

Fraunhofer IVV Report PA/4453/17 (English Version)

Investigations on the migration of Polycyclic Aromatic Hydrocarbons (PAH) from rubber products containing recycled tyres

Date: 06/12/2017

The results of the test report are property of the client. However duplication in an excerpted version or publication is subject to a written agreement with the Fraunhofer Institute for Process Engineering and Packaging.



Fraunhofer-Institut für Verfahrenstechnik und Verpackung, Giggenhauser Str. 35, D-85354 Freising

Page 2 of 35 PA/4453/17 Fraunhofer IVV Report 06/12/2017

Authors of the report:

Ludwig Gruber Dr. Martin Schlummer Dominik Fiedler Michael Barwitz Sonja Smolic Dr. Roland Franz

Recommended citation:

Ludwig Gruber, Martin Schlummer, Dominik Fiedler, Michael Barwitz, Sonja Smolic, Roland Franz (2017) Investigations on the migration of Polycyclic Aromatic Hydrocarbons (PAH) from rubber products containing recycled tyres. Fraunhofer IVV Report PA/4453/17, Freising.

© Fraunhofer-Institut für Verfahrenstechnik und Verpackung, Giggenhauser Str. 35, D-85354 Freisi

Table of Content

1	Scope	4
2	Initial situation	4
3	Method development	5
	3.1 Initial situation	5
	3.2 Fraunhofer IVV Method PA 1.601	5
	3.2.1 Sample cleanup	5
	3.2.2 Quantitative analysis of PAH	5
4	Development of a method for analysis of the migration behavior	6
	4.1 Methodical approach	6
	4.2 Samples	6
	4.3 Quantitative analysis	
	4.4 Migration experiments	7
	4 4 1 Migration onto Tenax	7
	4.5 Results during method development	8
	A 5.1 Concentration within the material	8
	4.5.7 Concentration within the matchairment $4.5.2$ Migration of PAH onto Tenax®	8
	1.6 Data evaluation	
5	4.0 Data evaluation	nishla
J	compositions	110010
	5.1 Mathodoical approach	13
	5.1 Investigated cample material	۲۱ ۱۸
	5.2 Investigated sample material	14 1E
	5.3 IVIELIOUS	15 1 Г
	5.4 Results	15
~	5.5 Discussion of the results	
6	Influence of the material thickness on the migration behavior	21
	6.1 Methodological approach	
	6.2 Samples	21
	6.3 Results	22
_	6.4 Discussion of the results	22
7	Comparison of migration experiments with Tenax and 20% Ethanol	23
	7.1 Methodical approach	23
	7.2 Samples	23
	7.3 Method description	23
	7.3.1 Migration onto Tenax®	23
	7.3.2 Migration in 20 % ethanol/water	24
	7.3.3 Cleanup and GC-MS-analysis	24
	7.3.4 Handling of internal standard	24
	7.4 Concentration within the material and migration of PAH	24
	7.5 Discussion of the results	27
8	Investigation of further samples for REACH-PAH	28
	8.1 Fitnessstudiobelag (Safety tiles for fitness studios), 6 mm	28
	8.2 Fallschutzplatte (Safety tile, red-brown, 45 mm)	30
	8.3 Evaluation of the results of further samples	31
9	Summary	32
10) Literature	34
A	cknowledgement	35

1 Scope

Scope of this report are investigations on the migration of Polycyclic Aromatic Hydrocarbons (PAH) from rubber products containing recycled tyres. PAH-containing extender oils have been used legally in car tyres until 2009. Besides extender oils a further source of PAH is black carbon. It is known that PAH are firmly bound to the carbon black surface under normal conditions. Unfortunately there are no evaluation guidelines for the rubber materials like they exist for plastic materials in EU 10/2011 (Plastic Implementation Measure, PIM). Scope of this report are therefore investigations on the migration behavior of Polycyclic Aromatic Hydrocarbons (PAH) and especially of the 8 REACH-PAH according to Annex XVII.

2 Initial situation

Rubber products containing recycled tyres are used e.g. in safety tiles for playgrounds. They are made from recycled tyres containing extender oils and black carbon which were known to likely contain PAH. Investigations were performed in several countries like Sweden, Norway, the Netherlands, Denmark, the USA and Germany with regard to safety issues on these playgrounds. (NIPH, 2006; Ilvonen, 2013; Kalbe et al., 2013; Schilirò et al., 2013; Celeiro et al., 2014: Bartsch et al., 2016; BGH et al., 2016; US EPA, 2016; Oomen and Mennen, 2017) Most of these studies observed no significant intake of PAH through breathing, skin contact or oral uptake, even in the years before 2010 when the EU-wide threshold value for PAH-containing extender oils in car tyres had been in effect. An EU-wide threshold value for PAH-containing extender oils in car tyres has been in effect since January 1, 2010. It was introduced because of a restriction in the European Chemicals Regulation REACH (Regulation (EC) No. 1907/2006) and led to a reduction of PAH. A number of products with a concentration of more than 1 mg/kg of one of the 8 REACH-PAH are banned since 27.12.2015. Till the end of 2017, the Commission shall 'review the limit values in paragraphs 5 and 6 in the light of new scientific information, including migration of PAHs from the articles referred to therein and information on alternative raw materials and, if appropriate, modify these paragraphs accordingly.' (Umweltbundesamt, 2016)

3 Method development

3.1 Initial situation

Usually a method for quantitative analysis of PAH in rubber materials is "ZEK 01-08 Harmonisierte Methode für Bestimmung von polycyclischen aromatischen Kohlenwasterstoffen (PAK) in Kunststoffproben" (Ausschuss für Technische Arbeitsmittel and Verbraucherprodukte (AtAV), 2008) which is used for GS approval. The experience of the Fraunhofer IVV shows that the use of toluene often leads to matrix effects interfering the analysis. The method is sufficient to reach a LOQ of 0.2 mg/kg, but matrix effects occur more often compared to the accredited Fraunhofer IVV Method PA 1.601.

3.2 Fraunhofer IVV Method PA 1.601

3.2.1 Sample cleanup

The samples are milled with a centrifugal mill (Retsch ZM-200) to a particle size of \leq 750 µm after a pretreatment with liquid nitrogen.

Approx. 0.5 g of the homogenized samples are extracted (isotope labelled PAH-Standard-Mix) with cyclohexane by means of ASE (Dionex/Thermo ASE 200) under the following conditions:

Pressure: 100 bar, Temperature: 100 °C, Cycles: 3 á 15 min (static).

To test the extraction efficiency a further extraction step is included. The extracts are treated with Solid Phase Extraction (SPE) with the following SPE-column: Strata SI-1 Silica; 55 μ m, 70 A; Phenomenex. The SPE-eluate will be evaporated under a gentle nitrogen flow to a volume of 1 ml and analysed with GC-MS.

3.2.2 Quantitative analysis of PAH

Quantitative analysis of PAH is performed with a GC-MS (Shimadzu QP 2010 Plus) in *Selected Ion Monitoring* (SIM)-mode.

The quantification is performed with deuterated internal standards.

Compound	Method ZEK 01-08 [mg/kg]	Method Fraunhofer PA 1.601 [mg/kg]
Benzo[a]anthracene	0.1	0.03
Chrysene	0.1	0.04
Benzo[b]fluoranthene	0.2	0.08
Benzo[k]fluoranthene	0.2	0.08
Benzo[j]fluoranthene	0.2	0.08
Benzo[e]pyrene	0.2	0.10
Benzo[a]pyrene	0.2	0.10
Dibenz[a,h]anthracene	0.2	0.06

Table 1: Comparison of the limits of detection in rubber materia	Fable	e 1: Comparison of t	he limits c	of detection	in rubber	materials
--	-------	----------------------	-------------	--------------	-----------	-----------

4 Development of a method for analysis of the migration behavior

4.1 Methodological approach

The following REACH-PAH in rubber granulate were analysed:

Benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[j]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, Dibenz[a,h]anthracene.

The analysis of the migration behavior was performed based on European Norm EN 1186-13b. The migration of the PAH was compared on Tenax® for PU-coated rubber mat and rubber granulate. Tenax® was chosen because of its specific surface area and good adsorption performance as a simulant for skin contact.

4.2 Samples

Table 2: Investigated sample material

	Description
Sample 1	Rubber granulate
Sample 2	PU-coated rubber mat, red



Graph 1: rubber granulate (on the left), PU-coated rubber mat

4.3 Quantitative analysis

The quantitative analysis was performed according to the accredited Fraunhofer IVV Method PA 1.601.

4.4 Migration experiments

Based on literature a method for migration experiments based on migration onto Tenax® was developed.

4.4.1 Migration onto Tenax®

Method: European Norm EN 1186-13b

Simulant: modified Polyphenylenoxide (MPPO, Tenax®)

Contact time and -temperatures:

1 d / 20 °C 10 d / 40 °C 10 d / 60 °C

The samples were placed into a Petri dish. The surface of the specimen was totally covered with Tenax[®]. The Petri dishes were closed and stored at the following conditions:

Contact area/volume:

11 g / 0.48 dm² Sample 1 / 3 g Tenax®

349 g / 1.5 dm² Sample 2 / 6 g Tenax®

After cooling down to ambient temperature the contact was ended. The Tenax® was extracted with n-Hexane under addition of an isotope-labelled PAH-Standard-Mix (internal standard) for 24 hours at 40 °C. Before GC-MS-analysis there was a SPE-cleanup as described in chapter 3.2.1. The tests were performed in triplicate.

4.5 Results during method development

A maximum of two significant digits is given for LOD.

