

Attenuation of Fluorocarbons Released from Foam Insulation in Landfills

CHARLOTTE SCHEUTZ,[†] YUTAKA DOTE,[‡]
ANDERS M. FREDENSLUND,[†]
HANS MOSBÆK,[†] AND PETER KJELDSEN[†]

Institute of Environment & Resources, Building 115, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark, and Department of Civil and Environmental Engineering, Miyazaki University, 1-1 Gakuen Kibanadai Nishi, Miyazaki 889-2192, Japan

Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) have been used as blowing agents (BAs) for foam insulation in home appliances and building materials, which after the end of their useful life are disposed of in landfills. The objective of this project was to evaluate the potential for degradation of BAs in landfills, and to develop a landfill model, which could simulate the fate of BAs in landfills. The investigation was performed by use of anaerobic microcosm studies using different types of organic waste and anaerobic digested sludge as inoculum. The BAs studied were CFC-11, CFC-12, HCFC-141b, HFC-134a, and HFC-245fa. Experiments considering the fate of some of the expected degradation products of CFC-11 and CFC-12 were included like HCFC-21, HCFC-22, HCFC-31, HCFC-32, and HFC-41. Degradation of all studied CFCs and HCFCs was observed regardless the type of waste used. In general, the degradation followed first-order kinetics. CFC-11 was rapidly degraded from $590 \mu\text{g L}^{-1}$ to less than $5 \mu\text{g L}^{-1}$ within 15–20 days. The degradation pattern indicated a sequential production of HCFC-21, HCFC-31, and HFC-41. However, 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. The degradation rate coefficient was directly correlated with the number of chlorine atoms attached to the carbon. The highest degradation rate coefficient was obtained for CFC-11, whereas lower rates were seen for HCFC-21 and HCFC-31. Equivalent results were obtained for CFC-12. HCFC-141b was also degraded with rates comparable to HCFC-21 and CFC-12. Anaerobic degradation of the studied HFCs was not observed in any of the experiments within a run time of up to 200 days. The obtained degradation rate coefficients were used as input for an extended version of an existing landfill fate model incorporating a time dependent BA release from co-disposed foam insulation waste. Predictions with the model indicate that the emission of foam released BAs may be strongly attenuated by microbial degradation reactions.

* Corresponding author phone: +45 45 25 16 07; fax: +45 45 93 28 50; e-mail: chs@er.dtu.dk.

[†] Technical University of Denmark.

[‡] Miyazaki University.

Sensitivity analysis suggests that there is a need for determination of degradation rates under more field realistic scenarios.

Introduction

Fluorocarbons are frequently used as blowing agents (BAs) for foam insulation used in appliances (e.g., refrigerators and freezers) and many building materials (1). From 1964 until 1996, when their use was banned by the Montreal Protocol due to its strong ozone depletion potential, CFC-11 (CCl_3F) was the most common BA (1). HCFC-141b ($\text{CCl}_2\text{-FCH}_3$) was used widely as a substitute for CFC-11, but by 2005 use of HCFC-141b was also banned in most developed countries due to recognition of its ozone depletion potential. CFC-12 (CCl_2F_2) has been used as coolant in appliances, and as a BA in polystyrene foams used for building insulation and food packing materials. HFCs such as HFC-134a ($\text{CH}_2\text{-FCF}_3$) or HFC-245fa ($\text{CF}_3\text{CH}_2\text{CHF}_2$) are expected to be used extensively in the future as foam BAs. In addition to depleting the ozone layer, fluorocarbons released to the atmosphere are potential greenhouse gases that may contribute to global warming. In 1990 the combined CO_2 -equivalent emissions of CFCs, HCFCs, and HFCs was estimated to be $7.5 \text{ GtCO}_2\text{-eq/year}$. This was equivalent to about 30% of the annual contribution due to global fossil fuel burning (2).

Many appliances are shredded after the end of their useful life. When this occurs, the foam insulation is reduced to small pieces that may be incinerated, landfilled or, in a minority of cases, recycled. In the United States, as in many other parts of the world, most foam insulation waste is disposed of in landfills, and very little is incinerated (3). The proportion of the BA content of foam insulation, which is released during shredding, is dependent on the sizes of the shredded foam fractions (4). A recent study concluded that >81% of foam insulation waste disposed in landfills is shredded into foam particles larger than 16 mm prior to disposal, and that an average of 75% of the initial CFC content in the foam remains in the foam particles after the shredding process (5). The BA remaining in the foam waste 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 (4).

The presence of BAs in landfills is evident in landfill gas (LFG), which typically includes CFC-11 and CFC-12 (6–9) released from foam insulation waste (10). Other BAs and fluorocarbons commonly detected in LFG include HCFC-21, HCFC-22, HCFC-31, CFC-113, and CFC-114 with typically concentration levels up to $500 \mu\text{g L}^{-1}$ (6–10). CFCs are generally considered to be chemically very stable as a result of the high bond energy between carbon and fluorine. As a consequence of their high stability, CFCs have been perceived historically to be biologically inert. In 1989, however, it was reported that CFC-11 and CFC-12 can be dechlorinated in anaerobic ecosystems such as termite mounds (11) and in rice fields (12).

The susceptibility of CFCs to anaerobic reductive chlorination is particularly relevant to landfill conditions, which are typically methanogenic and strongly reducing. CFC-11 degradation under anaerobic conditions has been observed in methanogenic sediment (13), anoxic aquifer material (14), contaminated groundwater (15), and in anoxic marine water (16). Under landfill conditions, CFC-11 has been shown to undergo reductive dechlorination via HCFC-21 to HCFC-31 (17–19). The presence of HCFC-21 and HCFC-31 in LFG

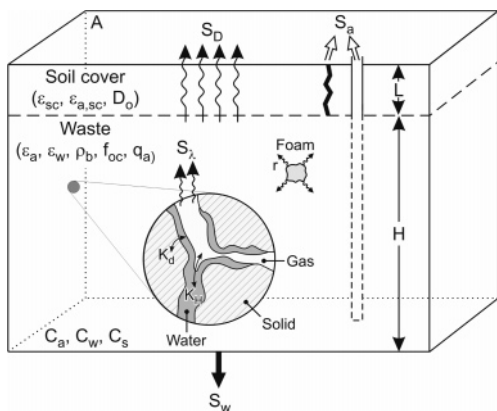


FIGURE 1. Setup for the MOCLA-FOAM model, showing the basic partition in the blown-up sketch and the fate routes: Gas flow (S_a), diffusion through soil cover (S_D), leaching (S_w), and degradation (S_d). The foam compartment releasing the BA with the rate, r , is also shown. The definition of other input parameters given in the figure is mentioned in the text following eqs 1–3 or in the SI.

thus indicates that anaerobic degradation of CFC-11 has occurred, because neither of these compounds have been produced for industrial applications. The frequent detection of CFC-11 degradation products in LFG suggests that landfills are sinks for CFCs disposed in foam waste. Landfills may also serve as sinks for HCFCs and HFCs; however, there is relatively little information available concerning the fate of these alternative BAs in landfills.

The importance of foam insulation waste in global fluorocarbon balances has been recognized for over a decade. Khalil and Rasmussen (20) projected that after production of CFC-11 ended, atmospheric concentrations of CFC-11 would depend primarily on the continued release from polyurethane foams. Due to the limited lifetime of products containing foam insulation, CFCs should cease to exist in waste being landfilled in most countries during the coming decades. Similar behavior is expected in the future for HCFCs and HFCs used as foam BAs. Thus, an understanding of the fluorocarbon behavior in landfills is crucial for accurate prediction of future fluorocarbon emission to the atmosphere.

