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Airborne emissions of asphalt/wax blends for warm mix asphalt production

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**Abstract:** During the asphalt heating process in the various stages of road pavement construction a complex mixture of hydrocarbon aerosols, vapors and gases is generated and emitted into the atmosphere. The reduction of these airborne asphalt emissions is a continuous issue and challenge for asphalt industry and operators. The scientific and technical communities had developed a number of new sustainable and cleaner technologies for asphalt materials, generally referred to as warm mix asphalts (WMA), that significantly reduce the manufacturing and application temperatures. Despite the great number of reported WMA methodologies, organic waxes, commonly defined "flow improvers", are mainly used for reducing the binder viscosity and as a result for enhancing the asphalt mixture workability already at lower temperatures (90-140 °C). Thus, the aim of the study was the analysis of the airborne emissions of different asphalt formulations and asphalt/wax blends to assess the role of both temperature and wax addition on their composition and extent. The gas chromatographic procedure has allowed the identification in the asphalt emissions of more than 200 compounds, showing at the same time a hierarchy of their appearance in relation to the temperature. In parallel, also the photoionization analyses have confirmed as the temperature represents the major factor in the generation of such airborne substances. The study of the binary asphalt/wax mixtures highlighted the twofold way in which the wax performs in reducing emissions.

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## COVER LETTER FOR SUBMISSION OF MANUSCRIPT

**Parma, 12<sup>th</sup> January 2017**

Dear Editor-in-Chief,

I am pleased to send you our research article entitled “AIRBORNE EMISSIONS OF ASPHALT/WAX BLENDS FOR WARM MIX ASPHALT PRODUCTION”, by Federico Autelitano, Federica Bianchi and Felice Giuliani for possible publication in “Journal of Cleaner Production”.

With the submission of this manuscript I would like to undertake that:

- I will be serving as the corresponding author for this manuscript and I have assumed responsibility for keeping my coauthors informed of our progress through the editorial review process, the content of the reviews, and any revisions made;
- This manuscript represents an original work;
- The contents of this manuscript have not been copyrighted or published previously;
- The contents of this manuscript are not now under consideration for publication elsewhere;
- All authors of this research have contributed substantially to the manuscript;
- All authors of this paper have read and approved the final version submitted;
- All previously published work cited in the manuscript has been fully acknowledged
- There is no type of real or perceived conflicts of interest

Please let me know of your decision at your earliest convenience.

Sincerely,

Felice Giuliani

**Title**

**Airborne emissions of asphalt/wax blends for warm mix asphalt production**

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7 Figures

## Abstract

During the asphalt heating process in the various stages of road pavement construction a complex mixture of hydrocarbon aerosols, vapors and gases is generated and emitted into the atmosphere. The reduction of these airborne asphalt emissions is a continuous issue and challenge for asphalt industry and operators. The scientific and technical communities had developed a number of new sustainable and cleaner technologies for asphalt materials, generally referred to as warm mix asphalts (WMA), that significantly reduce the manufacturing and application temperatures. Despite the great number of reported WMA methodologies, organic waxes, commonly defined “flow improvers”, are mainly used for reducing the binder viscosity and as a result for enhancing the asphalt mixture workability already at lower temperatures (90-140 °C). Thus, the aim of the study was the analysis of the airborne emissions of different asphalt formulations and asphalt/wax blends to assess the role of both temperature and wax addition on their composition and extent. The gas chromatographic procedure has allowed the identification in the asphalt emissions of more than 200 compounds, showing at the same time a hierarchy of their appearance in relation to the temperature. In parallel, also the photoionization analyses have confirmed as the temperature represents the major factor in the generation of such airborne substances. The study of the binary asphalt/wax mixtures highlighted the twofold way in which the wax performs in reducing emissions.

**Keywords:** asphalt emissions; pavement engineering; warm mix asphalt; photoionization, volatile organic compounds detection; wax

## 1. Introduction

Hot mix asphalt (HMA) is a paving material, consisting of asphalt binder and mineral aggregates, which is generally manufactured in stationary or mobile blending plants at 170-190 °C and laid down at 140-160 °C, with significant percentage of energy consumption and release of pollutant fumes (Almeida-Costa & Benta, 2016; Rubio et al., 2013). These emissions, which are defined as the complex mixtures (saturated and aromatic hydrocarbons) of aerosols, vapors and gases generated during asphalt binder heating processes, could have an impact on the ecosystem and on the human health (IARC, 2013; Chong et al., 2014). The scientific literature has generally analyzed asphalt fumes in terms of volatile organic compounds (VOCs), with particular attention to polycyclic aromatic hydrocarbons (PAHs) and total particulate matter (TPM), which are considered hazardous compounds. A variety of analytical techniques for sample collection, identification and quantification are available for evaluating asphalt emissions. After sample collection, fumes can be evaluated both by performing laboratory analyses or directly on-site using portable gas analyzer devices generally adopted for environmental monitoring (Gałuska et al., 2015; Gasthauer et al., 2008). The international requirements impose practical guidance for the assessment of threshold limit values for asphalt plants and worker exposure. The HMA plants require approval from local authorities which is given according to the pollutant thresholds, generally expressed as annual average emissions for combustion gases (CO, NO<sub>x</sub>, CO<sub>2</sub>, O<sub>2</sub>), total organic carbon (TOC), TPM, VOCs and PAHs (Jullien et al., 2010; Ventura, Lorino & Le Guen, 2015). Although most of the VOCs and PAHs are removed during the manufacturing process, some residues remain in the asphalt and are emitted during hot storage, transport and road paving (Boczka et al., 2014). Limits for occupational exposure to asphalt emissions have been set in more than 50 countries, often considering the 8-hour time-weighted average (TWA) concentration of TPM or PAHs (IARC, 2011; Kriech & Osborn, 2014).

