PROPOSAL FOR ASSESSMENT OF INDOOR AIR POLYCYCLIC AROMATIC HYDROCARBON (PAH)

C Zorn[*], M Köhler, N Weis and W Scharenberg

Bremer Umweltinstitut GmbH, Fahrenheitstraße 1, D-28359 Bremen

ABSTRACT

In indoor environment situations severe odour nuisances often limits or prevents use. This often is reason to check indoor Air PAH-contamination which mainly derive from a variety of building material containing coal tar constituents. Today the use of tar as an additive to wood-preservatives, solvents and building material is strongly restricted in Germany (GefStoffV) but other sources for similar odours are fire-events, asphalt and bitumen products. Using a modified VDI method 3875-1 including an additional sampling on Polyurethane-foam for analysing air-samples, very variable patterns of single PAH concentrations are obtained which correspond to the source-type. While high concentrations with naphthalene are regularly found indoors, not volatile and rather dust-borne PAH like Benzoapyrene (BaP) rarely occur in concentrations about 2 ng/m³. Some PAH have a very high carcinogenic potency in human, some smell intensively. However, as the absence of the characteristic smell does not implicate the absence of PAH, it cannot be used for remediation guidelines and health-concerns remain. For remediation official threshold guideline levels and remediation action criteria are needed. In this course a risk-assessment is proposed using PAH toxicity equivalence factors (TEF) against BaP. Multiplication with measured concentrations and summarising leads to the Cancerogenic Equivalence Sum (KE_{sum}). for the 16 measured PAH. Using data on the additional cancer risk through definite BaP-exposition in the PAH mixture of coking plant gas (unit risk) we can postulate a KE_{sum} of 1,36 for this gas. On a basis of this scaling we can quantify the additional cancer risk for various air samples. Accepted risks of 10^{-4} and $5 \cdot 10^{-4}$ lead to guideline values for successful remediation of KE_{sum} <= 2,0 and intervention of KE_{sum} >= 10.0. Case studies are shown where the scheme could successfully be applied as the main criteria for building remediations.

INDEX TERMS

Indoor air PAH, cancer risk assessment, TEF, remediation guideline

INTRODUCTION

Polycyclic aromatic hydrocarbons PAH are structurally derived from multiple benzene matrices. So far there could approximately be identified more than 200 PAH. PAH with boiling points up to 400°C usually consist of up to 4 condensed rings and can in particular be found in the gaseous phase while PAH with higher boiling points (400 - 550°C) and 4 - 6 condensed rings are more likely to occur in a particle-bound state. Toxicologically there is a special concern about PAH due to a remarkable carcinogenic potential of individual representatives. The American environmental protection authority EPA proposed to use a selection of 16 PAH which are frequently found in environmental monitoring samples as well as standard for assessment of indoor samples (EPA 1984). For comparability reasons also the formation of a total (PAH_{sum}) is common. PAH occur as a substantial content of hard coal tar-oil products. Through the production of tar from coal many different PAH are formed, while e.g. a careful processing from crude oil to bitumen or hydrocarbons (paraffin) yields only few PAH. From both bitumen and tar certain adhesives and other building materials were made (e.g. adehsives, paints and coatings, tarboards,...), which are more or less contaminated with PAH according to their origin. The use of these adhesives for instance represents a substantial cause for indoor air PAH contamination, since up to the 70's they were widely used under parquet-floorings. Nowadays PAH-containing tar is no longer in use for most purposes, while all remaining tar products indoors are still potential sources for indoor-air pollution with PAH (Köhler et al. 2001; Preuss et al. 2003). Hard-coal oil (Creosote, Carbolineum) itself is a strongly smelling impregnation oil, which was mainly used as insect repellent and wood preservative against mould in ambient areas. As a further source of PAH the incomplete combustion of organic material under oxygen deficiency can be named. This refers to exhaust gas (particularly of diesel fuel) as well as forest and domestic fire or cigarette smoke. Also smoked food contains PAH. Eventually an ubiquitous spreading of PAH results, so that the population is principally exposed to at least small

