

# Short- and Long-Term Releases of Fluorocarbons from Disposal of Polyurethane Foam Waste

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Several halocarbons having very high global warming or ozone depletion potentials have been used as a blowing agent (BA) for insulation foam in home appliances, such as refrigerators and freezers. Many appliances are shredded after the end of their useful life. Release experiments carried out in the laboratory on insulation foam blown with the blowing agents CFC-11, HCFC-141b, HCF-134fa, and HFC-245fa revealed that not all blowing agents are released during a 6-week period following the shredding process. The experiments confirmed the hypothesis that the release could be divided into three segments: By shredding foam panels, a proportion of the closed cells is either split or damaged to a degree allowing for a sudden release of the contained atmosphere in the cell (*the instantaneous release*). Cells adjacent to the cut surface may be only slightly damaged by tiny cracks or holes allowing a relative slow release of the BA to the surroundings (*the short-term release*). A significant portion of the cells in the foam particle will be unaffected and only allows release governed by slow diffusion through the PUR cell wall (*the long-term release*). The magnitude of the releases is for all three types highly dependent on how fine the foam is shredded. The residual blowing agent remaining after the 6-week period may be very slowly released if the integrity of the foam particles with respect to diffusion properties is kept after disposal of the foam waste on landfills. It is shown by setting up a national model simulating the BA releases following decommissioning of used domestic refrigerators/freezers in the United States that the release patterns are highly dependent on how the appliances are shredded.

## Introduction

The blowing agent (BA) for insulating foam used in appliances (e.g., refrigerators and freezers) and many building materials is frequently a fluorocarbon such as HCFC-141b or HFC-134a. Prior to 1996 the most common blowing agent was CFC-11 (1). New HFCs such as HFC-245fa are expected to be used extensively in the future in the United States. All of these compounds are strong greenhouse gases that contribute to global warming if released to the atmosphere. About 8 million refrigerators/freezers are being decommissioned in the United States each year. Each unit contains about 1 kg of blowing agent. Many appliances are shredded after the end of their useful life. When this occurs, the insulating foam

is reduced to small pieces that may be incinerated or disposed of in a landfill. In the United States most of the foam waste is disposed of directly in landfills and very little is incinerated (2). Relatively little information is available regarding the amount of the blowing agent that escapes, the time frame of the release, and how much remains in the foam after an appliance is shredded. Good data in this area are of interest because many climate change models assume 100% release at disposal. Furthermore basic understanding of the release mechanisms is very important for constructing facilities for refrigerator/freezer disposal allowing only minimal releases of the BA to the atmosphere.

The BA release is mainly controlled by slow outward diffusion from the polyurethane (PUR) foam, which is used as insulation material in refrigerators/freezers. The diffusion in nonshredded foam panels is very slow (1). Recent laboratory studies (1) performed on PUR foam containing CFC-11 studying the distribution of CFC-11 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 particles. For smaller particles the short-term release will be larger. This study did not quantify the instantaneous release from cutting closed cells during the shredding process, so the numbers given above exclude this release.

The objective of this study is to determine the fraction of the blowing agent that escapes when polyurethane insulation foam is shredded and the amount released as a function of time during the following 6 weeks. The objectives are met by performing laboratory experiments on cut foam cubes and foam particles obtained from realistic (i.e., comparable with industrial standards) shredding. Foam diffusion models are used for evaluating and extrapolating the results. The following blowing agents were studied: CFC-11, HCFC-141b, HFC-134a, and HFC-245fa.

**Conceptual Model of the Blowing Agent Release from Shredded Foam.** Insulation foam in refrigerators/freezers is rigid foam consisting of tiny bubbles of a blowing agent separated by very thin cell walls of PUR. When the foam is shredded, some of the cells at the edges are broken, which presumably will release the blowing agent to the surroundings very fast. Tiny cracks originally present in the cell walls or introduced by the shredding activity may release the blowing agent more slowly. A conceptual model is set up based on the foam structure: By cutting the foam, a proportion of the cells is either split or damaged to a degree allowing for a sudden release of the contained atmosphere in the cell (*the instantaneous release*). Cells adjacent to the cut surface may be only slightly damaged by tiny cracks or holes allowing a relative slow release of the BA to the surroundings (*the short-term release*). A significant portion of the cells in the foam particle will be unaffected and only allows release governed by slow diffusion through the PUR cell wall (*the long-term release*). A microscope picture of a cut foam piece is given in the Supporting Information.

By assuming that both the short-term and the long-term release can be described by diffusion processes with concentration independent diffusion coefficients, the initial part of both diffusion processes may be modeled by the equation (3)

$$\frac{M_{t,i}}{M_{0,i}} = 2\left(\frac{A}{V}\right)\sqrt{\frac{D_i t}{\pi}} \quad (1)$$

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TABLE 1. Diffusion Coefficients of Different Blowing Agents in PUR Foams Obtained from Literature<sup>b</sup>

reference	$D_{\text{eff},c}$ ( $10^{-14} \text{ m}^2 \text{ s}^{-1}$ )
CFC-11	
(17)	1.3
(18)	0.6–1.7
(19)	0.18
(20)	2.8–3.2
(8)	0.05–0.23
(21)	12
(22)	4.6
HCFC-22	
(20)	14.8 <sup>a</sup>
HCFC-141b	
(13)	19
(20)	3.0
HFC-134a	
(23)	3.8
HFC-245fa	
(13)	3.9
(23)	1.0

<sup>a</sup> Values of  $D_{\text{eff},c}$  obtained from the pressure related diffusion coefficient following the method given by Kjeldsen and Jensen (7). A gas-filled porosity,  $f_g$ , of 0.98 is used. <sup>b</sup> The values are valid for 25 °C. Values for CFC-11 are taken from the review given by Kjeldsen and Jensen (7).

where the index  $i$  refers to either the short- or the long-term release process,  $(A/V)$  is the ratio of the external surface area of the particle to the volume of the particle,  $M_t$  is the mass of the blowing agent released to time  $t$ ,  $M_0$  is the total mass of the blowing agent available for the diffusion process, and  $D$  is the diffusion coefficient valid for the diffusion process.

