Emission of Hexabromocyclododecane from Polystyrene Foams into Gas Phase – Modeling versus Experiment

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1. Introduction

Hexabromocyclododecane (HBCD) is a widely used flame retardant for polystyrene foams and textile back coating. HBCD is part of the EU Existing Chemicals Programme (Sweden as rapporteur country) for EU Risk Assessment. Additionally emissions into the environment are currently under discussion by Canadian and Japanese Environmental Protection Agencies.

While emissions during production and manufacturing can be measured by monitoring at the corresponding sites, there is some uncertainty about the emission during service life. The Technical Guidance Document (TGD) of ECB states a procedure derived from plasticized PVC-films, which would result in unrealistically high emission estimations. In addition, there are difficulties to directly measure emissions into the gas phase due to the very low vapor pressure of brominated flame retardants such as HBCD.

Recently a method for predicting emissions, based on diffusion modeling has been established by FABES [1], and has been proven to work for the assessment of migration of polymer additives into water and other solvents as well as for the evaluation of air emissions of volatile impurities.

For the present work, an experimental set-up has been developed to determine emissions into the gas phase and to compare the results with models including the approach used by the TGD.

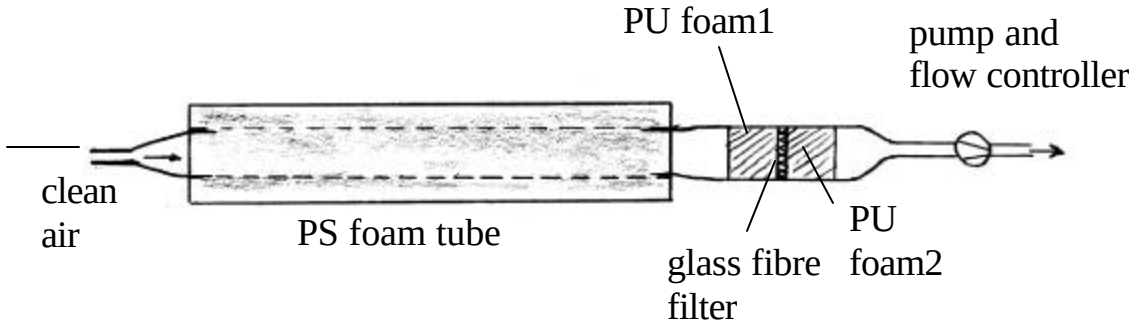
2. Materials and Methods

The materials used were commercial XPS-boards (extruded polystyrene foam) with a thickness of 6 cm. The HBCD concentration was 1.1% and 2.0 %. The XPS used had a density of 45 g/l.

The boards were cut with a hot wire to achieve a tube with the following dimensions: length: 1.2 m, internal diameter 4 cm, inner surface 0.15 m^2.

A flow of c. 15 l/h of purified air (Gas Chromatography quality) was passed through the XPS tube using a vacuum pump. At the end of the XPS tube an adsorption unit was installed consisting of two pieces of polyurethane foam (PU foams cleaned by extraction before use), which were separated by a glass fibre filter (See Fig 1). The dimensions of the cylindrical PU foams were: length 5 cm, diameter 4 cm each. The adsorption unit was separated in two compartments, the first was PU foam 1 and the second was the combination of the glass fibre filter and the PU foam 2. The extraction was carried out with dichloromethane for 4 hours in a Soxhlet extractor. The extract was concentrated by distillation, and finally transferred to acetonitrile. No further clean up of the extract was done. The final determination was done by LC-MS with a detection limit of 5 ng HBCD.

Fig. 1: Schematic set up of HBCD emission measurement



3. Results

Spiking with 79 ng HBCD was used to verify the validity of the test method. The HBCD-peak appeared at 0.92 min with a recovery of ~ 85%. The sampling was done at 5, 10, 15, and 30 days. Only at the first sampling time after 5 days HBCD could be detected above the detection limit of 5 ng.

The maximum amount found after 5 days was about 10 ng HBCD. Taking into account the surface of the tube the emission can be calculated to be 70 ng/m² per 5 days, corresponding to 5µg/m² per year.

