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Capacity for Biodegradation of CFCs and HCFCs in a Methane Oxidative Counter-Gradient Laboratory System Simulating Landfill Soil Covers

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The attenuation of methane and four chlorofluorocarbons was investigated in a dynamic methane and oxygen counter-gradient system simulating a landfill soil cover. Soil was sampled at Skellingsted Landfill, Denmark. The soil columns showed a high capacity of methane oxidation with oxidation rates of 210 g m^{-2} d^{-1} corresponding to a removal efficiency of 81%. CFC-11 and to a lesser extent also CFC-12 were degraded in the active soil columns. The average removal efficiency was 90% and 30% for CFC-11 and CFC-12, respectively. Soil gas concentration profiles indicated that the removal was due to anaerobic degradation, which was verified in anaerobic batch experiments where CFC-11 was rapidly degraded. HCFC-21 and HCFC-22 were also degraded in active soil columns (61% and 41%, respectively), but compared to the CFCs, the degradation was located in the upper oxic part of the column with overlapping gradients of methane and oxygen. High oxidation rates of methane and HCFCs were obtained in soil microcosms incubated with methane. When increasing the column inlet flow, the oxidation zone was moved upward in the column, and the removal efficiency of methane and HCFCs decreased. The removal of CFCs was, however, less affected since the anaerobic zone expanded with increasing inlet flow rates. This study demonstrates the complexity of landfill soil cover systems and shows that both anaerobic and aerobic bacteria may play a very important role in reducing the emission of not only methane but also trace components into the atmosphere.

Introduction

Landfill gas (LFG) is produced by the microbial degradation of the organic components in municipal refuse under anaerobic conditions. The main components in LFG are methane (55−60 vol %) and carbon dioxide (40−45 vol %). Besides methane and carbon dioxide, LFG also contains numerous trace compounds representing a maximum of a few volume percentages (*1*). The trace compounds originate from hazardous materials deposited in the landfill or from biological/chemical degradation of materials deposited in the landfill. The trace components in LFG include hydrocarbons, aromatics, halogenated hydrocarbons, and organic compounds containing oxygen and sulfur. Aromatic and chlorinated hydrocarbons are considered anthropogenic compounds, and their concentration in LFG is therefore mainly governed by waste composition (*2*). The chlorofluorocarbons (CFCs) have high volatility, high stability, and nontoxicity and have therefore been used in a number of industrial processes and products such as refrigerating aggregates, foaming agents, solvents, propellants, etc. CFCs are thus often found in LFG in relatively high concentrations because of their widespread use, their high volatility, and their high persistence. In LFGs sampled at seven disposal sites in the U.K., the chlorofluorocarbons accounted for up to 95% of the total chlorine content (*3*). The fluorinated halocarbons most frequently occurring in waste are CFC-11, CFC-12, HCFC-21, HCFC-22, CFC-113, and CFC-114 (*4*). Typical gas concentrations are in the range of 10−500 mg m^{-3} (*2*). The emission of CFCs can continue for long periods after waste disposal if the compounds are released slowly from their sources within the waste. The release from insulation foam is governed by closed cell diffusion, and it has been estimated that it can take 9−300 yr before 50% of the residual CFC is released from insulation foam that is shredded into 2-cm pieces (*5*). If refrigerator cabinets and cooling circuits are kept intact after disposal, the release will continue for an even longer period. As an example, high levels of CFC-12 and HCFC-22 (between 111 and 404 mg m^{-3}) have been found in more than 20-year-old waste (*3*).

Due to increasing concern about the global environment, production of CFCs has been intensively regulated through international conventions. Many governments signed the Montreal Protocol on substances that deplete the ozone layer, which stated a ban on production and use of most CFCs from 1996 on (*6*). Although the production of CFCs is decreasing, an increase in the atmospheric concentration will continue for years to come. Moreover, because of the CFCs long lifetimes in the atmosphere, they can be expected to be active in atmospheric chemistry for hundreds of years. The hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs) replacing the CFCs are less stable and have lower lifetimes in the atmosphere and lower ozone-depletion potential (*7*). However, some of the CFC replacements have significant global warming potential (*7*).

The LFG produced in landfills without control systems (gas collection systems) is transported through soil top covers due to pressure and concentration gradients, causing emission of gas into the atmosphere. Even at sites with gas collection systems a significant amount of the gas might still be emitted. In landfill top covers, methane and oxygen counter-gradients may appear due to emission of methane from the waste and diffusion of oxygen from ambient air. Landfill soil covers thus often appear with an upper aerobic zone of 20−50 cm and a lower anaerobic zone of 20−50 cm in a 1-m top cover, providing living conditions for different bacteria (*8*).

