

Biodegradation of volatile CFCs, H-CFCs and VC in compost and marl

The biodegradation of volatile fully chlorofluorinated hydrocarbons (CFCs), partly chlorofluorinated hydrocarbons (H-CFCs) and vinyl chloride (VC) were investigated in compost and marl in laboratory studies. Trichlorofluoromethane (R11), dichlorodifluoromethane (R12), 1,1,2-trichlorotrifluoroethane (R113), difluoromethane (R32) and VC were biodegradable in compost under anaerobic conditions, probably by methanogenic bacteria. The anaerobic decomposition products of R11 were dichlorofluoromethane (R21) and chlorofluoromethane (R31). The degradation product of R12 was chlorodifluoromethane (R22). R11 and its degradation products have the inhibiting effects of the R12 degradation under anaerobic conditions. The partly halogenated hydrocarbon R22 and VC were degraded preferentially under aerobic conditions in marl, probably by methanotrophic bacteria. Under aerobic conditions R22 and VC have inhibited the biodegradation of methane by methanotrophic bacteria.

Anna Deipser

Department of Waste Management, Technical University of Hamburg-Harburg, Schwetzingen, Germany

Keywords – CFCs, H-CFCs, trichlorofluoromethane, R11, dichlorofluoromethane, R21, chlorofluoromethane, R31, difluoromethane, R32, chlorodifluoromethane, R22, vinyl chloride, VC, trichlorotrifluoroethane, R113, anaerobic and aerobic biodegradation, compost, marl, landfill, landfill gas, LFG, cometabolism, inhibition competitive inhibition, methanogenic bacteria, methanotrophic bacteria

Corresponding author: Anna Deipser, Dipl.-Ing., Technical University of Hamburg-Harburg, Department of Waste Management, Helmholtzstraße 27, 68723 Schwetzingen, Germany

Received 23 September 1996, accepted in revised form 7 April 1998

Introduction

During the last few decades, many products manufactured in Germany used volatile chlorofluorocarbons (CFCs) and volatile chlorocarbons (VCCs). These products ended up, in relatively large quantities, in the landfills mixed with municipal solid waste (MSW) as well as with commercial and industrial wastes. These substances can be transported from the landfill into the environment in both the gaseous and liquid phases. Analyses of landfill gas (LFG) have proven that the compositions of trace substances change with time (Deipser & Stegmann, 1994; Deipser *et al.* 1996). It has, therefore, been suggested that the trace substances are microbiologically degradable (Deipser & Stegmann 1997a).

A number of biological degradation processes take place in conventional (reactor) landfills due to the concentration of organic matter and to the amount of moisture in the landfills. These are mainly anaerobic degradation processes, which usually lead to the decomposition of organic sub-

stances into primarily methane and carbon dioxide. Aerobic conditions may be found along the surface of the landfills, due to a higher supply of oxygen.

VCCs and CFCs are of significance due to their toxicological or environmentally damaging effects. It is, therefore, of interest to know if these compounds are biologically degradable under different milieu conditions (Christensen *et al.* 1994) and what the resulting decomposition products would be. The most quantitatively important CFCs (trichlorofluoromethane (R11), dichlorodifluoromethane (R12) and 1,1,2-trichlorotrifluoroethane (R113) (Deipser & Poller 1990; Deipser & Stegmann 1993, 1994)) and vinyl chloride (VC) as degradation product were chosen for this investigations, including the partly chlorofluorinated hydrocarbons (H-CFCs) dichlorofluoromethane (R21), chlorofluoromethane (R31), chlorodifluoromethane (R22), difluoromethane (R32) and fluoromethane (R41) which may occur as decomposition products and may, in some cases, be utilized as refrigerants in cooling units and as solvents like the CFCs.

Table 1. Compounds used in the experiment and their observed degradation products.

Compound CAS RN	Abbreviation	Formula	Degradation	Degradation paths
Trichlorofluoromethane 75-69-4	R11	CCl_3F	Reductive	$\text{R11} \rightarrow \text{R21} \rightarrow \text{R31} \rightarrow \text{R41} \rightarrow \text{CH}_4, \text{CO}_2, \text{CO}, \text{H}_2\text{O}$
Dichlorofluoromethane 75-43-4	R21	CHCl_2F	Hydrolytic Oxidative	$\text{R21} \rightarrow \text{chlorofluoromethanol} \rightarrow \text{fluoromethanal} \rightarrow \text{fluoromethanoic acid} \rightarrow \text{CH}_4, \text{CO}_2, \text{CO}, \text{H}_2\text{O}$
Chlorofluoromethane 593-70-4	R31	CH_2ClF	Hydrolytic Oxidative	$\text{R31} \rightarrow \text{fluoromethanol or chlorofluoromethanol} \rightarrow \text{methanal or fluoromethanal} \rightarrow \text{methanoic or fluoromethanoic acid} \rightarrow \text{CH}_4, \text{CO}_2, \text{CO}, \text{H}_2\text{O}$
Dichlorodifluoromethane 75-71-8	R12	CCl_2F_2	Reductive	$\text{R12} \rightarrow \text{R22} \rightarrow \text{R32} \rightarrow \text{R41} \rightarrow \text{CH}_4, \text{CO}_2, \text{CO}, \text{H}_2\text{O}$
Chlorodifluoromethane 75-45-6	R22	CHClF_2	Hydrolytic Oxidative	$\text{R22} \rightarrow \text{difluoromethanol} \rightarrow \text{fluoromethanal} \rightarrow \text{fluoromethanoic acid} \rightarrow \text{CH}_4, \text{CO}_2, \text{CO}, \text{H}_2\text{O}$
Difluoromethane 75-10-5	R32	CH_2F_2	Hydrolytic Oxidative	$\text{R32} \rightarrow \text{fluoromethanol or chlorofluoromethanol} \rightarrow \text{methanal or fluoromethanal} \rightarrow \text{methanoic or fluoromethanoic acid} \rightarrow \text{CH}_4, \text{CO}_2, \text{CO}, \text{H}_2\text{O}$
1,1,2-trichlorotrifluoroethane 76-13-1	R113	$\text{C}_2\text{Cl}_3\text{F}_3$	Reductive	See Fig. 1
Vinyl chloride 75-01-4	VC	$\text{C}_2\text{H}_3\text{Cl}$	Hydrolytic Oxidative	See Figs. 2 and 3

Anaerobic and aerobic biodegradation of CFCs, H-CFCs and VC

The compounds that were evaluated have damaging effects to the environment and to the human health. CFCs and H-CFCs are depleting the stratospheric ozone layer as a result of chemical reactions involving the chlorine atoms they contain. Therefore, they have a high global warming potential (GWP). In addition, VC and R31 are gases known to be carcinogenic. It could be assumed that reductive biodegradation of these substances can occur by replacement of chlorine and fluorine atoms by hydrogen, probably in cometabolism with similar biodegradation processes induced from methanogenic bacteria.

The decomposition products from R11, R12, R113 and R32, which may theoretically form after reductive dechlorination and perhaps even defluorination, are given in Table 1 and in Fig. 1.

