

Release of CFC-11 from Disposal of Polyurethane Foam Waste

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The halocarbon CFC-11 has extensively been used as a blowing agent for polyurethane (PUR) insulation foams in home appliances and for residential and industrial construction. Release of CFCs is an important factor in the depletion of the ozone layer. For CFC-11 the future atmospheric concentrations will mainly depend on the continued release from PUR foams. Little is known about rates and time frames of the CFC release from foams especially after treatment and disposal of foam containing waste products. The CFC release is mainly controlled by slow diffusion out through the PUR. From the literature and by reevaluation of an old reported experiment, diffusion coefficients in the range of $0.05\text{--}1.7 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$ were found reflecting differences in foam properties and experimental designs. Laboratory experiments studying the distribution of CFC in the foam and the short-term releases after shredding showed that about 40% of the CFC is solubilized in the PUR phase, and that up to 10% of the total content will be released within a few weeks if the foam is shredded down to 2-cm sized pieces. For smaller pieces the quick release will be larger. Fifty percent of residual CFC content will be released within 9–300 years from 2-cm pieces based on the range in diffusion coefficients reported. For larger pieces the initial release is insignificant, and the release time frames are much longer than for the shredded foam.

Introduction

Chlorofluorocarbons (CFCs) have had a widespread use for different industrial purposes (refrigeration and air conditioning fluid, propellant in spraying cans, and blowing agents for insulation foams) (1). CFCs have been shown to be a very important factor in the depletion of the Earth's ozone layer (2). Due to this a ban of production and use of most CFCs from 1996 was stated with the Montreal Protocol and further stressed in the Copenhagen Agreement (3). CFC-11 (CCl_3F) is one of the most important compounds, due to widespread use and high ozone depletion potential in comparison to other CFCs (3). CFC-11 has especially in the last period before the ban (1980–1996) been used to blow polyurethane (PUR) foams for insulation (3). The blown PUR forms rigid, closed cell foams containing CFC-11 gas in tiny gas bubbles. The bobbles are maintained in the foam after hardening of the PUR. The CFC is a low heat conductivity gas adding to the insulation properties of the foam (4). At the same time the loss of CFC from the foam due to diffusion is very low. This means that the insulation properties are mainly deteriorated

due to the diffusion into the foam of atmospheric air (4). The content of CFC-11 in closed cell PUR foam is in the range of 10–15% (w/w) (5) with a significant amount solubilized in the PUR itself (6).

PUR foams have been used for several applications. Gamlen et al. (5) reported on rigid PUR foam use in the U.S.A. together with estimated use lifetimes of the different applications. They showed that a substantial fraction has been used for construction purposes where the use lifetime is very long (30–80 years). Since the use of CFC-11 for rigid foams showed a strong increase in the middle of the 1960s, the first significant disposal of PUR constructional foams will take place through the next decade. Another significant fraction is used in household refrigeration and freezers. Here the expected use lifetime is estimated to 15–20 years, meaning that substantial amounts of PUR foam from home appliances all ready have been disposed of, and that the last home appliances containing CFC-11 will be disposed of through the next decade. Assuming that 8 million refrigerators/freezers are thrown away in the U.S. each year (7) and that each unit contains 500 g of CFC-11 in the insulation foam (8), the yearly U.S. disposal of CFC-11 with home appliances foam is about 4000 tons.

Several authors have recognized the significance of closed cell foams in global CFC balances. Khalil and Rasmussen (3) state that after production of CFC-11 has been terminated (i.e. after 1996), future atmospheric concentrations will mainly depend on the continued release from PUR foams. It is pointed out that the hardly unknown residence time of CFC in PUR foams is the factor, which by far gives the largest uncertainty of atmospheric CFC-11 lifetime estimation (3, 5).

Disposal of used PUR foam is managed differently from country to country. In the U.S.A. most is disposed of directly on landfills and very little is incinerated (9). This is the case for both constructional foams and foams in home appliances. The metal content of home appliances are recycled in many areas in the U.S. through shredding of the units and subsequently disposal of plastic and foam waste after recovering of the metal. Due to the diffusional nature of the CFC release from PUR foam, shredding of waste is believed to enhance the release of CFC. In Denmark regulation requires that the CFC in foam waste is destructured with efficiency of more than 80% (10). The destruction is in most places done in municipal solid waste incinerators. This significantly decreases CFC emission from the foam, but the halogen content of the CFC may have an adverse effect on any dioxine or furane formation in the incineration process (11).

Foam waste disposed of in landfills will continue to release CFC. Due to the very volatile nature of CFC-11, a substantial fraction of released CFC will be found in the air pore space of the landfilled waste (12) and will be emitted with the biogas produced in the landfill. Numerous measurements of the CFC-11 concentrations in landfill gas have shown concentrations in the range of $20\text{--}220 \text{ mg m}^{-3}$ (13). If the landfill gas is utilized in gas engines, the elevated halogen content of the gas leads to a significant wear and tear of the engine due to corrosion from formation of hydrogen chlorides and fluorides (14) and is considered a major problem (15). Investigations of the fate of CFC-11 in landfills have indicated that the CFC-11 may be degraded to a certain extent under the anaerobic environment prevailing in landfilled MSW (16).

Theories for the CFC release from PUR foam have been developed by foam insulation research looking at the aging of the foams, i.e., the deterioration of the insulation properties of the foams due to diffusion of CFC out of the foam and

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diffusion in of atmospheric air (4, 6, 17–20). The CFC loss is governed by diffusion through the closed cell wall and by simultaneous release of the fraction sorbed in the PUR. The diffusion is very slow, which means that experiments for measuring diffusion coefficients are very time consuming if not indirect methods are used (19). While the above-mentioned experiments were carried out in order to measure the diffusion coefficient for evaluating foam aging, Khalil and Rasmussen made experiments to directly measure the release of CFC-11 from 1 square foot foam samples over a period of 400 days (21, 22). The results were interpreted with an empirical model to obtain estimations of CFC retention times in the foam samples needed as part of global CFC balances. No release experiments have, however, looked at the initial release from shredded or demolished foam. A fraction of the CFC may eventually be released from fractures in the closed cell structure originating from the shredding/demolition process.