---

[*] corresponding autor email. zorn@bremer-umweltinstitut.de

proportions. For PAH the main focus regarding health-relevant effects lies within a possible cancer-risk. Historically this observations originates from certain working-places - coking plants, tar-processing industry and chimney sweeping, respectively - where persons are exposed to PAH to a much higher extent then in inhabited indoor-situations. But even in regular dwellings and public buildings indoor air concentrations can reach dimensions which must be regarded critical for health and require cautious assessment. So far in Germany there are no official threshold values, guideline levels or values of comparable objective for the assessment of PAH indoor air concentrations of variable PAH-content. Additionally there is a lack of toxicological knowledge for concrete evaluation of airborne PAH loads - with the exception of naphthalene[1]. In order to allow a health-based assessment, the Bremer Umweltinstitut suggests a concept which is in particular applicable in terms of remediation as it is shown, that the objectives are feasible even from a technical point of view.

METHOD

Especially in indoor inspections it must be considered that individual PAH rather occur in the gaseous state than particle-bound (i.e. dust-borne). Thus both the gaseous and the particle-bound airborne portion must be sampled and analysed. The used sampling-method according to former german standard VDI 3875-1 was advanced by additional adsorption at polyurethane-foam (Köhler et al. 2004). In this extended form it is suitable for the determination of all 16 EPA-PAH at regular indoor air levels. The detection limit lies in the range of 0.1-0.4 ng/m³ for each compound. It is however well-known that concerning the quite volatile naphthalene a loss by desorption during sampling must be expected. It is corrected by consideration of the recovery rate of ^{d8}naphthalene in each sample. The average recovery rate for this internal standard is approx. 25%.

ASSESSING INDOOR-AIR PAH USING CANCEROGENIC EQUIVALENCE SUM

Naturally PAH only occur in mixtures, since the formation processes do not lead to single compounds. If for a given type of PAH-mixture a fairly stable composition is observed, generally the inspection of a single component out of the total spectrum of PAH can be used as a simple and sufficient monitoring parameter. Thus BaP was selected as monitoring marker for environmental samples, due to its high and proven carcinogenic effect on human. The results of PAH-contamination levels given in

Table 1 have been obtained through 182 measurements during indoor inspections in 47 individual cases of the Bremer Umweltinstitut and corresponding outdoor controls (Zorn et al. 2005). The occurrence of PAH in air is determined by a variety of physical processes such as temperature, degradation rates, usage of rooms (Moriske 2002). Moreover in indoor environment the observed PAH-pattern is not homogenous, but strongly dependent on the type and strength of sources and the presence or absence of dust-borne contamination respectively (Köhler et al. 2001; Ohura et al. 2004). Often an intensive mixing of ambient- with outside-air is lacking. Particularly in the presence of certain emission sources this leads to a significantly different PAH-pattern indoors compared to outside air, as can be seen in

Table 1 by the remarkable width-span of individual PAH-contamination in indoor and outdoor air respectively. Relevant differences can be obtained for the somewhat volatile PAH like naphthalene, rather than for the more likely carcinogenic but only dust-borne PAH. Therefore guideline levels for a single compound are not appropriate for assessing the actual composition of air samples (Zorn et al. 2005).

Toxicological investigations showed a different cancerogenic potency for various PAH-mixtures, individual PAH and different application paths (oral, dermal and inhalative) which at present cannot be predicted quantitatively (Schneider et al. 2002). Of the 16 EPA-PAH analysed in this context some PAH - especially the slightly volatile ones - are not regarded cancerogenic. Within the remaining PAH there are substantial differences of potency in the size of several orders of magnitude - the most potent possibly being Benzo(a)pyrene BaP. Through several different studies it became evident that it is possible to specify the cancerogenic effect of individual PAH compared with BaP and to weight it by means of a conversion factor. These factors are called toxicity equivalence factors (**TEF**, Table 2).