Although carbon monoxide, carbon dioxide and water are set free as end products, they can also form via intermediate products which are not mentioned in this article (Krone *et al.* 1991; Lesage *et al.* 1992). In the presence of an electron donor atom it is likely that methane, ethane or ethene form

as decomposition products (e.g. Fathepure & Boyd 1988; Bouwer & McCarty 1983; Vogel *et al.* 1987).

Under aerobic and anaerobic conditions it is theoretically possible to hydrolytically dechlorinate and defluorinate the partly halogenated H-CFCs: R21, R22, R32, R31 and R41, which form by reductive dehalogenation (Müller & Lingens 1988; Hardman 1991). Furthermore, R32, R31 and R41 may be dechlorinated and defluorinated oxidatively with the help of an enzyme, the monooxygenase. This biodegradation method probably can also occur cometabolically (Cook *et al.* 1987; DeFlaun *et al.* 1992). The halogenated methanols which form during the hydrolytic dehalogenation process are unstable under aerobic conditions, a halogen can separate and, together with a hydrogen atom, the methanols can transform into a (halogenated) aldehyde. This aldehyde is oxidized with the help of a dehydrogenase into a (halogenated) carboxylic acid which can be degraded into carbon dioxide or methane, depending on the environmental conditions. Due to a lower binding energy, the splitting up of chlorine takes place before that of fluorine. Theoretically, there may also occur an oxidative dehalogenation of the halogenated methanol with a dihydroxymethane being formed. The theoretical hydrolytical dehalogenation of R22, R21 and R31 is given in Table 1.

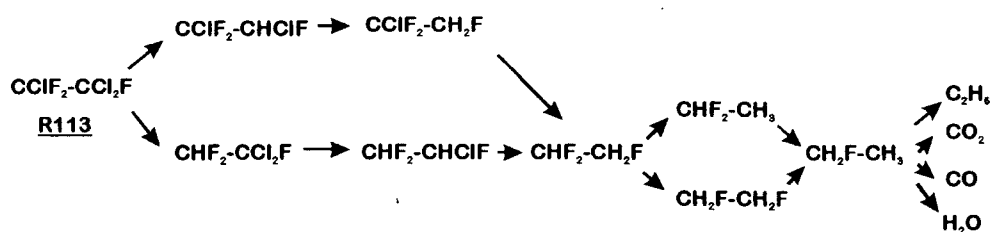


Fig. 1. Theoretical reductive dechlorination and defluorination of 1,1,2-trichlorotrifluoroethane (R113).

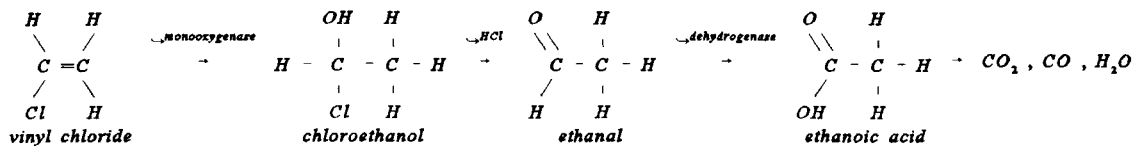


Fig. 2. Theoretical oxidative dechlorination of vinyl chloride.

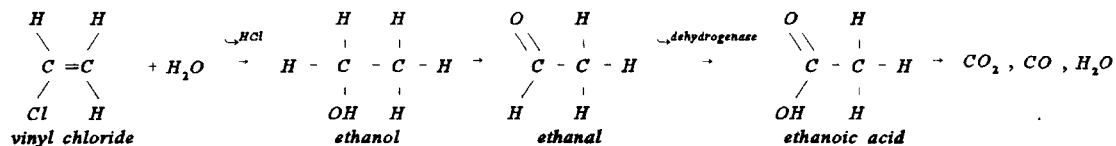


Fig. 3. Theoretical hydrolytic dechlorination of vinyl chloride.

The aerobic biodegradation of vinyl chloride to carbon dioxide has been described in the literature (e.g. Hartmans *et al.* 1985; Vogel & McCarty 1987). The oxidative dechlorination of vinyl chloride could take place as shown in Fig. 2.

Hydrolytic dechlorination under anaerobic conditions would also be a possible degradation path (Fig. 3).

The actual degradation path is not generally known. The possibility of biological decomposition of vinyl chloride in marl (under aerobic conditions) and in compost (under anaerobic conditions) was investigated.

Biodegradation of CFCs, VC and R32 under anaerobic conditions

Materials and methods

In the experiments, 3-liter glass digesters (Fig. 4) were filled with 1.6 kg of mature sieved compost. The compost was made from organic waste collected from private households in Hamburg (Germany). The biological processes in the compost had largely come to an end so that only a relatively low gas production was expected.

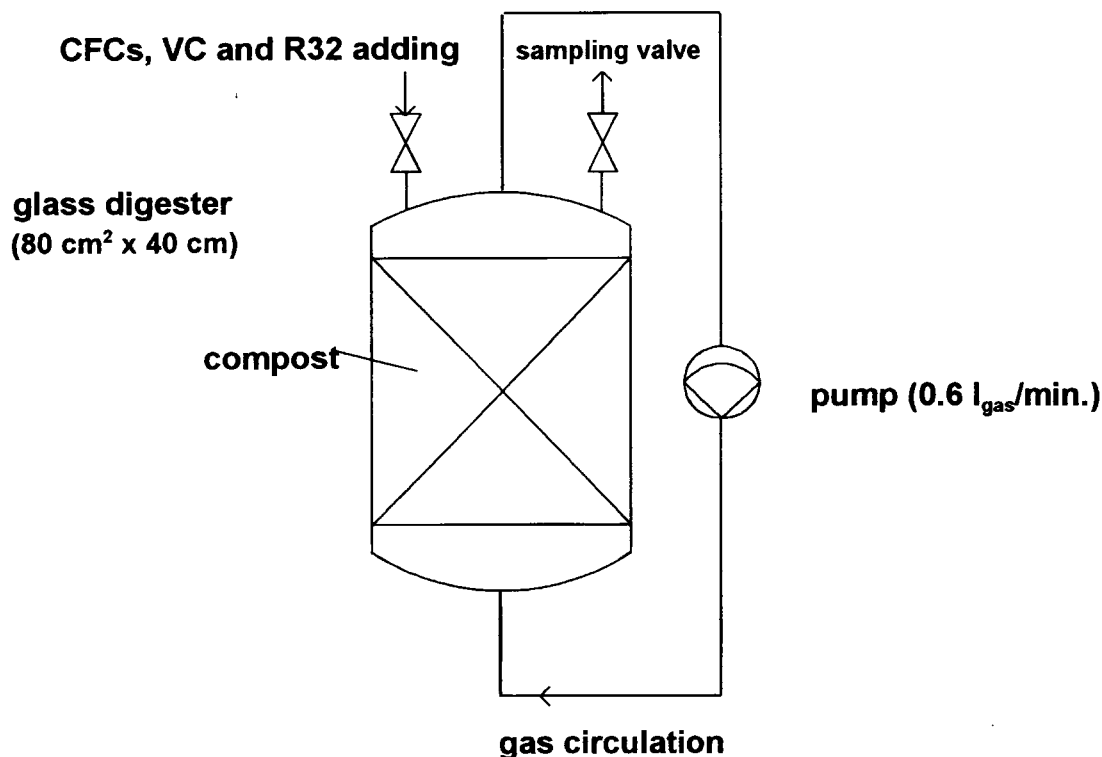


Fig. 4. Scheme for the anaerobic microbiological degradation of CFCs, vinyl chloride and difluoromethane in 3-liter test digesters filled with compost.