The objectives of this paper are to evaluate the initial release of CFC-11 from foam waste particles based on short-term laboratory batch experiments and the long-term release based on model simulations using developed physical-chemical diffusion models of the CFC release and input data obtained from literature. Results from the experiments will be interpreted in order to determine valid diffusion coefficients for the initial release phase as well as the initial released CFC fractions. Khalil and Rasmussen (21, 22) well-performed experiment will be reevaluated using the same diffusion model.

Theory and Data Evaluation

Basic Theory. The transport of gases in PUR foam is assumed to follow Fickian diffusion (19). The gas composition as a function of time can be found by solving for each compound the diffusion equation (19):

$$\frac{\partial C}{\partial t} = \nabla \cdot D_{\text{eff},c} \nabla C \quad (1)$$

Here C is the concentration depending on time, t , and position. $D_{\text{eff},c}$ is the effective diffusion coefficient of the component in the foam (in $\text{m}^2 \text{s}^{-1}$). Besides the diffusion equation with a known diffusion coefficient, we also need an initial distribution of the gas in the foam and the boundary conditions to be able to solve the equation.

The relation between the concentration of the compound in polymer material that surrounds a void and the concentration of the compound in the void is supposed to be proportional as given by Henry's law (19)

$$C_p = K \cdot C_g \quad (2)$$

where C_p is the concentration in the polymer material (in $\text{mol} \cdot (\text{m}^3 \text{ polymer material})^{-1}$), C_g is the concentration in the void (in $\text{mol} \cdot (\text{m}^3 \text{ gas})^{-1}$), and K is the distribution factor (in $(\text{m}^3 \text{ gas}) \cdot (\text{m}^3 \text{ polymer material})^{-1}$).

Bart and du Cauzé de Nazelle (19) developed an expression for the effective diffusion coefficient for a differential equation similar to eq 1, but with the pressure, p , of the compound as the variable in stead of the gas concentration. The expression was developed for a one-dimensional cubical foam model, where the cells were assumed cubical with the side length, l , and the wall thickness of polymer material between the voids of d . Following the development by Bart and du Cauzé de Nazelle (19), but for the gas concentration as the dependent variable, the following dependency for $D_{\text{eff},c}$ is obtained (assuming relationship between concentration and pressure by the ideal gas law)

$$D_{\text{eff},c} = \frac{D_p \cdot (l/d)}{f_g + K(1 - f_g)} = \frac{1}{K} \cdot D_{\text{eff},p} \quad (3)$$

where D_p is the diffusion coefficient in the solid polymer material (in $\text{m}^2 \text{s}^{-1}$), f_g is the void volume fraction of the foam, and $D_{\text{eff},p}$ is the diffusion coefficient in the differential equation with the pressure as the depending variable. The equation shows that it is very important to specify if a given diffusion coefficient is valid for the concentration or the pressure related differential equation. The factor (l/d) can be interpreted as a geometrical factor, which can be different for other foam geometric models than the cubical model.

Solutions to Different Geometries. Specific solutions to Ficks second law (eq 1) depends on the size and geometry of the foam waste particles. Crank (23) compiled many solutions to Ficks second law, which was further elaborated by Grathwohl (24). The solutions can be divided into two cases: the infinite bath and the bath of limited volume. In the first case the CFC in the foam particle is released to a very large volume, which concentration can be assumed constant and independent of the release from the given particle. These solutions are valid for evaluating releases to the atmosphere, to containers with a considerable exchange of gas, or to the pore gas in a landfill where landfill gas continuously is produced. Solutions of the second case can be used for interpreting release experiments carried out in batch containers of limited volume. The diffusion coefficient is called D in the following equations.

For the *infinite bath* release from a foam slab with the thickness, L , the following equation gives the residual mass of CFC in the slab to time t , M_t (in g m^{-2}), in relation to the initial mass, M_0 . The initial total concentration of CFC in the slab, C_0 , is assumed constant in space (giving $M_0 = C_0 \cdot L$) (23):

$$\frac{M_t}{M_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\{-D(2n+1)^2 \pi^2 t / L^2\} \quad (4)$$

The equivalent equation for the flux out of the slab, F_t (in $\text{g m}^{-2} \text{s}^{-1}$) is obtained by differentiating the equation for the residual mass:

$$F_t = \frac{8M_0 D}{L^2} \sum_{n=0}^{\infty} \exp\{-D(2n+1)^2 \pi^2 t / L^2\} \quad (5)$$

The release from foam slabs is in some cases limited to one side of the slab. Insulation plates are often covered with aluminum foil on one side. Insulation foam in refrigerators or freezers is covered with a metal plate on one side. In this case the above-mentioned solutions can be used according to a symmetry consideration. The equivalent equations for this case are

$$\frac{M_t}{M_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\{-D(2n+1)^2 \pi^2 t / 4L^2\} \quad (6)$$

$$F_t = \frac{M_0 D}{L^2} \sum_{n=0}^{\infty} \exp\{-D(2n+1)^2 \pi^2 t / 4L^2\} \quad (7)$$

The equivalent solution for a spherical particle with the radius a is (here $M_0 = C_0 \cdot V = 4\pi a^3 C_0 / 3$, where V is the volume of the sphere and M_0 is in g) (23):

$$\frac{M_t}{M_0} = 1 - \frac{6}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{n^2} \exp\{-Dn^2 \pi^2 t / a^2\} \quad (8)$$

The equation for the flux out of the sphere, F_t (in g s^{-1}), is

$$F_t = \frac{6M_0D}{a^2} \sum_{n=0}^{\infty} \exp\{-Dn^2\pi^2 t/a^2\} \quad (9)$$

For cubical foam particles the solution for spheres can be used without too large errors. The following equation can be used for calculated the value for the term "a" to be used in the equations (25)

$$a = c\left(\frac{4}{3}\pi\right)^{-1/3} \quad (10)$$

where *c* is the side length of the cube. For other geometrical shapes the following short-term approximations (only valid for the first release) can be used (24)

$$\frac{M_t}{M_0} = 2\left(\frac{A}{V}\right)\sqrt{\frac{D \cdot t}{\pi}} \quad (11)$$

$$F_t = M_0\left(\frac{A}{V}\right)\sqrt{\frac{D}{\pi \cdot t}} \quad (12)$$

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

For the batch experiments, solutions to bath of limited volume are used. The solution for spherical particles is (23)

$$\frac{M_t}{M_0} = 1 - \sum_{n=19}^{\infty} \frac{6\beta(\beta + 1)}{9\beta + q_n^2\beta^2} \exp\{-q_n^2 D n^2 / a^2\} \quad (13)$$

where the *q_n*s are the nonzero roots of

$$\tan q_n = \frac{3q_n}{3 + \beta q_n^2} \quad (14)$$

and *β* denotes the ratio of mass in the batch gas phase to the mass in the foam particles in the batch at equilibrium. Equation 13 was solved using a spreadsheet program with *D* and *β* as fitting parameters where *q_n*s were interpolated based on values given by Crank (23).

