POLITECNICO DI TORINO
Repository ISTITUZIONALE

Development of a laboratory test procedure for the evaluation of potential gaseous emissions of asphalt rubber bituminous mixtures

Original
Development of a laboratory test procedure for the evaluation of potential gaseous emissions of asphalt rubber bituminous mixtures / Zanetti, Mariachiara; Fiore, Silvia; Ruffino, Barbara; Santagata, Ezio; Lanotte, MICHELE ANTONIO; Dalmazzo, Davide. - ELETTRONICO. - (2014), pp. 119-128. (Intervento presentato al convegno ICTI 2014 International Conference on Transportation Infrastructure tenutosi a Pisa nel 22-25 aprile 2014).

Availability:
This version is available at: 11583/2543149 since: 2015-11-27T12:45:19Z

Publisher:
Taylor & Francis Group

Published
DOI:

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

12 October 2024

Development of a laboratory test procedure for the evaluation of potential gaseous emissions of asphalt rubber bituminous mixtures

M.C. Zanetti, S. Fiore, B. Ruffino, E. Santagata, M. Lanotte & D. Dalmazzo
Politecnico di Torino, Turin, Italy

ABSTRACT: The superior performance of bituminous mixtures containing crumb rubber from end-of-life tyres has been widely documented from a structural and functional point of view. However, potential impact of the use of crumb rubber on the health of workers in pavement construction sites has been the subject of a limited number of investigations, with a consequent gap in currently available technical knowledge. Following previous research work focused on the chemical analysis of fumes sampled on site, in this paper the Authors present results obtained in the development of a laboratory test procedure for the evaluation of gaseous emissions of asphalt rubber bituminous mixtures in standard, controlled conditions unaffected by site-specific factors. The investigation included monitoring of emissions at the paver's driving seat and at the screed during the laying of gap- and dense-graded wearing course mixtures in three different sites. Laboratory tests were performed by following a fume-generation protocol and by measuring the contents of volatile organic compounds and polycyclic aromatic hydrocarbons in produced emissions. Comparison of results derived from laboratory and field data was carried out in absolute terms and within a carcinogenic risk assessment model. It was found that the proposed laboratory procedure yields emissions which in most cases are similar to those recorded on site at the paver's screed and that lead to a conservative risk estimate.

1 INTRODUCTION

Benefits which derive from the use of crumb rubber (CR) from end-of-life tyres in bituminous mixtures for paving applications have been clearly highlighted by experimental research and field implementation in the last 50 years. In particular, it has been observed that the so-called "asphalt rubber" (AR) binders produced by means of the "wet" technology can be incorporated into gap- and dense-graded mixtures which exhibit a superior performance in terms of resistance to fatigue, permanent deformation, ageing and water damage. Moreover, positive records have been collected with respect to functional properties such as skid resistance and noise absorption (Hicks 2002, Caltrans 2005, Way et al. 2012).

Although the diffusion of AR bituminous mixtures is increasing worldwide, concerns still exist with respect to the potential impact they may have on health of construction workers. In general terms it has been noticed that odour of emissions of such paving materials is distinctively different from that of standard mixtures and that in some cases severe eye, nose and throat irritation episodes have been reported (Santagata & Zanetti 2012b). However, few studies have analysed the potential toxic and carcinogenic effects of fumes produced on site.

The most relevant investigation documented in literature on this specific subject was performed in the United States by the National Institute for Occupational Safety and Health (NIOSH) in cooperation with the Federal Highway Administration (FHWA) (Burr et al. 2001). Based on data gathered at seven pavement construction sites, occupational exposures among asphalt workers were evaluated by comparing conventional and AR bituminous mixtures.

The study included the evaluation of workers' medical data and a massive amount of chemical analyses carried out on fumes sampled at paving sites in different positions. In particular, tests were carried out for total particulate, benzene soluble particulate, polycyclic aromatic compounds, organic sulphur-containing compounds and benzothiazole.

It was found that the highest exposures were from jobs near the paver of asphalt delivery trucks. Moreover, irritation symptoms were more frequently reported in association with laying of AR mixtures. It was concluded that exposure to emissions of bituminous mixtures containing CR may be potentially more hazardous than that associated to conventional paving materials. However, such a conclusion was not supported by quantitative models for the assessment of workers' health risks.

A personal exposure monitoring study was carried out by Watts et al. (1998), that analysed gaseous emissions of bituminous mixtures containing CR and of the standard type by focusing on fine respirable particles (< 2.5 microns) and particle-bound polycyclic aromatic hydrocarbons (PAHs). Obtained results showed that in some of the considered sites the presence of AR mixtures led to greater potential carcinogenic PAH exposures of road workers. However, a statistical analysis indicated that there were no significant differences with respect to standard mixtures.

Stout and Carlson (2003) reviewed the results of investigations carried out in three US states on stack emissions at production plants in which bituminous mixtures were prepared with and without CR. Even though the studies were performed with different approaches and methods, in all cases the effects of CR, if any, were reported to be relatively small when compared to the effects of other variables.

Health effects of gaseous emissions produced by AR bituminous mixtures have been recently studied by the Authors of this paper by means of a sanitary-environmental risk analysis procedure which was employed to model experimental data obtained from field monitoring activities (Zanetti et al. 2013a, 2013b). Such an approach is totally different not only from those of the investigations described above, but also from those which in the past have been performed, with the support of toxicological and epidemiological studies, to evaluate the toxic and carcinogenic properties of standard bituminous binders and mixtures (Concawe 1992, NIOSH 2000, ACGIH 2001, German Bitumen Forum 2006, IARC 2013).

Emission samples taken at paving sites according to a specific protocol were subjected to laboratory analyses for the evaluation of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). It was found that composition of fumes is affected by several material-specific (i.e. mixture composition, CR type and bitumen base type) and site-specific (i.e. layer thickness, laying and air temperature, air pressure, relative humidity and wind speed) factors. Nevertheless, relative contributions of bitumen quantity, type and composition seemed to be the most relevant.