Landfills are estimated to release between 9 and 70 Tg of CH_4/yr, out of an estimated annual global emission of 600 Tg of methane to the atmosphere (*9, 10*). However, it is important to note that these projections are based on estimated rates of methane production applied to national statistics for landfilled refuse and not on field emission measurements (*10*). Oxidation of methane by methanotrophic bacteria in landfill top cover soil has been shown to reduce the amount of methane emitted to the atmosphere (*11*−*14*). Methanotrophic bacteria are unique in their ability to utilize CH_4 as a sole C and energy source. The enzymes, methane monooxygenases (MMOs), exhibit a striking lack of substrate specificity, resulting in the fortuitous metabolism of a very large number of compounds including some halogenated hydrocarbons (*15*), thus offering a potential of

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mitigating the emission of trace gases from landfills. Kjeldsen and co-workers (*16*) published results on oxidation of methane and degradation of trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) in soil affected by LFG. High methane oxidation potentials and high degradation rates for benzene and toluene were found. In addition, slow cometabolic degradation of TCE and TCA was observed in the presence of methane. Recent research confirms that a high number of halogenated compounds can be co-oxidized in landfill cover soils offering a potential of mitigating the emission of trace gases from landfills (*17*). To our knowledge, these are so far the only research projects concerning degradation of volatile organic compounds (VOCs) in LFG-affected soil reported in the open international literature.

The objective of the present study was to determine the capacity of methane oxidation and degradation of halocarbons in landfill soil cover systems. The investigations have been carried out through laboratory experiments using a dynamic column setup. Simple batch experiments were conducted to support the observed degradation pattern in the column experiments. The selected trace components included four halocarbons: trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), dichlorofluoromethane (HCFC-21), and chlorodifluoromethane (HCFC-22).

Materials and Methods

Chemicals. CFC-11, CFC-12, HCFC-21, and HCFC-22 were purchased from Flourochem Limited, U.K. All solvents were obtained in high purity. All other gases (CH_4, O_2, Ne, and the 50/50% CH_4/CO_2 gas mixture) were obtained from Hede-Nielsen, Denmark.

Field Site and Soil Sampling. Soil samples were collected at Skellingsted Landfill south of Holbæk, Western Sealand, Denmark. Skellingsted Landfill received a total of approximately 420 000 t 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 uncontrolled with no liners or gas extraction system. The LFG migration has been intensively studied because of a gas explosion accident in 1991 (*18*). The LFG 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 1-yr field campaign (*19*). The soil was sampled in 5-cm intervals from the surface to 30 cm depth and in 10-cm intervals from 30 to 90 cm below the surface. Soil samples were collected using a hand auger and stored at 4 °C in darkness in closed containers to avoid dehydration. Before storage, 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, copper content, ammonium, chloride, nitrate, and sulfate. All soil analyses were conducted according to standard methods approved by the Danish EPA. The soil analyses are described in ref *17*.

Column Experiments. Column experiments simulating a landfill top cover soil matrix through which gas was transported were carried out. The degradation process was examined in a methane and oxygen counter-gradient system. The columns were packed with landfill cover soil and continuously fed in opposite ends with methane gas (containing trace components) and air. The soil was packed in the columns in the same sequence as sampled in the field. The system consisted of a tube made of rigid PVC, 100 cm long by 8 cm i.d (Figure 1). The PVC tube was closed at both ends with PVC end caps fitted with rubber O-rings to ensure a gastight fit. The PVC cap positioned at the bottom end of the column had one inlet while the PVC cap positioned at the top end of the column had 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 3-cm layer of sterilized gravel (grain size of 2−3 mm) was placed at the bottom of the column to ensure homogeneous 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 silcone septa, which enabled taking gas samples by a gastight syringe needle. The gas samples (3 mL) were transferred into evacuated glass tubes (Venoject, Terumo Europe n.v., Belgium) and analyzed by gas chromatography. The artificial LFG, which consisted of 50/50% v/v CH_4/CO_2 was kept in Tedlar bags (SKC Inc., Eighty Four, PA) and fed to the bottom inlet of the column by gastight piston pumps (FMI Lab Pump, model QG, Fluid Metering Inc., Syosset, NY). CFC and HCFC mixtures were added to the CH_4/CO_2 mixture in the Tedlar bag. The inlet concentrations varied between 15 and 250 μg L^{-1} depending on the compound, which are within the range of typical LFG concentrations of trace gases. Atmospheric conditions were obtained at the top of the column by passing an air stream through the chamber on top of the soil column (approximately 100 mL min^{-1}). This simulated ambient air over

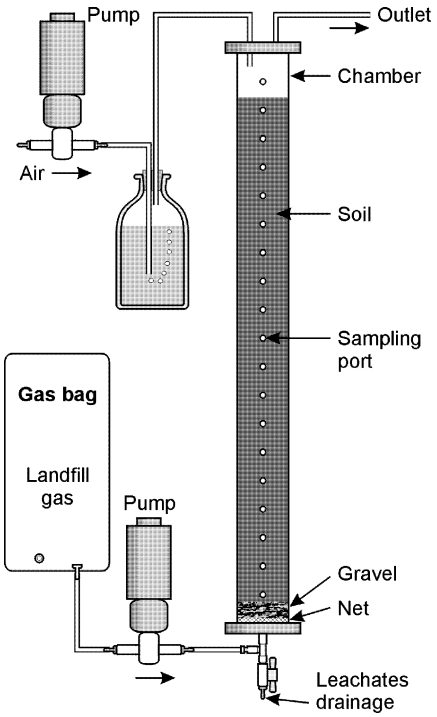

FIGURE 1. Dynamic column setup.