Literature Values of Diffusion Coefficients

Very few data on the foam diffusion coefficient of CCl₃F has up to the present been obtained by direct permeability measurement because of the very long time needed to achieve steady state. Table 1 shows the diffusion coefficients for CCl₃F in PUR foam based on literature data. Due to the very long time needed for measuring the diffusion coefficient directly, most values are calculated using eq 3 based on determination of the diffusion coefficient, *D_p*, in rigid PUR. The geometrical factor (*l/d*) in eq 3 can be estimated from the porosity of the foam using eq 20:

$$\frac{l}{d} = \frac{1}{1 - f_g} \quad (15)$$

The equation assumes that all the polymer material in the foam is present in the cell walls and therefore slightly overestimates the thickness of the cell wall.

A rapid steady-state measurement technique has also been used in a single case (17). Here the steady-state conditions (i.e. a constant concentration gradient through the foam sample) achieved prior to the measurement was obtained by increasing the temperature of the sample, which significantly increases the diffusion process. The technique gave reproducible results for gases such as O₂, CO₂, and N₂; however, for CCl₃F the reproduction was somewhat lower.

The distribution factor, *K*, is also contained in eq 3. This value was determined by Bart and du Cauzé de Nazelle (19)

TABLE 1. Diffusion Coefficients of CCl₃F in PUR Foams Obtained from Literature^f

reference	<i>D_p</i> (m ² s ⁻¹)	<i>D_{eff,p}</i> (m ² s ⁻¹)	<i>D_{eff,c}</i> (m ² s ⁻¹)
Brandreth and Ingersoll ^a (17)	n.s. ^d		1.3·10 ⁻¹⁴
Ostogorsky and Glicksman ^b (18)	n.d. ^e	22–57·10 ⁻¹⁴	0.6–1.7·10 ⁻¹⁴
Bart and du Cauzé de Nazelle ^a (19)	1.0·10 ⁻¹⁸	6.0·10 ⁻¹⁴	0.18·10 ⁻¹⁴
Hong and Duda ^a (6)	8–10·10 ⁻¹⁶		1.1–1.4·10 ⁻¹⁴

^a Values of *D_{eff,c}* obtained by measurement of *D_p* and calculating *D_{eff,c}* using eqs 3 and 12. ^b Values obtained by steady-state measurements on foam samples. ^c Calculated using eq 3 (last part) and a *K*-value of 33 as determined as the average value determined by Hong and Dudas and our self (confer Table 4). ^d n.s.: not stated. ^e n.d.: not determined. ^f The values are valid for 25 °C.

TABLE 2. Description of the Sampled Refrigerators

refrigerator	A	B	C
type	combi ^a	refrigerator	refrigerator
brand	Atlas	Gram	Arctic Gaesti
prod. no.	9244208–10	282718	31164111–312
series no.	620–0066	234	75019330
country of production	Denmark	Denmark	Rumania
year of production	1986	1984	
samples	A1 (side, bottom) A2 (side, top)	B1 (side, mid)	C1 (side, mid)

^a Combined refrigerator and freezer.

on milled foam samples measuring the total mass change of the foam sample after equilibrium was settled. Their determined value was 10.0. Recently, Hong and Dudas (6) determined a *K*-value of 30–37 by sorption experiment on micrometer thin PUR slices. They also measured the polymer diffusion into very thin slices of rigid PUR (slice thickness of about 7 μm) and determined the polymer diffusion coefficient, *D_p*. The use of very thin slices made it possible to measure the diffusion coefficient, *D_p*, over a reasonable time frame. They observed that *D_p* decreased with decreasing concentration of CCl₃F. The foam related diffusion coefficients in this paper is given as pressure-related values, and has been recalculated to *D_{eff,c}* using eq 3 and a *K*-value of 33 (an average value of values determined by Hong and Dudas and our self (see discussion under foam characterization).

Table 1 shows that observed PUR foam diffusion coefficients are in the range of 0.18–1.7·10⁻¹⁴ m² s⁻¹. The magnitude probably depends on the foam type (i.e. the real geometric factor to be used in eq 3, and on the method used). Directly determined values may be relative higher than the values calculated by use of eq 3, because some open cells are introduced by cutting the foam sample (17).

Experimental Section

Reagents and Materials. CCl₃F was obtained in high purity. A stock solution of CCl₃F was prepared by dissolving CCl₃F (obtained in methanol (5000 μg mL⁻¹) from Supelco, Bellefonte, PA) in ethylene acetate. *N,N*-Dimethylformamide (DMF) was obtained from Merck.

PUR foam samples from three used refrigerators were obtained. Details of the refrigerators are given in Table 2. All three units were intact prior to sampling. A square of the outer metal plate was carefully removed. The foam sample was cut out with a knife and transferred to composite aluminum/plastic bags, which were rapidly closed with tape,

TABLE 3. Description of the Batch Experiment

expt no.	sample ^a	cube side length (cm)/ no. of cubes	replicates	expt no.	sample ^a	cube side length (cm)/ no. of cubes	replicates
A1-2	A1	2/1	3	B1-2	B1	2/1	2
A2-1	A2	1/8	2	C1-1	C1	1/8	2
A2-2	A2	2/1	2	C1-2	C1	2/1	2
B1-1	B1	1/8	2				

^a As described in Table 2.

and the atmosphere in the bags was evacuated. The bags were stored at 4 °C. The density of the foam samples were measured by weighing 2 × 2 × 2 cm cubes (three replicates for each sample) cut out of the foam samples. Gas filled porosity was calculated based on the density measurements using a density of solid PUR of 1240 g/L (4) and a density of CCl₃F gas in the voids of 5.6 g/L (assuming 25 °C and 1 atm.). The total content of CCl₃F in the foam samples was measured by GC analysis after extraction.