Table 2. Test parameters for the 3-liter glass digesters filled with compost.

Glass digester	1	2
Built-in mass of compost [g _{WM}]	1 600	1 600
Water content of compost [%WM]	50	50
Built-in density [kg _{WM} /l]	0.737	0.743
Built-in volume [m ³]	2.16×10 ⁻³	2.2×10 ⁻³
Components added	VC (1.4 mg) R113 (3.2 mg) R32 (2.4 mg) R12 (2.5 mg)	R11 (3 mg) R12 (2.5 mg)

WM: wet mass
VC: vinyl chloride
R113: 1,1,2-trichlorotrifluoroethane
R32: difluoromethane
R12: dichlorodifluoromethane

The gas phase was pumped continuously (at approximately 0.6 l_{gas}/min.) through the substrate, in cycles from the bottom to the top of the digesters, by means of a tube connected to the top and bottom of the digester and interconnected to a pump. A glass valve with a septum connected to the top of the digester was used to take gas samples and to add the CFCs, VC and R32.

The methane concentrations in all of the experiments ranged between 10 and 20 vol%, whereas the carbon dioxide concentrations were approximately 30 vol% in the gas phase. All digesters received a maximum of 3 mg of substrate per kg dry mass of CFCs, VC and R32. The maximum concentration

was set such that competitive inhibition of the biological process was avoided. Available data in the literature indicate that the minimum concentration of halogenated methane analogues at which level an inhibition of methane production can be clearly seen at approximately 10 mg per kg dry mass (Poller 1990). The test parameters are shown in Table 2.

Analyses

The halogenated trace substances and their metabolites in the gas phase of the test digesters were examined with standard analytical methods by means of gas chromatography. In order to control the environmental conditions, the gas composition (methane; carbon dioxide; hydrogen; oxygen; nitrogen) was also analyzed by means of gas chromatography.

The same analytical methods were used for the experiments described in the section titled H-CFCs and VC biodegradation under aerobic conditions.

Results

In the experiments carried out in the laboratory under idealized conditions (room temperature 30 °C and material moisture content > 50%) all the halogenated decomposition products could be determined with the exception for analytical reasons of R41, R32 and the decomposition products of R113, because of insufficient selectivity of the used analytical gas chromatography columns (non-ventilated experimental systems: 50 m × 0.53 mm PLOT capillary column

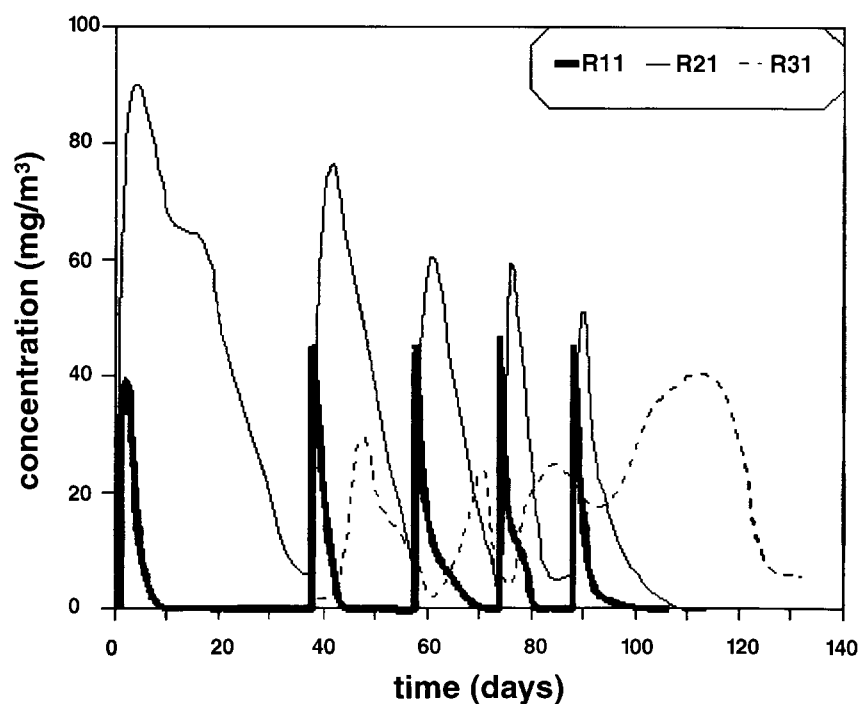


Fig. 5. Concentration diagrams of R11, R21 and R31 in the gas phase of 3-liter test digester number 2 filled with compost.

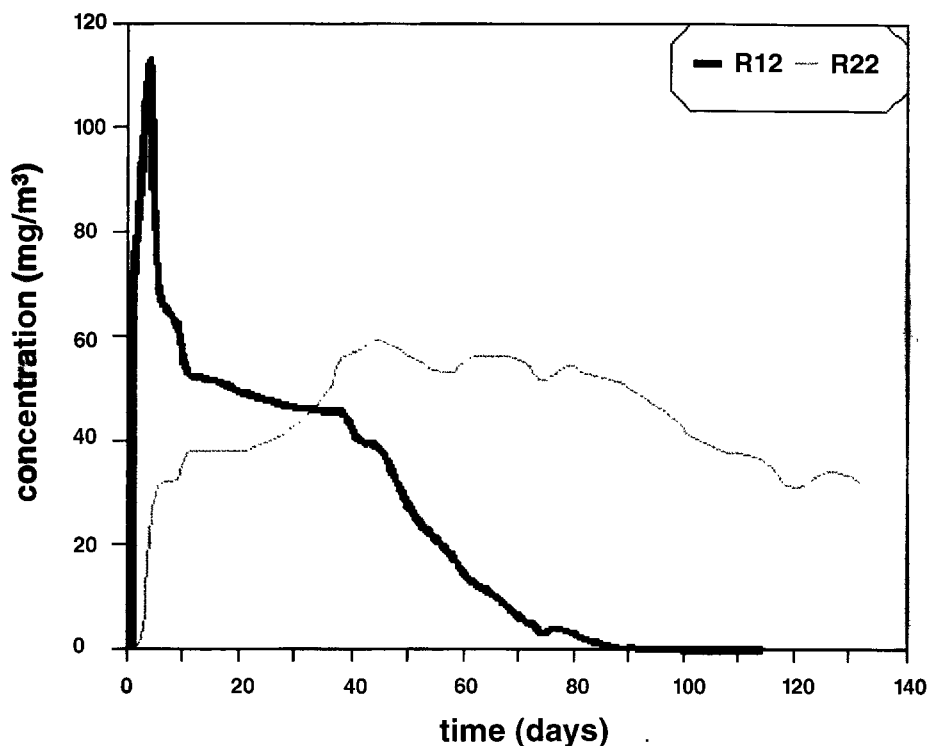


Fig. 6. Concentration diagrams of R12 and R22 in the gas phase of 3-liter test digester number 2 filled with compost.