4.5.1 Concentration within the material

Table 3: Concentration within the material - Sample 1 (rubber granulate)

Compound	Concentration within the material [mg/kg]	Limit of detection (LOD) [mg/kg]
Benzo[a]anthracene	0.05	0.03
Chrysene	0.06	0.04
Benzo[b]fluoranthene	0.29	0.08
Benzo[k]fluoranthene	0.12	0.08
Benzo[j]fluoranthene	0.08	0.08
Benzo[e]pyrene	1.61	0.10
Benzo[a]pyrene	0.75	0.10
Dibenz[a,h]anthracene	< LOD	0.06
Sum of PAH	2.96	

4.5.2 Migration of PAH onto Tenax®

Table 4: Migration per weight onto Tenax® - Sample 1 (rubber granulate)

Compound	Migra	tion per weight [µg/kg] *
Compound	1 d / 20 °C	10 d / 40 °C	10 d / 60 °C
Benzo[a]anthracene	n.d.	0.78	3.36
(BaA)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Chrysen	n.d.	2.25	7.89
(CHR)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Benzo[b]fluoranthene	n.d.	0.59	2.58
(BbFA)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Benzo[k]fluoranthene	n.d.	0.30	0.87
(BkFA)	(LOD: 0.20)	(LOD: 0.20)	(LOD: 0.20)
Benzo[j]fluoranthene	n.d.	0.53	0.73
(BjFA)	(LOD: 0.20)	(LOD: 0.20)	(LOD: 0.20)
Benzo[e]pyrene	n.d.	0.89	6.46
(BeP)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Benzo[a]pyrene	n.d.	0.39	2.86
(BaP)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Dibenz[a,h]anthracene	n.d.	n.d.	n.d.
(DBAhA)	(LOD: 0.20)	(LOD: 0.20)	(LOD: 0.20)
Sum	n.d.	5.73	24.75

Remark*: Values with regard to migration of the analytes per μ g/kg rubber granulates.

Commound	Migra	ation per area [µg/dm	2] *
Compound	1 d / 20 °C	10 d / 40 °C	10 d / 60 °C
Benzo[a]anthracene	n.d.	0.02	0.07
(BaA)	(LOD: 0.002)	(LOD: 0.002)	(LOD: 0.002)
Chrysen	n.d.	0.05	0.17
(CHR)	(LOD: 0.002)	(LOD: 0.002)	(LOD: 0.002)
Benzo[b]fluoranthene	n.d.	0.01	0.06
(BbFA)	(LOD: 0.002)	(LOD: 0.002)	(LOD: 0.002)
Benzo[k]fluoranthene	n.d.	0.01	0.02
(BkFA)	(LOD: 0.004)	(LOD: 0.004)	(LOD: 0.004)
Benzo[j]fluoranthene	n.d.	0.01	0.02
(BjFA)	(LOD: 0.004)	(LOD: 0.004)	(LOD: 0.004)
Benzo[e]pyrene	n.d.	0.02	0.14
(BeP)	(LOD: 0.002)	(LOD: 0.002)	(LOD: 0.002)
Benzo[a]pyrene	n.d.	0.01	0.03
(BaP)	(LOD: 0.002)	(LOD: 0.002)	(LOD: 0.002)
Dibenz[a,h]anthracene	n.d.	n.d.	n.d.
(DBAhA)	(LOD: 0.004)	(LOD: 0.004)	(LOD: 0.004)
Sum	n.d.	0.13	0.51

Table 5: Migration per area onto Tenax® - Sample 1 (rubber granulate)

Remark*: Values are calculated on the basis of the contact area/volume – ratio of 22 g/dm².

Table 6: Comparison of tenax migration - Sample 1 (rubber granulate) under simulated conditions (Sample 2)

Compound	Calculated	migration per area [ug/dm²] *
Compound	1 d / 20 °C	10 d / 40 °C	10 d / 60 °C
Benzo[a]anthracene	n.d.	0.17	0.71
(BaA)	(LOD: 0.02)	(LOD: 0.02)	(LOD: 0.02)
Chrysen	n.d.	0.47	1.66
(CHR)	(LOD: 0.02)	(LOD: 0.02)	(LOD: 0.02)
Benzo[b]fluoranthene	n.d.	0.12	0.54
(BbFA)	(LOD: 0.02)	(LOD: 0.02)	(LOD: 0.02)
Benzo[k]fluoranthene	n.d.	0.06	0.18
(BkFA)	(LOD: 0.04)	(LOD: 0.04)	(LOD: 0.04)
Benzo[j]fluoranthene	n.d.	0.11	0.15
(BjFA)	(LOD: 0.04)	(LOD: 0.04)	(LOD: 0.04)
Benzo[e]pyrene	n.d.	0.19	1.36
(BeP)	(LOD: 0.02)	(LOD: 0.02)	(LOD: 0.02)
Benzo[a]pyrene	n.d.	0.08	0.60
(BaP)	(LOD: 0.02)	(LOD: 0.02)	(LOD: 0.02)
Dibenz[a.h]anthracene	n.d.	n.d.	n.d.
(DBAhA)	(LOD: 0.0044)	(LOD: 0.04)	(LOD: 0.0044)
Sum	n.d.	1.20	5.20

Remark*: To compare the values with the PU-coated rubber mat a surface area weight of 233 g/dm² was assumed with a PU-content of 10 % in the final product (Source: Supplier data sheet).

Compound	Migratic	on per weight [µg/kg] *
compound	1 d / 20 °C	10 d / 40 °C	10 d / 60 °C
Benzo[a]anthracene	n.d.	0.28	1.27
(BaA)	(LOD: 0.05)	(LOD: 0.05)	(LOD: 0.05)
Chrysen	n.d.	0.47	1.84
(CHR)	(LOD: 0.05)	(LOD: 0.05)	(LOD: 0.05)
Benzo[b]fluoranthene	n.d.	n.d.	0.28
(BbFA)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Benzo[k]fluoranthene	n.d.	n.d.	n.d.
(BkFA)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Benzo[j]fluoranthene	n.d.	n.d.	n.d.
(BjFA)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Benzo[e]pyrene	n.d.	n.d.	0.47
(BeP)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Benzo[a]pyrene	n.d.	n.d.	0.27
(BaP)	(LOD: 0.05)	(LOD: 0.05)	(LOD: 0.05)
Dibenz[a.h]anthracene	n.d.	n.d.	n.d.
(DBAhA)	(LOD: 0.10)	(LOD: 0.10)	(LOD: 0.10)
Sum	n.d.	0.75	4.13

Table 7: Migration per weight onto Tenax® - Sample 2 (PU-coated rubber mat)

Remark*: Values with regard to migration of the analytes per $\mu\text{g/kg}$ PU-coated rubber mat.

Compound	Migrati	on per area [µg/dm²]	*
Compound	1 d / 20 °C	10 d / 40 °C	10 d / 60 °C
Benzo[a]anthracene	n.d.	0.07	0.38
(BaA)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Chrysen	n.d.	0.11	0.43
(CHR)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzo[b]fluoranthene	n.d.	n.d.	0.07
(BbFA)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzo[k]fluoranthene	n.d.	n.d.	n.d.
(BkFA)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzo[j]fluoranthene	n.d.	n.d.	n.d.
(BjFA)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzo[e]pyrene	n.d.	n.d.	0.11
(BeP)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzo[a]pyrene	n.d.	n.d.	0.06
(BaP)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Dibenz[a,h]anthracene	n.d.	n.d.	n.d.
(DBAhA)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Sum	n.d.	0.18	1.05

Table 8: Migration per area onto Tenax® - Sample 2 (PU-coated rubber mat)

Remark*: Calculated on the basis of a rubber mat weight of 233 g/dm².

4.6 Data evaluation

Migration from rubber granulate and from PU-coated rubber mats onto Tenax® was analysed for several contact conditions to evaluate the effects on possible transfer rates. Effects could observed especially at test temperatures of 40 °C and 60 °C. The PU-coating seems to decrease migration of semivolatile PAH by a approximate factor 4 - 5 in relation to the contact area.

After a short-time contact of the PU-coated rubber mat (1 d / 20 °C) there was no detectable transfer of the 8 investigated PAH onto Tenax® with a limit of detection of 0.01 μ g/dm². After a contact time of 10 d / 40 °C a transfer of benzo[a]anthracene with 0.07 μ g/dm² and Chrysene with 0.11 μ g/dm² was observed. At 10 d / 60 °C the levels of benzo[b]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, benzo[a]anthracene and chrysene were in a range of 0.07 to 0.43 μ g/dm². Not mentioned PAH (see chapter 4.2, Table 5) were not detectable (approx. LOD = 0.01 μ g/dm²). There is no current legislation for the evaluation of PAH migration from these materials. It is helpful to keep in mind the following definitions for the discussion:

- External exposition = Transfer of PAH from the rubber mat onto skin (simulated by the Tenax®-test)
- Internal exposition = bioavailable amount of PAH in the human body.

For benzo[a]pyrene there is an oral reference dose of the EPA (US Environmental Protection Agency) for drinking water (2012 Edition of the Drinking Water Standards and Health Advisories). For benzo[a]pyrene the maximum allowable concentration is 0.2 μ g/L (200 ng/L).

Under the worst case assumption that the external exposition leeds to an equivalent internal exposition and the external exposition is completely bioavailable in the human body this oral reference dose of the EPA can be used for evaluation.

We used a contact time of 10 d / 40 °C, which is conservative because 30 - 60 minutes of contact are more realistic. The migration of benzo[a]pyrene was not detectable with a limit of detection of 0.01 µg/dm².

Assuming a skin area of 6 dm² in contact with the rubber mat the maximum internal exposition would be 0.06 μ g/person. This equates to a concentration of 0.06 μ g/kg benzo[a]pyrene in water for a consumtion of 1 L per day. This means a factor 3.3 below the EPA values.

