STUDY ABOUT THE CONTAMINATION OF PAH IN ROOMS WITH TAR PARQUETRY ADHESIVES

UNTERSUCHUNG VON PAK-BELASTUNGEN DURCH TEERHALTIGE PARKETTKLEBER IN INNENRÄUMEN

UNE ETUDE SUR LA CONTAMINATION EN HAP DUE AUX ADHESIFS POUR PARQUETS A BASE DE GOUDRON

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SUMMARY

In former times it was usual to use tar parquetry adhesives. Tar could be responsible for the contamination of the rooms with **p**olycyclic **a**romatic **h**ydrocarbons (PAH). In this study we investigated parquetry adhesives, dust, indoor air and outdoor air. The most important PAH compound is the benz(**a**)**p**yrene (BaP).

The indoor air was not significant contaminated with BaP. The values for the BaP in the parquetry adhesives were very high. But only in one case, it was possible to find a contamination of the dust. In this room the parquetry by itself was defect. In all the other rooms we could not find any contamination of the dust. The contamination of the rooms with BaP depends on conditions of the parquetry.

ZUSAMMENFASSUNG

Bis Ende der 70iger Jahre wurden teerhaltige Parkettkleber eingesetzt. Inwieweit von diesen Parkettklebern eine Belastung der Innenräume durch **p**olyzyklische **a**romatische **K**ohlenwasserstoffe (PAK) ausgeht, sollte in dieser Studie untersucht werden. Hierzu wurden die Gehalte an **B**enz(**a**)**p**yren (BaP), dem wichtigsten PAK, im Parkettkleber, im Boden- und Altstaub und in der Innenraum- und Außenluft bestimmt. Eine signifikante BaP -Belastung der Innenraumluft konnte in keinem Gebäude festgestellt werden.

Für die Parkettkleber wurden BaP-Werte bis zu 19000 mg/kg gemessen. Trotz dieser hohen Werte konnte nur in einem Fall eine Belastung des Boden- und Altstaubes ermittelt werden. Der Grund für diese Belastung liegt im Zustand des Parkettbodens, u.a. war die Versiegelung stark beschädigt. Bei intakten Parkettoberflächen konnten auch bei hohen BaP – Gehalten des Klebers keine Belastung der Innenräume gefunden werden. Der Zustand des Parkettbodens ist eine entscheidende Voraussetzung für eine Einschätzung der BaP – Belastung in Innenräumen.

RESUME

Les adhésifs pour parquets à base de goudron ont été utilisés jusqu'à la fin des années 70. L'influence de ces adhésifs sur la contamination de l'air d'intérieur en hydrocarbures aromatiques polycycliques (HAP) est analysé dans cette étude. Nous avons pour cela mesuré la contenance en benz(a)pyèrne (BaP), le principal HAP, de l'adhésif, de la poussière, ainsi que de l'air d'intérieur et d'extérieur. Une contamination significative en BaP de l'air d'intérieur n'a pu être constatée dans aucun des bâtiments considérés.

La concentration en BaP dans les adhésifs variait entre 20 et 19000 mg/kg. Malgré ces hautes valeurs, une contamination de la poussière n'a pu être décelée que dans un seul cas. Dans cette pièce, le parquet était endommagé, en particulier le cachetage était défectueux. Une contamination n'a pu être décelée dans aucune pièce dont le parquet était intact, même si l'adhésif utilisé avait une haute concentration en BaP. L'état du parquet constitue une condition décisive pour une contamination en BaP.

KEYWORDS: tar parquetry adhesives, dust, indoor air, benz(a)pyrene

1. INTRODUCTION

A lot of buildings in Germany belonged to the American army. After the Americans left Germany these buildings were sold. At the beginning of this year it was suspected, that these buildings were contaminated with **p**olycyclic **a**romatic **h**ydrocarbons (PAH). This was suspected by mesasurements of the “Frankfurter Housing Area”. These measurements showed contamination’s of dust and indoor air with PAH’s. The use of tar parquetry adhesives in these

buildings could be responsible for this contamination. The PAH from the tar parquetry adhesives could be transported to the floor dust. Parents were fret about the contamination of the floor dust, because their infants often play at the floor. A study about the oral taking up of dust [AGLMB, 1995] shows, that infants (between 0 and 6 years) are taking up average 20 mg (95. percentile 100 mg) dust per day.