1 The composition of asphalt emissions varies and depends on crude oil and asphalt type, whereas  
2 temperature is the key parameter in order to control their extent. Asphalt contains a complex  
3 mixtures of aliphatic compounds, cyclic alkanes, aromatic hydrocarbons, PAHs and heterocyclic  
4 compounds. Elemental analyses indicate the presence of carbon (80-88%), hydrogen (8-12%),  
5 sulfur (0-9%), oxygen (0-2%), nitrogen (0-2%) and traces of several metals, such as vanadium,  
6 nickel, iron, magnesium and calcium (Lesueur, 2009). Some strategies for the characterization of  
7 asphalt composition are based on the organic compounds identification according to molecular  
8 weight and polarity: it is usually given in terms of the relative quantity of asphalt SARA fractions,  
9 acronym for saturates, aromatics, resins and asphaltenes (Corbett, 1969; Rostler, 1965). A number  
10 of solvent based separation procedures to identify and measure SARA fractions have been  
11 developed, including thin layer chromatography-flame ionization detection (TLC-FID), gravimetric  
12 adsorption chromatography, high performance liquid chromatography (HPLC), and automated  
13 asphaltene determinator coupled with saturates, aromatics, and resins separation (SAR-AD)  
14 (Bissada et al., 2016).

15 The reduction of airborne asphalt emissions related with production, mixing, transportation and  
16 paving operations is a continuous issue and challenge for asphalt industry and operators.

17 Recently, a line of research has examined the possibility of using fume suppression agents as  
18 additives for HMA in order to reduce asphalt emissions (Peng & Li, 2010; Qian & Wang, 2012,  
19 Xiao et al., 2010). The functioning principle is to increase molecular stability in the asphalt concrete  
20 and to reduce the light component content. Flame retardants (melamine and P-, N- and triazinic  
21 compounds) could increase the volatilization temperature of the light components and form  
22 hyalence film on asphalt layer, suppressing VOCs emissions. Activated carbon and expanded  
23 graphite use their strong physical and chemical absorption and swelling potential to suppress  
24 asphalt fumes. Through physical and chemical crosslinking reactions, polymers (SBS and PE) are  
25 able to form a network with the light asphalt components, transforming the small organic molecules  
26 into macromolecules, limiting their volatilization.



In parallel, a growing international pressure on the reduction of fossil fuels consumption and the emission of greenhouse effect gases has led the scientific and technical communities to develop a number of new sustainable and cleaner technologies for asphalt materials, generally referred to as warm mix asphalts (WMA), that significantly reduce the manufacturing and application temperatures (Capitão et al., 2012; D'Angelo et al., 2008; Rubio et al., 2012). WMA is generally produced in a temperature range from 90 to 140 °C, with a temperature decrease of about 30 °C with respect to HMA. Despite the great number of reported WMA technologies, they can be basically grouped in three main classes: organic waxes (viscosity reductants), chemical additives (surfactants, emulsifiers, aggregate coating enhancers and anti-stripping additives) and foaming technologies. Specifically, thanks to the compatibility between asphalt and waxes and their melting/crystallizing characteristics, several studies have been conducted to evaluate the influence of these products on the asphalt properties. Essentially, waxes, generally defined “flow improvers”, are mainly used for reducing the binder viscosity at typical asphalt production and compaction temperatures, depending on their melting temperature (Capitão et al., 2012; Polacco et al., 2012, Rubio et al., 2012). Moreover, waxes can be used to develop ternary asphalt/polymer/wax systems which combine the mechanical and workability properties of their constituents to produce technologically advanced warm mix polymer modified asphalts (WMPMA) (D'Angelo et al., 2008; Rossi et al., 2013). Irrespective of the WMA production process, a significant decrease of combustion gases (10-60%) and asphalt emissions (30-50%) has been observed both at plant and at site construction (Capitão et al., 2012; Pérez-Martínez et al., 2014; Sol-Sanchez et al., 2016). Thus, the aim of the study was the analysis of the airborne emissions of different asphalt formulations and asphalt/wax blends to assess the role of both temperature and wax addition on their composition and extent.

## 2. Materials

Three 70/100 penetration neat asphalt binders (A1, A2 and A3), produced in different refineries, were used. Asphalt A2 was manufactured using crude oil from Adriatic basin (Mediterranean Sea), whereas asphalts A1 and A3 were obtained by Middle-Eastern crude oils. Table 1 summarizes the penetration grade (EN 1426:2015) and the softening point (EN 1427:2015) of the neat binders.

Table 1 – Specification of the neat asphalts

Property	Unit	Test result		
		A1	A2	A3
Penetration (25 °C)	0.1 mm	84	75	86
Softening point	°C	46.4	49.6	46,2

Two different waxes, referred in the text as M and S, were added (3% by weight) to the three binders to produce asphalt/wax blends. The asphalt/wax mixtures were labelled using an alphanumeric acronym consisting of three characters: the first letter represents the neat asphalt, while the number and the second letter indicate respectively the content and the type of the added wax. Specifically, M is an amidic-modified hydrocarbon wax (Montan wax by Romonta GmbH with fatty acid amide) and S is a hydrocarbon paraffinic wax (Fisher Tropsch wax by Sasol Wax). Montan wax (lignite wax) contains a combination of non-glyceride long-chain carboxylic acid esters, free long-chain organic acids, long-chain alcohols, ketones, hydrocarbons, and resins. Fischer-Tropsch wax consists mainly of saturated, straight-chain hydrocarbons without functional groups (Rubio et al., 2012). Both waxes showed a melting temperature equal to 110 °C (Polacco et al., 2012). The preparation of wax-modified asphalts was as follows. An asphalt sample of 300 g was heated in a ventilate oven at 160 °C for 30 min and subsequently placed on a heating plate. Pre-weighted wax was added to asphalt and the blend was mixed for 15 min at 160 °C.