TABLE 1. Parameters for Column Experiments Conducted with Variable Inlet Flow Rates[a]

inlet flow (mL min^{-1})	gas flux (m^3 m^{-2} d^{-1})	retention time (h)	CH_4 load (g m^{-2} d^{-1})	CFC load (g m^{-2} d^{-1})	HCFC load (g m^{-2} d^{-1})
0.82	0.24	31.0	77	0.008	0.094
1.23	0.37	19.3	120	0.013	0.155
2.66	0.76	9.7	250	0.027	0.333
4.24	1.22	6.1	398	0.040	0.489
5.39	1.55	4.7	506	0.054	0.656
7.39	2.12	3.4	693	0.070	0.851
11.08	3.18	2.3	1040	0.105	1.276
14.25	4.09	1.8	1336	0.135	1.641

[a] The calculated retention time is based on a gas-filled porosity of 0.35.

soil cover surface with O_2 supply by vertical diffusion into the soil column. Dehydration of the surface soil was avoided by passing the inlet air stream through a washing bottle containing distilled water. The air stream through the chamber on top of the soil column was measured with a soap film flow meter. Gas samples were taken from the Tedlar bags and from the outlet of the columns to control mass balance for the system. Neon was added as conservative tracer during periods of the experimental run. The experiments were carried out at room temperature (22 °C). The average porosity of the packed soil column was 0.52 while the gas filled pore space was 0.22. The porosity of the packed soilcolumn was calculated based on the volume of the column, the soil mass, and the particle density. The experimental setup included three soil columns: two microbial active columns permeated with CFCs and HCFCs, respectively, and a sterilized control column. In the first experimental trial, the degradation was studied under stable conditions with a constant inlet flow. The inlet flow at the bottom of the column was 2.6 mL min^{-1} corresponding to a gas flux of 0.76 m^3 of LFG m^{-2} d^{-1} and a methane flux of 250 g m^{-2} d^{-1}, which is in the mid to high range of reported landfill methane fluxes (*10*). Assuming a 20-m-deep layer of waste, this is equivalent to a generation rate of about 13.9 m^3 of LFG (m of waste)$^{-3}$ yr^{-1}, which can be expected within the first 10−15 yr after disposal (*20*). The inlet bottom flow was measured by timing the transport of water drops through a defined glass tube inserted between the pump and the column inlet. To obtain steady-state conditions (homogeneous distribution of gas, extinction of sorption capacity of the soil profile) columns were left with gas for 5 d before initial sampling; thereafter, the experiments were run for at least 3 weeks.

To study the degradation processes under more dynamic conditions, column experiments with variable flow were performed. Under natural conditions, the gas flux and the gas gradient system varies, influenced both by changes in the LFG production and by changes in barometric pressures. The experiment was carried out with CFC-11, CFC-12, HCFC-21, and HCFC-22. Experiments were carried out with eight different inlet flows varying between 0.82 and 14.25 mL min^{-1} corresponding to a gas fluxes range of 0.24−4.09 m^3 m^{-2} d^{-1} (Table 1), which are realistic gas fluxes from the top covers of landfills. Gas fluxes of approximately 0.25 m^3 m^{-2} d^{-1} are representative for older landfills or sites with gas collection systems, while new and active landfills with high gas production can have gas fluxes of up to 5 m^3 m^{-2} d^{-1}. For each flow condition, samples were extracted daily over a period of 5 d. The system was given a period of 2 d between different flow conditions to adjust and reach a steady state. At the end of the experiment, soil samples were taken for analysis of chloride from the column permeated with HCFCs. The analytical procedure for chloride analysis is described in ref *17*.

The control column was identical to the active columns except that the soil had been sterilized by autoclaving (three times for 1 h each time) and mercury chloride (0.5 g kg^{-1}) had been added thereafter to avoid microbial activity. The control column was run in parallel and operated similar to the active column.