In April 1998 the Umweltbundesamt Germany gave an information about the investigation of rooms with tar parquetry adhesives [UMWELTBUNDESAMT, 28.04.1998]. Regarding to the toxicity of PAH's only benz(a)pyrene (BaP) should be investigated in dark parquetry adhesives. For further information please have a look at appendix 1.

Our study was carried out to check these points. In this summer we started the examination of 10 US-flats, 10 new-building flats and 10 public buildings (like schools and kindergartens) in co-operation with the Sozialministerium Baden-Württemberg and the Landesgesundheitsamt Baden-Württemberg. We investigated parquetry adhesives, floor dust, old dust, indoor air and outdoor air. 15 EPA – PAH (except naphthaline) were determined.

2. SAMPLE COLLECTION

Some special points, like age and condition of parquetry, heating and ventilation of room, smoking in room, were noted in a catalogue, which has been developed by the Landesgesundheitsamt Baden-Württemberg [LANDESGESUNDHEITSAMT, 1998]. All samples were collected in the nursery. In order to compare the results and to exclude contamination's of the samples, the samples were collected by the following general conditions:

- collection of indoor and outdoor air over 7 days
- room cleaned up four days before dust collection
- order of succession: first dust collection, second collection of parquetry

adhesives

2.1 Parquetry adhesives

An expert opened the parquetry and collected the tar parquetry adhesives. It was difficult to get a representative sample. The parquetry should not be destroyed and therefore it was opened at the periphery. The quantity of used parquetry adhesives is very different (from punctiform to wing loading). Impurities (like wood, cardboard, mineral compounds) could be attached at the parquetry adhesives and, at least, in one single room the use of different parquetry adhesives is possible.

2.2 Floor dust

For the collection of the dust it is not possible to use a normal vacuum cleaner, because the vacuum cleaner absorbers dust and parquetry adhesives out of the joints. Further it is also not possible to get the fine dust.

We used an absorber with a special jet (diameter: 0.5 cm), a glass-fiber filter and a flow rate of 15 l/min. It is very important, to keep a distance between jet and joint. It must be about 1 cm. Only in this case no dust and no parquetry adhesives out of the joint will be collected. The examined surface measured 2 m^2. The collected dust was weighted several times under definite moisture conditions. This sample is called “absorber dust”.

We also collected dust by wiping the surface (1 m^2) with a dry polyurethane-foam (diameter: 2 cm). This dust sample is called “wipe dust”.

2.3 Old dust

Old dust is defined as the normal old dust on wardrobes, bookcases, cupboards, door-cases etc. The old dust was collected by the “absorber dust” method, see above, please.

2.4 Indoor air

The indoor air was collected with a polyurethane foam. The collection was realised over 7 days under normal conditions [VDI 4300 Bl. 2] with a rate of 0.2 – 1 l/min.

2.5 Outdoor air

Corresponding to VDI 4300 Bl. 2 the outdoor air was collected at the same time like the indoor air.

3. ANALYTICAL METHOD

The samples were spiked with a quantitation standard, before collection (air sample) or before extraction (dust sample) respectively after extraction (parquetry adhesives). The samples were extracted with cyclohexane, the extrakt was cleaned by solid phase extraction with silicagele. Before measurement the extract was spiked with a recovering standard (except: parquetry adhesives).

We analysed the PAH with the **g**as **c**hromatograophy coupled with the **h**igh **r**esolution **m**ass **s**pectrometer (GC-HRMS). This is a very selective and sensitive process. It is often use to identify complex mixtures with low detection limits.

Another advantage of the mass spectrometer is the possibility of using isotope standards. The quantitation standard was a ^{13}C – isotope standard of all 15 PAH. The recovering standard included deuterate PAH – isotope. The comparision between the quantitation standard and the recovering standard gave the recovering rate.

The parquetry adhesives is very heterogeneous. Impurities (like wood, cardboard, mineral compounds) could be attached at the parquetry adhesives and falsified the weight. Therefore the evaporation residue of the cyclohexane

extration by 40°C over 24 hours was determined. This evaporation residue reproduced the soluble part of the parquetry adhesives. For the quantification this soluble part was used.