($\text{Al}_2\text{O}_3/\text{KCl}$, film thickness $10\mu\text{m}$) and ventilated experimental systems: $50\text{ m} \times 0.53\text{ mm}$ Fused Silica WCOT capillary column (CP-Sil 5; film thickness $5\mu\text{m}$), Chrompack 1992).

During the first 140 days of the test period, 3 mg of R11 were added five times and 2.5 mg of R12 were added once. Only a few hours after the addition of R11 substantially higher concentrations of R21 than of R11 could be measured,

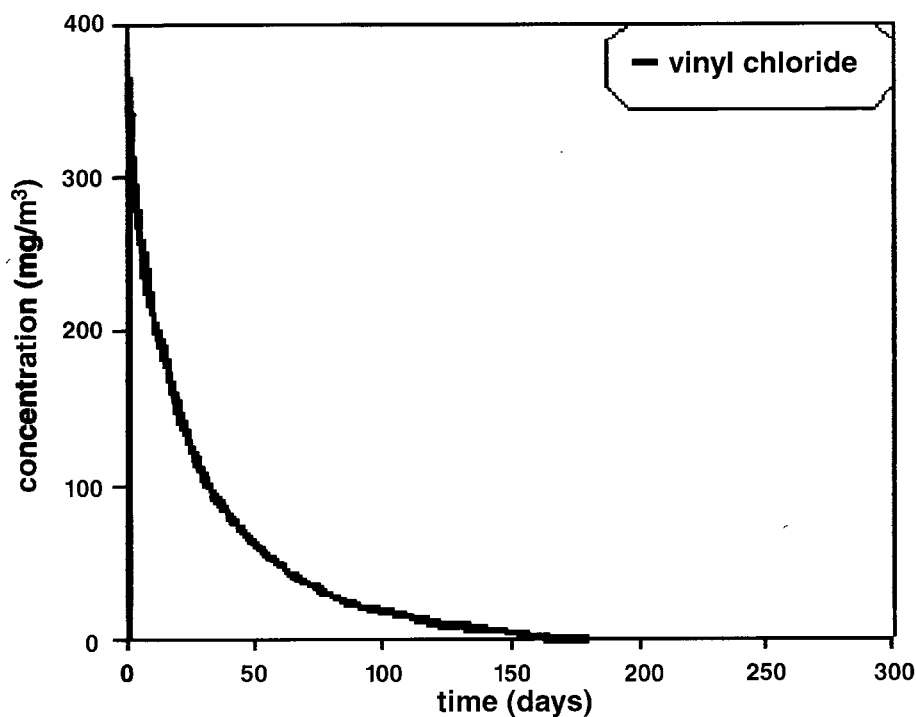


Fig. 7. Concentration diagram of vinyl chloride in the gas phase of 3-liter test digester number 1 filled with compost.

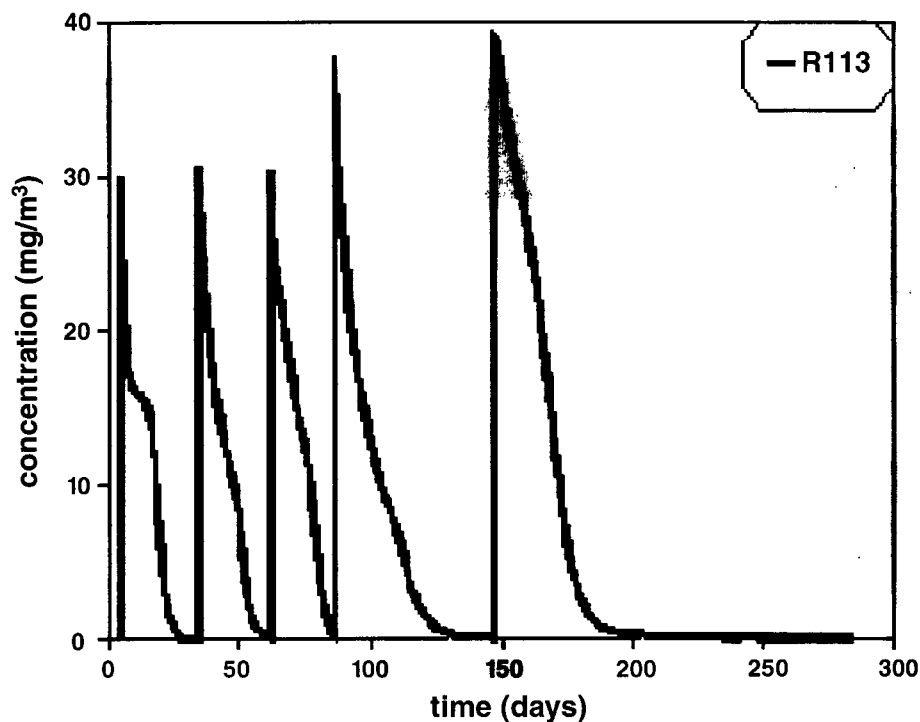


Fig. 8. Concentration diagram of R113 in the gas phase of 3-liter test digester number 1 filled with compost.

which was presumably due to the adsorption of R11 at the moist material. The curves in Fig. 5 show the concentrations of R11 and of R31 in the digester.

The R21, reduced by microorganisms from R11, was further degraded within 40 days after the first addition. At that

point the biodegradation product of R21 (R31) could be detected, whose concentration first increased and then decreased as well, but in a longer degradation time than R21. Hence, it must be assumed that R31 had been decomposed as well. Because of the distinctly declining degradation time of

