Biological monitoring as a useful tool for the detection of a coal-tar contamination in bitumen-exposed workers

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Introduction

Polycyclic aromatic hydrocarbon (PAH) metabolites in human urine can be used as biomarkers of internal dose to assess recent exposure to PAHs. In contrast to coal-tar that exposes to PAH at high air concentrations, the hot application of bitumen-containing materials, e.g. during indoor mastic asphalt application, road paving or roofing, leads to exposure of fumes that contain only small traces of PAHs. In an ongoing research project „Chemical irritative and/or genotoxic effect of fumes of bitumen under high processing temperatures on the airways", where multiple parameters of external exposure and irritative and genotoxic effects were raised we identified coal-tar exposure during mastic asphalt application with biological monitoring of urinary PAH metabolites.

Methods

In a cross-shift study 73 mastic asphalt workers exposed to fumes of bitumen and 49 construction workers without exposure to fumes of bitumen were analysed regarding PAH exposure and exposure-related health effects (Table 1).
The monohydroxylated metabolites of phenanthrene [1,2+9,3,4-hydroxyphenanthrene (OHPH)] and pyrene [1-hydroxypyrene (1-OHP)] were measured in pre- and post-shift urinary samples in order to assess the internal exposure. Exposure to fumes of bitumen was assessed by personal air monitoring. For data analysis a mixed linear model was performed on the different outcomes with exposure group, time of measurement (pre-, post-shift), current smoking, German nationality and age as fixed factors and subjects as random factor.

Table 1: Description of the study population

			Exposure		
			Reference N=49	Bitumen only N=66	Bitumen and tar N=7
Age [yrs]		Median	36	40	34
		Range	19-61	17 - 63	27 - 48
Current smoking		N (%)	20 (40.8)	44 (66.7)	5 (71.4)
German nationality		N (%)	44 (89.8)	38 (57.6)	5 (71.4)
Duration of employment [months]		Median	78	72	60
		Range	1 - 288	1 - 456	11 - 206
Chronic bronchitis		N (%)	3/49 (6.1)	6/35 (17.1)	2/7 (28.6)
Wheezing within the last 12 months	In the chest	N (%)	4/49 (8.2)	9/35 (25.7)	0/6 (0)
	With shortness of breath	N (%)	2/48 (4.2)	3/21 (14.3)	0/6 (0)
	Without having a cold	N (%)	1/48 (2.1)	4/21 (19.1)	0/6 (0)
Symptoms of the lower airways (cough)	Prior to shift	N (%)	2/49 (4.1)	4/35 (11.4)	3/6 (50.0)
	After shift	N (%)	3/48 (6.3)	8/34 (23.5)	0
	During time off work	N (%)	1/30 (3.3)	1/21 (4.8)	1/6 (16.7)
Symptoms of the eye (irritation, itching, burning)	Prior to shift	N (%)	0/49 (0)	1/35 (2.9)	0/6 (0)
	After shift	N (%)	0/48 (0)	5/35 (14.3)	0
	During time off work	N (%)	0/30 (0)	0/21 (0)	0/6 (0)
Symptoms of the nose (irritation, blocked)	Prior to shift	N (%)	0/49 (0)	6/35 (17.1)	1/6 /(16.7)
	After shift	N (%)	0/48 (0)	8/34 (23.5)	0
	During time off work	N (%)	0/30 (0)	1/21 (4.8)	0/6 (0)

Results

Significantly higher concentrations of PAH-metabolites (1-OHP and OHPH) were determined in the post-shift urine samples of seven mastic asphalt workers working on same construction site compared to the reference workers and all other 66 mastic asphalt workers (Table 2 and 3).
In addition, there was a more than twelvefold increase of the PAH-metabolites from pre- to post-shift in these seven workers, whereas in the other mastic asphalt workers only a doubling of the PAH-metabolites between pre- and post-shift were measured (Fig. 1a-c; 2a-c). The smoking attitudes of the seven workers were not different compared to the other workers. Also exposures by motor fumes could be excluded, as in the hall, in which the mastic asphalt works were carried out, no car traffic took place.
Intensive examinations led to the detection of the substantially PAH-exposure during the working shift of the seven workers: coal tar plates, which were without knowledge of the workers and the coordinators, the underground material of the mastic asphalt layer (Fig. 3 and 4).