Batch Experiments. To verify observed degradation patterns in the soil columns, simple batch experiments were conducted. Soil was incubated with trace components under both aerobic and anaerobic conditions. A fixed amount of soil (20 g of moist soil) was added to a 117-mL batch container equipped with Mininert (VICI AG, Schenkon, Switzerland) valves made of Teflon. The valves enabled gas to be sampled or injected by a hypodermic needle and a syringe. To simulate landfill conditions, the gas phase in the batch containers was flushed with a 50/50% mixture of methane and carbon dioxide. To obtain methane oxidation conditions, air was withdrawn from each container using a syringe and replaced with methane and oxygen, which gave an initial mixture of methane (15% v/v), oxygen (35% v/v), and nitrogen (50% v/v). The soil in the aerobic experiments was sampled at 15−20 cm depth, while the soil used in the anaerobic experiments was sampled at 50−60 cm depth. Gas samples containing the test compound were removed from gaseous stock solutions by a gastight glass syringe and injected into the batch containers. The degradation of the VOCs was studied in single compound tests. The initial concentrations were generally selected in the order that they were in the range of typically trace gas concentrations in LFG (10−250 mg m^{-3}). Gas samples withdrawn from headspace were sampled periodically and analyzed by gas chromatography. The gas chromatographic setup and the procedure for data evaluation are described in ref *17*. The batch experiments were conducted at room temperature (22 °C). All aerobic batch experiments were carried out in series of four, while the anaerobic batch experiments were conducted in duplicate. The aerobic batch experiments are presented in ref *17*. To check if any disappearance could be due to nonmicrobial processes (abiotic degradation, sorption, and volatilization) control batches with sterilized soil (autoclaving followed by addition of sodium azide (0.2 g kg^{-1})) were conducted.

Gas Chromatographic Analysis. The halogenated compounds were measured by manual injection via an on-column inlet to Carlo Erba HRGC 5300 equipped with an electron capture detector and a WCOT fused silica capillary column (CP-Sil-19 CB) with nitrogen being the carrier gas flow. All compounds were analyzed with an isotherm column temperature of 35 °C. Concentrations of the target compounds were calibrated by injection of gas standards (no fewer than 12 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 main gas components (CH_4, CO_2, O_2, N_2, and Ne) 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 were quantified 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% volume were used for calibration.

Results and Discussion

Soil Characteristics. The soil was characterized and analyzed for different soil parameters as a function of sampling depth prior to column startup. The soil was characterized according to the USDA classification. Three soil layers based on the granulometric composition could be identified: loamy sand (0−35 cm), sandy loam (35−70 cm), and coarse sand/gravel (70−90 cm) (Table 2). The bulk density of the loamy sand layer was 1.55 while the porosity was 0.38. The soil moisture content varied between 9 and 33% w/w with the upper 35 cm being wettest. The soil organic carbon content showed a maximum of 3.2% w/w around 20-cm depth and decreased to 0.3 at 85-cm depth. The total nitrogen content showed a similar pattern with a maximum content of 3.5 g of N (kg of dry soil)$^{-1}$ at 20-cm depth. The soil pH_{CaCl_2} also showed a maximum (6.9) at 20 cm below the surface and decreased downward to 5.1 at 85 cm. The copper content varied between 2.5 and 8.9 mg of Cu (kg of dry soil)$^{-1}$ and showed no trend according to depth distribution. The highest chloride concentration (7.5 mg kg^{-1}) was found in the surface soil. Two other minor chloride maxima (3.8 and 3.0 mg (kg of soil)$^{-1}$)

TABLE 2. Soil Parameters[a]

depth (cm)[b]	soil texture	H_2O (% w/w)	TOC (% w/w)	TON (mg kg^{-1})	pH	Cu (mg kg^{-1})	NH_4^+ (mg-N kg^{-1})	Cl^- (mg kg^{-1})	NO_3^- (mg-N kg^{-1})	SO_4^{2-} (mg-S kg^{-1})
5−10	loamy sand	27	2.1	2220	7.6	3.9	1.2	7.6	27	0.2
10−15	loamy sand	25	2.1	2220	8.0	3.8	1.4	2.7	16	0.1
15−20	loamy sand	33	3.2	3540	7.6	4.7	2.3	3.8	73	0.4
20−25	loamy sand	30	2.7	3180	7.0	4.5	3.1	3.4	94	0.6
30−35	loamy sand	25	2.2	2610	6.0	5.4	3.1	3.3	109	2.1
40−50	sandy loam	21	1.5	1650	6.3	4.1	1.7	2.0	63	5.0
50−60	sandy loam	18	1.2	1010	6.3	2.5	1.1	1.1	41	5.5
70−80	coarse sand	9	0.6	632	6.3	8.9	13.5	1.8	16	3.9
80−90	coarse sand	11	0.3	230	6.2	3.0	16.3	3.0	10	1.9

[a] TOC, total organic carbon. TON, total organic nitrogen. Maximal measured bromide = 0.06 μg g^{-1}. Maximal measured nitrite = 0.4 μg g^{-1}. [b] Below surface.