Multiplying the TEF of each individual PAH with its actual indoor air concentration and summarising these 16 products yields a Cancerogenic Equivalence Sum (short KE_{sum}) of an air sample. There is an underlying assumption, that due to similar cancer provoking mechanisms cancerogenic potencies of PAH lead to a linear increase of risks and thus the concentration-weighted risks can be added. The KE_{sum} represents the inhalative

---

[1] a RW II value of 20 µg/m³ is published, giving the threshold value for indoor long-term exposition

cancerogenic potency caused by airborne-PAH and shall be used for further assessment.

Table 1. *182 indoor and 47 outdoor PAH-measurements of the Bremer Umweltinstitut.*

PAH		**Indoor** [ng/m³]				**Outdoor** [ng/m³]			
		min	median	90th percentile	max	min	median	90th percentile	max
Naphthalene	NAP	20	813	3 000	30 909	0.8	121	883	1 429
Acenaphthylene	ACY	<dl	10	82	3 200	<dl	2.6	14	37
Acenaphthene	ACE	0.5	29	308	4 800	<dl	4.2	73	98
Fluorene	FLU	0.5	34	169	1 700	<dl	5.5	33	60
Anthracene	PHE	0.6	109	509	5 500	3.5	12.0	65	410
Phenanthrene	ANT	<dl	9	45	420	<dl	1.1	11	14
Fluoranthene	FLA	<dl	9	47	470	<dl	2.7	16	28
Pyrene	PYR	<dl	6	25	200	<dl	2.1	11	15
Chrysene	BAA	<dl	0.5	2.8	56	<dl	<dl	2.4	3.2
Benzo[a]anthracene	CHR	<dl	0.5	3.2	120	<dl	0.4	2.9	4.7
Benzo[b]fluoranthene	BbF	<dl	0.5	3.1	110	<dl	0.5	2.9	4.7
Benzo[k]fluoranthene	BkF	<dl	0.5	1.4	110	<dl	0.4	2.2	4.6
Benzo[a]pyrene	BaP	<dl	0.5	2.1	21	<dl	<dl	2.5	5.0
Indeno[1.2.3-cd]pyrene	IND	<dl	0.5	1.4	30	<dl	0.5	4.1	5.0
Dibenzo[a.h]anthracene	DBA	<dl	0.5	1.5	11	<dl	0.5	2.7	5.0
Benzo[g.h.i]perylene	BgP	<dl	0.5	2.0	90	<dl	0.5	3.6	5.0
PAH$_{sum}$		**48**	**1 095**	**4 465**	**32 517**	**36**	**48**	**648**	**1 608**

Table 2. *Classification of the 16 EPA PAH (ordered by boiling point) regarding their carcinogenic potentials (MAK list DFG 2004, grey shading: carcinogenic PAH) and TEF. TEF I (Larsen and Larsen 1998), TEF II (Nisbeth and LaGoy 1992, Malcom and Dobson 1994) following Schneider et al. 2002. C_{PAH} taken from* ***Table 1****: medians and* $^{dl}/_{2}$.

PAH		MAK list III	RL 67/548/E WG app. I	toxicity equivalence factor		KE-medians of indoor air	KE-medians of outdoor air
				TEF I	TEF II	$C_{PAH} \cdot$ TEF II	$C_{PAH} \cdot$ TEF II
Naphthalene	NAP	2	K 3		0.001	0.813	0.121
Acenaphthylene	ACY				0.001	0.010	0.003
Acenaphthene	ACE				0.001	0.029	0.004
Fluorene	FLU				0.001	0.034	0.006
Anthracene	ANT			0.0005	0.001	0.109	0.012
Phenanthrene	PHE			0.0005	0.01	0.087	0.011
Fluoranthene	FLA			0.05	0.001	0.009	0.003
Pyrene	PYR			0.005	0.001	0.006	0.002
Benzo[a]anthracene	BAA	2	K 2	0.005	0.1	0.005	0.004
Chrysene	CHR	2	K 2	0.03	0.01	0.050	0.040
Benzo[k]fluoranthene	BkF	2	K 2	0.05	0.1	0.050	0.050
Benzo[b]fluoranthene	BbF	2		0.1	0.1	0.050	0.040
Benzo[a]pyrene	BaP	2	K 2	1	1	0.500	0.350
Indeno[1,2,3-cd]pyrene	IND	2		0.1	0.1	0.050	0.050
Dibenzo[a,h]anthracene	DBA	2	K 2	1.1	5;1	0.500	0.500
Benzo[g,h,i]perylene	BgP			0.02	0.01	0.005	0.005
						KE$_{sum}$: **2.305**	KE$_{sum}$: **1.199**