The total content of the blowing agent,  $M_0$ , in the particle is divided into two parts

$$M_0 = M_{0,1} + M_{0,2} \quad (2)$$

where  $M_{0,1}$  is the content in the affected (broken) fraction of the foam particle, and  $M_{0,2}$  is the content in the intact fraction of the foam particle. For both of the releases the first initial part of the release process, eq 1, can be used. This means that if the mass released,  $M_t$ , is shown as a function of the square root to the time ( $t^{1/2}$ ) the curve would be composed of two straight lines with different slopes, one for each of the release processes. By estimating  $M_{0,1}$  and  $M_{0,2}$  (see under the Results and Discussion section how that is done) the governing diffusion coefficients for the two release processes,  $D_1$  and  $D_2$ , can be calculated using the slopes of the lines.

The long-term release from a given foam particle can then be estimated using the calculated  $D_2$  and a model valid for the whole release period as given by Kjeldsen and Jensen (1). This model omits any concentration dependency of the long-term diffusion coefficient. Therefore the model may overestimate the long-term release to a specific point in time.

**Literature Values of Diffusion Coefficients.** Very few data on the foam diffusion coefficient of blowing agents in PUR foam 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 different blowing agents in PUR foam based on literature data. In general typical diffusion coefficients are in the range of  $1\text{--}4 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$ , and only a few observations are lying outside this range. There seems not to be a strong dependency of the BA used. Some studies (4, 20) find that the diffusion coefficient is concentration dependent.

## Experimental Section

**Chemicals.** The CFC-11, HFC-134a, HCFC-141b, and HFC-245fa used were all obtained in high purity. CFC-11, HFC-134a, and HFC-245fa were obtained from Interchim, France, while HCFC-141b was obtained from Honeywell, Netherlands. The chemicals were mainly used for calibration and control experiments.

**Foam Samples.** Foam samples blown with four different blowing agents (CFC-11, HCFC-141b, HFC-134a, and HFC-245fa) were included in this study. The Appliance Research Committee under Association of Home Appliances Manufacturers, Washington, DC, U.S.A. supplied the foam panels containing HCFC-141b, HFC-245fa, and HFC-134a. Panels manufactured by three different manufacturers were provided. PUR foam samples containing CFC-11 were obtained from a used refrigerator. Experiments with these four blowing agents were in general carried out in parallel. After removing the aluminum foil/plastic liner covering the foam panels, a large foam sample ( $10 \cdot 10 \cdot 5 \text{ cm}$ ) was cut of the panel. Smaller cylindrical foam samples were cut out from the center of the large foam sample using a cork bore.

The total content of the blowing agent in the foam samples was determined using a heating method: A 1 cm diameter by 1 cm height cylinder cut out by the cork bore was placed in a closed bottle. To release the halocarbons from the foam, the bottle was incubated in an oven for 48 h at 140 °C. When cooled to room temperature gas samples were redrawn from headspace and analyzed by gas chromatography. Initial investigations showed that only one heating step was required since only small masses of the blowing agent were released by a second heating step. To measure the distribution of the BA between the voids and the PUR phase in the foam samples, compression tests were carried out following the method presented by Kjeldsen and Jensen (1).

To investigate typical size distribution of foam particles from a real shredder, an old combined refrigerator and freezer was shredded at the Danish Recycling Center, Aarhus, Denmark. The size distribution was determined on a sample of the shredded foam using standard soil sieves. Besides, a subsample of the shredded foam was collected at the exit of the shredding unit and kept in gastight bags at low temperature until arrival at the laboratory. This sample was divided by sieving in the lab, and short-term release experiments were performed on the sieved fractions.

**Instantaneous Release Experiments.** To quantify the instantaneous release during shredding due to breakage of closed cells, an experimental setup was used where foam was shredded in a closed environment. Foam blown with three types of blowing agents (CFC-11, HCFC-141b, and HFC-245fa) was included in the experiment. The release experiments were conducted in a glovebox made of thick transparent polyvinyl film. The glovebox had a volume of  $1.3 \text{ m}^3$ . The glovebox has as standard equipment two ventilators, which should ensure that the gas phase in the glovebox always is fully mixed. In addition a fan was also placed in the box. A large foam sample was cut out of the test panels and placed in the glovebox. The shredding of the foam was carried out by a combination of cutting using a knife and breaking by hand the foam, simulating real shredding. To obtain smaller size fractions a grater and a food blender were used. After 5 min the foam particles were enclosed in a container, and the thoroughly mixed air space in the glovebox was sampled and analyzed by gas chromatographic analysis. On the basis of the result the fraction of the instantaneously released blowing agent was calculated. After the experiment the size distribution of the shredded foam was determined by sieving.

**Short-Term Release Experiments.** To quantify the short-term release two types of experiments (flux chamber experiments and batch release experiments) were carried out over

TABLE 2. Measured and Calculated Parameters for the Four Foam Panels Provided by Supplier B<sup>c</sup>

parameter	unit	blowing agent			
		CFC-11	HFC-134a	HCFC-141b	HFC-245fa
density, $\rho_{\text{foam}}$	g/L	24.6	39.0 (38.6,33.7)	32.2	30.7 (30.5,30.3)
porosity, $f_g$ (calculated <sup>a</sup> )		0.985	0.972	0.978	0.980
total content of BA	g/L	3.43	2.78 (3.32,2.52)	3.77	3.66 (4.20,5.63)
	% w/w	13.9	7.1 (8.6, 7.5)	11.7	11.9 (13.7,18.3)
fraction sorbed in PUR	%	29.5	22.7	27.8	24.8
distribution coeff, $K^b$	m <sup>3</sup> gas·(m <sup>3</sup> PUR) <sup>-1</sup>	24.6	10.1	16.5	14.9

<sup>a</sup> Gas-filled porosity was calculated based on the density measurements using a density of solid PUR of 1240 g/L, and densities of the BA gas in the voids were calculated using an assumption of 25 °C and 1 atm. <sup>b</sup> Calculated as described in ref 1. <sup>c</sup> Densities and total BA contents for foam panels provided from supplier C and D, respectively, are given in parentheses for HFC-134a and HFC-245fa.

a 6-week period. The advantage of the flux chamber technique to the batch release technique is that the atmosphere in the chamber can be controlled and that a mass buildup is avoided. However, the flux chambers are technically more complex and time-consuming.