Table 2: Urinary metabolites of workers with and without exposure to fumes of bitumen and tar

			Exposure to fumes of bitumen			
		Reference N=49		Bitumen only N=66		Bitumen and tar N=7	
Variable		Pre shift	Post shift	Pre shift	Post shift	Pre shift	Post shift
Urine	Creatinine [g/l] Median	1.2	1.2	1.3	1.6	1.2	1.8
	Creatinine [g/l] P25-P75	0.9-1.6	0.9-1.7	0.9-1.9	1.3-2.3	0.8-1.6	1.3-3.2
	1-OH Pyrene [ng/g crn] Median	175	182	252	455	442	6605
	1-OH Pyrene [ng/g crn] P25-P75	88-325	112-287	133-456	216-827	133-775	4628-11598
	Sum OH-Phenanthrenes [ng/g crn] Median	948	992	954	1770	1494	12774
	Sum OH-Phenanthrenes [ng/g crn] P25-P75	568-1390	636-1529	655-1443	1249-2281	539-1659	9741-19010

Table 3: Adjusted means and effect estimates of the mixed model analysis[1] in workers with and without exposure to bitumen and tar

			Pre shift			Post shift			During shift	
Variable	Group	N [3]	Adjusted mean [2]	Exposure effect	p	Adjusted mean [2]	Exposure effect	p	Shift effect	p
Urine	Creatinine [g/l] Reference	97	1.10	1.00		1.18	1.00		1.07	0.45
	Creatinine [g/l] Bitumen	131	1.18	1.08	0.51	1.54	1.30	0.02	1.30	0.001
	Creatinine [g/l] Bitumen and tar	14	1.08	0.98	0.92	1.98	1.67	0.03	1.84	0.012
	1-OH-pyrene [ng/g crn] Reference	97	170.07	1.00		205.43	1.00		1.21	0.11
	1-OH-pyrene [ng/g crn] Bitumen	131	176.92	1.04	0.84	309.69	1.51	0.04	1.75	0.00001
	1-OH-pyrene [ng/g crn] Bitumen and tar	14	296.54	1.74	0.17	5498.83	26.77	0.00001	18.54	0.00001
	Sum OH-phenanthrenes [ng/g crn] Reference	97	968.07	1.00		1021.82	1.00		1.06	0.53
	Sum OH-phenanthrenes [ng/g crn] Bitumen	131	878.27	0.91	0.39	1543.68	1.51	0.0004	1.76	0.00001
	Sum OH-phenanthrenes [ng/g crn] Bitumen and tar	14	952.77	0.98	0.95	12918.67	12.64	0.00001	13.56	0.00001

[1] with subject as random factor and shift, exposure group and interaction between both as fixed factors. Effect estimates as factor for log-transformed variables and percentages of change for untransformed variables with respect to the reference group.
[2] adjusted for smoking
[3] number of observations

Table 4 shows the results of the analysis of the drilling core. Thereby it becomes apparent, that the measured concentrations in the lower layer (coal-tar) are significant higher than in the upper layer (mastic asphalt).
A closer evaluation of the stationary workplace concentration (ambient monitoring) showed enhanced concentration of phenathrene, pyrene, fluoren, anthracen and acenaphthen during working shift at the construction site of these seven workers (Table 5).

Tab. 4: Results of the analysis of the drilling core from the special workplace (presented in Fig. 4)

	Upper layer [µg/g]	Lower layer [µg/g]
Phenanthrene	5.8	1590
Anthracene	2.0	424
Fluoranthrene	7.8	2822
Pyrene	5.9	2034
Benz[a]anthracene	0.6	1063
Chrysene	0.5	1007
Benzo[e]pyrene	<0.3	699
Benzo[b]fluoranthrene	<0.3	767
Benzo[k]fluoranthrene	<0.4	406
Benzo[a]pyrene	<0.3	768
Dibenzo[ah]anthracene	<0.4	144
Benzo[ghi]peryene	<0.5	262
Indeno[1,2,3-cd]pyrene	<0.3	524

Table 5: Workplace concentrations at two different mastic asphalt construction sites (assessed by stationary sampling 300 min duration)

	Bitumen and coal-tar exposure	Only bitumen exposure (exemplarily)
Bitumen, aerosols	2.2 [mg/m³]	4.6 [mg/m³]
Bitumen, fumes and aerosols	5.9 [mg/m³]	6.4 [mg/m³]
Naphthaline	2.0	<1.12
Acenaphthylene	<1.98	<3.41
Acenaphthene	1.27	<1.24
Fluorene	3.69	<0.38
Phenanthrene	7.60	0.24
Anthracene	0.44	0.04
Fluoranthene	0.87	<0.27
Pyrene	0.94	<0.23
Benzo[*a*]anthracene	<0.15	<0.9
Chrysene	<0.6	<0.82
Benzo[*e*]pyrene	<0.94	<3.57
Benzo[*b*]fluoranthene	<0.08	<0.15
Benzo[*k*]fluoranthene	<0.59	<0.54
Benzo[*a*]pyrene	<0.18	<0.44
Dibenz[*ah*]anthracene	<0.14	<0.54
Benzo[*ghi*]perylene	<0.01	<1.46
Indeno[1,2,3-*cd*]pyrene	<0.12	<1.17

All values in [µg/m³], if not others are indicated

Fig. 1a-c: Urinary sum OH-Phenathrene.