Compression Test. To measure the distribution factor, *K*, foam cubes (2 × 2 × 2 cm) were compressed by a 30 tons press (Model C-30, Research & Industrial Instruments Company, London, U.K.). The samples were compressed with 15 tons (or 370 MPa). The sides of the compressed sample were measured with a slide gauge, and the volume of the PUR material was calculated (assuming that the compression has fully removed the gas phase). The CCl₃F content in compressed (*M_f* in g) and uncompressed (*M_s* in g) samples were measured. The distribution factor is calculated (assuming that the CCl₃F content in the compressed samples equals the sorbed CCl₃F in the PUR material) with the equation

$$K = \frac{f_g \cdot M_f}{(1 - f_g) \cdot (M_s - M_p)} \quad (16)$$

Batch Release Experiments. To measure the diffusion coefficients valid for the initial, dynamic release of CCl₃F from foam waste particles as well as the initial released CFC fractions, batch experiments were carried out in glass containers (volume: 605 mL) fitted with screw caps with Teflon coated silicon septa. Foam sample cubes (with side length of 1 or 2 cm) were carefully cut out of the large foam sample and placed in the batch containers. For all experiments a total foam volume of 8 cm³ was used (i.e. 8 cubes were used for the 1 cm side length experiments). Headspace samples were withdrawn from the batches with a syringe at different times after the start of the experiment and analyzed on GC. Due to high concentrations the samples were diluted in 1.5 mL glass containers fitted with Teflon coated silicon septa prior to GC analysis. Table 3 gives an overview of the different batches according to sample, cube number and size, and batch replicates. A control batch was run in quadruple using an initial CCl₃F gas concentration of 0.9 mg/L, which is close to the range of the final gas concentrations in the batches containing foam cubes. Identical gas sample procedures were used in foam and control batches.

Infinite Bath Experiment. To evaluate the release of CCl₃F from foam particles under maximal concentration gradient, 50 1 × 1 × 1 cm cubes were prepared from the C1 foam sample (confer Table 2). The cubes were placed on a wire frame in room temperature. Single cubes were withdrawn from the tray at different times. The cube was extracted, and the CCl₃F content in the cube was determined by analysis on GC. The experiment lasted for 50 days.

Extraction of Foam Samples. A sample of foam (either 1 cm or 2 cm cubes) was placed in 10 mL test tubes and 5 mL of DMF was added. For the compressed samples 10 mL were added. The samples were extracted for 72 h. Preliminary

TABLE 4. Measured and Calculated Parameters for the Four Foam Samples

parameter	foam sample			
	A1	A2	B1	C1
density (g/L)	32	30	37	36
porosity, <i>f_g</i> (–)	0.979	0.980	0.975	0.975
CCl ₃ F content (g/L)	3.85	3.48	5.39	4.14
CCl ₃ F content (%w/w)	12.2	11.8	14.5	11.4
CCl ₃ F content after compression (g/L)	1.58	1.50	2.37	n.d.
distribution coeff., <i>K</i> (m ³ gas (m ³ PUR) ^{–1}) ^a	32	37	30	n.d.

^a As calculated by use of eq 16.

extraction tests showed that no further extraction of CCl₃F from the foam took place after 24 h. Preliminary tests using additional extraction steps showed that at least 90% was extracted in the first step. Only one extraction test was used in the following. The extracts were diluted in ethyl acetate before analysis on GC.

GC Analysis. Both headspace samples and extracts were analyzed by gas chromatography. Diluted extract samples (0.2–1.0 μL) were injected for analysis via an on-column inlet to a HP 5890 series II gas chromatograph equipped with a HP 19233 electron capture detector. The gas chromatograph contained a (encapsulated) PLOT fused silica (capillary) column (25 m × 0.53 mm – CP-PoraPLOT Q) with an isothermal oven temperature at 170 °C. Nitrogen was used as carrier gas. The CCl₃F concentrations were quantified using standards prepared in ethyl acetate solution. For the headspace samples the same equipment was used, here injecting 20 μL of diluted sample, and using standards prepared in air. Detection limit for CCl₃F was 0.01 mg/L.

Results and Discussion

Foam Characteristics. Table 4 shows the characterization of the four foam samples. The found densities (and calculated gas porosities) are within the range expected for PUR foams (4, 17). The observed range in CCl₃F content of 11–15%w/w is close to expected values, which are in the range of 10–15%w/w (5, 21). The volume reduction of the foam samples after compression was in the range of 94–96% (data not shown), which is close to the calculated gas porosities of 97–98%. The volume reduction was measured after compression was over, and it is likely that the value under compression was slightly larger. This means that the CCl₃F content after compression resembles the fraction sorbed in the PUR, which was from 41 to 44%. The calculated distribution coefficients of 30–37 are very close to values from a recent study (6), which for sorption of CCl₃F to solid slices of PUR found *K*-values in the range of 30–36. Another study obtained a *K*-value of 10 for a release experiment performed with a pulverized foam sample (19). Details of the performed experiment are, however, not given in the study.