The objective of this research was to evaluate the potential for degradation of foam BAs in batch landfill microcosms, and to develop a model that could simulate the fate of foam BAs in landfills using the degradation rate coefficients derived from the microcosm tests. The investigation was performed using organic household waste or refuse excavated from a landfill. The BAs studied were CFC-11, CFC-12, HCFC-141b, HFC-134a, and HFC-245fa. In addition, experiments were performed investigating the fate of expected BA degradation intermediates, including HCFC-21, HCFC-22, HCFC-31, and HFC-41. The model was developed as a spreadsheet model capable of simulating the dynamic behavior and fate of BAs released from shredded foam insulation waste in landfills. The Supporting Information (SI) gives details on the model and the model input parameters.

Model for Emissions and Degradation of Foam Released Halocarbons in Landfills. The fate of halocarbons contained in foam insulation waste in a landfill was simulated using a modified version of the MOCLA (Model for Organic Chemicals in Landfills) spreadsheet model (21). The modified model, MOCLA-FOAM, contains a source term (i.e., foam insulation) module to simulate the continuous release of BA into the pore air space of the landfilled waste. The processes simulated in MOCLA-FOAM are shown in Figure 1. The model is based on the box model assumption that fully mixed conditions exist and all phase concentrations are uniform within the landfill model domain. Others have modeled landfills as a plug flow reactor with respect to the flow of LFG and water.

The few full-scale tracer studies that have been carried out on landfills (22, 23) suggest that the retention time distribution in a landfill is closer to that of a fully mixed reactor than a plug flow reactor, probably due to a high flow of the water in channels within the waste (21). In addition, modeling the landfill as a fully mixed reactor offers the advantage of simpler mathematics and requires less input data than models for plug flow reactors.

The model assumes that, within a volume of waste, an organic chemical will be in equilibrium with the waste components and will be distributed among aqueous (leachate), gaseous (pore space), and sorbed (solid waste) phases (see Figure 1). At equilibrium, two equations describe the relationship between the phases. The relationship between the gaseous phase and the aqueous phase is described by Henry's constant, K_H ($\text{m}^3 \text{ water m}^{-3} \text{ air}$). The relationship between the solid phase and the aqueous phase is described by the distribution coefficient, K_d ($\text{m}^3 \text{ water metric tons}^{-1} \text{ dry waste}$). The model also assumes that the landfill contains shredded foam insulation waste that is releasing BA at a rate, r .

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

$$C_T(t) = \frac{r \cdot R_a}{k} \left(1 - \exp \left(-\frac{k}{R_a} \cdot t \right) \right) + C_{T,0} \exp \left(-\frac{k}{R_a} \cdot t \right) \quad (1)$$

where

$$k = q_a + q_D + \frac{N}{H \cdot K_H} + \frac{\epsilon_w \lambda}{K_H} \quad (2)$$

R_a is the retardation factor:

$$R_a = \frac{\rho_b \cdot K_d + \epsilon_w}{K_H} + \epsilon_a = \frac{\rho_b \cdot f_{oc} \cdot K_{oc} + \epsilon_w}{K_H} + \epsilon_a \quad (3)$$

$C_{T,0}$ is the initial total concentration (g chemical m^{-3} of landfill); r is a constant release rate of the chemical (in g chemical m^{-3} of landfill year^{-1}); k is the first-order decay coefficient (year^{-1}); q_a is the specific gas production rate ($\text{m}^3 \text{ LFG m}^{-3} \text{ waste year}^{-1}$); q_D is the diffusion equivalent specific gas flow (year^{-1}); N is the yearly net precipitation (m year^{-1}); H is the total depth of waste (m); K_H is the dimensionless Henry's laws constant ($\text{m}^3 \text{ water m}^{-3} \text{ air}$); K_d is the distribution coefficient between the solid phase and the aqueous phase ($\text{m}^3 \text{ water metric tons}^{-1} \text{ dry waste}$); f_{oc} is the fraction of organic carbon in the dry waste (metric tons organic carbon metric tons $^{-1}$ dry waste); K_{oc} is the distribution coefficient onto solid organic carbon ($\text{m}^3 \text{ water metric tons}^{-1} \text{ carbon}$); λ is the first-order degradation coefficient related to the aqueous phase (year^{-1}); ρ_b is the dry bulk density of the waste in the landfill (metric tons dry waste m^{-3} of landfill); ϵ_w is the volumetric content of water in the landfill (m^3 of water m^{-3} of landfill); ϵ_a is the volumetric content of air in the landfill (m^3 of air m^{-3} of landfill).

As described above K_d is calculated from the well-known relationship to the solid organic carbon content, f_{oc} and the distribution coefficient, K_{oc} , onto solid organic carbon. Since a large part of the organic carbon is lost over time due to waste decomposition and LFG generation, it is expected that f_{oc} will decrease with time. However, at the same time K_{oc} may increase due to the general aging of the organic waste. Such trends have been observed for soils by comparing soils containing young and very old organic material (24, 25). Due to this and to keep the model as simple as possible, the K_d -value is kept constant over time.

TABLE 1. Chemical Names, Synonyms, Physical/chemical Properties of the Halocarbons Included in This Study^a

chemical name	synonyms	formula	CAS no.	molecular weight g mol ⁻¹	Henry law constant K_H	Log K_{ow}
Trichlorofluoromethane	CFC-11	CCl ₃ F	75-69-4	137.37	3.96	2.53
Dichlorodifluoromethane	CFC-12	CCl ₂ F ₂	75-71-8	120.91	14.02	2.16
Dichlorofluoromethane	HCFC-21	CCl ₂ FH	75-43-4	102.92	0.44	1.55
Chlorodifluoromethane	HCFC-22	CClF ₂ H	75-45-6	86.47	1.66	1.08
Chlorofluoromethane	HCFC-31	CClFH ₂	593-70-4	68.48	0.27	0.51
Difluoromethane	HFC-32	CF ₂ H ₂	75-10-5	52.02	11.94	0.2
Fluoromethane	HFC-41	CFH ₃	593-53-3	34.03	0.69	0.51
1,1,1,2-tetra-fluoroethane	HFC-134a	CH ₂ FCF ₃	811-97-02	102.03	2.04	1.68
1,1-dichloro-1-fluoroethane	HCFC-141b	CCl ₂ FCH ₃	1717-00-6	116.95	0.9	2.37
1,1,1-trifluoro-3,3-difluoro-propane	HFC-245fa	CF ₃ CH ₂ CHF ₂	460-73-1	134.05	ndf	ndf

^a ndf: no data found; K_H (dimensionless, 25 °C) and Log K_{ow} -values were taken from Syracuse Research Corporation Environmental Science PhysProp Database: <http://www.syrres.com/esc/physdemo.htm>.

Additional details regarding the calculation of q_D and K_{oc} are given in Kjeldsen and Christensen (21) and are summarized in the SI. The SI also gives details on calculating accumulative mass losses (referred to as fate routes in the model) due to the different processes (gaseous and aqueous emissions and degradation), and provides instruction on how to use the model with a time-dependent release rate, r .

Materials and Methods

Chemicals and Foam Samples. The CFC-11, HCFC-21, HCFC-22, HCFC-31, HFC-32, HFC-41, HFC-134a, HCFC-141b, and HFC-245fa used were all obtained in high purity (>98%). CFC-11, CFC-12, HCFC-21, and HCFC-22 were purchased from Fluorochem Ltd., England. HCFC-31, HFC-32, and HFC-41 were purchased from SynQuest Labs. Inc., Alachua, FL. HFC-134a, HFC-245fa were obtained from Interchim, France whereas HCFC-141b was obtained from Honeywell, Netherlands. Table 1 shows chemical names, synonyms and selected physical/chemical properties for the halocarbons used in this study.

The potential of organic waste to have a mitigating effect on the release of BAs from foam insulation was tested in anaerobic microcosm experiments supplemented with foam pieces. Foam samples blown with four different BAs (CFC-11, HCFC-141b, HFC-134a, HFC-245fa) were included in this study. The characteristics of the four foam panels are described in Table 1 in Kjeldsen and Scheutz (4).

