MODELLING THE BEHAVIOUR OF SLOWLY RELEASED ORGANIC COMPOUNDS IN LANDFILLS

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SUMMARY: The integrated evaluation of the fate of halocarbons contained in foam waste disposed of in a landfill was carried out by extending a model for fate of organic compounds in landfills (the MOCLA model) to include a compartment (i.e. foam) continuously releasing blowing agent to the pore air space of the landfilled waste. The new model, MOCLA-FOAM, takes into account the time-dependent release patterns of blowing agent from foam. The extended model can estimate the fate route of the mass of blowing agent released from the foam waste over a specified period. The model specifies the fraction of the released blowing agent which is degraded or emitted with landfill gas. Setting up the model for a landfill reactor scenario, where biodegradable waste and foam is mixed, and using the laboratory determined degradation rates for CFC-11, it is shown that a strong reduction of the emission of CFC-11 is simulated, due to microbial degradation. The model is set up using certain assumptions, which realization has not been fully investigated under full-scale landfill conditions.

1. INTRODUCTION

Landfills receive municipal solid waste and other types of waste which contain different organic compounds, such as aromatic hydrocarbons (originating from solvents and oil products), chlorocarbons (solvents), fluorocarbons (from insulation foam), brominated flame retardants and others. The received organic compounds have very different physical-chemical properties and degradability, which will govern the fate of the compound in the landfill. Many of the compounds may be slowly released from the waste matrix. The potential emission of such compounds may lead to different environmental impacts ranging from global warming and ozone depletion to human health risks, and there is a need for a better understanding of the factors controlling the emission of the non-methane organic compounds from landfills both as components of gas and leachate. Due to the very different physico-chemical properties of the organic compounds the behavior of the compounds in a landfill is to a large extend governed by the different controlling processes: releases from waste materials, sorption onto the solid waste, dissolution into the leachate, volatilization into the gas phase or degradation in the waste body or in soil covers. Compounds may also be produced as transformation products from degradation of other organic compounds.

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There is a need for evaluating long term environmental impacts of older landfills which have received significant volumes of hazardous waste. Waste types acceptable to be received in existing landfills without prior treatment are evaluated only by leaching tests which do not take volatilization or formation of degradation products into account. A predicting tool is also needed for including end-of-life issues in risk assessment of new chemicals. The predictive tool should be dynamic in order to evaluate the fate routes of different organic compounds in landfills. Due to the extremely heterogeneous nature of landfills, a relatively simple model approach is the natural first step. The model MOCLA (Model of Organic Compounds in Landfills), which was introduced in a former Sardinia Symposium (Kjeldsen and Christensen, 1997), is such a model which can be used for estimating the behavior of organic compounds in landfills. However, the original model did not take into account slow kinetic release of the organic compound from special waste residuals (such as blowing agents in insulation foam or additives from polymer waste, nor transformation processes leading to production of potentially toxic new chemicals.

The release of fluorocarbons used as blowing agents for insulation foam in refrigerators/freezers and building insulation panels is mainly controlled by slow outward diffusion from the foam material. The diffusion in non-shredded foam panels is very slow (Kjeldsen & Jensen 2001). Landfills are potential significant sinks for chlorinated compounds and for fluorocarbons disposed of in foam waste. Figure 1 shows the potential attenuating microbial processes, consisting of anaerobic processes within the waste body, and coupled anaerobic/methanotrophic processes in soils surrounding the waste (Scheutz and Kjeldsen, 2002). Studies have shown that in very reduced environments like anaerobic sediments or landfills, chlorinated aliphatic compounds (as trichloroethylene or chloroform), chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are being dechlorinated with the production of degradation products (Ejlertson et al., 1996, Lovley and Woodward,1992, Deipser and Stegmann, 1997) as shown on Figure 1. A significant emission of the chloro- and fluorocarbon degradation products is therefore expected at landfills, if the degradation compounds are not further degraded in the landfill top covers.

