VOC- AND SVOC-EMISSIONS FROM ADHESIVES, FLOOR COVERINGS AND COMPLETE FLOOR STRUCTURES

O Wilke*, O Jann and Brödner

Federal Institute for Materials Research and Testing, 12200 Berlin, Germany

ABSTRACT
VOC/SVOC-Emissions from materials for flooring installation (primer, screed, adhesive, floor covering) were measured by means of emission test chambers and cells over a time period of at least 28 days at 23°C, 50 % relative humidity and an area specific air flow rate of q = 1.25 m³/m²h. Single components were tested in comparison to three complete structures (same concrete, primer, screed, adhesive) with different types of floor covering (PVC, carpet, linoleum). Sorption into concrete/screed and different sealing by the flooring materials affected the emissions from the complete structures. The complete structures with linoleum and PVC showed the same emissions and emission rates as the flooring materials alone. Emissions from the carpet-covered structure resulted mainly from the lower layers. For two adhesives the formation of secondary emissions (aldehydes and organic acids) was observed starting after the standard testing time of 28 days.

INDEX TERMS
Test chambers, VOCs and SVOCs, Secondary emissions, Construction and renovation

INTRODUCTION
The emission of volatile organic compounds from materials and building products used indoors is an important parameter for the chemical impact on the indoor air quality. Especially materials used on large areas are of importance. One example are building products used for flooring installation. The flooring structure consists of different layers. Normally these are concrete, primer, screed, adhesive and floor covering. They are often applied onto the complete floor area (loading about 0,4 m²/m³) with about 100 g/m² (primer), 1000 g/m²mm (screed) and 300-600 g/m² (adhesive) making them an important possible source for VOC/SVOC-emissions, additionally to the flooring itself. A labeling system with different classification criteria for those flooring installation materials is the GEV-EMICODE® (Oppl, 1999). For this the components are tested separately on glass plates with 300 g/m².

Investigations on the emission behavior of low-emitting adhesives for flooring materials have been described before (Wilke, 2000) and were carried on in the present paper. This time the focus was put on the comparison between complete structures and single components to see possible differences in the emission spectrum. The test conditions were more realistic (complete structure) and gave the possibility to look out for reaction products (secondary emissions) resulting e.g. from the combination of the flooring installation materials. The single components were tested in parallel at the same time to get knowledge of their emitting substances.
Measurements of emissions from floor structures have already been reported under different aspects (Saarela, 2000; Sjöberg, 2000).

* Contact author email: Olaf.Wilke@bam.de

METHODS

Materials

The flooring materials were bought in carpet stores or were obtained from producers. Flooring installation material used for this study was procured from producers. 36 adhesives were investigated for screening with direct thermal desorption (Wilke, 2000) and 9 of these were investigated by chamber testing. All of these 9 had the EC1-label according to GEV. Concrete plates were self made with dimensions of 25 cm x 20 cm x 2 cm and conditioned at 23°C and 50 % relative humidity for 4 weeks before use.

Emission test chambers and cells

The investigations were performed in 0.02 m³ emission test chambers (glass exsiccators), FLEC and emission cells (V=1 l, with ventilator) made from the top of a reaction vessel. The 0.02 m³ chambers were constructed for SVOC and VOC measurements (Jann, 1999) and showed very good comparability (Jann, 1997) with 1 m³ chambers which also are in accordance with the European standard ENV 13419-1. The chambers and cells were operated at a temperature of 23°C ± 0.3°C and a relative humidity of 50 % ± 5 %. The area specific air flow rate was adjusted to q = 1.25 m³/m²h (this value results from an assumed loading of 0,4 m²/m³ and an air exchange of 0,5 h^{-1} in a real room, see ENV 13419, part 1, annex B). For the 0.02 m³ chambers this was obtained with a material surface A = 0.1 m² and an air flow °V = 0.125 m³/h. For the FLEC and for the other cells A = 0.0177 m² and °V = 0.0221 m³/h for testing of floorings and A = 0.0154 m² and °V = 0.0192 m³/h for testing of adhesives.