Waste Samples. The potential of anaerobic bacteria to degrade BAs under landfill conditions was tested in presence of three types of waste material: A, B, C.

A: 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 waste materials differed in terms of composition, origin, and age. The methane gas production rate of the different waste types was determined using the method by Hansen et al. (26).

The organic waste (waste A) was collected from private Danish households in an area where the citizens as a part of a research program were sorting their waste into different fractions including an organic fraction. The organic waste had the highest methane gas production rate (0.014 g CH₄ g⁻¹ waste d⁻¹) of the three types of waste tested, and consisted of well-sorted easily degradable food wastes including fruits, vegetables, bread, rice, corn. The organic material was therefore expected to provide the anaerobic bacteria with a labile carbon source to maximize growth.

Older predisposed waste (waste B) was excavated from an American landfill situated in North Carolina. Although the landfill was producing methane, the gas production rate

was lower (0.002 g CH₄ g⁻¹ waste d⁻¹) in comparison with the Danish organic refuse, probably due to the higher degree of maturity of the organic material. Unlike waste A, however, waste B may have contained anaerobic bacteria that had been preexposed to different BAs in the landfill environments and could therefore hold a potential to degrade some of the halocarbons evaluated in these experiments.

Samples from a laboratory experimental digester containing refuse (waste C) was the third type of waste tested. The digester was in its methanogenic phase and contained well-decomposed waste, which was also confirmed by a low methane production rate (0.001 g CH₄ g⁻¹ waste d⁻¹).

Microcosms were inoculated with methanogenic digested sludge from either a mesophilic biogas reactor receiving agricultural waste (Hashøj Biogas, Denmark) or a biological sewage treatment plant (Lundtofte sewage treatment plant, Denmark).

Degradation of BAs Under Methanogenic Conditions.

Anaerobic degradation of selected BAs and associated degradation products was examined in glass microcosm bottles (327 mL in total volume) equipped with Teflon-coated butyl rubber septa (8 mm thick) held in place by an aluminum screw caps. The septum enabled gas to be sampled or injected by a hypodermic needle and a syringe. A fixed amount of waste (10 g) was placed in each bottle. The waste was homogenized in a blender before use in the experiments. The bottles were inoculated with sludge (40 mL) to ensure anaerobic microbial activity. To obtain anaerobic conditions during microcosm construction, the bottles were flushed with a nitrogen/carbon dioxide mixture (80:20%).

The degradation of halocarbons was studied in single compound tests. Microcosms were spiked with one test compound (CFC-11, CFC-12, HCFC-21, HCFC-22, HCFC-31, HFC-41, HCFC-141b, HFC-134a, or HFC-245fa) using gaseous stock solutions and a glass barrel gastight syringe. Halocarbon initial concentrations, which varied between 150 and 600 µg L⁻¹, were generally selected so they were in the range typically observed in LFG (6–9).

The headspace (50 µL) in the microcosms was sampled periodically and analyzed by gas chromatography (GC). Approximately 20 gas samples were extracted during an experimental period (approximately 80–200 days), utilizing less than 1% of the gas volume in the batch microcosm, which was found not to influence the results. Furthermore, a leakage test was performed using argon as a conservative tracer to account for losses through the septum due to perforation during sampling. The test showed that up to 30 gas samples could be extracted over a period of approximately 200 days before the septum started to leak if the syringe was inserted in a new place every time a sample was taken (results not shown). The microcosm experiments were conducted at

TABLE 2. Average First-Order Degradation Rate Coefficients (k_1) and Half-Lives ($t_{1/2}$) for Anaerobic Degradation of BAs in Microcosm Experiments Added Different Types of Waste Materials and Inoculated with Digested Sludge from a Biogas Plant Receiving Agricultural Waste^a

blowing agent		average degradation rate coefficients					methane production
		C_0^b $\mu\text{g L}^{-1}$	k_1 d^{-1}	$t_{1/2}$ d	R^2	λ d^{-1}	T^c d
waste A: fresh organic waste collected from Danish households – 1. round							
CFC-11	CCl_3F	215	0.426 ± 0.046	1.6	> 0.958	16.14	16
HCFC-21	CCl_2FH	210	0.029 ± 0.002	24.1	> 0.943	0.14	nd
HCFC-31	CClFH_2	137	0.011 ± 0.004	65.4	> 0.900	0.03	nd
HFC-41	CFH_3	164	—	—	—	—	nd
CFC-12	CCl_2F_2	225	0.029 ± 0.004	23.9	> 0.910	2.90	15
HCFC-22	CClF_2H	215	0.015 ± 0.002	46.2	> 0.901	0.19	26
HCFC-141b	CCl_2FCH_3	246	0.026 ± 0.001	26.7	> 0.951	0.36	12
HFC-134a	CH_2FCF_3	367	—	—	—	—	18
HFC-245fa	$\text{CF}_3\text{CH}_2\text{CHF}_2$	348	—	—	—	—	26
waste B: Older pre-disposed waste from an American landfill							
CFC-11	CCl_3F	589	0.259 ± 0.026	2.7	> 0.983	9.81	26
CFC-11	CCl_3F	555	0.251 ± 0.032^c	2.8	> 0.962	9.51	21
CFC-11	CCl_3F	520	0.096 ± 0.012^d	7.2	> 0.976	3.64	nd
HCFC-21	CCl_2FH	420	0.024 ± 0.001	28.9	> 0.881	0.12	92
HCFC-31	CClFH_2	252	0.011 ± 0.006	63.0	> 0.670	0.03	70
HFC-41	CFH_3	102	—	—	—	—	150
HCFC-141b	CCl_2FCH_3	202	0.012 ± 0.003	57.8	> 0.869	0.17	45
HFC-134a	CH_2FCF_3	215	—	—	—	—	55
HFC-245fa	$\text{CF}_3\text{CH}_2\text{CHF}_2$	289	—	—	—	—	35
waste C: Waste from a laboratory experimental digester simulating landfill conditions							
CFC-11	CCl_3F	210	0.298 ± 0.006	2.3	> 0.960	11.29	25
HCFC-141b	CCl_2FCH_3	197	0.010 ± 0.003	69.3	> 0.867	0.14	50
HFC-134a	CH_2FCF_3	210	—	—	—	—	67
HFC-245fa	$\text{CF}_3\text{CH}_2\text{CHF}_2$	283	—	—	—	—	46

^a The minimum regression coefficient (R^2) obtained from fitting the experimental data to a first-order degradation process out of triplicate replicates. The water-based first-order degradation rate coefficients, λ , calculated by eq S115 and S116 in the SI are also given. Microcosm parameters used for calculation of λ are listed in Table 1 in the SI. —, no degradation observed. nd, not determined as methane analysis were only conducted in the end of the experiments. ^b Average initial concentrations; C_0 . ^c Sludge from a wastewater treatment plant. ^d Not inoculated with sludge. ^e The average time period; T for production of an amount of methane corresponding to 20% vol in the headspace.

room temperature (22 °C). All experiments were carried out in triplicate. Sterile control microcosms were prepared to investigate halocarbon loss due to nonbiological processes (i.e., abiotic degradation, sorption, and volatilization). Control reactors were sterilized by autoclaving (three times for 1 h at 121 °C). Halocarbons were added to the control experiments after autoclaving.

Degradation kinetics were examined by plotting the measured headspace concentrations of the individual compounds versus time and fitting the data to an exponential regression. In all cases, degradation followed first-order kinetics, and degradation rate coefficients were estimated from an exponential fit to the data. For each compound, an average degradation rate coefficient (k_1) was calculated based on three replicates. The average degradation rate coefficient (k_1), which was based on gas phase measurements, was converted to an aqueous phase rate coefficient (λ) for use as input in the fate model (see the SI for additional details). In this paper, the term degradation is used to describe significant decreases in gas concentration over time in live microcosms relative to sterile controls.