## 3. Methods

Analysis of asphalt emissions was carried out following a two-step experimental program. A preliminary evaluation of asphalts macro-chemical composition (assessment of SARA fractions)

1 was conducted by means of TLC-FID analysis. Then, VOCs qualitative and semi-quantitative  
2 analyses were performed on asphalt headspaces generated in laboratory at different temperatures,  
3 referable to those registered during the manufacturing and the laying of HMA and WMA (range  
4 90÷200 °C), through two different techniques. The temperature of 90 °C was considered as the  
5 lower limit value reported in the literature for the WMA applications, whereas 200 °C represents an  
6 upper limit situation found in plant as a result of asphalt binder overheating. The potential of both  
7 headspace gas chromatography-mass spectrometry (HS-GC/MS) and photoionization detection  
8 (PID) were exploited, using in the first case a stationary analytical instrument and in the second  
9 case a portable device. The experiments were carried out both on neat asphalts and on asphalt/wax  
10 blends.  
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### 25 *3.1 TLC-FID*

26 The determination of SARA fractions was carried out by using a IATROSCAN MK-5 (Iatron  
27 Laboratories Inc.) TLC-FID analytical system. The separation was based on the TLC method using  
28 the so called chromarods, i.e. quartz rods coated with a thin layer adsorbents, as stationary phase  
29 and different solvents as mobile phases. The detection was performed using a flame ionization  
30 detector. Asphalts samples (0.10 g) were dissolved in 5 mL of dichloromethane and applied on the  
31 chromarods by means of a 1 µL syringe. The separation was achieved by using a three-stage solvent  
32 development sequence. Saturates were eluted with heptane, aromatics with a solution of toluene and  
33 heptane (80:20 by volume) and resins with a solution of dichloromethane and methanol (95:5 by  
34 volume): the most polar asphaltenes remain at the origin place. After the separation, the chromarods  
35 were scanned (30 sec/scan) through a hydrogen/air flame: hydrogen flow rate of 160 mL/min and  
36 air flow rate of 2 mL/min. For each asphalt binder and asphalt/wax blend, 20 chromarods were  
37 tested and the mean value of the 20 measurements was calculated.  
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### 3.2 HS-GC/MS

The headspace analysis was performed by using the PAL COMBI-xt autosampler (CTC Analytics AG). 0.12 g of each binder class were weighted in 10 mL glass vials and heated at 90, 110, 130, 160 and 200 °C for 15 min. The agitator speed was set at 250 rpm. Finally, 1 mL of the headspace was collected by using a gastight syringe and injected into the GC inlet. Three replicated measurements for each sample were performed. A HP 6890 Series Plus gas chromatograph (Agilent Technologies) equipped with a MSD 5973 mass spectrometer (Agilent Technologies) was used. The gas chromatograph was operated in splitless mode with the PTV injector (Agilent Technologies) maintained at the temperature of 270 °C and equipped with a 1.5 mm i.d. multibaffled liner (Agilent Technologies). Helium, at a constant flow rate of 1.3 mL/min, was used as the carrier gas. Chromatographic separation was performed on a 30 m × 0.25 mm, df 0.25 μm MDN-5S capillary column (Supelco) using the following temperature program: 50 °C for 1 min, then 10 °C/min up to 300 °C and 300 °C for 4 min. The transfer line and source were maintained at the temperatures of 280 °C and 150 °C, respectively. Full scan EI data were acquired under the following conditions: ionization energy, 70 eV; mass range, 35-500 amu; scan time, 1.6 scan/s; electron multiplier voltage, 1920 V. Signal acquisition and data handling were performed using the HP Chemstation (Agilent Technologies). The identification of the volatile compounds was carried out by comparing the experimental mass spectra with those stored in the Wiley 275 library.

### 3.3 PID

Asphalt emissions were also measured by the PhoCheck Tiger 3.1 (Ion science) photoionization detector. Asphalt samples (2.00 g) were put in 50 mL glass vials and heated at 90, 110, 130, 160 and 180 °C for 20 min. In this analysis, the maximum heating temperature has been fixed at 180 °C to avoid the instrument pump failure. The headspace was drawn, using a flow rate of 220 mL/min, into the ionization chamber in which is housed a Krypton lamp (10.6 eV) and the PID sensor. The sampling procedure was based on the use of a flexible extension hose with a disposable 20 G inlet

needle ( $\phi_{\text{int}} = 0.90$  mm;  $L = 35$  mm) to collect the emissions. A chip microcomputer measured the PID sensor readings and calculated the gas concentrations based on the calibration to isobutylene. The gas concentration of each specimen, expressed in ppmv, is referred to the sum of 10 consecutive measurements registered in 10 sec (1 per sec). Ten replicated measurements on independent specimens were performed for each binder at each temperature.

## 4. Results

### 4.1 Solid matrix asphalt analysis

The preliminary analyses on the SARA fractions highlighted a similarity in the macro-molecular composition of asphalt A1 and A3, in comparison to asphalt A2, especially in terms of fraction molecular weight (Tab. 2) (Ecker, 2001; Lesueur, 2009).