In order to compare the experiment with theoretical estimations diffusion models were applied. This model is based on the diffusion laws taking into account the mobility of molecules within polymer matrices using polymer depending parameters. For polystyrene these parameters have been well established and the diffusion model could be successfully applied to calculate the emission of styrene from polystyrene into gas phase[2]. Furthermore, the diffusion model has been well established for the use in food contact migration and has been approved by authorities[3].

The major results of the diffusion modeling are that the emission rate is decreasing significantly with time, linearly increases with increasing concentration and almost exponentially increases with increasing temperature. The modeling predicts an emission of ~ 400 µg/m² per year by assuming that all HBCD which reaches the surface will be vaporized immediately, thus ending up in the gas phase. However, when taking into account the very low vapor pressure of HBCD ($6*10^{-5}$ Pa)[4] the value predicted is significantly reduced to 17µg/m² per year, which is much closer to the experimentally derived value. In summary diffusion modeling predicts values far above experimentally determined data and thus can be seen as a worst-case estimate. However, when taking into account saturation effects and considering the low vapor pressure the values predicted by the model are in the same order of magnitude compared to experimentally determined data.

4. Discussion

HBCD emissions into the gas phase could be detected by a sampling method comparable to the set-up used for dioxin analyses. The detection limit was around 5 ng. However, only in one experiment after 5 days a detectable amount was found. Using this value one can calculate the theoretical total emissions of HBCD into the gas phase from the use of polystyrene foams. For this calculation the consumption data of EPS (expanded polystyrene

foam) and XPS in Europe as collected from the respective associations (APME/EXIBA) were used with an average thickness of 6 cm and 8 cm, for the EPS and XPS boards, respectively. The corresponding emissions can be calculated to be below 2kg/a for the total EU. This value is about a factor of 30000 lower than the number calculated using the TGD procedure.

Modeling of emission is a valuable alternative to experimental measurements. However, the results from modeling must be regarded as worst-case estimates.

At least modeling provides much more realistic values than compared to the approach based on the TGD using the default factors[5].

This can be explained by the experimental basis from which the TGD-factors were derived. The TGD-factors were derived from experiments with highly plasticized PVC containing plasticizer in concentrations up to 50%. In these experiments it was found that the emission could be described using the vapor pressure of the plasticizer. While this might be justified for additives present at high concentrations, for low concentrations interactions with the polymer matrix have to be expected. This leads to a reduction of the vapor pressure above the polymer matrix in which the additive is dissolved. As this reduced vapor pressure is unknown in most cases it is very difficult to apply the approach as outlined in the TGD.

In addition the TGD is only applicable for thin films such as for plasticized PVC. For the emission from thicker materials such as PS foam boards diffusion has to be taken into account because the additive must move from inner parts of the material to the surface. This is very critical in those cases where the polymer has a very low diffusion parameter like polystyrene. The model shows that only the outer layer of the board with a thickness of approximately 1 µm is contributing to HBCD emissions to the surrounding atmosphere. Generally, any additive below that surface layer cannot be emitted because its restricted mobility. In the case of polystyrene foam boards with a thickness of 6 cm atmospheric emissions of HBCD have to be reduced by a factor of 30000, what could be verified by the presented experimental data.

