) and many building materials is frequently a fluorocarbon. Prior to 1996 the most common blowing agent was CFC-11, but the compound was banned by the Montreal Protocol due to its strong ozone depletion potential. HCFC-141b, the compound that in most cases was used to substitute CFC-11, will be banned in most developed countries by 2005. HFCs such as HFC-134a or HFC-245fa are expected to be used extensively in the future as foam blowing agents. The HFCs are greenhouse gases that contribute to global warming if released to the atmosphere.

Many appliances are shredded after the end of their useful life. When this occurs, the insulating foam is reduced to small pieces that may be incinerated, or disposed of in a landfill or, in a minority of cases, further processed for re-use. In the USA most is disposed of directly on landfills and very little is incinerated (1). A recent study showed that the proportion of the BA content of foams, which is released from foams within the first six weeks after shredding (including the instantaneous release) is in the order of 13-60% depending on particle size (valid for a particle size range of 2 to 32 mm). The remaining BA may be released very slowly if the integrity of the foam particles is maintained with respect to diffusional properties after disposal of the foam waste on landfills occurs (2).

Landfills are used for disposing of organic waste in most countries worldwide. Waste deposited in landfills will undergo anaerobic decomposition resulting in generation of landfill gas (LFG). The main components in LFG are methane (55-60 vol.%) and carbon dioxide (40-45 vol.%) (3). LFG also contains trace compounds at levels of up to a few volume percentages (4,5). Chlorofluorocarbons (CFCs), especially CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) are observed in LFG (6), and mainly originate from insulation foams disposed of at the landfill (7). Several authors have recognized the significance of insulation foams in the global fluorocarbon balances. Khalil and Rasmussen (8) state that after production of CFC-11 was terminated (i.e. after 1996), future atmospheric concentrations will mainly depend on the continued release from polyurethane foams. Due to the limited lifetime of products containing insulation foam, CFCs will end in landfills in most countries during the coming decades. Similar behavior is expected in the future for the HCFCs and HFCs used as foam blowing agents. CFCs are known to undergo reductive dechlorination under anaerobic conditions, however, relatively little information is available concerning the fate of blowing agents in landfills.

US landfills are in most cases equipped with a passive gas extraction system including flares where the LFG is burned. In a few cases (150-200 landfills) active gas extraction systems including gas utilization facilities are present at the landfill. However, the passive systems are not especially effective, and a significant fraction of the generated LFG is emitted through the soil cover or the soil strata in the surrounding areas. Even the active extraction systems are not regarded as 100% effective.

Microbial oxidation of methane plays a significant role in reducing the emission of methane from landfills (9,10). Indeed, field studies have shown methane oxidation of up to 100% at some landfills (11,12). The methanotrophic bacteria facilitate transformation of a number of halogenated hydrocarbons including fluorinated hydrocarbons; thus the potential exists for attenuation of selected blowing agents in landfill soil covers. However, research in this area has only recently been initiated.

2. OBJECTIVES

The objective of this project was to evaluate the potential for degradation of alternative foam blowing agents in landfills and landfill soil covers, and to develop a landfill model which could simulate the fate of foam blowing agents in landfills using the laboratory determined degradation rates. The investigation was performed by batch and column studies using soil collected from a landfill soil cover and organic household waste or refuse excavated from a landfill. The blowing agents studied were CFC-11, HCFC-141b, HFC-134a, and HFC-245fa. CFC-11 was mainly used as a reference compounds to evaluate the overall reactivity of the soil and waste samples. The landfill model was developed as a spreadsheet model with possibilities of simulating the dynamic behavior and fate of the foam released blowing agents.

3. LITERATURE REVIEW – STATE OF THE ART

Landfills are potential significant sinks for CFCs disposed of in foam waste. Figure 3.1 shows the potential attenuating microbial processes, consisting of anaerobic processes within the waste body, and coupled anaerobic/methanotrophic processes in soils surrounding the waste. The soil covers often consist of a lower anaerobic zone where the pore gas consists mainly of LFG, and an upper methanotrophic zone characterized by a pore gas mixture of LFG and atmospheric air diffusing into the top cover from the atmosphere.

CFCs are generally considered to be chemically very stable as a result of the high bond energy between carbon and fluoride. As a consequence of their high stability, CFCs first were expected to be biologically inert. In 1989, however, it was reported that CFC-11 and CFC-12 can be de-chlorinated in anaerobic ecosystems such as termite mounds (13) and in rice fields (14). CFC-11 bio-transformation under anaerobic conditions has been observed since in methanogenic sediment (15), anoxic aquifer (16), contaminated groundwater (17), and in anoxic marine water (18). CFCs serve as electron acceptors and CFCs are degraded primarily by dechlorination reactions that produce hydrochlorofluorocarbons (HCFCs). The fate of CFCs under landfill conditions has only been studied in a few cases. Deipser and Stegmann (19) investigated the microbial degradation of CFCs in simulated landfill conditions. Under both acid phase and methanogenic condition CFC-11 was degraded, with HCFC-21 as the sole product. Under methanogenic conditions the degradation rate was nearly 37-fold higher than observed under acid phase conditions, and further degradation of HCFC-21 was observed. Also CFC-12 and CFC-113 were similarly decomposed under methanogenic conditions. Ejlertson et al. (20) studied the potential for biological transformation of CFC-11, CFC-12, CFC-13, CFC-114, and HCFC-22 by microorganisms in municipal solid waste samples from a laboratory scale landfill reactor. CFC-11 was completely transformed to HCFC-31 with HCFC-21 being a transient intermediate. After 100 days of incubation a 5% portion of the added CFC-12 was transformed to HCFC-22, while less than 1% of the added CFC-114 was converted to C_2HClF_4. CFC-13 and HCFC-22 were not transformed. Balsiger et al. (21) investigated the potential of bio-transformation of ten chlorofluorocarbons and hydrochlorofluorocarbons under methanogenic conditions. CFC-11 was transformed to HCFC-21 and to HCFC-31. CFC-113 was transformed to two products, which were deduced to be 1,2-dichloro-1,2,2-trifluoroethane (HCFC-123a) and chlorotrifluoroethene. No transformation was observed for CFC-12, HCFC-22, CFC-114, CFC-115, HCFC-141b, HCFC-142b, and HFC-134a.

Chlorofluorocarbons are often found in landfill gas in relatively high concentrations because of their wide-spread use, their high volatility, and high persistence. The fluorinated halocarbons most frequently measured in landfill gas are: CFC-11, CFC-12, HCFC-21, HCFC-22, HCFC-31, CFC-113, and CFC-114 (22,23). The presence of HCFC-21 and HCFC-31 in landfill gas thus indicates that anaerobic degradation of CFC-11 is occurring since neither of these compounds have been produced for industrial applications.

Under anaerobic conditions the degradation rate of halogenated compounds decreases with decreasing number of halogen substituents (24). Hence, HCFC-31, HCFC-41, and HCFC-22 may accumulate during anaerobic degradation of CFC-11 and CFC-12. Hardly any studies have looked at degradation of the alternative blowing agents under strict anaerobic conditions. HCFC-141b has some similarities to HCFC-22, which has been observed to be anaerobically degraded (31). Thus anaerobic degradation of HCFC-141b may occur. Defluorination (i.e. rupture of the carbon-fluorine bond) has only been rarely observed, and seems to require

extreme reducing conditions (25). However, very reducing conditions are often observed in landfilled waste, which may then imply a possible defluorination of the HFCs.
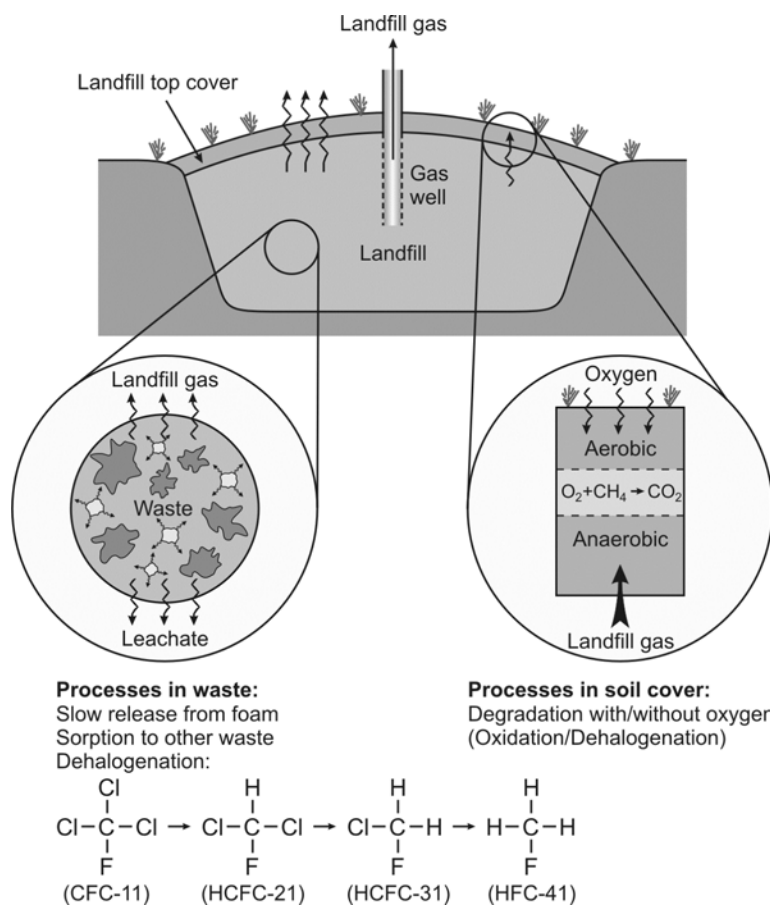
Figure 3.1 Conceptual model of the attenuation processes in landfills including processes within the waste body and processes in the soil cover.

The attenuation of methane in landfill top covers by methane oxidation has been subject to several studies (26,27,28,29,30). The anaerobic and methanotrophic degradation of the volatile organic compounds in landfill top covers has only been studied in a few cases. Kjeldsen and co-workers (31) showed in laboratory experiments using soil samples from a single landfill, that CFC-11 and CFC-12 were degraded due to co-metabolic reactions in the methanothrophic zone of the top cover in combination with an initial dechlorination in the lower anaerobic zone.

The methane oxidation is carried out by methane oxidizing bacteria, the methanotrophs, in the upper aerobic soil layer. In landfills, type II methanotrophs are reported to dominate (32). Several of the type II methanotrophs carry besides the membrane bound methane monooxygenase (pMMO), also a soluble variant of the enzyme (sMMO) having a broad substrate spectrum enabling them to oxidize halogenated hydrocarbons (33,34). Co-metabolic oxidation of chlorinated hydrocarbons (especially trichloethylene) by methanotrophs has been intensively studied. However, the metabolic pathways have only been fully elucidated for trichloroethylene and involve both biological and abiotic processes (35,36,37). In general, 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 (38).

Highly chlorinated hydrocarbons including perchloroethylene, tetrachloroethane, carbon tetrachloride, and CFCs are not degraded by methanotrophs (39,40).

Methanotrophs have also been shown to transform fluorinated hydrocarbons such as HCFCs and HFCs (41,42,43,44,45,46). The order of reactivity was found to be HCFC-22>HCFC-142b>HFC-134a>HCFC-123 (42). Further compounds reported to be bio-transformed by methanotrophs are HCFC-21, HCFC-141b, and HCFC-143 (45,46). Streger and co-workers (45) found that full mineralization was observed for HCFC-141b by specific methanotrophs. This was shown by a full recovery of formed Cl⁻ and F⁻ in the experiments. HCFC-124, HFC-134, and HFC-245fa were not degradable by methanotrophs (45,46). No studies were found concerning degradation of HFC-245fa under environmental conditions.

4. MATERIALS AND METHODS

4.1 Chemicals

The CFC-11, HCFC-21, HCFC-31, HFC-41, HFC-134a, HCFC-141b, and HFC-245fa used were all obtained in high purity. CFC-11, and HCFC-21 were purchased from Flourochem Limited, England. HCFC-31 and HFC-41 were purchased from SynQuest Labs. Inc., Alachua, FL. HFC-134a, HFC-245fa were obtained from Interchim, France while HCFC-141b was obtained from Honeywell, Netherlands. Table 4.1 lists physical and chemical properties of the four blowing agents included in this study. HCFC-21, HCFC-31, and HFC-41 were mainly used to identify degradation products of CFC-11. Physical and chemical properties for these compounds are included in appendix 1.

Table 4.1 Physical and chemical properties of CFC-11, HFC-134a, HCFC-141b, and HFC-245fa.

Chemical name	Unit	Trichlorofluoro methane	1,1,1,2-tetra-fluoroethane	1,1-dichloro-1-fluoroethane	1,1,1-trifluoro-3,3-difluoro-propane
Synonyms		CFC-11	HFC-134a	HCFC-141b	HFC-245fa
Structure		CCl_3F	CH_2FCF_3	CCl_2FCH_3	$CF_3CH_2CHF_2$
CAS no.		000075-69-4	000811-97-02	001717-00-6	460-73-1
Molecular weight	g/mol	137.37	102.03	116.95	134.05
Boiling point	°C	23.8	-26.2	32	15.3
Vapor pressure	mmHg	802.8	430	707	1.24bar
Water solubility	mg/L	1100	67	2632	n.d.f
Log K (octanol-water)		2.53	1.68	2.37	n.d.f
Saturated gas concentration	g/L (1atm, 25°C)	5.62	4.17	4.78	5.48
Ozone depletion potential[1]		1.0	0	0.09	0
Global warming potential[1]		4600	1600	700	820

Note: n.d.f.: no data found
1: From database compiled by Air-Conditioning and Refrigeration Technology Institute (www.arti-21cr.org/db/qa.html).

4.2 Characteristics of waste samples used in anaerobic batch experiments

The potential of anaerobic bacteria to degrade blowing agents under landfilling conditions was tested in presence of three types of waste material: A, B, C. The waste materials mainly differed in age.

A: Fresh organic waste collected from Danish households
B: older pre-disposed waste from an American landfill
C: waste from a laboratory experimental digester simulating landfill conditions

The fresh organic waste was collected from private Danish households in an area were the citizens as a part of a research program are sorting their waste into different fractions including an organic fraction. The organic waste is expected to be easily degradable and to have a high gas potential as the material is fresh, well sorted, and consists of easily degradable materials like fruits, vegetables, bread, rice, corn – no paper. The organic material may therefore provide the anaerobic bacteria with an easily available carbon source to maximize growth.

Older pre-disposed waste was excavated from an American landfill situated in North Carolina. Even though the landfill is producing methane the waste is expected to have a lower gas potential due to the higher degree of maturity of the organic material. However, anaerobic bacteria in the waste might have been exposed to different blowing agents in the landfill environments and therefore have a potential to degrade some of these compounds.

Furthermore, waste samples from a laboratory experimental digester containing fresh refuse were included in the study. The digester is in its methanogenic phase and contains some well-decomposed waste.

4.3 Characteristics of foam samples used in batch experiments

The potential of organic waste to have a mitigating effect on the release of blowing agents from insulation foam was tested in anaerobic batch experiments with added foam pieces. Foam samples blown with four different blowing agents (CFC-11, HCFC-141b, HFC-134a, HFC-245fa) were included in this study. Experiments with these four blowing agents were in general carried out in parallel.

The ARC Monitoring committee supplied foam panels blown with three different blowing agents (HCFC-141b, HFC-245fa, and HFC-134a). The foam panels were 2 ft. square by 2 in. thick, encased in aluminum foil. The foam panels were all produced in late 1997 by the same manufacturer. PUR foam samples containing CFC-11 were obtained from a used refrigerator produced in 1977.

In general samples were taken by cutting out a larger piece (10 x 10 x 5 cm^3) of foam from the test panels. After removing the aluminum foil, smaller foam samples were cut out from the center of the large foam sample using a cork bore. To avoid further loss of BA from the foam panels during storage after cutting out samples they were sealed by vapor-tight tape. In order to compare results from previously conducted experiments, foam samples had the same shape and size, i.e., a cylinder with a diameter of 1 cm and a height of 1 cm. The foam cylinders containing CFC-11 were cut out from foam cubes (4 by 4 cm) from a refrigerator door, which had been stored in closed glass containers. These cubes were used as the original refrigerator was lost in a fire at the department.