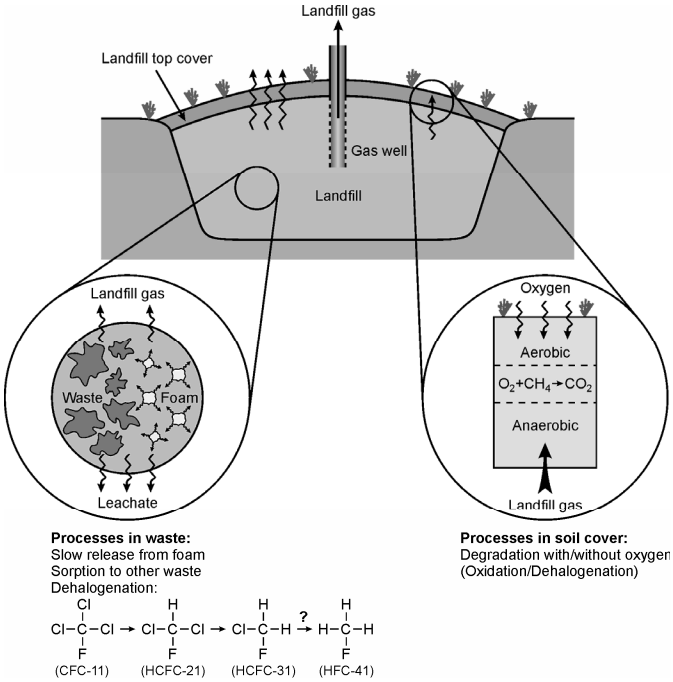

Figure 1. Conceptual model of the attenuation processes in landfills including processes within the waste body and processes in the soil cover.

The objective of this study is to develop simple models based on extensions of the MOCLA (Model for Organic Chemicals in LAndfills) model (Kjeldsen and Christensen, 1997, 2001) which allows for taking into account slow releases of the organic compound from the waste material. The presented model does not take into account the potential production of degradation products but a model incorporating degradation product formation from the anaerobic transformation of organic compounds is currently under development. The slow release MOCLA model is presented and is demonstrated with use of laboratory determined release and degradation parameters for the compound CFC-11.

2. MODEL FOR EMISSIONS AND DEGRADATION OF SLOWLY RELEASED COMPOUND

2.1 Extension of MOCLA to MOCLA-FOAM

The original MOCLA model, did not contain a compartment (for instance insulation foam waste) continuously releasing the organic compound to the pore air space of the landfilled waste. The setup for the new model, called MOCLA-FOAM is shown in Figure 2. The model is based on the box model principle assuming fully mixed conditions within the landfill. This means that all phase concentrations are assumed to be constant in space. Others have modeled landfill as a plug flow reactor both regarding the flow of gas and water. The few full scale tracer studies that have been carried out on landfills, suggest that the retention time distribution is closer to a retention time distribution for a fully mixed reactor than for a plug flow reactor, probably due to a significant flow of the water in channels within the waste (Kjeldsen and Christensen, 2001). The advantages of the fully mixed reactor assumption are that simpler mathematics and less input data are required.

The model assumes that, within a volume of waste, an organic chemical will be in equilibrium with the waste components and will be distributed in the water/leachate phase, in the air/gas phase and sorbed to the solid waste (see Figure 2). At equilibrium, two equations describe the relationship between the phases. The relationship between the gas phase and the water phase is described by Henry's constant, K_H (m^3 water/m^3 air). The relationship between the solid phase and the water phase is described by the distribution coefficient, K_d (m^3 water/tonne dry waste). Besides, the landfill contains foam waste which is releasing the blowing agent with a rate, r.

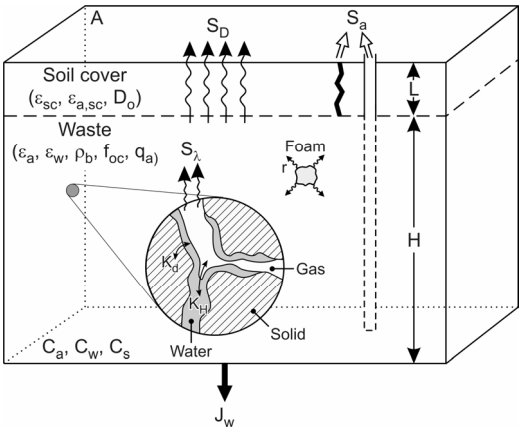

Figure 2. Setup for the MOCLA-FOAM model

Box 1. The concentration-time-dependency in MOCLA-FOAM.