In order to highlight health-related effects caused by the use of CR, toxic and carcinogenic risk parameters considered within the risk analysis procedure (Hazard Quotient, HQ, and Individual Excess Life Cancer Risk, IELCR) were expressed in relative terms, by comparing absolute values with analogous data obtained in other paving sites where no CR was employed. As a consequence of such an analysis, it was concluded that the toxic and carcinogenic risk to which workers are exposed on site in the case of AR mixtures is comparable to that of standard paving materials (produced by employing neat or polymer-modified bitumen).

Following the research work cited above, the Authors observed it would be useful to develop a laboratory test procedure for the assessment of gaseous emissions of bituminous mixtures in standard, repeatable conditions (Zanetti et al. 2013b).

Analysis of literature revealed that such an issue has been addressed in the case of standard materials (i.e. not containing CR) by considering in most cases the generation of fumes from the binder only. Different prototype units have been developed and thereafter employed either by comparing composition of laboratory-produced and field-generated fumes or by analyzing the effects caused by variations in bitumen composition (including tar content and added steam) and temperature (Brandt & de Groot 1999, Kurek et al. 1999, Bonnet et al. 2000, Binet et al. 2002, Budija et al. 2004, Hugener et al. 2004, Gasthauer et al. 2008, de La Roche et al. 2008). Studies also focused on the critical analysis of the fume generation protocol adopted by NIOSH (Sivak et al. 1989) as part of the animal skin painting studies carried out in the 80s to assess the carcinogenic response of roofing asphalt (McCarthy et al. 1999).

A laboratory procedure for the production and analysis of fumes from bituminous mixtures was developed by the research group of the Laboratoire Central des Ponts et Chaussées (LCPC, now part of IFSTTAR, the French Institute of Science and Technology for Transport, Development and Networks) as part of a scientific collaboration with Shell Bitumen (Paranhos et al. 2006, Paranhos 2007).

According to such a procedure, emissions are generated during mixing of aggregates and bitumen in a thermo-regulated epicycloidal mixer. Fumes are collected through a stainless steel stack linked to the mixer and are thereafter subjected to analysis for the evaluation of total organic compounds, semi-volatile organic compounds and benzene soluble matter. The actual mixing protocol has been fine-tuned to mimic the various phases of production and laying during which mixtures are subjected to movement (Gaudefroy et. al 2010, Viranaiken et al. 2010). Developments have also been implemented with respect to chemical analysis of sampled emissions.

Preliminary investigations performed with such an apparatus highlighted the effects on gaseous emissions of mixing time and temperature, bitumen content and bitumen type (Gaudefroy et al. 2008). Subsequently, the procedure was employed for the evaluation of non-standard materials such as half-warm mixtures (Gaudefroy et al. 2009, Olard & Gaudefroy 2012) and mixtures containing reclaimed asphalt pavement material (Enell et al. 2012).

In this paper the Authors present the results obtained during the development of a laboratory test procedure for the assessment of gaseous emissions of bituminous mixtures containing CR. Investigations started in the field, where fumes were sampled

at three paving sites during laying of AR wearing course mixtures of the gap- and dense-graded type. The same mixtures were thereafter subjected to the laboratory procedure under development, by means of which emissions were generated in controlled conditions. Results of chemical analyses performed on the fumes sampled in the field and in the laboratory, expressed in terms of concentration of VOCs and PAHs, were compared in absolute terms and by taking into account the specific carcinogenic effects of each detected compound.

Even though the proposed test procedure may require further improvements and a more extended validation, experimental results obtained in this preliminary investigation were certainly encouraging. Laboratory emissions of the considered AR bituminous mixtures were compared in the absence of site-specific biasing effects and were found to be associated to conservative values of carcinogenic risk parameters.

2 FIELD INVESTIGATION

2.1 *Construction sites*

Experimental activities were based on observations and measurements performed during pavement construction/rehabilitation operations carried out in three different paving projects, respectively indicated as BV-G, ZA-G and CE-D (Santagata et al. 2012, Zanetti et al. 2013a).

Mixtures constituting wearing courses contained AR binder supplied by the only Italian plant which currently employs the "wet" production technology (with a typical declared CR content of 18%). After being produced in the central plant, where they are cured at 190°C for approximately 45 minutes, AR binders are usually left to cool down overnight and thereafter transported to the hot mix plant. Before starting mixture production, the heating system of the transport tank is turned on and after reaching a sufficiently low viscosity (comprised between 1500 and 5000 cP) the binder is pumped through the supply line of the hot mix plant.

The above described steps were followed in the case of projects BV-G and ZA-G. However, due to the specific characteristics of the binder supply line of the involved hot mix plant, in project CE-D asphalt rubber was stored overnight at high temperature in one of the plant's tanks were it was kept in continuous agitation. Finally, before mixture production, the AR binder was partially diluted with an additional neat bitumen, thus leading to a low viscosity final binder with CR content of the order of 5% (Zanetti et al. 2013a).

Since the three construction sites were located in different Italian provinces, for each of them, aggregates of different origin and characteristics were employed.

Mix design was based on the requirements of available technical specifications which refer to gap-graded and dense-graded mixtures (CIRS 2009, ARI 2012, CIRS 2001).

A description of the sites, including information on length (L) and areal extension (A) of test sections, is provided in Table 1. In all cases, design thickness of the wearing course was equal to 3 cm.

Table 1. Construction sites.

Site	Road	Mixture	L [m]	A [m^2]
BV-G	Provincial	Gap-graded	1,200	16,000
ZA-G	Urban road	Gap-graded	650	5,000
CE-D	Urban road	Dense-graded	250	2,000

2.2 *Construction monitoring*

During construction works, mixture temperature (T_m) behind the paver's screed was recorded by means of hand-held immersion thermometers. By making use of a multi-purpose probe, site-specific conditions were also assessed by measuring air temperature (T_a) and, in the case of sites ZA-G and CE-D, air pressure (p_a), relative humidity (φ_a) and wind speed (v_w). Average values deriving from such measurements are given in Table 2.

Table 2. Laying conditions at the construction sites.

Site	T_m [°C]	T_a [°C]	p_a [bar]	φ_a [%]	v_w [m/s]
BV-G	170	9	-	-	-
ZA-G	145	28	1014	34	0.4
CE-D	170	26	1004	48	0

2.3 *Sampling of emissions and mixtures*

Samples of gaseous emissions produced by the AR bituminous mixtures were taken at the driver's seat of the paver and at the screed. This was done in the most severe exposure conditions which respectively correspond to mixture discharge operations from delivery trucks and to the forward movement of the paver during laying.