Batch Experiments. Figure 1 shows two representative examples of the measured concentration of CCl₃F in the

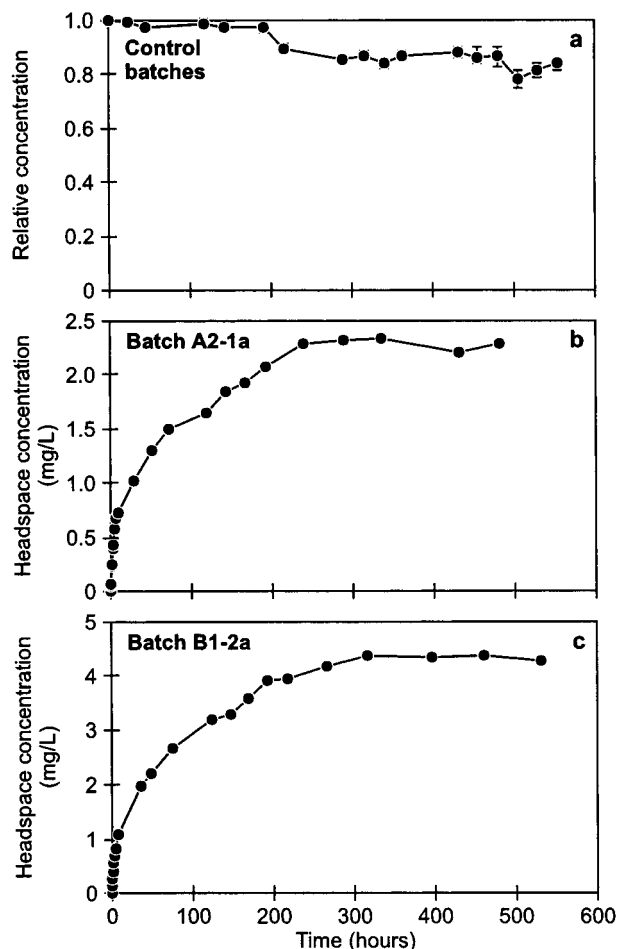


FIGURE 1. (a) Average relative headspace concentration of CCl_3F versus time for the control batches. The initial concentration has been used for normalizing the concentrations. Horizontal bars show the standard deviation determined from the four identical batches. (b) Headspace concentration of CCl_3F versus time in the batch A2-1a. (c) Headspace concentration of CCl_3F versus time in the batch B1-2a.

headspace in the batch versus time together with the results of the control experiment. All four control batches showed constant relative concentrations the first 200 h followed by a sudden drop at the same time in all four batches. After the drop the concentration is constant through the rest of the experimental time. The reason for the sudden drop has not been established. The control experiment, however, shows no indications of continuous CFC losses through needle holes in the septa or by sorption to the septa material.

For the foam batches, all curves show increased concentrations with time up to a pseudoequilibrium, which is reached after 300–500 h, indicating that a certain fraction of the CFC content of the foam is released relative quickly. All curves are fitted to the analytical solution (eq 13) by use of the spreadsheet solution to the equation. It is hypothesized that only the fraction of the CFC in the open foam pores introduced by the cutting is active in the diffusion process out of the foam and that the time frame is so short that release of the sorbed fraction of CFC can be neglected. Since the available CFC fraction in the open pores, f_{avail} , is unknown as well as the effective diffusion coefficient in the foam particles, D , both parameters need to be fitted using the spreadsheet solution. The spreadsheet solution uses the value F (= the fraction of the total content in the batch left in the foam at equilibrium) as fitting parameter. The parameter β in eq 13 equals $(1-F)/F$. The concentration of CFC available

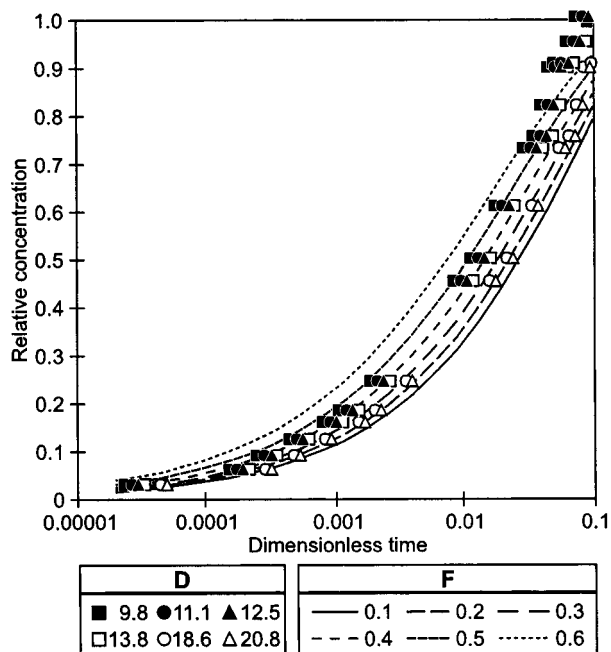


FIGURE 2. Fitting of experimental data from batch experiment B1-2a. Experimental results are normalized using the equilibrium headspace concentration for normalizing the y-axis and an array of five different D -values ($9.8\text{--}20.8 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$) to obtain dimensionless times (shown with symbols). The data are compared to theoretical model curves calculated for an array of F -values (0.1–0.6).

for the quick release, $C_{\text{s,avail}}$ can be calculated using the equation

$$C_{\text{s,avail}} = \frac{C_{\text{a,eq}} \cdot V}{c^3(1-F)} \quad (17)$$

where $C_{\text{a,eq}}$ is the concentration in the air space in the batch at equilibrium (g/m^3), V is the volume of the batch (m^3), and c is the cube side length (m). This equation is only valid for the experiments using a single cube. For the batches using eight cubes, the system is equivalent to a system with one cube of the same side length and a batch volume of $V/8$. The fraction available for quick release, f_{avail} , is then

$$f_{\text{avail}} = \frac{C_{\text{s,avail}}}{C_{\text{s,tot}}} \quad (18)$$

where $C_{\text{s,tot}}$ is the initial total content of CFC in the foam (g/m^3).

Figure 2 shows the fitting of results from batch experiment B1-2a. Values of D between $9.8 \cdot 10^{-12}$ and $20.8 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$ is used for calculating dimensionless times ($= D \cdot t/a^2$) from experimental data. In the figure, series calculated from experimental data using different D 's are shown with symbols. The series are compared with analytical solutions for different values of F (between 0.1 and 0.6). The two curves which fits the best over the longest time range is $D = 20.8 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $F = 0.2$. In general the data was difficult to fit for the last period of the experiment probably due to deviation from using a spherical model for cubic particles.