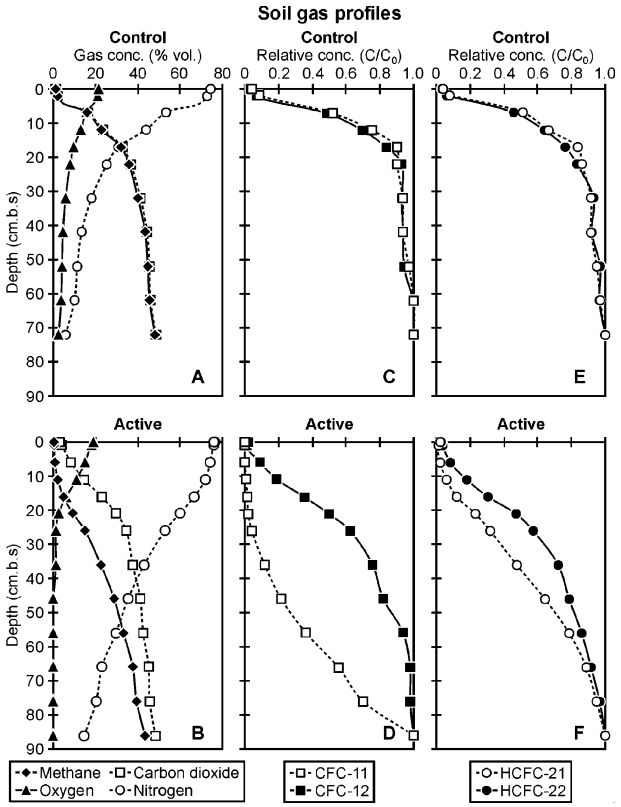

FIGURE 2. Vertical concentration profiles in a control and an active soil column permeated with artificial LFG (50% CH_4:50% CO_2) added trace concentrations of CFCs and HCFCs. Inlet LFG flow rate = 0.76 m^3 m^{-2} d^{-1}.

were observed at 20- and 85-cm depth.

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 LFG (60% CH_4 and 40% CO_2)—with only very low or no oxygen presence (*17*). The ionic composition of the soil water indicated zonation as a result of different redox conditions. From around 25-cm depth, where oxygen became limited, the nitrate concentration decreased while the sulfate concentration increased. At 50-cm depth, where soil became anaerobic, sulfate decreased and elevated ammonium concentrations were observed.

Methane Oxidation and Degradation of Trace Components in a Stable Column System. *Methane.* Figure 2A 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 from 20 cm to the top. The concentration profiles for O_2 and N_2 show that air was penetrating throughout the whole column. Figure 2B 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, with a maximum decline around 20 cm. Compared to CH_4, the upward decrease in the concentration for CO_2 is 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 35 cm down the column becomes anoxic. The removal of O_2 and increasing CO_2/CH_4 ratio upward in the column indicates methane oxidation. The N_2 concentration is much higher in the lower part of the active column as compared to the control column. This is caused by a volume reduction from methane oxidation (3 mol turning into 1 mol) creating an underpressure and thereby enhancing the transport of atmospheric air into soil system. Increasing the 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 column directly. Steady-state gas profiles were obtained within the first 4 d after start-up, indicating that a microbial community of methane oxidizers was already well-established in the soil.

TABLE 3. Removal Capacities of Methane and Halocarbons Obtained in Soil Column Experiments Permeated with Artificial Landfill Gas[a]

		methane oxidation		degradation of halocarbons	
trace gas	C_{inlet} (μg L^{-1})	efficiency (%)	capacity (g m^{-2} d^{-1})	efficiency (%)	capacity (g m^{-2} d^{-1})
CFC-11	15	81 ± 3	210	90 ± 6	1.0×10^{-2}
CFC-12	25	81 ± 3	210	30 ± 3	5.8×10^{-3}
HCFC-21	250	74 ± 4	185	61 ± 5	1.1×10^{-1}
HCFC-22	250	74 ± 4	185	41 ± 3	7.6×10^{-2}

[a] 50% CH_4 and 50% CO_2, v/v. Inlet LFG flow rate = 0.76 m^3 m^{-2} d^{-1}.

In general, the soil columns showed a high capacity of methane oxidation giving methane oxidation rates between 185 and 210 g m^{-2} d^{-1} corresponding to a reduction of 74−81% (Table 3). The columns showed stable activity, as the removal was fairly constant during the 3-week period that the experiment lasted (Figure 3). These methane oxidation rates are consistent with results reported by Kightley et al. (*21*), 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 et al. (*22*) also found comparable oxidation capacities of up to 240 g (m of column)$^{-2}$ d^{-1} in columns packed with soil originating from

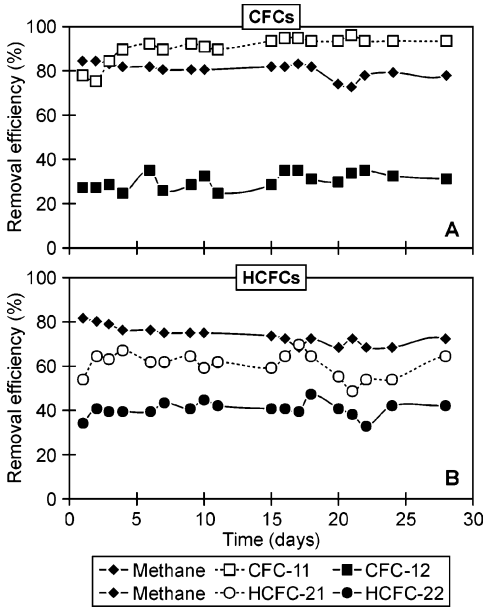

FIGURE 3. Removal efficiency in soil columns over time. Inlet LFG flow rate = 0.76 $m^3\ m^{-2}\ d^{-1}$.