Table 2 - SARA fractions of analyzed asphalts (n = 20)

Asphalt	Saturates <sup>*</sup> [%]	Aromatics <sup>*</sup> [%]	Resins <sup>*</sup> [%]	Asphaltenes <sup>*</sup> [%]
A1	5.2 (0.4)	52.6 (2.7)	26.6 (1.7)	15.6 (1.2)
A1-3S	5.1 (0.4)	48.3 (2.1)	26.4 (1.5)	20.2 (1.1)
A1-3B	5.9 (0.2)	45.1 (2.7)	27.7 (1.3)	21.3 (1.7)
A2	5.8 (0.2)	45.5 (1.6)	25.9 (0.6)	22.8 (1.1)
A2-3S	5.9 (0.3)	41.9 (1.5)	25.7 (0.7)	26.5 (1.1)
A2-3B	6.0 (0.4)	40.6 (1.4)	25.5 (0.9)	27.9 (1.4)
A3	2.3 (0.2)	55.3 (2.0)	25.5 (1.8)	16.9 (0.7)
A3-3S	2.8 (0.4)	47.1 (2.3)	27.2 (1.4)	22.9 (1.2)
A3-3B	2.4 (0.3)	47.3 (2.2)	26.6 (1.3)	23.9 (1.4)

<sup>\*</sup>Mean (SD)

Specifically, asphalt A2 was characterized by a high amount of asphaltenes (22.8%), i.e. highly polar aromatic compounds having high molecular weight, thus including porphyrines with metal atoms (Corbett, 1969; Speight, 2004). In addition, the asphalt A2 showed a less content of the lower molecular weight fractions, comprising saturates and aromatics. Saturates are predominantly characterized by straight and branched-chain aliphatic hydrocarbons, and to a minor extent by alkyl naphthenes and alkyl aromatics. The aromatics, also called naphthene aromatics, comprise aromatic

compounds with paraffinic and naphtenic carbons including sulphur elements. The resin fraction was similar in the three asphalt binders (Speight, 2004). Resins mainly contain compounds of relatively high molecular weight and are usually characterized by the presence of polar chemical groups bearing oxygen, nitrogen or sulphur atoms (Lesueur, 2009). With regards to the asphalt/wax blends, the addition of both waxes produced an increase of the asphaltene fraction at the expense of the aromatics in all the asphalts. It is emphasized that the waxes are not soluble in any of the considered solvents: they are not eluted in the separation process remaining at the origin spot place on the chromarods and thus being calculated as asphaltenes.

#### 4.2 Asphalt emissions analysis

The heating temperature is the main and significant parameter for asphalt emissions. As expected, the HS-GC/MS chromatograms obtained from the analysis of the investigated asphalt formulations heated at different temperatures showed an increase of the GC responses in correspondence to the temperature increase (Fig. 1).

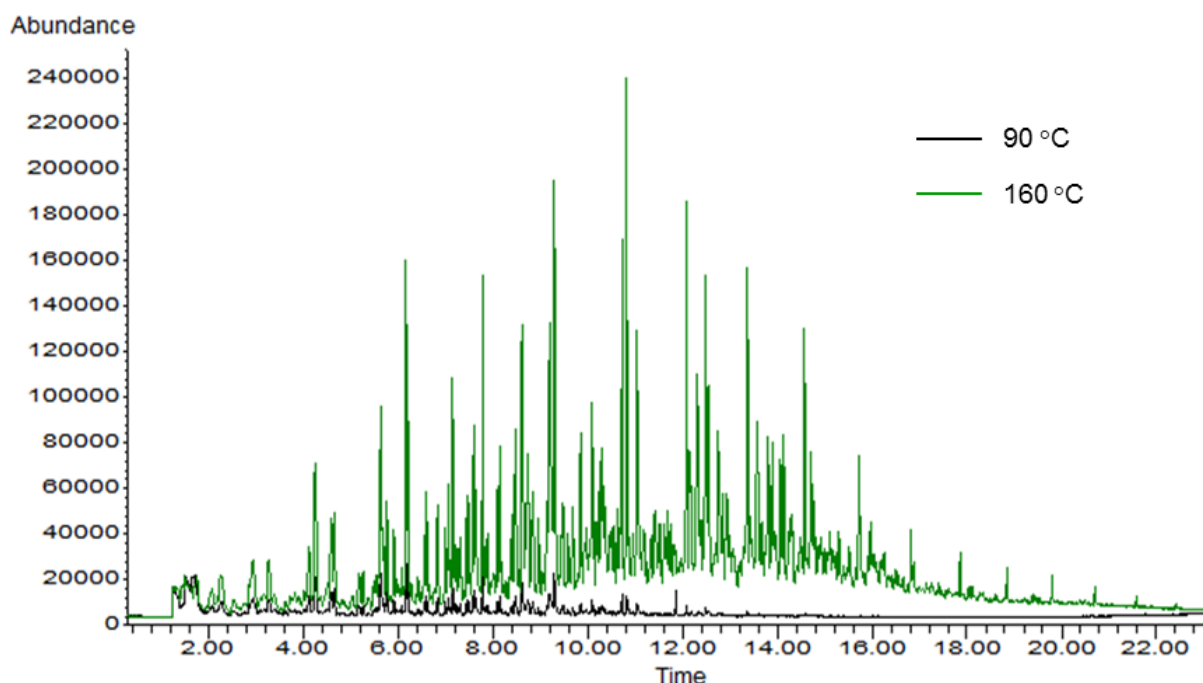


Figure 1 - HS-GC/MS chromatograms of sample A3 heated at 90 °C (black) and 160 °C (green).

