Occupational health risk assessment for the workers exposed to rubberized asphalt fumes

A comparative study based on monitoring campaigns

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ABSTRACT. *The incremental health risk for workers of the road-paving sector using rubberized asphalt was assessed based on the outcome of monitoring campaigns carried out during paving operations where both rubberized and standard asphalt were used. The exposure of workers to Polycyclic Aromatic Hydrocarbons (PAHs) released in the asphalt fumes were measured by means of personal samplers and dermal sampling pads, followed by laboratory analysis. Based on monitoring data, the incremental cancer resulted significantly lower for rubberized asphalt in comparison with standard asphalt. The laboratory measurement of PAH released by the 2 asphalt mixtures to understand the cause of the observed difference and the PAH emission potential of rubberized and standard asphalt mixtures is undergoing.*

KEYWORDS: *asphalt fumes, rubberized asphalt, tire recycling, rubber dust, PAHs, occupational exposure.*

1. Introduction

The safety of recycled materials is a key aspect when assessing its suitability for being placed on the market. A thorough characterization of the chemical and toxicological aspects is crucial in ensuring that a recycled material can fulfil the highest safety standards so that it can be considered compliant with "end of waste" rules. In this framework, the assessment of the exposure of road-paving workers to Polycyclic Aromatic Hydrocarbons (hereinafter PAHs) released from "rubberized asphalt", i.e. asphalt modified with the addition of small amount of rubber dust derived from End of Life Tires (ELTs), is of primary concern as the use of rubber modified asphalt can significantly contribute to the recycling of end of life tires.

The research aims at measuring the incremental health risk deriving from the exposure of workers to PAH contained in asphalt fumes during the placement of roads with either rubberized asphalt or standard asphalt.

The research is based on several steps including:

- monitoring of the inhalatory exposure to PAHs for different categories of workers during road paving operations by means of personal samplers;

- monitoring of the dermal exposure to PAHs for one category of workers during road paving operations by means of dermal pads;

- measurement of environmental concentrations of PAHs during road paving operations

- laboratory measurement of the PAH released from samples of rubberized and standard asphalt at different temperatures and in controlled conditions (ongoing, results not reported in this article).

The sampling of PAHs in the breathing zone of workers, carried out by personal samplers, resulted in concentrations which were in most cases higher for standard asphalt than for rubberized asphalt operations. Similar results were obtained for the dermal exposure. From the statistical standpoint (Wilcoxon extended pair test), the difference was significant. For one site, it was possible to compare directly the rubberized asphalt with the standard asphalt, as the paving operations were carried out in the same day by the same workers, and the two asphalt types were placed in two parallel lanes of the same stretch of the road. In the other cases, the comparability was not directly possible as the operations with rubberized or asphalt rubbers were carried out in different places / days.

The asphalts were characterized before the monitoring campaigns, and the temperature of asphalt placement was measured by thermoscan cameras. As of now, 5 environmental and personal monitoring trials have been completed in 4 sites: Zola Predosa(BO), Finale Emilia (MO) Imer (TN)) where rubberized asphalt was used, and two (again Zola Predosa (BO) and Giardini di Corcolle (RM)) where standard asphalt was used. The monitoring is still ongoing in additional sites to expand the monitoring database and increase the reliability of the estimates.

Although the observed differences resulted significant, the monitoring activities by alone cannot provide any insight on the cause of this difference. For this reason, a parallel activity, carried out at laboratory scale, is undergoing to verify, in controlled conditions, whether the addition of rubber dust in asphalt mixtures may result is a differential release of PAH. At the same time, if the results will be confirmed by additional studies, the reduced health risk could represent an additional reason for recommending the use of rubber dust from recycled tires in asphalt mixtures.

2. Materials and Methods

2.1. *Sampling Design*

In Italy, the teams in charge of road paving operations are usually made of four staff: a paver, two screedmen and a roller. These workers are likely exposed to a different extent to asphalt fumes, due to their different distance from the source of asphalt fumes and due to the different physical intensity of their respective tasks. Therefore, it was decided to monitor each staff separately, with dedicated personal samplers and dermal sampling pads.

Air samples were therefore collected within the breathing zone of each worker by means of portable pumps (Tecora, Ayron) and analysed in accordance with the methods USEPA TO 13A, NIOSH 5515 and UNICHIM 2010:2011, respectively for PAHSs and respirable inhalable particulate. For dermal exposure, a specific method based on absorption pads made of polypropylene, modified from the ones described by McClean et al. (2004), Jongeneelen et al. (1988) and Van Rooij et al. (1993), was developed and used. The dermal patch samples were collected from 2 workers carrying out the same task (screedmen) to reduce method uncertainty.

For each sampling campaign, the sampling scheme was therefore as following:

- Rollers: breathing-zone sampling for PAHs.
- Screedmen 1: breathing-zone sampling for respirable particulate, dermal pads for PAHs.
- Screedmen 2: breathing-zone sampling for PAHs, dermal pads for PAHs.
- Paver drivers: breathing-zone sampling for PAHs.

In addition to that, air samples for the measurement of PAHs were collected by means of high volume samplers (Tecora Hi Vol) located within road paving yards.