Table 4.2 shows the characteristics of the four foam panels. For further discussion of analysis methods used to determine foam characteristics please consult the report "Determination of the Fraction of Blowing Agent Released from Refrigerator/Freezer Foam after Decommissioning the Product by Scheutz & Kjeldsen, 2001 (2).

Table 4.2 Measured and calculated parameters for the four foam panels

Parameter	Unit	Blowing agent			
		CFC-11	HFC-134a	HCFC-141b	HFC-245fa
Density, ρ_{foam}	g/L	24.6	39.0	32.2	30.7
Porosity, f_g (calculated)		0.985	0.972	0.978	0.980
Porosity, f_g (measured)		0.964	0.929	0.919	0.933
Total content of BA a)	g/L	3.43	2.78	3.77	3.66
	% w/w	13.3	7.0	11.6	11.6
Total content of CO_2	g/L	0.14	1.50	0.75	0.48
	% w/w	0.58	3.86	2.34	1.61
Fraction of CO_2 b)	% w/w	3.9	35.0	16.6	11.6
Content of BA in polymer	g/L	1.01	0.63	1.05	0.91
Fraction sorbed in PUR	%	29.5	22.7	27.8	24.8
Distribution coeff., K	m^3 gas$\cdot$ $(m^3$ PUR$)^{-1}$	24.6	10.1	16.5	14.9

a): as measured by the heating method

b): calculated as $M_{CO_2}/(M_{CO_2}+M_{BA})$

4.4 Soil characteristics and sampling

4.4.1 Field site

Soil samples for batch and column experiments were collected at Skellingsted Landfill south of Holbæk, Western Sealand, Denmark. Skellingsted Landfill received a total of approximately 420,000 metric tons of waste between 1971 and 1990. The composition of the waste was approximately 60% municipal solid waste and 40% bulky waste, industrial waste, and sewage treatment sludge. The landfill is situated in an abandoned gravel pit located in an area of alluvial sand and gravel sediments. The landfill is un-controlled with no liners or gas extraction system. The landfill gas migration has been intensively studied due to a gas explosion accident in 1991 (47). The landfill gas is mainly migrating horizontally through the sides of the landfill due to the stratified compaction of the waste. The soil was sampled at a test station on the landfill border where the average methane emission was 25 mmol m^{-2} h^{-1} (maximal emission was 189 mmol m^{-2} h^{-1}) measured during a one-year field campaign (12). The soil was sampled in 5 to 10-cm intervals from the surface to 100-cm depth below the surface. Soil samples were collected using a spade and kept cold and in darkness in closed containers prior to the laboratory experiments. The soil was sieved through an 8-mm mesh to increase homogeneity. The soil was analyzed for the following parameters: grain size distribution, soil moisture content, organic carbon content, pH, total nitrogen, ammonium, and nitrate. All soil analyses were conducted according to standard methods approved by the Danish EPA.

4.4.2 Soil characteristics

The soil was characterized and analyzed for different soil parameters as a function of sampling depth prior to column start up. The soil was characterized according to the USDA classification. Three soil layers based on the granulometric composition could be identified: loamy sand (0-40 cm), sandy loam (40-70 cm), and coarse sand/gravel (70-100 cm) (table 4.3). The soil moisture content varied between 10 and 27%w/w with the upper 20 cm being driest. The highest soil organic carbon content was obtained in the upper 20 cm below the surface with values up to 5.7%w/w and decreased to 0.9 at 100-cm depth. The total nitrogen content showed a similar pattern with a maximum content of 4.3 g-N kg^{-1} dry soil.

The soil pH_{CaCl2} showed a maximum (7.6) at 25 cm below the surface and decreased downwards.

Vertical soil gas profiles showed that both methane and oxygen often were present between 20 and 40-cm depth. From 60-cm depth the soil gas consisted of almost pure landfill gas (60%CH_4 and 40%CO_2) – with only very low or no oxygen.

Table 4.3 Soil parameters

Depth cm.b.s.	Soil texture	H_2O % w/w	TOC % w/w	TON mg kg^{-1}	pH	NO_3^- mg kg^{-1}	NH_4^+ mg-N kg^{-1}
5-10	Loamy sand	10	5.7	4300	6.9	98	12
10-15	Loamy sand	13	4.4	3690	7.2	81	22
15-20	Loamy sand	11	3.7	3190	7.5	93	13
25-30	Loamy sand	17	3.0	3320	7.6	98	11
30-35	Loamy sand	27	2.2	2600	7.2	160	7.9
40-45	Sandy loam	24	1.7	1860	6.7	99	3.8
50-55	Sandy loam	23	1.7	1570	6.4	56	2.2
60-70	Sandy loam	22	2.0	1650	6.4	45	<2
75-80	Coarse sand	22	1.3	896	5.7	88	<2
85-90	Coarse sand	22	1.0	326	6.5	12	<2
95-100	Coarse sand	18	0.9	338	6.7	63	<2

TOC: Total organic carbon. TON: Total organic nitrogen.

4.5 Gas Chromatographic Analysis

4.5.1 Gas chromatographic analysis of halogenated compounds using mass spectrometry

Analysis of the halogenated compounds (CFC-11, HFC-134a, HCFC-141b, HFC-245fa, HCFC-21, HCFC-31, and HFC-41) was performed on an Agilent 6890N gas chromatograph coupled with an Agilent 5973N mass spectrometer. The gas samples were injected manually as direct on-column injections on a DB-VRX column (20m×0.18mm×1.00μm) with helium as carrier gas. The compounds were analyzed with an isotherm column temperature of 35°C. The carrier gas flow is set at 0.6 ml/min, and a sample split of 5:1 is used. Injection volume of samples was 50 μl throughout the project period. Injection of gas samples was done using a 100 μl VICI Precision Sampling Inc Pressure Lock Gas Syringe.

Concentrations of the target compounds were calibrated by injection of gas standards (no fewer than 5 concentration levels) and constructing a standard curve. Calibration standards were made by adding a specific volume of a saturated pure gas at atmospheric pressure to a known volume of air. The standard curves were linear throughout the whole concentration range. Gas chromatograph conditions for analysis of halocarbons are shown in Table 4.4.

4.5.2 Gas Chromatographic Analysis – main components

The main gas components (CH_4, CO_2, O_2, and N_2) were analyzed on a transportable CP-2002P Chrompack Micro GC (Chrompack International BV, The Netherlands) gas chromatograph equipped with a thermal conductivity detector and two columns. Oxygen and nitrogen were quantified on a 4 m long Molsieve 5A column and methane and carbon dioxide on a 10 m long Poraplot Q column. Carrier gas was helium and the column temperature was 40°C. Gas standards produced by MicroLab, Aarhus, Denmark ranging from 0,02 to 50 %vol. are used for calibration.

Table 4.4 Gas chromatograph conditions for analysis of halocarbons

Compound	Target ion m/z	Relative response factor compared to CFC-11	Highest standard (µg/l)	Lowest standard (µg/l)	Detection limit (µg/l)
CFC-11	101	1	820	82	0.04
HCFC-21	67	0.7	620	62	0.03
HCFC-31	33	6.9	400	40	0.3
HFC-41	33	5.3	200	20	0.2
HFC-134a	83	3.2	600	60	0.1
HCFC-141b	81	1.2	700	70	0.05
HFC-245fa	115	4.4	800	80	0.2

5. ANAEROBIC BATCH EXPERIMENTS WITH ORGANIC WASTE

The potential of anaerobic bacteria to degrade blowing agents under landfill conditions was tested in presence of three types of waste material, which mainly differed in age.

A: fresh organic waste collected from Danish households
B: older pre-disposed waste from an American landfill
C: waste from a laboratory experimental digester simulating landfill conditions

5.1 Experimental set-up

The anaerobic degradation process was examined in glass incubation bottles (320 mL in total volume) equipped with Teflon coated rubber septum held in place by an aluminum screw cap. The septum enables gas to be sampled or injected by a hypodermic needle and a syringe. A fixed amount of waste (1 g) was added to each batch container. The waste was homogenized in a blender before being added to the experiments. To obtain anaerobic conditions, the bottles were flushed with a nitrogen/carbon dioxide mixture ($80\%N_2:20\%CO_2$). The carbon dioxide buffers the bottles and prevents acidification of the waste material due to build up of fermentation products like organic acids. The bottles were inoculated with sludge (40mL) from a mesophilic biogas reactor to insure anaerobic microbial activity. To some bottles glucose (1g) was added instead of organic waste to study the effect of an easily degradable carbon source. In experiments with added organic household waste (waste A) the bottles were opened after 60 days, septa were changed and blowing agents re-added. This was done as leakage through the septa was suspected as a result of the high sampling frequency. In the following experiments a lower sampling frequency was used. Gas samples containing the test compound (CFC-11, HCFC-141b, HFC-134a, and HFC-245fa) were removed from gaseous stock solutions by a gas tight glass syringe and injected into the batch containers. The initial concentrations, which varied between 200-600 µg/L, were generally selected so they were in the range of typical trace gas concentration in landfill gas (10-500 mg m^{-3}). The degradation of the halocarbons was studied in single compound tests. Gas samples withdrawn from headspace were sampled periodically and analyzed by gas chromatography. The batch experiments were conducted at room temperature (22°C). All batch experiments were carried out in triplicate.

In order to check if any disappearance could be due to non-microbial processes (abiotic degradation, sorption and volatilization) bottles were sterilized by autoclaving to avoid microbial growth in control batches. In addition, bottles where only the blowing agent or the blowing agent and water were added were analyzed in parallel. To be able to account for losses due to pressure build-up as a result of methane production in the microbial active bottles, argon was used as a conservative tracer. Pictures of the anaerobic batch experiments are shown in appendix 2.

5.2 Anaerobic degradation of blowing agents under landfill conditions

CFC-11 was relatively rapidly degraded in all experiments regardless of the type of waste. CFC-11 was virtually 100% degraded under present experimental conditions within 10-14 days. The degradation of CFC-11 followed first order kinetics. Figure 5.1 shows the results of the degradation experiments conducted with organic house hold waste (Waste A – 2. round). Table 5.1 shows the first-order degradation rates as well as the regression coefficient from

fitting the experimental data with a first-order model equation. Table 5.1 includes degradation rates from the conducted experiments whereas degradation curves for wastes B and C are shown in appendices 5 and 6 respectively. HCFC-141b was also degraded by a mechanism following first order degradation kinetics, as with CFC-11. The degradation of HCFC-141b occurred at a slower rate compared to CFC-11 giving approximate half-lifes of 50 days and 2 days respectively. Anaerobic degradation of HFC-134a and HFC-245fa was not observed in any of the experiments within a run time of up to 210 days.

Methane was produced in all bottles indicating active methanogenic bacteria. For comparison, the time period for a production of 20%vol methane is listed in table 5.2. Methane production curves for the different experiments are showed in appendices 4 to 6. Higher methane production was observed in the bottles containing fresh organic household waste (A) when compared to bottles containing pre-disposed waste (B, C). This also correlates with the higher degradation rates for CFC-11 and HCFC-141b observed in bottles with fresh organic waste. The fresh waste most likely contains more easily degradable/available organic carbon compared to the more mature pre-disposed waste. In general, the methane production was a little higher in bottles containing both inoculum and organic waste when compared with bottles only containing inoculum. This is especially evident in batches containing fresh organic waste indicating that the bacteria benefit from the added carbon in the form of organic waste. A high methane production and degradation rate of CFC-11 and HCFC-141b was also obtained in bottles with added glucose instead of waste, since glucose is an easily degradable carbon source.
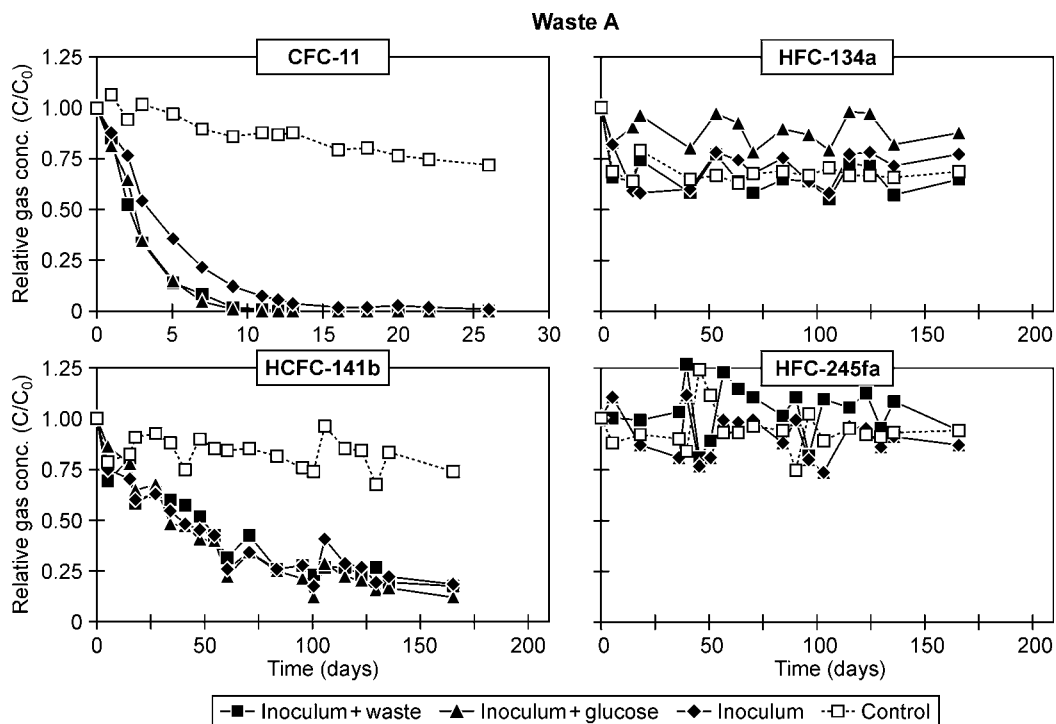

Figure 5.1 Relative gas concentration of blowing agents in batch experiments with added organic household waste.

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Table 5.1 First-order rate constants (k_1) and half-lifes ($t_{1/2}$) for anaerobic degradation of CFC-11 and HCFC-141b in batch experiments added three different types of waste materials.

Blowing agent	CFC-11			HCFC-141b		
	k_1	$t_{1/2}$	R^2	k_1	$t_{1/2}$	R^2
	d^{-1}	d		d^{-1}	d	
Waste A: Fresh organic waste collected from Danish households – 1. round						
Inoculum + waste	0.426	1.6	0.958	0.026	26.7	0.951
Inoculum + glucose	0.485	1.4	0.965	0.027	25.7	0.916
Inoculum	0.249	2.8	0.997	0.018	38.5	0.906
Waste A: Fresh organic waste collected from Danish households – 2. round						
Inoculum + waste	0.494	1.4	0.974	0.010	69.3	0.912
Inoculum + glucose	0.530	1.3	0.991	0.013	53.3	0.880
Inoculum	0.427	1.6	0.992	0.009	77.0	0.812
Waste B: Older pre-disposed waste from an American landfill						
Inoculum + waste	0.259	2.7	0.983	0.012	57.8	0.869
Inoculum + glucose	0.225	3.1	0.974	0.012	57.8	0.866
Inoculum	0.248	2.8	0.981	0.013	53.3	0.867
Waste C: Waste from a laboratory experimental digester simulating landfill conditions						
Inoculum + waste	0.298	2.3	0.960	0.010	69.3	0.867

Table 5.2 Time periods in days to reach a methane production of 20% vol. in anaerobic batch experiments with three different types of added waste materials.