1 The only exception was represented by the samples heated at 110 °C and 130 °C, respectively for  
2 which no significant differences were observed. In addition, the detection of the less volatile  
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4 compounds was feasible only when the samples were heated at temperatures higher than 160 °C.  
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7 A complex mixture of aliphatic compounds (about 200 compounds), including linear and branched  
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9 hydrocarbons, cyclic alkanes, aromatic hydrocarbons, polycyclic aromatic hydrocarbons, and  
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11 heterocyclic compounds mainly containing sulfur atoms was observed in the samples. More  
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13 precisely, among PAHs, naphthalene, methyl-, dimethyl- and trimethyl- naphthalenes, phenanthrene,  
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15 anthracene, methyl- and dimethyl-phenanthrenes were identified. The group of *S*-heterocyclic PAHs  
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17 was constituted mainly by thiophenic compounds like dimethyl-, diethyl-, trimethyl-  
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19 benzo[*b*]thiophenes, methyl- and dimethyl-naphtho[2,3-*b*]thiophenes, methyl- and dimethyl-  
20  
21 dibenzothiophenes whereas toluene, ethylbenzene, xylenes, propylbenzene, diethyl-, trimethyl-,  
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23 tetramethyl-benzenes, ethyl-methyl/dimethyl/trimethyl-benzenes, diethyl-methyl-benzenes, and  
24  
25 methyl-propyl-benzenes were the major compounds belonging to the class of the substituted  
26  
27 monoaromatic hydrocarbons. Figure 2 depicts a non-exhaustive list of the compounds identified in  
28  
29 the asphalt headspace.  
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36 In order to represent the different classes of analytes found in the asphalt emissions, toluene (RT:  
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38 2.93 min), octane (RT: 3.28 min), trimethylthiophene (RT: 5.99 min), diethylbenzene (RT: 7.01  
39  
40 min), naphthalene (RT: 9.22 min), methylnaphthalene (RT: 11.05 min), tetradecane (RT: 12.10  
41  
42 min), methylnaphthothiophene (RT: 17.83 min), dimethyldibenzothiophene (RT: 18.61 min) and  
43  
44 docosane (RT: 20.69 min) were chosen as model compounds. Multivariate analysis of variance  
45  
46 (MANOVA) was applied to evaluate the presence of significant differences among the mean  
47  
48 responses of the samples analysed under different heating temperatures. Since significant  
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50 differences among the mean responses obtained under different heating temperatures were observed  
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56 ( $\Lambda^*=3.45\text{E-}72$ ,  $\chi^2_{(\alpha:0.05,40)}=55.76$ ), the Bonferroni approach was then used for pairwise comparisons.  
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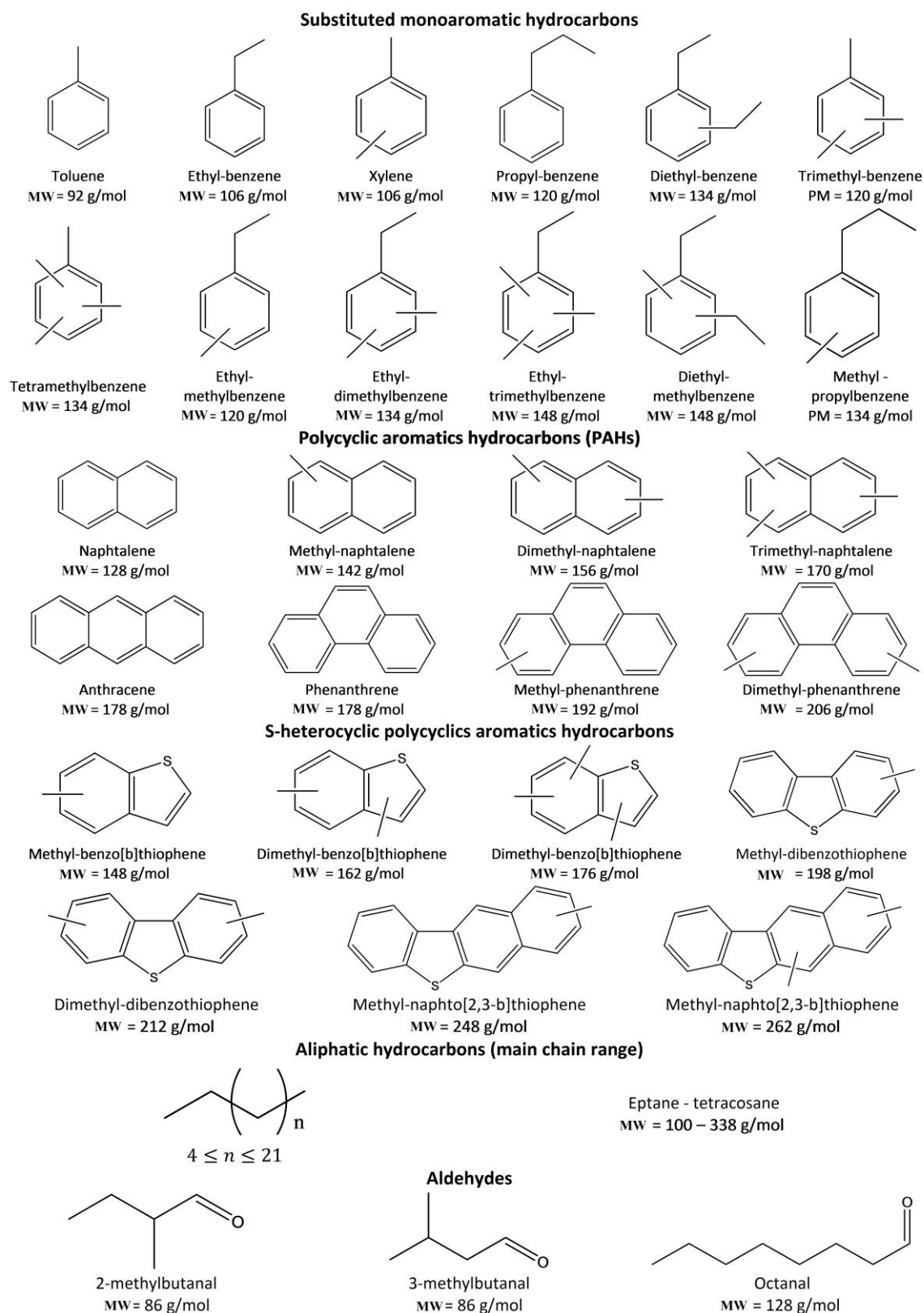


Figure 2 - Molecular structures of some compounds identified in the asphalt headspace



Table 3 shows the results of the Bonferroni test on the GC mean responses of the 10 selected volatiles for asphalt A3. As shown in table 3, a significant increase in the mean responses for each compound was observed in accordance with the temperature increase. Similar results were obtained for all the other formulations, thus including the asphalt/wax blends. As a general remark, it has to be observed that when the temperature of 200 °C was used to heat asphalt, GC responses 3÷1000 times higher than those achieved by applying the temperature of 90 °C were obtained for all the investigated analytes.