The temperature of placement of asphalt, which is directly related to the release of PAHs from asphalt (biblio here) was measured by thermoscan camera in the Zola Predosa fieldwork and by thermocouple devices in the other yards.

2.2. *Environmental sampling*

In accordance with the sampling method USEPA TO13A, samples for the measurement of particulate and vapour PAHs in the environment air were collected by means of a high volume sampler (Tecora Hivol) equipped with a two stage sampling head containing a particulate filter (quartz fibre filter Munktell MK360, 102 mm) and a Poly Urethane Foam (PUF) filter (PUF Tecora h50mm). Both the quartz and PUF filter were pre-conditioned before their use in accordance with method requirements. The sampling inflow was set at 200 l/min. Sampling was continued during the whole road paving operations, for 2 to 4 hours.

The following blanks were analysed:

- sampling media blanks: new, unused quartz and PUF filters representative of each package were set aside right after their conditioning for laboratory measurement of PAHs.
- conditioning solvent blanks: solvent used for the pre-treatment of PUF were analyzed after PUF pre-treatment to determine their content of PAHs.
- sampling method blanks: PAHs were determined on pre-conditioned PUF and quartz filter placed in the sampling head and then immediately removed and stored for analysis;
- laboratory blanks: PAHs were measured in new unused extraction solvents.

In general, the analysis of the blank proved a very low presence of PAHs, confirming the good performance of sampling and laboratory activities. For each PAH substance, the analytical value determined in the actual samples was therefore corrected by subtracting the corresponding PAH value of either sampling media or sampling method blank, whichever was the lowest.

2.3. "*Breathing zone" sampling*

PAH: samples of the air inhaled by the workers were taken in the breathing zone of each worker in accordance with method NIOSH 5515. Personal air samplers (Tecora Ayron) compliant with the UNI-EN standard 1232:1999 were used. The samplers were equipped with a sampling train composed by a particulate filter and an adsorbent vial (XAD2 200-400 mg Jumbo). The sampling method was improved with the use of quartz filter (Munktell MK360, 25mm) instead of the PTFE (Polytetrafluoroethylene) filters indicated by the sampling method, due to their better extractability and higher cleanliness which allowed fully benefitting of the GC/MS (Gas Chromatography- Mass Spectrometry) analytical method adopted. The sampling flow was set at 2l/min for PAH sampling and 1.7 l/min for respirable particulate. The sampling lasted for 2 to 4 hours, the whole duration of each worker's shift. Similarly, to environmental sampling, sampling media blanks, sampling method blanks and laboratory blanks were analyzed for PAHs. The sampling flow timeseries with a time interval of one minute were downloaded from the data logger of each sampler and checked to verify the proper functioning of the samplers after each monitoring.

Respirable particulate: The sampling in the workers' breathing zone was conducted in compliance with the method NIOSH 0600 (1998). A centrifugal Dorr-Oliver pre-selector was used for the selection of the particulate fraction to be sampled. In compliance with the common practice, and the standard UNI EN 481 (1994), pretreated (oven dried) glass filters of 25 mm were used for intercepting the respirable fraction of the particulate. The amount of particulate intercepted by the filters was measured by a gravimetric method. For each particulate sample, at least 2 blank filters were measured. Particulate results were always far below the regulatory level for occupational exposure.

2.4. *Sampling for dermal exposure*

To date there are no standardized and validated methods for skin contamination measurements (Joost et al., 2007). The most used methodologies for the assessment of occupational dermal exposure to PAHs during asphalt paving operations are based on the "interception principle", as for this type of workplace, skin contamination is mostly caused by the direct deposition of pollutants on the skin. These sampling methods use a sorbent layer placed on the skin or on the clothing, which intercepts the contaminant before it reaches the skin; after the exposure, the sorbent pad is removed and sent for laboratory analysis to determine the mass of contaminant collected on it.

The dermal sampling method adopted in this study was modified after the ones described by McClean et al. (2004), Jongeneelen et al. (1988) and Van Rooij et al. (1993). During each monitoring activity, dermal patches were placed on two workers performing the same job (screedmen) to reduce uncertainty. For each worker, four patches were placed (chest, shoulder, wrist, calf). The patches were placed directly on the skin or on the protective clothing. This configuration was specially designed to allow a good mapping of distribution of skin contamination on the entire body surface, reducing at the same time the discomfort for the workers.

Each patch was made by a polypropylene filter (Millipore, AN1H4700, 47 mm diameter, 10 µm size) placed between two layers of adhesive films: only a small area (diameter 15 mm) was left uncovered and used as monitoring area. Sampling time lasted generally from 2 to 4 hours, which for most of the PAHs was long enough to allow the collection of analytically detectable amounts.

Immediate after sampling, pad samples were removed, packed in aluminium foil and stored at 4°C until analysis. Each set of 4 pads for each worker was extracted together and analysed using HRGC-HRMS (High Resolution Gas Chromatography/ High Resolution Mass Spectrometry) system following the same analytical methods adopted for the other samples.