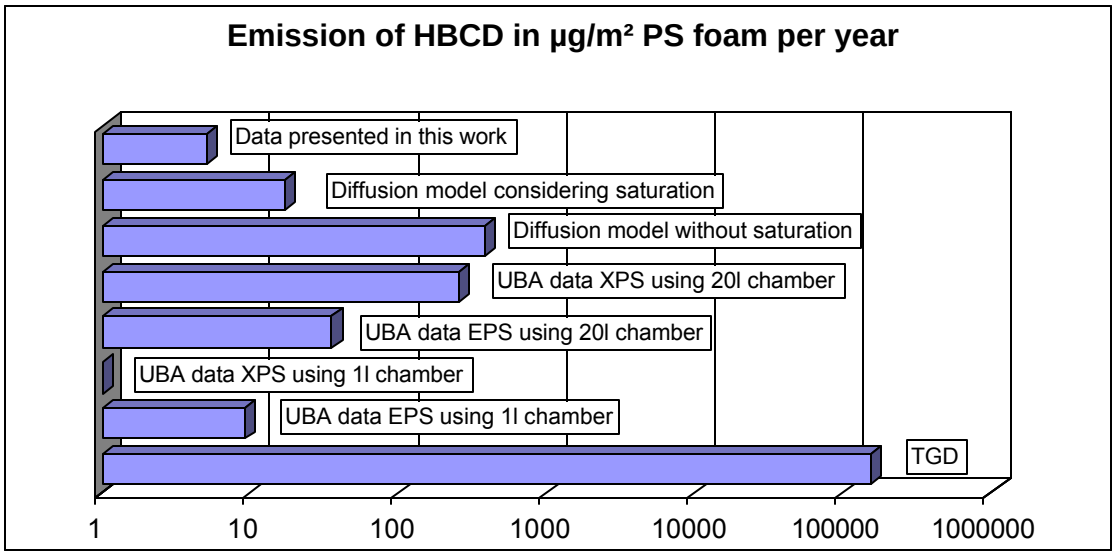
Additionally, because the TGD procedure is based on thermodynamically controlled processes, it does not take into account the decrease of the emission rate with time due to the kinetic (diffusion) control of emissions. Therefore diffusion based modeling gives a much better tool to estimate emissions during service life. Finally, as the model is independent of the chemical nature of the additive this tool can be used for the estimation of emission of other flame retardants where needed.

Recently the German Umweltbundesamt carried out an investigation of emission of HBCD into the gas phase from XPS and EPS with two different experimental set-ups using 1l and 20l chambers[6] giving similar results. The conclusion from the UBA was consistent with our results stating that emission of HBCD from polystyrene foams is negligible. The emission was in almost all cases below the detection limit and only traces of HBCD were found on the surface of the test chambers. Taking into account these trace amounts from the chamber walls the emission rate was calculated to be between 0.1ng/(m²h) and 29ng/(m²h) giving values between 12ng/m² - 3.5µg/m² per 5 days.

In figure 2 various values of HBCD emissions from PS foams in µg/m² per year are summarized. The data presented in this work are compared to values derived from diffusion

modeling and from the UBA measurements. In summary the emission calculated by applying the TGD procedure is much higher than all other values. The result derived from diffusion modeling without taking into account any saturation effects are comparable to the data found by UBA for XPS using the 20l chamber. The data presented here are comparable to the values found by UBA in the 1l chamber as well to the emission predicted by using diffusion modeling under consideration of saturation effects.

Fig. 2



5. Conclusion

The air emission of HBCD from polystyrene foam has been measured and compared to both modeling calculations based on diffusion and a procedure following the EU TGD. It could be clearly shown that the TGD procedure is not applicable for the estimation of air emissions. This finding could be explained using validated computer modeling. The diffusion based computer model however has proven to be a reasonable tool to estimate worst-case emission providing much more realistic values than the TGD procedure.

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[1] Migratest Lite 2001, Otto Piringer et.al, FABES GmbH Munich, Germany

[2] "Migrations from Styrenic Polymers", Martin Klatt, BASF Aktiengesellschaft, Proceedings of teh 19th International Plastics and Polymers in Contact with Foodstuffs Conference, Edinburgh, Scotland, 2002

[3] EU Directive 2002/72/EEC, Whereas No (14)

[4] JI Stenzel and WB Nixon, He xabromocyclododecane (HBCD): Determination of the vapor pressure using a spinning rotor gauge, 1997, 439C-117, pp44. Wildlife international LTD., Easton, Maryland

[5] Emission scenario documents for several use categories as included in Appendix 3 to Chapter 11 of the Technical Guidance Document for the Risk Assessment of notified New Substances (EC, 1993)

[6] "Emissionen von Flammschutzmitteln aus Bauprodukten und Konsumgütern", Sabine Kemmlein et al., UBA report Förderkennzeichen 299 65 321, 2003