The preliminary examination of the parquetry adhesives was carried out by the **n**uclear **r**esonance **s**pectrometry (NMR). With this method we got first information's about the compounds.

4. RESULTS AND DISCUSSION

4.1 Air

The readily volatile PAH as fluorene, acenaphthene and acetanphthaline were discriminated by this collection method. This is shown by the recovering rates. The less volatile compound phenanthrene has a recovering rate above 50% and the recovering rate of BaP is higher than 70 %. So BaP could be determinate with this method.

We measured BaP concentrations in the indoor air between 0.1 ng/m³ and 1.2 ng/m³ and in the outdoor air between 0.1 ng/m³ and 0.3 ng/m³. In summer times this BaP concentrations are normal. A study [UMEG, 1996] showed, that the concentration of BaP in outdoor air in winter times is significantly higher than in summer times.

4.2 Dust

The recovering rates for the 15 PAH were between 80 % and 120 %. Only in one room we found BaP concentrations above 1 mg/kg in the old dust and in the floor dust. In all the others the concentration of BaP in the old dust and in the floor dust were lower than 1 mg/kg.

The exception with a high level for BaP was a public building. The old dust

had a concentration of 32 mg/kg and the floor dust about 45 mg/kg. According to the Umweltbundesamt Germany [UMWELTBUNDESAMT, 28.04.1998] (see also appendix 1) the limit for BaP was 10 mg/kg. Therefore it was necessary to repeat the measurement of the floor dust. The room was cleaned a short time before the repeat measurement. (Contrast to the general conditions for sample collection see point 2) The repeat test showed BaP values of 15 mg/kg and 10 mg/kg. Therefore, the first measurement was verified. Table 1 shows the comparison of the old dust and the floor dust for all 15 PAH.

Table 1: *Comparison old dust and floor dust*

	old dust 1	floor dust 1	floor dust 2a	floor dust 2b
PAH	mg/kg	mg/kg	mg/kg	mg/kg
acenaphthaline	0.1	0.1	0.2	0.1
acenaphthene	2.0	8.2	2.4	1.6
fluorene	2.3	14	3.8	2.2
phenanthrene	76	180	49	31
anthracene	4.1	33	8.3	4.2
fluoranthene	86	147	35	23
pyrene	41	72	25	17
benzo(a)anthracene	26	64	18	12
chrysene	42	61	22	17
benzo(b)fluoranthene	36	43	12	9.8
benzo(k)fluoranthene	39	51	15	11
benzo(a)pyrene	**32**	**45**	**15**	**10**
indeno(1,2,3-c,d)pyrene	16	18	7.5	5.2
dibenz(a,h)anthracene	5.3	5.5	1.1	0.8
benzo(g,h,i)perylene	16	18	7.3	5.1
sum 15 PAH	425	762	220	149

old dust 1, floor dust 1: first measurement
floor dust 2a, floor dust 2b: repeat measurement

The PAH concentration in the floor dust is slightly higher than in the old dust. The values for the repeat measurement are comparable.

Table 2 shows the comparison of the technique for the collection of the floor dust, once the absorber dust and once the wipe dust.

Table 2: *Comparision absorber dust and wipe dust*

	room A		room B		room C	
	absorber dust	wipe dust	absorber dust	wipe dust	absorber dust	wipe dust
PAH	ng/m²	ng/m²	ng/m²	ng/m²	ng/m²	ng/m²
acenaphthaline	0.1	21	0.84	26	1.5	24
acenaphthene	6.8	91	5.0	135	18	117
fluorene	13	231	9.2	258	21	197
phenanthrene	84	409	119	312	155	399
anthracene	8.0	35	5.5	21	14	34
fluoranthene	41	177	43	152	38	103
pyrene	29	137	25	107	26	95
benzo(a)anthracene	12	16	4.6	6.8	9.4	8.7
chrysene	13	33	14	40	12	29
benzo(b)fluoranthene	7.8	11	5.2	13	6.4	7.5
benzo(k)fluoranthene	13	11	4.7	11	6.9	6.8
benzo(a)pyrene	**8.5**	**8.3**	**1.7**	**2.2**	**5.6**	**3.1**
indeno(1,2,3-c,d)pyrene	1.9	3.8	1.4	1.1	3.3	1.5
dibenz(a,h)anthracene	< 0.1	0.3	0.1	< 0.1	0.8	< 0.1
benzo(g,h,i)perylene	3.0	5.1	2.2	1.2	3.6	2.8
sum 15 PAH	240	1191	242	1086	321	1028