2.5. *Analytical methods for PAHs*

The concentration of the following PAH substances were measured in all the samples collected: Acenaphthene; Acenaphthylene; Anthracene; Benzo [a] anthracene; Benzo [b] Fluoranthene; Benzo [j] Fluoranthene; Benzo [k] Fluoranthene; Benzo [g, h, i] Perylene; Benzo [a] Pyrene; Benzo [e] Pyrene; chrysene; Dibenzo [a, h] Anthracene; Dibenzo [a, e] Pyrene; Dibenzo [a, h] Pyrene; Dibenzo [a, i] Pyrene;

Dibenzo [a, l] Pyrene; Phenanthrene; Fluoranthene; Fluorene; Indeno [1,2,3-cd] Pyrene; Naphthalene; Pyrene.

All the samples were labeled and signed to fulfil chain of custody procedures, and delivered to the laboratory in refrigerated containers within five days after sampling.

PAHs were measured in compliance with the US EPA TO-13A 1999C method. High resolution mass spectrometry was used for the quantification. The internal calibration was carried out by means of isotopic dilution using deuterated and / or C13 markers.

In specific cases, the extracts from quartz filters and from the XAD2 / PUF filters were analyzed separately to measure the relative amount of PAHs in the vapor phase or adsorbed to particulate.

2.6 Asphalt Mixtures

In table 1 asphalt mixtures used in the five monitoring campaigns are reported.

In general, standard asphalts contain bitumen as a binder (normally between 4.5 and 8 %), stone aggregate and filler. These asphalts are usually placed at a temperature ranging from 150° to 160 °C depending on the type of conglomerate, the distance between the production site and the yard, the season and the weather conditions. All the standard asphalts used in this study were Split Mastix Asphalt (SMA) type.

Rubberized asphalts are obtained with the addition of rubber powder (normally <10% weight basis) using the so called "dry process". In this type of process, rubber powder replaces a part of stone aggregates and it is added directly at the production plant as an additional component of the mixture.

Table 1. *Asphalt Mixtures.*

	Zola Predosa	**Zola Predosa**	**Zola Predosa**	**Imer**	**Finale Emilia**	**Giardini di Corcolle**
Grain size	**SMA**	**SMA 8.5 ELT 1.2**	**SMA 7.5 ELT 0.75**	**SMA 7.5 ELT 0.75**	**SMA 7.5 ELT 0.75**	**SMA**
UNI EN sieve (mm)	Pass through (%)	Pass through (%)	Pass through (%)	Pass through (%)	Pass through (%)	Pass through (%)
10	100	100	100	100	100	N.A
8	98.2	98.5	98.1	99.5	99.7	N.A
6.3	85	88.1	87.4	91.5	98.4	N.A
4	46	51.2	50.5	55.7	61.8	N.A
2	26	25.2	24.6	25.4	27.7	N.A
1	19.9	18.2	17.8	17.5	18.8	N.A
0.5	16.3	14.2	13.9	14	13.5	N.A
0.25	13.4	9.6	9.5	11.7	9.8	N.A
0.125	10.5	6.7	6.5	8.9	7.6	N.A
0.063	8	4.7	4.5	7	5.8	N.A
Composition						

	Zola Predosa	Zola Predosa	Zola Predosa	Imer	Finale Emilia	Giardini di Corcolle
Bitumen [%]	6.55%	8.53%	7.51%	7.49%	7.91%	6.55%
Rubber dust [%]	0%	1.20%	0.75%	0.75%	0.75%	0%
Placement temperature [°C]	145°C	150°C	160°c	145°c	145°c	160°C

2.7 *The studied road paving yards*

Zola Predosa. The monitoring of the Zola Predosa paving yard (Figure 1), a 300m stretch of a road located in the Bologna province, Italy, was carried out on July 31, 2014. This was the only yard site where rubberized asphalt (SMA 7.5 ELT 0.75 and SMA 8.5 ELT 1.2) and standard asphalt (SMA) mixtures where placed in the same day in two parallel lanes, allowing therefore for a direct comparison among the two. As it can be seen from figure 1, in this yard the following asphalt mixtures were placed:

- SMA: the whole 300m stretch of the lane toward Bologna;
- SMA 8.5 ELT 1.20: the first 155m of the lane toward Modena;
- SMA 7.5 ELT 0.75: the second 145m of the lane toward Modena;

The paving operations lasted for around 2 hours for each stretch. The air temperature ranged from 23.2°C to 26.3 during the paving with standard asphalt, with a maximum wind speed of 4.8 km/h, and from 27.7°C to 29.5°C degree during the placement of rubberized asphalt, with a maximum wind speed of 9.7 km/h.

Figure 1. *Zola Predosa road paving yard*.

Imer. Imer (Trento province, Italy) was the second yard studied. (September 25th, 2014) In this case, only rubberized asphalt mixture (SMA 7.5 ELT 0.75) was placed on both lanes of a 600 m stretch. The paving operations lasted for around 4 hours. During the paving operation, the average temperature was 12.9°C, and the average wind speed was 1.4 m/s.

Figure 2. *Imer road paving yard*.