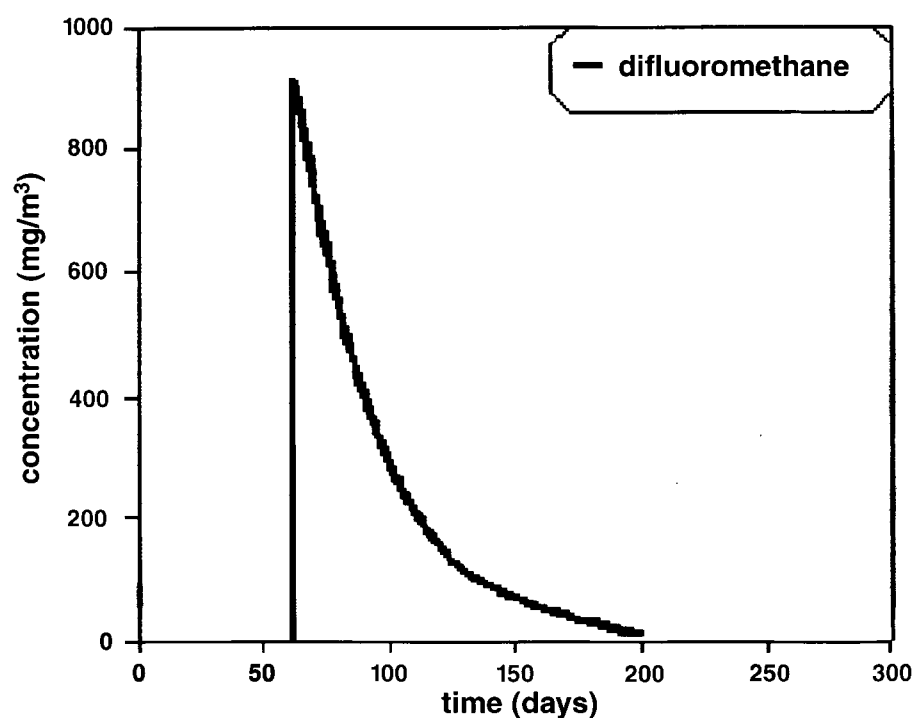


Fig. 9. Concentration diagram of difluoromethane in the gas phase of 3-liter test digester number 1 filled with compost.

Table 3. Average degradation rates of CFCs, vinyl chloride and difluoromethane in 3-liter test digesters under anaerobic test conditions.

Glass digester (filled with compost)	Simulated conditions of landfill	Components added	Max. gas concentrations (mg/m ³ gas)	Products of degradation	Average values of degradation rates (mg/m ³ mat vol./h)
1	Stable methanephase	R12	117.3	R22	~1
		R113	39.1	(?)	1.2
		Vinyl chloride	364.7	CO ₂ (?), H ₂ O	0.2
		Difluoromethane	912.0	(?)	0.3
2	Stable methanephase			R41 (?)	
		R11	47.0	R21, R31,	7
		R12	112.1	R41 (?)	0.5
				R22	

R12: dichlorodifluoromethane; R113: 1,1,2-trichlorotrifluoroethane;
 R11: trichlorofluoromethane; R22: chlorodifluoromethane; R21: dichlorofluoromethane
 R31: chlorofluoromethane; R41: fluoromethane

R21 it is supposed that adaptation of the microorganisms degrading R21 had taken place.

Under anaerobic conditions, R12 is not as easily biodegradable as R11. The resulting metabolite, R22, either was not decomposed or decomposed slowly. The results are shown in Fig. 6.

Adaptation of the bacteria that probably are responsible for the biodegradation of the fully halogenated CFCs under anaerobic conditions (methanogenic and acetogenic bacteria) did not occur.

The concentration diagrams of the substances VC, R113 and R32 in digester number 1 can be seen in Figs. 7 to 9.

The results of the tests show that R12 was degraded twice as fast in this experiment as in the tests where R11 had also been added. This is probably due to the absence of R11 and its biodegradation products, since they have inhibiting effects.

Vinyl chloride was dehalogenated at a low degradation rate under anaerobic conditions (Vogel & McCarty 1985; Freedman & Gossett 1989). Difluoromethane was also degraded slowly.

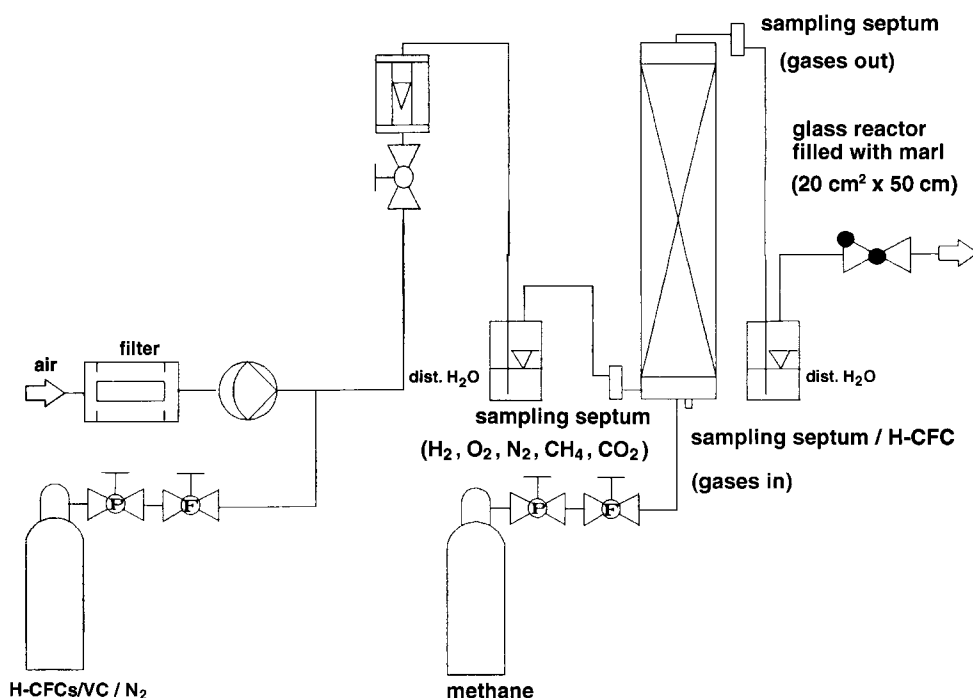


Fig. 10. Scheme of the continuous aerobic microbiological degradation of H-CFCs/VC in 1-liter reactors.

