EMISSION OF PHTHALATES FROM PVC FLOORING IN TWO VERY DIFFERENT TEST CHAMBERS

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ABSTRACT

PVC flooring containing ca. 17% (w/w) di-(2-ethylhexyl)phthalate (DEHP) as plasticizer has been emission tested in two FLECs (Field and Laboratory Emission Cell) and one CLIMPAQ (Chamber for Laboratory Investigations of Materials, Pollution and Air Quality) over a 300 days period. In spite of large differences in test conditions, the measured DEHP concentrations in all the chambers were comparable (~ 1µg/m^3). However, the corresponding specific emission rates were 5-10 times higher in the FLECs. Furthermore, the time required to reach an expected constant concentration was unexpectedly long (~ 150 days) in all the chambers. There appears not to be problems with the sampling, the analysis or the background. Backpressure effect may explain the differences in the specific emission rates and sink effects may explain the long equilibration time.

INDEX TERMS

PVC, Phthalate esters, Emission, Chamber test, Sink effect

INTRODUCTION

The prevalence of allergic airway diseases is rapidly increasing in Western Europe and North America. This increase may be associated with phthalates esters that are suspected to possess adjuvant effects that enhance the health damaging potential of common allergens. An epidemiological study has shown that the area of polyvinyl chloride (PVC) in homes was associated with development of bronchial obstruction in children (Jaakkola et al, 1999). It has been proposed that deposition of di(2-ethylhexyl)phthalate (DEHP) in the lungs increases the risk of inducing inflammation which is characteristic of asthma (Øie et al, 1997). DEHP is expected to be metabolized to mono(2-ethylhexyl)phthalate that has shown to posses adjuvant effect with simultaneous injection of the allergenic ovalbumin in mice (Larsen et al, 2001). Phthalate esters are used as plasticizers in PVC and are slowly emitted as vapors. They are common pollutants in indoor air (Sheldon et al, 1993; Clausen et al, 1999) and surface dust (Øie et al, 1997; Pöhner et al, 1997). The existence of phthalate esters in indoor air may be due to resuspension of sedimented dust (Øie et al, 1997) and/or emission from phthalate containing building products, furniture and office equipment. Due to difficult analytical procedures, only a few studies have been carried out regarding emission behavior of especially high boiling plasticizers. We are aware of only one study on emission of DEHP published in a peer reviewed journal (Uhde et al, 2001). The aim of this study was to compare emission of DEHP from one type of PVC flooring in two widely used and very different climate chambers.

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METHODS

Test piece

PVC flooring (Tarkett) that contains ca. 17% (w/w) DEHP as plasticizer.

Chambers and test conditions

Two different types of chambers were used, the CLIMPAQ (Chamber for Laboratory Investigations of Materials, Pollution and Air Quality) (Gunnarsen et al, 1993) and the FLEC (Field and Laboratory Emission Cell) (Wolkoff et al, 1991), respectively. The test was conducted in duplicate in the FLEC (two FLECs on two separate test pieces) and in one CLIMPAQ. An additional empty CLIMPAQ was blank chamber. The tests have been conducted for 11 month. Test conditions are shown in Table 1.

The CLIMPAQ is made of panes of window glass assembled with low emitting two-component epoxy glue. Other main surface materials are stainless steel and eloxated aluminum. The ventilation rate and air speed may be varied independently around typical indoor values. One internal fan recirculates the air over the test piece.

The FLEC is a micro emission cell made of stainless steel that is positioned upon the test piece. The test piece and the inner surface of the FLEC form a cone-shaped cavity. Planar materials are sealed to the FLEC by means of an O-ring. The supplied air flows from a circular slit at the periphery of the cell over the material surface and into the center, where it exits the FLEC outlet. Thus the air velocity over the surface depends on the chamber airflow (Wolkoff, 1996).

Before testing the chambers were cleaned and background measurements were performed. For the background measurements the FLEC is placed on a cleaned glass plate. The temperature, the humidity, and the flow through the FLEC was checked before and after each sampling.