A flux chamber consists of a stainless steel cylinder, 25-cm long by 15-cm i.d. The steel cylinder is closed at one end and equipped with a steel lid fitted with rubber O-rings to ensure a gastight fit. The lid contains an inlet port for gas. An outlet port is positioned at the bottom-end of the cylinder. A perforated screen is located 8 cm above the bottom of the cylinder to place the foam cubes. A sampling port is located at the bottom of the cylinder to enable taking gas samples with a syringe needle. The sample port is equipped with a Teflon coated silicone septum. Both inlet and outlet are equipped with a valve, which enables closing the container when changing the gas supply.

The nitrogen (>99.999%) gas flask, which feeds the test chamber, is equipped with a special reduction valve in order to obtain a very low pressure above atmospheric pressure. The pressure was 0.03 bar above atmospheric pressure. To calculate the exact gas amount released from the foam, the flow must be kept constant. A gastight piston pump (FMI Lab Pump, model QG, Fluid Metering Inc.) controls the flow through the system. The gas outflow can be measured by a bubble flow meter. The inlet flow was 12 mL/min resulting in a retention time of 6.2 h. The chamber experiment was carried out at room temperature.

In total 10 flux chambers experiments were carried out in two series. In the first series, four chambers with foam and one control chamber were set up. The four chambers contained four foam types all manufactured by Manufacturer B blown with the four different blowing agents. The foam was cut into a number of small cylinders using a cork bore (diameter = 1 cm; height = 1 cm) and placed in the chamber. The number of foam cylinders placed in each chamber was determined by the sensibility on the GC—so that fewer foam cylinders were needed to get a measurable concentration for CFC-11 in comparison with HFC-134a. The chamber was closed, and the first gas sample was taken after 15 min.

In the second series similar experiments were carried out but containing foam blown with HFC-134a and HFC-245fa from Manufacturers C and D (four chambers). A chamber containing foam blown with CFC-11 collected from Aarhus Recycling Company (the “large” fraction obtained by sieving the collected sample) was included in the second series.

The control flux chamber contained a known amount of liquid HCFC-141b in a small glass container equipped with a stopper and a needle. Before start up and at the end of the experiment the liquid sample was weighed. The mass loss of HCFC-141b from the container was measured over the full experiment time by analyzing gas samples taken in the outlet and measuring the gas flow.

The batch release experiment was performed in order to evaluate the importance of foam particle size to the short-

term release. A series of batches using foam blown with HCFC-141b was set up. In the batch release experiments foam cylinders were cut using the cork bore and placed in a 1-L closed glass container equipped with a Teflon coated rubber septum. Foam cylinders with sizes ranging from 0.8 cm<sup>3</sup> to 12.8 cm<sup>3</sup> were used. Headspace samples were withdrawn and analyzed by gas chromatography over time. The experiments ran for 6 weeks at room temperature. Control experiments (without foam but containing BA) were run in parallel.

**Analysis.** The halogenated compounds were measured on a Carlo Erba HRGC 5300 gas chromatograph equipped with an electron capture detector (ECD) and a flame ionization detector (FID) in parallel. The FID is mainly used for analysis of HFC-134a since the sensibility on the ECD for this compound was very low. Samples (10–500  $\mu$ L gas) were injected on a WCOT fused silica capillary column (CP-Sil-19 CB) with nitrogen being the carrier gas. The compounds were analyzed with an isotherm column temperature of 40 °C. Concentrations of the target compounds were calibrated by injection of gas standards (no fewer than 12 concentration levels) and constructing a standard curve.

## Results and Discussion

**Foam Characteristics.** Table 2 shows the characteristics of the four foam panels. The densities found (and calculated gas porosities) are within the range expected for PUR foams (5, 6). The total content of BA in foam is for CFC-11, HCFC-141b, and HFC-245fa in the range of 11.6–13.3% w/w, which is close to the expected values which are in the range of 10–15% w/w (7–9). The foam panel blown with HFC-134a is in the lower end with a total content of 7.0% w/w.

The amount of the BA dissolved in the polymer was measured by compression, assuming that the amount in the compressed foam sample consists only of the fraction sorbed in the PUR. The amount of the BA dissolved in PUR varied between 23% and 30%. Swanström and Ramnäs (10) found that approximately half of the total content of CFC-11 in the foam was dissolved in the polymer in 10–20 year old foam samples. However a significant variation in BA solubility has also been observed in a study performed by Bomberg and Kumaran (11). Samples taken from different foams showed a total content of CFC-11 in the range of 10–12.2% w/w. However, the distribution of the BA between the cell gas and the polymer showed large variations: from 22% up to 60% of the CFC-11 was dissolved in the polymer. In another study by Bomberg and Brandreth<sup>12</sup> foam samples showed that around 30% of the CFC-11 was present in the PUR phase after 11 years of laboratory storage.