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

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

where

$$k = q_a + q_D + \frac{N}{H\, K_H} + \frac{\varepsilon_w \lambda}{K_H} \quad \text{(B1.2)}$$

R_a is the retardation factor:

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

$C_{T,0}$ 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 and year),
q_a is the specific gas production rate (m^3 landfill gas/(m^3 waste· year))
q_D is the diffusion equivalent specific gas flow ($year^{-1}$)
N is the yearly net precipitation (m/year)
H is the total depth of waste (m)
K_H is the dimensionless Henry's laws constant (m^3 water/m^3 air)
f_{oc} is the fraction of organic carbon in the dry waste (tonne organic carbon/tonne dry waste)
K_{oc} is the distribution coefficient onto solid organic carbon (m^3 water/tonne carbon)
λ is the first order transformation constant related to the water phase ($year^{-1}$)
ρ_b is the dry bulk density of the waste in the landfill (tonne 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)

Solving the differential equation derived from the landfill mass balance with a constant release term, r, incorporated, the equation given in Box 1 is obtained. Calculation of fate routes can be made by use of the equations in Box 2. A fate route, F_x is defined as the fraction of the initial compound mass which has volatilized (F_a), leached (F_w) or degraded (F_λ) during the time period from t = 0 to t.

2.1 MOCLA-FOAM with time dependent release rate.

The release rate, r, is in a real scenario over longer time scales not constant. Kjeldsen et al.(2001) gave equations for estimating the time dependency of the release rate. MOCLA-FOAM can be set up in a spreadsheet version in a step-vise mode using successive time steps each with a constant release rate, r. The time dependency of the release rate is calculated assuming an *infinite bath* scenario (i.e. the release is independent of the concentration in the space surrounding the foam particle). The release, F_t (in g $year^{-1}$) from a spherical particle with the radius *a* ($M_0 = C_0 \cdot V_p = 4\pi a^3 C_0/3$, where V_p is the volume of the sphere and M_0 is in g) is (Kjeldsen and Jensen, 2001):

Box 2. Equations for calculating fate routs in MOCLA-FOAM.

From the solution given in equation B1.1 the following fate routes can be determined. The equations is given for time t= 0 until time t and for constant release rate, r.

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

$$F_\lambda = \frac{\varepsilon_w \cdot V \cdot \lambda}{R_a \cdot K_H} \int_0^t C_T(t)dt \qquad \text{(B2.1)}$$

Mass emitted with landfill gas (including diffusional loss through cover) from time=0 until t (in kg):

$$F_a = \frac{(q_a + q_D) \cdot V}{R_a} \int_0^t C_T(t)dt \qquad \text{(B2.2)}$$

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

$$F_w = \frac{N \cdot A}{R_a \cdot K_H} \int_0^t C_T(t)dt \qquad \text{(B2.3)}$$

where

$$\int_0^t C_T(t)dt = \frac{r \cdot R_a}{k}\left[t - \frac{R_a}{k}\left(1 - e^{-\frac{k}{R_a}t}\right)\right] + C_{T,0} \cdot \frac{R_a}{k}\left(1 - e^{-\frac{k}{R_a}t}\right) \qquad \text{(B2.4)}$$

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

D is the diffusion coefficient of the blowing agent in the foam (in m^2 $year^{-1}$). For other geometrical shapes the following short-term approximations (only valid for the first release) can be used:

$$F_t = M_0\left(\frac{A}{V_p}\right)\sqrt{\frac{D}{\pi \cdot t}} \qquad (2)$$

where (A/V_p) is the ratio of the external surface area of the particle to the volume.
The release rate, r (in g/ m^3 landfill · year) is:

$$r = \frac{\varepsilon_f \cdot F_t}{V_p} \qquad (3)$$

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

Table 1. Data for waste and landfill reactor used in MOCLA-FOAM set up.