With carcinogenic compounds it is supposed, that no minimum concentration with a residual carcinogenic risk of zero can be given. However through statistic data the additional cancer risk effected by this compound may be quantified. Only the additional risk is regarded, any general basic cancer-risk is not considered. In the case of PAH an additional cancer risk associated with defined exposition against coking plant gases of $7 \cdot 10^{-5}$ at 1 ng BaP/m³ is published (LAI, 1992). This standardisation defines the **unit risk** of coking plant gas. The life risk therefore is 1 of 700.000 exposed persons (lifetime exposure at 8h/d). Given that the published (Björseth and Becher 1984) PAH-composition of coking plant gas is constant, at a level of 1 ng BaP/m^3 a KE_{sum} of 1,360 is obtained. For any two samples an equality of KE_{sum} in this approach signifies equivalent carcinogenic potencies. On the basis of this normalisation and comparison additional cancer risks of PAH-containing air-samples can be derived from the unit-risk. For directive purposes it still must be decided, which additional carcinogenic risk appears acceptable. The "virtually safe dose" of EPA refers to an excess lifetime cancer risk of 10^{-6} which corresponds to a KE_{sum} of 0.02. As can be seen from Table 2 this value by far cannot by be maintained in outside air and therefore can not stand as a target value for remediation. But an "accepted risk" of about 10^{-4} according to EPA which corresponds with $KE_{sum} = 2$ can be kept after experiences of the Bremer Umweltinstitut both for outside and uncontaminated indoor air. Additionally, this risk lies within an order of magnitude where other risk of cancerogenesis still play a more important role (Sagunski 1999). With the selected "accepted risks" the following target values for Cancerogenic Equivalence Sum are proposed Table 3.

Table 3. *Scheme of target values for KE_{sum} used for assessing PAH-concentration in indoor environments and following remediation action*

KE_{sum}	cancer risk	Action criteria and evaluation
2	$1 \cdot 10^{-4}$	Proposed **Remediation guide value**. In the case of an obtained KE_{sum} of <2.0 a still acceptable additional cancer risk is present. In relation to overall cancer risk this persisting additional risk is regarded as negligible.
10	$5 \cdot 10^{-4}$	**Intervention value**. If exceeded a relevant additional risk is stated. A suspension of use of the areas concerned is preferred. Remediation is regarded necessary before a further long-term use.
Based on considerations of health care a reduction of the air burden is recommended in the range of $2 < KE_{sum} < 10$		

EXAMPLES

Followed are a few case samples (Table 4) which show characteristically varying concentration of PAH-contamination and the effect on KE_{sum}. In each case specific sources are cause of the air burden. By application of the scheme in Table 3 success of remediation can be documented.

Table 4. *PAH-concentration in 5 case studies:*

PAH concentration [ng/m^3]	**1**	**2**	**3a**	**3b**	**4**	**5**
Naphthalene	8 500	500	7 100	12.000	7 300	19 200
Acenaphthylene	97	2.5	2	200	51	5 600
Acenaphthene	240	20	230	740	13 000	150
Fluorene	460	20	47	260	2 600	1 000
Anthracene	440	85	51	110	4 300	1 400
Phenanthrene	47	9.2	2	7.9	310	200
Fluoranthene	38	20	2	11	170	200
Pyrene	15	16	1	8.3	80	140
Chrysene	1.7	5.9	<dl	<dl	2.7	1.9
Benzo[a]anthracene	2.3	6.4	<dl	0.9	4.1	2.6
Benzo[b]fluoranthene	1.1	13	<dl	<dl	2.7	1.8
Benzo[k]fluoranthene	0.8	4.1	<dl	<dl	1.2	<dl
Benzo[a]pyrene	1.4	9.3	<dl	<dl	1.5	1.1
Indeno[1.2.3-cd]pyrene	0.9	<dl	<dl	<dl	1.5	<dl
Dibenzo[a.h]anthracene	0.2	11	<dl	<dl	1.1	1.0
Benzo[g.h.i]perylene	1.4	7.1	<dl	<dl	1.8	<dl
PAH_{sum}	**9 800**	**730**	**7 400**	**13 338**	**27828**	**27 900**
KE_{sum}	**12.4**	**23.6**	**7.5**	**18.5**	**34.2**	**32.3**
KE_{sum} after remediation	**0.9**	**1.8**	**1.3**	**1.5**	**---**	**---**