**Instantaneous Release.** Figure 1 shows the instantaneous loss of the BA in percentage of the total BA content as a function of time from foam blown with two different blowing agents. The calculation of the total loss is based on the measured gas concentrations, the total volume of the



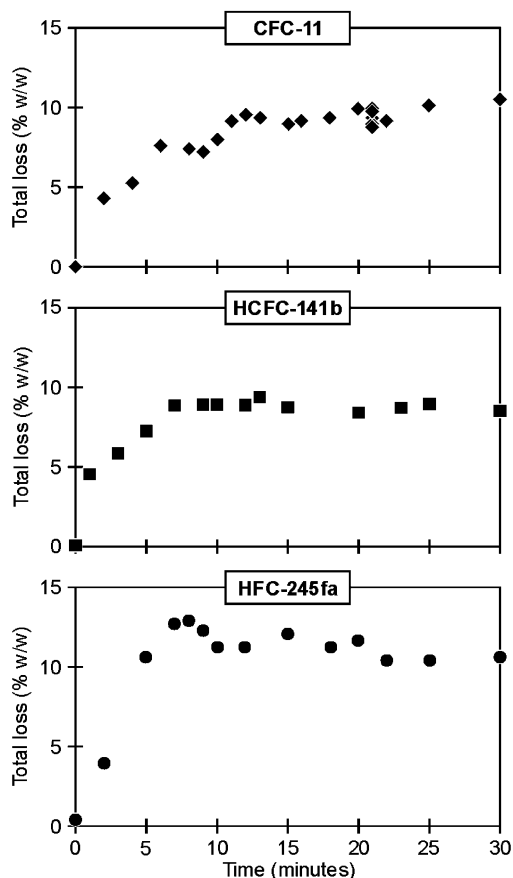


FIGURE 1. The instantaneous release in percentage during shredding of foam blown with different blowing agents within the first 30 min. For CFC-11 results from the samples taken after 21 min at different locations within the glovebox are also shown.

glovebox, and the total content of the BA in the foam. The experiments show the same trend in the release of the BA from all the different foams. The figure shows that the BA is released instantaneously at the shredding of the foam and continues for 6–7 min, which corresponds to the time it takes to shred all the foam. The release decreases thereafter rather rapidly, and after 12 min no further release is observed. Fifteen minutes after start up the shredded foam is collected and placed in a closed container inside the box. In the experiment with foam blown with CFC-11, six gas samples were taken in different places in the glovebox (including corners) in order to check if the glovebox was fully mixed. The samples were taken 21 min after start up as can be seen from Figure 1a. The gas samples showed very similar results (standard deviation of 5%), indicating that the box was fully mixed.

The results of the instantaneous release experiments are summarized in Table 3. The table shows that most of the foam weight in each category is within the desired particle fraction (between 65 and 74%). It also shows that the instantaneous release—at least from the X-large fraction—is nearly independent of the type of blowing agent (total release in the range of 9–11%). The total instantaneous release is, however, highly dependent on the particle size, which is expected due to the higher fraction of cut cells for the small particles.

Based on the results of the instantaneous release experiments and the measured size distribution of foam shredded in a full-scale refrigerator shredder (Table 4), the expected instantaneous release during full-scale shredding is estimated to be 18–24% based on the two foam samples taken from the full-scale shredder unit. This range is not universal but

TABLE 3. Instantaneous Release during Shredding from Foam Particles of Different Sizes and—for the X-Large Fraction—from Foam with Different Blowing Agents

blowing agent	size	main fraction (mm)	%age of total content wt in main fraction (%)	total content of BA (% w/w)	total release (% w/w)
CFC-11	small	2–4	65	13.30	39
CFC-11	medium	4–8	77	13.30	34
CFC-11	large	8–16	83	13.30	18
CFC-11	X-large	16–32	84	13.30	9
HCFC-141b	X-large	16–32	74	11.62	9
HFC-245fa	X-large	16–32	74	11.62	11

TABLE 4. Size Distribution of Two Foam Samples Taken from the Full-Scale Refrigerator Shredder Unit at the Danish Recycling Center<sup>a</sup>

	size fraction (mm)					
	<1	1–2	2–4	4–8	8–16	16–32
sample A	9.7	3.9	7.8	19.7	42.9	15.9
sample B	3.5	0.3	1.3	10.0	54.5	30.4

<sup>a</sup> Numbers are in percentage of total weight.

highly dependent on how fine the foam is shredded.

**Short-Term Release.** Figure 2 shows the results of the flux chamber release experiments. Each graph gives the total accumulated loss in percentage of the total initial content of BA.

In the control experiment it was found that a total mass of 2.0664 g determined by weight had been lost from the liquid source of HCFC-141b. This mass loss was compared with the measured accumulated mass loss based on outlet concentration and flow measurements as shown in Figure 2a. After 1100 h the measured accumulated mass loss was 102% of the mass reduction in the liquid source. The small deviation is believed to be within the measurement error. The control experiment therefore shows that there are no losses in the experimental set up.

The graphs in Figure 2 for all foam types show the same trend: most of the BA loss happens during the first 150–200 h and decreases afterward. The total relative loss ranges from 5 to 28% depending on the BA and foam manufacturer. The graphs indicate that some of the differences in release among types of blowing agents may be due to differences in the manufacturing of the foam boards, since the experiments with HFC-134a and HFC-245fa gave a significant variation in released mass between the three manufacturers. The difference could not be explained by differences in foam densities and total BA content (confer Table 2) and may be due to differences in foam cell structures. Comparing the two graphs for CFC-11 in Figure 2 it is seen that the release behavior of the foam shredded in an industrial shredding unit is equivalent to the behavior of the cutted foam particles.