Analysis of chamber air samples

Sampling was done using glass tubes (length 178 mm, o.d. 6 mm, i.d. 4 mm) filled with Tenax TA (200 mg, 60-80 mesh) fixed with glass wool (deactivated) stoppers. Sampling volume was between 1 and 2 l with an airflow of 100 ml/min. Before sampling cyclodecane and toluene-d_8 in methanol (1 µl) were spiked onto the glass wool as internal standards. For calibration also 1 µl of standard substance mixtures in methanol were added and a volume of 1 l clean air from an empty emission test chamber was sucked through the tube.
The analysis was carried out by thermal desorption (Gerstel TDS-2) combined with gas chromatography (HP 5890 II plus) and a mass spectrometer (HP MSD5972). The conditions for the thermal desorption were: heating from 40°C to 280°C with 40°C/min, 280°C hold for 5 minutes, cryofocussing at -150°C (Gerstel CIS-3), Helium desorption flow 25 ml/min. After desorption the cooled injection system (CIS-3) was heated to 280°C with 12°C/s in splitless mode. For separation a 30 m analytical column from Restek (Rtx-200, film 1 µm, i.d. 0.25 mm) was used. The GC temperature program was: 40°C hold for 4 min, increase 5°C/min to 140°C, increase 10°C/min to 240°C, increase 25°C/min to 290°C hold for 3 min. The MSD was operated in scan modus (25-400 amu) with 1.9 scans/s at 300°C interface temperature.

RESULTS

1. Emission rates from single products

The area specific emission rates from different flooring materials are shown in tables 1 and 2. Substances are listed in the order of the emission rate on the 28th day of chamber testing. The results for emission rates and emission behavior (time dependence) of the tested materials differ very much even inside the different classes of materials. Adhesives had the fastest decrease of emission rates with time, PVC showed the slowest decrease. Carpets had the smallest emission rates after 28 days in average. PVC 5 is remarkable for the high emission rate of TXIB even after 28 days, showing the potential for a long term emission. SVOCs were

the main compounds after 28 days for adhesives 22 and 23, too. The complete emission results are published in the final report of the project (Wilke, 2002).

Table 1. Emission rates from flooring material (main substances)

Flooring material	main substances	area specific emission rate in µg/m²h			
		1st day	3rd day	10th day	28th day
PVC 1	ethylhexanol	55	-	20	13
	sum VOC/SVOC (n*=5)	139	-	34	21
PVC 2	ethylhexanoic acid	120	-	96	75
	N-methylpyrrolidon	55	-	43	31
	sum VOC/SVOC (n>18)	315	-	300	229
PVC 3	butyldiglycol	500	329	308	286
	butanone	830	861	570	208
	butoxyethanol	296	246	180	124
	sum VOC/SVOC (n>13)	2638	2103	1546	929
PVC 4	phenol	520	273	74	46
	butyldiglycol	266	125	37,5	25
	sum VOC/SVOC (n>11)	1728	911	328	205
PVC 5	TXIB (SVOC)	1564	1079	873	674
	alkylated benzenes (SVOC, n>5)	1014	820	563	361
	sum VOC/SVOC (n>30)	3598	2575	1949	1365
carpet 1	4-phenylcyclohexene	94	-	35	23
	sum VOC/SVOC (n=3)	246	-	55	30
carpet 2	propandiolderivates (n=3)	923	561	238	35
	alkylated benzenes (SVOC, n=5)	73	34	34	30
	4-phenylcyclohexene	136	104	54	15
	ethylene glycol	949	425	99	< 50 (l.d.)
	sum VOC/SVOC (n=10)	2139	1161	440	83
carpet 3	n-alkanes, iso-alkanes (n>70)	990	674	631	338
	sum VOC/SVOC (n>72)	1016	698	646	346
carpet 4	sum VOC/SVOC	10	-	-	< 1
carpet 5	sum VOC/SVOC	268	-	-	< 1
linoleum 1	acetic acid	495	-	98	56
	hexanal	68	-	26	28
	sum VOC/SVOC (n=14)	701	-	188	134
linoleum 2	acetic acid	365	288	94	131
	hexanoic acid	105	108	41	28
	sum VOC/SVOC (n=8)	1274	1259	331	185
polyolefin	N-methylpyrrolidon	296	-	116	83
	sum VOC/SVOC (n=1)	296	-	116	83
rubber	benzothiazol	261	-	133	86
	sum VOC/SVOC (n=10)	390	-	196	126