Microbial Mitigation of BA Releases from Foam Insulation Under Methanogenic Conditions. Microcosm experiments with waste mixed with pieces of foam insulation were performed to study whether the presence of anaerobic bacteria can have a mitigating effect on the release of BAs from foam insulation in landfill waste. The experimental procedure was similar to the procedure described in the previous section except that cut pieces of foam insulation were supplemented to bottles instead of a fixed amount of BA. Foam cylinders were cut using a cork bore (1 cm diameter and 1 cm height). Four foam pieces cut as cylinders were supplemented to each foam-containing bottle. The experiment also included use of sterile controls to quantify release

of BAs in the absence of degradation. Headspace samples were withdrawn and analyzed by GC over time. The experiments ran for 14 weeks at room temperature. Experiments with four BAs (CFC-11, HCFC-141b, HFC-134a, and HFC-245fa) were performed in parallel.

Gas Chromatography Analysis. Analysis of the halogenated compounds (CFC-11, CFC-12, HFC-134a, HCFC-141b, HFC-245fa, HCFC-21, HCFC-22, HCFC-31, HFC-32, and HFC-41) was performed on an Agilent 6890N gas chromatograph (GC) coupled with an Agilent 5973N mass spectrometer (MS) (Agilent Technologies Denmark A/S, Naerum, Denmark). The gas samples were injected manually as direct on-column injections on a GS-CarbonPLOT column (30m × 0.32 mm × 1.5 μm) (J&W Scientific Inc., Folsom, CA) with helium as carrier gas. For compound separation, the oven was set to 45 °C for 1.2 min and then increased to 260 °C at 30 °C min⁻¹. The carrier gas flow was set at 2 mL min⁻¹, and a sample split of 1:2 was used. The GC-MS was operated in a SIM-mode. The target and qualifier ions are listed in Table 2 in the SI. Injection volume of samples was 50 μL throughout the project period. Injection of gas samples was performed using a 100 μL VICI Precision Sampling Inc Pressure Lock Gas Syringe (VICI Valco Instruments Co. Inc., Houston, TX).

Calibration curves were prepared by injection of at least five different concentration levels from gaseous standards. 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 standards ranging from app. 20 to 820 $\mu\text{g L}^{-1}$ were used for calibration. The detection limit varied between 0.05 and 0.3 $\mu\text{g L}^{-1}$ for the individual halocarbons included in this study.

Methane was analyzed on a transportable CP-2002P Chrompack Micro GC (Chrompack International BV, The

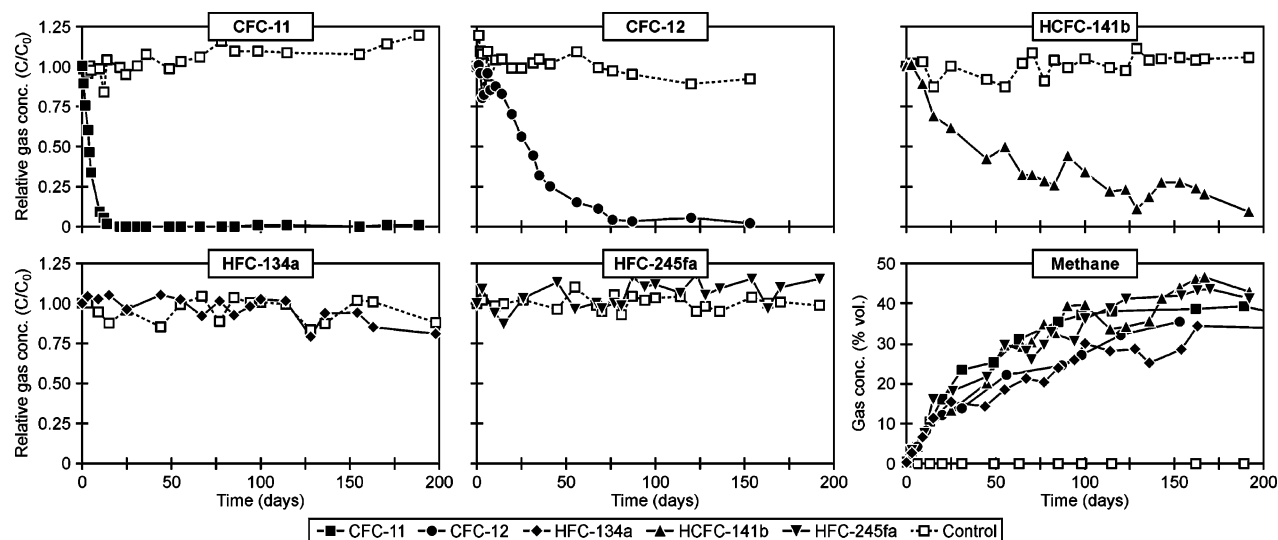


FIGURE 2. Headspace concentrations of halocarbons; CFC-11, CFC-12, HCFC-141b, HFC-134a, HFC-245fa and methane in microcosm experiments containing organic household waste inoculated with anaerobic digester sludge. Open symbols represents the results from sterilized control experiments. All values are average values based on triplicate replication.

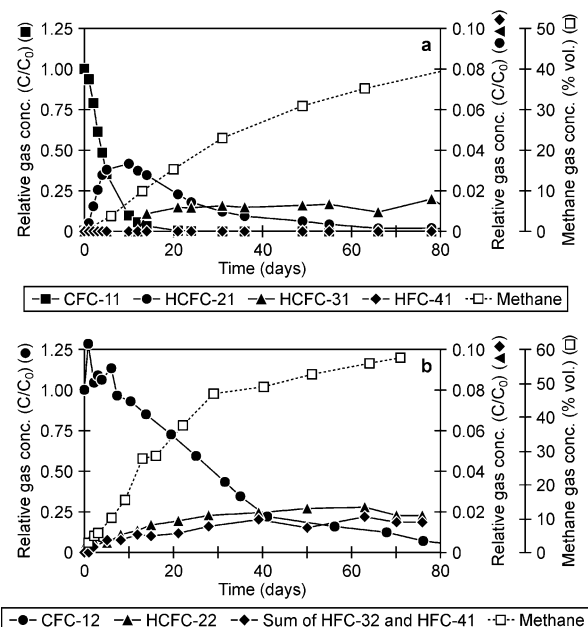


FIGURE 3. Anaerobic degradation of CFC-11 (a) and CFC-12 (b) and formation of degradation products in microcosm experiments containing organic household waste inoculated with anaerobic digester sludge. All values are average values based on triplicate replication. Relative concentrations are calculated based on molar concentrations.

Netherlands) gas chromatograph equipped with a thermal conductivity detector and two columns. Methane was quantified on a 10 m long Poraplot Q column. Helium was used as the carrier gas and the column temperature was 40 °C. Gas standards produced by MicroLab, Aarhus, Denmark ranging from 0.02 to 50 %vol were used for calibration.

Results and Discussion

Degradation of BAs Under Methanogenic Conditions. Degradation of CFC-11, CFC-12, HCFC-21, HCFC-22, HCFC-31, HCFC-141b was observed in microcosms containing waste inoculated with digested sludge (Figures 2–4). The degradation was microbially mediated as seen from comparison with the sterilized control batch (Figure 2 and Figure 1 in the SI).