Figure 3 shows the accumulated release of HFC-245fa in one of the flux chamber experiments. The accumulated released mass is pictured as a function of square root to the time, since this, according to the diffusion process described by eq 1, should give straight lines. The figure shows that two diffusion processes are working simultaneously in the foam particles. In the first stage, the blowing agent available in the short-term release reservoir is adding most significantly to the release. The last part of the curve is only representing the long-term release, because the release from the short-term release reservoir has been exhausted. Graphs showing the close fit between the model and the experimental results are given in the Supporting Information. Based on the shown experiment and similar experiments with other blowing

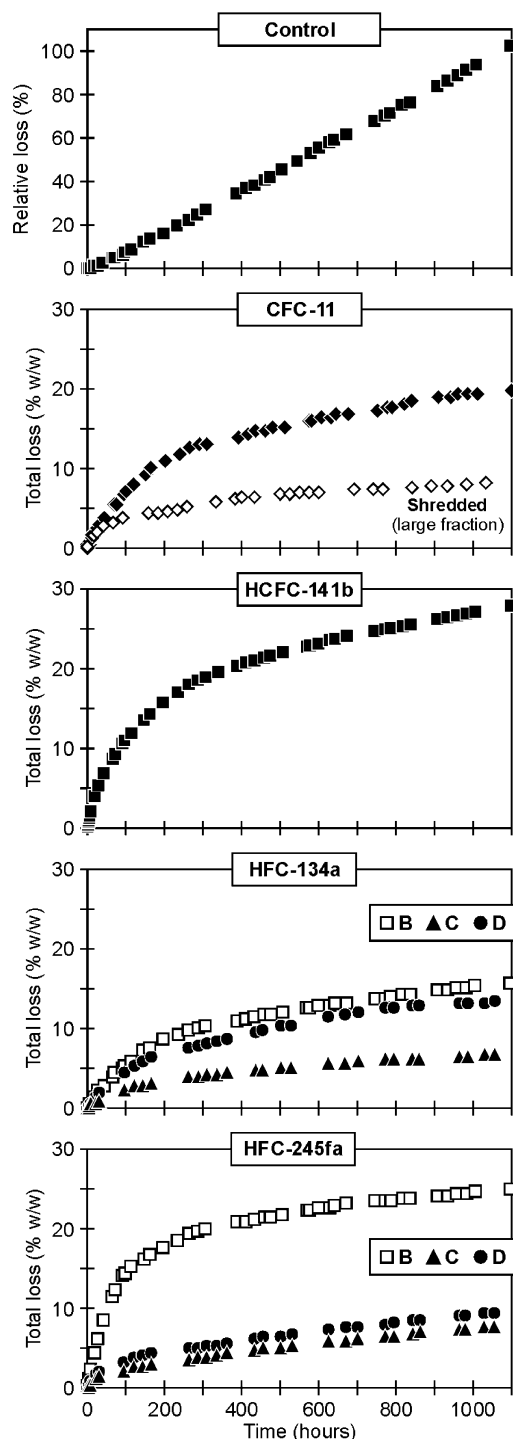


FIGURE 2. Results from the flux chamber release experiments showing the accumulative release in percentage of the initial blowing agent content as a function of time (for the control experiment the release is relative to the mass loss from the small container inside the chamber). For CFC-11 results from the experiment using the large fraction of real shredded foam is also shown. For HFC-134a and HFC-245fa foam from three different manufacturers (B, C, and D) was used.

agents, diffusion coefficients representing both the short-term and the long-term release are calculated and presented in Table 5. The total mass of the blowing agent available in the short-term reservoir,  $M_{0,1}$ , is determined as the intercept to the y-axis of the linear relation of the long-term release ( $M_{0,1}$  equals 565  $\mu\text{g}$  for HFC-245fa as shown in Figure 3).  $M_{0,2}$  is then calculated as the difference between the measured

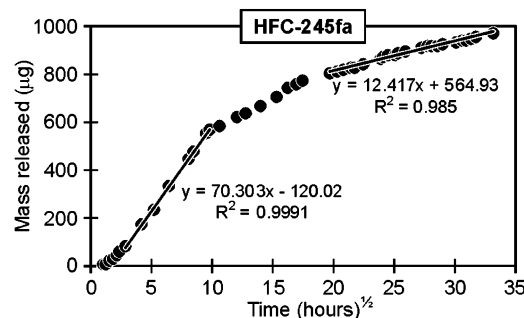


FIGURE 3. Mass released (in  $\mu\text{g}$ ) as a function of the square root of time for flux chamber experiment using foam blown with HFC-245fa. The fitted lines for the short-term release and the long-term release are shown with the slope and the correlation coefficient ( $R^2$ ).

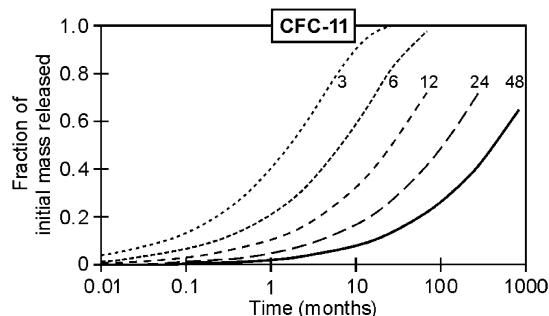


FIGURE 4. The fraction of initial mass released as a function of time and particle size for CFC-11 calculated by the release model.

total content (as given in Table 2 and  $M_{0,1}$ ). The magnitude of the diffusion coefficients for the short-term and long-term releases given in the table are close to the observed values found in other investigations (1). Three out of four long-term diffusion coefficients are very close to each other. The diffusion coefficient for HCFC-141b is about 50% larger. Others have also found larger diffusion for foams blown with HCFC-141b (13). Extrapolating the long-term releases by use of the determined diffusion coefficients and the model valid for long-term releases (1), it is shown that it may take on the order of 10 years to release 50% of the initial content for a 24 mm foam particle (confer Figure 4). This assumes that the particle keeps its diffusion properties after product decommissioning and disposal of foam in a landfill.