This scenario is conservative, i.e. the PAH-exposition of persons in contact with the rubber mats are expected to be much lower than calculated. The test conditions are harsh and external and internal exposition are assumed to be identical. It has to be taken into account that this is an outdoor application with some leaching, therefore there is a decreasing exposition potential.

5 Investigation of the migration behavior from rubber products with variable compositions

5.1 Methological approach

Scope of the investigations described in this chapter was the migration behavior of PAH from rubber products with variable compositions.

Investigated were seven samples, three rubber mats, two samples of rubber granulate and two extender oils for the production of rubber mats. Two of the rubber mats were specialy produced for this investigations. Aim was to understand the influence of the source of PAH (deriving from extender oil and/or rubber granulates). It was expected that PAH from extender oil are more mobile then from granulates. If the extender oil migrates from the rubber product, the oil will be acompanied from the PAH present in the oil.

The investigations should also test the theory that the PAH present in the recycled tyres itself are tightly adsorbed to the carbon black surface under normal handling conditions.

Some governmental bodies, including the European Union (REACH regulation) as well as the Environmental Protection Agency in the US, regulate concentrations of PAH. The PAH were selected accordingly. 25 PAH were investigated (see table). The selection of PAH was done according to existing regulation in the EU (REACH and the SCF 15+1 PAH) and the US EPA (Environmental Protection Agency).

Compound	CAS Number	List
Naphthalene (Naph)	91-20-3	EPA
Acenaphthylene (Aceny)	208-96-8	EPA
Acenaphthene (Acen)	83-32-9	EPA
Fluorene (FLO)	86-73-7	EPA
Phenanthrene (PHE)	85-01-8	EPA
Anthracene (A)	120-12-7	EPA
Fluoranthene (FLU)	206-44-0	EPA
Pyrene (PYR)	129-00-0	EPA
Benzo[c]fluoren (BcL)	205-12-9	SCF
Cyclopenta[cd]pyrene (CPP)	27208-37-3	SCF
Benzo[a]anthracene (BaA)	56-55-3	EPA, SCF, REACH
Chrysene (CHR)	218-01-9	EPA, SCF, REACH
5-Methylchrysene (5MC)	3697-24-3	SCF
Benzo[b]fluoranthene (BbFA)	205-99-2	EPA, SCF, REACH
Benzo[k]fluoranthene (BkFA)	207-08-9	EPA, SCF, REACH
Benzo[j]fluoranthene (BjFA)	205-82-3	SCF, REACH
Benzo[e]pyrene (BeP)	192-97-2	REACH
Benzo[a]pyrene (BaP)	50-32-8	EPA, SCF, REACH
Indeno[1,2,3-cd]pyrene (lcP)	193-39-5	epa, scf
Dibenz[a,h]anthracene (DBAhA)	53-70-3	EPA, SCF, REACH

Table 9: Investigated PAH

Benzo[g,h,i]perylene (BghiP)	191-24-2	EPA, SCF
Dibenzo[a,e]pyrene (DeP)	192-65-4	SCF
Dibenzo[a,h]pyrene (DhP)	189-64-0	SCF
Dibenzo[a,i]pyrene (DiP)	189-55-9	SCF
Dibenzo[a,l]pyrene (DlP)	191-30-0	SCF

The quantitative analysis of PAH in the material was performed to estimate the migration potential. Migration experiments were performed onto Tenax® with a contact time of 24 hours and 10 days at 40 ° Celsius.

5.2 Investigated sample material

Table 10: Investigated sample material

Sample		Description
	1	Rubber mat "sample A, recycled tyre granulate, stearic acid, Catenex T 145"
	2	Rubber mat "sample B, EPDM-Granulate, Chemba 3, Tudalen 65"
Number	3	Rubber mat sample C, unknown product of non-european origin
	4	Granulate "Recycled tyre granulate"
	5	Granulate "EPDM-Granulate"
	6	Extender oil "Tudalen 65"
	7	Extender oil "Catenex T 145"



Graph 2: Sample 1 to 7

5.3 Methods

The methods described in chapter 4 were used.

5.4 Results

Table 11: Concentration within the material and migration onto Tenax $\mbox{$\mathbb R$}$ using a contact time of 10 days at 40 ° Celsius .

	Sample 1: rubber mat "Sample A, Recycled tyre granulate, Stearic acid, Catenex T 145"					
Compound	Concentration in the material [µg/kg]	Migration per weight [µg/kg]	Migration per area [µg/dm²]			
Naphthalene (Naph)	344.9 (LOD: 5)	57.91 (LOD: 0.01)	13.69 (LOD: 0.002)			
Acenaphthylene (Aceny)	839.0 (LOD: 5)	15.79 (LOD: 0.01)	3.73 (LOD: 0.002)			
Acenaphthene (Acen)	58.0 (LOD: 5)	2.59 (LOD: 0.01)	0.61 (LOD: 0.002)			
Fluorene (FLO)	210.0 (LOD: 5)	3.82 (LOD: 0.01)	0.90 (LOD: 0.002)			
Phenanthrene (PHE)	4644.5 (LOD: 5)	32.27 (LOD: 0.01)	7.63 (LOD: 0.002)			
Anthracene (A)	671.6 (LOD: 5)	4.07 (LOD: 0.01)	0.96 (LOD: 0.002)			
Fluoranthene (FLU)	5823.4 (LOD: 5)	46.96 (LOD: 0.01)	11.10 (LOD: 0.002)			
Pyrene (PYR)	20933 (LOD: 5)	116.77 (LOD: 0.01)	27.60 (LOD: 0.002)			
Benzo[c]fluorene (BcL)	532.3 (LOD: 5)	2.06 (LOD: 0.01)	0.49 (LOD: 0.002)			

Cyclopenta[cd]pyrene (CPP)		3381.6 (LOD: 5)	2.86 (LOD: 0.01)	0.68 (LOD: 0.002)
Benzo[a]antl	hracene (BaA)	445.9 (LOD: 5)	0.42 (LOD: 0.01)	0.10 (LOD: 0.002)
Chrysene (CH	IR)	948.9 (LOD: 5)	0.98 (LOD: 0.01)	0.23 (LOD: 0.002)
5-Methylchry	/sene (5MC)	789.8 (LOD: 5)	0.38 (LOD: 0.01)	0.09 (LOD: 0.002)
Benzo[b]fluc	oranthene (BbFA)	595.3 (LOD: 5)	0.06 (LOD: 0.01)	0.02 (LOD: 0.002)
Benzo[k]fluc	oranthene (BkFA)	138.0 (LOD: 5)	0.03 (LOD: 0.01)	0.002 (LOD: 0.002)
Benzo[j]fluoranthene (BjFA)		224.2 (LOD: 5)	0.02 (LOD: 0.01)	0.002 (LOD: 0.002)
Benzo[e]pyrene (BeP)		2317.2 (LOD: 5)	0.13 (LOD: 0.01)	0.03 (LOD: 0.002)
Benzo[a]pyrene (BaP)		891.2 (LOD: 5)	0.05 (LOD: 0.01)	0.002 (LOD: 0.002)
Indeno[1,2,3-cd]pyrene (IcP)		325.6 (LOD: 5)	n.d. <i>(LOD: 0.01)</i>	n.d. <i>(LOD: 0.002)</i>
Dibenz[a,h]a	nthracene (DBAhA)	n.d. <i>(LOD: 50</i>)*	n.d. <i>(LOD: 0.01)</i>	n.d. <i>(LOD: 0.002)</i>
Benzo[g,h,i]	perylene (BghiP)	5212.7 (LOD: 5)	n.d. <i>(LOD: 0.01)</i>	n.d. <i>(LOD: 0.002)</i>
Dibenzo[a,e]	pyrene (DeP)	n.d. <i>(LOD: 20)</i>	n.d. <i>(LOD: 0.01)</i>	n.d. <i>(LOD: 0.002)</i>
Dibenzo[a,h]pyrene (DhP)		n.d. <i>(LOD: 20)</i>	n.d. <i>(LOD: 0.01)</i>	n.d. (LOD: 0.002)
Dibenzo[a,i]pyrene (DiP)		n.d. <i>(LOD: 20)</i>	n.d. <i>(LOD: 0.01)</i>	n.d. (LOD: 0.002)
Dibenzo[a,l]pyrene (DIP)		n.d. <i>(LOD: 20)</i>	n.d. <i>(LOD: 0.01)</i>	n.d. (LOD: 0.002)
	8 REACH PAH	5561	1.69	0.40
Sum	15 + 1 EU PAH	13485	6.86	1.62
	16 EPA PAH	42082	281.73	66.59

	Table 11	- continue	d
--	----------	------------	---

n.d.: not detectable, LOD: limit of detection, * Coelution

Table	12:	Conc	entratio	on	within	the	materia	l as	well	as	migration	onto	Tenax®
using	а со	ntact	time of	f 24	1 hours	and	10 day	s at	40°	Cel	sius.		