* n: number of substances >1.25 µg/m²h on the28th day of chamber testing
l.d.: limit of determination

Table 2. Emission rates from materials for flooring installation

materials for flooring installation	main substances	area specific emission rates in µg/m²h			
		1st day	3rd day	10th day	28th day
adhesive 6	acetone	0	0	0	76
	heptanal	0	0	0	25
	ethylhexanol	944	248	33	23
	nonenal	0	0	0	13
	acetic acid	2036	650	108	< 50 (l.d.)
	ethylene glycol	1645	536	< 50 (l.d.)	< 50 (l.d.)
	sum VOC/SVOC (n=6)	4849	1560	161	160
adhesive 12	dibutylglycol	3624	2304	383	2
	acetic acid	2543	1059	200	< 50 (l.d.)
	propylene glycol	1044	404	81	< 50 (l.d.)
	sum VOC/SVOC (n=3)	9409	4219	678	6
adhesive 22	unknown SVOCs (n>11)	201	218	241	216
	phenoxypropanol (SVOC)	653	288	200	68
	sum VOC/SVOC (n>12)	1125	564	470	301

Table 2. **continued** Emission rates from materials for flooring installation

materials for flooring installation	main substances	area specific emission rates in µg/m²h			
		1st day	3rd day	10th day	28th day
adhesive 23	unknown SVOCs (n>11)	80	59	71	66
	ethylhexanol	234	106	45	9
	acetic acid	769	518	< 50 (l.d.)	< 50 (l.d.)
	sum VOC/SVOC (n>12)	1373	799	170	75
adhesive 36	acetic acid	4076	-	1363	288
	acetone	0	-	170	111
	unkown SVOCs (n>11)	263	-	116	74
	ethylhexanol	969	-	94	18
	sum VOC/SVOC (n>21)	5913	-	1889	561
screed	methylpropanol	59	-	0	0
	sum VOC/SVOC	65	-	0	0
primer	propandiolderivates	5015	-	388	198
	dimethylphthalate (SVOC)	48	-	21	19
	sum VOC/SVOC (n=3)	5096	-	421	221

2. Secondary emissions from adhesives

For two of the tested adhesives secondary emission products were detected. In one case this was due to longer testing time. Acetone and some aldehydes were observed from adhesive 4 (Wilke, 2000) after 46 days for the first time. From the 56th day also n-alkane acids from formic to nonanoic acid were observed with increasing concentrations with heptanoic acid as the main compound.

As you can see from table 2 for adhesive 6 the aldehydes could already be detected within the 28 days of standard testing time. The emission of acids started later than 28 days, again. They were detected on the 48th day also with heptanoic acid having the highest emission rates. The secondary emissions were also found when covering the adhesive with a carpet. However, the emission of the organic acids started later in comparison to the test without the carpet.
Figure 1 shows the course over 130 days for some of the detected carbonyl compounds.