By following the sampling protocol developed in previous research work (Santagata & Zanetti 2012a, 2012b), fumes were adsorbed on active granular carbon cartridges by means of a portable pump which was operated in each point of interest for 5 minutes with a flow rate of 0.5 l/min. Samples were then marked for identification and transferred to the laboratory where they were stored at freezing temperature until analysis.

Finally, during laying operations, samples of loose mixtures were taken at the paver for subsequent laboratory testing.

2.4 *Composition of mixtures*

Compliance of mixture composition with requirements set by technical specifications was checked in the laboratory by subjecting samples taken on site to tests for the determination of binder content and aggregate size distribution.

Binder content was determined by means of ignition tests carried out according to EN 12697-39 (2012). Mean values, expressed as a percentage of dry aggregate mass (%B), are listed, together with acceptance intervals (Δ%B), in Table 3.

Table 3. Binder content of AR bituminous mixtures.

Site	%B	Δ%B
BV-G	7.8	7.5-8.5
ZA-G	8.5	7.5-8.5
CE-D	5.6	4.8-5.8

Size distribution of the aggregates recovered from ignition tests was evaluated in wet conditions. Average results are plotted in Figure 1.

2.5 *Analysis of gaseous emissions*

Analysis of fumes sampled on each construction site was carried out by subjecting test cartridges to solvent extraction (with methylene chloride, Fluka, HPLC grade) in an ultrasound bath for 60 minutes (EN 13689 2002, Lindberg et al. 2008) and by then analysing the resulting fluid with an Agilent 7890/5975 gas chromatograph, equipped with a HP5-MS capillary column (30m×0.25mm×0.25μm). Based on the evaluation of the position and area of response peaks, concentrations of VOCs and PAHs were determined.

Results of these analyses are synthesized in Tables 4 and 5, which show average concentrations of detected chemical compounds (two samples per site and position). These include all those which typically reach measureable threshold values and those which are potentially harmful for human beings in the case of extended exposure (ISS 2012).

AR binders employed for the production of mixtures ZA-G and CE-D contained the same CR and base bitumen type. Moreover, it was observed that the neat dilution bitumen added to the AR binder at the hot mix plant of site CE-D had a composition which was similar to that of the base bitumen (Zanetti et al. 2013a). As a result of these common factors, for the two sites similar results were obtained in terms of both VOCs and PAHs (total contents and concentrations of single compounds). Thus, it can be hypothesized that the effects of the higher binder content of mixture ZA-G (8.5% vs. 5.8%) were compensated by the lower laying temperature (145°C vs. 170°C). The overall influence of site-specific factors (Table 2) was in this case of minor relevance.

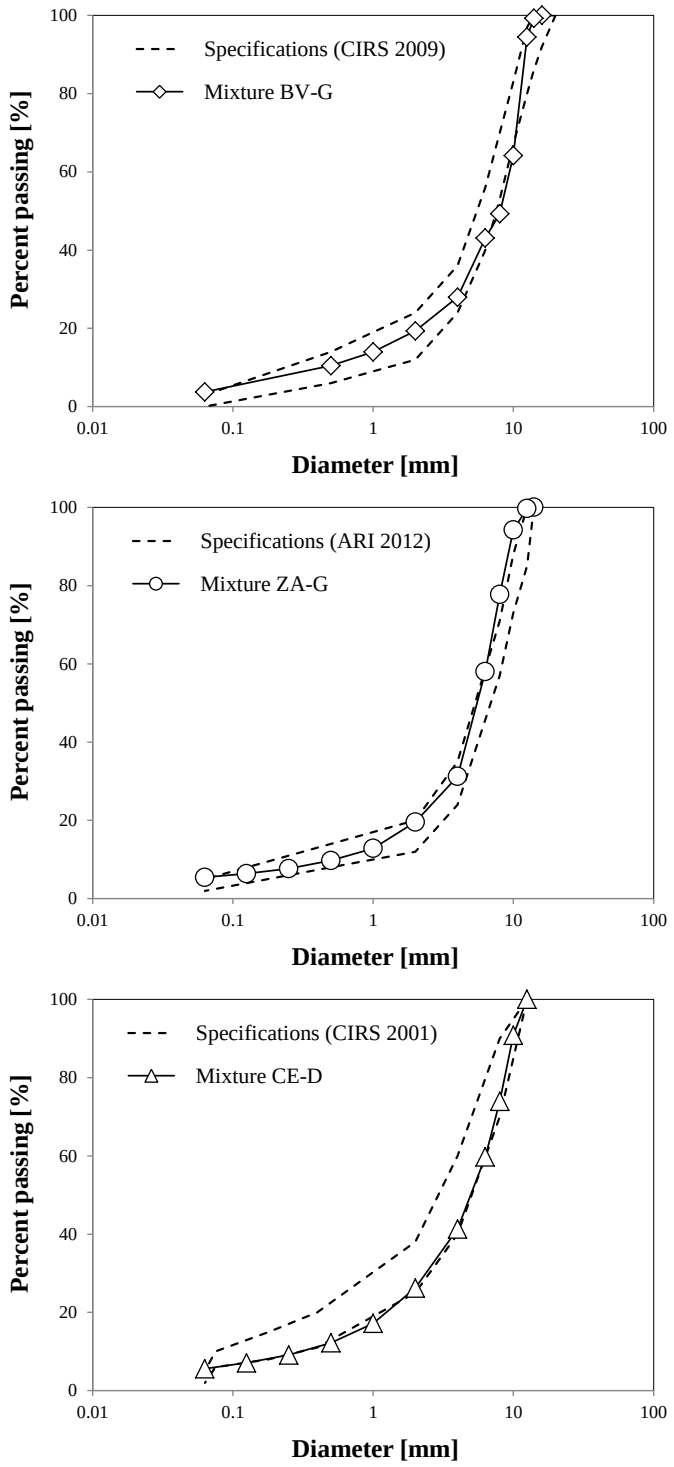

Figure 1. Particle size distribution of aggregates extracted from AR bituminous mixtures.