Finale Emilia. The third yard studied (Septermber 26th, 2014) was located in "Viale della Rinascita", a new road in Finale Emilia (Modena Province). The whole new road, 700 m length, was paved using rubberized asphalt mixture (SMA 7.5 ELT 0.75). The monitoring was carried out during the placement of the first lane, and lasted for around 3.30 hours. During the paving operation, the average temperature was 19.8°C, and the average wind speed was 6.4 km/h

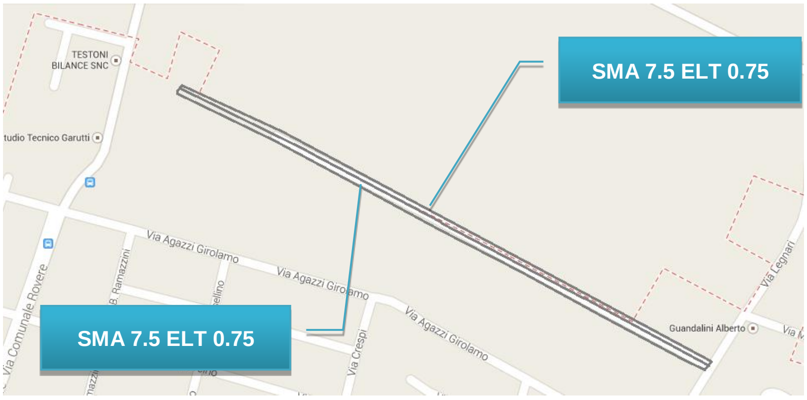

Figure 3. *Finale Emilia road paving yard.*

Giardini di Corcolle. The monitoring of the Giardini di Corcolle (Rome Province) paving yard occurred on November 24th, 2014. In this case, only standard asphalt mixture (SMA) was used for the road paving works. The monitoring was carried out during the first 3 hours of the road paving operations. During the monitoring, the temperature ranged from 13°C to 18°C, and the average wind speed was 3 km/h

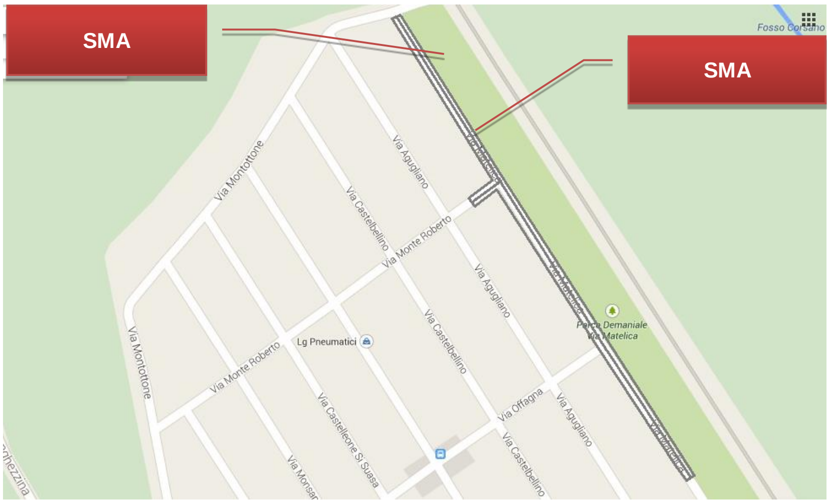

Figure 4. *Giardini di Corcolle paving yard.*

2.8 *Statistical Methods*

In spite of the limited number of samples available, the statistical comparison among samples was made possible by the large number of analytes determined for each sample.

Each sample was indeed considered as an array of data and the analysis studied therefore the frequency of pairwise differences between samples, being each pair the concentration of a single PAH in the two samples being compared. For the statistical analysis of the blanks, all the 22 analytes were included in the statistical analysis, whilst for actual samples the statistical analysis was limited to the 11 PAHs of toxicological relevance regulated by EU (European Union) or Italian laws.

Clearly, being the data for each sample related to the measurement of different analytes, it has to be assumed that their distribution is not normal; or at least that the normality of their distribution was not demonstrable. For this reason, it was necessary to use a non-parametric statistical test, independent from any assumption related to the normal distribution of the data. The Wilcoxon Matched Pairs Signed Ranks Test was therefore used for the analysis. The Wilcoxon test analyzes the difference between pairs in two sets of data: in this case the pairs are the analytical results of the same PAH in the two samples.

The Wilcoxon test explores simultaneously the magnitude of the differences and their direction. In other words, unlike other non-parametric tests such as the sign test, the Wilcoxon test is quantitative, i.e. it provides an indication of the size of the difference and its direction. Is therefore particularly strong when used with quantitative values.

The Wilcoxon test was used to test for differences between the following sets of homogeneous data:

- Comparison of different blank samples: field blanks, unused filter blanks, laboratory within the same site and among different sites;
- Comparison between samples taken during paving with rubberized asphalt against standard asphalt;
- Comparison between samples between staff performing different tasks.

3. Results

3.1 *Environmental concentration of PAHs in the vicinity of the paving yards.*

In table 2 the environmental concentration of the 11 PAHs regulated by the EU or Italian regulation in the proximity of paving yards is reported. The environmental concentration of PAHs resulted in all cases compliant with the Italian regulatory limit of $1ng/n^3$ of Benzo[a]Pyrene (B(a)P) (Table 1)

The measured environmental concentrations were not different from the background concentrations of PAHs usually observed in other Italian urban areas (Legambiente, Ministry of Environment, FS (Ferrovie dello Stato), ARPA (Regional Agency for Environmental Protection) (Campaign *“Treno Verde”:1990-2001*).