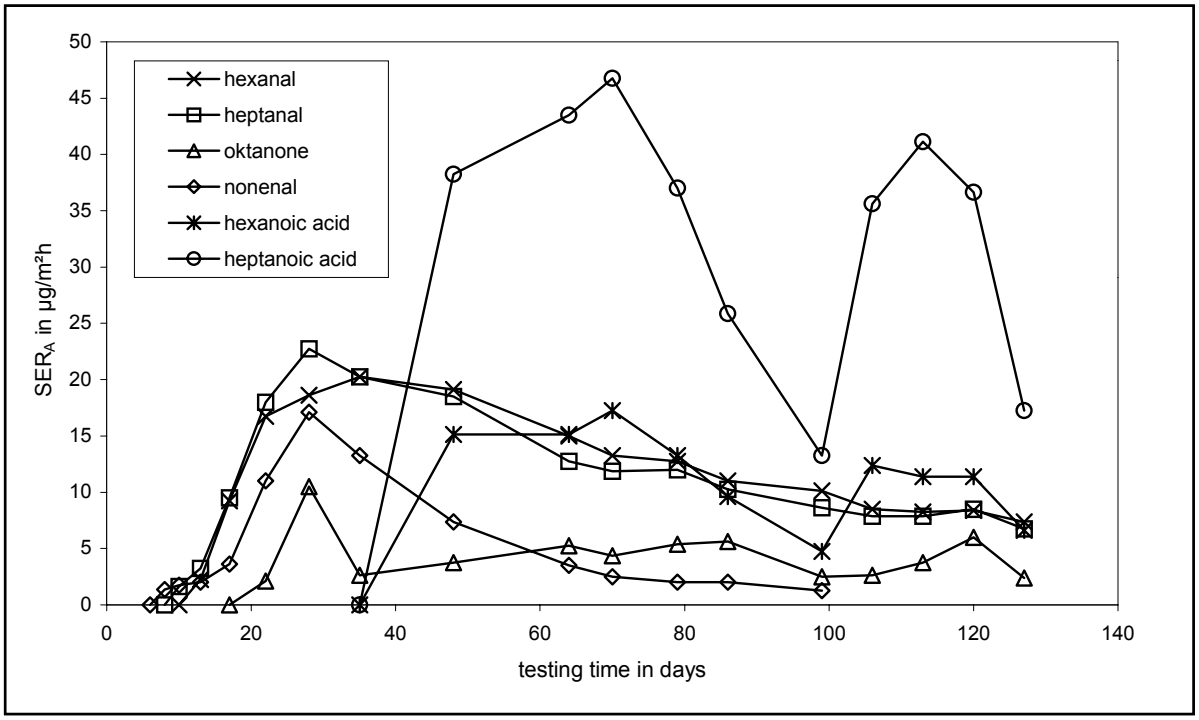

Figure 1. Secondary emissions from adhesive 6

3. Emission rates from complete structures

Three complete structures were made from three different types of flooring material (PVC 1, linoleum 1, carpet 1) in combination with the same adhesive (adhesive 36), screed, primer and concrete. Emission testing was done in parallel with the single components. All measurements were made by means of emission cells. Figure 2 shows the results for the carpet-covered structure where emissions from the lower layers could be detected. Mainly all compounds from the adhesive were observed. Dioxane and butanol had higher emission rates after 24 hours compared to the adhesive alone. Acetic acid was not found from the complete structure at all but was the main compound when testing the adhesive alone (on glass). This should be due to reaction with the alkaline screed. Phenoxypropanol and other not identified SVOCs which were observed from the adhesive could not be detected from the complete structure even not after 204 days of testing. This might indicate adsorption onto the carpet.
After 28 days the total emissions from the complete structure are less than total emissions from the structure without carpet and also less than from the primer and adhesive (figure 2). The complete structures with linoleum and PVC showed the same emissions and emission rates as the flooring materials alone.