The data interpretation method used is as described in the section "Conceptual Model of the Blowing Agent Release from Shredded Foam" based on a double compartment with a constant diffusion coefficient for each compartment. Other studies (20) have shown that the diffusion coefficient is decreasing with decreasing concentration of the blowing agent in the PUR material. Incorporating this dependency in the release model would probably improve the fit to the data presented in Figure 3. The concentration dependency cannot be determined from the existing data presented in this study, but future studies should focus on this aspect. The decreasing diffusion coefficient with concentration would prolong the time needed for the long-term release as estimated in Figure 4.

Figure 5 shows the result of the batch release experiments using cylinders of different sizes. The figure gives the total short-term loss in percentage of the original content of the BA in the foam samples over a 6-week period. Each graph describes one experiment, and the volume of the foam sample is shown in the top of the graph. The graphs show that the largest loss is obtained from the smallest foam particle: in the experiment with a 0.8  $\text{cm}^3$  particle the loss is 19% of the total content of BA, while it is only 3% for a 12.8  $\text{cm}^3$  particle.

TABLE 5. Parameters in the Double Compartment Model Using the Four Blowing Agents<sup>d</sup>

BA	short-term release				long-term release			
	$M_{0,1}$ ( $\mu\text{g}$ )	$\alpha_1^a$ ( $\mu\text{g t}^{-1/2}$ )	$R^2$ <sup>b</sup>	$D_1^c$ ( $10^{-12} \text{ m}^2 \text{ s}^{-1}$ )	$M_{0,2}$ ( $\mu\text{g}$ )	$\alpha_2$ ( $\mu\text{g t}^{-1/2}$ )	$R^2$	$D_2$ ( $10^{-14} \text{ m}^2 \text{ s}^{-1}$ )
CFC-11	155	28.8	0.997	21	2540	13.8	0.998	1.8
HFC-134a	58	15.3	0.997	42	2125	11.0	0.999	1.6
HCFC-141b	293	37.3	0.999	9.8	2580	17.2	0.999	2.7
HFC-245fa	565	70.3	0.999	9.3	2308	12.4	0.985	1.8

<sup>a</sup> Slope of best fitting line to  $M_t$  versus  $t^{1/2}$ . <sup>b</sup> Correlation coefficient for the line fit. <sup>c</sup> Calculated diffusion coefficient from eq 1. <sup>d</sup> All experiments used cylinders with  $d = 1 \text{ cm}$  and  $h = 1 \text{ cm}$ .

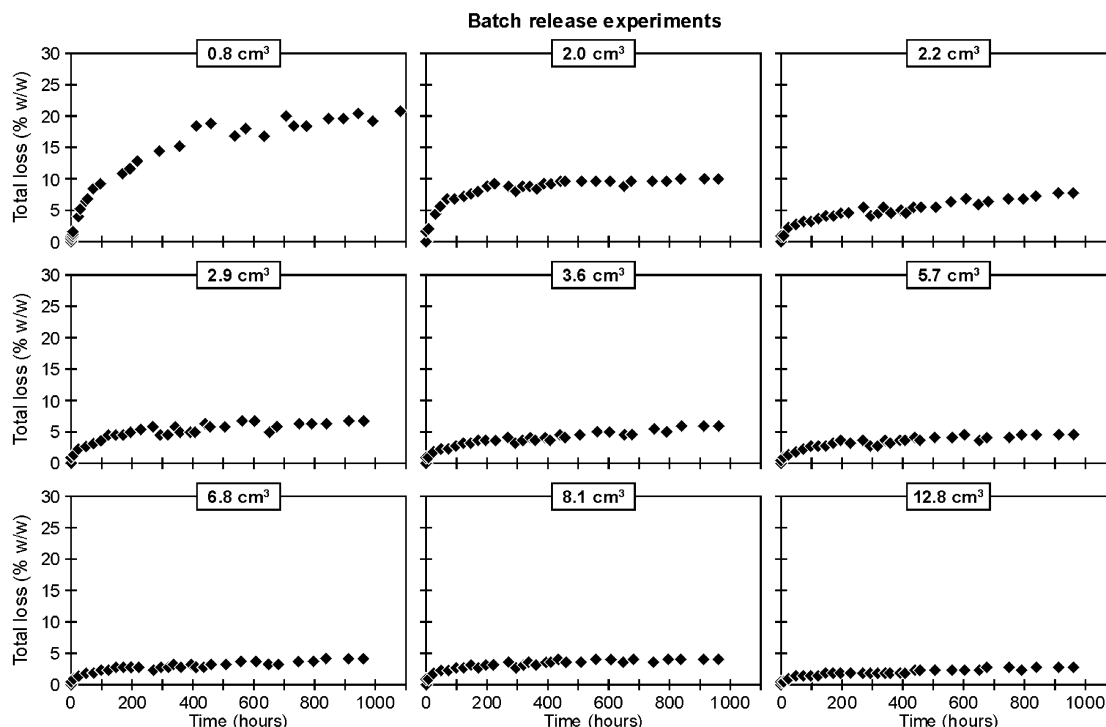


FIGURE 5. The time dependency of the total loss of HCFC-141b in percentage of initial content from foam particles with different sizes determined in batch experiments.

TABLE 6. Fractional Distribution of the Instantaneous, Short-Term and Long-Term Releases as a Function of Foam Particle Size

release type	particle size category (mm)				
	<4	4–8	8–16	16–32	>32
instantaneous release (% w/w)	40	34	18	10	5
short-term release (% w/w)	60	40	10	4	2
long-term release (% w/w)	0	26	72	86	93

The loss appears to increase significantly when the particle is smaller than  $2.2 \text{ cm}^3$ . These results indicate that not only the instantaneous release but also the short-term release is highly dependent on particle size.