For both methods, the BaP concentrations are comparable. But there is a great difference for the sum of PAH. The wipe dust showed substantially higher values for the sum of PAH than the absorber dust. The readily volatile PAH were discriminated by the collection with a absorber. This effect can be shown until benzo (a) anthracene.

The dust collection in private household was complicated, because the amount of the dust were often very low.

In public buildings the dust included gross impurities. In this cases the dust was fractionated. By the sample collection a sieve (mash width: 500 µm) were used. There was no relevant difference in the PAH concentrations between the

non fractionated and the fractionated dust.

4.3 Parquetry adhesives

The preliminary examination with NMR showed the different compounds of the parquetry adhesives like bitumen, tar and combinations of bitumen and tar. Table 3 presents the concentration of BaP [mg/kg] and sum 15 PAH [g/kg] once for the original sample and once for the soluble part of the sample. The soluble part of the parquetry adhesives were determined under defined conditions (see point 3).

Table 3: *BaP and sum 15 PAH for original and soluble part of adhesives*

adhesives sample	BaP mg/kg original	BaP mg/kg soluble part	Σ15 PAH g/kg original	Σ15 PAH g/kg soluble part	NMR	soluble part
A	2	20	0.05	0.56	bitumene	8 %
B	15	19	0.21	0.26	bitumene	80 %
C	730	7430	22	224	tar	10 %
D	1990	15000	39	293	tar	13 %
E	1060	3380	18	57	tar, bitumene	31 %
F	280	430	14	22	tar, bitumene	64 %

Depending on the impurities of adhesives the soluble part was very different. The limit value of 10 mg/kg for the parquetry adhesives [UMWELTBUNDESAMT, 28.04.1998] (see also appendix 1) was exceeded even by pure bitumen parquetry adhesives.

Table 4 shows some BaP concentrations of the outdoor air, the indoor air, the old dust, the floor dust and the parquetry adhesives (refer to soluble part).

Table 4: *Summary of the BaP concentrations*

outdoor air ng/m³	indoor air ng/m³	old dust mg/kg	floor dust mg/kg	adhesives mg/kg
< 0.1	< 0.1	< 1	< 1	20

< 0.1	0.5	32	45	7400
0.3	< 0.1	< 1	< 1	8500
< 0.1	< 0.1	< 1	< 1	7800
< 0.1	0.1	< 1	< 1	14000
< 0.1	0.2	< 1	< 1	19000

In no event we found a contamination of BaP in the indoor air (compare to[UMWELTBUNDESAMT, 28.04.1998]).

The BaP values for the parquetry adhesives are lying all over 10 mg/kg, by half of the samples they are lying above 3000 mg/kg. But only in one case we found a contamination of the dust. In this room the parquetry by itself was defect, especially the parquetry sealing was destroyed, joint width was large and the parquetry slats were disconnected.

5. CONCLUSION

According to the information of the Umweltbundesamt Germany [UMWELTBUNDESAMT, 28.04.1998] we could not find any contamination of the indoor air with BaP.

The BaP limit for the parquetry adhesives (by the Umweltbundesamt Germany) at about 10 mg/kg is not convenient, because pure bitumen parquetry adhesives already shows a higher concentration.

Responsible for BaP contamination of rooms with tar parquetry adhesives is the condition of the parquetry. Investigations in our institute show, that also the condition of the floor basis can cause a BaP contamination. By a damaged state of the floor basis, the parquetry can move and at stressing parts it can smash up. By this alternating effects, the tar parquetry adhesives can be pulverize and by a pump effect the tar can come to the surface of the parquetry.

By an uninjured parquetry we ca not find any BaP contamination’s of the

room, even if the tar parquetry adhesives shows very high values (e.g. 19 g/kg).

The description of the condition of the parquetry floor is very important for a assess of a BaP contamination.