	Sample 2: rubber mat "Sample B, EPDM-Granulate, Chemba 3, Tudalen 65"					
Compound	Conc. in the material [µg/kg] ¹	Migration p [µg/k	er weight [3] ²	Migration per area [µg/dm²] ³		
Contact time and temperature	-	24 h / 40° C	10 d / 40° C	24 h / 40° C	10 d / 40° C	
Nanhthalana (Nanh)	457.3	34.43	85.79	8.46	21,08	
Napitrialerie (Napit)	(LO <i>D: 5)</i>	(LOD: (0.01)	(LOD: 0.002)		
A seperativelana (A sepu)	321.3	6.44	10.31	1.58	2,53	
Acenaphthylene (Aceny)	(LO <i>D: 5)</i>	(LOD: ((LOD: 0.01)		0.002)	
Acaranhthana (Acar)	n.d.	0.39	1.21	0.10	0,30	
Acenaphtnene (Acen)	(LO D:100)*	(LOD: 0.01)		(LOD: 0.002)		
Elucropo (ELO)	165.6	2.11	4.13	0.52	1,02	
Fluorene (FLO)	(LO <i>D: 5)</i>	(LOD: 0.01)		(LOD: 0.002)		
Phononthrong (PHE)	1074.8	5.74	15.71	1.41	3,86	
Filenantinene (FHE)	(LO <i>D: 5)</i>	(LOD: (0.01)	(LOD: 0.002)		
Apthracopo (A)	150.1	0.64	1.76	0.16	0,43	
Antiliacene (A)	(LO <i>D: 5)</i>	(LOD: 0.01)		(LOD: 0.002)		
Eluoranthono (ELLI)	510.0	1.03	5.20	0.25	1,28	
Fluorantinene (FLO)	(LO <i>D: 5</i>)	(LOD: 0.01)		(LOD: 0.002)		

Table 12 - continued

Pyrene (D	(R)	2208.8	3.04	17.35	0.75	4,26
i yrene (P		(LO <i>D: 5)</i>	(LOD	: 0.01)	(LOD:	0.002)
Renzolcifi	uorene (Bcl.)	803.8	0.60	4.40	0.15	1,08
Denzo[e]n		(LO <i>D: 5)</i>	(LOD	: 0.01)	(LOD:	0.002)
Cyclonent	a[cd]nvrene (CPP)	1625.7	0.30	2.26	0,07	0,56
cyclopent	a[ca]pyrene (en)	(LO <i>D: 5)</i>	(LOD	. 0.01)	(LOD:	0.002)
Benzolala	nthracene (BaA)	793.8	0.13	1.00	0,03	0,25
Denzolaja		(LO <i>D: 5)</i>	(LOD	. 0.01)	(LOD:	0.002)
Chrysene	(CHR)	2870.2	0.52	3.95	0,13	0,97
emysene	(erm)	(LO <i>D: 5</i>)	(LOD	: 0.01)	(LOD:	0.002)
5-Methylc	hrvsene (5MC)	2238.0	0.17	2.09	0,04	0,51
5 Wiedrigie		(LO <i>D: 5)</i>	(LOD	. 0.01)	(LOD:	0.002)
Benzo[b]f	luoranthene	809.2	n.d.	0.20	n.d.	0,05
(BbFA)		(LO <i>D: 5)</i>	(LOD	: 0.01)	(LOD:	0.002)
Benzo[k]fluoranthene		1084.2	n.d.	0.04	n.d.	0,01
(BkFA)		(LO <i>D: 5)</i>	(LOD	: 0.01)	(LOD:	0.002)
Benzo[i]fluoranthene (BiFA)		270.2	n.d.	0.04	n.d.	0,01
		(LO <i>D: 5</i>)	(LOD	: 0.01)	(LOD:	0.002)
Renzolejnyrene (ReP)		3841.9	0.05	0.45	0,01	0,11
Denzolejp	yrene (Ber)	(LO <i>D: 5</i>)	(LOD	: 0.01)	(LOD:	0.002)
Benzo[a]pyrene (BaP)		652.0	n.d.	0.07	n.d.	0,02
		(LO <i>D: 5</i>)	(LOD	: 0.01)	(LOD:	0.002)
Indono[1,2,2,cd]nyrono (IcD)		229.9	n.d. n.d.		n.d.	n.d.
indeno[1,		(LO <i>D: 5)</i>	(LOD	: 0.01)	(LOD:	0.002)
Dibenz[a,	h]anthracene	427.5	n.d.	n.d.	n.d.	n.d.
(DBAhA)		(LO <i>D: 5)</i>	(LOD	: 0.01)	(LOD:	0.002)
Benzola h	ilpen/lene (BahiP)	3094.5	n.d.	n.d.	n.d.	n.d.
benzolg,	, ijperviene (bgini)	(LO <i>D: 5)</i>	(LOD: 0.01)		(LOD: 0.002)	
Dibenzola	elovrene (DeP)	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzola	a,ejpyrene (Dei)	(LO <i>D: 20</i>)	(LOD: 0.01)		(LOD: 0.002)	
Dibenzola	hlovrene (DhP)	n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzo[a,n]pyrene (DNP)		(LOD: 50)	(LOD	: 0.01)	(LOD:	0.002)
Dibenzo[a,i]pyrene (DiP)		n.d.	n.d.	n.d.	n.d.	n.d.
		(LOD: 50)	(LOD	: 0.01)	(LOD:	0.002)
Dihanzala Universa (DID)		n.d.	n.d.	n.d.	n.d.	n.d.
Dibenzola	а, прутепе (DIP)	(LOD: 50)	(LOD	: 0.01)	(LOD:	0.002)
	8 REACH PAH	10749	0.70	5.76	0.17	1.42
Sum	15 + 1 EU PAH	14899	1.71	14.06	0.42	3.46
	16 EPA PAH	14978	54.47	146.74	13.39	36.06

Remark ¹: Values with regard to the concentration in μ g per kg in the sample. Remark ²: Values with regard to migration of the analyte in μ g per kg sample. Remark ³: Values with regard to migration of the analyte in μ g per dm² sample. n.d.: not detectable , LOD: limit of detection, * Coelution

		Sample 3: rubber mat "Sample C, unknown product of non-european origin "						
Compound		Concentration in the material [µg/kg] ¹	Migration [µg/	per weight /kg] ²	Migration per area [µg/dm²] ³			
Contact and	and Contact time temperature	-	24 h / 40° C	10 d / 40° C	24 h / 40° C	10 d / 40° C		
Naphthale	ene (Naph)	18458 (LOD: 5)	186.20 (LOD:	1087.55	41.66 (LOD:	243.35 0.002)		
Acenapht	hylene (Aceny)	884.9 (LOD: 5)	2.00 (LOD)	4.77	0.45 (LOD:	1.07 0.002)		
Acenapht	hene (Acen)	8584.2 (LOD: 5)	10.47 (LOD)	19.69	2.34 (LOD:	4.41 0.002)		
Fluorene (FLO)	26021 (LOD: 5)	16.14 (LOD)	32.65	3.61 (LOD:	7.31		
Phenanth	rene (PHE)	257240 (LOD: 5)	39.14 (LOD)	111.54	8.76 (LOD:	24.96 0.002)		
Anthracer	ne (A)	22558 (LOD: 5)	12.68 (LOD)	34.61	2.84 (LOD:	7.74 0.002)		
Fluoranth	ene (FLU)	87694 (LOD: 5)	74.13 (LOD)	236.11	16.59 (LOD:	52.83 0.002)		
Pyrene (P)	(R)	263004 (LOD: 5)	154.40 (LOD)	416.36	34.55 (LOD:	93.16		
Benzo[c]fluorene (BcL)		220162 (LOD: 5)	102.02	348.81	22.83	78.05		
Cyclopenta[cd]pyrene (CPP)		42110 (LOD: 5)	6.38 (LOD)	24.94	1.43	5.58 0.002)		
Benzo[a]anthracene (BaA)		48378 (LOD: 5)	26.96	120.66	6.03	27.00		
Chrysene (CHR)		64654 (LOD: 5)	33.27 (I OD	148.46	7.44	33.22		
5-Methylchrysene (5MC)		69601 (LOD: 5)	6.07	36.78	1.36	8.23 0.002)		
Benzo[b]fluoranthene		10681 (LOD: 5)	1.20	6.99	0.27	1.56		
Benzo[k]f	uoranthene (BkFA)	2472 (LOD: 5)	0.29	1.77	0.06	0.40		
Benzo[j]fl	uoranthene (BjFA)	3077 (LOD: 5)	0.50	3.03	0.11	0.68		
Benzo[e]p	yrene (BeP)	30415 (LOD: 5)	1.98	13.03	0.44	2.92		
Benzo[a]p	yrene (BaP)	18194 (LOD: 5)	1.25	8.98	0.28	2.01		
Indeno[1,2	2,3-cd]pyrene (lcP)	1665 (LOD: 5)	0.02	0.18	0.002	0.04 0.002)		
Dibenz[a,h]anthracene		5976 (LOD: 5)	0.03	0.26	0.002	0.06		
Benzo[g,h,i]perylene (BghiP)		25612 (LOD: 5)	0.14	0.93	0.03	0.21		
Dibenzo[a,e]pyrene (DeP)		546.9 (LOD: 20)	n.d.	n.d.	n.d. n.d.			
Dibenzo[a,h]pyrene (DhP)		2306 (LOD: 20)	n.d.	n.d.	n.d.	n.d. 0.002)		
Dibenzo[a	i,i]pyrene (DiP)	3603 (LOD: 20)	n.d.	n.d.	n.d.	n.d. 0.002)		
Dibenzo[a	,l]pyrene (DIP)	1277 (LOD: 20)	n.d.	n.d.	n.d.	n.d. 0.002)		
	8 REACH PAH	183846	65.48	303.19	14.65	67.84		
Sum	15 + 1 EU PAH	520313	178.13	701.81	39.86	157.04		
	16 EPA PAH	862075	558.32	2231.52	124.93	499.33		

Table 13: Concentration within the material as well as migration onto Tenax® using a contact time of 24 hours and 10 day at 40° Celsius.