Overall, the release experiments revealed that the BA release process from shredded foam conceptually can be divided into the three phases described previously: an instantaneous release (typical time frame in minutes), a short-term release (typical time frames in 250–500 h for larger foam particles), and a long-term release. The release in the last phase is governed by closed cell diffusion. Based on the experiments performed, the average fractional distribution of the instantaneous, short-term, and long-term releases as a function of foam particle size is given in Table 6. The very significant particle size dependency of all three types of

releases clearly demonstrates that the shredding conditions govern the magnitude and time frame of the BA releases from PUR foam waste.

**Estimating the Future Releases of Halocarbons from Decommissioning Used Refrigerator/Freezers in the United States.** Based on the laboratory experiments presented in the previous chapters the future releases of halocarbons from decommissioning used refrigerator/freezers (R/Fs) in the United States are estimated. The evaluation is carried out for R/Fs produced in the period 1985–2010. The estimation is based on (a) numbers of R/Fs produced in the United States from 1985 until now as given by The Association of Home Appliance Manufacturers (14), (b) an estimated 3% growth in U.S. production of R/Fs from 2003 until 2010 (14), (c) an estimate of the types of the BA used as a function of year as given in Table 7 (14), (d) a fixed lifetime of a unit of 15 years (14), (e) a foam volume per unit of  $10 \text{ ft}^3$  (283 L) (14), (f) foam densities and BA weight fraction in foam as measured in foam board used in this research (confer Table 7), and (g) release patterns (instantaneous and short- and long-term releases) from foam after decommissioning, i.e., the fraction of the BA for one unit released for each year following the decommissioning.

The experimental results have shown that the release patterns of the blowing agent from the foam to a high degree depend on how the home appliances are being decommis-

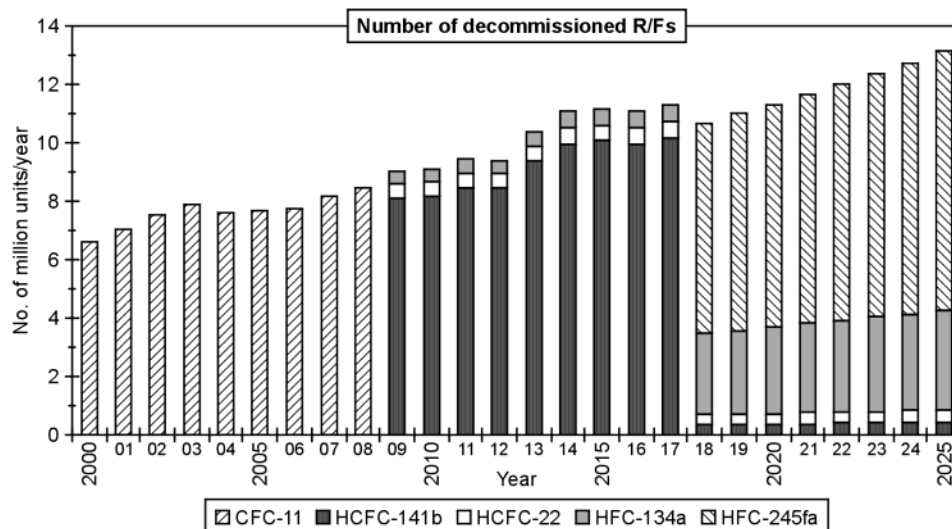


FIGURE 6. Estimated number of yearly decommissioned domestic refrigerator/freezer unit (in millions) in the United States for the period 2000–2025. The expected type of the blowing agent is given as shown in the legend.

TABLE 7. Foam Density and BA Content Used in the Model<sup>c</sup>

	CFC-11	HCFC-141b	HFC-134a	HCFC-22	HFC-245fa
foam density (g/L)	25	32	39	25	31
BA content (% w/w) <sup>a</sup>	15.3	13.3	8.1	15.0	13.3
BA content (g/unit) <sup>b</sup>	1083	1209	889	1062	1171
BA Used (%)					
1985–1993	100	0	0	0	0
1994–2002	0	90	5	5	0
2003–2010	0	3	24	62	8

<sup>a</sup> 15% added to measured total content to account for instantaneous loss, which is not accounted for with the used method. <sup>b</sup> Using the foam content of 283 L/unit and the determined foam densities. <sup>c</sup> The values are based on the determined values.

TABLE 8. Foam Particle Size Distribution Used in the Three Shredding Scenarios Used in Estimation of the BA Release Decommissioned Refrigerator/Freezers in the United States

shredding scenario/ size distr	particle size category (mm)				
	<4	4–8	8–16	16–32	>32
A	14.5	15	48.1	22.4	0
B	5	15	15	45	20
C	2	3	5	15	75

sioned. If the foam is shredded into very fine particles the release is fast, and nearly all the blowing agent is released within a short period. On the other hand, the release may be slow if the foam is cut into larger pieces. Table 6 gives an estimate of the fractional distribution of the instantaneous, short-term, and long-term releases as a function of foam particle size. To evaluate the significance on the shredding process, three scenarios are selected: (1) shredding scenario A: foam is shredded as in the Danish recycling facility (Danish Recycling Center), (2) shredding scenario B: foam is shredded to a more coarse particle distribution, and (3) shredding scenario C: foam is cut into larger pieces with dimensions close to typical foam thicknesses in R/F units. Table 8 gives the assumed foam particle size distributions for the three scenarios.