As expected, different results were recorded for mixture BV-G, prepared by employing AR which contained base materials different from those of mixtures ZA-G and CE-D and laid in conditions in which the mixture-air temperature differential was very high. In particular, while VOC data were found to be similar to the other paving sites at the screed, very high concentrations were recorded for all PAH compounds in both sampling positions.

Table 4. VOCs of gaseous emissions (μg/m^3) at the paver (D: driver's seat; S: screed).

	BV-G		ZA-G		CE-D	
	D	S	D	S	D	S
Benzene	4.0	-	11.9	3.7	1.2	2.7
Toluene	9.0	13.4	24.1	21.1	23.5	31.6
Ethylbenzene	-	-	7.2	6.1	13.3	7.7
p-Xylene	19.5	81.2	16.0	1.9	15.1	5.1
Styrene	-	-	0.56	0.25	0.55	0.56
Bromobenzene	-	-	1.9	2.9	1.4	2.5
1,3,5-Trimethylbenzene	11.6	17.1	40.0	66.1	36.5	55.0
1,2,4-Trimethylbenzene	30.1	12.2	42.2	16.9	24.5	38.8
p-Isopropiltoluene	5.4	57.3	15.5	3.9	10.3	14.0
Butylbenzene	-	6.0	8.5	1.9	2.9	18.0
1,3,5-Trichlorobenzene	-	-	-	-	-	-
1,2,4-Trichlorobenzene	-	-	-	-	-	-
total VOCs	80	187	168	125	129	176

Table 5. PAHs of gaseous emissions (μg/m^3) at the paver (D: driver's seat; S: screed).

	BV-G		ZA-G		CE-D	
	D	S	D	S	D	S
Naftalene	7.2	5.2	2.0	3.3	1.4	2.4
Acenaphthylene	1.65	1.2	0.14	0.17	-	0.09
1-Bromonaphthalene	11.1	9.2	2.4	3.9	2.3	3.0
Acenaphthene	2.1	1.4	-	0.08	-	-
Fluorene	1.2	0.99	1.8	2.2	2.3	1.3
Phenanthrene	2.1	1.1	0.37	0.15	-	0.10
Anthracene	2.0	0.63	0.17		-	-
Fluoranthene	3.2	0.95	1.7	0.08	-	0.09
Pyrene	3.1	0.90	0.65	0.38	0.23	0.32
Triphenylene	3.5	1.5	-	-	-	-
Benz[a]anthracene	5.9	4.3	-	-	-	-
Benzo[b]fluoranthene	3.5	0.81	3.2	1.6	2.1	1.6
Benzo[a]pyrene	3.2	3.5	2.4	8.1	4.1	6.7
Indeno[1,2,3-cd]pyrene	8.5	-	-	-	-	-
Dibenzo[a,h]antracene	-	-	-	-	-	-
Benzo[ghi]perylene	3.7	1.2	0.26	-	-	-
total PAHs	62	33	15	20	12	16

3 LABORATORY GASEOUS EMISSION TESTS

3.1 *Experimental approach and test protocol*

As previously mentioned, a laboratory test procedure was developed with the purpose of obtaining quantitative data on gaseous emissions produced in standard conditions by bituminous mixtures containing CR.

Such a development was deemed necessary in order to reach the following goals:

- supplement field emission measurements with a more objective evaluation, independent from site-specific factors which may have a major influence on composition of fumes and on the relative concentrations of VOCs and PAHs;
- perform an evaluation of the potential gaseous emission of mixtures even when site measurements are not available (e.g. in the design phase when different candidate mixtures may be compared).

As proven by the results of previous studies performed by the Authors, the major emphasis of emission studies should be placed on the evaluation of effects which fumes may have on workers' health, with the consequent assessment of carcinogenic risk (Zanetti et al. 2013a, 2013b). Thus, in the context of a conservative approach to this very delicate issue, preliminary tests were performed in the laboratory by trying to identify a protocol capable of yielding emissions that do not lead to an underestimate of potential risks.

AR bituminous mixtures employed in the development of the test procedure were those sampled at sites BV-G, ZA-G and CE-D, subjected to a full characterization in terms of composition and monitored for emissions during construction activities.

The device used for fume generation was the same employed by the LCPC research group (Paranhos et al. 2006, Paranhos 2007, Gaudefroy et. al 2008, 2009, 2010, Viranaiken et al. 2010, Olard & Gaudefroy 2012, Enell et al. 2012): a high-capacity (80 kg) temperature-controlled laboratory mixer equipped with a vertical-axis screw mixing tool. As described below, definition of the exact test protocol adopted during the development phase of the procedure derived both from practical needs and from the analysis of expected emission phenomena.

Mass of samples subjected to testing was fixed at 30 kg with the purpose of leaving inside the mixer a significant free volume available for saturation with gaseous emissions.

Test duration was set at 1 hour in order to guarantee a complete fume development in stationary conditions.

Test temperature, which has a major effect on fume production, was initially set at 150°C (for mixture BV-G) since in literature such a temperature is indicated as the threshold which corresponds to the onset of emission phenomena (Riley 2004). However, further on in the investigation, temperature was increased to 175°C (for mixtures ZA-G and CE-D) in order to obtain the release not only of light boiling point hydrocarbons but also of semi-volatile and aerosol fractions. According to the Authors' experience such a temperature also represents the maximum value which is rarely exceeded during laying in the field (Santagata & Zanetti 2012b).

Given that gaseous emissions are influenced by the equilibrium which occurs at the interface between the hot bituminous mixture and surrounding air, it was decided that static temperature conditioning should be supplemented by a mixing action applied to the material according to a given pattern.

This was done by making use of the vertical mixing tool which was operated with its standard rotational speed for defined time periods during the test.

In order to guarantee coherency between laboratory and on-site experimental data, sampling of gaseous emissions from the head-space of the mixer at the end of the controlled heating period was performed with the same apparatus and procedure employed in field investigations.

In summary, the adopted laboratory test procedure can be described by referring to the following operative steps.

Step 1. Preliminary conditioning. 30 kg of mixture are kept at target test temperature (typically 175°C) for 4 hours in a forced draft oven, while the mixer, completely closed (including aspiration conduits), is preconditioned at the same temperature.