Blowing agent	CFC-11	HFC-134a	HCFC-141b	HFC-245fa
Waste A: Fresh organic waste collected from Danish households – 1. round				
Inoculum + waste	16	18	12	26
Inoculum + glucose	19	20	22	35
Inoculum	35	35	65	70
Waste A: Fresh organic waste collected from Danish households – 2. round				
Inoculum + waste	26	108	115	108
Inoculum + glucose	27	116	117	117
Inoculum	33	113	122	116
Waste B: Older pre-disposed waste from an American landfill				
Inoculum + waste	26	55	45	35
Inoculum + glucose	22	45	42	35
Inoculum	38	85	52	61
Waste C: Waste from a laboratory experimental digester simulating landfill conditions				
Inoculum + waste	25	67	50	46

5.3 Anaerobic degradation of CFC-11 and formation of degradation products

The anaerobic degradation of CFC-11 and the formation of the lower chlorinated fluoro-methanes were studied in inoculated batch experiments added organic household waste. CFC-11 was degraded to HCFC-21, HCFC-31, and HFC-41 (c.f. figure 5.2). However, the degradation pattern did not indicate sequential dechlorination but rather a simultaneous production of HCFC-21, HCFC-31, and HFC-41. Furthermore, the production of degradation products did not correlate with a stoichiometric removal of CFC-11 indicating that other degradation products were produced. HCFC-21 and HCFC-31 were further degraded whereas no further degradation of HFC-41 was observed. No transformation of CFC-11 occurred in the sterilized control experiments and degradation products could not be identified.

To verify observed degradation patterns, batch experiments with high initial concentration of HCFC-21, HCFC-31 and HFC-41 were conducted. Figure 5.3 shows the anaerobic degradation of CFC-11, HCFC-21, HCFC-31, and HFC-41 in batch experiments containing organic household waste. The degradation rate was directly correlated with the number of chloride atoms attached to the carbon as the highest degradation rate was obtained for CFC-11, the lowest for HCFC-31, whereas no degradation of HFC-41 was observed (no difference between sterilized controls and active batch experiments – results not shown). The degradation of CFC-11 occurred approximately 10 times as fast as the degradation of HCFC-21, which occurred three times as fast as the degradation of HFC-31 (table 5.3). In experiments with HCFC-21 and HCFC-31, production of their respective lower chlorinated compounds were observed, however, never in amounts corresponding to a stoichiometric release. CFC-11 is generally considered to undergo reductive dechlorination through HCFC-21 to HCFC-31 (19,20). However, Krone et al. (48) studied the reductive dehalogenation of $CFCl_3$ by corrinoids with titanium (III) citrate as electron donor. The corrinoid protein $[Co^I]$ may mediate the dehalogenation of chlorinated C_1-hydrocarbons in anaerobic bacteria. CFC-11 was reduced by titanium (III) citrate in the presence of aquocobalamin. The major product was CO (67%); $CHFCl_2$ (<10%); and formate (<5%). CH_2FCl, CH_3F, $C_2F_2Cl_2$, and $C_2F_2Cl_4$ were identified as side products at low concentrations. The recovery was 90%. Lovley and Woodward (15) obtained transformation of both CFC-11 and CFC-12 during anaerobic incubation of samples from fresh water sediments and soils. Since no intermediates or end-products were detected, these authors suggested that the CFCs were transformed via CO as reported by Krone et al. (48).
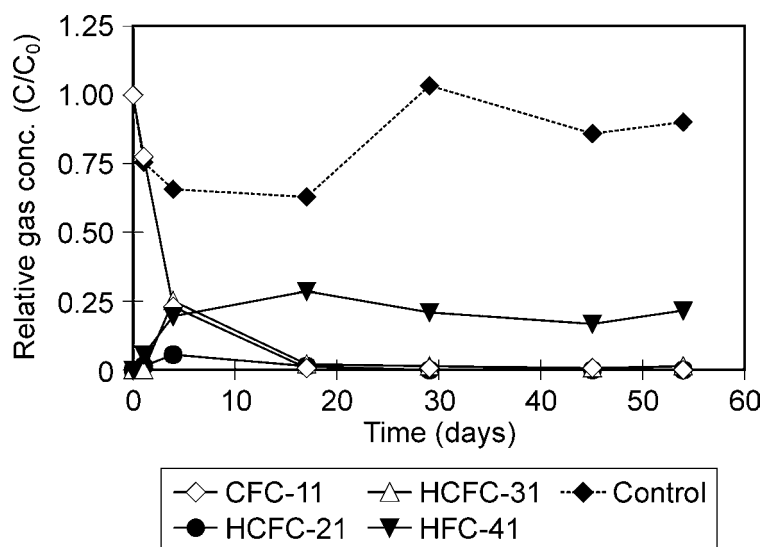

Figure 5.2 Anaerobic degradation of CFC-11 and formation of degradation products in a batch experiment containing organic household waste
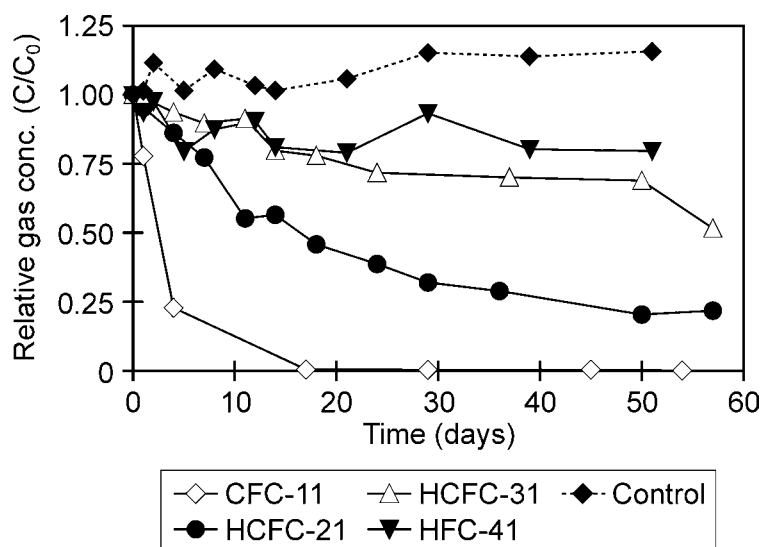
Figure 5.3 Anaerobic degradation of CFC-11, HCFC-21, HCFC-31, and HFC-41 in batch experiments containing organic household waste.

Table 5.3 First-order rate constants (k_1) and half-lifes ($t_{1/2}$) for anaerobic degradation of CFC-11, HCFC-21, HCFC-31, and HFC-41 in batch experiments containing organic household waste.

Blowing agent	Degradation rate k_1 days^{-1}	Half-life $t_{1/2}$ days	Regression coefficient R^2
CFC-11	0.317	2.2	0.998
HCFC-21	0.029	24.1	0.943
HCFC-31	0.011	65.4	0.900
HFC-41	n.d.	-	-

n.d.: no degradation observed

6. ANAEROBIC BATCH EXPERIMENTS WITH DIFFERENT AMOUNTS OF ORGANIC WASTE

Batch experiments with different amounts of waste (1, 5, 10g) were conducted in order to study the impact of the amount of waste on the degradation of CFC-11 and HCFC-141b compared to the amount of inoculum. Experiments were amended with two types of waste: fresh organic waste (A) and older pre-disposed waste from an American landfill (B). The experimental set-up is similar to the anaerobic batch experiments described in section 5.1 except that CFC-11 and HCFC-141b was added as a mixture instead of as single components.

6.1 Anaerobic degradation of CFC-11 and HCFC-141b in un-inoculated waste

In all inoculated experiments a fast degradation of CFC-11 was observed regardless of the type of waste and the amount of waste material (figure 6.1). The degradation followed first-order kinetics giving half-life times of 1.9-2.9 days (c.f. table 6.1), which are comparable with the results obtained in the similar experiments presented in section 5. However, degradation of CFC-11 was also observed in un-inoculated bottles only amended with pre-disposed waste even though at a slower rate compared to the inoculated experiments. The highest degradation rates were obtained in bottles containing 10g waste material, whereas almost no degradation was observed in bottles containing only 1g waste. In experiments with fresh household waste no degradation of CFC-11 was observed regardless of the amount of waste. The higher activity of the pre-disposed waste is probably a result of the fact that the micro-organisms have previously been exposed to halocarbons. They are therefore likely to be adapted to degradation of these components. The fresh organic waste, which consists of fruits, vegetable peals, bread and the like, holds only a small number of anaerobes (if any) and they have not previously been exposed to halocarbons. However, when methanogens are added in the form of the inoculum, the fresh waste material may have a high methane potential due to the more easily degradable carbon, which is observed in inoculated experiments. Similar degradation patterns were obtained for HCFC-141b, however, to a lesser degree due to the slower degradation rate. The degradation curves for HCFC-141b are shown in appendix 7, whereas the first-order degradation constants are listed in table 6.1. In the inoculated experiments HCFC-141b was degraded giving half-lifes of 35 days. However, in the un-inoculated experiments degradation was not really significant. The experiments have currently been running for 66 days, which based on the inoculated anaerobic batch experiments is the approximate time for 50% degradation of HCFC-141b when inoculum is added. However, when inoculum is omitted an degradation rate approximately 10 times slower rate is expected, based on the degradation results of CFC-11. This implies that a removal of HCFC-141b of only 10% after 66 days, which would be difficult to observe in the experiments. To obtain more significant degradation curves a longer run time for experiments with HCFC-141b would be desirable.
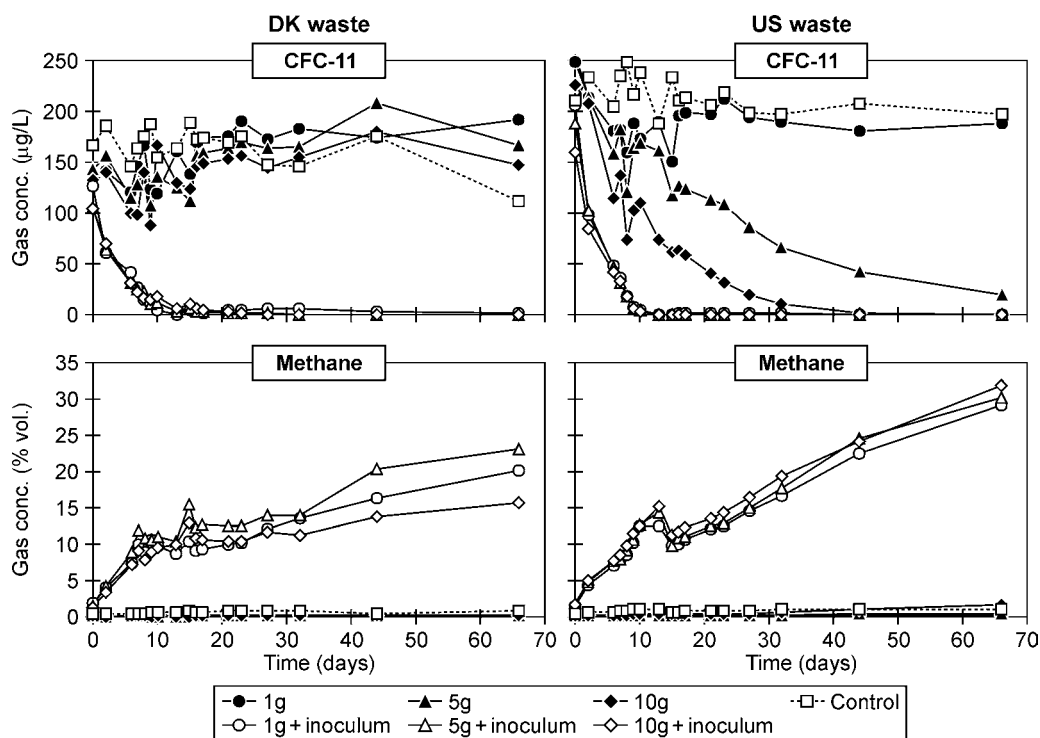
Figure 6.1 Anaerobic degradation of CFC-11 in inoculated (open symbols) and un-inoculated (filled symbols) batch experiments containing fresh household waste (first column) or waste from an anaerobic digester feed with US refuse (second column).

Table 6.1 First-order rate constants for anaerobic degradation of CFC-11 and HCFC-141b un-inoculated and inoculated batch experiments containing different amount of organic waste

Blowing agent	CFC-11			HCFC-141b		
	k_1 days^{-1}	$t_{\frac{1}{2}}$ days	R^2	k_1 days^{-1}	$t_{\frac{1}{2}}$ days	R^2
Waste A: Fresh organic waste collected from Danish households – 1. round						
Inoculum + 1g waste	0.293	2.4	0.897	0.020	34	0.661
Inoculum + 5g waste	0.220	3.2	0.956	0.020	34	0.729
Inoculum + 10g waste	0.205	3.4	0.957	0.020	34	0.623
1g waste	-	-	-	-	-	-
5g waste	-	-	-	-	-	-
10g waste	-	-	-	-	-	-
B: Older pre-disposed waste from an American landfill						
Inoculum + 1g waste	0.355	2.0	0.910	0.028	25	0.872
Inoculum + 5g waste	0.362	1.9	0.907	0.023	30	0.840
Inoculum + 10g waste	0.349	2.0	0.880	0.020	35	0.659
1g waste	-	-	-	-	-	-
5g waste	0.037	18.8	0.967	-	-	-
10g waste	0.096	7.2	0.976	-	-	-

7. ANAEROBIC BATCH EXPERIMENTS WITH WASTE AND FOAM

Batch experiments with waste mixed with pieces of insulation foam have been carried out. The purpose of the experiments was to study whether the presence of anaerobic bacteria can have a mitigating effect on the release of blowing agents from foam sources in landfilled waste.

7.1 Experimental set-up

The experimental procedure was similar to the procedure for the anaerobic batch experiment except that cut pieces of foam have been added to bottles instead of a fixed amount of blowing agent. Foam cylinders were cut using a cork bore (1cm diameter and 1cm height) and placed in 320mL incubation bottles equipped with Teflon coated rubber septa. Four foam pieces cut as cylinders were added to each foam-containing bottle. For comparison with batch release experiments reported in (2) all experiments were conducted with foam obtained from supplier B. The experimental set-up also included release experiments - bottles containing foam pieces and no waste plus different controls (bottles with a constant amount of blowing agent, bottles with sterile waste and foam etc. – table 7.1). The foam to air volume in the release experiments was approx. 105. Headspace samples were withdrawn and analyzed by gas chromatograph over time. The experiments ran for 14 weeks at room temperature. To the experiments with sterilized waste a fixed amount of CFC-11 was added instead of foam cylinders as there was a shortage of insulation foam blown with CFC-11.