Table 3. Bonferroni's t-test: comparison of the mean responses (GC peak areas) for the selected volatile organic compounds released from bitumen A3 at 90, 110, 130, 160 and 200 °C (n = 3)

Compound	Temperature				
	90 °C	110 °C	130 °C	160 °C	200 °C
	GC peak area *				
Toluene (RT: 2.93 min)	113100±3500 <sup>a</sup>	204000±2700 <sup>b</sup>	201000±3600 <sup>b</sup>	310000±4800 <sup>c</sup>	364000±8300 <sup>d</sup>
Octane (RT: 3.28 min)	36500±1800 <sup>aI</sup>	74600±1500 <sup>bI</sup>	69000±1400 <sup>bI</sup>	105200±800 <sup>cI</sup>	140100±4100 <sup>dI</sup>
trimethyl thiophene (RT: 5.99 min)	6130±330 <sup>aII</sup>	13870±570 <sup>bII</sup>	13390±850 <sup>bII</sup>	42800±1900 <sup>cII</sup>	41500±2500 <sup>cII</sup>
Diethyl benzene (RT: 7.01 min)	10770±520 <sup>aIII</sup>	25200±2200 <sup>bIII</sup>	23700±1400 <sup>bIII</sup>	88200±2100 <sup>cIII</sup>	90100±3400 <sup>cIII</sup>
Naphthalene (RT: 9.22 min)	66900±4100 <sup>aIV</sup>	206350±520 <sup>bIV</sup>	209360±950 <sup>bIV</sup>	1000000±20000 <sup>cIV</sup>	1230000±71000 <sup>dIV</sup>
Methyl naphthalene (RT: 11.05 min)	35500±2000 <sup>aV</sup>	126200±3600 <sup>bV</sup>	134400±1200 <sup>bV</sup>	977000±38000 <sup>cV</sup>	1320000±146000 <sup>dV</sup>
Tetradecane (RT: 12.10 min)	11500±730 <sup>aVI</sup>	52500±1000 <sup>bVI</sup>	54500±2600 <sup>bVI</sup>	621000±9000 <sup>cVI</sup>	752000±15000 <sup>dVI</sup>
Methyl naphtothiophene (RT: 17.83 min)	n.d.	n.d.	n.d.	23300±600 <sup>cVII</sup>	44700±2100 <sup>dVII</sup>
Dimethyl dibenzothiophene (RT: 18.61 min)	n.d.	n.d.	n.d.	23300±720 <sup>cVIII</sup>	32310±970 <sup>dVIII</sup>
Docosane (RT: 20.69 min)	n.d.	n.d.	n.d.	41100±600 <sup>aIX</sup>	116700±4400 <sup>bIX</sup>

\*Area values obtained by using the extracted ion chromatogram mode on the basis of the base peaks for each compound (Area ± SD)

Same letters: absence of significant differences among the mean values

Different letters: presence of significant differences among the mean values

n.d.: not detected

According to the results achieved by TLC-FID analysis (Tab. 2), different chromatographic profiles were obtained when different formulations were analyzed. More precisely, when headspace analyses of samples A1, A2 and A3 were compared, sample A2 was characterized both by a reduced amount of the most volatile compounds and by stronger signals due to the presence of linear hydrocarbons in the C14 - C24 range, especially when higher temperatures were used (Figg. 3 and 4).