Waste		Landfill reactor	
Bulk density, ρ_b (dry tonne/m^3)	0.6	Area of landfill reactor, A (m^2)	5625
Organic carbon fraction, f_{oc}	0.25	Average landfill height, H (m)	10
Foam content, ε_f (m^3 foam/m^3 LF)	0.1	Total infiltration to waste, N (m/year)	0.25
Foam cube side length (m)	0.05	Specific landfill gas production rate, q_a (m^3 LFG/m^3 waste · year)	2
Blowing agent content in foam (%w/w)	13	Volumetric water content in waste, ε_w	0.4
Foam density, ρ_{foam} (g/L)	25	Volumetric gas content in waste, ε_a	0.1
		Thickness of cover, L(m)	0.5

Due to the time-dependency of the release rate, r, from the foam, the fate routes (mass degraded or emitted) as given in equations B2.1-3 must be calculated for each discrete time step in the spreadsheet model and summed up to obtain information about the importance of each potential fate route for the blowing agent in relation to the period starting with disposal until present.

3. MODELLING THE EMISSION AND DEGRADATION OF FOAM RELEASED CFC-11 IN LANDFILLS

In order to evaluate the determined degradation rates in a landfill scenario incorporating all governing processes to the overall fate of the blowing agent, a landfill reactor scenario is set up. It is assumed that the foam is cut into pieces (5 cm cubes) and co-disposed together with a mixture of organic wastes without any compaction. The landfill reactor is assumed of limited size (in comparison to typical whole landfill sizes). Compaction is avoided to deteriorate the foam structure as little as possible, because any deterioration will enhance the release of blowing agent from the foam. Tables 1 give the default input data used for the model run using MOCLA-FOAM for the given scenario. The physical-chemical data for CFC-11 are all based on data given in the referenced literature or are estimated as described in Table 2. The waste and landfill data are either based on references or judgment.

The degradation rate used in MOCLA, λ, is referring to the water concentration of the compound while the batch determined, k_1, is referring to the gas concentration. The following equation was used for conversion:

$$\lambda = \frac{K_H \cdot k_1 \cdot R_{a,batch}}{V_{w,batch} / V_{T,batch}} \tag{4}$$

where $R_{a,batch}$ is calculated by the equation:

Table 2. Chemical data for CFC-11 (from Kjeldsen and Christensen, 2001)

Chemical data	
Molar weight, MW (g/mole)	137.4
Henrys constant, K_H	4.5
Octanol/water distribution coefficient, $LogK_{ow}$	2.5
Anaerobic 1. order degradation constant, k_1 ($day^{-1)}$	0.4
Anaerobic 1. Order degradation constant, λ (day^{-1})	12.4
Derived constants	
Estimated free air diffusion coefficient, D_0 (m^2/s)	$6.9 \cdot 10^{-6}$
Anaerobic degradation half-life, $T_{½}$ (days)	0.021
Estimated organic carbon/water distribution coefficient, K_{oc}[a] (L/kg)	195

a: estimated using method from Kjeldsen and Chrsitensen(2001)

$$R_{a,batch} = \frac{m_{s,batch} \cdot f_{oc,batch} \cdot K_{oc} + V_{w,batch}}{V_{T,batch} \cdot K_H} + \frac{V_{a,batch}}{V_{T,batch}} \quad (5)$$

The anaerobic degradation rate in the waste, λ, for CFC-11used in the base-case is 12.4 d^{-1} based on the average batch determined rates, k_1 (0.4 d^{-1}) using equation 4 and 5 for the conversion (more details is given in Scheutz et al., 2005).

Based on the foam characteristics the time-dependent release rate is determined using the release model summarized in section 2.1 using the assumptions given in Table 1 and the diffusion coefficient given in Table 3.

Model runs with the defined landfill scenario (Table 1) shows that the leachate and the diffusive loss through the cover soil are insignificant fate routes, the released blowing agent is either released with landfill gas or being degraded. Figure 3 shows in more details the importance of the degradation rate 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 observed in the batch experiments significantly decreases the emission of CFC-11 in landfill gas to the atmosphere.