Table 7.1 Experimental set-up of the anaerobic experiments with waste and foam

Contents	CFC-11	HFC-134a	HCFC-141b	HFC-245fa	Total
Inoculum + waste (type A) + foam	3	3	3	3	12
Inoculum + waste (type A) + foam sterile	2	2	2	2	8
Only foam	2	2	2	2	8
Blowing agent		2		2	4
Total amount of bottles					**32**

7.2 Release of blowing agents from insulation foam blown with four different BAs

Figure 7.1 shows accumulation of BA versus time (■-symbols). In general, similar releases are observed in bottles containing only foam pieces and bottles containing foam pieces and sterilized waste material. Release patterns are similar to previously conducted experiments reported in (2) where a high initial release rate, which subsequently decreases, is observed. For all foam types most of the BA loss happens during the first 120 to 240 hours, and decreases afterwards. The total loss when normalized to one foam cylinder was between 425 and 616 µg for CFC-11, HCFC-141b, and HFC-245fa, but was lower for HFC-134a, at approx. 228 µg. In order to compare the different foam types the loss is calculated as a percentage of the total initial BA concentration. The foam blown with CFC-11 and HFC-134a lost approx. 9%, while the foams blown with HCFC-141b and HFC-245fa lost approx. 16-19%.
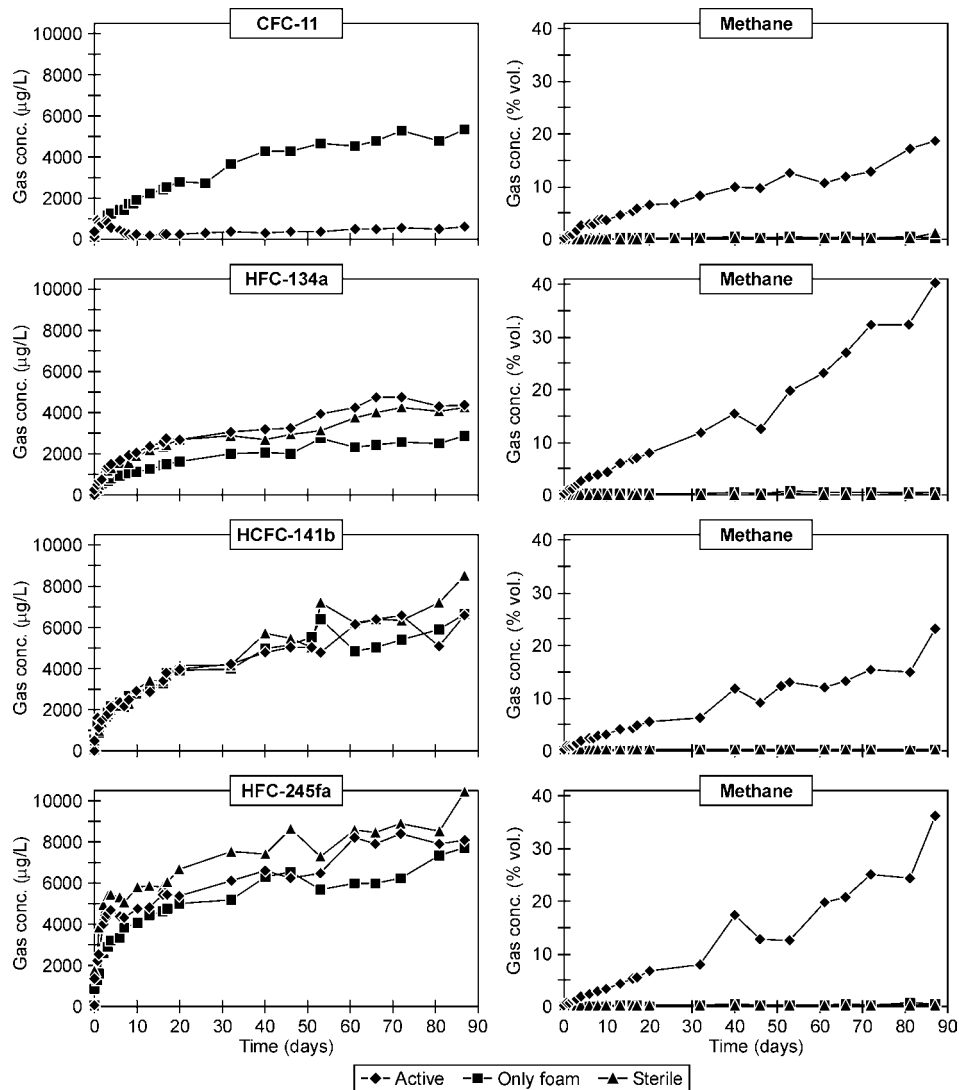
Figure 7.1 Anaerobic batch experiments with waste and foam.

Calculation of short term diffusion coefficients from batch experiments.

From the batch experiments only containing foam cylinders, the short term release is further evaluated by calculating diffusion coefficients using the double compartment release model as presented and used in Scheutz & Kjeldsen (2). The calculated diffusion coefficients are presented in Table 7.2, which also gives the diffusion coefficients determined in flux chamber experiments in Scheutz & Kjeldsen (2) for the same foam panels (supplier B). The experiments with foam blown with CFC-11 were, as mentioned previously, carried out on 1cm by 1cm cylinders cut from foam-cubes (5cm by 5cm) sampled from the original panel. Therefore some of the short term release had probably already occurred explaining the lower release compared to previous conducted release experiments. The numbers determined in this study are generally slightly lower than the original values. For HCFC-141b the value is significantly lower. The reason for this is not known but may be due to the fact that these values are determined in batch experiments, where the original values were determined from flux chamber experiments. Furthermore, the batch release experiments were conducted in 320mL containers with a foam to air volume of 105 compared to 1000mL containers in the previous project were the foam to air volume was 1444. It is therefore likely that the diffusion

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of blowing agent out of the foam in the current experiments was reduced due to accumulation of blowing agent in the gas phase which would lower the concentration gradient between foam and gas.

Table 7.2 Determination of short-term diffusion coefficients from batches containing only foam cylinders. The values are compared to diffusion coefficients determined in flux chamber experiments from Scheutz & Kjeldsen (2). All experiments used cylinders with d=1cm and h=1cm.

	Short-term release				Scheutz & Kjeldsen (2)
BA	$M_{0,1}$[a] (μg)	α_1[b] $(\mu g\ t^{-1/2})$	R^2[c]	D_1[d] $(10^{-12} m^2 s^{-1})$	D_1[d] $(10^{-12} m^2 s^{-1})$
CFC-11	250	10	.98	1.0[e]	4.1
HFC-134a	150	6	.993	1.0	1.5
HCFC-141b	370	13	.975	1.1	6.0
HFC-245fa	300	26	.9759	4.5	7.5

a: $M_{0,1}$ used as fitting parameter
b: Slope of best fitting line to M_t versus $t^{1/2}$
c: Correlation coefficient for the line fit

d: Calculated diffusion coefficient from expression $D = \dfrac{\pi \cdot \alpha^2}{4 M_0^2 \cdot (A/V)^2}$ given from Scheutz & Kjeldsen (2002) (2)

e: Approximatetive value since the foam cylinders were cut from smaller foam sample.

7.3 The potential of anaerobic bacteria in waste to mitigate the release of blowing agents from insulation foam

In experiments with active waste and inoculum, the microbial bacteria degrading CFC-11 mitigate the release of CFC-11 (figure 7.1). In experiments with HCFC-141b no tendency toward a microbial removal is observed, which is due to the degradation rate of HCFC-141b being almost 30 times slower than that of CFC-11. Simple calculations using the degradation rates obtained in the anaerobic degradation experiments showed that the microbial removal of HCFC-141b is insignificant compared to the release rate from foams. In experiments with HFC-134a and HFC-245fa no difference between microbially active and sterile bottles is observed, which was also expected based on the anaerobic degradation experiments where none of the two compounds were degraded.

In a landfill the distribution between phases (solid to liquid and solid to gas-ratios) is quite different from the experimental conditions in the batch containers. To predict the fate of CFC-11 and HCFC-141b under real conditions, these circumstances need to be included. This is covered in section 11 by use of a developed landfill model incorporating the BA release from foam.

8. AEROBIC BATCH EXPERIMENTS WITH SOIL

The potential for degradation of blowing agents was investigated in soil microcosms incubated with methane and atmospheric air, simulating the gas composition in landfill soil covers.

8.1 Experimental set-up

The oxidation process was examined in glass bottles (320 mL in total volume) equipped with Teflon-coated septa, which enables gas to be sampled or injected by a hypodermic needle and a syringe. A fixed amount of soil (50 g moist soil) was added to each batch container and the water content was adjusted to 25% w/w. The batch experiments were conducted with soil sampled at 15-20 cm below the surface. To obtain methanotrophic conditions, air was withdrawn from each container using a syringe and replaced with methane and oxygen, which gave initial mixture of methane (15% v/v), oxygen (30% v/v) and nitrogen (55% v/v). The initial concentrations of the blowing agents were selected so that they were in the range of typical trace gas concentrations in landfill gas (300 mg m^{-3}). Gas samples withdrawn from headspace were sampled periodically and analyzed by gas chromatography. Between sampling, the bottles were gently turned to ensure total mixed conditions in the batches. The batch experiments were conducted at room temperature (22°C). All batch experiments were carried out in series of three. In order to check if any disappearance could be due to non-microbial processes (abiotic degradation, sorption and volatilization) sodium azide (25 mg kg^{-1} soil) was added to avoid microbial growth in control batches. Table 8.1 shows the experimental set up.

Table 8.1 Experimental set up of aerobic batch experiments with soil pre-exposed to landfill gas.

Contents	CFC-11	HFC-134a	HCFC-141b	HFC-245fa	Total
Blowing agent + soil	3	3	3	3	12
Blowing agent + soil sterile		3		3	6
Total amount of bottles					**18**

8.2 Methane oxidation and degradation of blowing agents in soil microcosms.

In general, very good reproducibility was obtained and results from three replicate batches were almost identical. The soil showed a high capacity for methane oxidation resulting in very high oxidation rates of up to 132 μg CH$_4$ g^{-1} h^{-1} (table 8.2). In all soil microcosms methane and oxygen concentrations declined over time while carbon dioxide increased, showing that methane oxidation was taking place (figure 8.1). Lag phases were never observed, which indicates that the methanotrophic bacteria were present and well adapted to oxidizing methane. Lag phase is here defined as the duration of time between the addition of substrate to the soil and evidence of its detectable loss. The oxidation was microbially mediated as seen from comparison with the sterilized control batch (figure 8.1). The methane oxidation followed zero-order kinetics (R^2>0.977), indicating that the oxidation was not methane-limited. In all experiments the oxygen concentrations were never below 10% v/v and methane oxidation was therefore not limited by low oxygen concentration (as exemplified by figure 8.1). Czepiel et al. (49) found that methane oxidation in incubation experiments

became sensitive to oxygen mixing ratios when below approximately 3 % v/v, resulting in lower oxidation rates. The methane oxidation rates are very high compared to those reported by Whalen et al. (28) and Jones and Nedwell (27), who obtained maximum oxidation rates between 0.65 and 2.7 µg CH_4 g^{-1} h^{-1}. The obtained methane oxidation rates fit well with the results gained by Figueroa (50) who reported maximum rates between 40 and 128 µg CH_4 g^{-1} h^{-1} for different landfill cover soils. Maximal methane oxidation rates reported in the literature show a wide range between 0.0024-128 µg CH_4 g^{-1} h^{-1}, even when comparing experiments conducted with landfill cover soils (51). This variation is probably due to differences in methane concentrations during incubation, organic content, soil moisture, and temperature, which will influence the activity of the soil.

However, none of the four blowing agents studied were degraded during the run of the experiment as no difference between microbially active and sterilized experiments was observed (figure 8.2). The concentration loss over time observed in both active and sterilized batches is probably due to sorption to the soil. In order to ensure a sufficient exposure time the experiment was repeated in total four times where methane and blowing agents were re-added to all bottles. For each re-addition of methane an increase in the methane oxidation rate was observed indicating bacterial growth (figure 8.3). However, re-addition of methane did not have an effect on the concentrations of blowing agents.

Information on co-oxidation of fluorinated hydrocarbons reported in the open literature is very limited. DeFlaun et al. (41) studied the oxidation of hydrochlorofluorocarbons by *Methylosinus trichosporium* OB3b and obtained aerobic degradation of three out of the five halocarbons tested - including HCFC-21, and HCFC-141b. However, CFC-11 and HFC-134a were not degraded, which is in line with the aerobic experiments conducted in this study. Streger et al. (45) studied the degradation of hydrohalocarbons by three bacterial strains of naturally occurring methanotrophs. One of the bacterial strains *Methylosinus trichosporium* OB3b transformed HCFC-141b. None of the tested bacteria were able to degrade HFC-134a. Chang and Criddle (42) report bio-transformation of HFC-134a in a mixed methanotrophic culture. The mixed methanotrophic culture also contained at least three heterotrophs and it is therefore possible that they facilitated the transformation of HFC-134a. The negative impact of CFCs and HCFCs on the stratospheric ozone layer has prompted an effort for environmentally acceptable alternatives like the non-chlorinated hydrofluorocarbons. HFC-245fa is a new substitute for the HCFCs used as blowing agents used in insulation foams - no references in the open literature on co-metabolic degradation by methanotrophs are know to the authors. CFCs are considered inert towards bio-transformation under aerobic conditions (25,40). The presence of one or more hydrogen atoms in HCFCs and HFCs make these compounds susceptible to undergo oxidation. The strong chemical carbon-fluoride bond provides greater stability to the HFCs compared to chlorinated hydrocarbons, suggesting that HFCs in general would be more resistant to microbial degradation. Although HFCs are good replacements for HCFCs as a result of their zero ozone depletion potential. Even though the HFCs have lower global warming potential compared to the HCFCs their contribution to global warming may still be important if they are resistant to microbial transformation.
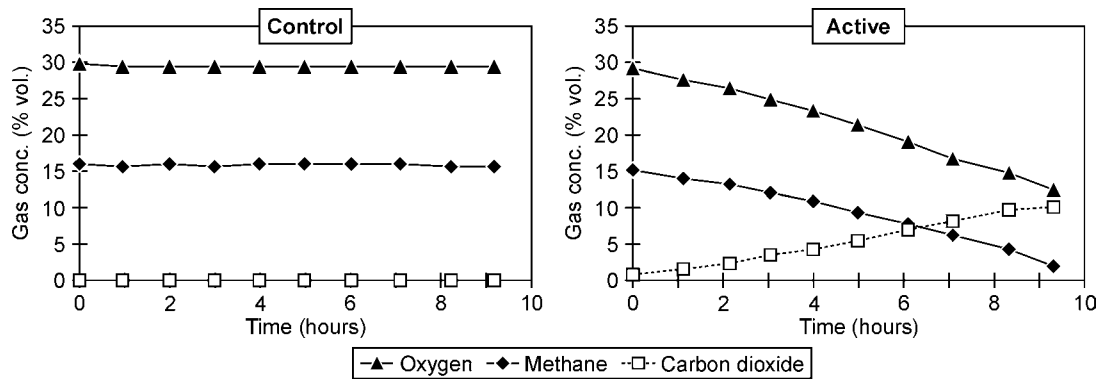
Figure 8.1 Headspace concentration of methane, oxygen and carbon dioxide as function of time, showing methane oxidation in a batch experiment containing 50 g soil sampled at 15-20 cm below the soil surface. A. Control experiment. B. Active batch experiment.
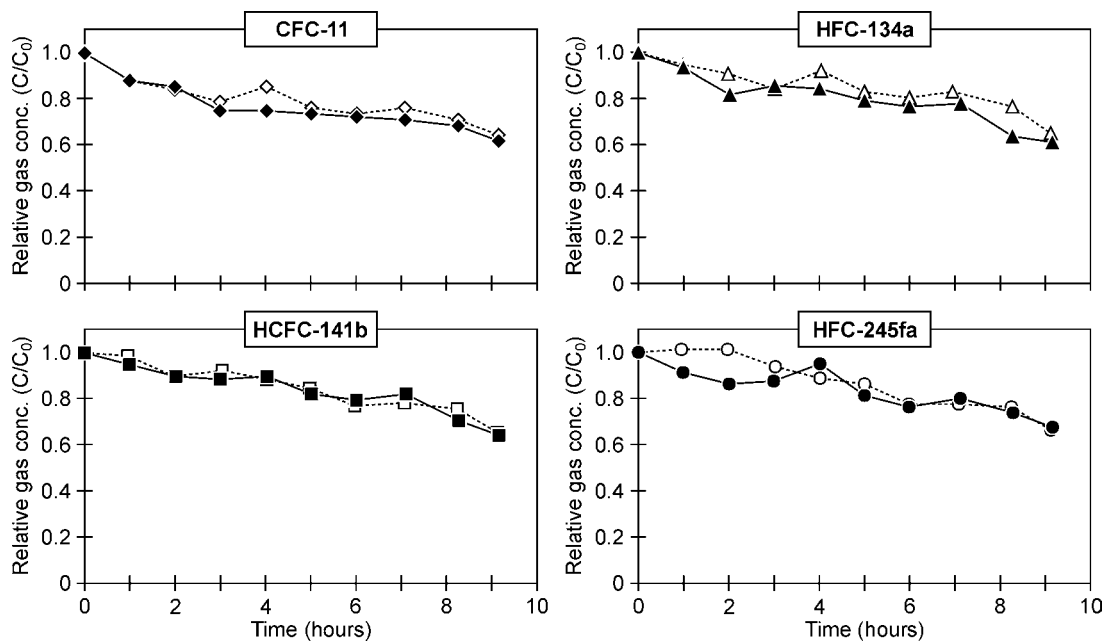

Figure 8.2 Relative headspace concentration of halocarbons as a function of time in aerobic batch experiment, containing 50 g soil pre-exposed to landfill gas.
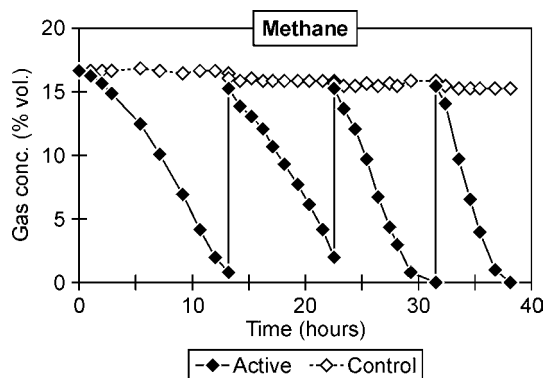
Figure 8.3 Methane oxidation by re-addition of methane in a batch experiment, containing 50 g soil pre-exposed to landfill gas.