The environmental concentration of PAHs resulted, on the average, lower during the paving with rubberized asphalt in comparison with the paving with standard asphalts. Although this difference is relatively small, it resulted statistically significant (Wilcoxon test $P<0.01$).

Table 2. *Environmental concentration of PAHs during the sampling campaign.*

	Environmental concentrations of PAHs				
	Standard Asphalt		Rubberized Asphalt		
	Giardini di Corcolle(RM)	Zola Predosa (BO)	Zola Predosa (BO)	Imer (TN)	Finale Emilia (MO)
PAHs	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)
Benzo [a] anthracene	1,22	0,64	0,21	0,03	0,04
Benzo[b]Fluoranthene	0,40	0,00	0,00	0,20	0,09

	Environmental concentrations of PAHs				
	Standard Asphalt		Rubberized Asphalt		
	Giardini di Corcolle(RM)	Zola Predosa (BO)	Zola Predosa (BO)	Imer (TN)	Finale Emilia (MO)
PAHs	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)
Benzo[j]Fluoranthene	0,06	<lod	0,01	0,02	0,00
Benzo[k]Fluoranthene	0,25	0,09	0,00	0,10	0,06
Benzo[g,h,i]Perylene	0,18	0,18	0,21	0,34	0,75
Benzo[a]Pyrene	0,26	0,26	0,03	0,25	0,33
Benzo[e]Piyene	0,68	0,29	0,05	0,31	0,16
Crhysene	2,16	0,57	0,37	0,10	0,08
DiBenzo[a,h]Anthracene	0,01	0,01	<lod	<lod	0,08
Indeno[1,2,3-cd]Pyrene	0,17	0,02	<lod	<lod	0,10
Pyrene	3,20	5,15	3,95	2,22	1,60

3.2. *Concentration of PAHs in the worker breathing zone*

In tables 3 to 5 the concentration of the 11 PAHs regulated by the EU or Italian regulation in the breathing zone of pavers, screedmen and rollers is reported. Due to a malfunctioning of the personal sampler, the exposure of the roller in the Finale Emila site was not measured. Based on these data, the following can be said:

- All levels of inhalation exposure measured in the five monitoring campaigns resulted by far within the available and more restrictive reference limits for occupational exposure to PAHs: compared for instance to the German regulatory limit, (TRK-Technical guidance concentration for B(a)P = 2 µg/m3), the highest values measured for both types of asphalt was ten times lower;
- For the Zola Predosa site, pavers (Table 3) are exposed to higher concentration of PAHs when standard asphalt is placed, in comparison with rubberized asphalt. In this case the difference is not significant. Although the inhalatory exposure of pavers to B(a)P is similar for all the five monitoring sites (in the range of 34 to 47 ng/m3), when all the sites are considered, the average exposure to 11 PAHs was significantly higher for standard asphalt in comparison with rubberized asphalt.
- For the Zola Predosa site, screedmen (Table 4) are exposed to significantly higher concentration of PAHs when standard asphalt is placed, in comparison with rubberized asphalt. The difference is significant also when the average exposure concentration for standard and rubberized asphalt is considered (Wilcoxon $p < 0.005$).
- For the Zola Predosa site, rollers (Table 5) are exposed to significantly higher concentration of PAHs when standard asphalt is placed, in comparison with rubberized asphalt (Wilcoxon $p < 0.005$) The difference is significant also when the average exposure concentration for standard and rubberized asphalt is considered (Wilcoxon $p < 0.005$).
- Regardless to the type of asphalt placed, in most of the monitored yards rollers and screedmen resulted exposed to higher concentration of PAHs compared to the

pavers. The only exception to that rule is the roller in Giardini di Corcolle, who resulted exposed to the lowest concentration of PAHs.

Table 3. *Concentration of PAHs in the breathing zone of pavers*

	Inhalatory exposure to PAHs				
	Paver				
	Standard Asphalt		Rubberized Asphalt		
	Giardini di Corcolle(RM)	Zola Predosa (BO)	Zola Predosa (BO)	Imer (TN)	Finale Emilia (MO)
PAHs	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)
Benzo [a] anthracene	41,11	22,31	19,71	4,46	19,89
Benzo[b]Fluoranthene	20,42	37,92	24,81	4,07	3,76
Benzo[j]Fluoranthene	3,68	3,02	4,24	1,06	6,57
Benzo[k]Fluoranthene	10,71	71,81	65,97	5,93	8,00
Benzo[g,h,i]Perylene	5,33	95,20	64,98	14,58	53,81
Benzo[a]Pyrene	33,59	40,40	38,16	35,72	47,64
Benzo[e]Piyene	43,58	27,82	41,13	35,67	36,31
Crhysene	83,94	21,42	43,01	6,24	8,63
DiBenzo[a,h]Anthracene	7,55	22,93	7,48	3,54	18,36
Indeno[1,2,3-cd]Pyrene	7,06	75,84	31,89	6,90	28,81
Pyrene	146,27	70,00	74,75	45,90	110,92