The instantaneous and short-term releases are allocated to the year where the unit is decommissioned. For the long-term release the particles are assumed cylindrical. For instance for particles in the 8–16 mm range, the particles are assumed cylindrical with a radius of 12 mm and a height of 12 mm. For the largest fraction a diameter/height of 40

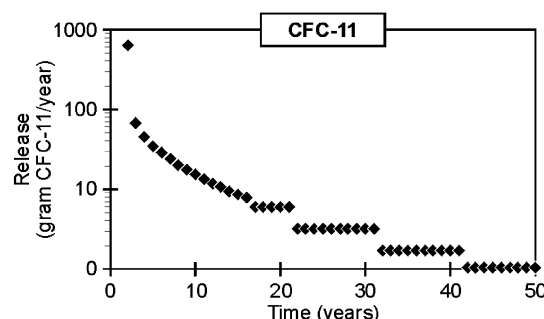
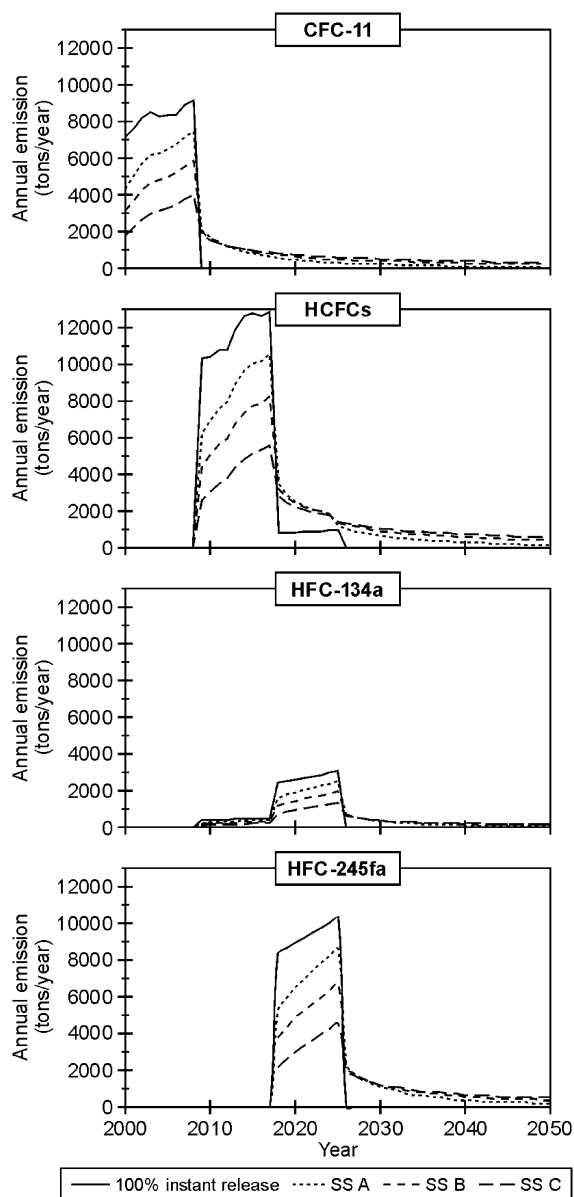


FIGURE 7. The estimated yearly release of CFC-11 from one unit as a function of year after decommissioning assuming that the unit is shredded according to shredding scenario A.

mm is assumed, since most foam particles originating from a R/F will have a maximal dimension of approximately 48 mm. For the smallest fraction it is assumed that the long-term release is insignificant.

The release-time dependency (grams BA released per year per unit) is calculated by use of the model also used for constructing Figure 4. After calculating the fraction of the initial mass released ( $M_t/M_0$ ) for each year, the release for one single year is calculated by subtracting  $M_t/M_0$  calculated for 2 succeeding years, multiplying by the mass of the blowing agent in the particle range category in question, and finally summing up all five particle size categories. For simplification the long-term diffusion coefficient is set to  $2.0 \cdot 10^{-14} \text{ m}^2/\text{s}$  for all five BAs (which is an average value determined for the four blowing agents), since the flux chamber experiments only found minor differences in diffusion coefficients among BAs (confer Table 5). The dependency is calculated for a 50-year time period after decommissioning. Figure 7 is an example of the calculated release-time dependency for a unit blown with CFC-11 under scenario A. Due to the rather extensive calculations the releases are interpolated after the first 15 years for periods of 10 years. This simplification has no significant effect on the final calculated releases. For scenario A almost the entire BA is released over the 50-year period (i.e., 98%). However, for the scenarios B and C, the release over the 50-year period is 89% and 74%, respectively. From data as presented in Figure 7 the total yearly release for a specific BA is calculated by adding up contributions from units decommissioned the specific year and from the previous years' decommissioned units.





**FIGURE 8.** Results of the emission model for the three shredding scenarios regarding the blowing agents CFC-11, HCFCs (HCFC-141b and HCFC-22 are pooled together), HFC-134a, and HFC-245fa. The annual emission in tons/year is given as a function of year for the period 2000–2050 for units decommissioned in the period 1985–2010. For comparison a curve is shown assuming that the total BA content of a unit is released instantaneously at decommissioning.

The result of the modeling is presented in Figure 8. The BA emissions are given in tons BA/year. *It should be emphasized that the emissions are only related to decommissioning of the R/Fs produced in the period 1985–2010.* For comparison, a curve assuming that all the BA is instantaneously released the year of decommissioning is given in the figure as well. The figure shows that the magnitude of the peak emission is very much dependent on how the shredding is carried out. For scenarios B and C a small but significant fraction of the release will take place after the 50-year period. The curve assuming instantaneous release gives obviously the highest peak.

The model assumes that the long-term releases from the foam waste after disposal at landfills are still governed by closed cell diffusion behavior with a concentration inde-

pendent diffusion coefficient. Future studies should look into the importance of using more advanced modeling using concentration dependent diffusion processes.

Due to mechanical forces within the landfilled waste, the foam structure may be further damaged leading to faster releases. The model also assumes that all the BA released from the foam particles is readily emitted and does not take into account any attenuation of the BA in the landfill or the soil covers surrounding the landfill, which may lead to reduced emissions. There is evidence that such an attenuation may take place (15, 16).

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## Supporting Information Available

Microscope picture of the edge of a foam piece cut out of the panel blown with CFC-11 (Figure 1), measured and simulated (using the double compartment model) mass release in flux chamber with foam blown with HFC-245fa (Figure 2), and measured and simulated (using the double compartment model) fluxes in flux chamber with foam blown with HFC-245fa (Figure 3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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