Table 8.2 Calculated maximal oxidation concentrations based on zero-order oxidation rates obtained from batch experiments.

Blowing agent	Addition of methane	Methane oxidation rate $\mu g \cdot g^{-1} \cdot h^{-1}$	Regression coefficient R^2
CFC-11	1	56	0.980
	2	66	0.989
	3	98	0.987
	4	125	0.977
HFC-134a	1	56	0.978
	2	70	0.989
	3	102	0.985
	4	132	0.983
HCFC-141b	1	56	0.977
	2	70	0.978
	3	99	0.983
	4	122	0.982
HFC-245fa	1	59	0.979
	2	71	0.985
	3	102	0.978
	4	114	0.977

9. ANEROBIC BATCH EXPERIMENTS WITH SOIL

The potential for anaerobic degradation of blowing agents was investigated in soil microcosms flushed with nitrogen. Soil sampled from approximately 60-70 cm below the surface, which is in the anaerobic zone of the cover layer at Skellingsted Landfill, was used in the experiments. The experimental set-up was similar to the aerobic batch experiments described in 8.1.

9. 1 Anaerobic degradation of blowing agents in soil microcosms

CFC-11 and HCFC-141b were degraded over time in anaerobic soil microcosms, whereas no degradation of HFC-134a and HFC-245fa was observed within the run of the experiment (Figure 9.1). For both CFC-11 and HCFC-141b degradation occurred after a lag phase of 40 days. The degradation of CFC-11 occurred almost twice as fast as the degradation of HCFC-141b giving degradation rates of 0.02 and 0.01 $\mu g \, g \, soil^{-1} d^{-1}$ respectively. The oxidation was microbially mediated as seen from comparison with the sterilized control batch. Figure 9.1 shows the results of a control experiment with CFC-11. Scheutz and Kjeldsen (31) found anaerobic degradation rates for CFC-11 of 0.2 $\mu g \, g \, soil^{-1} d^{-1}$ in similar soil microcosms. The relatively low degradation capacity obtained in the current study may be due to a longer exposure time to oxygen during sample preparation (soil was left to dry in the laboratory) and storage, as some anaerobes are sensitive to oxygen. This will cause a longer adaptation period to re-establish an anaerobic microbial community, as also indicated by the relatively long lag phase.
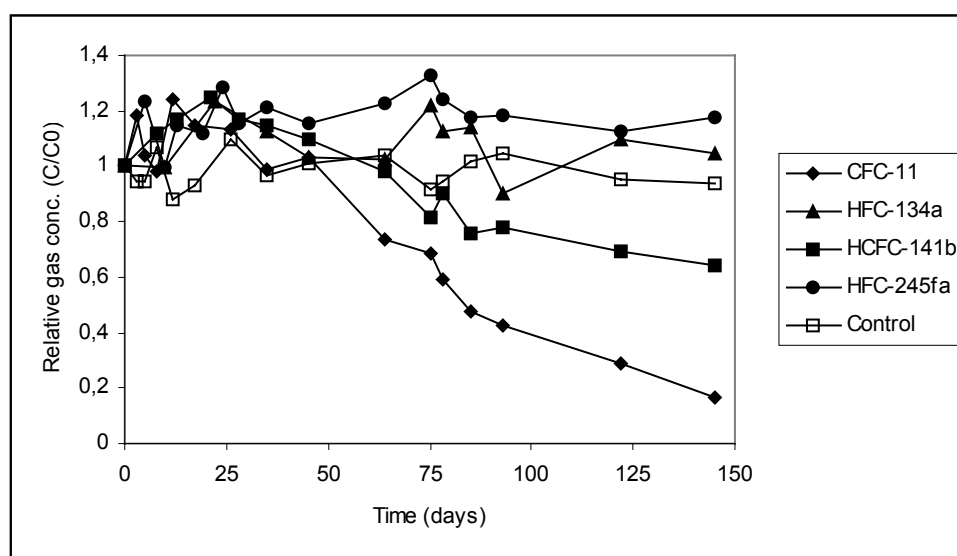

Figure 9.1 Relative headspace concentration of halocarbons as a function of time in anaerobic batch experiment, containing 50 g soil pre-exposed to landfill gas. The control curve is for CFC-11.

10. SOIL COLUMNS EXPERIMENTS

The potential of degradation of the four blowing agents was studied in a dynamic column set-up simulating a landfill top cover soil matrix through which gas is transported. The system allows the degradation process to be studied in a methane and oxygen counter-gradient system.

10.1 Experimental set-up

The columns were packed with landfill cover soil from Skellingsted Landfill, and continuously fed in opposite ends with artificial landfill gas containing the blowing agents and air. The system consists of a tube made of rigid PVC, 100 cm long by 8 cm internal diameter (figure 10.1). The PVC tube is closed at both ends with PVC end caps fitted with rubber O-rings to ensure a gas-tight fit. The PVC cap positioned at the bottom end of the column has one inlet while the PVC cap positioned at the top end of the column has one inlet and one outlet. A perforated plate was located at the bottom of the column so that soil could be packed in the tube. A layer of sterilized gravel (3 cm) was placed at the bottom of the column to ensure homogenous gas distribution. Sampling ports were located along the column length at intervals of 5 cm from the first port, which was positioned 5 cm from the inlet at the bottom. The sampling ports were equipped with teflon-coated silicone septa, which enabled the taking of gas samples by a gas tight syringe needle. The gas samples (3 mL) were transferred into evacuated glass tubes (Venoject, Terumo Europe n.v., Belgium) and analyzed on a gas chromatograph equipped with a mass spectrometer. The artificial landfill gas, which consisted of 50:50% vol. CH_4/CO_2 was kept in Tedlar bags (SKC Inc., Eighty Four, PA) and fed to the bottom inlet of the column by gas tight piston pumps (FMI Lab Pump, model QG, Fluid Metering Inc., Syosset, NY). The blowing agents (CFC-11, HFC-134a, HCFC-141b, HFC-245fa) were added to the CH_4/CO_2-mixture in the gas-bags – one compound per column. The inlet concentrations varied between 100 and 500 μg/L, which is within the range of typical landfill gas concentrations of trace gasses. Atmospheric conditions were obtained at the top of the column by passing an air stream through the chamber on top of the soil column (60 mL/min). This simulates ambient air over soil cover surface with O_2 supply by vertical diffusion into the soil column. To control mass balance for the system, gas samples were taken from the gas-bags and from the outlets of the columns. The experiments were carried out at room temperature (22°C). The inlet flow at the bottom of the column was 3 mL/min corresponding to a gas flux of 0.86 m^3 LFG·m^{-2}·d^{-1} and a methane flux of 280 g·m^{-2}·d^{-1}, which is in the mid-range of reported landfill methane fluxes. The experimental set-up included five soil columns: four microbial active columns permeated with CFC-11, HFC-134a, HCFC-141b, and HFC-245fa respectively and a control column permeated with a mixture of the four blowing agents. The control column was identical to the active columns except that the soil had been sterilized by autoclaving to avoid microbial activity.
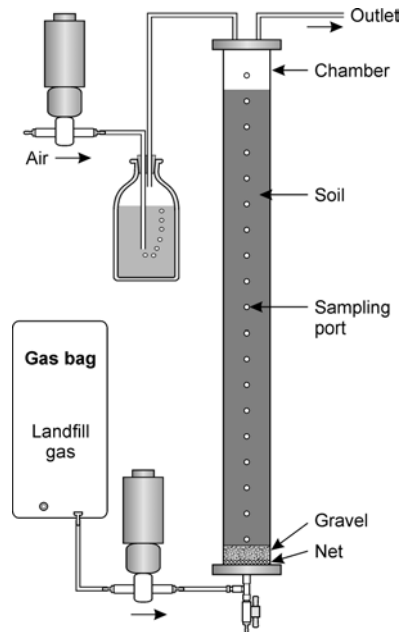
Figure 10.1 The dynamic column set-up

10.2 Methane oxidation and degradation of blowing agents in a dynamic column systems

Methane.
Figure 10.2 shows a representative gas depth profile of methane, carbon dioxide, oxygen, and nitrogen for the control column. In the control column the concentration profiles for CH_4 and CO_2 were almost identical and showed a decrease upwards to the top. The concentration profiles for O_2 and N_2 show that air was penetrating throughout the whole column diluting the concentration of CH_4 and CO_2. Figure 10.2 shows a representative gas depth profile of methane, carbon dioxide, oxygen, and nitrogen for an active column. The CH_4-concentration profile shows a decrease upward toward the surface. Compared to CH_4 the upward decrease in the concentration for CO_2 is much less pronounced, indicating CO_2 production. The O_2 and N_2 concentration profiles show that air is diffusing into the soil matrix from the ambient air. The O_2 concentration declines downward with depth and from 20 cm down the column become anaerobic. The removal of O_2 and increasing CO_2/CH_4 ratio upward in the column strongly indicates methane oxidation, as the methanotrophic bacteria use methane and oxygen while they produce carbon dioxide. The N_2 concentration is a little higher in the lower part of the active column compared to the control column. This is caused by a volume reduction from methane oxidation (three moles turning into one mole) creating an under-pressure and thereby enhancing the transport of atmospheric air into soil system. Increasing supply of O_2 into the column will have a positive effect on methane oxidation. The significant effect of the methane oxidation process on the physical gas transport behavior in the column causes the mechanisms controlling the gas flow to be complex including both advective and diffusive transport and makes it difficult to compare gas profiles from the active and control columns directly.

All four soil columns show a high capacity of methane oxidation giving maximal methane oxidation rates up to 240 g m^{-2} d^{-1} corresponding to a reduction of 93% (table 10.1). Steady state gas profiles were obtained within the first four days after start-up, indicating that a microbial community of methanotrophs was already well established in the soil. During the first two-month measuring campaign, the columns showed a relatively stable activity, as the removal was fairly constant during this period. A second measuring campaign conducted four

months after start-up showed a small reduction in the methane oxidation capacity probably due to accumulation of oxidation products (table 10.1). The methane mass balance for the control column was 98 % (±6) recovery indicating no losses and insuring a tight system. The obtained methane oxidation rates are consistent with results reported by Kightley and co-workers (52) who obtained maximum rates of 166 g m^{-2} d^{-1} in soil cores of porous coarse sand collected from a landfill site known to emit methane. De Visscher and co-workers (30) also found comparable oxidation capacities of up to 240 g m^{-2} column d^{-1} in columns packed with soil originating from a landfill cover.

Blowing agents.
Figure 10.3 shows the vertical concentration profiles for column experiments permeated with CFC-11, HFC-134a, HCFC-141b and HFC-245fa. In the control column the concentration profiles for the four blowing agents are almost identical and show a decrease towards the top due to dilution with air. Based on mass balances no degradation was observed in the control column. The mass balances for the four compounds varied between 97-98 % (±6) recovery indicating no losses and insuring a tight system. CFC-11 and HCFC-141b were degraded in the active soil columns. The average degradation capacities for CFC-11 and HCFC-141b during the first two months were both.03 g m^{-2} d^{-1} corresponding to a removal efficiency of 38% and 27% respectively. An increase in the degradation capacities for CFC-11 and HCFC-141b was observed during the four-month operation period of the soil columns indicating growth of the microbial population. The average degradation capacities for CFC-11 and HCFC-141b during the second measuring campaign were 0.07 and 0.05 g m^{-2} d^{-1} corresponding to a removal efficiency of 75% and 42% respectively. Figure 10.4 shows the removal efficiency of the blowing agents as a function of time. Table 10.1 shows the removal efficiencies and degradation capacities obtained based on total mass balances. Appearance of very low concentrations of HCFC-21 in the column indicated that CFC-11 was partly anaerobically dechlorinated, resulting in accumulation of HCFC-21 (figure 10.5). The concentration profile for HCFC-21 showed a maximum around 20-cm depth in the column indicating oxidation of HCFC-21 in the upper part of the column with overlapping O$_2$ and CH$_4$ gradients. HCFC-31 and HFC-41 could not be detected. Similarly, HCFC-21, HCFC-31, and HFC-41 could not be detected in the control column. The expected degradation pathway for highly chlorinated methanes under anaerobic conditions is through reductive dechlorination, resulting in accumulation of HCFC-21 and HCFC-31 (24). However, as demonstrated by Scheutz et al. (31), HCFC-21 can be oxidized in the upper aerobic zone in landfill top covers due to their rapid oxidation by the methanotrophic bacteria. Degradation products of HCFC-141b were not targeted. The degradation of HCFC-141b is most likely also a result of anaerobic degradation in the lower part of the columns, as no degradation was observed in the aerobic batch experiments. Furthermore, HCFC-141b was degradable in anaerobic batch experiments even though the degradation occurred relatively slowly and only after a long lag phase. The removal rates obtained for CFC-11 are lower than results previously reported by Scheutz and co-workers (31) who obtained removals of 92% in similar soil columns also with soil from Skellingsted landfill. The reason for has not been identified. However, several possible explanations exist, such as differences in gas porosity and soil moisture content. Finally the soil was collected at two different sites approximately 6 meters apart – and the two soils could therefore have different microbial populations due to differences in gas migration and thereby gas exposure.