Table 1. Test conditions

Parameter	CLIMPAQ	FLEC
Temperature (°C)	ca. 22	20.1 – 23.6
Relative humidity (%RH)	ca. 50	47.9 – 52.0
Chamber volume (l)	51	0.035
Chamber air flow (l/min)	8.3 – 9.4	0.444 – 0.465
Air exchange rate (N) h^{-1}	9.8 - 11	760 – 796
Air velocity at test piece surface (m/s)	0.14 – 0.16	0.016*
Area of test piece (m^2)	1.6	0.018
Chamber loading (L) (m^2/m^3)	31	510
L/N	2.8 - 3.2	0.64 – 0.67

* Estimate based on geometry.

Sink effect and vapor pressure experiments

FLEC: A clean (empty) FLEC with a hand polished stainless steel plate as the bottom part (instead of a test piece) was connected to the outlet of each of the test FLECs that was still positioned upon the PVC flooring. For DEHP analysis air was sampled from the outlet of the empty FLECs. Several air samples were collected over a 50 days period.

CLIMPAQ: The PVC test piece was removed after the last measurement and the CLIMPAQ was closed immediately again. For DEHP analysis air was sampled three times from the outlet of this CLIMPAQ over a 25 days period.

An open beaker containing ca. 50 ml of pure DEHP was placed in an empty clean CLIMPAQ under the conditions shown in Table 1. The vial was heated to ca. 150°C for two hours in order to saturate the CLIMPAQ (including all sinks) with DEHP vapor. After the beaker was cooled air was sampled three times from the outlet of this CLIMPAQ over a 25 days period.

Sampling of DEHP in the effluent air from the chambers
A filter/adsorbent sampling device was previously developed for indoor air sampling of semivolatile organic compounds (Clausen and Wolkoff, 1997). However, in this case the chamber air was assumed to contain an insignificant amount of particles. Therefore DEHP was sampled directly on Tenax TA tubes with a pump (Alpha-1, Ametek) calibrated to a nominal flow of 200 ml/min. The sampling time was 24 h ~ volume of 288 l. All samples were in duplicate. In pilot emission tests conducted over a two-month period 11 sample tubes were connected to backup tubes to check for breakthrough. The sampling volumes were between 130 l and 440 l.

TD-GC-MS/FID analysis of the air samples
A thermal desorber (TD) (Perkin Elmer ATD 400) was connected to a gas chromatograph (GC) with mass spectrometric (MS) detector (Perkin Elmer Autosystem XL / TurboMass) or flame ionization detector (FID). The Tenax TA tubes were desorbed for 20 min at 300°C, a He flow of 50 ml/min and a cold trap temperature of –30°C. The cold trap was narrow bore (Low Flow Trap Tube) packed with a small piece of silylated glass wool. Flash heating of the cold trap to 350°C transferred the analytes through the valves at 250°C and the transfer line at 225°C to the GC. The GC-MS/FID had a pressure controlled He (carrier gas) flow of ca. 1 ml/min and was equipped with 60-m x 0.25 mm-i.d. Chrompack CP Sil 8 CB Low Bleed/MS (0.25 µm film thickness) column. Temperature programming was 120°C, held for 2 min, increased to 300°C at 15°C/min, held for 8 min and finally increased to 320°C at 20°C/min and held for 4 min. The MS transfer line and the FID temperature was 275°C. The mass spectrometer was operated in the electron impact ionization mode (EI+, 70 eV) with a source temperature of 175°C using full scan mode (m/z 30 – 400). No internal standard was used and ion m/z 149 was used for quantification.

All tubes were analyzed by two successive desorptions to test for complete desorption of both the tube and the TD system. Randomly selected clean tubes were used to estimate the background in the sampling and analytical system. Calibration curves (six points) were made for each analysis series.

Data treatment
The Microsoft® Excel spreadsheet has been used for all plots and calculations from the raw GC peak area counts to the concentrations and specific emission rates (SER) (calculated for each data point assuming a constant source). The GC-MS gave unreliable results in a period (from day 72 to day 142) and five data points were rejected. At day 259 the FLEC temperature was 2°C below the mean temperature and one data point was rejected.