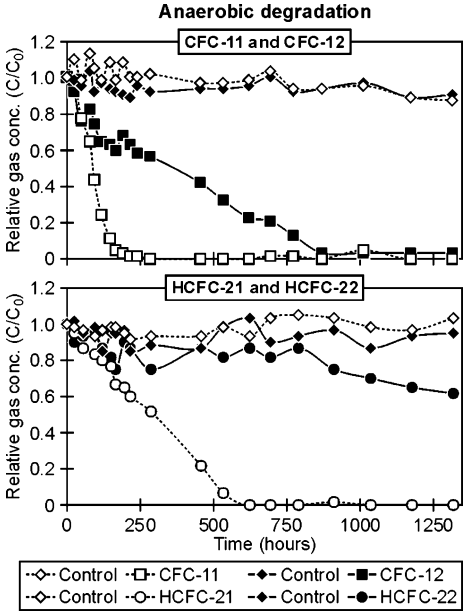

FIGURE 4. Headspace concentrations of (hydro)chlorofluorocarbons as a function of time in anaerobic batch experiment containing 20 g of moist soil preexposed to LFG.

a landfill cover. The lower methane oxidation rates observed in soil columns with HCFCs are probably a result of increased competition between methane and the trace components for the enzyme, due to the higher initial concentration as compared to the soil column with CFCs or due to buildup of toxic byproducts that inhibit the microbial activity. Matheson and co-workers (*23*) observed irreversible inhibition of methane oxidation by HCFC-21 and HCFC-22. Furthermore, the HCFCs also proved inhibitory to the methanol dehydrogenase (driving the second step in methane oxidation pathway), suggesting that the HCFCs also disrupt other aspects of C_1 catabolism in addition to MMO activity. The methane mass balance for the control column was 102% (± 6) recovery indicating no losses and ensuring a tight system. The tracer mass balance showed an average recovery of 101% (± 5) for the control column and an average recovery of 99% (± 8) for the active columns measured over a 10-d period.

CFCs. Figure 2C,D shows the vertical relative concentration profiles for column experiments permeated with CFC-11 and CFC-12. In the control column, the relative concentration profiles for CFC-11 and CFC-12 are almost identical and show a sharp decrease from 20-cm depth to the top. On the basis of mass balances, no degradation was observed in the control column. CFC-11 and, to a lesser extent, CFC-12 were degraded in the active soil columns. The average degradation capacities for CFC-11 and CFC-12 were 1.0×10^{-2} and 5.8×10^{-3} g m^{-2} d^{-1} corresponding to a removal efficiency of 90% and 30%, respectively. Figure 3A shows the removal efficiency of the CFCs as a function of time. Table 3 shows the removal efficiencies and degradation capacities obtained based on total mass balances. The decline in the CFC-11 concentration profile in the lower part of the column indicates that the removal was due to anaerobic degradation (Figure 2D). This was verified by anaerobic batch experiments where CFC-11 was rapidly degraded (Figure 4). In Table 4, the degradation rates obtained in the batch experiments are listed together with the regression coefficients obtained from fitting the data with a zero-order equation. Also CFC-12 was degraded in anaerobic batch experiments, however at a lower rate, which is consistent with the column results and with observations of other authors (*24*, *25*). No degradation of CFC-11 and CFC-12 was observed in aerobic batch experiments despite the fact that rapid methane oxidation occurred with rates up to

TABLE 4. Maximal Degradation Rates Obtained from Batch Experiments Conducted under Both Anaerobic and Aerobic Conditions[a]

batch experiments		methane		halocarbons	
trace gas	initial gas concn (μg L^{-1})	oxidation rate (μg (g of soil)$^{-1}$ h^{-1})	R^2	degradation rate (μg (g of soil)$^{-1}$ h^{-1})	R^2
Aerobic Condition					
CFC-11	35	112	>0.982	no degradation	
CFC-12	20	108	>0.983	no degradation	
HCFC-21	250	92	>0.970	0.509	>0.916
HCFC-22	250	93	>0.977	0.343	>0.922
Anaerobic Condition					
CFC-11	35			0.0086	>0.957
CFC-12	50			0.0004	>0.937
HCFC-21	100			0.0013	>0.981
HCFC-22	100			0.0002	>0.811

[a] Regression coefficients (R^2) obtained from fitting the experimental data to a zero-order oxidation process. The batches held soil water content of 25% w/w and were conducted at room temperature.