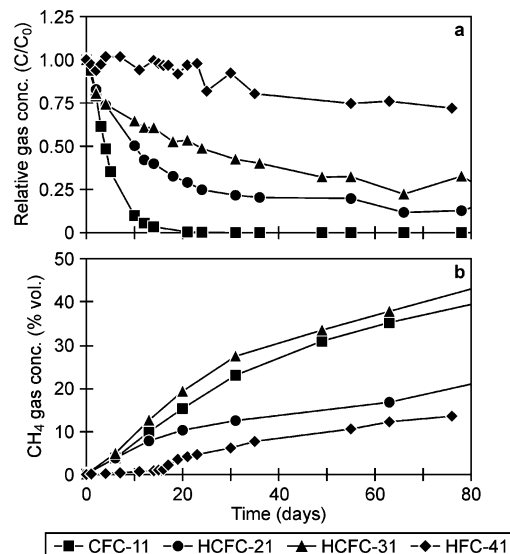


FIGURE 4. a. Anaerobic degradation of CFC-11, HCFC-21, HCFC-31, and HFC-41 in microcosm experiments containing organic household waste inoculated with anaerobic digester sludge. b. Methane production in microcosm experiments containing CFC-11, HCFC-21, HCFC-31, and HFC-41, respectively. Note that the degradation of the halocarbons was studied in single compound tests.

In general the degradation followed first-order kinetics. Table 2 shows the first-order degradation rate coefficients (k_1) as well as the regression coefficients (R^2) from fitting the experimental data with a first-order model equation. In general, good reproducibility was obtained and results from three replicate batches were almost identical with standard deviations of less than 10% between the obtained degradation rate coefficients (see Table 2). For the three HFCs (HFC-134a, HFC-245fa, and HFC-41) the evidence of degradation is more unclear. A statistical evaluation of the data for the three HFCs is included in the SI. The analysis shows weak (low regression coefficients) but statistically significant indications of microbially mediated degradation for HFC-41 and HFC-134a (on a 95% confidence level). However, for HFC-245fa the statistical analysis indicates a production of HFC-245fa in the active microcosm, which is highly unlikely. Defluorination (i.e., rupture of the carbon–fluorine bond) has only rarely been observed, and seems to require extreme

reducing conditions (27, 34). Balsiger et al. (19) did not see any degradation of HFC-134a in microcosms inoculated with sludge or sediment. No data on anaerobic degradation of HFC-245fa is currently reported. Due the low regression coefficients obtained in the statistical analysis and the fact that anaerobic degradation of HFCs only in a few cases has been observed, we think that these findings are too weak as a final proof of anaerobic HFC degradation. However, the findings clearly indicate that there is a need for future research with more focus on HFC degradation under methanogenic conditions performing experiments with much longer time frames.

Methane was produced in all bottles supplemented with waste and inoculum, indicating the presence of active methanogenic bacteria. The average time period for production of an amount of methane corresponding to 20 %vol in the headspace is listed in Table 2. In experiments supplemented with the lower halogenated HCFCs and HFCs an inhibition of the methane production was observed in comparison with experiments supplemented with CFC-11 and CFC-12 (cf. Table 2). No methane production was observed in sterilized bottles with waste and sludge, indicating that the sterilization process was effective (see Figure 2).

CFC-11 was relatively rapidly degraded in all experiments regardless of the type of waste. A similar degradation pattern was observed regardless whether the microcosms were inoculated with sludge from a biogas plant or sludge from a wastewater sewage treatment plant. CFC-11 was degraded from up to $590 \mu\text{g L}^{-1}$ to less than $5 \mu\text{g L}^{-1}$ under present experimental conditions within 15–20 days. CFC-11 was degraded to HCFC-21, HCFC-31, and HFC-41 (Figure 3a). However, the production of degradation products did not correlate with a stoichiometric removal of CFC-11 suggesting that other degradation products were produced. HCFC-21 and HCFC-31 were further degraded, whereas no further degradation of HFC-41 was observed. Figure 3a shows the degradation of CFC-11 in experiments conducted with organic household waste. In uninoculated microcosms containing older predisposed waste, CFC-11 was also degraded even though the degradation rate coefficient was lower compared to the inoculated experiments (Table 2). There was no transformation or loss of CFC-11 in the sterile controls.

To verify observed degradation patterns, microcosm experiments with high initial concentration of HCFC-21, HCFC-31, and HFC-41 were conducted. Figure 4a shows the anaerobic degradation of CFC-11, HCFC-21, HCFC-31, and HFC-41 in microcosms containing organic household waste inoculated with methanogenic digested sludge from a mesophilic biogas reactor receiving agricultural waste. The degradation rate coefficient was directly correlated with the number of chlorine atoms attached to the carbon as the highest degradation rate coefficient was obtained for CFC-11, the lowest for HCFC-31, whereas no degradation of HFC-41 was observed (see the discussion provided in the SI). 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 HCFC-31 (Table 2). In experiments with HCFC-21 and HCFC-31, production of their respective lower chlorinated compounds was observed, however, in amounts consistently lower than the corresponding stoichiometric release. This was the case regardless of the type of waste or the source of inoculum used. CFC-11 is generally considered to undergo reductive dechlorination through HCFC-21 to HCFC-31 (17, 18). However, Krone et al. (27) studied the reductive dehalogenation of CFC-11 (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. Krone et al. (27) found that CFC-11 was reduced by titanium (III) citrate in the presence of aquocobalamin with

the major degradation products being: CO (67%); CHFCl_2 (<10%); and formate (<5%). CH_2FCl , CH_3F , $\text{C}_2\text{F}_2\text{Cl}_2$, and $\text{C}_2\text{F}_2\text{Cl}_4$ were identified as side products at low concentrations. Lovley and Woodward (13) observed degradation 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. (27). Also, Olivas et al. (28) found the degradation pathway of CFC-11 to be only partially reductive since the production of reduced metabolites was low in comparison with the total amount of original compound added.

To verify whether degradation products similar to those observed by Krone and co-workers (27) were produced, the experiments supplemented with CFC-11 were periodically analyzed for $\text{C}_2\text{F}_2\text{Cl}_2$ and $\text{C}_2\text{F}_2\text{Cl}_4$ with GC-MS and GC equipped with ECD, respectively, but none of the products were observed. After 70 days, gas samples were analyzed by GC-MS operated in a SCAN-mode (10–325 m/z), however chromatograms showed no peaks, suggesting that nonvolatile products were produced. Based on the conducted experiments it can be concluded that CFC-11 was only partly dechlorinated to HCFC-21, HCFC-31, and HFC-41 under methanogenic conditions, and it is likely that CFC-11 is degraded into nonvolatile compounds. Whether CFC-11 was completely dehalogenated to produce mass balance quantities of chloride and fluoride could not be determined in this study because high background concentrations of these anions in the wastes tested and analytical interference from volatile acids prevented quantitative determination of these ions via ion chromatography. Elucidation of the degradation pathway of CFC-11 in landfills is important as a complete stoichiometric degradation of CFC-11 to HCFC-21, and HCFC-31 could be problematic as both HCFC-21 and HCFC-31 are toxic (29). Fortunately, HCFC-21 and HCFC-31 are rapidly microbially oxidized in landfill cover soils, a process that serves to mitigate the emission of these two compounds from landfills (30, 31).

In microcosms that were initially spiked with HCFC-21, methane production was lower compared to microcosms spiked with CFC-11 and HCFC-31 (Figure 4b). Balsiger et al. (19) observed inhibition of methane production in sediment microcosms supplemented with CFC-11. In addition, CFC-11 was not completely consumed and no further conversion of HCFC-21 to HCFC-31 occurred. Deipser (32) reported that CFC-11 inhibited the degradation of CFC-12 and HCFC-21 in anaerobic compost. These observations suggest that either CFC-11 or a CFC-11 degradation product is responsible for the inhibition of methanogens and of the degradation of CFC-11. However, as no inhibition of methane production was observed in microcosms supplemented with CFC-11, and as the primary degradation product did not seem to be HCFC-21, this indicates that HCFC-21 (and not CFC-11) was inhibitory to the methanogens in the experiments conducted in this study. In addition, HFC-41 was found to inhibit methane production and this in a higher degree than in experiments run with any of the other compounds.