DESCRIPTION OF SITUATION

Case 1: gaseous contamination. PAH source - Creosote

In a three-storey office building the cause and health relevance of a odour nuisance were to be examined. The highest PAH burden was obtained in a single bureau and surrounding floor area. Selective air sampling proved a concentration gradient towards the emission sources: Part of a wooden beam behind the suspended ceiling was contaminated with a spilled creosote. The gaseous contamination could be remediated through complete removal of the beam (Zorn et al. 2004).

Case 2: dust-borne contamination. PAH source: tar-coatings

In an antique water castle which was in authority use there have been intensive remediation efforts. The concern was the removal of a tar coating which contained particular high amounts of high-boiling PAH and at random appeared as a paint on the inner walls. (Köhler et al. 2001). In the progress of removing the layer, occurred situations of dust release. The adequate countermeasures were fine dust control and special cleaning.

Case 3: gaseous contamination. PAH source: a) tar-adhesive; b) bituminised boards

In an office building a tar adhesive under the parquet flooring was detected. Indoor air analysis revealed significant emissions of naphthalene. Precautionary the adhesive was removed (3a). By mistake, afterwards bituminised boards were laid out and heat bonded anew, which again lead to a remarkable rise of low-boiling PAH concentrations (3b). After removal of the bituminised boards the burden instantly dropped to uncritical dimension.

Case 4: Dust- and gaseous contamination. PAH source: removal of asphalt-tiles

In a school building the working classes were paved with asphalt tiles. On removing a distinct mixture of dust and gaseous contamination prevailed. The indoor air burden is shown. Remediation by intensive fine dust control and cleaning is ongoing.

Case 5: Dust- and gaseous contamination PAH source: fire event

An example of the possible PAH-burden stemming from a severe fire event is shown. Relevant proportions of high-boiling PAH were formed and a typical burnt smell prevailed. Any reasonable remediation advice to lower PAH-contamination is dependent on the situation.

CONCLUSIONS AND IMPLICATIONS

For some remediation projects primary intent was lowering odour nuisance. But if a PAH contamination remains olfactory unidentified no remediation recommendation can be derived. Using single monitoring parameter like BaP can not reflect the overall situation and as a general rule is not advised in indoor situations where PAH-spectrum differ largely. Following evaluation through orientation values or comparison with outside air situation (Köhler et al. 2004) is always applicable but lacks a toxicological basis. In order to cope with this requirement and achieve a health-oriented scale for remediation decisions, the criterion of the Cancerogenic Equivalence Sum via TEF offers a proper basis and is a technically feasible tool. It must be stated, that the scheme is of recommendatory nature. Certain circumstances in the particular case must be taken into account and can lead to deviating decisions. Additionally it must be kept in mind that probable alterations regarding estimations about the carcinogenic potency of individual EPA-PAH (Pufulete et al. 2004) and an obvious need to extent the analytical spectrum to further health-relevant PAH (Collins et al. 1998).

REFERENCES

Björseth A, Becher G. 1984. “PAH in work atmospheres: occurrence and determination”. *CRC Press Boca Raton.* pp 117-139.

Collins JF, Brown JP, Alexeeff GV, Salom AG. 1998. „Potency equivalency factors for some polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbon derivatives“ Regul Toxicol Pharmacol Vol 28, pp 45-54

DFG - Deutsche Forschungsgemeinschaft. 2004. *MAK- und BAT-Werte-Liste.* Wiley-VCH, Weinheim.