No degradation of HFC-134a and HCFC-245fa was observed within the duration of the experiment. The resistance to degradation of HCF-134a and HFC-245fa is probably a result of the higher stability owing to the presence of carbon-fluoride bonds.
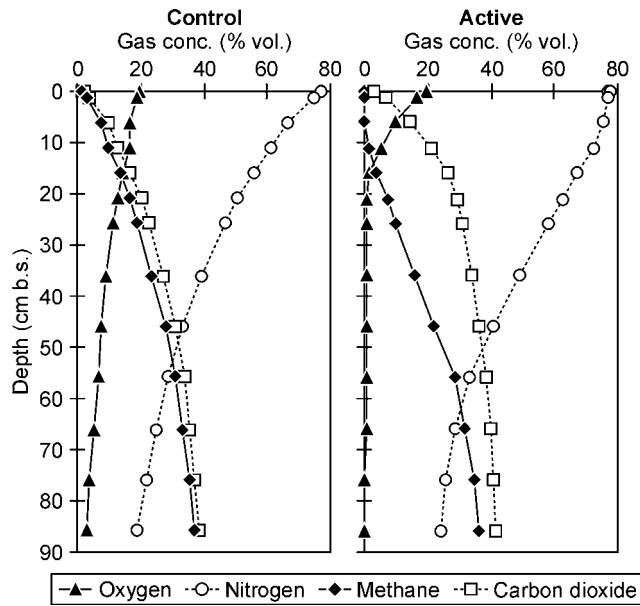
Figure 10.2 Vertical concentration profiles in a control and an active soil column permeated with artificial landfill gas.
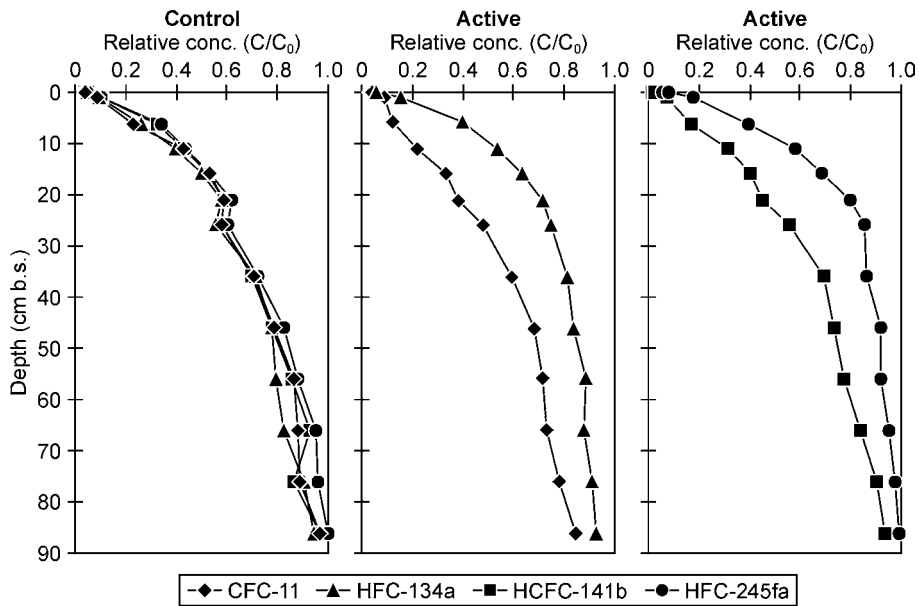

Figure 10.3 Vertical concentration profiles in a control and an active soil column permeated with artificial landfill gas.
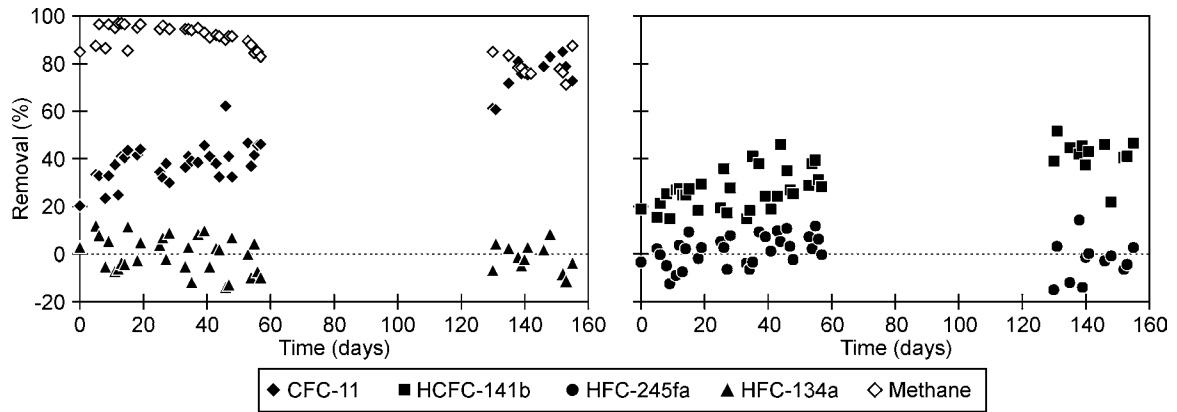
Figure 10.4 Removal efficiency in soil columns over time.

Table 10.1 Average removal capacities of methane and halocarbons obtained in soil column experiments permeated with artificial landfill gas (50% vol. CH_4 and 50% vol. CO_2).

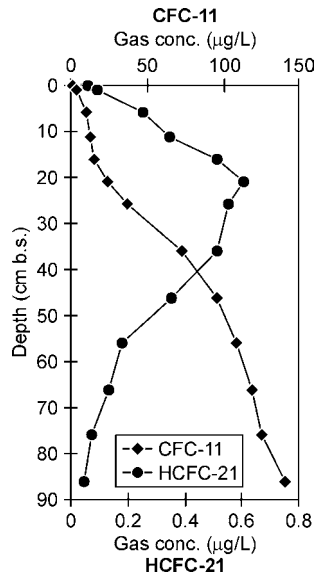| Blowing agent | C_{inlet} | Active column | | | |
| | | Methane oxidation | | Degradation of blowing agents | |
		Efficiency	Capacity	Efficiency	Capacity
	$\mu g\ L^{-1}$	%	$g\ m^{-2}\ d^{-1}$	%	$g\ m^{-2}\ d^{-1}$
1. period					
CFC-11	86	92	240	38	0.03
HCFC-141b	133	85	221	27	0.03
HFC-134a	143	84	207	n.d.	n.d.
HFC-245fa	193	84	221	n.d.	n.d.
2. period					
CFC-11	108	79	194	75	0.07
HCFC-141b	161	78	203	42	0.05
HFC-134a	290	79	207	n.d.	n.d.
HFC-245fa	275	66	175	n.d.	n.d.

Figure 10.5 Accumulation of HCFC-21 in columns permeated with CFC-11. Note the different concentration scales.

11. MODELING OF EMISSIONS AND DEGRADATION OF FOAM RELEASED HALOCARBONS IN LANDFILLS

The integrated evaluation of the fate of halocarbons contained in foam waste disposed of in a landfill was carried out by extending the MOCLA model, which was developed at Environment & Resources DTU (53). The original model, which is described in the following section, did not contain a compartment (i.e. foam) continuously releasing the blowing agent to the pore air space of the landfilled waste. In section 12.2 a new version of MOCLA, which has been developed as part of this project is presented. A typical landfill scenario is given and results of the fate modeling of the blowing agent in the landfill scenario are presented.

11.1 Overview of the MOCLA model

The setup for the simple model, called MOCLA (Model for Organic Chemicals in LAndfills) is shown in Figure 11.1. The model is based on the box model principle assuming fully mixed conditions within the landfill. This means that all phase concentrations are assumed to be constant in space. Others have modeled landfill as a plug flow reactor both regarding the flow of gas and water. The few full scale tracer studies that have been carried out on landfills (54,55), suggest that the retention time distribution is closer to a retention time distribution for a fully mixed reactor than for a plug flow reactor, probably due to a significant flow of the water in channels within the waste (53). The advantages of the fully mixed reactor assumption are that simpler mathematics and less input data are required.
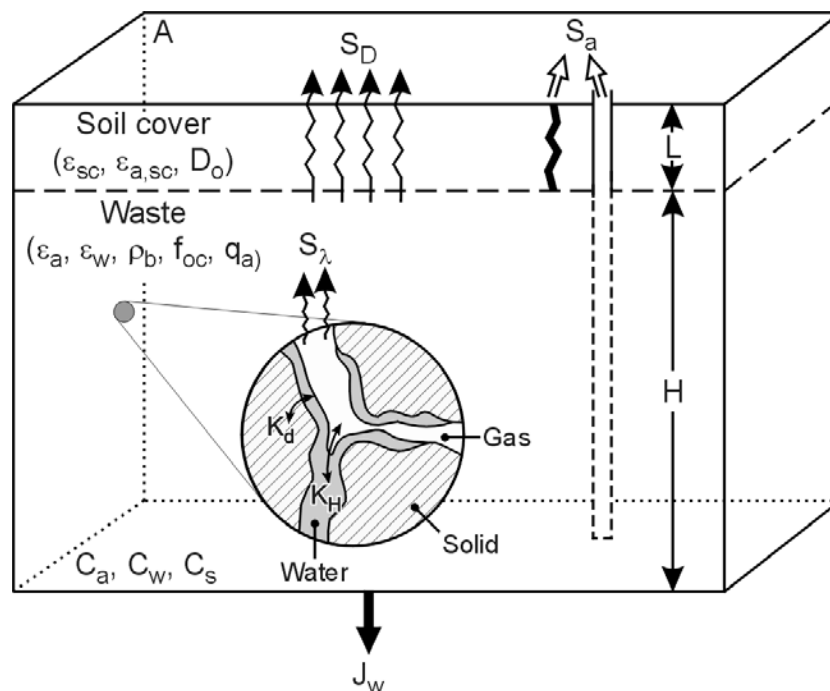

Figure 11.1   Setup for the MOCLA model, showing the basic partition in the blown-up sketch and the fate routes: Gas flow (S_a), diffusion through soil cover (S_D), leaching (S_w) and transformation (S_λ).

The model assumes that, within a volume of waste, an organic chemical will be in equilibrium with the waste components and will be distributed in the water/leachate phase, in the air/gas phase and sorbed to the solid waste (see Figure 11.1).

At equilibrium, two equations describe the relationship between the phases. The relationship between the gas phase and the water phase is described by Henry's constant, K_H (m^3 water/m^3 air). The relationship between the solid phase and the water phase is described by the distribution coefficient, K_d (m^3 water/tonne dry waste). K_d may be estimated according to the following relation, which is often used in soils and sediments:

$$K_d = f_{oc} K_{oc}$$

where:

f_{oc} is the fraction of organic carbon in the dry waste (tonne organic carbon/tonne dry waste)

K_{oc} is the distribution coefficient onto solid organic carbon (m^3 water/tonne carbon)

The overall result of the degradation processes is expressed in terms of a first order transformation constant related to the concentration in the leachate by λ, the first order transformation constant (year^{-1}).

The leachate and gas generated in the landfill may transport organic chemicals out of the waste and significantly affect the fate of the chemicals. The flows of leachate and gas are expressed as annual averages and are related to volume and area of the landfill, respectively, and to net precipitation.

Organic chemicals may also be transported out of the landfill by gas diffusion through the top soil cover of the landfill. The diffusion is controlled by Fick´s law, and the diffusional transport through the top cover is considered quasi-stationary. The diffusion coefficient in the soil pore air of the top cover is calculated from the free air diffusion coefficient by the Millington-Quirk relationship (56). The model does not take into account any attenuating processes that may occur in the top cover. One important process for some of the contaminants may be aerobic degradation in the top soil due to diffusion of oxygen into the top cover (31,57). This means that in the case where diffusive transport is more significant than advective flux, the model may, for some chemicals, overestimate the amount entering the atmosphere.

The MOCLA model is described in Box 11.1 and 11.2 where the basic equations are given. More details are given in Kjeldsen and Christensen (53).

11.2 Extending the MOCLA model to use time dependent release of organic compounds from waste co-disposed in the landfill: MOCLA-FOAM

The original MOCLA model did not contain the option that an organic compound may be released from special waste, such as the blowing agent used in insulation polyurethane foam. Scheutz & Kjeldsen (2) showed that the release is highly time dependent and can be described by a diffusion controlled model assuming an initial content of blowing agent in the foam, a known geometry of the foam waste particles and a controlling diffusion coefficient. Since the release rate is time dependent, a new spreadsheet version of MOCLA has been developed. The new version is based on a step-wise solution, with a fixed blowing agent release rate for each time step. The fixed release rate for a certain time step is first calculated from a release sub-model (see box 11.3). A new basic MOCLA model containing a compartment which is releasing the blowing agent with a constant rate, MOCLA-FOAM is developed (Box 11.3)

Using the release rate given by the release sub-model, the MOCLA-FOAM model is used to calculate the resulting total concentrations of blowing agent at the end of the time step. These values are then used as the new initial total concentration for the following time period in a new MOCLA-FOAM calculation. This method is continued through the whole period, and accumulative emissions were calculated by summing up contributions for each time step as calculated by the equations given in Box 11.4.

Box 11.1.   The basic equations of the MOCLA model

The total concentration of the chemical C_T (g chemical/m³ of landfill) at any time, t, can be calculated with the equation:

$$C_T = C_{T,o} \exp\left(-\frac{k}{R_a} \cdot t\right) \qquad (B1.1)$$

where:

$C_{T,0}$ is the initial total concentration (g chemical/m³ of landfill)

$$k = q_a' + \frac{N}{H K_H} + \frac{\varepsilon_w \lambda}{K_H} \qquad (B1.2)$$

R_a is the retardation factor:

$$R_a = \frac{\rho_b \cdot f_{oc} \cdot K_{oc} + \varepsilon_w}{K_H} + \varepsilon_a \qquad (B1.3)$$

q_a' is calculated as shown in Box 11.2 (equation B2.1)
N is the yearly net precipitation (m/year)
H is the total depth of waste (m)
$K_{H,j}$ is the dimensionless Henry's laws constant (m³ water/m³ air)
f_{oc} is the fraction of organic carbon in the dry waste (tonne organic carbon/tonne dry waste)
K_{oc} is the distribution coefficient onto solid organic carbon (m³ water/tonne carbon) as calculated as shown in Box 11.2
λ is the first order transformation constant (year^{-1})
ρ_b is the dry bulk density of the waste in the landfill (tonne dry waste/m³ of landfill)
ε_w is the volumetric content of water in the landfill (m³ of water/m³ of landfill)
ε_a is the volumetric content of air in the landfill (m³ of air/m³ of landfill)

The emissions with LFG (E_a), by diffusion through top cover (E_D) and with leachate (E_w) can be calculated by the following equations

$$E_a(t) = \frac{V q_a}{R_a} \cdot C_T(t) \qquad (B1.4)$$

$$E_D(t) = \frac{Q_D}{R_a} \cdot C_T(t) \qquad (B1.5)$$

$$E_w(t) = \frac{NA}{K_H R_a} \cdot C_T(t) \qquad (B1.6)$$

where $Q_D = V \cdot q_D$

Box 11.2.   More equations for use in the MOCLA model

The sum of specific gas flow and diffusional "flow" is seen as a resulting specific gas flow $q_a^{'}$:

$$q_a^{'} = q_a + q_D \qquad \text{(B2.1)}$$

where q_a is the specific gas production rate (m^3 landfill gas/(m^3 waste· year))

The diffusional flow q_D is calculated from the equation:

$$q_D = \frac{\varepsilon_{a,SC}^{10/3} D_o A}{\varepsilon_{SC}^2 LV} \qquad \text{(B2.2)}$$

where

D_o is the diffusion coefficient of the chemical in air at given temperature (m^2/year)
ε_{SC} is the total porosity of the soil cover (m^3 of pore space/m^3 of soil cover)
$\varepsilon_{a,SC}$ is the volumetric content of air in the soil cover (m^3 of air/m^3 of soil cover)
L is the thickness of the soil cover (m)
A is the surface area of the landfill (m^2)
V is the total volume of waste in the landfill (m^3)

D_o can be estimated from the following equation and data for a reference chemical:

$$D_{0,2} = D_{0,1} \sqrt{\frac{MW_1}{MW_2}} \qquad \text{(B2.3)}$$

where $D_{0,1}$ and MW_1 are diffusion coefficient in air and mole weight respectively for a reference chemical, and MW_2 is the mole weight for the chemical in question. (Data for benzene as a reference can be used ($D_{0,1} = 9.1 \cdot 10^{-6}$ m^2 s^{-1}, $MW_1 = 78.1$ g/mole).

K_{oc}, the distribution coefficient onto solid organic carbon (m^3 water/tonne carbon) is calculated from the equation:

$$logK_{oc} = 0.72 \cdot logK_{ow} + 0.49 \qquad \text{(B2.4)}$$

where

K_{ow} is the octanol-water distribution coefficient (dimensionless)

Box 11.3   Basic equations of the MOCLA-FOAM model

Besides the processes contained in the MOCLA model a constant release rate of the chemical, r (in g chemical/(m^3 of landfill and year), is assumed. Including that in the original mass balance of the landfill gives (see Figure 11.1):

$$\frac{d(VC_T)}{dt} = -(S_a + S_D + S_w + S_\lambda) + r \cdot V$$

This equation is changed to the following differential equation using the symbols given in Box x.1 and x.2):

$$\frac{d(C_T)}{dt} = -\frac{k}{R_a}C_T + r$$

The total concentration of the chemical C_T (g chemical/m^3 of landfill) at any time, t, can be calculated with the equation:

$$C_T(t) = \frac{r \cdot R_a}{k}\exp\left(-\frac{k}{R_a} \cdot t\right) + C_{T,o}\exp\left(-\frac{k}{R_a} \cdot t\right) \tag{B3.1}$$

The definitions of the symbols are given in Box 11.1.

The time dependency of the release rate is calculated assuming an *infinite bath* scenario (i.e. the release is independent of the concentration in the space surrounding the foam particle). The release, F_t (in g year^{-1}) from a spherical particle with the radius a ($M_0 = C_0 \cdot V_p = 4\pi a^3 C_0/3$, where V_p is the volume of the sphere and M_0 is in g) is (2):

$$F_t = \frac{6M_0 D}{a^2}\sum_{n=1}^{\infty}\exp\left\{-Dn^2\pi^2 t / a^2\right\} \tag{4}$$

D is the diffusion coefficient of the blowing agent in the foam (in m^2 year^{-1}).