CFC-12 and HCFC-22 were degraded in microcosms supplemented with organic household waste (Figures 2 and 3b). CFC-12 and HCFC-22 were degraded from ca. $225 \mu\text{g L}^{-1}$ to less than $25 \mu\text{g L}^{-1}$ within 70 and 150 days, respectively. As for experiments with CFC-11, the degradation pattern of CFC-12 did not indicate a stoichiometric sequential dechlorination as the sum of the observed degradation products HCFC-22, HFC-32, HFC-41 never exceeded 10% of the initial content of CFC-12 (Figure 3b). Similar observations were made in microcosm experiments supplemented HCFC-22 (results not shown). In general, the degradation rate coefficient of CFC-12 was much slower compared to CFC-11, resulting in approximate half-lives of 24 days and 2 days,

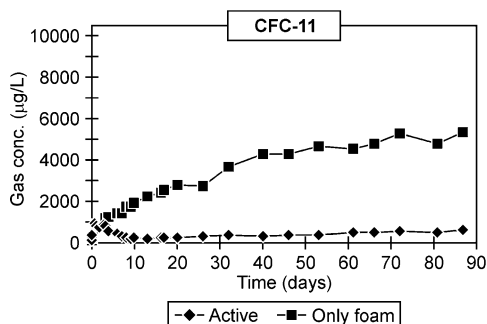


FIGURE 5. Headspace concentration of CFC-11 in anaerobic microcosm experiments with organic household waste and foam (◆). Also shown is the release of CFC-11 from foam insulation in a control batch experiment without waste and inoculum (■). Figure 1 in the SI shows the results of the corresponding experiments with HCFC-141b, HFC-134a, and HFC-245fa.

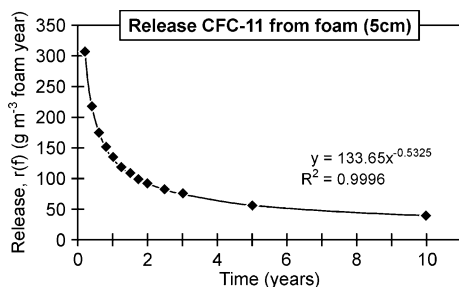


FIGURE 6. The time-dependent release rate, r , of BA (CFC-11) from foam, modeled according to the equations SI13 and SI14 and the parameters in Table 1 in SI.

respectively. Theoretical predictions of the rates for halomethane degradation by reductive dechlorination suggest that the rates for CFC-11 and CFC-12 should be almost equal (19), but experimental evidence shows that CFC-12 is degraded at rates that are at least 10 times slower than those for CFC-11 (13, 19, 28, 32, 33), a result that was also apparent in this study.

HCFC-141b was also degraded with rates comparable to HCFC-21 and CFC-12. In comparison with CFC-11, the degradation of HCFC-141b occurred at a slower rate ($t_{1/2} = 50$ days). The degradation pathway of HCFC-141b was not investigated. Balsiger et al. (19) observed degradation of HCFC-141b in microcosms inoculated with contaminated sediment, whereas no degradation was observed in microcosms inoculated with sewage sludge. In the experiments reported by Balsiger et al. (19) the rate of degradation of HCFC-141b was slower than CFC-12 but higher than HCFC-21.

Microbial Mitigation of BAs Releases from Foam Insulation Under Methanogenic Conditions. Figure 2 in the SI shows accumulation of BAs versus time. As expected, similar releases were observed in bottles containing only foam pieces and bottles containing foam pieces and sterilized waste material. Release patterns showed a high initial release rate, which subsequently decreased. In experiments with active waste and inoculum, the microbial bacteria degrading CFC-11 mitigated the release of CFC-11 (Figure 5). In experiments with HCFC-141b no tendency toward a microbial removal was observed, which was due to the degradation rate coefficient of HCFC-141b being almost 30 times lower than that of CFC-11 (cf. Table 2). Simple calculations using the degradation rate coefficients obtained in the anaerobic degradation experiments showed that the microbial removal of HCFC-141b was insignificant compared to the release rate from foams (cf. Figure 2 in the SI). In experiments with HFC-134a and HFC-245fa no difference between microbially active

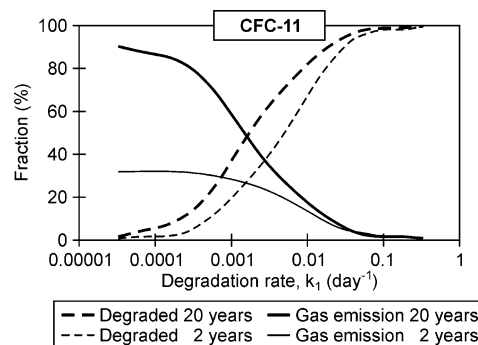


FIGURE 7. The fraction (%) of released BA (CFC-11), which has been degraded or emitted with LFG for the first 2 or 20 years, respectively, as a function of degradation rate coefficient, k_1 .

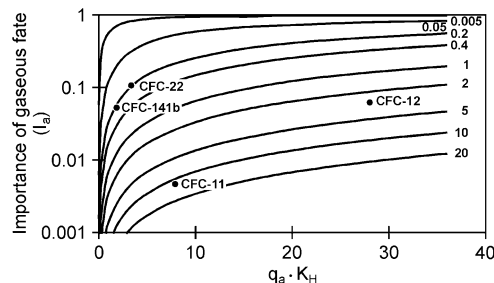


FIGURE 8. The relative importance of the gaseous fate route to the total fate as a function of the product $K_H \cdot q_g$ (The Henry's law constant multiplied by the specific gas production rate) on the x-axis, and the degradation rate coefficient, λ (in days⁻¹) as legends for each curve. Example values for the four BAs, CFC-11, CFC-12, HCFC-22, and HCFC-141b is plotted in the graph fraction based on the specific gas production rate used in the landfill scenario (see the SI for more details).

and sterile bottles was observed, which was also expected based on the anaerobic degradation experiments where none of the two compounds were degraded (cf. Figure 2 in the SI).

Modeling the Emission and Degradation of Foam Released Halocarbons in Landfills. To evaluate the determined degradation rates in a landfill scenario incorporating all governing processes to the overall fate of the BA, a landfill reactor scenario was set up. It is assumed that the foam waste was disposed of under ideal conditions for microbial degradation of the continuously released BA. Ideal conditions would be to cut the foam panels in moderate sizes, avoid too much compaction, and to mix in anaerobic sludge as inoculum. It was assumed that the foam was cut into pieces (5 cm cubes) and codisposed together with a mixture of organic wastes without any compaction. Compaction was avoided to deteriorate the foam structure as little as possible because any deterioration will enhance the release of BA from the foam. Table 1 in the SI gives 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 were all based on data given in the referenced literature or were estimated as described in Table 1. The waste and landfill data were based on typical landfill scenarios as defined in the original MOCLA description (21). The model is used to evaluate the fate of the degrading BAs (CFC-11, CFC-12, HCFC-22, and HCFC-141b). The HFCs were not shown degradable in the microcosm experiment, and their fates in landfills are, therefore, not modeled.