Table 5 shows a summary of obtained diffusion coefficients for all batch experiments. The observed diffusion coefficients are in the range of $1.9 \cdot 10^{-12}$ and $2.1 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$. The variation may reflect differences in the open pore structure, which again may depend on slight differences in foam structure and how the foam cubes were cut out. The observed values are between 100 and 10 000 higher than the

TABLE 5. Results and Interpretations from the Batch Experiments

batch	$C_{a,eq}$ (mg L ⁻¹)	D (10 ⁻¹² m ² s ⁻¹)	F	$C_{s,avail}$ (mg L ⁻¹)	f_{avail} (%)	time for 95% release (h) ^a
A2-1a	2.30	2.8	0.5	0.35	10	1000
A2-1b	2.80	2.8	0.6	0.53	15	
A1-2a	2.00	11	0.3	0.22	6	900
A1-2b	2.50	14	0.2	0.24	6	
A1-2c	2.00	14	0.1	0.17	4	
A2-2a	1.80	21	0.4	0.23	7	500
A2-2b	2.10	21	0.4	0.26	8	
B1-1a	6.70	2.8	0.4	0.84	16	950
B1-1b	7.50	2.8	0.4	0.95	18	
B1-2a	4.35	21	0.2	0.41	8	550
B1-2b	4.45	21	0.1	0.37	7	
C1-1a	4.70	1.9	0.4	0.59	14	1400
C1-1b	5.80	1.9	0.4	0.73	18	
C1-2a	3.30	13	0.2	0.31	8	780
C1-2b	3.75	14	0.1	0.32	8	

^a An average value of D for the replicates is used in the calculation

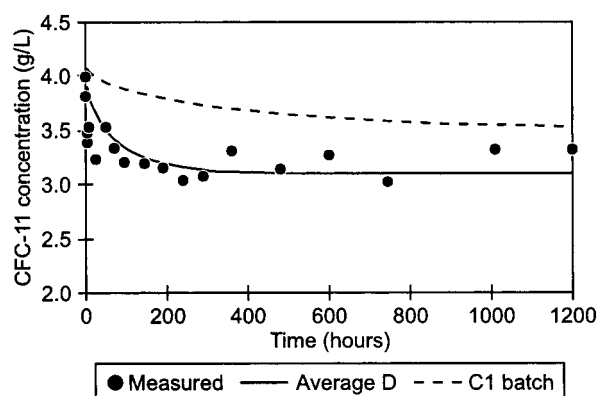


FIGURE 3. Result of the infinite bath experiment using the foam sample C1. The measured foam concentrations versus time (●) and simulations using (a) diffusion coefficient and available foam concentration from the C1-1 batch experiment (broken line) and (b) the average diffusion coefficient from all batch experiments and the observed available fraction in the infinite bath $8.3 \cdot 10^{-12}$ and $20.8 \cdot 10^{-12}$ m² s⁻¹ experiment (full line).

values obtained in intact PUR foam without open pores (confer Table 1).

The calculated available fractions, f_{avail} , shows generally higher numbers for the small 1-cm cubes, where values in the range of 10–18% are obtained, in comparison to the larger 2-cm cubes, where values of 4–8% are seen.

To evaluate the time scale of the quick release process, the obtained diffusion coefficients are used in calculating the time needed for a 95% release of the available fraction. The infinite bath solution (eq 8) is used to evaluate the release to an open system such as the atmosphere or the pore gas of a landfill. The result of the calculations is shown in Table 5. The time scales observed are in the range of 500–1400 h. This means that the quick release after shredding PUR foams to particle sizes of 1–2 cm is most significant the first week after shredding and is more or less over after 3–8 weeks. The fraction, which is lost over this period, is less than 20% of the total initial CFC content for the particles of 1-cm size and even below 8% for particles in the 2-cm size.

Infinite Bath Experiment. Figure 3 shows the result of the infinite bath experiment. Some scatter is observed in the data in comparison to results obtained in the batch experiments. This may be due to the fact that a new cube represents each data point (after extraction and analysis). Slightly

TABLE 6. Data, Results, and Interpretations from the Khalil and Rasmussen Experiments

	foam sample			
	SN001	SN002	SN003	SN004
aluminum-cladded	yes	no	yes	yes
thickness, h (cm)	5.7	4.8	5.1	5.0 ^a
sample size length, c (cm)	30.5	30.5	30.5	30.5
sample weight (gram)	179	113	163	175
initial CFC content (% w/w)	10	10	10	10
initial CFC content, $M_{eq(g)}$	17.9	11.3	16.3	17.5
initial release (%) ^b	0.2	0.3	0.2	0.1
initial release time (hours)	600	400	800	550
experimental time (days)	394	388	390	279
total release (%)	1.0	0.9	0.5	0.9
effective diffusion coeff, D (10 ⁻¹⁵ m ² s ⁻¹)	2.3	0.45	0.56	1.5
calculated half-life (years) ^c	9000	8000	35000	10800

^a Estimated value, number not given in original paper. ^b Defined as the released mass until the linear relationship between flux, F , and reciprocal squared time is valid. Given as percentage of the initial CFC content. ^c Calculated using the determined effective diffusion coefficient and the eq 4 or—for the aluminum-cladded case—eq 6.

different cube sizes and a generally higher uncertainty of the CFC analysis of foam samples in comparison to headspace analysis may be the reason for the observed higher scatter. Figure 3 also includes two simulated releases. The obtained diffusion coefficient for the C1 samples in the batch experiments together with the obtained available fractions from the same experiments is used to calculate a theoretical release curve using eqs 8 and 10. A similar curve is included based on an average diffusion coefficient from all batch experiments and on the actual observed available fraction in the infinite bath experiment. The figure shows that the average diffusion coefficient better simulates the time scale of the quick release in the infinite batch experiment than specific diffusion coefficients obtained for the foam sample C1. The available CFC fraction determined for sample C1 in the batch experiment (14–18%) is slightly lower than the released fraction of 23% observed in the infinite bath experiment. However, the experiment supports the general finding that the quick release is finalized after a time period of a few weeks and that the released fraction is in the order of 20% for 1-cm foam particles.

Reinterpretation of the Khalil and Rasmussen Data.