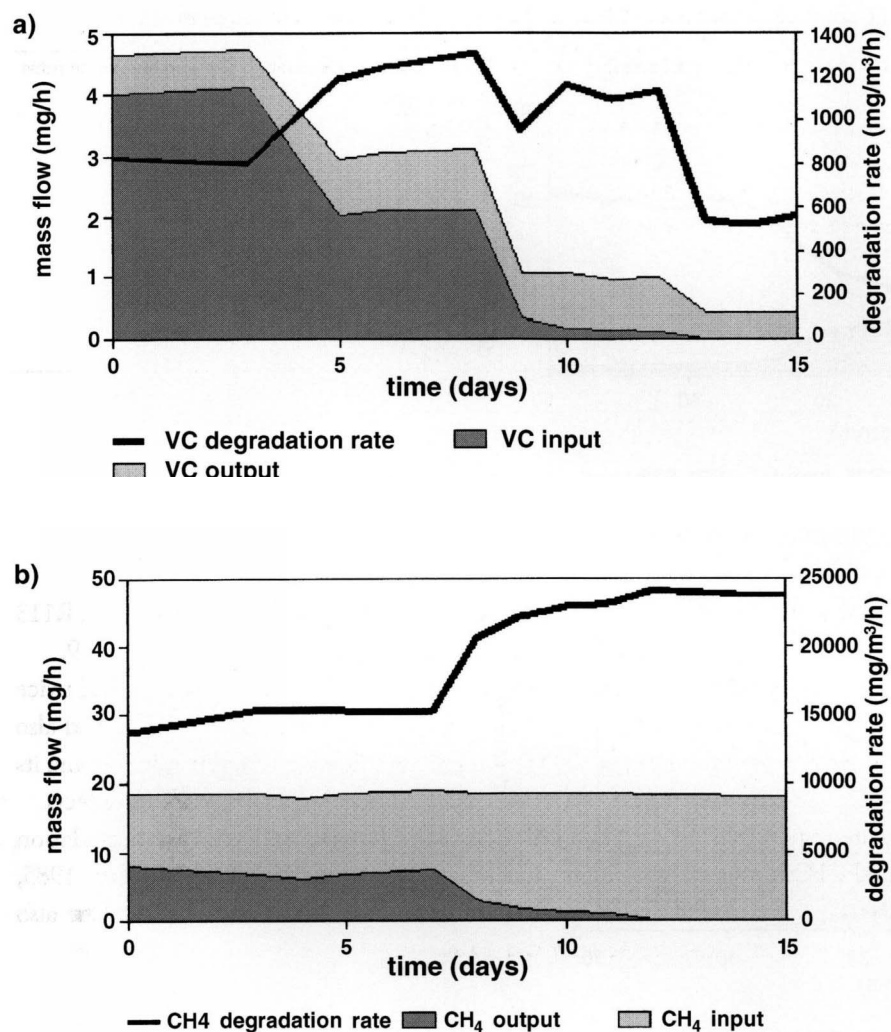


Fig. 11. Degradation of: a) vinyl chloride; and b) methane under aerobic conditions by methanotrophic bacteria (reactor number 1).

To ensure a comparability of the results, the degradation rates were determined as follows:

$$r = \frac{m}{V \cdot t_h} \quad [1]$$

degradation rate	r	[mg/m ³ _{mat} /h]
mass of CFCs/VC adding	m	[mg]
material volume	V	[m ³]
degradation time	t_h	[h]

It can be shown that R11 was degraded in all digesters with an average degradation rate of approximately 7 mg/m³_{co}/h; leading to the biodegradation products R21 and R31. The compound R12 was decomposed as well; but at a considerably lower degradation rate (approximately 0.5 to 1 mg/m³_{co}/h). The compound R22 occurred as biodegradation product of R12, which is not likely to be decomposed under anaerobic conditions. The degradation rates of vinyl chloride and difluoromethane were low at 0.2 mg/m³_{co}/h and at 0.3 mg/m³_{co}/h, respectively. R113

ranked second after R11 with a degradation rate of 1.2 mg/m³_{co}/h. The results have been summarized in Table 3.

Table 4. Test parameters of the 1-liter reactors filled with marl.

Reactor	1	2
Built-in mass of marl [g _{wM}]	1 000	1 000
Built-in mass of adapted marl [g _{wM}]	100	100
Water content of marl [%WM]	8.86	8.86
Water content of adapted marl [%WM]	4.43	4.43
Density of wet mass [kgWM/l]	1.448	1.357
Built-in volume [m ³]	0.760×10 ⁻³	0.811×10 ⁻³
Components (continuously added)	VC	R21, R22
Methane concentration [vol%]	3	2
Gas flow [ml/min.]	15	15

WM: wet mass
R21: dichlorofluoromethane
R22: chlorodifluoromethane
VC: vinyl chloride

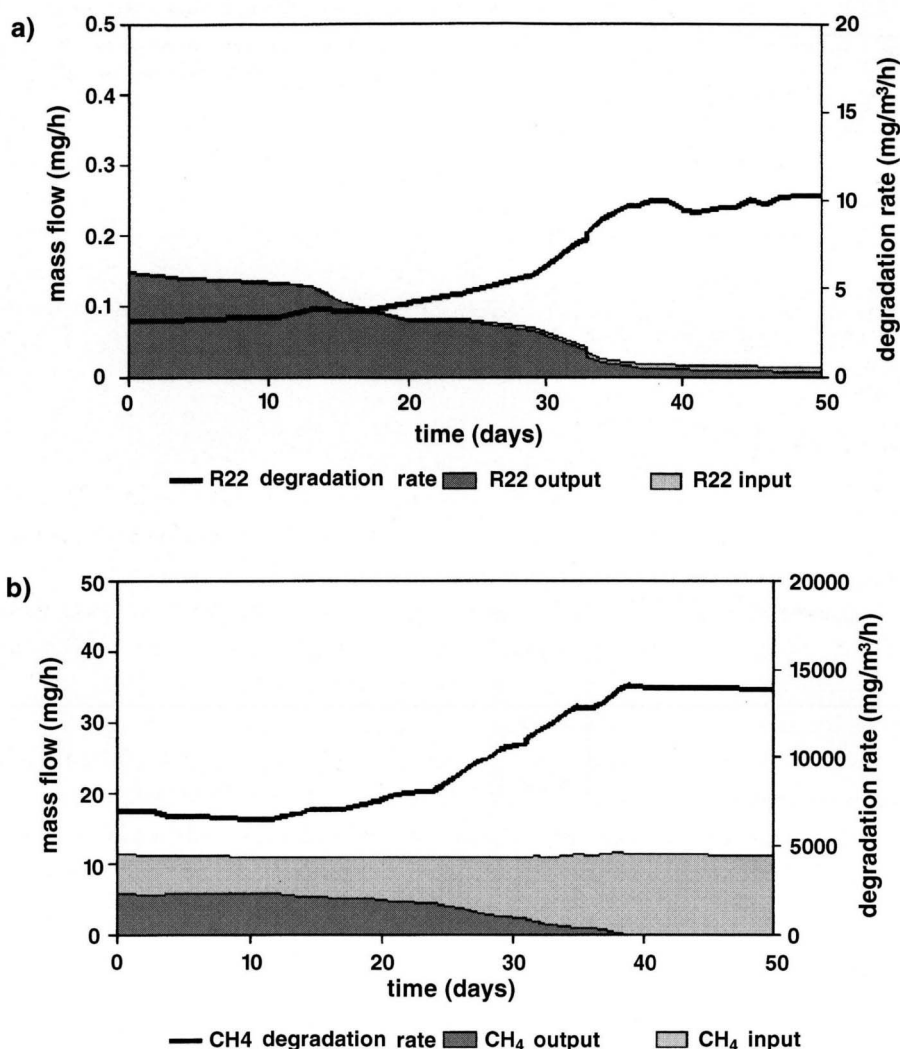


Fig. 12. Degradation of: a) R22; and b) methane under aerobic conditions by methanotrophic bacteria (reactor number 2).

H-CFCs and VC biodegradation under aerobic conditions

Materials and methods

In the aerobic experiments carried out in the laboratory under idealized conditions and with the introduction of methane a biodegradation of the partly chlorofluorinated hydrocarbons R22, R21 and VC (probably by methanotrophic bacteria (Fogel *et al.* 1986; Hanson *et al.* 1990; Chang & Criddle 1995)) were investigated in marl (Deipser & Stegmann 1997b).