The degradation rate coefficient, λ , used in MOCLA-FOAM is referring to the water concentration of the compound while the microcosm determined, k_1 , is referring to the gas concentration. Conversion of microcosm-determined degradation rate coefficients based on gaseous concentrations

TABLE 3. An Analysis Using MOCLA-FOAM for Evaluating Compound Fate Sensitivity to Diffusion Coefficient, D ($\text{m}^2 \text{s}^{-1}$) and Degradation Rate Coefficient, $k_1(\text{d}^{-1})^a$

	polyurethane foam				polystyrene foam			
	CFC-11		HCFC-141b		CFC-12		HCFC-22	
	$0.1k_1$	k_1	$0.1k_1$	k_1	$0.1k_1$	k_1	$0.1k_1$	k_1
diffusion: D^b								
fraction of initial content released (%)	35	35	41	41	52	52	100	100
released amount which has been emitted with gas/degraded (%)	5/94	0.5/99	29/48 ^c	6/92 ^c	40/60	6/94	57/43	12/88
diffusion: $10D$								
fraction of initial content released (%)	83	83	91	91	98	98	100	100
released amount which has been emitted with gas/degraded (%)	5/94	0.5/99	29/48 ^c	6/92 ^c	40/60	6/94	57/43	12/88

^a The table also presents the effect of lower degradation rate coefficient (a factor of 10; $0.1k_1$) and a higher diffusion coefficient (a factor of 10; $10D$). ^b Diffusion coefficients used: $2.0 \cdot 10^{-14} \text{ m}^2 \text{s}^{-1}$ (CFC-11)(4); $2.9 \cdot 10^{-14} \text{ m}^2 \text{s}^{-1}$ (HCFC-141b)(4); $5.1 \cdot 10^{-14} \text{ m}^2 \text{s}^{-1}$ (CFC-12)(36); $5.4 \cdot 10^{-12} \text{ m}^2 \text{s}^{-1}$ (HCFC-22)(36). The degradation rate coefficients, k_1 , in the runs with MOCLA-FOAM are average microcosm rates based on values listed in Table 2 (0.309, 0.029, 0.015, and 0.016 for CFC-11, CFC-12, HCFC-22, and HCFC-141b, respectively). ^c The remaining amount to close the mass balance is contained in the landfill as a sorbed fraction (due to the relatively high K_{ow} -value and low K_H -value).

to degradation rate coefficients based on aqueous concentrations valid for field scenarios is shown in the SI. The anaerobic degradation rate coefficient in the waste, λ , for the different compounds is given in Table 2 together with the microcosm determined rate coefficients, k_1 . The microcosm parameters used for the conversion are given in Table 1 in the SI. The chosen degradation rate coefficients, k_1 , in the runs with MOCLA-FOAM were average microcosm rate coefficients (0.309d^{-1} , 0.029d^{-1} , 0.015d^{-1} , and 0.016d^{-1} for CFC-11, CFC-12, HCFC-22, and HCFC-141b, respectively).

Based on the foam characteristics, the time-dependent release rate was determined using the release model presented in Kjeldsen and Jensen (35) and summarized in the SI. Figure 6 shows the release rate-time dependency for CFC-11 using the assumptions given in Table 1 in the SI and the diffusion coefficient given in Table 3.

Model runs with the defined landfill scenario (Table 1 in the SI) showed that the leachate and the diffusive loss through the cover soil were negligible fate routes; the release of BA was either released with LFG or being degraded. Especially for CFC-11, which had the highest observed degradation rate coefficient of the BAs studied, removal by degradation was very important. Figure 7 shows in more details the importance of the degradation rate coefficient to the amounts degraded and emitted after both 2 and 20 years for CFC-11. It is obvious that the degradation process even at much lower rates than those observed in the microcosm experiments decreased the emission of CFC-11 in LFG to the atmosphere.

To evaluate the relative importance of the fraction of BA release emitted to atmosphere, F_a , to the fraction of BA release emitted through all routes (degradation, F_d , water, F_w , and gas, F_g), an expression of the relative importance of gaseous emission, I_a , has been established (see the SI for details):

$$I_a = \frac{F_a}{F_a + F_w + F_d} = \frac{1}{1 + \frac{N/H + \epsilon_w \cdot \lambda}{K_H(q_a + q_D)}} \approx \frac{1}{1 + \frac{\epsilon_w \cdot \lambda}{K_H \cdot q_a}} \quad (4)$$

The assumption for the equation following the “almost equal sign” is that the water infiltration and the diffusional loss through the soil cover are negligible. This will be valid for clay covers made to prevent infiltration. Figure 8 is made using this equation with typical values of the degradation rate coefficient, λ (in days^{-1}) and $K_H \cdot q_a$. Using the determined average degradation rate coefficients for the BAs, CFC-11, CFC-12, HCFC-22, and HCFC-141b and the specific gas production rates used in the example ($q_a = 2 \text{ m}^3 \text{ LFG m}^{-3} \text{ waste year}^{-1}$) the I_a -values are calculated and plotted in Figure 8. The figure shows that gas emission

makes out about 10% of the fate for HCFC-22, and that lower values are obtained for the other three BAs. The plot can be used to evaluate the relative importance of the gaseous emission to the overall fate for other compounds having different degradability and volatility.

Table 3 shows an analysis of the BAs most widely used for polyurethane and polystyrene foam (CFC-11, HCFC-141b, CFC-12, and HCFC-22) using the same landfill scenario as mentioned above. Since the diffusion coefficient is depending both on the BA and the polymer, different diffusion coefficients were used. A sensitivity analysis on changing diffusion coefficient and degradation rate is performed. The table presents the effect of lower degradation rate coefficient (a factor of 10; $0.1k_1$) and higher diffusion coefficient (a factor of 10; $10D$) to how much BA has been released over a 20-year period, and the percentage of the released amount, which was emitted with gas or degraded. The table shows that CFC-12 and HCFC-22 released from polystyrene had the largest tendency of the four BAs to be emitted with the gas. Especially if the degradation rate coefficient is 10 times lower than that observed in our experiments a large fraction (40 and 57%, respectively) of the BA released will be emitted with the gas from the landfill. In general, it is clearly shown that the degradation rate coefficient valid under field conditions is a very crucial parameter, and that there is a need for larger scale experiments to determine degradation rate coefficients under even more realistic landfill conditions. The table also shows that increasing the release rate (by increasing the diffusion coefficient by a factor of 10) does not have an effect on the relative fraction being emitted or degraded (which is consistent with the simple evaluation method given by eq 4). However, the absolute mass being emitted increases since more BA is released over the 20 year period (for instance, from 35% to 83% for CFC-11).

The evaluation by using the model MOCLA-FOAM clearly indicates that the emission of BAs disposed of at landfills in foam insulation waste may be attenuated by microbial degradation reactions. However, to which extend the BAs are being attenuated depends especially on how fast a degradation can be obtained under real landfill conditions and also on the release rate of BA from the foam waste. For the current disposal of foam waste in landfills it is difficult to predict the fate of the released BA. In normal landfill operation, waste is compacted to gain landfill volume. How the compaction is affecting initial and long-term release rates of BA is not known. In the future, the use of HFCs as BAs will increase. Since the HFCs seem persistent in landfill environments a larger fraction of the HFC disposed of in foam waste

is expected to be emitted to the atmosphere in comparison to the previously used CFCs and HCFCs.

Acknowledgments

The project was funded by The Appliances Research Committee, Association of Home Appliances Manufacturers, Washington, D.C. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of The Appliances Research Committee. We thank Morton A. Barlaz and Trine L. Hansen for supplying waste samples. We also thank Henrik Poulsen for lab assistance.

Supporting Information Available

More details of the MOCLA-FOAM model can be found along with the waste and landfill reactor parameters used in the model. Conversion of microcosm-determined degradation rate coefficients based on gaseous concentrations to degradation rates based on aqueous concentrations valid for field scenarios is also shown.