Table 3 shows a further analysis for the blowing agent, CFC-11 using the same landfill scenario as mentioned above. The table presents the effect of lower degradation rate and higher diffusion coefficient to how much blowing agent has been released over a 20 year period, and the percentage of the release amount which was emitted with gas or degraded. In general, it is clearly shown that the degradation rate valid under field condition is a very crucial parameter, and that there is a need for larger scale experiments to determine degradation rates under more real landfill conditions. The table also shows that increasing the release rate significantly (by increasing the diffusion coefficient by a factor ten) do not have an effect on the relative fraction being emitted or degraded. However the absolute mass being emitted increases since more blowing agent 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 blowing agents disposed of at landfills in insulation foam waste may be attenuated by microbial degradation reactions. However to which extend the blowing agents are being attenuated depends especially on how fast a degradation can be obtained under the real landfill conditions and also on the release rate of blowing agent from the foam waste.

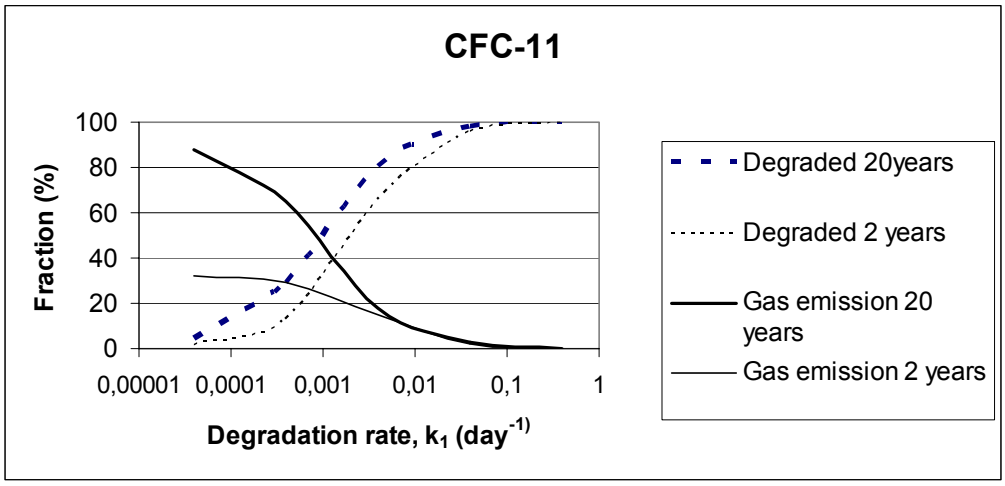

Figure 3. The fraction (%) of released blowing agent which has been degraded or emitted with landfill gas for the first 2 or 20 years, respectively as a function of degradation rate, k_1. The laboratory-determined k_1-value was 0.4 d^{-1}.

Table 3. An analysis using MOCLA-FOAM for evaluating CFC-11 fate sensitivity to diffusion coefficient, D and degradation rate, k_1.

	CFC-11	
	$0.1k_1$	k_1
Diffusion: D[a]		
Fraction of initial content released (%)	35	35
Released amount which has been emitted with gas/degraded (%)	5/94	0.5/99
Diffusion: 10D		
Fraction of initial content released (%)	83	83
Released amount which has been emitted with gas/degraded (%)	5/94	0.5/99

a: Diffusion coefficients used: $2.0 \cdot 10^{-14}$ m^2/s (Kjeldsen & Scheutz, 2003)

4. CONCLUSIONS AND PERSPECTIVES

Preliminary results of landfill fate model simulations using an extended version of the MOCLA model, which takes into consideration the time-dependent release of blowing agent from foam waste and assuming a first order degradation of the blowing agent showed for CFC-11 that even with much lower degradation rates than observed in the laboratory experiments a very significant emission reduction is expected. The model does not incorporate any attenuation in landfill soil covers, which from others studies is found to be significant. Based on the conducted study, it can be concluded that there exists a very large potential for degradation of the originally used blowing agent, CFC-11, in landfill environments. This research, coupled with previous work done by the authors regarding the amount of blowing agent released during shredding, provides a plausible explanation for at least some of the discrepancy between the predicted and the observed atmospheric concentrations of CFCs noted by others.

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