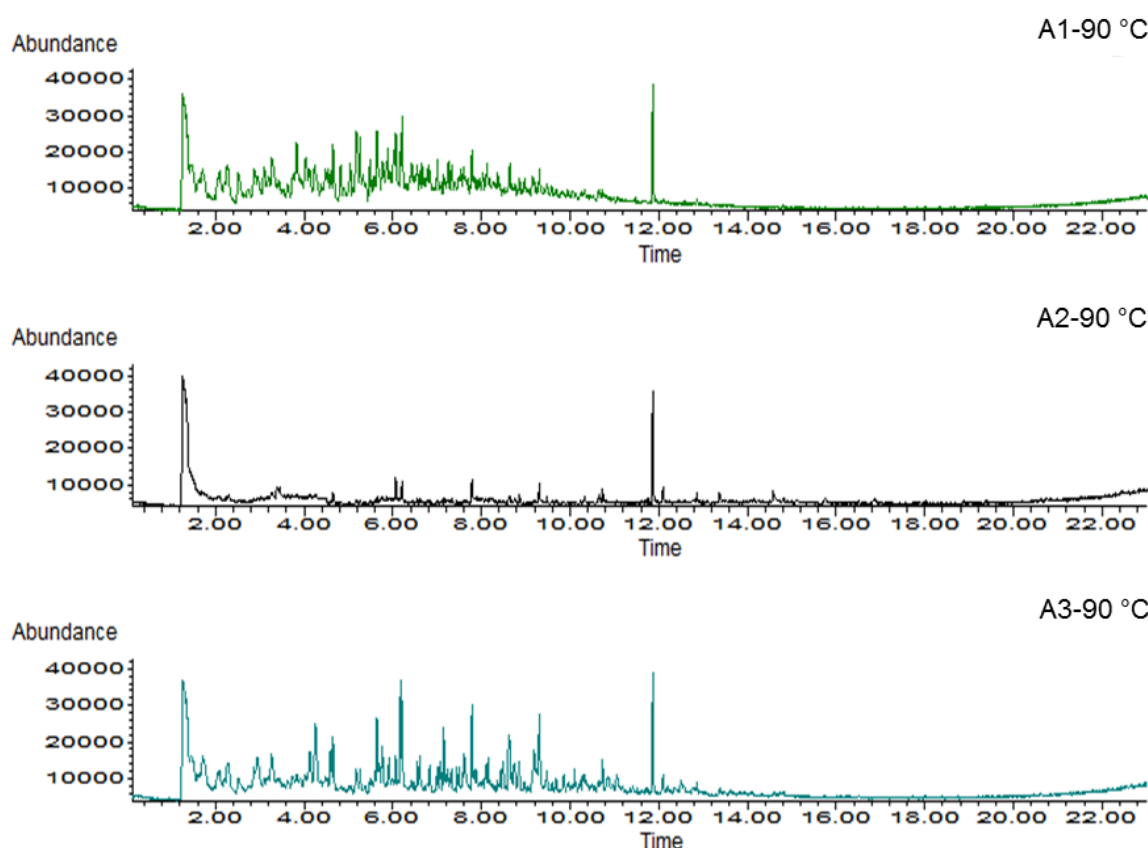


Figure 3 - HS-GC/MS chromatograms of asphalts A1, A2 and A3 heated at 90 °C

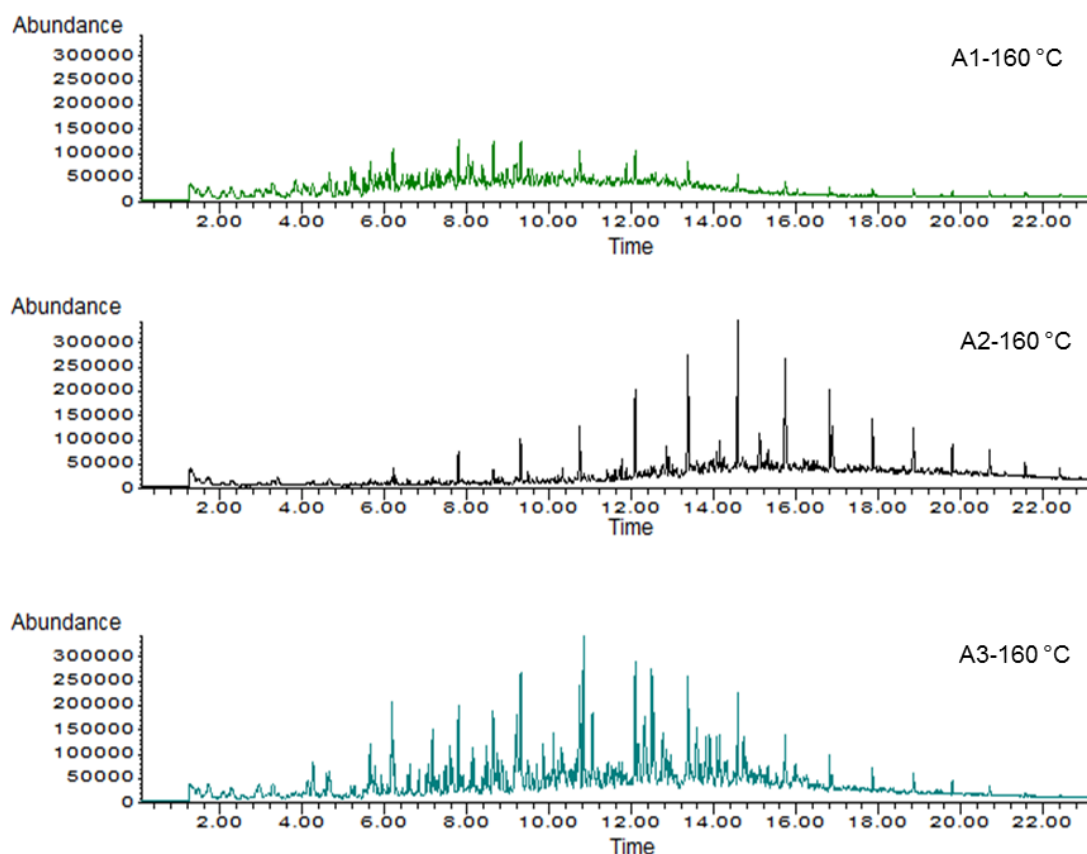


Figure 4 - HS-GC/MS chromatograms of asphalts A1, A2 and A3 heated at 160 °C

Photoionization analyses provided additional information about the total detectable volatile organic contaminants (TVOC) present in the asphalt headspaces. Figure 5 shows the neat asphalt vapors concentration trend versus temperature. According to both HS-GC/MS and TLC-FID results, an increment of the PID responses in correspondence to the temperature rise was observed for all the investigated binders with a dramatic increase for temperatures above 130 °C (pseudo-hyperbolic trend). It was registered an increase of about 1200%, from 90 to 180 °C (incremental ratio of about 12), whereas an increase of 120% in the range 130÷160 °C. Asphalt A2, which is characterized by an high amount of asphaltenes, registered lower VOCs concentration in its headspace in comparison to asphalts A1 and A3, which are richer of volatile compounds (saturates and aromatics), quantifiable in 80% up to 130 °C and in 60% for the higher temperatures.