Literature Cited

- (1) UNEP. *Montreal Protocol On substances that Deplete the Ozone Layer*; Report of the Technology and Economic Assessment Panel (TEAP). Volume 3: Task Force On foam End-of-Life Issues; May 2005.
- (2) IPCC/TEAP. *Safeguarding the ozone layer and the global climate system: Issues related to hydrofluorocarbons and Perfluorocarbons. IPCC/TEAP Special Report*; Summary for Policymakers and Technical Summary; Intergovernmental Panel on Climate Change: Switzerland, 2005; ISBN 92-9169-118-6.
- (3) U.S. Environmental Protection Agency. *Protecting the Ozone Layer: Safe Disposal of Home Appliances Containing Ozone-Depleting Substances. Air and Radiation*; National Service Center for Environmental Publications: Cincinnati, OH, 1993; EPA 430-K-93-001.
- (4) Kjeldsen, P.; Scheutz, C. Short- and long-term releases of fluorocarbons from disposal of polyurethane foam waste. *Environ. Sci. Technol.* **2003**, *37*, 5071-5079.
- (5) Scheutz, C.; Fredenslund, A. M.; Tant, M.; Kjeldsen, P. Release of fluorocarbons from insulation foam in home appliances during shredding. Accepted for publication in *J. Air Waste Manage.* **2007**.
- (6) Eklund, B.; Anderson, E. P.; Walker, B. L.; Burrows, D. B. Characterization of landfill gas composition at the Fresh Kills municipal solid-waste landfill. *Environ. Sci. Technol.* **1998**, *32*, 2233-2237.
- (7) Brosseau, J.; Heitz, M. Trace gas compound emissions from municipal landfill sanitary sites. *Atmos. Environ.* **1994**, *28*, 285-293.
- (8) Rettenberger, G.; Stegmann, R. Landfill gas components. In *Landfilling of Waste: Biogas*; Christensen, T. H., Cossu, R.; Stegmann, R., Eds.; E & FN Spon: London, GB, 1996; pp 51-58.
- (9) Allen, M. R.; Braithwaite, A.; Hills, C. C. Trace organic compounds in landfill gas at seven U.K. waste disposal sites. *Environ. Sci. Technol.* **1997**, *31*, 1054-1061.
- (10) Deipser, A.; Poller, T.; Stegmann, R. Emissions of volatile halogenated hydrocarbons from landfills. In *Landfilling of Waste: Biogas*; Christensen, T. H., Cossu, R.; Stegmann, R., Eds.; E & FN Spon: London, GB, 1996; pp 59-72.
- (11) Khalil, M. A. K.; Rasmussen, R. A. The potential of soils as a sink of chlorofluorocarbons and other man-made chlorocarbons. *Geophys. Res. Lett.* **1989**, *16*, 679-682.
- (12) Khalil, M. A. K.; Rasmussen, R. A. Emissions of trace gases from Chinese rice fields and biogas generators—CH₄, N₂O, CO, CO₂, chlorocarbons, and hydrocarbons. *Chemosphere*. **1990**, *20*, 207-226.
- (13) Lovley, D. R.; Woodward, J. C. Consumption of freons CFC-11 and CFC-12 by anaerobic sediments and soils. *Environ. Sci. Technol.* **1992**, *26*, 925-929.
- (14) Semprini, L.; Hopkins, G. D.; McCarty, L. P.; Roberts, P. V. In situ transformation of carbon tetrachloride and other halogenated compounds resulting from biostimulation under anoxic conditions. *Environ. Sci. Technol.* **1992**, *26*, 2454-2461.
- (15) Sonier, D. N.; Duran, N. L.; Smith, G. B. Dechlorination of trichlorofluoromethane (CFC-11) by sulfate-reducing bacteria from an aquifer contaminated with halogenated aliphatic compounds. *Appl. Environ. Microbiol.* **1994**, *60*, 4567-4572.
- (16) Lee, B. S.; Bullister, J. L.; Whitney, F. A. Chlorofluorocarbon CFC-11 and carbon tetrachloride removal in Saanich Inlet, an intermittently anoxic basin. *Mar. Chem.* **1999**, *66*, 171-185.
- (17) Deipser, A.; Stegmann, R. Biological degradation of VCCs and CFCs under simulated anaerobic landfill conditions in laboratory test digesters. *Environ. Sci. Pollut. Res. Int.* **1997**, *4*, 209-216.
- (18) Ejlerstson, J.; Johansson, E.; Karlsson, A.; Meyerson, U.; Svensson, B. H. Anaerobic degradation of xenobiotics by organisms from municipal solid waste under landfilling conditions. *Antonie van Leeuwenhoek* **1996**, *69*, 67-74.
- (19) Balsiger, C.; Holliger, C.; Höhener, P. Reductive dechlorination of chlorofluorocarbons and hydrochlorofluorocarbons in sewage sludge and aquifer sediment microcosms. *Chemosphere*. **2005**, *61*, 361-373.
- (20) Khalil, M. A. K.; Rasmussen, R. A. The environmental history and probable future of fluorocarbon 11. *J. Geophys. Res.* **1993**, *98* (12), 23,091-23,106.
- (21) Kjeldsen, P.; Christensen, T. H. A simple model for the distribution and fate of organic chemicals in a landfill: MOCLA. *Waste Manage. Res.* **2001**, *19*, 201-216.
- (22) Rosqvist, H.; Destouni, G. Solute transport through preferential pathways in municipal solid waste. *J. Contam. Hydrol.* **2000**, *46*, 39-60.
- (23) Christiansen, K.; Prismo, M.; Skov, C. *Undersøgelse af lossepladens selvrensende effekt ved recirkulering af perkolat. (Investigation of natural attenuation in landfills by leachate recirculation, in Danish)*; Report. Enviroplan A/S: Lyngby, Denmark, 1985.
- (24) Kile, D. E.; Chiou, C. T.; Zhou, H. D.; Li, H.; Xu, O. Y. Partition of nonpolar organic pollutants from water to soil and sediment organic matters. *Environ. Sci. Technol.* **1995**, *29*, 1401-1406.
- (25) Huang, W. L.; Weber, W. J. A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis, the chemical characteristics of organic domains. *Environ. Sci. Technol.* **1997**, *31*, 2562-2569.
- (26) Hansen, T. L.; Schmidt, J. E.; Angelidaki, I.; Marca, E.; Jansen, J. I. C.; Mosbæk, H.; Christensen, T. H. Method for determination of methane potentials of solid organic waste. *Waste Manage.* **2004**, *24*, 393-400.
- (27) Krone, U. E.; Thauer, R. K.; Hogenkamp, H. P. C.; Steinbach, K. Reductive formation of carbon-monoxide from CCl₄ and Freon-11, Freon-12, and Freon-13 catalyzed by corrinoids. *Biochemistry* **1991**, *30*, 2713-2719.
- (28) Olivas, Y.; Dolfing, J.; Smith, G. B. The influence of redoxpotential on the degradation of halogenated methanes. *Environ. Toxicol. Chem.* **2002**, *21*, 493-499.
- (29) Deutsche Forschungsgemeinschaft. *List of MAK and BAT values 1997*; Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, Report No. 33; WILEY-VCH Verlag GmbH: Weinheim, 1997.
- (30) Scheutz, C.; Mosbæk, H.; Kjeldsen, P. Attenuation of methane and volatile organic compounds in landfill soil covers. *J. Environ. Qual.* **2004**, *33*, 61-71.
- (31) Scheutz, C.; Kjeldsen, P. Capacity for biodegradation of CFCs and HCFCs in a methane oxidative counter gradient laboratory system simulating landfill soil covers. *Environ. Sci. Technol.* **2003**, *37*, 5143-5149.
- (32) Deipser, A. Biodegradation of volatile CFCs, H-CFCs and VC in compost and marl. *Waste Manage. Res.* **1998**, *16*, 330-341.
- (33) Oster, H.; Sonntag, C.; Munnich, K. O. Groundwater age dating with chlorofluorocarbons. *Water Resour. Res.* **1996**, *32*, 2989-3001.
- (34) Key, B. D.; Howell, R. D.; Criddle, C. S. Fluorinated organics in the biosphere. *Environ. Sci. Technol.* **1997**, *31*, 2445-2454.
- (35) Kjeldsen, P.; Jensen, M. H. Release of CFC-11 from disposal of polyurethane foam waste. *Environ. Sci. Technol.* **2000**, *35*, 3055-3063.
- (36) Vo, C. V.; Paquet, A. N. An evaluation of the thermal conductivity of extruded polystyrene foam blown with HFC-134a or HCFC-142b. *J. Cell. Plast.* **2004**, *40*, 205-228.

Received for review March 28, 2007. Revised manuscript received August 28, 2007. Accepted August 30, 2007.

ES0707409