Table 4. *Concentration of PAHs in the breathing zone of screedman*

	Inhalatory exposure to PAHs				
	Screedman				
	Standard Asphalt		Rubberized Asphalt		
	Giardini di Corcolle(RM)	Zola Predosa (BO)	Zola Predosa (BO)	Imer (TN)	Finale Emilia (MO)
PAHs	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)
Benzo [a] anthracene	256,79	62,99	7,56	7,65	5,16
Benzo[b]Fluoranthene	48,63	41,57	7,73	4,81	7,53
Benzo[j]Fluoranthene	11,25	4,54	2,86	0,41	1,55
Benzo[k]Fluoranthene	41,71	187,54	42,07	1,16	4,95
Benzo[g,h,i]Perylene	12,07	130,11	55,63	11,05	65,81
Benzo[a]Pyrene	61,23	98,57	18,63	11,69	71,37
Benzo[e]Piyene	63,76	132,04	24,65	21,39	46,77
Crhysene	264,50	75,53	14,23	13,23	8,85
DiBenzo[a,h]Anthracene	4,90	50,54	16,48	2,87	7,28
Indeno[1,2,3-cd]Pyrene	3,17	129,81	23,54	7,28	14,83
Pyrene	981,41	109,50	25,67	35,41	25,15

Table 5. *Concentration of PAHs in the breathing zone of rollers*

	Inhalatory exposure to PAHs			
	Roller			
	Standard Asphalt		Rubberized Asphalt	
	Giardini di Corcolle(RM)	Zola Predosa (BO)	Zola Predosa (BO)	Imer (TN)
PAHs	(ng/m^3)	(ng/m^3)	(ng/m^3)	(ng/m^3)
Benzo [a] anthracene	15,36	86,82	64,80	40,13
Benzo[b]Fluoranthene	2,98	90,25	37,75	20,54
Benzo[j]Fluoranthene	1,80	31,95	7,94	4,08
Benzo[k]Fluoranthene	2,47	287,07	189,42	25,12
Benzo[g,h,i]Perylene	14,38	356,29	102,71	46,29
Benzo[a]Pyrene	5,13	199,96	52,89	52,13
Benzo[e]Piyene	10,31	241,56	80,78	38,07
Crhysene	16,87	159,31	59,48	28,28
DiBenzo[a,h]Anthracene	0,00	81,18	25,35	9,62
Indeno[1,2,3-cd]Pyrene	2,21	238,74	101,84	13,62
Pyrene	52,63	115,05	103,79	25,59

3.3. *Amount of PAHs intercepted by the dermal sampling pads*

In tables 6 and 7 the surface amount of the 11 PAHs regulated by the EU or Italian regulation in the sampling pads for the screedmen is reported. The dermal pads data show in general a large variability and a significant number of analytes falling below the analytical limit of detection. Based on the analytical results,the following was found:

- The highest exposed worker was screedman 1 in Giardini di Corcolle (standard asphalt), for this worker, an average surface amount of 3.8 ng/cm2 for the 11 PAHs was measured in the dermal pads, in comparison with an average amount ranging from 0.08 to 038 ng/cm2 for all the other sites.

- For the Zola Predosa site, screedmen (Table 6 and 7) undergo to a significantly higher dermal exposure to PAHs when standard asphalt is placed, in comparison with rubberized asphalt. (Wilcoxon $p < 0.005$).

Table 6. *Surface amount of PAHs in dermal sampling pads for Screedman 1*

	Dermal exposure to PAHs				
	Screedman 1				
	Standard Asphalt		Rubberized Asphalt		
	Giardini di Corcolle(RM)	Zola Predosa (BO)	Zola Predosa (BO)	Imer (TN)	Finale Emilia (MO)
PAHs	(ng/cm^2)	(ng/cm^2)	(ng/cm^2)	(ng/cm^2)	(ng/cm^2)
Benzo [a] anthracene	7,55	<lod	0,05	0,13	0,07
Benzo[b]Fluoranthene	0,56	<lod	<lod	0,37	0,02
Benzo[j]Fluoranthene	0,18	<lod	<lod	0,04	0,01
Benzo[k]Fluoranthene	1,06	0,04	<lod	0,08	<lod
Benzo[g,h,i]Perylene	0,84	<lod	0,03	0,49	0,45
Benzo[a]Pyrene	7,82	<lod	0,42	0,31	<lod
Benzo[e]Piyene	4,25	0,39	0,41	0,62	<lod
Crhysene	5,34	<lod	0,01	0,18	<lod
DiBenzo[a,h]Anthracene	0,58	<lod	0,05	0,09	0,00
Indeno[1,2,3-cd]Pyrene	0,91	<lod	<lod	0,16	0,02
Pyrene	12,68	0,88	0,47	1,72	0,32