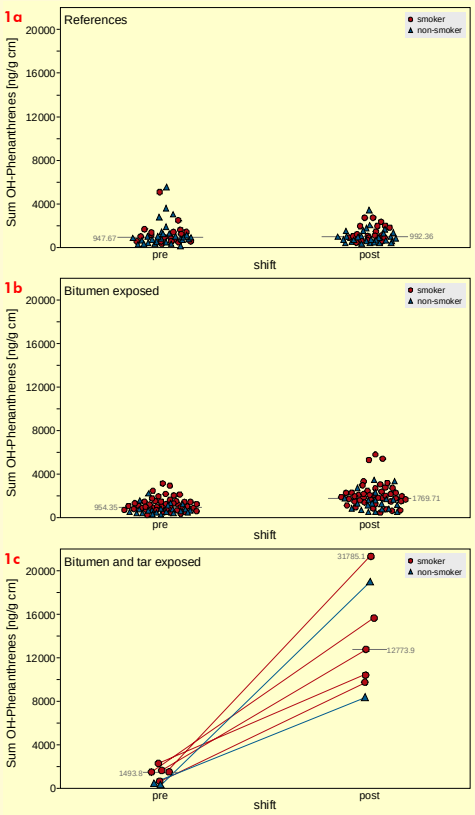
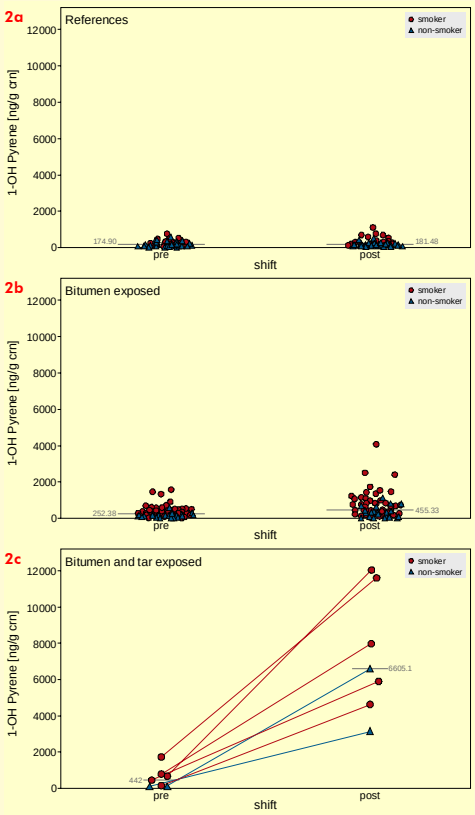


Fig. 2a-c: Urinary sum 1-OH-Pyrene.



In all groups the pre-shift concentrations of OHPH (Fig. 1a-c) and 1-OHP (Fig. 2a-c) were in the same range, but the PAH-metabolite concentrations of the group of workers with bitumen and especially with bitumen and coal-tar exposure increased significantly during the shift.

Fig. 3: Workplace at the examined construction site.

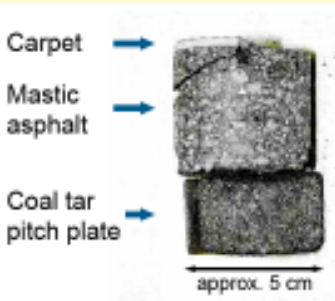


Fig. 4: Withdrawal of a drilling core from the workplace. Already the optical inspection of the drilling core made clear, that under the mastic asphalt layer another black layer, the coal tar pitch plate is located.

Conclusion

Biological monitoring led to the detection of the extremely high urinary PAH-concentrations in a subgroup of mastic asphalt workers. Further analysis at the working place demonstrated that the cause of significantly enhanced PAH-exposure during handling with bitumen under high processing temperatures was not exclusively bases on the fumes of bitumen itself, but contamination with coal-tar traces in the underground material have to keep in mind.