Remark ¹: Values with regard to the concentration in μ g per kg in the samples. Remark ²: Values with regard to migration of the analyte in μ g per kg sample. Remark ³: Values with regard to migration of the analyte in μ g per dm² sample.

n.d.: not detectable , LOD: limit of detection

Compound		Sample 4: granulate "Recycled tyre- granulate"	Sample 5: granulate "EPDM- Granulate"	Sample 6: extender oil "Tudalen 65"	Sample 7: extender oil "Catenex T 145"
			Concentration w [µg/	ithin the material ˈkg] ¹	
Naphthale	ene (Naph)	190.9 (LOD: 5)	327.8 (LOD: 5)	1881 (LOD: 50)	n.d. <i>(LOD: 500)</i>
Acenapht	hylene (Aceny)	725.0 (LOD: 5)	335.1 (LOD: 5)	471.5 (LOD: 50)	n.d. <i>(LOD: 200</i>)
Acenapht	hene (Acen)	71.6 (LOD: 5)	38.3 (LOD: 5)	498.2 (LOD: 50)	n.d. <i>(LOD: 200</i>)
Fluorene ((FLO)	179.8 (LOD: 5)	113.7 (LOD: 5)	477.8 (LOD: 50)	n.d. <i>(LOD: 100</i>)
Phenanth	rene (PHE)	4529 (LOD: 5)	514.7 (LOD: 5)	4376 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Anthracer	ne (A)	796.1 (LOD: 5)	60.8 (LOD: 5)	600.4 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Fluoranth	ene (FLU)	7927 (LOD: 5)	477.2 (LOD: 5)	594.7 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Pyrene (P)	YR)	26812 (LOD: 5)	1546.6 (LOD:5)	13014 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Benzo[c]fluorene (BcL)		551.7 (LOD: 5)	n.d. <i>(LOD: 20</i>)	21487 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Cyclopenta[cd]pyrene (CPP)		3656 (LOD: 5)	n.d. <i>(LOD: 15)</i>	17029 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Benzo[a]anthracene (BaA)		631.9 (LOD: 5)	n.d. <i>(LOD: 5</i>)	4666 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Chrysene (CHR)		1415 (LOD: 5)	n.d. <i>(LOD: 5</i>)	22910 (LOD: 50)	n.d. <i>(LOD: 50</i>)
5-Methylchrysene (5MC)		879.9 (LOD: 5)	n.d. <i>(LOD: 5</i>)	48417 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Benzo[b]fluoranthene (BbFA)		903.3 (LOD: 5)	n.d. <i>(LOD: 10</i>)	n.d. <i>(LOD: 2000)</i>	n.d. <i>(LOD: 50</i>)
Benzo[k]f	luoranthene (BkFA)	173.7 (LOD: 5)	n.d. <i>(LOD: 5</i>)	8086 (LOD:2000)	n.d. <i>(LOD: 50</i>)
Benzo[j]fl	uoranthene (BjFA)	334.4 (LOD: 5)	n.d. <i>(LOD: 5</i>)	n.d. <i>(LOD: 2000)</i>	n.d. <i>(LOD: 50</i>)
Benzo[e]p	yrene (BeP)	2943 (LOD: 5)	n.d. <i>(LOD: 50)</i> 26679 (LOD: 5		n.d. <i>(LOD: 50</i>)
Benzo[a]p	yrene (BaP)	999.9 (LOD: 5)	n.d. <i>(LOD: 50</i>)	5194 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Indeno[1,2	2,3-cd]pyrene (IcP)	333.1 (LOD: 5)	n.d. <i>(LOD: 5</i>)	855.5 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Dibenz[a,h]anthracene (DBAhA)		n.d. <i>(LOD: 5)</i>	n.d. <i>(LOD: 20</i>)	2365.4 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Benzo[g,h,i]perylen (BghiP)		6507 (LOD: 5)	n.d. <i>(LOD: 5)</i>	29185 (LOD: 50)	n.d. <i>(LOD: 50</i>)
Dibenzo[a,e]pyrene (DeP)		n.d. <i>(LOD: 20)</i>	n.d. <i>(LOD: 20</i>)	n.d. <i>(LOD: 200</i>)	n.d. <i>(LOD: 200</i>)
Dibenzo[a	n,h]pyrene (DhP)	n.d. <i>(LOD: 20)</i>	n.d. <i>(LOD: 20</i>)	1061 (LOD: 200)	n.d. <i>(LOD: 200</i>)
Dibenzo[a	ı,i]pyrene (DiP)	n.d. <i>(LOD: 50)</i>	n.d. <i>(LOD: 20</i>)	2619 (LOD: 200)	n.d. <i>(LOD: 200</i>)
Dibenzo[a	ı,l]pyrene (DIP)	n.d. <i>(LOD: 50)</i>	n.d. <i>(LOD: 20</i>)	496.5 (LOD: 200)	n.d. <i>(LOD: 200</i>)
<u>Cump</u>	8 REACH PAH	7401.1	n.d.	69901	n.d.
Sum	16 EPA PAH	52195	3414.3	95176	n.d.

Table 14: PAH-concentration within the material

Remark $^1\!\!:$ Values with regard to the concentration in μg per kg in the samples. n.d.: not detectable $\,$, LOD: limit of detection

5.5 Discussion of the results

The performed experiments on rubber mat Sample 1 "rubber mat Sample A, Recycled tyre granulate, Stearic acid, Catenex T 145" and Sample 2 "rubber mat Sample B, EPDM-Granulate, Chemba 3, Tudalen 65" showed that the percentage of migrated PAH is very low compared to the initial concentrations within the material (i.e. the migration potential). Furthermore for semivolatile PAH like Benzo[e]pyrene and benzo[a]pyrene it could be demionstrated that the migration rates are lower for the PAH deriving from the recycled tyre granulate itself compared to extender oil.

The limits of detection of the migration experiments that were reached are sufficient for further analyses. The rubber mat sample 3 "Sample C, unknown product of non-european origin", a heavily PAH-contaminated product with an unknown producer, was used for worst-case investigations.

6 Influence of the material thickness on the migration behavior

6.1 Methological approach

To investigate the influence of the material thickness on the migration behaviour mats (Safety tiles) made from identical material were analysed in 3 mm and 10 mm thickness.

6.2 Samples

Table 15: Investigated samples

Sample		Description Description		
	3 Safety tiles 3 mm made of rubber fibers			
Number	5	Safety tiles 10 mm made of rubber fibers		

6.3 Results

Compound	Safety tiles 3 n Mig	Sample 3: nm made of r ration per are [µg/dm ²]	ubber fibers ea	Sample 5: Safety tiles 10 mm made of rubber fibers Migration per area [µq/dm ²]		
	1 d / 20 °C	10 d / 40 °C	10 d / 60 °C	1 d / 20 °C	10 d / 40 °C	10 d / 60 °C
Benzo[a]anthracene (BaA)	< LOD (LOD: 0.002)	0.116 (LOD: 0.002)	0.307 (LOD: 0.002)	0.016 (LOD: 0.006)	0.09 (LOD: 0.006)	0.322 (LOD: 0.006)
Chrysene (CHR)	< LOD (LOD: 0.002)	0.151 (LOD: 0.002)	0.413 (LOD: 0.002)	0.008 (LOD: 0.006)	0.121 (LOD: 0.006)	0.422 (LOD: 0.006)
Benzo[b]fluoranthene (BbFA)	< LOD (LOD: 0.002)	0.003 (LOD: 0.002)	0.045 (LOD: 0.002)	< LOD (LOD: 0.006)	0.008 (LOD: 0.006)	0.046 (LOD: 0.006)
Benzo[k]fluoranthene (BkFA)	< LOD (LOD: 0.002)	< LOD (LOD: 0.002)	0.025 (LOD: 0.002)	< LOD (LOD: 0.006)	< LOD (LOD: 0.006)	< LOD (LOD: 0.006)
Benzo[j]fluoranthene (BjFA)	< LOD (LOD: 0.002)	0.009 (LOD: 0.002)	0.029 (LOD: 0.002)	< LOD (LOD: 0.006)	0.008 (LOD: 0.006)	0.018 (LOD: 0.006)
Benzo[e]pyrene (BeP)	< LOD (LOD: 0.002)	0.013 (LOD: 0.002)	0.108 (LOD: 0.002)	< LOD (LOD: 0.006)	0.014 (LOD: 0.006)	0.113 (LOD: 0.006)
Benzo[a]pyrene (BaP)	< LOD (LOD: 0.002)	0.003 (LOD: 0.002)	0.043 (LOD: 0.002)	< LOD (LOD: 0.006)	0.009 (LOD: 0.006)	0.035 (LOD: 0.006)
Dibenz[a,h]anthracene (DBAhA)	< LOD (LOD: 0.002)	< LOD (LOD: 0.002)	< LOD (LOD: 0.002)	< LOD (LOD: 0.006)	< LOD (LOD: 0.006)	< LOD (LOD: 0.006)
Sum of migrated PAH	< LOD	0.295	0.970	0.024	0.245	0.956

Table 16: Migration per area onto Tenax® for variable material thickness

6.4 Discussion of the results

The comparison of the migration behavior between safety tiles of differing thickness (3 mm and 10 mm) showed that not the total amount of PAH is the main influence factor for migration, it is the contact area. This is clearly visible especially at migration conditions 10 d / 60° C. The sum of migrated PAH per area is 0.970 bzw. 0.956 µg/dm² although the thickness differs by a factor of 3.

7 Comparison of migration experiments with Tenax and 20 % Ethanol

7.1 Methological approach

A comparison between migration experiments with Tenax and 20% Ethanol.was performed. Experiments for 20 % ethanol were performed according to N. Bartsch, J. Heidler, B. Vieth, C. Hutzler & A. Luch (2016) Skin permeation of polycyclic aromatic hydrocarbons: A solvent-based in vitro approach to assess dermal exposures against benzo[a]pyrene and dibenzopyrenes. Journal of Occupational and Environm. Hygiene, 13:12. 969-979. DOI:10.1080/15459624.2016.1200724. Bartsch et al. noted that "... the usage of 20% ethanol as simulant revealed good agreement to the actual exposure of human skin against B[a]P migrating out of contaminated products." Conditions for the experiments were 24h, 37°C.