Table 7. *Surface amount of PAHs in dermal sampling pads for Screedman 2*

	Dermal exposure to PAHs				
	Screedman 2				
	Standard Asphalt		Rubberized Asphalt		
	Giardini di Corcolle(RM)	Zola Predosa (BO)	Zola Predosa (BO)	Imer (TN)	Finale Emilia (MO)
PAHs	(ng/cm^2)	(ng/cm^2)	(ng/cm^2)	(ng/cm^2)	(ng/cm^2)
Benzo [a] anthracene	1,78	0,27	0,07	0,20	<lod
Benzo[b]Fluoranthene	0,45	1,37	0,67	0,12	0,01
Benzo[j]Fluoranthene	0,05	0,22	0,20	<lod	<lod
Benzo[k]Fluoranthene	0,55	1,81	0,64	<lod	<lod
Benzo[g,h,i]Perylene	0,59	2,12	1,95	0,60	0,23
Benzo[a]Pyrene	0,31	1,63	0,82	<lod	<lod
Benzo[e]Piyene	<lod	1,88	1,12	0,30	<lod
Crhysene	1,96	0,74	0,60	0,13	0,03
DiBenzo[a,h]Anthracene	0,22	0,36	0,34	0,13	<lod
Indeno[1,2,3-cd]Pyrene	0,19	2,04	1,80	0,14	0,02
Pyrene	5,52	1,12	0,70	1,84	0,03

4. Risk Assessment

4.1 *Equations for the calculation of carcinogenic incremental risk*

The incremental cancer risk associated to the exposure to PAHs in the workplace has been calculated as the sum of the inhalatory and dermal risk. The following equation has been used for the calculation of inhalation risk (RI):

$$[1] \quad R_I = SF_I \frac{(C_p + C_v) \times I_R \times HE \times EF \times ED}{BW \times AT \times 365\ \boldsymbol{days/year}}$$

As far as risk associated to dermal exposure (RD) is concerned, the following equation has been used:

$$[2] \quad R_D = SF_d \frac{C_{pad} \times HE \times BF \times S \times EF \times ED}{ET \times BW \times AT \times 365\ days/year}$$

4.2.*Carcinogenic slope factors*

In table 8 the carcinogenicity data for the 11 PAHs regulated in Europe are reported. The Inhalation Slope Factor (SFi) was used for assessing the incremental cancer risk deriving for workers associated with the inhalatory exposure to PAHs, whilst dermal slope factor SFd ([mg/kg-day]-1) was calculated using equation provided by USEPA (2007) and parameters provided by OEHHA (2014). For the selected PAHs studied, the SFd value has the same value of the SFo reported in the table.

Table 8. *Summary of carcinogenicity information for selected PAHs*

PAH	IARC	Carcinogenic Target Risk (United States Environmental Protection Agency, 2014) (TR)=1x10^{-6}		Inhalation Slope Factor (SFi) (California Environmental Protection Agency 2014)	Slope Factor, Oral (United States Environmental Protection Agency, 2014)
		Residential Air	***Worker Ambient Air***		
	Class	**[μg/m^3]**	**[μg/m^3]**	**[(mg/kg-day)$^{-1}$]**	**[(mg/kg-day)$^{-1}$]**
Benzo [a] anthracene	2B	9.2×10^{-3}	1.1×10^{-1}	3,9×10^{-1}	7,3×10^{-1}
Benzo[b]Fluoranthene	2B	9.2×10^{-3}	1.1×10^{-1}	3,9×10^{-1}	7,3×10^{-1}
Benzo[j]Fluoranthene	2B	2.6×10^{-2}	1.1×10^{-1}	3,9×10^{-1}	1,2

Benzo[k]Fluoranthene	2B	9.2×10^{-3}	1.1×10^{-1}	$3,9\times10^{-1}$	$7,3\times10^{-2}$
Benzo[g,h,i]Perylene	3	N.A.	N.A.	N.A.	N.A.
Benzo[a]Pyrene	1	9.2×10^{-4}	1.1×10^{-2}	3,9	7,3
Benzo[e]Piyene	3	N.A.	N.A.	N.A.	N.A.
Crhysene	2B	9.2×10^{-2}	1.1	$3,9\times10^{-2}$	$7,3\times10^{-3}$
DiBenzo[a,h]Anthracene	2A	8.4×10^{-4}	1.0×10^{-2}	4,1	7,3
Indeno[1,2,3-cd]Pyrene	2B	9.2×10^{-3}	1.1×10^{-1}	$3,9\times10^{-1}$	$7,3\times10^{-1}$
Pyrene	3	N.A.	N.A.	N.A.	N.A.

4.3. *Contact rate factors*

Inhalation volumes (IR): based on the assumed intensity of the activity performed, the following inhalatory volumes (ECETOC, 2001) as where adopted for the calculation of inhalation exposure:

- Rollers: 1.67 m3/h (calculated as the average of 1hr intense activity and 5 hours of moderate activity;
- Screedman: 2.5 m3/h (intense activity)
- Pavers: 1.5 m3/h (moderate activity).

Life expectancy (AT): a 75 year life expectancy was assumed.

Duration of Exposure Events (HE):a 6 hours duration of each exposure event, based on direct observation and on personal communication received from the operators, has been adopted.