112 μg g^{-1} h^{-1}. Unfortunately, it was not possible to measure degradation products in the soil columns because of much higher detection limits for HCFCs as compared to CFCs.

HCFCs. Average degradation capacities for HCFC-21 and HCFC-22 were 1.1×10^{-1} and 7.6×10^{-2} g m^{-2} d^{-1}, respectively. However, as compared to the CFCs, the degradation of the HCFCs seems to be located in the upper oxic part of the column (Figure 2F). For both compounds, the steepest decline in the concentration profile is observed at 20 cm corresponding to the methane oxidation zone with overlapping O_2 and CH_4 gradients. In aerobic batch experiments incubated with methane, both HCFC-21 and HCFC-22 were rapidly oxidized, and the degradation occurred in parallel with the oxidation of methane (*17*). The faster oxidation of HCFC-21 as compared to HCFC-22 is probably a result of the higher stability of HCFC-22 due to the presence of two carbon−fluoride bonds. This is consistent with the higher removal efficiency of HCFC-21 (61%) as compared to HCFC-22 (41%) observed in the soil column. On the contrary, HCFC-21 and HCFC-22 were slowly degraded under anaerobic conditions in anaerobic batches (Figure 4). The degrada-

tion of HCFC-22 was very slow, and only 35% degradation was obtained within the duration of the experiment. The degradation of the HCFCs was more than 400 times slower under anaerobic conditions as compared to the oxidative experiments (Table 4). In a previous study (*17*), soil samples from different depths incubated with methane showed that the methane oxidizers were very active in oxidizing HCFCs down to a depth of 50 cm below the surface. Maximum rates were obtained with soil from 15- to 20-cm depth, which is consistent with results obtained in the column experiments. The oxidation rates decreased dramatically at 50-cm depth, indicating that the methane oxidizers were located in the upper part of the soil profile where both methane and oxygen were present.

Methanotrophs expressing the soluble form of MMO (sMMO) were dominating in the upper 20 cm of the soil at Skellingsted Landfill: 15 isolates of type II (where 10 carried the genes for sMMO) were identified and only one type I (*26*). This is compatible with the low copper concentration of 4.7 mg g^{-1} measured in the soil, which corresponds to a copper concentration of 4.7 μg L^{-1} in soil water (using a soil−water distribution coefficient of 1000 (*27*)) as sMMO is only produced in the wild-type organism at very low copper concentrations (<16 μg L^{-1}) (*28*). Methanotrophs producing sMMO are particularly valuable in landfill soil covers as the enzyme sMMO has a broad substrate specificity and is known to catalyze faster cometabolic degradation than particulate MMO (*29*).

Dehalogenation in the column study was measured by evaluation of the stoichiometric release of chloride by ion chromatographic analysis at the end of the experiment. Approximately 60% of the total HCFC chloride was released and mainly in the upper part of the column. Maximal chloride content (45 mg kg^{-1}) was located at 20-cm depth as compared to the initial concentration of 3.5 mg kg^{-1}. In comparison, the chloride concentration in the lower part of the column (50 cm) was less than 7 mg kg^{-1}.

Methane Oxidation and Degradation of Trace Components in Column Experiments with Variable Inlet Flow. Figure 5A−C shows removal efficiency of methane, CFCs, and HCFCs as a function of the inlet flow. Figure 5A shows that very high methane reductions of 88−97% were obtained with low inlet flows between 0.24 and 0.76 m^3 m^{-2} d^{-1}. Increasing the inlet flow led to a drop in methane oxidation (i.e., for a flow of 4.1 m^3 m^{-2} d^{-1} only 24% of the methane was oxidized). Soil gas profiles of methane and oxygen also showed that the oxidation zone was moved upward in the column when the inlet flow was increased (Figure 6). Similarly, the degradation of HCFCs decreased from approximately 75 to 20% when increasing the flow from 0.24 to 4.1 m^3 m^{-2} d^{-1}. In column experiments with CFCs, a drop in degraded mass was also observed when increasing the inlet flow. However, the drop was much less pronounced than for HCFCs, with values falling from 98% to 86% for CFC-11 and from 40% to 10% for CFC-12 when increasing the flow from 0.24 to 4.1 m^3 m^{-2} d^{-1}. Enhanced inlet flow results in diminished retention time and thereby a diminished oxidation. However, when increasing the inlet flow, the oxidative zone is moved upward in the column and thereby increases the anaerobic zone (Figure 6). An increased anaerobic zone will enhance the degradation of compounds that are anaerobically degraded and will thereby mitigate the effect of a lower retention time. This again indicates that anaerobic degradation of the CFCs takes place. This experiment clearly demonstrates the complexity of degradation of trace gases in soil covers when both oxidative and reductive processes are in play under variable flow conditions.