Step 2. Sample charge. The pre-heated mixture is transferred to the mixer which is thereafter closed and turned on, with a mixing speed of 20.4 rpm, for 2 minutes in order to obtain a homogeneous distribution of the material and to quickly return to target test temperature.

Step 3. Emission generation. With the aspiration system closed, the mixer is operated by setting the mixing tool in movement for 2 minutes with 15 minutes intervals (1 hour total fume generation time).

Step 4. Emission sampling. A sampling tube is inserted in the mixing chamber through a small opening and emissions are aspired by means of the same pump employed for field monitoring (5 minutes sampling time, flow rate of 0.5 l/min).

Step 5. Chemical analyses. Active granular carbon cartridges which are part of the sampling device are transferred to the laboratory where they are subjected to the necessary treatments and tests for the determination of VOC and PAH content.

3.2 *Results and discussion*

Average results obtained from the analyses of gaseous emissions sampled during laboratory tests (two samples per test) are given in Tables 6 and 7, which also contain values of slope factors (SFs) associated to considered compounds within a carcinogenic risk assessment model of the following type (ISS 2012):

$$R = SF \cdot C \cdot E \qquad (1)$$

where R is carcinogenic risk, C is concentration of the compound in the exposure point, E is exposure.

Increasing values of SF indicate more severe health risks for pavement construction workers for a given concentration and exposure.

Experimental data recorded in the laboratory are also shown in Figures 2 and 3, where they are compared to field data in terms of single compounds.

Table 6. Laboratory tests. VOCs of gaseous emissions (μg/m^3) and SFs (mg^{-1}·kg·days).

	BV-G	ZA-G	CE-D	SF
Benzene	14.5	2.5	14.1	0.0273
Toluene	11.1	20.5	27.1	-
Ethylbenzene	2.3	5.3	7.1	-
p-Xylene	2.6	2.7	1.9	-
Styrene	-	1.4	0.22	-
Bromobenzene	1.3	1.6	2.9	-
1,3,5-Trimethylbenzene	54.9	75.6	6.2	-
1,2,4-Trimethylbenzene	35.3	13.5	4.0	-
p-Isopropiltoluene	15.8	1.9	6.2	-
Butylbenzene	5.9	2.3	1.1	-
1,3,5-Trichlorobenzene	-	-	-	-
1,2,4-Trichlorobenzene	-	-	-	-
total VOCs	144	127	71	-

Table 7. Laboratory tests. PAHs of gaseous emissions (μg/m^3) and SFs (mg^{-1}·kg·days).

	BV-G	ZA-G	CE-D	SF
Naftalene	2.5	2.1	2.5	0.031
Acenaphthylene	0.73	-	-	0.031
1-Bromonaphthalene	8.4	4.6	13.5	0.031
Acenaphthene	1.1	-	-	0.031
Fluorene	1.1	2.3	13.9	0.031
Phenanthrene	0.61	0.12	0.12	0.031
Anthracene	0.14	-	-	0.031
Fluoranthene	0.53	0.18	0.14	0.031
Pyrene	0.46	0.38	0.77	-
Triphenylene	-	-	-	0.031
Benzo[a]anthracene	-	-	-	0.6
Benzo[b]fluoranthene	1.5	2.8	1.8	0.6
Benzo[a]pyrene	5.7	11.3	4.9	7.32
Indeno[1,2,3-cd]pyrene	-	-	-	0.031
Dibenzo[a,h]antracene	-	-	-	0.031
Benzo[ghi]perylene	-	-	-	-
total PAHs	23	24	38	-

Given that in laboratory tests there are no biasing effects of site-specific factors, and despite the fact that test on mixture BV-G was carried out at a lower temperature (150°C vs. 175°C), from the data shown in Tables 6 and 7 it can be observed that results for the three mixtures are contained in a range that is more narrow than that of field measurements. The only exception is represented by total VOC content of emissions produced by mixture CE-D, which was found to be significantly lower than that of mixtures BV-G and ZA-G. This may be due to the peculiar thermal history of the asphalt rubber binder employed for the preparation of mixture CE-D, which after the previously mentioned overnight heating may have lost most of the volatile compounds (e.g. 1,3,5 and 1,2,4trimethylbenzene). Such an hypothesis is coherent with results obtained in previous studies by Binet et al. (2002) which observed the progressive exhaustion of light 2-ring PAHs as a result of prolonged laboratory heating.