RESULTS

The concentration versus time data for all the chambers (incl. the blank CLIMPAQ) are shown in Figure 1 and the corresponding SERs are shown in Figure 2. Concentrations at

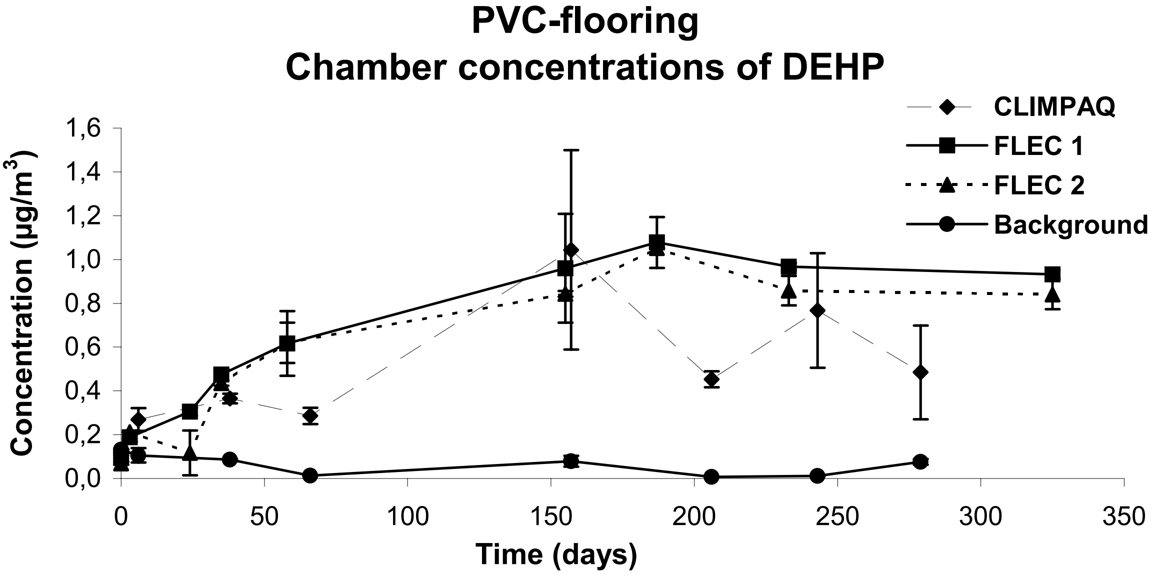

Figure 1. Concentration (± 1 standard deviation) versus time data for emission of DEHP from PVC flooring in two FLECs and one CLIMPAQ and additional background concentration for an empty CLIMPAQ.

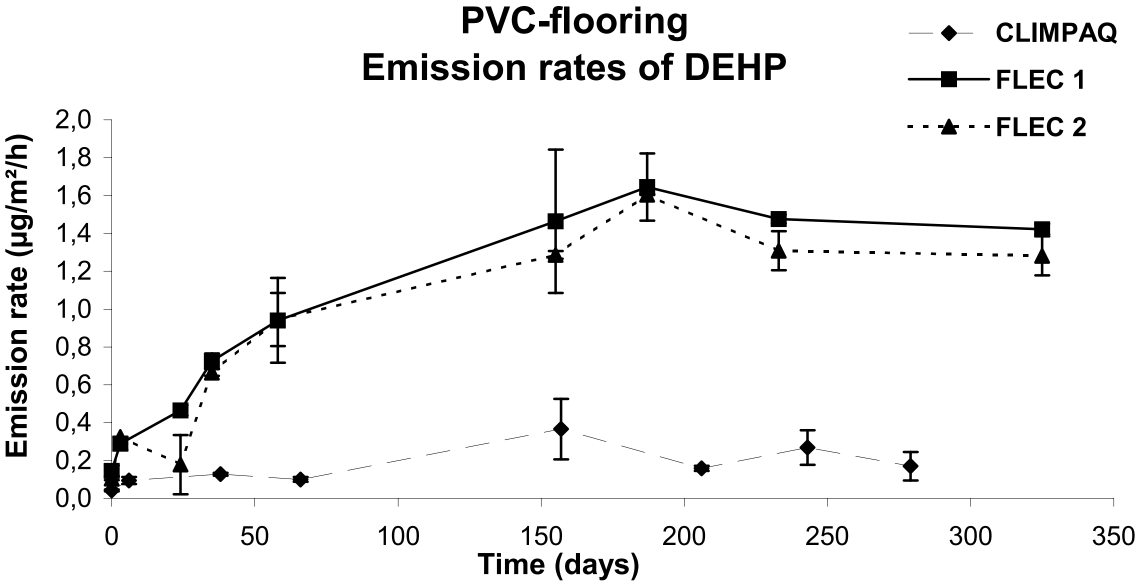

Figure 2. Specific emission rates (SERs) (± 1 standard deviation) versus time calculated for each measured concentration of DEHP from PVC flooring in two FLECs and one CLIMPAQ.

time = 0 are the chamber background. No model was used to evaluate the emission.