Conditions at Fraunhofer were chosen as 24 h, 40 °C whichmight increase migration values slightly.

7.2 Samples

Table 17: Investigated samples

Sample		Description
Number	1	Rubber mat "Fitnessstudiobelag: 6 mm"
Number	2	Rubber mat "Estrichdämmung: 17 mm"





Graph 3: Sample 1 and 2

7.3 Method description

7.3.1 Migration onto Tenax® As described in chapter 4.

7.3.2 Migration in 20 % ethanol/water

Simulans medium:	20 % Ethanol/Water
Contact time/temperature:	24 h / 40 °C Sample 1 and 2
Contact area/Volumen:	0.19 dm ² / 22 ml 20 % ethanol/water Sample 1 0.26 dm ² / 22 ml 20 % ethanol/water Sample 2
Contact weight:	3.3 g Sample 1 and 2

The samples were immersed in appropriate glass vials (full contact) in 20 % ethanol/water and stored for 24 hours at 40° Celsius. Every sample was weighed and the complete surface area was calculated (including the cutting edges !). After end of the contact time migration contact was stopped.

7.3.3 Clean-up and GC-MS-analysis

The migration solutions were extracted against n-Hexane (Liquid Liquid Extraktion; LLE) and the n-hexane fraction was evaporated to 1 ml and analysed via GC-MS, evaporated with a gentle nitrogen flow to 1 ml and analysed by GC-MS in duplicate.

7.3.4 Handling of internal standard

For quantification an isotope-labelled PAH-Standard-Mix (internal standard) is used. Performing migration experiments the addition of internal standard before the start of the experiment may lead to a loss of internal standard within the sample material itself. This may overestimate migration. This assumption is backed up by the results of recovery experiments with internal standards.

	d10-Pyrene	d12-	d12-	d12-	
		Benzo[a]pyrene	Perylene	Benzo[a]perylene	
Fitnessstudiobeläge 6 mm	28.4 %	75.3 %	104.0 %	70.7 %	
Estrichdämmung 17 mm	5.4 %	16.1 %	27.8 %	19.9 %	

 Table 18: Recovery of internal standard

It is therefore recommended to add the standard after the end of the contact time. An additional "recovery standard" might improve the quality of the analysis.

7.4 Concentration within the material and migration of PAH

			Rubber mat	Sample 1:	lag: 6 mm"	
Commonweal			Migratio	on onto	Migration in 20 %	
Com	pound	Conc.	Ter	nax	Ethano	l/Water
		[µg/kg] ¹	per weight	per area	per weight	per area
			[µg/kg] ²	[µg/dm²] ³	[µg/kg] ²	[µg/dm²] ³
Naphthalene (Naph)	1104.1	222.96	12.90	49.2	0.86
1 .	1 1	(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Acenaphthyler	ne (Aceny)	(100:5)		6.29	262.99 (LOD: 0.01)	4.59 (100:001)
		799.3	(LOD. 0.07) 42 35	2.45	(LOD. 0.01) 72 32	(LOD. 0.07) 1 26
Acenaphthene	(Acen)	(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
		789.3	42.99	2.49	68.95	1.20
Fluorene (FLO)		(LO <i>D: 5)</i>	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Phenanthren (PHF)	9442.2	158.67	9.18	376.41	6.57
	,	(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Anthracen (A)		1397.9	21.39	1.24	32.16	
		8706.7	(LOD. 0.01) 29 38	(LO <i>D.</i> 0.07) 1 70	(LOD: 0.07) 56 91	(LOD. 0.07)
Fluoranthene ((FLU)	(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
		21686	61.19	3.54	140.54	2.45
Pyrene (PYR)		(LO <i>D: 5)</i>	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzolcifluore	ne (Rcl.)	873.5	1.95	0.11	6.48	0.11
Denzolejnuore		(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Cyclopenta[cd]	pyrene (CPP)	3157.8	0.62	0.04	6.29	0.11
		(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzo[a]anthra	Benzo[a]anthracene (BaA)		(100.001)	(100.02)	$(1 \cap D^{*} \cap O^{1})$	$(1 \cap D^{*} \cap O^{*})$
	\ \	4098.7	0.23	0.01	0.25	0.01
Chrysene (CHR	Chrysene (CHR)		(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
5-Methylchryse	ene (5MC)	316.9	n.d.	n.d.	n.n	n.n
, ,	. ,	(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzo[b]fluoranthene (BbFA)		(LOD: 5)	(LO <i>D: 0.01</i>)	(LO <i>D: 0.01</i>)	(LOD: 0.01)	(LOD: 0.01)
Popzo[k]fluora	nthong (PkEA)	522.0	n.d.	n.d.	n.n	n.n
Benzo[k]nuora	Inthene (BKFA)	(LO <i>D: 5)</i>	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzo[j]fluora	nthene (BjFA)	1135.7	n.d.	n.d.	n.n	n.n
		(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Benzo[e]pyren	e (BeP)	(IOD: 5)	$(I \cap D^{*} \cap O^{*})$	$(I \cap D^{*} \cap O 1)$	(I OD: 0 01)	(100, 0, 0, 0, 1)
	(0, 0)	2471.0	n.d.	n.d.	n.n	n.n
Benzo[a]pyren	e (BaP)	(LO <i>D: 5</i>)	(LO <i>D: 0.01)</i>	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Indeno[1.2.3-co	dløvrene (IcP)	1097.3	n.d.	n.d.	n.d.	n.d.
Dihan-la hlant	hracana	(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
(DRAhA)	Inracene	(10D: 5)	$(1 \cap D^{*} \cap O^{*})$	$(1 \cap D^{*} \cap O^{*})$	$(1 \cap D^{*} \cap O^{*})$	$(1 \cap D^{*} \cap O^{*})$
		13054	n.d.	n.d.	n.d.	n.d.
Benzo[g.h.i]pe	rylene (BghiP)	(LOD: 5)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)	(LOD: 0.01)
Dibenzo[a.e]p	/rene (DeP)	n.d.	n.d.	n.d.	n.d.	n.d.
21261120[010]p]		(LOD: 20)	(LOD: 0.04)	(LOD: 0.04)	(LOD: 0.04)	(LOD: 0.04)
Dibenzo[a.h]py	/rene (DhP)	n.d. (LO <i>D: 20</i>)	n.d. (LO <i>D: 0.04</i>)	n.d. (LOD: 0.04)	n.d. (LO <i>D: 0.04)</i>	n.d. (LOD: 0.04)
Dibenzo[a.i]py	rene (DiP)	n.d. (LO <i>D· 20</i>)	n.d. (LO <i>D[.] 0 04</i>)	n.d. (LOD: 0.04)	n.d. (LO <i>D[.] 0 04</i>)	n.d. (LOD: 0.04)
		n.d.	n.d.	n.d.	n.d.	n.d.
Ulbenzo[a.l]py	rene (DIP)	(LOD: 20)	(LOD: 0.04)	(LOD: 0.04)	(LOD: 0.04)	(LOD: 0.04)
	8 REACH PAH	21503	0.55	0.03	0.25	0.01
Sum	15 + 1 EU PAH	32497	3.13	0.18	13.01	0.23
	16 EPA PAH	72664	688.28	39.82	1059.7	18.49

Table 19: Concentration within the material as well as migration onto Tenax®. and 20 % ethanol/water using a contact time of 24 hours at 40° Celsius .

Remark ¹: Values with regard to the concentration in μ g per kg in the Samples. Remark ²: Values with regard to migration of the analyte in μ g per kg Samples. Remark ³: Values with regard to migration of the analyte in μ g per dm² Samples.