Frequency of Exposure Events (EF): conservatively assumed 240 days of road paving work per year;

Exposure duration, yearss: (ED): 30 years (personal communication received from the operators and interviews with workers);

Dermal Adsorbtion Coefficient (BF): Specific studies related to PAH adsorption provided adsorption coefficient values in the range of 0.3% to 1.4% (VanRooij JG, 1993) for pyrene and in the range 0.15% to 1.1% for benzo(a)pyrene (Stroo HF, 2005). Based on these data, a BF value of 1% has been adopted.

Exposed body surface (S). The surface area of workers was calculated by formula proposed by Du Bois and Du Bois and parameters provided by USEPA (2011), using weight and height data of workers collected through interviews before monitoring activities. Total exposed surface area was calculated summing the skin surface area for each body part, calculated as rate of total surface area (USEPA, 2011).

4.4 Results for the incremental carcinogenic risk assessment

The results of the carcinogenic risk assessment are reported in Table 9 (risk from Inhalation exposure), Table 10 (Risk from dermal exposure) and Table 11 (total risk).

Inhalatory exposure: In general, the incremental risk associated to the inhalatory exposure to rubberized asphalt fumes is lower than or in the worse case equal to the risk associated to the inhalatory exposure to standard asphalt fumes.
The comparison within jobs categories for the 2 types of asphalt reveals that the risk for the rollers is around 2 times lower for rubberized asphalt in comparison with standard asphalt ($1.13x10^{-5}$ against $2.15x10^{-5}$); for screedmen, the inhalation associated risk is 3 times lower for rubberized asphalt in comparison with standard asphalt; ($8.89x10^{-6}$ against $2.78x10^{-5}$), whilst for pavers, the risk, although slight lower for the rubberized asphalt, is comparable ($6.24x10^{-6}$ against $7.23x10^{-6}$).

Dermal Exposure: similarly, the risk associated to dermal exposure is lower for the exposure to rubberized asphalt fumes in comparison with standard asphalt.
In this case, the incremental risk for rubberized asphalt resulted in a value of $7.79x10^{-7}$, whilst the incremental risk for standard asphalt resulted almost ten times higher, with a value of $5.6x10^{-6}$.

Overall Exposure. the risk associated to the overall exposure can be calculated only for screedmen, as dermal exposure was measured only for these jobs.
For these workers, it is interesting to see that the relative contribution of the dermal exposure is around one tenth of the overall incremental risk.

Table 9. *Carcinogenic risk for Inhalation Exposure*

R_i- Risk associatied to Inhalation Exposure						
PAH	**Standard Asphalt**			**Rubberized Asphalt**		
	Roller	Screedman	Paver	Roller	Screedman	Paver
Benzo[a]Pyrene	$1,20\times10^{-5}$	$1,48\times10^{-5}$	$3,92\times10^{-6}$	$6,13\times10^{-6}$	$6,28\times10^{-6}$	$4,30\times10^{-6}$
∑ PAHs	$2,15\times10^{-5}$	$2,78\times10^{-5}$	$7,24\times10^{-6}$	$1,13\times10^{-6}$	$8,89\times10^{-6}$	$6,24\times10^{-6}$

Table 10. *Carcinogenic risk for Dermal Exposure*

R_d- Risk associated to Dermal Exposure		
PAH	**Standard Asphalt**	**Rubberized Asphalt**
	Screedman	Screedman
Benzo[a]Pyrene	$4,35\times10^{-6}$	$4,64\times10^{-7}$
∑ PAHs	$5,60\times10^{-6}$	$7,79\times10^{-7}$

Table 11. *Combined Incremental Carcinogenic Risk*

PAH	R tot	
	Standard Asphalt	**Rubberized Asphalt**
	Screedman	Screedman
Benzo[a]Pyrene	$1{,}92\times10^{-5}$	$6{,}74\times10^{-6}$
∑ PAHs	$3{,}34\times10^{-5}$	$9{,}67\times10^{-6}$

5. Conclusions

Based on the outcome of the monitoring activities, the use of rubberized asphalt resulted in a significant, though slight reduction of the incremental carcinogenic risk for workers. At this stage, given the limited number of monitored field, is not possible to prove that the observed benefit has to be associated to site-specific conditions rather than to an actual reduction of the release of PAHs from rubberized asphalts. To understand this aspect, a specific laboratory activity aimed at studying the release of PAHs in controlled conditions from a range of rubberized and standard asphalts is undergoing. In the meanwhile, monitoring activities are also planned on a number of additional sites.

The monitoring also showed that the risk for the workers in the observed road paving yards was limited. The highest calculated incremental risk resulted, (screedman, standard asphalt) in the order of $3.4\text{x}10^{-5}$, which is slightly higher than the generally accepted incremental risk for occupational exposure of $1\text{x}10^{-5}$, whilst all the workers placing rubberized asphalt were exposed to a risk lower than $1\text{x}10^{-5}$

The risk associated to dermal exposure is around one order of magnitude lower than the risk associated to inhalation exposure, ranging from $7.79\text{x}10^{-7}$ to $5.6\text{x}10^{-6}$

Although the risk for workers is not alarming, the use of simple PPE (Personal protective equipment) like disposable facial masks equipped with activated charcoal cartridges, of light, disposable suits could easily lower it of one order of magnitude, and is therefore recommended for this type of activity.

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