For other geometrical shapes the following short-term approximations (only valid for the first release) can be used (2):

$$F_t = M_0\left(\frac{A}{V_p}\right)\sqrt{\frac{D}{\pi \cdot t}} \tag{7}$$

where (A/V_p) is the ratio of the external surface area of the particle to the volume.

The release rate, r (in g/ m^3 landfill · year) is:

$$r = \frac{\varepsilon_f \cdot F_t}{V_p}$$

where ε_f is the volumetric content of foam (m^3 foam/m^3 landfill)

Box 11.4   Equations in the MOCLA-FOAM model

From the solution given in Box 11.3 the following fate routes can be determined. The equations is given for time t= 0 until time t and for constant release rate, r. Due to the time-dependency of the release rate, r, from the foam, the mass degraded or emitted must be calculated for each discrete time step in the spreadsheet model and summed up to obtain information about the importance of each potential fate route for the blowing agent in relation to the period starting with disposal until present.

Mass degraded from time=0 until t (in kg):

$$F_\lambda = \frac{\varepsilon_w \cdot V \cdot \lambda}{R_a \cdot K_H} \int_0^t C_T(t)dt$$

Mass emitted with landfill gas from time=0 until t (in kg):

$$F_a = \frac{(q_a + q_D) \cdot V}{R_a} \int_0^t C_T(t)dt$$

Mass emitted with landfill leachate from time=0 until t (in kg):

$$F_a = \frac{N \cdot A}{R_a \cdot K_H} \int_0^t C_T(t)dt$$

where

$$\int_0^t C_T(t)dt = \frac{r \cdot R_a}{k} \left[t - \frac{R_a}{k} \left(1 - e^{-\frac{k}{R_a}t} \right) \right] + C_{T,0} \cdot \frac{R_a}{k} \left(1 - e^{-\frac{k}{R_a}t} \right)$$

11.3 Input data for default model runs

A landfill reactor scenario is given where the foam is cut into pieces (5 cm cubes) and co-disposed together with a mixture of organic wastes without any compaction. The landfill reactor is assumed of limited size (in comparison to typical whole landfill sizes). Compaction is avoided to deteriorate the foam structure as little as possible, because any deterioration will enhance the release of blowing agent from the foam. Tables 11.1-3 give the default input data used for the model run using MOCLA-FOAM for the given scenario. The physical-chemical data for CFC-11 and HCFC-141b are all based on data given in the referenced literature or are estimated as described in Box 11.2. The waste and landfill data are either based on references or judgment.

   The anaerobic degradation rate in the waste given in Tables 11.2 and 11.3 is based on the rates determined in the batch experiments as shown in Table 5.1. The degradation rate used in MOCLA, λ, is referring to the water concentration of the compound while the batch determined, k_1, is referring to the gas concentration. The following equation is used for conversion:

$$\lambda = \frac{K_H \cdot k_1 \cdot R}{\varepsilon_w}$$

where the used parameters is defined in Box 11.1.

Table 11.1 Data for waste and landfill reactor used in MOCLA-FOAM set up.

Waste

Bulk density, ρ_b (dry tonne/m^3)	0.6
Organic carbon fraction, f_{oc}	0.25
Foam content, ε_f (m^3 foam/m^3 LF)	0.1
Foam cube side length (m)	0.05

Landfill reactor

Area of landfill reactor (m^2)	5625
Average landfill height, H (m)	10
Total precipitation, P (m/year)	1.1
Specific landfill gas production rate, q_a (m^3 LFG/m^3 waste · year)	2
LFG rate (m^3/day)	308
Volumetric water content in waste, ε_w	0.4
Volumetric gas content in waste, ε_a	0.1
Specific infiltration to waste, f_i	0.23
Thickness of cover, L(m)	0.5
Volumetric air content in cover soil, $\varepsilon_{a,SC}$	0.1
Total porosity of cover soil, ρ_{SC}	0.35
Gas extraction efficiency (%)	0
Leachate collection (%)	100

Table 11.2 Chemical data for CFC-11 (from Kjeldsen and Christensen (53))

Chemical data

Molar weight, MW (g/mole)	137.4
Henrys constant, K_H	4.5
Octanol/water distribution coefficient, $LogK_{ow}$	2.5
Anaerobic 1. order degradation constant, k_1 (day^{-1})	0.4
Anaerobic 1. Order degradation constant, λ (year^{-1})	11000

Derived constants

Estimated free air diffusion coefficient, D_0 (m^2/s)	$6.9 \cdot 10^{-6}$
Anaerobic degradation half-life, $T_{\frac{1}{2}}$ (days)	0.021
Estimated organic carbon/water distribution coefficient, K_{oc}[a] (L/kg)	195

a: estimated using formula B2.4 in Box 11.2

Table 11.3 Chemical data for HCFC-141b.

Chemical data	
Molar weight, MW (g/mole)	117.0
Henrys constant, K_H (-)	1.0
Octanol/water distribution coefficient, Log K_{ow}	2.37
Anaerobic 1. order degradation constant, k_1 (day$^{-1)}$)	0.01
Anaerobic 1. Order degradation constant, λ (year^{-1})	220
Derived constants	
Estimated free air diffusion coefficient, D_0 (m^2/s)	$7.4 \cdot 10^{-6}$
Anaerobic degradation half-life, $T_{\frac{1}{2}}$ (days)	1.15
Estimated organic carbon/water distribution coefficient., $K_{oc}{}^a$ (L/kg)	157

a: estimated using formula B2.4 in Box 11.2

11.4 Results from the model run

The results of the model run for CFC-11 and HCFC-141b are shown in table 11.4. The table shows the fate of the two blowing agents at 2 and 20 years after the landfill reactor was constructed. For both blowing agents, results for three different degradation rates, k_1, are given. The highest value is close to the average value found in the anaerobic waste incubation experiments that are presented in table 5.1. The mid column is calculated for a k_1 10% of the measured value. The first column contains results of a model run assuming no degradation of the blowing agents (k_1=0). The table shows that, for CFC-11, even for a degradation rate of only 10% of the observed rate in the laboratory experiments, the degradation significantly reduces the emission of CFC-11 to below 2% of that released from the foam waste. Figure 11.2 shows in more details the importance of the degradation rate to the amounts degraded and emitted after both 2 and 20 years.

Assuming that the degradation rate observed in the lab for HCFC-141b is valid, a significant emission reduction due to microbial degradation is observed also for this blowing agent. For a rate of only 10% of that observed, the emission with gas is lower that for the case with no degradation (18.7% and 64.4% with and without degradation, respectively after 20 years).

Table 11.4 Results of the model run with spreadsheet version of MOCLA-FOAM using the scenario given in tables 11.1-3.

|	k_1 (CFC-11) (day^{-1})			k_1 (HCFC-141b)		
	0	0.04	0.4	0	0.001	0.01
	2 y;20y	2 y;20y	2 y;20y	2 y;20y	2 y;20y	2 y;20y
1. Fraction of blowing agent remaining in foam (%)	88;64	88;64	88;64	n.d	n.d	n.d
2. Fraction of blowing agent released which has been degraded (%)	0;0	96;97.7	99.7;99.7	0;0	33.3;75.3	89.7;96.9
3. Fraction of blowing agent released which has been emitted with gas (%)	32;91	2.1;2.6	0.2;0.2	10.7;64.4	8.3;18.7	2.2; 2.4
4. Fraction of blowing agent released which has been emitted with leachate (%)	0.08;0.24	<0.01;<0.01	<0.01;<0.01	0.12;0.75	0.10;0.21	0.03;0.03
5. Fraction sorbed at time=t (%)	65.8;8.4	1.9;0.2	0.15;0.02	87.4;34.1	57.1;5.7	7.9;0.66
6. Fraction contained in gas phase at time=t (%)	1.0;0.13	0.03;<0.01	<0.01;<0.01	0.37;0.14	0.24;0.02	0.03;<0.01
7. Fraction contained in water phase at time=t (%)	0.9;0.11	0.03;<0.01	<0.01;<0.01	1.5;0.58	0.97;0.10	0.13;<0.01
8. Emitted + degraded + present in three phases (kg)	1830;5980	1830;5980	1830;5980	2515;8110	2515;8110	2516;8110
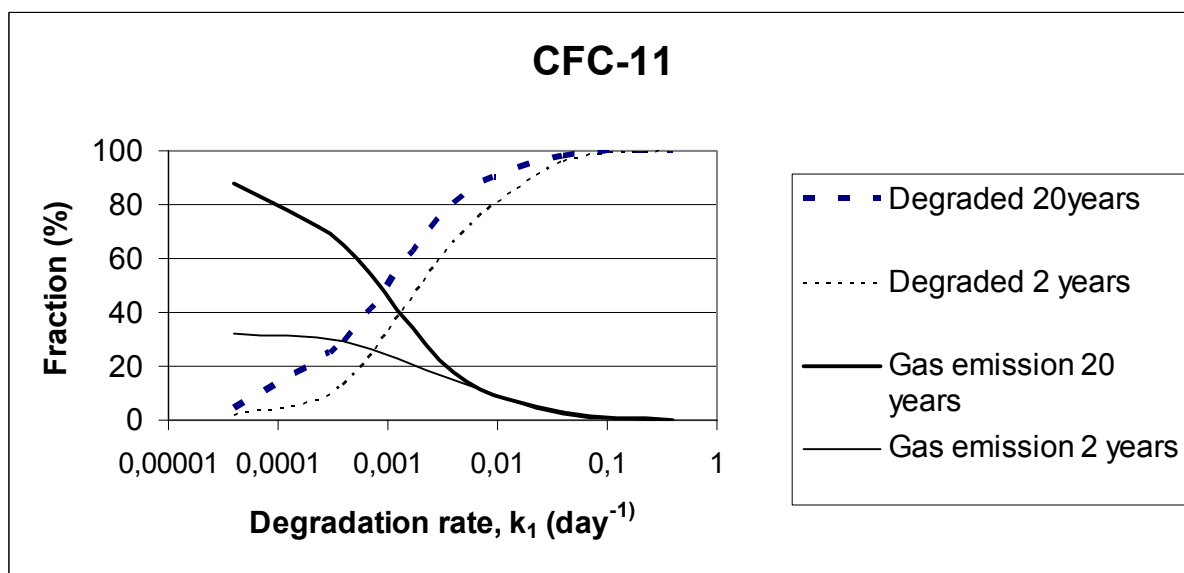
Figure 11.2 The fraction (%) of released blowing agent which has been degraded or emitted with landfill gas for the first 2 or 20 years, respectively as a function of degradation rate, k_1.
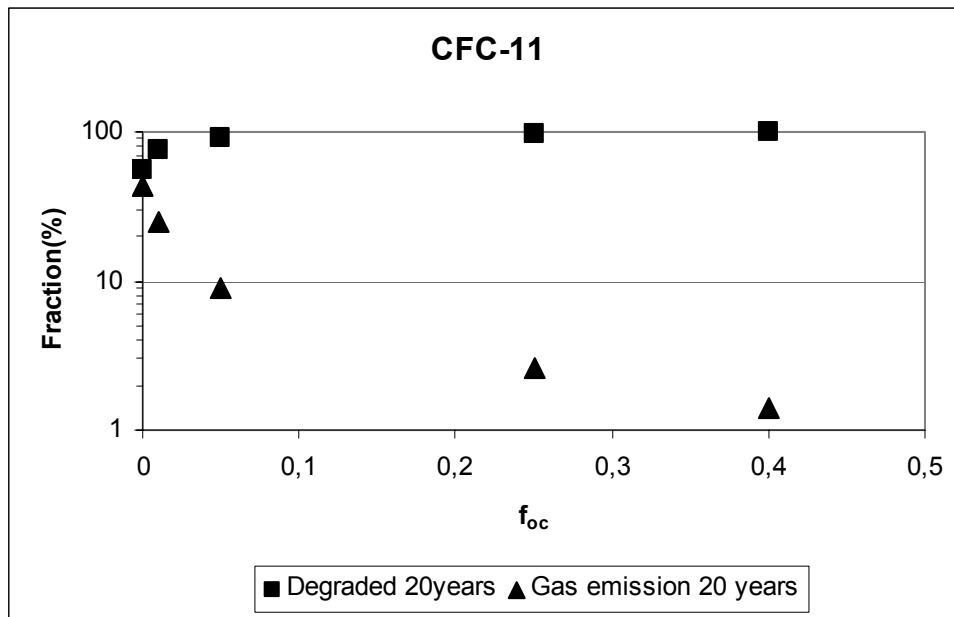
Figure 11.3 Fraction of BA released from foam being degraded or emitted with gas over the first 20 year period.

Figure 11.3 shows a sensitivity analysis focusing on the effect of the waste content of organic carbon, f_{oc} for a case assuming a degradation rate of k_1=0.04 day^{-1}. It clearly shows the advantage of having a high organic carbon content in the land-filled waste. The fraction being degraded is clearly higher at higher f_{oc}. The emission is also lower; however, this may be a retardation of the emission due to higher sorptive effect of the waste body.

A very preliminary model run with foam waste assuming a 10 times higher diffusion coefficient shows, as expected, a much faster release rate. For this scenario about 25% of the BA content of the foam has been released over the first year (only 8% for the case with a 10 times lower diffusion coefficient). In spite of that a very significant emission reduction due to degradation processes can still be observed (assuming k_1 =0.04 day^{-1}). In this scenario, however, it becomes very important that the anaerobic degradation is active from the very start. This means that the initial composition of the waste used in the landfill reactor is very important.

12. CONCLUSIONS AND IDEAS FOR FURTHER/RELATED RESEARCH

This project has clearly shown that there exists a significant potential for degradation of CFC-11 in landfilled waste. The laboratory experiments performed yielded high degradation rates for CFC-11. Degradation of HCFC-141b under anaerobic conditions was also observed; however, with much lower rates than observed for CFC-11. Possible degradation products of HCFC-141b were not looked for. It would be interesting to evaluate whether any known products could be observed under the degradation of HCFC-141b. The developed MOCLA-FOAM model using the observed degradation rates showed that the emission reduction by the anaerobic degradation processes which take place in the landfill is significant for CFC11, and maybe also for HCFC-141b. The success of treating foam waste in constructed landfill bioreactor cells is especially depending on the following questions:

1. Can the refrigerator/freezer units be decommissioned without destroying the structure of the foam pieces?
2. Can the foam pieces be built into the landfill reactor – together with bio-waste without deteriorating the foam structure?
3. How is a fast initiation of the anaerobic degradation secured so the high initial BA release is not lost with escaping landfill gas?
4. What intermediates are formed in the anaerobic degradation of HCFC-141b, and are the intermediates degradable?
5. Is it possible to develop microbes that specifically target HFC blowing agents?

It is recommended to initiate a pilot scale project to test the bio-treatment of foam waste in landfill reactor cells and to evaluate the feasibility of the proposed technology.

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ATTENUATION OF ALTERNATIVE BLOWING AGENTS IN LANDFILLS

APPENDIX

Appendix 1

Physical and chemical properties of CFC-11, HCFC-21, HCFC-31, and HFC-41.

Chemical name	Unit	Trichlorofluoro methane	Dichlorofluoro methane	Chlorofluoro methane	Fluoromethane
Synonyms		CFC-11	HCFC-21	HCFC-31	HFC-41
Structure		CCl_3F	$CHCl_2F$	CH_2ClF	CH_3F
CAS no.		000075-69-4	000075-43-4	000593-70-4	000593-53-3
Molecular weight	g/mol	137.37	102.92	68.48	34.03
Boiling point	°C	23.8	9	-9.1	-78.4
Vapor pressure	mmHg	802.8	1360	2450	2850
Water solubility	mg/L	1100	18800	10400	22700
Log K (octanol-water)		2.53	1.5	0.51	0.51
Henry´s Law constant	atm m^3/mole	0.097	0.0108	0.00659	0.017

Appendix 2

Anaerobic batch experiments.