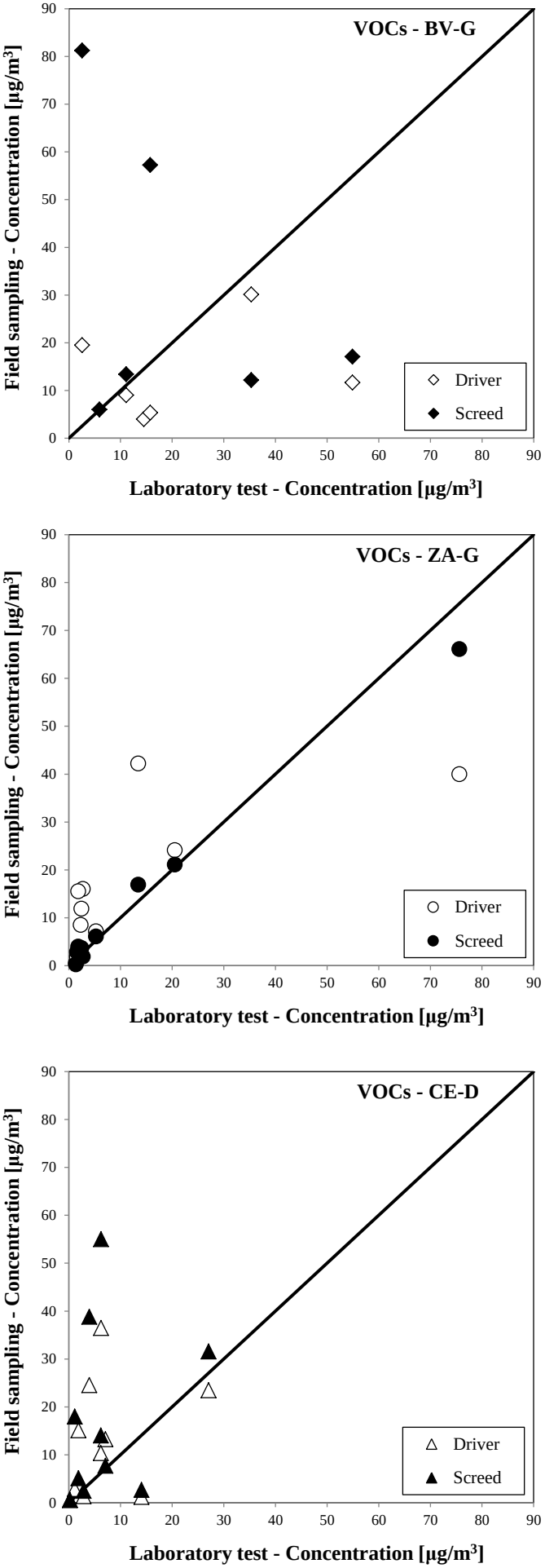

Figure 2. Volatile organic compounds (VOCs). Comparison between results of laboratory tests and field monitoring of gaseous emissions.

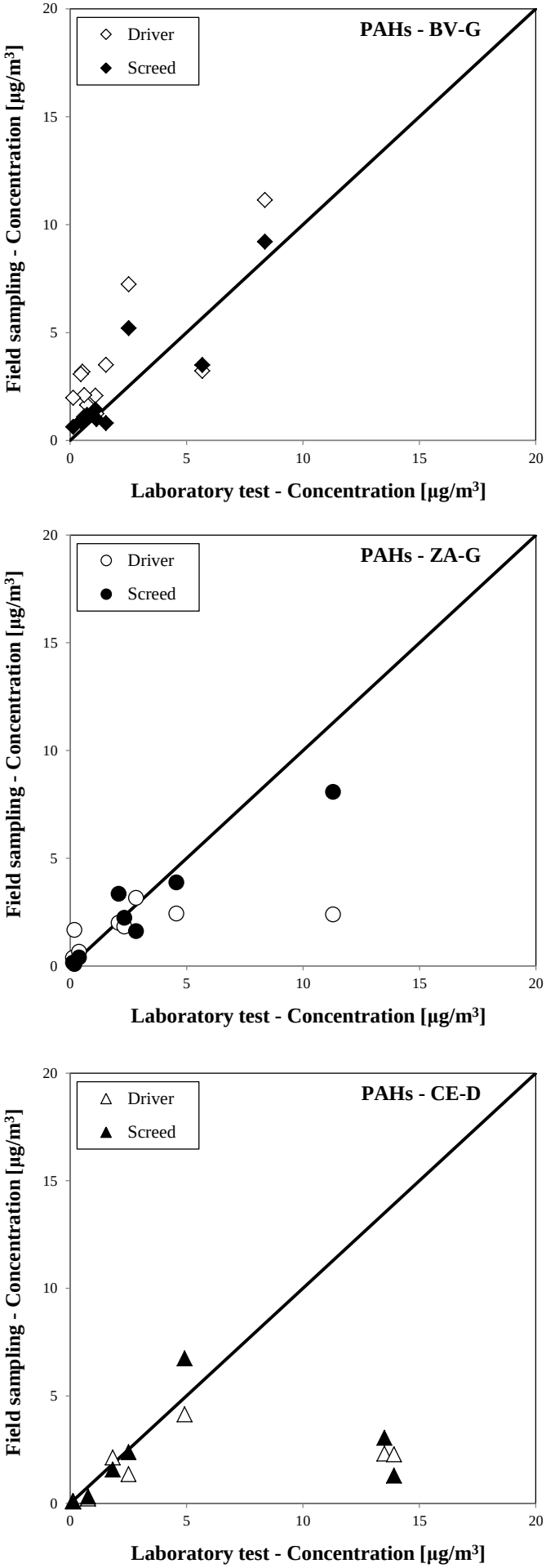

Figure 3. Polycyclic aromatic hydrocarbons (PAHs). Comparison between results of laboratory tests and field monitoring of gaseous emissions.

Plots represented in Figures 2 and 3 indicate that emissions produced in standard laboratory conditions deviate from those recorded on site. This is not surprising since the purpose of the test is not to exactly reproduce field scenarios which in any case are extremely variable. Nevertheless, by considering the overall distribution of data points (above and below the equality lines in Figures 2 and 3), the following general deductions can be drawn with respect to compared experimental results:

- differences between field and laboratory emissions are significant in the case of VOCs, as a result of their low molecular weight which makes them very sensitive to variations of site-specific factors and subjected to uncertainties in chemical analyses;
- differences are comparatively smaller in the case of PAHs, which are more stable and subjected to minor uncertainties;
- for each mixture and construction site, laboratory data are closer to screed measurements than to those obtained at the paver's driving position, which are unpredictably affected by the specific dynamics of fume migration.

Since the ultimate purpose of emission monitoring is to assess potential health risks for construction workers, comparative analysis of experimental data should take into account the specific carcinogenic effects of each detected compound. Thus, for each construction site and measurement position the sum of weighted concentrations was calculated as indicated below:

$$R_1 = \sum_{i=1}^{n} \frac{SF_i \cdot C_i}{1000} \qquad (2)$$

where R_1 represents carcinogenic risk for unit exposure, $(SF_i \cdot C_i)/1000$ is the weighted concentration of the i-th carcinogenic compound. Such an approach to data analysis is similar to the one proposed by Posniak (2005) for the assessment of workers' exposure in several asphalt-related production processes.

Field and laboratory experimental results expressed in terms of parameter R_1 are given in Figure 4. It can thus be observed that the assessment based on laboratory data is fully conservative for two of the considered sites (BV-G and ZA-G). However, in the case of mixture CE-D, risk associated to the screed position is slightly underestimated as a result of the high concentration of benzo[a]pyrene which was detected on site (unfortunately based on a single emission sample).