In the experiments, 1-liter reactors were filled with marl (Fig. 10).

The air flow rate was fixed at 15 ml per minute with a methane concentration of 2 and 3 vol%, respectively. The concentration of H-CFCs was between 10 and 200 mg/m³_{gas} in the gas phase of the reactors. The test parameters are shown in Table 4.

The retention times were calculated as follows:

$$t_r = \frac{V}{\dot{V}} \quad [2]$$

retention time	t_r	[h]
material volume	V	[m ³]
gas volume flow rate	\dot{V}	[m ³ _{gas} /h]

The degradation rates were calculated on the basis of the mass inflow and outflow rates and the material volume as follows:

$$r = (\dot{m}_i - \dot{m}_o) \cdot \frac{1}{V} \quad [3]$$

degradation rate	r	[mg/m ³ _{mat.} /h]
mass inflow rate	\dot{m}_i	[mg/h]
mass outflow rate	\dot{m}_o	[mg/h]
material volume	V	[m ³]

Results

The maximum degradation rate of vinyl chloride was $1300 \text{ mg/m}^3_{\text{ma}}/\text{h}$ ($V_{\text{ma}}=0.760 \times 10^{-3} \text{ m}^3$) as an input mass flow rate of 3 mg/h . As an input mass flow rate of 0.5 mg/h and a gas concentration of $550 \text{ mg/m}^3_{\text{gas}}$ ($t_r = 51 \text{ min.}$) methane would be degraded completely first. Before this value, methane biodegradation was inhibited (Fig. 11). The degradation rate of R21 could not be determined.

The maximum degradation rate of R22 was $10 \text{ mg/m}^3_{\text{ma}}/\text{h}$ ($V_{\text{ma}}=0.811 \times 10^{-3} \text{ m}^3$) as an input mass flow rate of 0.015 mg/h and a gas concentration of $17.3 \text{ mg/m}^3_{\text{gas}}$. At this concentration methane would be completely degraded first. At higher concentrations of R22 the methane biodegradation was competitively inhibited (Fig. 12).

The experiments showed that the degradation rate depends on the presence of methanotrophic bacteria. The nutrient supply seems to be less important, as experiments with nutrient-poor marl have shown (see also Witt 1991). It is assumed that the biodegradation occurs in form of a hydrolytic and oxidative dehalogenation which takes place in cometabolism. So the H-CFCs can probably be dehalogenated hydrolytically (cometabolically) under aerobic and anaerobic conditions. Under both conditions degradation rates were relatively low (only some $\text{mg/m}^3_{\text{ma}}/\text{h}$; Table 5).

Significance of the results on conventional reactor landfills

Under anaerobic conditions, typical of conventional reactor landfills with activity of methanogenic bacteria, the concentrations of volatile fully halogenated CFCs will decrease with time. As a result partly halogenated hydrocarbons can occur. In deficiency of active or passive LFG collection, permanent gases and trace substances can reach the mineral layer of landfill surfaces.

On the basis of the results of the tests the concentration of vinyl chloride will be reduced significantly when the gas leaves the surface of landfills. For example, if LFG with 3 vol% methane penetrate a 39 cm nutrient-poor mineral landfill covering (e.g. marl with circa 9%_{wet mass} water content) with 15 ml per minute - a realistic value for landfill surfaces (Figueroa & Stegmann 1991) - $550 \text{ mg/m}^3_{\text{gas}}$ vinyl chloride (approximately twice the maximum quantity of measured LFG concentration in Germany (Poller 1990)) could be degraded. At this concentrations of methanotrophic bacteria; methane degradation would not be reduced significantly.

The partly halogenated H-CFCs with a small quantity of halogen atoms in the molecule and from it the H-CFCs with a lower quantity of fluoroatoms were degraded with priority under aerobic conditions.

R21 could be degraded at a concentration lower than $19 \text{ mg/m}^3_{\text{gas}}$ (maximum concentration measured in LFG was $14 \text{ mg/m}^3_{\text{gas}}$ in Germany). For this, the area loading of R21 must be lower than $35 \text{ mg/m}^2/\text{h}$.

At a methane concentration of 2 vol%, a 36 cm high marl layer and a R22 concentration of $30 \text{ mg/m}^3_{\text{gas}}$ (near the maximum concentration of R22 measured in LFG in Germany), the R22 could be degraded about 38%. The methane oxidation would not be inhibited at a concentration lower than $17.3 \text{ mg/m}^3_{\text{gas}}$.

The values of the examples are valid for the experimental conditions and only partly valid for actual landfill surface conditions. Essentially, the volatile trace substance composition, methane and oxygen concentration, physical conditions (like temperature; water content; porosity; void spaces; grain size distribution, etc.) and kinetic parameters (like gas flow rate and speed; gas distribution and area loading of substance, etc.) affect the biodegradation.

Table 5. Degradation rates of vinyl chloride and H-CFCs in 1-liter reactors under aerobic conditions.

reactor (filled with marl)	H-CFCs/ VC added	max. degradation rate ($\text{mg/m}^3_{\text{m}}/\text{h}$)	max. degradation rate (%)	input ($\text{mg/m}^3_{\text{gas}}$)	retention time (min.)	CH ₄ (v.%)	CH ₄ -inhibit.	CH ₄ -degradation rate ($\text{g/m}^3_{\text{gas}}/\text{h}$)	subst. area loading ($\text{mg/m}^2_{\text{m}}/\text{h}$)
1	VC	1 300	>99	550	51	3	yes (<50%)	24	2 300
2	R22	10	41	17.3	54	2	yes	14	80
	R21	n.m.	n.m.	19.5			yes (Σ <50%)		<35

n.m.: not measurable

VC: vinyl chloride

R21: dichlorodifluoromethane

R22: chlorodifluoromethane

Summary and conclusions

The experiments have shown that the volatile fully halogenated CFCs R11, R12 and R113, which for a long time have been considered non-biodegradable, and R21, R31, R32 and VC can be microbiologically decomposed under methanogenic anaerobic conditions. The theoretical biodegradation paths of fully halogenated CFCs and of partly halogenated H-CFCs and VC were partly confirmed by the investigations carried out in compost and marl.

Theoretically, depending on their molecular structure, the partly halogenated H-CFCs and VC can be degraded hydrolytically under aerobic and anaerobic conditions or oxidatively under aerobic conditions. The investigations have shown that under aerobic conditions VC was degraded in relatively high concentrations in marl. The partly halogenated H-CFCs R22 and R21 were dehalogenated at a low degradation rate. Under aerobic conditions they have competitively inhibited the biodegradation of methane by methanotrophic

bacteria (from a concentration higher than about 20 mg/m³_{gas}).