Khalil and Rasmussen made experiments with 1 square foot samples of four different commercial PUR foam panels blown with CFC-11 (21, 22). Each sample was supported on a wire frame in a hermetically sealed chamber. A measured amount of air was constantly passed over the foam sample using a pump. A small sample of air was extracted periodically from the chamber and the amount of CFC-11 was measured. Using a mass balance the emission of CFC was calculated (in $\mu\text{g/day}$). Data for the experiments using the four samples (SN001–SN004) is given in Table 6. Three of the four samples were cladded with aluminum-foil on one side as shown in Table 6. By integrating the original figures, which showed flux (in $\mu\text{g/day}$) as a function of time, the total released amounts are calculated. The releases were below 1% for all four foam samples (confer Table 6), indicating that the diffusion process is in its very early stage. This means that the short-term approximation of the flux can be used (eq 12). The value for the term A/V to be used is for the non-aluminum-cladded sample: $A/V = 4/c + 2/h$ and $A/V = 4/c + 1/h$ for the aluminum-cladded sample. The value, c , is the side length of the square foam sample, and h is the thickness of the sample.

Equation 12 shows that for short times the flux should be proportional to the square root of the reciprocal time. Figure

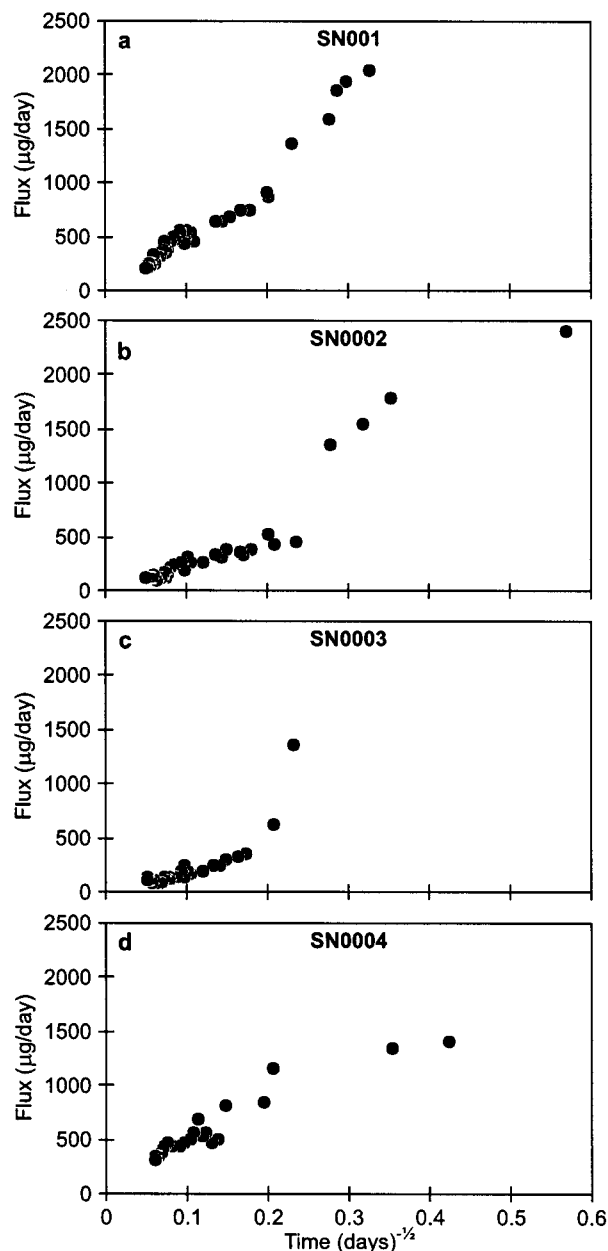


FIGURE 4. Results from the Khalil and Rasmussen experiment (27). The observed flux of CFC-11 from each of the four foam samples (SN001–SN004) is shown as a function of the square root to the reciprocal time (in days).

4 shows the original flux data with the x -axis, square root of the reciprocal time. All four curves show linear dependencies to $t^{-1/2}$ except for the first initial period (large values of $t^{-1/2}$). The initial release period last between 400 and 800 h (Table 6), which agree very well with the time frames of the initial release from the cubes in the batch and infinite bath experiments (confer Table 5). Thus the initial release period is probably controlled by enhanced releases due to the sample cutting. However the fraction initially released for the large square samples (0.1–0.2%—Table 6) are much lower than found for the 1 and 2 cm cubes (5–20%—Table 5).

On the basis of the slope of fitted lines to the data in Figure 4, effective diffusion coefficients are calculated from eq 12. The numbers are between 0.05 and $0.23 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$ (Table 6), which are in the low end of the range reported in other studies. The lowest value found by traditional diffusion methods is $0.18 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$ (confer Table 1). However, evaluating the experimental techniques used for obtaining

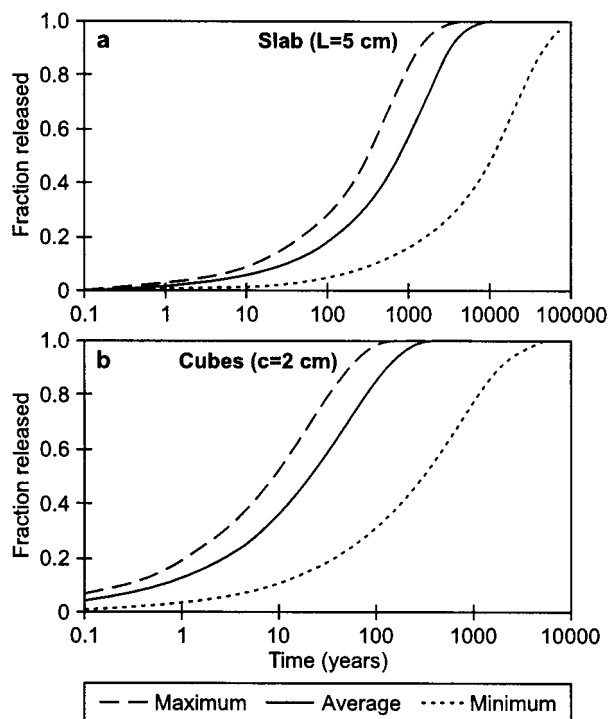


FIGURE 5. The fraction of CFC-11 released from the foam as a function of time for the slab (a) and the cube (b) scenario. Curves for the minimum ($0.05 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$), average ($0.7 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$), and maximum ($1.7 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$) diffusion coefficient observed are shown.