n.d.: not detectable . LOD: limit of detection

	Sample 2:							
		Rubber mat "Estrichdämmung: 17mm"						
Compound	Conc.	Migration	onto Tenax	Migration in 20 % Ethanol/Water				
	[µg/kg] ¹	per weight [µg/kg] ²	per area [µg/dm²] ³	per weight [µg/kg] ²	per area [µg/dm²] ³			
Naphthalene (Naph)	534.1 (LOD: 5)	72.02 (LOD: 0.01)	5.68 (LOD: 0.002)	7.80 (LOD: 0.01)	0.10 (LOD: 0.001)			
Acenaphthylene (Aceny)	1234 (LOD: 5)	94.70 (LO <i>D: 0.01)</i>	7.47 (LOD: 0.002)	182.71 (LO <i>D: 0.01)</i>	2.35 (LO <i>D: 0.001)</i>			
Acenaphthene (Acen)	1027 * (LOD: 5)	29.56 (LO <i>D: 0.01)</i>	2.33 (LO <i>D: 0.002)</i>	47.89 (LO <i>D: 0.01)</i>	0.61 (LOD: 0.001)			
Fluoren (FLO)	726.4 (LOD: 5)	59.95 (LOD: 0.01)	4.73 (LOD: 0.002)	54.73 (LOD: 0.01)	0.70 (LOD: 0.001)			
Phenanthren (PHE)	8652 (LOD: 5)	242.96 (LOD: 0.01)	19.15 (LOD: 0.002)	314.66 (LOD: 0.01)	4.04 (LOD: 0.001)			
Anthracen (A)	1243 (LOD: 5)	30.63 (LOD: 0.01)	2.41 (LOD: 0.002)	23.15 (LOD: 0.01)	0.30 (LOD: 0.001)			
Fluoranthene (FLU)	7583 (LOD: 5)	37.20 (LOD: 0.01)	2.93 (LOD: 0.002)	453.19 (LOD: 0.01)	5.82 (LOD: 0.001)			
Pyrene (PYR)	19778 (LOD: 5)	71.92 (LOD: 0.01)	5.67 (LOD: 0.002)	979.12 (LOD: 0.01)	12.57 (LOD: 0.001)			
Benzo[c]fluoren (BcL)	850.5 (LOD: 5)	2.31 (LOD: 0.01)	0.18 (LOD: 0.002)	32.39 (LOD: 0.01)	0.42 (LOD: 0.001)			
Cyclopenta[cd]pyrene (CPP)	3117 (LOD: 5)	0.96 (LOD: 0.01)	0.08 (LOD: 0.002)	393.14 (LOD: 0.01)	5.05 * (LOD: 0.001)			
Benzo[a]anthracene (BaA)	1525 (I O/D: 5)	0.61	0.05	2.66	0.03			
Chrysene (CHR)	1774	0.74	0.06	3.35	0.04			
5-Methylchrysene (5MC)	451.1 (LOD: 5)	0.05 n.d. (LOD: 0.01) (LOD: 0.002)		n.n (I OD: 0.01)	n.n (I OD: 0.001)			
Benzo[b]fluoranthene (BbFA)	939.3 (LOD: 5)	n.d.	n.d.	n.n (LOD: 0.01)	n.n (LOD: 0.001)			
Benzo[k]fluoranthene (BkFA)	219.8	n.d.	n.d.	n.n	n.n			
Benzo[j]fluoranthene (BjFA)	475.6	n.d.	n.d.	n.n	n.n			
Benzo[e]pyrene (BeP)	2938 (LOD: 5)	0.05	n.d.	n.n	n.n			
Benzo[a]pyrene (BaP)	899.8	n.d.	(LOD: 0.002) n.d.	(LOD: 0.01) n.n	n.n			
Indeno[1.2.3-cd]pyrene (IcP)	(LOD: 5) 192.1	n.d.	n.d.	(LOD: 0.01) n.d.	n.d.			
Dibenz[a.h]anthracene	45.8	(LOD: 0.01) n.d.	n.d.	(LOD: 0.01) n.d.	n.d.			
Benzo[g.h.i]perylene (BghiP)	4258	(LOD: 0.01) 0.05	(LOD: 0.002) n.d.	(LOD: 0.01) n.d.	n.d.			
Dibenzo[a.e]pyrene (DeP)	n.d. (LOD: 20)	n.d. (LO <i>D: 0.04</i>)	n.d. (LO <i>D: 0.002)</i> (LO <i>D: 0.003</i>)	n.d. (LO <i>D: 0.04</i>)	n.d. (LO <i>D: 0.001)</i> (LO <i>D: 0.001</i>)			

Table 20: Concentration within the material as well as migration onto Tenax $\mbox{@}$. and 20 % ethanol/water using a contact time of 24 hours at 40° Celsius .

Table 20 - continued

Dibenzo[a.h]pyrene (DhP)		n.d.	n.d.	n.d.	n.d.	n.d.
		(LO <i>D: 20</i>)	(LO <i>D: 0.04)</i>	(LOD: 0.003)	(LO <i>D: 0.04)</i>	(LOD: 0.001)
Dibenzo[a.i]pyrene (DiP)		n.d.	n.d. <i>n.d.</i>		n.d.	n.d.
		(LO <i>D: 20</i>)	(LOD: 0.04) (LOD: 0.003)		(LO <i>D: 0.04)</i>	(LOD: 0.001)
Dibenzo[a.l]pyrene (DIP)		n.d.	n.d.	n.d.	n.d.	n.d.
		(LO D: 20)	(LO <i>D: 0.04)</i>	(LOD: 0.003)	(LO <i>D: 0.04)</i>	(LOD: 0.001)
	8 REACH PAH	8818	1.39	0.11	6.01	0.08
Sum	15 + 1 EU PAH	5 + 1 EU PAH 14748		0.37	431.54	5.54
	16 EPA PAH	50631	640.3	50.48	2069.3	26.56

Remark ¹: Values with regard to the concentration in μ g per kg in the Samples. Remark ²: Values with regard to migration of the analyte in μ g per kg Samples. Remark ³: Values with regard to migration of the analyte in μ g per dm² Samples. n.d.: not detectable . LOD: limit of detection, * Coelution

7.5 Discussion of the results

There is a good coincidence between the migration experiments into 20 % ethanol/water (Bartsch et al.. 2016) and Tenax using a contact time of 24 hours at 40 ° Celsius especially for semivolatile PAHs.

Both migration experiments show that they do not achieve the theoretical migration potential (total mass transfer). Therefore "worst case"-assumptions based on total mass transfer are highly overestimative (and lead to a completely unrealistic) migration estimation.

This shows a comparison in Graph 4, where the results of both migration experiments for acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[c]fluorene, cyclopenta[cd]pyrene and benzo[a]anthracene are given. Naphthalene was not included in the graph due to his ubiquity in the environment; other PAH compounds were below or near LOD in this case.



Graph 4: Tenax-Migration versus Migration in 20% EtOH for Fitnessstudiobelag 6 mm

The comparison of Tenax-Migration versus Migration in 20 % EtOH show a linear correlation with $R^2 = 0.9837$. For Estrichdämmung 17 mm this is not as distinct. The influence of the bigger cutting edges and "soaking effects" may cause this effects.

It is imprtant to note that both migration experiments do not achieve the theoretical migration potential (total mass transfer). Therefore "worst case"-assumptions based on total mass transfer are highly overestimative (and lead to a completely unrealistic) migration estimation.

Work is ongoing at Fraunhofer IVV to predict the migration behaviour of PAH.

8 Investigation of further samples for REACH-PAH

8.1 Fitnessstudiobelag (Safety tiles for fitness studios), 6 mm

The concentration within the material and migration onto Tenax® as well as 20 % ethanol/water was investigated using a contact time of 24 hours at 40° Celsius.

Description				
Sample	Rubber mat "Fitnessstudiobelag: 6 mm"			

Table 21: Investigated	sample material
------------------------	-----------------



Graph 5: Sample "Fitnessstudiobelag, 6 mm"

Table 22: Concentration within the material and migration onto Tenax® as well as 20 % ethanol/water using a contact time of 24 hours at 40° Celsius .

		Sample: Rubber mat "Fitnessstudiobelag: 6 mm"					
Compound		Conc. within	Migratio	on onto	Migration in 20 %		
		the Material	Ter	nax	ethanol/water		
		[µg/kg] ¹	per weight [µg/kg] ²	per area [µg/dm²] ³	per weight [µg/kg] ²	per area [µg/dm²] ³	
Benzo[a]anthrace	ene (BaA)	1169 (LO <i>D: 5</i>)	0.19 (LO <i>D: 0.2)</i>	0.01 (LO <i>D: 0.01)</i>	n.d. (LO D: 0.2)	n.d. <i>(LOD: 0.01)</i>	
Chrysen (CHR)		22679 (LO <i>D: 5</i>)	0.37 (LO <i>D: 0.2)</i>	0.02 (LOD: 0.01)	1.05 (LO <i>D: 0.2)</i>	0.02 (LOD: 0.01)	
Benzo[b]fluoranthene (BbFA)		1616.2	n.d. n.d.		n.d.	n.d.	
		(LO <i>D: 5</i>)	(LO <i>D: 0.2)</i> (LO <i>D: 0.01)</i>		<i>(LOD: 0.2)</i>	(LOD: 0.01)	
Benzo[k]fluoranthene (BkFA)		232.3	n.d.	n.d.	n.d.	n.d.	
		(LO <i>D: 5</i>)	(LO <i>D: 0.2)</i>	(LO <i>D: 0.01)</i>	(LO <i>D: 0.2</i>)	(LOD: 0.01)	
Benzo[j]fluoranth	iene (BjFA)	490.6 (LO <i>D: 5)</i>	n.d. (LO <i>D: 0.2)</i>	n.d. (LO <i>D: 0.01)</i>	n.d. <i>(LOD: 0.2)</i>	n.d. (LO D: 0.01)	
Benzo[e]pyrene (BeP) 5940		n.d.	n.d.	n.d.	n.d.	
	(LOD: 5)		(LO <i>D: 0.2)</i>	(LO <i>D: 0.01)</i>	<i>(LOD: 0.2)</i>	(LO D: 0.01)	
Benzo[a]pyrene (BaP)		2018	n.d. n.d.		n.d.	n.d.	
		(LO <i>D: 5</i>)	(LO <i>D: 0.2</i>) (LO <i>D: 0.01</i>)		<i>(LOD: 0.2)</i>	(LO D: 0.01)	
Dibenz[a.h]anthracene		52.6	n.d.	n.d.	n.d.	n.d.	
(DBAhA)		(LO <i>D: 5</i>)	(LO <i>D: 0.2)</i>	(LO <i>D: 0.01)</i>	(LO <i>D: 0.2</i>)	(LO <i>D: 0.01)</i>	
Sum	8 REACH PAH	13787	0.56	0.04	1.05	0.02	

Remark ¹: Values with regard to the concentration in μ g per kg in the Samples. Remark ²: Values with regard to migration of the analyte in μ g per kg Samples.