The CFC/H-CFC/VC concentrations in LFG will decrease with time because they can be removed with the LFG that is emitted or extracted from the landfill and, secondly, they can be partly or completely biologically degraded. But the reduction rates in the landfill will be lower than those calculated on the basis of the degradation rates in laboratory tests. This is, in particular, due to varying physical conditions in the landfills like temperature and humidity. When mining or reconstructing old landfills today it should thus be considered that there are still VCCs/CFCs and increasing concentrations of H-VCCs/H-CFCs, which might escape into the atmosphere.

Acknowledgements

This project was funded by the "Deutsche Forschungsgemeinschaft (DFG)".

References

- Bouwer, E. J. & McCarty, P. L. (1983) Transformation of 1- and 2-carbon halogenated aliphatic organic compounds under methanogenic conditions. *Applied and Environmental Microbiology* **45**, 1286–1294.
- Chang, W. & Criddle, C. S. (1995) Biotransformation of HCFC-22; HCFC-142b; HCFC-123; and HFC-134a by methanotrophic mixed culture MM1. *Biodegradation* **6**, 1–9.
- Christensen, T. H., Kjeldsen, P., Albrechtsen, H.-J., Heron, G., Nielsen, P. H., Bjerg, P. L. & Holm, P. E. (1994) Attenuation of Landfill Leachate Pollutants in Aquifers. *Environmental Science and Technology* **24** (2), 119–202.
- Cook, A. M., Scholtz, R. & Leisinger, T. (1987) Mikrobieller Abbau von halogenierten aliphatischen Verbindungen (Microbiological degradation of halogenated aliphatic compounds). 5. DECHEMA-Fachgespräch Umweltschutz. *gwf Biotechnologie* **128**, 7–15.
- DeFlaun, M. F., Ensley, B. D. & Steffan, R. J. (1992) Biological oxidation of hydrochlorofluorocarbons (HCFCs) by a methanotrophic bacterium. *Bio/Technology* **10** (12), 1576–1578.
- Deipser, A. & Poller, T. (1990) Laborbestimmung von FCKW und LCKW im Hausmüll (Laboratory determination of CFCs and VCCs in MSW). *Entsorgungs-Praxis* **6**, 373–375.
- Deipser, A. & Stegmann, R. (1993) Untersuchungen von Hausmüll auf leichtflüchtige Spurenstoffe, (Investigations on volatile trace substances in MSW). *Müll und Abfall* **2**, 69–81.
- Deipser, A. & Stegmann, R. (1994) The Origin and Fate of Volatile Trace Components in Municipal Solid Waste Landfills. *Waste Management & Research* **12**, 129–139.
- Deipser, A., Poller, T. & Stegmann, R. (1996) Emissions of Volatile Halogenated Hydrocarbons from Landfills. In: Christensen, T. H., Cossu, R. & Stegmann, R. (eds.) *Landfilling of Waste: Biogas*. London, UK: E & FN Spon. pp. 59–72.
- Deipser, A. & Stegmann, R. (1997a) Biological degradation of VCCs and CFCs under simulated anaerobic landfill conditions in laboratory test digesters. *Environmental Science and Pollution Research* **4** (4), 209–216.
- Deipser, A. & Stegmann, R. (1997b) Deponiegas: Biologischer Abbau von teilhalogenierten H-FCKW und Vinylchlorid unter aeroben Bedingungen bei Anwesenheit von Methan. (Landfill gas: Biological degradation of partly halogenated H-CFCs and vinyl chloride under aerobic conditions in presence of methane.) *Umweltwissenschaften und Schadstoff-Forschung* **9** (6), 309–316.
- Fathepure, B. Z. & Boyd, S. A. (1988) Dependence of Tetrachloroethylene Dechlorination on Methanogenic Substrate Consumption by *Methanosarcina* sp. Strain DCM. *Applied and Environmental Microbiology* **54** (12), 2976–2980.
- Figueroa, R. A. & Stegmann, R. (1991) Gas Migration through Natural Liners. In: Christensen, T. H., Cossu, R. & Stegmann, R. (eds) *Proceedings Sardinia '91, Third International Landfill Symposium*. Cagliari, Italy: CISA. pp. 167–177.
- Fogel, M. M., Taddeo, A. R. & Fogel, S. (1986) Biodegradation of Chlorinated Ethenes by a Methane-Utilizing Mixed Culture. *Applied and Environmental Microbiology* **51** (4), 720–724.
- Freedman, D. L. & Gossett, J. M. (1989) Biological Reductive Dechlorination of Tetrachloroethylene and Trichloroethylene to Ethylene under Methanogenic Conditions. *Applied and Environmental Microbiology* **55** (9), 2144–2151.
- Hanson, R. S., Tsien, H. C., Tsuji, K., Brusseau, G. A. & Wackett, L. P. (1990) Biodegradation of low-molecular-weight halogenated hydrocarbons by methanotrophic bacteria. *FEMS Microbiology Reviews* **87**, 273–278.
- Hardman, D. J. (1991) Biotransformation of Halogenated Compounds. *Critical Reviews in Biotechnology* **11** (1), 1–40.
- Hartmans, S., De Bont, J. A. M., Tramper, J. & Luyben, K. Ch. A. M. (1985) Bacterial Degradation of Vinyl Chloride. *Biotechnology Letters* **7** (6), 383–388.
- Krone, U. E., Thauer, K., Hogenkamp, H. P. C. & Steinbach, K. (1991) Reductive Formation of Carbon Monoxide from CCl₄ and FREONs 11; 12; and 13 Catalyzed by Corrinoids. *Biochemistry* **30**, 2713–2719.

- Lesage, S., Brown, S. & Hosler, K. R. (1992) Degradation of chlorofluorocarbon-113 under anaerobic conditions. *Chemosphere* **24** (9), 1225–1243.
- Müller, R. & Lingens, F. (1988) Der mikrobielle Abbau von chlorierten Kohlenwasserstoffen (The microbiological degradation of chlorinated hydrocarbons). *gwf Biotechnologie* **129**, 55–60.
- Poller, T. (1990) *Hausmüllbürtige LCKW/FCKW und deren Wirkung auf die Methangasbildung* (VCCs/CFCs from domestic wastes and their function of the methane gas production). Bonn, Germany: Economics Verlag.
- Vogel, T. M., Criddle, C. S. & McCarty, P. L. (1987) Transformations of halogenated aliphatic compounds. *Environmental Science and Technology* **21**, 722–736.
- Vogel, T. M. & McCarty, P. L. (1985) Biotransformation of tetrachloroethylene to trichloroethylene; dichloroethylene; vinyl chloride; and carbon dioxide under methanogenic conditions. *Applied and Environmental Microbiology* **5**, 1080–1083.
- Vogel, T. M. & McCarty, P. L. (1987) Abiotic and Biotic Transformations of 1,1,1-Trichloroethane under Methanogenic Conditions. *Environmental Science and Technology* **21** (112), 1208–1213.
- Witt, D. (1991) *Mikrobieller Abbau von Kohlenwasserstoffen und Kohlenwasserstoffverbindungen* (Microbiological degradation of hydrocarbons and combinations of hydrocarbons). DGMK-Forschungsbericht 461-01. Hamburg, Germany: DGMK Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e. V.