the values in Table 1, the values obtained by the reevaluation of the Khalil and Rasmussen data are probably not of lower quality. Khalil and Rasmussen worked on relative large samples as compared to others, which means that edge effects and releases from open pores had a much lower importance. On the basis of the determined diffusion coefficient the half-lives of CFC in the foam slabs are calculated using eq 4 (non aluminum-cladded case) or eq 6 (aluminum-cladded case). The half-life is defined as the time needed for a release of 50% of the total CFC content in the slab. The numbers are given in Table 6. Khalil and Rasmussen (22) used an empirical first-order approximation (release rate proportional to the average CFC content in the sample) to calculated half-lives. They reported half-lives in the order of 140–400 years, which are nearly a factor 50–100 lower than values obtained by using the diffusion-based analytical solution. The first-order approximation is only valid for long time periods (24), which is by no means the case for the Khalil and Rasmussen experiment, as already discussed.

Perspectives

The time frame of CFC release is evaluated using the range of observed diffusion coefficients based on values in Table 1 and the values obtained from reevaluating the Khalil and Rasmussen data (minimum: $0.05 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$; average: $0.7 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$; maximum: $1.7 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$). Figure 5 shows calculations for two scenarios. The one scenario resembles the release from a nonshredded, noncladded foam panel with a thickness of 5 cm. The other scenario resembles the release from shredded foam represented by 2 cm cubes. For both scenarios the following data has been used: foam density, 34 g L^{-1} (average value for foam used in our experiments) and CFC-content, 10%w/w. Figure 6 gives the calculated releases (in $\text{mg CFC (L foam)}^{-1} \text{ year}^{-1}$) for both scenarios. Figure 5 shows that the diffusion coefficient used has a significant effect on the time frame of the release process in both scenarios. For instance for the cube scenario, the

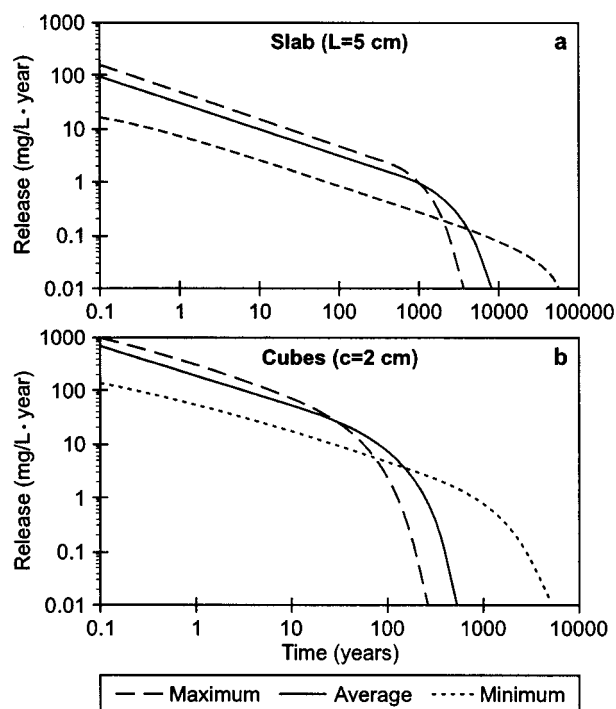


FIGURE 6. The release of CFC-11 (in $\text{mg CFC (L foam)}^{-1} \text{ year}^{-1}$) from the foam as a function of time for the slab (a) and the cube (b) scenario. Curves for the minimum ($0.05 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$), average ($0.7 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$), and maximum ($1.7 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$) diffusion coefficient observed are shown.

TABLE 7. Evaluation of the Effect on Particle Size after Shredding Using the Average Diffusion Coefficient of $0.7 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$

cube side length, c (cm)	0.5	1	2	3	4	5
half-life (years) ^a	1.3	5	22	50	85	135

^a Half-life defined as the time needed for a 50% release of the initial CFC content.

half-life (fraction released = 0.5) varies from 9 years to 300 years between the minimum and the maximal value. Also the magnitude of the release is strongly depending on the diffusion coefficient used. This clearly shows that there is a need for systematic research determining diffusion coefficient for different foam products and different measuring techniques in order to evaluate if the observed differences in diffusion coefficients truly reflect differences in foam properties or merely are due to experimental artifacts using different measuring techniques.

By comparing the calculations presented in Figures 5 and 6 in relation to disposal practices it becomes obvious that shredding the foam waste before disposal in landfills leads to enhanced releases of CFC in comparison to disposing of the foam in larger pieces. Using the average D -value, the half-lives are 22 years and 800 years, respectively, for the cube and slab scenario. Also the particle size obtained from the shredding is important. Table 7 shows the calculated half-lives for particle sizes between 5 mm and 5 cm (cube side length). The large differences in half-life shown will even be more evident if the initial release from pores made open in the shredding process was taken into account (our studies showed that for particles lower than 2 cm this release, which only last for a few weeks, is substantial). The initial release due to shredding will in many cases be directly emitted to the atmosphere before the waste is compacted and covered with new waste layers. However, an effective shredding may still lead to very high CFC concentrations in landfill gas, which

may be detrimental for gas engines used in landfill gas utilization. The initial release after disposal of shredded foam may eventually be even higher due to compression of the foam by machinery initially compacting received waste at the landfill or after a while by the weight of overlying waste layers. However the 40% which is bound in the PUR phase is not affected by compression and will still be slowly released.

As mentioned in the Introduction, the global release from PUR foam is probably the most important factor for the future development in CFC-11 concentrations in the atmosphere. In a detailed global model evaluation of future CFC-11 concentrations in the atmosphere (3) half-lives in the order of 11–100 years for the release from PUR foam are used. These numbers may be vastly underestimated (for insulation foam boards still in place in constructions or nonshredded waste) or strongly overestimated (for shredded foam waste from disposed of home appliances) depending on the disposal practice used and lifetimes of the foam containing products. A more differentiated global model analysis based on diffusional governed release may be appropriate using information on lifetimes and disposal practices for different foam containing products.

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