Under methanogenic conditions, which exist within the waste, CFC-11 and CFC-12 may undergo reductive dehalogenation leading to accumulation of lesser chlorinated

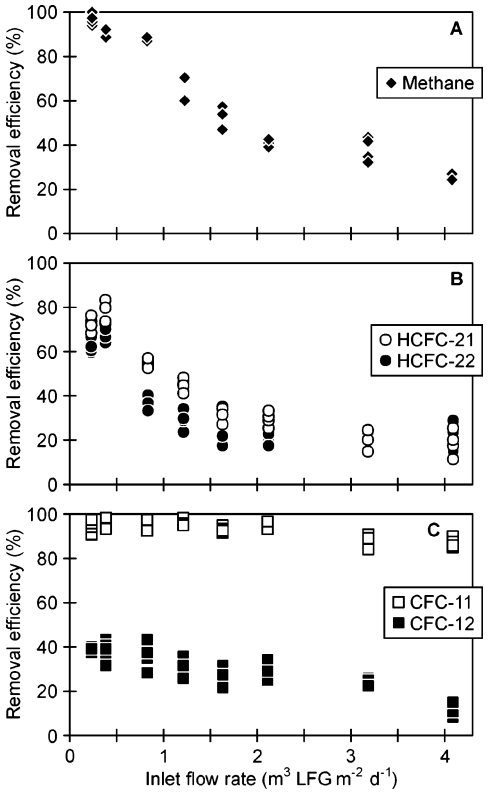

FIGURE 5. Removal efficiency of methane (A), HCFCs (B), and CFCs (C) as a function of the inlet flow.

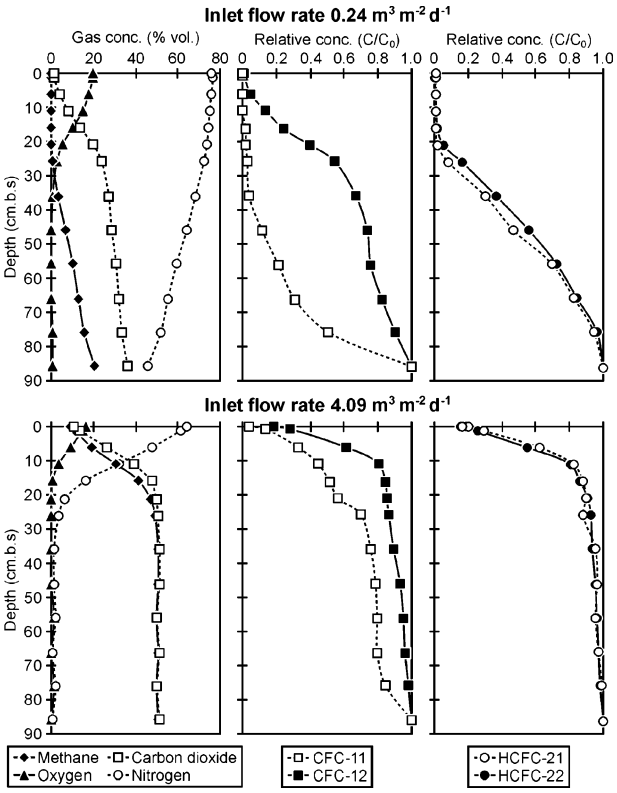

FIGURE 6. Soil gas profiles in soil columns at low (top) and high (bottom) inlet flows.

compounds such as HCFC-21, HCFC-31, and HCFC-22 (*30*, *31*), which often are more toxic than the prime compound (*32*). However, this study shows that the lower halogenated compounds such as HCFC-21 and HCFC-22 can be rapidly degraded in the upper oxidative zone in landfill soil covers

or in the surrounding soil due to their rapid oxidation by the methanotrophic bacteria. The same could be valid for other highly halogenated organic compounds, which are resistant to degradation or only slowly degradable in the aerobic zone, like perchloroethylene, trichloroethanes, etc.

Attenuation of methane in landfill top covers has been intensively studied in order to evaluate the contribution from landfills to global warming. This study shows that not only methane but also halogenated trace components can be degraded in surface soils. Landfill top covers are complex systems with counter-gradient gas migration, different redox zones, and a complex microbial community where both anaerobic and aerobic bacteria may play a very important role in reducing the emission of both methane and trace components into the atmosphere. At old landfills with lower gas production, methane oxidation and degradation of trace components in top soils may play a very important role in reducing the emission into the atmosphere. Worldwide, a significant part of the waste is still landfilled including chlorofluoro-containing waste. However, the fate of chlorofluoro compounds in landfill environments (e.g., release from waste sources, transformation capacity, and air emissions) is only sparsely enlightened. Transformation of CFCs and HCFCs both within the waste and in the surrounding soils should be taken into account in global mass balances for these compounds. Finally, future engineering of soil covers should not only focus on methane but also on trace components in order to develop good biostrategies for remediation of old landfill or as an add-on to modern controlled landfills.

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