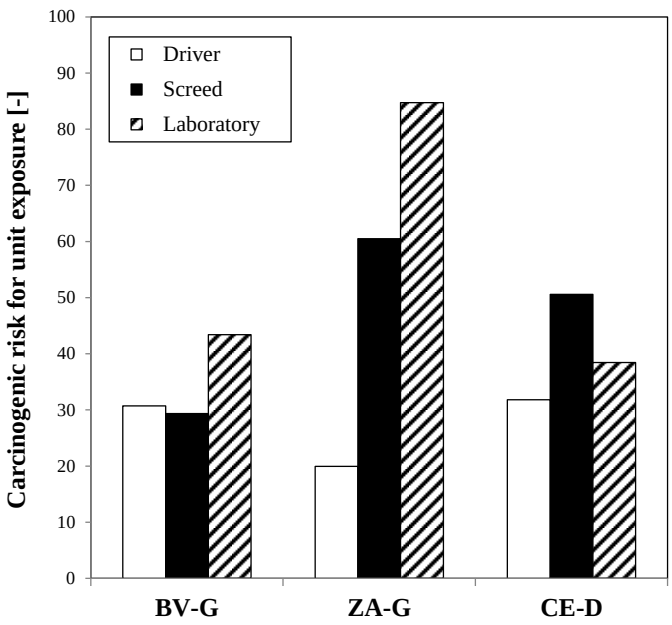

Figure 4. Carcinogenic risk for unit exposure of the three AR bituminous mixtures.

4 CONCLUSIONS

Results presented in this paper suggest that the laboratory procedure developed by the Authors for the evaluation of gaseous emissions of AR bituminous mixtures can be extremely useful in assessing the impact of such materials on paving workers' health.

It was shown that while emissions recorded in the field may be affected by site-specific factors, those which are produced in the laboratory by means of the proposed test procedure can be more clearly analysed with the purpose of highlighting effects of material-specific factors. Moreover, it was found that in most cases laboratory data are similar to those recorded at the paver's screed and that they lead to a fully conservative estimate of carcinogenic risk.

It is envisioned that the test method may be employed as a supplement to field investigations and/or as a design tool for the comparison between different AR bituminous mixtures. Nevertheless, improvements to the procedure may still be sought by investigating in more detail the influence of test temperature and time on the concentrations of VOCs and PAHs in generated fumes. Moreover, the significance of test results may be increased further by expanding the available database and by expressing carcinogenic risk values in relative terms with respect to data obtained from the analysis of standard bituminous mixtures.

ACKNOWLEDGEMENTS

The investigation described in this paper was carried out as part of the POLIPNEUS and TYREC4LIFE research projects, respectively funded by Ecopneus S.c.p.A. and by the European Commission.

REFERENCES

ACGIH. 2001. *Documentation of the threshold limit values for chemical substances. Asphalt (Bitumen) fumes*, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, USA.

ARI. 2012. *Technical specifications for gap-graded asphalt concrete with asphalt rubber*, Asphalt Rubber Italia, Agliana, Italy.

Binet, S., Bonnet, P., Brandt, H., Castegnaro, M., Delsaut, P., Fabries, J.F., Huynh, C.K., Lafontaine, M., Morel, G., Nunge, H., Rihn, B., Vu Duc, T. & Wrobel, R. 2002. Development and validation of a new bitumen fume generation system which generates polycyclic aromatic hydrocarbon concentrations proportional to fume concentrations, *Ann. Occup. Hyg.*, 46(7): 617-628.

Bonnet, P., Binet, S., Brandt, H., Kriech, A.J., Nunge, H., Morele, Y., de Groot, P., Wissel, H. & Castegnaro, M. 2000. Inhalation study on exposure to bitumen fumes. Part 1: Development and validation of the equipment, *Ann. Occup. Hyg.*, 44(1): 15-29.

Brandt, H.C.A. & de Groot, P.C. 1999. "A laboratory rig for studying aspects of workers exposure to bitumen fumes", *American Industrial Hygiene Association Journal*, 60(2): 182-190.

Budija, M., Cornelius, P., Johnson, S., Parry, M. & Webb, C. 2004. *The development of high performance polymer modified binders for asphalt use with improved fuming characteristics*, BP Australia Limited, Altona North, Victoria, Australia.

Burr, G., Tepper, A., Feng, A., Olsen, L. & Miller, A. 2001. Crumb-rubber modified asphalt paving: occupational exposures and acute health effects, *NIOSH Health Hazard Evaluation Report 2001-0536-2864*, National Institute for Occupational Safety and Health, Cincinnati, OH, USA.

Caltrans. 2005. *Use of scrap tire rubber. State of the technology and best practices*. State of California Department of Transportation, Sacramento, CA, USA.

CIRS. 2001. *Performance-based technical specifications*, InterUniversity Road Research Center, Ancona, Italy.

CIRS. 2009. Asphalt Rubber bituminous mixtures, *Final Report*, InterUniversity Road and Airport Research Center, Ancona, Italy.

CONCAWE. 1992. Bitumen and bitumen derivatives, *Product dossier 92/104*, Concawe, Brussels, Belgium.

de La Roche, C., Gaudefroy, V., Viranaiken, V. & Paranhos, R. 2008. A new experimental trial protocol for laboratory investigations of bitumen fumes: influence of stirring and steamed water on emissions, *Proceedings, ISAP Symposium on Asphalt Pavements and Environment*, Zurich, Switzerland, 18-20 August 2008, pp. 297-306.

EN 13649. 2002. Stationary source emissions - Determination of the mass concentration of individual gaseous organic compounds - Active carbon and solvent desorption method. European Committee for Standardization (CEN), Brussels, Belgium.

EN 12697-39. 2012. Test methods for hot mix asphalt - Binder content by ignition. European Committee for Standardization (CEN), Brussels, Belgium.

Enell, A., Quinn, A., McNally, C., Huzlik, J., Wik, O., Licbinsky, R., Gaudefroy, V. & Mouillet, V. 2012. Test methods for environmental characterization of reclaimed asphalt, *Deliverable 1.6, Re-road – End of life strategies of asphalt pavements*, European Commission, DG Research, Brussels, Belgium.

Gasthauer, E., Mazé, M., Marchad, J.P. & Amouroux, J. 2008. Characterization of asphalt fume composition by GC/MS and effect of temperature, *Fuel*, 87: 1428-1438.