Clean tube background concentrations were all below the detection limit that was estimated to be 0.01 µg/tube or 0.03 µg/m^3 (based on 3 times the standard deviation of 13 runs of low standards). Complete desorption of the tubes and the TD system was confirmed by the second desorption of the tubes that in all cases showed concentrations below the detection limit. Furthermore, there appeared not to be interference from other m/z 149 ions. No calibration curves had intercepts significantly different from zero and r^2 was between 0.99 and 0.999. The pilot experiments showed that the SER was as low as 1 µg/m^2/h. Therefore the large sampling volume was chosen. In spite of that phthalate ester concentrations on the backup tubes were below the detection limit. The background measurements in the chambers (time = 0) and the highest concentration of the blank CLIMPAQ were ca. 10 times lower than the corresponding highest measured chamber concentrations. The test chamber conditions were relatively constant over the entire period of time (Table 1).

DEHP in the outlet air of the empty FLECs was below the detection limit within the first month of the sink experiment. After 50 days the DEHP concentration was 0.2 µg/m^3. The concentration of DEHP in the outlet air of the CLIMPAQ from which the PVC was removed was 0.6 µg/m^3 and constant over the study period (25 days).

The three measurements of the dynamic equilibrium concentration of DEHP in the empty CLIMPAQ were 30 µg/m^3, 3.7µg/m^3, 3.4 µg/m^3 within the first day, at 21 days, and 25 days, respectively.

DISCUSSION

The sampling, analyses and background appeared to be satisfactorily. The curves in Figures 1 and 2 show a slow increase of the chamber concentrations over time. There is a tendency to stabilization of the levels after 150 days in all chambers. There appears to be a good agreement between the two FLECs and comparable concentration levels in the FLECs and the CLIMPAQ. Even though the observed SERs are 5-10 times higher in the FLECs.

The first question is why the observed SERs are different in the two types of chambers. One reason could be influence of the actual test conditions on the emission. However, this should only be expected by emissions controlled by diffusion in the boundary layer. If this is assumed to be the case the emission should be driven by the concentration difference between the PVC surface and the air and depend on the thickness of the boundary layer. Since the air concentrations in all the chambers are close to each other and the emitted amount of DEHP is small compared to the content of the PVC (few mg compared to several grams) the concentration difference must be approximately the same in all the chambers. However, a high air velocity over the material surface should increase the SER because the thickness of the boundary layer decreases. This is not in agreement with the high surface air velocity in the CLIMPAQ (Table 1). However, it appears that the dynamic equilibrium concentration of pure DEHP in the CLIMPAQ was relatively close to the measured maximum concentrations. This indicates that back pressure effect may decrease the SER in the CLIMPAQ and explain the comparable concentrations in the two types of chambers. This could be confirmed by experiments with different chamber loading. However, L/N must be much smaller than shown in Table 1.

The second question is why it takes so long time to reach an equilibrium concentration. The sink experiments showed that DEHP has sink effects in both types of chambers. It was expected due to its low vapor pressure. It was also expected that the emission was so slow that the PVC could be considered as a constant source of DEHP. The idea was to follow the concentration over time until it had stabilized at a constant concentration. However, it was not expected to take several months! In total few mg DEHP was emitted in the chambers and this amount could easily be adsorbed to the walls. If sink effects cause the long equilibration time a chamber without sinks should be constructed. It could consist of a thin steel gasket with an air inlet and outlet placed between two PVC sheets.

Concentrations of DEHP in the indoor environment are usually lower than observed in this chamber study (1 μg/m^3) (Sheldon et al, 1993; Clausen et al, 1999). If the DEHP emission from PVC is controlled by backpressure effect, the SER in the indoor environment are probably higher than measured in this study.

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