Köhler M, Weis N, Zorn C. 2004. „Luftgetragene PAK-Belastungen. In Innenräumen – Vorkommen, Quellen und Bewertung“ *AGÖF - 7 Fachkongress*. pp 156-165.

Köhler M, Hörnes U, Zorn C. 2001.“PAK-Belastungen durch Teeranstriche und ihre Sanierung.“ In: „Umwelt, Gebäude und Gesundheit“. *AGÖF - 6 Fachkongress*. pp 241-250.

LAI (Länderausschuss für Immissionsschutz). 1992. „Krebsrisiko durch Luftverunreinigungen Entwicklung von "Beurteilungsmaßstäben für kanzerogene Luftverunreinigungen" im Auftrag der Umweltministerkonferenz Ministerium für Umwelt, Raumordnung und Landwirtschaft des Landes Nordrhein-Westfalen Düsseldorf“.

Larsen JC und Larsen PB. 1998. „Chemical carcinogens“. In: Hester RE und Harrison RM. (eds.). *Air Pollution and Health*. The royal Society of Chemistry, Cambridge UK, pp 33-56.

Malcom HM, Dobson S. 1994. “The Calculation of an Environmental Assessment Level (EAL) for Atmospheric PAHs Using Relative Potencies”. *Department of the Environment*, London.

Moriske HJ. 2002. „Chemische Luftverunreinigungen, Außenlufthygiene III-31“. In: Moriske HJ and Turowski E (eds.). *Handbuch für Bioklima und Lufthygiene*. Ecomed Verlag, Landsberg.

Nisbet ICT, La Goy PK. 1992. “Toxicity equivalence factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs)”. *Regul Toxicol Pharm*, Vol 16, pp 290-300.

Ohura T, Amagai, T, Fusya M, Matsushita H. 2004. “Polycyclic aromatic hydrocarbons in indoor and outdoor environments and factors affecting their concentrations”. *Environ Sci, Technol,* Vol 38, pp 77-83.

Preuss R, Angerer J, Drexler H 2003. “Naphthalene - an environmental and occupational toxicant.” *In ternational. Archives of Occupational and Environmental He*alth, Vol 76, pp 556 –576.

Pufulete M, Battershill J, Boobis A, Fielder R. 2004. “Approaches to carcinogenic risk assessment for polycyclic aromatic hydrocarbons: a UK perspective”. Regul Toxicol Pharmacol Vol 40, pp 54-66

Sagunski H. 1999. “Regulating Indoor air carcinogens: current considerations in Germany on radon and implications for other indoor carcinogens”. *Proceedings of indoor air*, Vol. 1, pp 212-217.

Schneider K, Schumacher US, Oltmanns J, Kalberlah F, Roller M. 2000. “PAK (Polyzyklische aromatische Kohlenwasserstoffe)”. In: Eikmann T, Heinrich U, Heinzow B, Konietzka R. (eds.): *Gefährdungsabschätzung von Umweltschadstoffen*. Loseblattsammlung, Kennziffer D 815, Berlin.

Schneider K, Roller M, Kalberlah F, Schuhmacher-Wolz U. 2002. “Cancer risk assessment for oral exposure to PAH mixtures”. *Journal of Applied Toxicology,* Vol 22, pp 73-83.

Zorn C, Köhler M, Weis N, Scharenberg W. 2004. „Luftgetragene PAK-Belastungen durch unsachgemäße Ausbringung eines Teerölpräparates im Baukörper - Beispiel der Erkundung, Bewertung und Sanierung“.. *Verein für Wasser-, Boden- und Lufthygiene* - 11. WaBoLu-Innenraumtage Vol. 114 / F14.

Zorn C, Köhler M, Weis N, Scharenberg W. 2005. „Bewertungsschema für PAK-Innenraumluftbelastungen auf der Basis von Toxizitätsäquivalentfaktoren gegenüber BaP“. *Bundesgesundheitsbl – Gesundheitsforsch – Gesundheitsschutz*, handed in for publication.

US-EPA - United states environmental protection agency. 1984. „poylnuclear hydrocarbons“ Vol 10.