Anaerobic batch experiments with organic waste. The two bottles to the left function as control experiments.

Anaerobic batch experiments with soil. Gas samples for GC-analysis are taken using the shown syringe (gas tight with pressure lock).
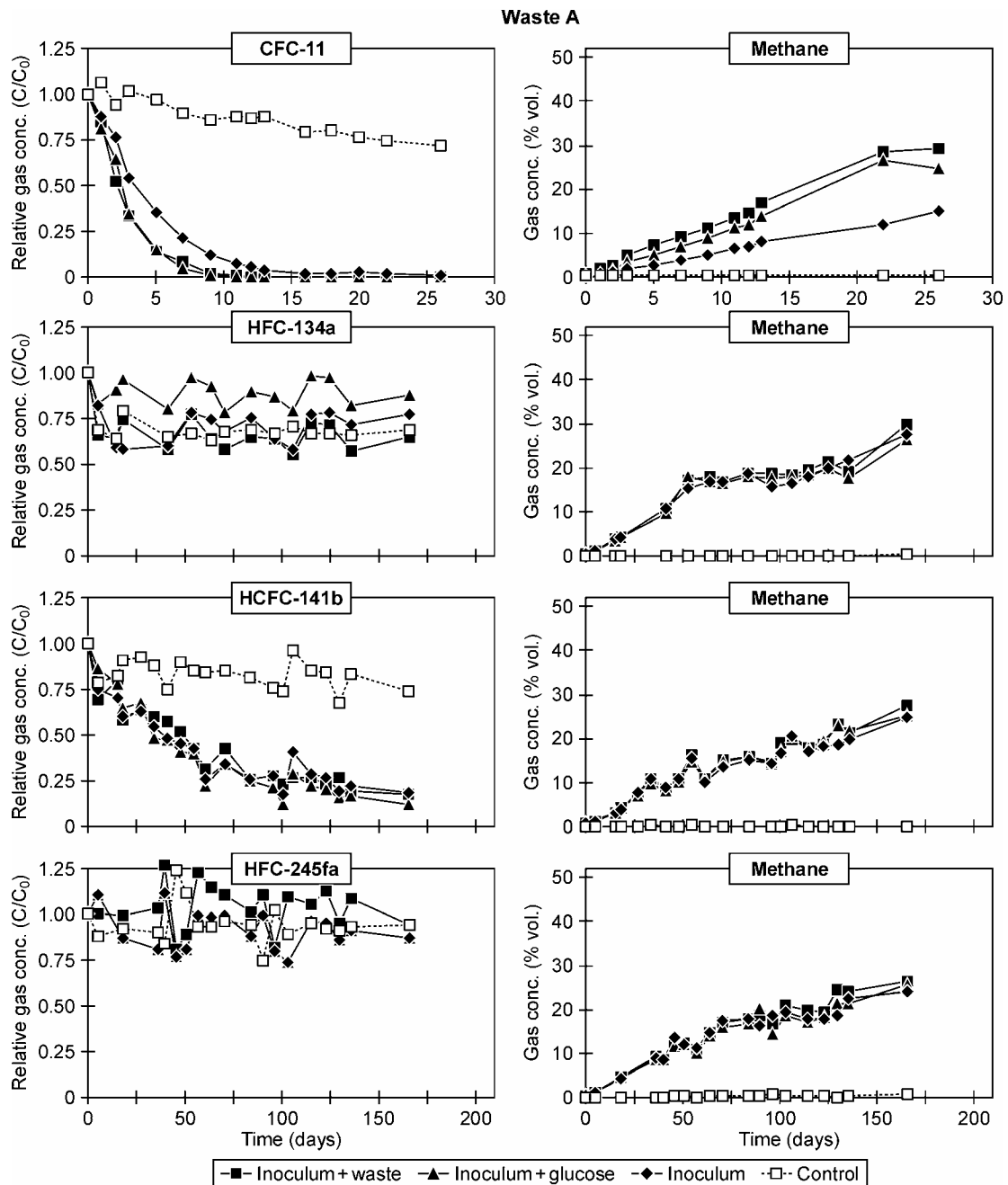
Appendix 3

Experimental set-up of soil columns

Soil columns equipped with gas sampling port and permeated with artificial landfill gas
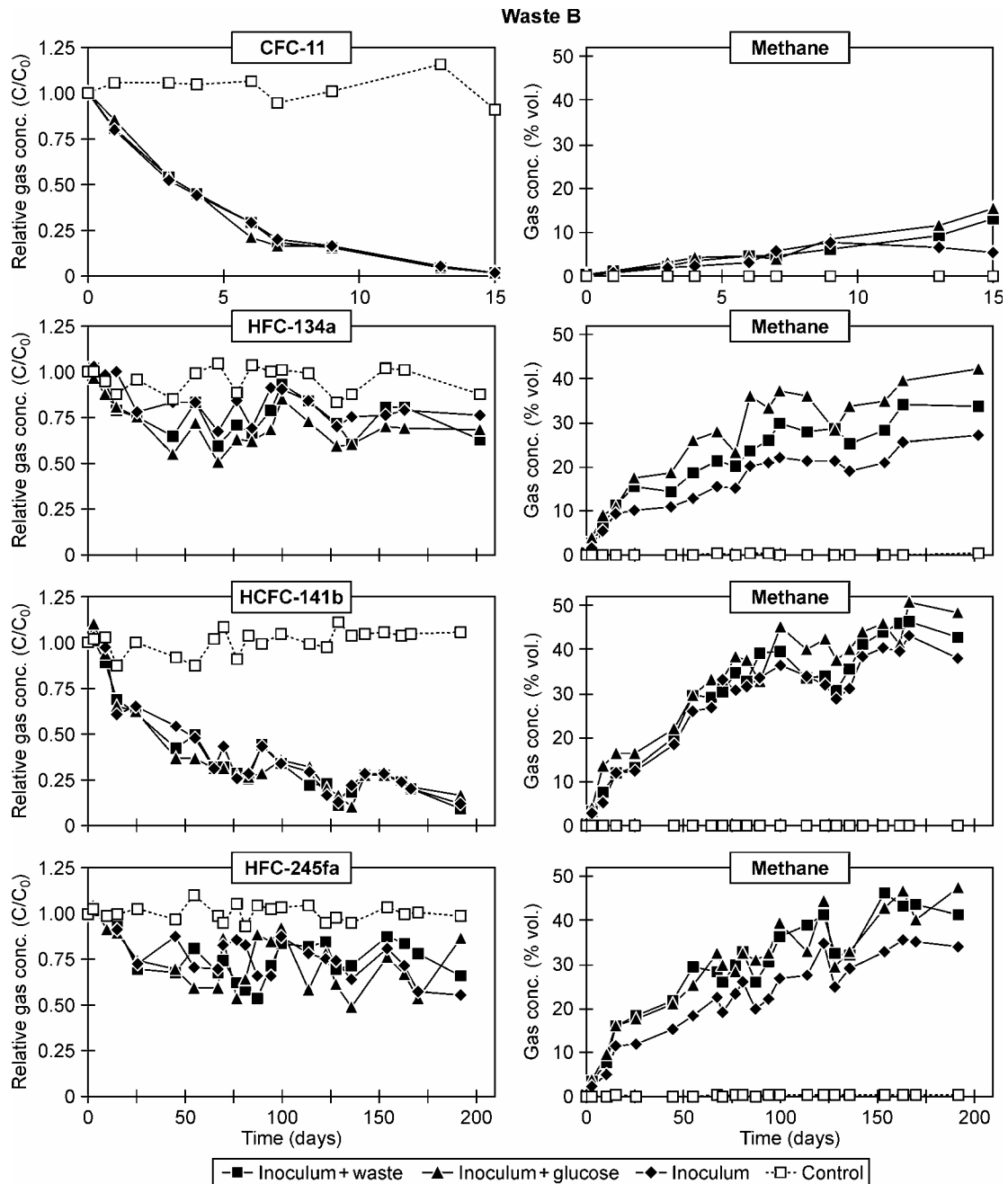

In-let system to soil column

Results of anaerobic batch experiments added fresh organic household

Relative gas concentration of blowing agents in batch experiments added fresh organic household waste (Type A). Figures in the second column show the production of methane during incubation. Bottles have been open flushed and blowing agents re-added.
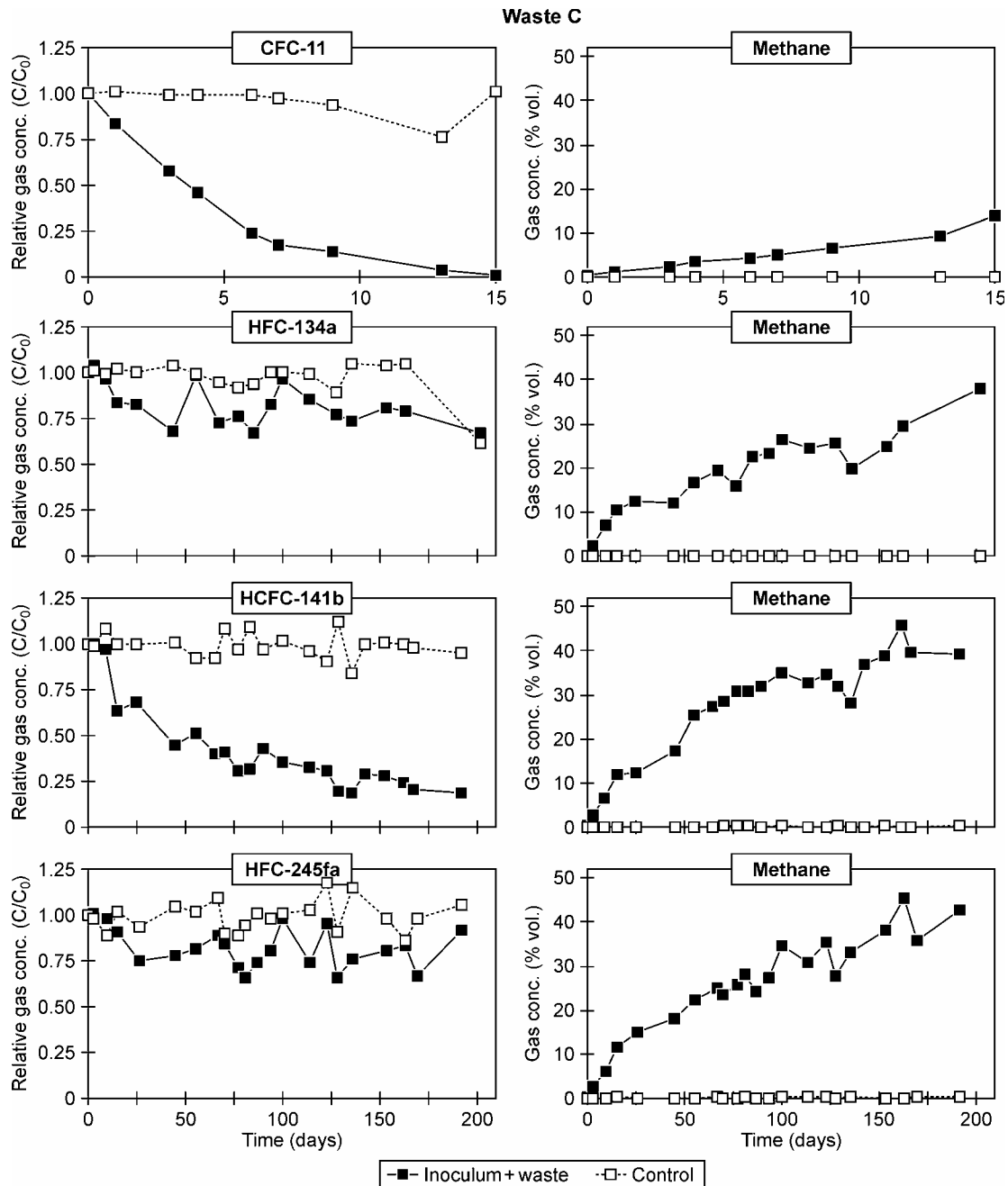
Results of anaerobic batch experiments added older pre-disposed waste from an American landfill

Relative gas concentration of blowing agents in batch experiments added older pre-disposed waste from an American landfill (Type B). Figures in the second column show the production of methane during incubation.

Appendix 6

Results of anaerobic batch experiments added from a laboratory experimental digester simulating landfill conditions


Relative gas concentration of blowing agents in batch experiments added waste from a laboratory experimental digester simulating landfill conditions (Type C). Figures in the second column show the production of methane during incubation.

Results of anaerobic degradation of HCFC-141b in un-inoculated waste
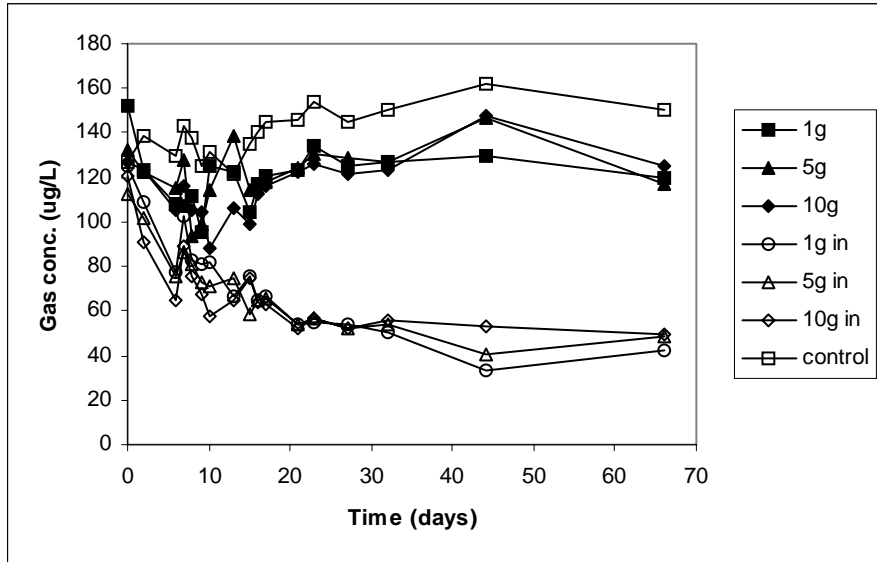
Anaerobic degradation of HCFC-141b in inoculated (open symbols) and un-inoculated (filled symbols) batch experiments containing fresh household waste.
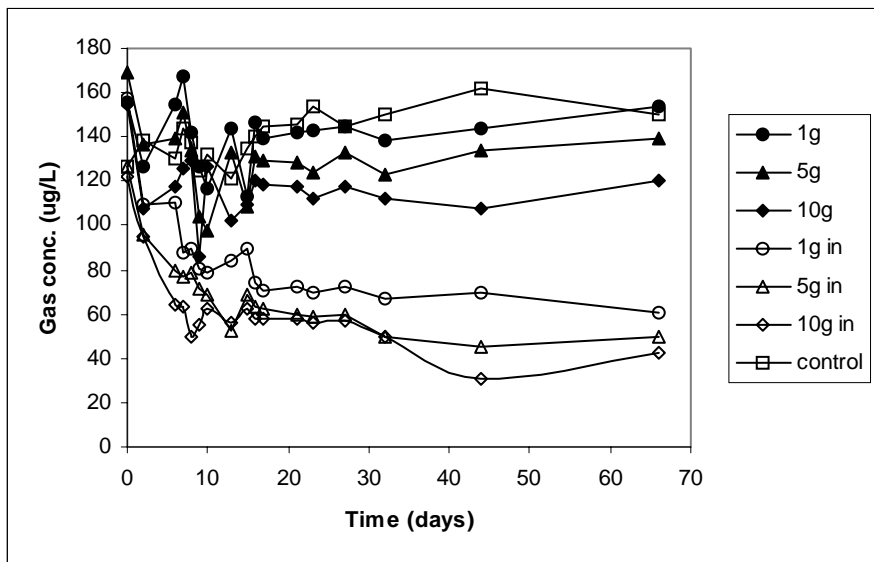
Anaerobic degradation of HCFC-141b in inoculated (open symbols) and un-inoculated (filled symbols) batch experiments containing waste from an anaerobic digester feed with US refuse (second column).