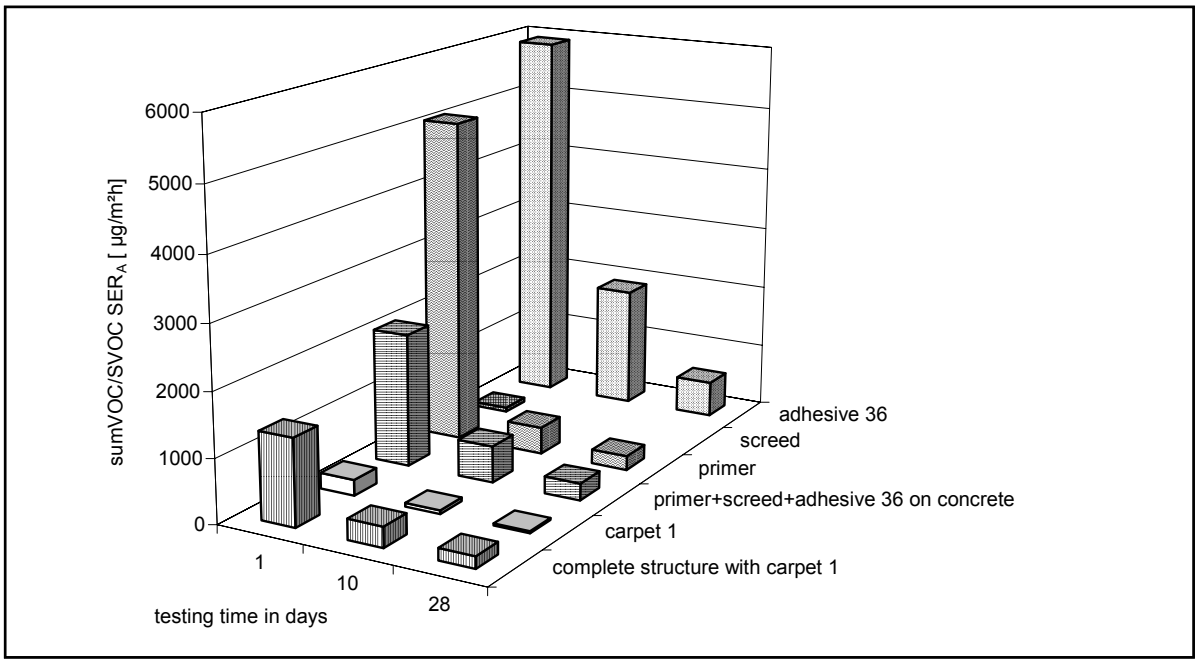

Figure 2. Comparison of sumVOC/SVOC of single components and complete structure with and without carpet

DISCUSSION

For the complete structures with linoleum and PVC no emissions from the lower layers were observed. This is in contrast to an experiment where adhesive 12 was covered with PVC 1 (thickness: 2 mm) on a glass plate. Dibutylglycol was detectable from the 21st day with 6 µg/m²h and increased to 15 µg/m²h after 104 days. N-methylpyrrolidon was also detected from the 62nd day with 3 µg/m²h. This experiment shows that depending on the type of compound (volatility, concentration, polarity, solvent character) and type of material migration through tight flooring materials is possible. However, in complete structures the concrete and screed have a strong sorption capacity which can be estimated from figure 2 by comparing the beams for adhesive, primer and adhesive+screed+primer+concrete.

Ongoing research indicates that some of the absorbed compounds are released after removing the PVC or linoleum with emission rates close to those after fresh application of the adhesive. In addition secondary emissions are released which were formed by reaction under the sealing floorings.

The secondary emissions which were found from the adhesive 6 (see figure 1) and also adhesive 4 (Wilke, 2000) gave reason to look out for possible sources. One was found to be tall oil or tall resin which are used as raw material for adhesives and contain linoleic acid and oleic acid. This would explain the occurrence of some of the detected aldehydes and also of the acids as further oxidation products. However, it is yet not clear why heptanoic acid had the highest emission rate of these secondary emissions. Emission rates for heptanal are the same than for hexanal from adhesive 6 and adhesive 4 showed even higher emission rates for hexanal than for heptanal. That should favorite hexanoic acid as oxidation product.

CONCLUSION AND IMPLICATIONS

It seems to be difficult or not applicable at all to use emission tests of single components for flooring installation as basis for the calculation of total emissions from the complete floor structure. Generally, the use of low-emitting components will give low-emitting complete structures. Another problem arises for the labeling of products because of delayed occurrence of secondary emissions which in this case might have a big influence for the sensoric perception of indoor air.

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