6. ACKNOWLEDGEMENT

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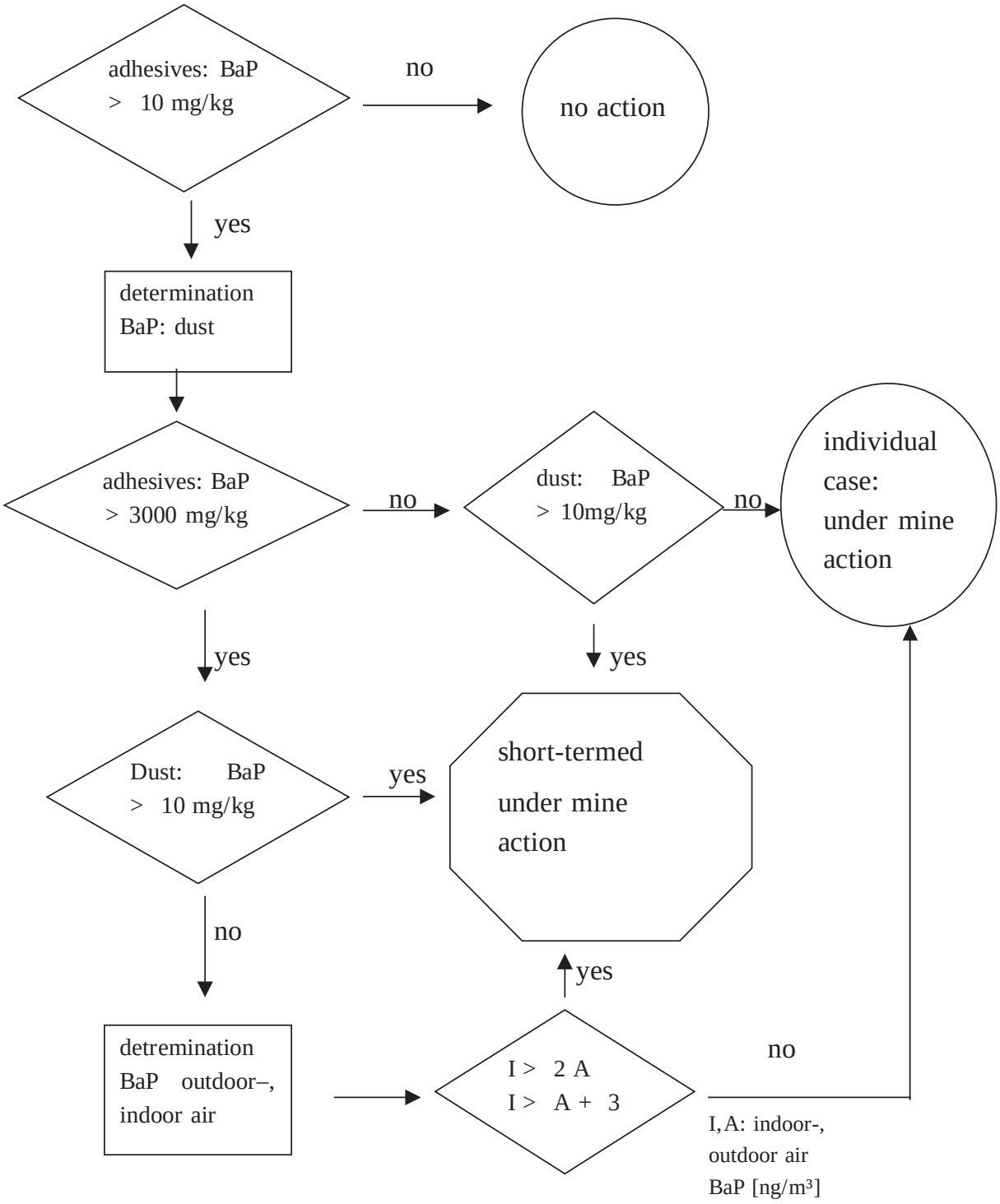
7. APPENDIX 1

Information from the Umweltbundesamt Germany 28.04.1998



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VDI-RICHTLINIE VDI 4300 BLATT 2: *Messen von Innenraumluftverun-reinigungen*