Gaudefroy, V., Viranaiken, V., Paranhos, R., Jullien, A. & de La Roche, C. 2010. Laboratory assessment of fumes generated by bituminous mixtures and bitumen, *International Journal of Road Materials and Pavement Design*, 11: 83-100.

Gaudefroy, V., Deygout, F., Viranaiken, V., Le Coutaller, P., Paranhos, R. & de La Roche, C. 2008. Laboratory identification of fumes during manufacturing of hydrocarbon mixtures, *Proceedings, ISAP Symposium on Asphalt Pavements and Environment*, Zurich, Switzerland, 18-20 August 2008, pp. 278-286.

German Bitumen Forum. 2006. *Progress report 2006*.

Hicks, R.G. 2002. *Asphalt rubber design and construction guidelines*. Northern California Rubberized Asphalt Concrete Technology Center - California Integrated Waste Management Board, Sacramento, CA, USA.

Hugener, M., Mattrel, P. & Emmenegger, L. 2004. Laboratory emission measurements from tar-containing binders, *Proceedings, 3rd Eurasphalt & Eurobitume Congress*, Vienna, Austria, 12-14 May 2004.

IARC. 2013. Bitumens and bitumen emissions and some n- and s-heterocyclic polycyclic aromatic hydrocarbons, *Monograph volume 103*, International Agency for Research on Cancer, Lyon, France.

ISS. 2012. *ISS-INAIL database for sanitary environmental risk analysis*, Istituto Superiore di Sanità, Rome, Italy.

Kurek, J.T., Kriech, A.J., Wissel, H.L., Osborn, L.V. & Blackburn, G.R. 1999. Laboratory generation and evaluation of paving asphalt fumes, *Transportation Research Record*, 1661: 35-40.

Lindberg, H.K., Väänänen, V., Järventaus, H., Suhonen, S., Nygren, J., Hämeilä, M., Valtonen, J., Heikkilä, P. & Norppa, H. 2008. Genotoxic effects of fumes from asphalt modified with waste plastic and tall oil pitch. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*, 653(1-2): 82-90.

McCarthy, B.M., Blackburn, G.R., Kriech, A.J., Kurek, J.L., Wissel, H.L. & Osborn, L.V. 1999. Comparison of field versus laboratory generated asphalt fumes, *Transportation Research Record*, 1661: 54-59.

NIOSH. 2000. *Health effects of occupational exposure to asphalt*, National Institute for Occupational Safety and Health, Cincinnati, OH, USA.

Olard, F. & Gaudefroy, V. 2012. Laboratory assessment of mechanical performance and fume emissions of LEA half-warm mix asphalt versus traditional hot mix asphalt, *Proceedings, 2nd International Warm-Mix Conference*, St. Louis, MO, USA, 11-13 October 2012.

Paranhos, R., Béghin, A., Petiteau, C., Monéron, P. & de La Roche, C. 2006. Laboratory characterization on hot mix asphalt fumes during mixing linked with mechanical performances, *Proceedings, 10th International Conference on Asphalt Pavements*, Quebec City, Canada, 12-17 August 2006.

Paranhos, R. 2007. *Approche multi-échelle des emissions d'un procédé d'élaboration des enrobes à chaud*, PhD Thesis, Université de Rouen, France.

Posniak, M. 2005. Polycyclic aromatic hydrocarbons in the occupational environment during exposure to bitumen fumes, *Polish Journal of Environmental Studies*, 14(6): 809-815.

Riley, T. 2004. Bitumen occupational health. Update on recent activities, *Proceedings, 8th Conference on Asphalt Pavements for Southern Africa (CAPSA'04)*, Sun City, South Africa, 12-16 September 2004.

Santagata, E. & Zanetti, M.C. 2012a. Evaluation of the possible use in road pavements of crumb rubber derived from end-of-life tyres, *Final report*, Province of Turin, Turin, Italy.

Santagata E. & Zanetti M.C. 2012b. *The use of products from end-of-life tyres in road pavements*, ECOPNEUS, Milan, Italy.

Santagata, E., Riviera, P.P., Dalmazzo, D., Lanotte, M., Zanetti, M.C., Fiore, S. & Ruffino, B. 2012. Design and construction of a full-scale test section with asphalt rubber gap-graded wearing course mixture, *Procedia: Social & Behavioral Sciences*, 53:524-534.

Sivak, A., Menzies, K.T., Beltes, K., Worthington, J., Ross, A. & Latta, R. 1989. Assessment of the carcinogenic/promoting activity of asphalt fumes, *Contract 200-83-2612*, U.S. Department of Health and Human Services, Washington, D.C., USA.

Stout, D. & Carlson, D.D. 2003. Stack emissions with asphalt rubber. A synthesis of studies, *Proceedings, Asphalt Rubber Conference 2003*, Brasilia, Brazil, 2-4 December 2003.

Viranaiken, V., Gaudefroy, V., Le Coutaller, P., Deygout, F. & Bujoli,, B. 2010. A new asphalt fumes generator: development of an original mixing and sampling sequential protocol, *89th Annual Meeting of the Transportation Research Board*, Washington, D.C., USA.

Watts, R.R., Wallingford, K.M., Williams, R.W., House, D.E. & Lewtas, J. 1998. Airborne exposures to PAH and PM2.5 particles for road paving workers applying conventional asphalt and crumb rubber modified asphalt, *Journal of Exposure Analysis and Environmental Epidemiology*, 8(2): 213-229.

Way G.B., Kaloush, K.E. & Biligiri K.P. 2012. *Asphalt-rubber standard practice guide*, Second edition, Rubber Pavements Association, Tempe, AZ, USA.

Zanetti, M.C., Fiore, S., Ruffino, B. & Santagata, E. 2013a. Use of crumb rubber in road paving applications: workers' health risk assessment, *Proceedings, Sardinia 2013, Fourteenth International Waste Management and Landfill Symposium*, S. Margherita di Pula, Italy, 30 September - 4 October 2013.

Zanetti, M.C., Fiore, S., Ruffino, B., Santagata, E. & Lanotte, M. 2013b. Assessment of gaseous emissions produced on site by bituminous mixtures containing crumb rubber, *1st Annual International Recycled Rubber Products (R2P) Technology Conference*, Las Vegas, NV, USA, 10-11 October 2013.