Remark ³: Values with regard to migration of the analyte in µg per dm² Samples.

n.d.: not detectable . LOD: limit of detection

8.2 Fallschutzplatte (Safety tile, red-brown, 45 mm)

The concentration within the material as well as migration onto Tenax and 20 % ethanol/water was investigatedt

Table 23: Investigated sample material

Description					
Sample	Rubber mat "Fallschutzplatte. rotbraun. 45 mm"				



Graph 6: "Fallschutzplatte. rotbraun. 45 mm"

	Sample: Rubber mat "Fallschutzplatte. rotbraun. 45 mm"						
		Migration onto Tenax at 24h, 40° C				Migration in 20 % Ethanol at 24 h, 40° C	
Compound	Material content	per weight [µg/kg] ²		per area [µg/dm²] ³		per	per area
	[µg/kg] '	24 h	10 d	24 h	10 d	weight [µg/kg] ²	[µg/dm²] ³
Benzo[a]anthracene (BaA)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chrysene (CHR)	119	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	183	n d	n d	n d	: 0.02 n d	<i>LOD: 0.1</i> n d	<i>LOD: 0.01</i> n d
Benzo[b]fluoranthene (BbFA)	LOD: 50	LOE): 0.05	LOD	: 0.02	LOD: 0.1	LOD: 0.01
Benzo[k]fluoranthene (BkFA)	n.d. <i>LOD: 50</i>	n.d. LOE	n.d. D: 0.05	n.d. LOD	n.d. : 0.02	n.d. <i>LOD: 0.1</i>	n.d. LOD: 0.01
Benzo[j]fluoranthene (BjFA)	n.d. <i>LOD: 50</i>	n.d. LOE	n.d. D: 0.05	n.d. LOD	n.d. : 0.02	n.d. LOD: 0.1	n.d. LOD: 0.01
Benzo[e]pyrene (BeP)	1028 LOD: 10	n.d. LOE	n.d. D: 0.05	n.d. LOD	n.d. : 0.02	n.d. LOD: 0.02	n.d. LOD:0.005
Benzo[a]pyrene (BaP)	423 LOD: 10	n.d. LOE	n.d. D: 0.05	n.d. LOD	n.d. : 0.02	n.d. LOD: 0.02	n.d. LOD:0.005
Dibenz[a.h]anthracene (DBAhA)	n.d. <i>LOD: 20</i>	n.d. LOE	n.d. D: 0.05	n.d. LOD	n.d. : 0.02	n.d. LOD: 0.05	n.d. LOD: 0.01
Sum 8 REACH PAH	1752	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 24: Concentration within the material as well as migration onto Tenax® and 20 % ethanol/water

Remark ¹: Values with regard to the concentration in μ g per kg sample. Remark ²: Values with regard to migration of the analyte in μ g per kg sample. Remark ³: Values with regard to migration of the analyte in μ g per dm² sample. Remark ⁴: influence of blank values n.d.: not detectable . LOD: limit of detection

8.3 Evaluation of the results of further samples

The sum of 8 REACH-PAH in the material "Fitnessstudiobelag: 6 mm" was 13787 μ g/kg. The main compounds were chrysene (CHR) with 2267, benzo[e]pyrene (BeP) with 5940 and benzo[a]pyrene (BaP) with 2017 μ g/kg. The results for migration tests (both Tenax and 20 % ethanol/water) were below or nearby the LOD (limit of detection).

The sum of 8 REACH-PAH in the material "Fallschutzplatte (rotbraun. 45 mm)" was 1752 μ g/kg. The main compounds were benzo[e]pyrene (BeP) with 1028 and benzo[a]pyrene (BaP) with 423 μ g/kg. The results for migration tests (both Tenax and 20 % ethanol/water) were below the LOD (limit of detection).

9 Summary

The analytical method for the total content of PAH in the material was applied to a widevariation of rubber materials. The use of cyclohexane as solvent for the ASE reduces matrix problems compared to the use of toluene. The Fraunhofer IVV method for the PAH analysis of rubber material based on ASE leads to reduced matrix problems.

Based on current literature and norms two methods of migration experiments were developped and evaluated:

- Migration onto Tenax
- Migration in 20 % Ethanol

The comparison of the migration behavior between safety tiles of differing thickness (3 mm and 10 mm) shows that not the total amount of PAH is the main influence factor for migration, it is the contact area. This is clearly visible especially at stronger migration conditions like 10 d / 60 °C.

Experiments for 20 % ethanol were performed according to Bartsch et al. 2016. They noted that "... the usage of 20 % ethanol as simulant revealed good agreement to the actual exposure of human skin against B[a]P migrating out of contaminated products." Contact conditions were 24h, 37 °C

There is a good coincidence between the migration experiments into 20 % ethanol/water (Bartsch et al.. 2016) and Tenax using a contact time of 24 hours at 40° Celsius. Both migration experiments seem to be adequate testing methods for the risk evaluation of rubber materials.

Results for both types migration experiments show that they do not achieve the theoretical migration potential (total mass transfer). Therefore "worst case"-assumptions based on total mass transfer are highly overestimative (and lead to a completely unrealistic) migration estimation. The modelling of the migration processes is ongoing work at Fraunhofer IVV. This is an important issue because by end of 2017, the European Commission shall 'review the limit values in paragraphs 5 and 6 in the light of new scientific information, including migration of PAH from the articles referred to therein, and information on alternative raw materials and, if appropriate, modify these paragraphs accordingly.'

In general both types of migration experiments seem to be adequate testing methods for a realistic risk evaluation of rubber materials. At the moment there is a lack of methods for rubber materials like they exist in Regulation 10/2011 (Plastics Implementation Measure, PIM) for plastics in food contact. Both types of migration experiments seem to be applicable. Thick materials might be sometimes problematic for the experiments with 20% ethanol due to problems with cutting edges (due to *"Total* immersion*"*)

A toxicological risk evaluation is not task of the project and needs further works of experts. For a first orientation it is possible to use existing guidelines for benzo[a]pyrene. There is an oral reference dose of the EPA (US Environmental Protection Agency) for drinking water (2012 Edition of the Drinking Water Standards and Health Advisories). For benzo[a]pyrene the maximum allowable concentration is 0.2 μ g/L (200 ng/L).

Under the worst case assumption that the external exposition leeds to an equivalent internal exposition and the external exposition is completely bioavailable in the human body this oral reference dose of the EPA can be used for evaluation. The following experiments were used for this scenario: Migration results of PU-coated rubber mats with a contact time of 10 d / 40 °C (see table 8) and for 2 types of rubber mats "Fitnessstudiobelag: 6 mm" with a contact time of 1 d / 40 °C (see table 19 und 22)

Contact times are conservative because 30 - 60 minutes of contact are more realistic. The migration of benzo[a]pyrene (assumption: similar to skin transfer) was not detectable with a limit of detection of 0.01 µg/dm².

Assuming a skin area of 6 dm² (e.g. both hands) in contact with the rubber mat the maximum internal exposition would be 0.06 μ g/person. This equates to a concentration of 0.06 μ g/kg benzo[a]pyrene in water for a consumtion of 1 L per day. This means a factor 3.3 below the EPA values in this very conservative scenario.

10 Literature

Ausschuss für Technische Arbeitsmittel und Verbraucherprodukte (AtAV), 2008. ZEK 01-08 Prüfung und Bewertung von Polycyclischen Aromatischen Kohlenwasserstoffen (PAK) bei der GS-Zeichen-Zuerkennung.

Bartsch, N., Heidler, J., Vieth, B., Hutzler, C., Luch, A., 2016. Skin permeation of polycyclic aromatic hydrocarbons: A solvent-based in vitro approach to assess dermal exposures against benzo[a]pyrene and dibenzopyrenes. J Occup Environ Hyg 13, 969-979.

Bokkers, B.G.H., Guichelaar, S.K., Bakker, M.I., 2016. Assessment of the product limit for PAHs in rubber articles : The case of shock-absorbing tiles. RIVM, The Netherlands.

Celeiro, M., Lamas, J.P., Garcia-Jares, C., Dagnac, T., Ramos, L., Llompart, M., 2014. Investigation of PAH and other hazardous contaminant occurrence in recycled tyre rubber surfaces. Case-study: restaurant playground in an indoor shopping centre. Int J Environ an Ch 94, 1264-1271.

Ilvonen, O., 2013. Assessing release of hazardous substances from construction products- Review of 10 years of experience with a horizontal approach in the European Union. Building and Environment 69, 194-205.

Kalbe, U., Krüger, O., Wachtendorf, V., Berger, W., Hally, S., 2013. Development of leaching procedures for synthetic turf systems containing scrap tyre granules. Waste Biomass Valori 4, 745-757.

NIPH, 2006. Artificial turf pitches an assessment of the health risks for football players. Norwegian Institute of Public Health and the Radium Hospital,.

Oomen, A., Mennen, M., 2017. Evaluation of health risks of playing sports on synthetic turf pitches with rubber granulate. RIVM, The Netherlands.

Schilirò, T., Traversi, D., Degan, R., Pignata, C., Alessandria, L., Scozia, D., Bono, R., Gilli, G., 2013. Artificial turf football fields: Environmental and mutagenicity assessment. Archives of Environmental Contamination and Toxicology 64, 1-11.

Umweltbundesamt, 2016. Polyzyklische Aromatische Kohlenwasserstoffe -Umweltschädlich! Giftig! Unvermeidbar? Hintergrundreport. Umweltbundesamt, Dessau-Rosslau.

US EPA, 2012. 2012 Edition of the Drinking Water Standards and Health Advisories.

US EPA, 2016. Federal Research Action Plan on Recycled Tire Crumb Used on Playing Fields and Playgrounds.

Page 35 of 35 PA/4453/17 Fraunhofer IVV Report 06/12/2017

Acknowledgement

The following companies were involved in this R&D project in the years 2016/17 and provided samples for the project:

- Berleburger Schaumstoffwerk GmbH, 57319 Bad Berleburg
- Conradi+Kaiser GmbH, 56271 Kleinmaischeid
- Gummiwerk KRAIBURG Elastik GmbH & Co. KG, 84529 Tittmoning
- KRAIBURG Relastec GmbH & Co. KG. 29410 Salzwedel
- KRAIBURG Holding GmbH & Co. KG, 84478 Waldkraiburg
- PVP Triptis GmbH, 07819 Triptis

The project was performed in cooperation with the *wdk Wirtschaftsverband der deutschen Kautschukindustrie e.V.*,60487 Frankfurt am Main.