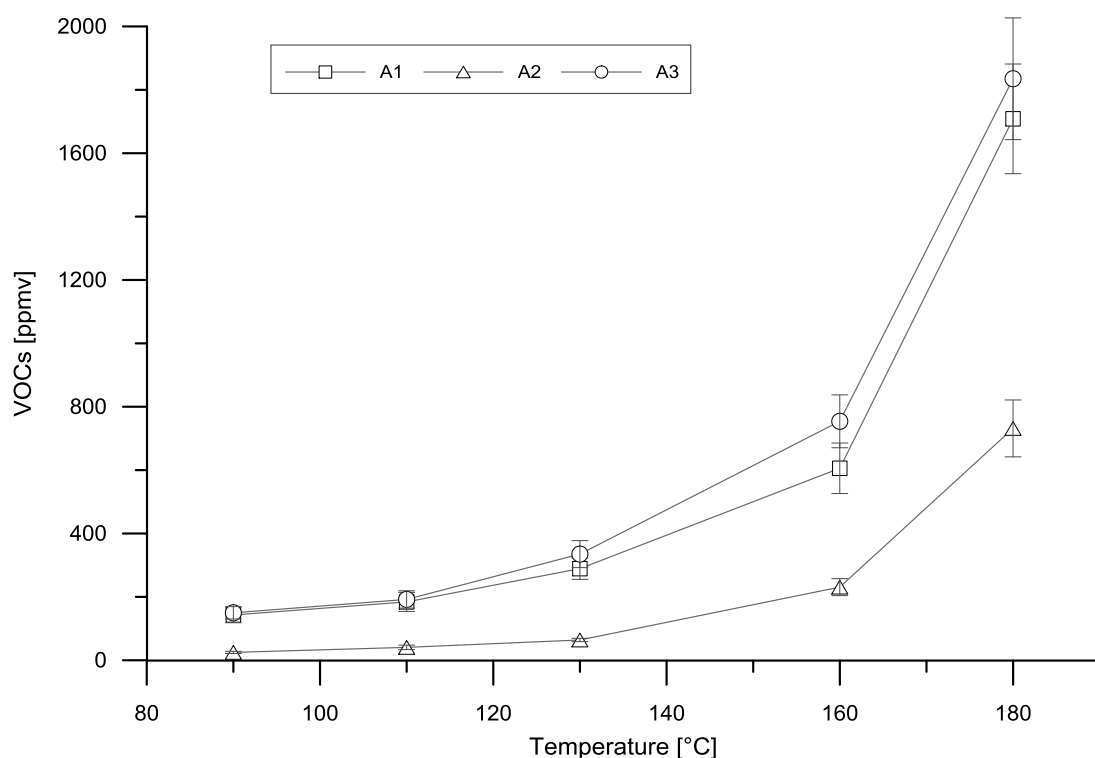


Figure 5 - PID responses (VOCs concentration) vs temperature in asphalts headspaces (A1, A2 and A3)

#### 4.3 Asphalt/wax blends emissions analysis

Differences in the chromatographic profiles of the pure asphalt vs asphalt/wax blends were observed with a decrease in the GC responses when the asphalt/wax blends were considered. As an example, table 4 shows the comparison of the GC mean responses of the 10 volatiles used as model compounds in the formulations A3, A3-3S and A3-3B after heating at 160 °C. A significant decrease in the emission of the volatile compounds was observed when the asphalt/wax blends were used. More precisely, MANOVA revealed the presence of significant differences among the mean values of the investigated samples: subsequently, the Bonferroni approach, used for pairwise comparisons, showed the presence of significant differences between the sample with and without wax. The addition of both waxes (M and S) produced a significant decrease of the GC signals for all the investigated volatiles with the sole exception of tetradecane and docosane for which a strong increase in the GC signal was observed when asphalt A3-3B was analyzed. Further investigations on the entire volatile profile of sample A3-3B showed the presence of very high GC responses

belonging to C14-C24 linear hydrocarbons (Fig. 6). The observed behavior could be ascribed to the characteristics of the wax M, from which, under the utilized operating conditions, linear hydrocarbons were better released with respect to the S wax.

Table 4 - Bonferroni's t-test: comparison of the mean responses (GC peak areas) for the selected volatile organic compounds released from asphalts A3, A3-3M and A3-3S at 160 °C (n = 3)

Compound	Asphalt mixture		
	A3	A3-3M	A3-3S
	GC peak area *		
Toluene (RT: 2.93 min)	310000±4800 <sup>a</sup>	215300±1200 <sup>b</sup>	177500±2500 <sup>c</sup>
Octane (RT: 3.28 min)	105200±800 <sup>aI</sup>	62300±700 <sup>bI</sup>	68000±1000 <sup>cI</sup>
Trimethyl thiophene (RT: 5.99 min)	42800±1900 <sup>aII</sup>	26700±600 <sup>bII</sup>	24730±620 <sup>cII</sup>
Diethyl benzene (RT: 7.01 min)	88200±2100 <sup>aIII</sup>	49600±900 <sup>bIII</sup>	49100±1100 <sup>bIII</sup>
Naphthalene (RT: 9.22 min)	1000000±20000 <sup>aIV</sup>	786000±18000 <sup>bIV</sup>	739000±25000 <sup>cIV</sup>
Methyl naphthalene (RT: 11.05 min)	977000±38000 <sup>aV</sup>	754000±31000 <sup>bV</sup>	677000±22000 <sup>cV</sup>
Tetradecane (RT: 12.10 min)	621000±9000 <sup>aVI</sup>	2899000±15000 <sup>bVI</sup>	442700±2200 <sup>cVI</sup>
Methyl naphthothiophene (RT: 17.83 min)	23300±600 <sup>aVII</sup>	12500±700 <sup>bVII</sup>	14100±400 <sup>bVII</sup>
Dimethyl dibenzothiophene (RT: 18.61 min)	23300±720 <sup>aVIII</sup>	13700±800 <sup>bVIII</sup>	14800±500 <sup>bVIII</sup>
Docosane (RT: 20.69 min)	41100±600 <sup>aIX</sup>	174600±1200 <sup>bIX</sup>	31000±400 <sup>cIX</sup>

\* Area values obtained by using the extracted ion chromatogram mode on the basis of the base peaks for each compound (Area ± SD)

Same letters: absence of significant differences among the mean values

Different letters: presence of significant differences among the mean values

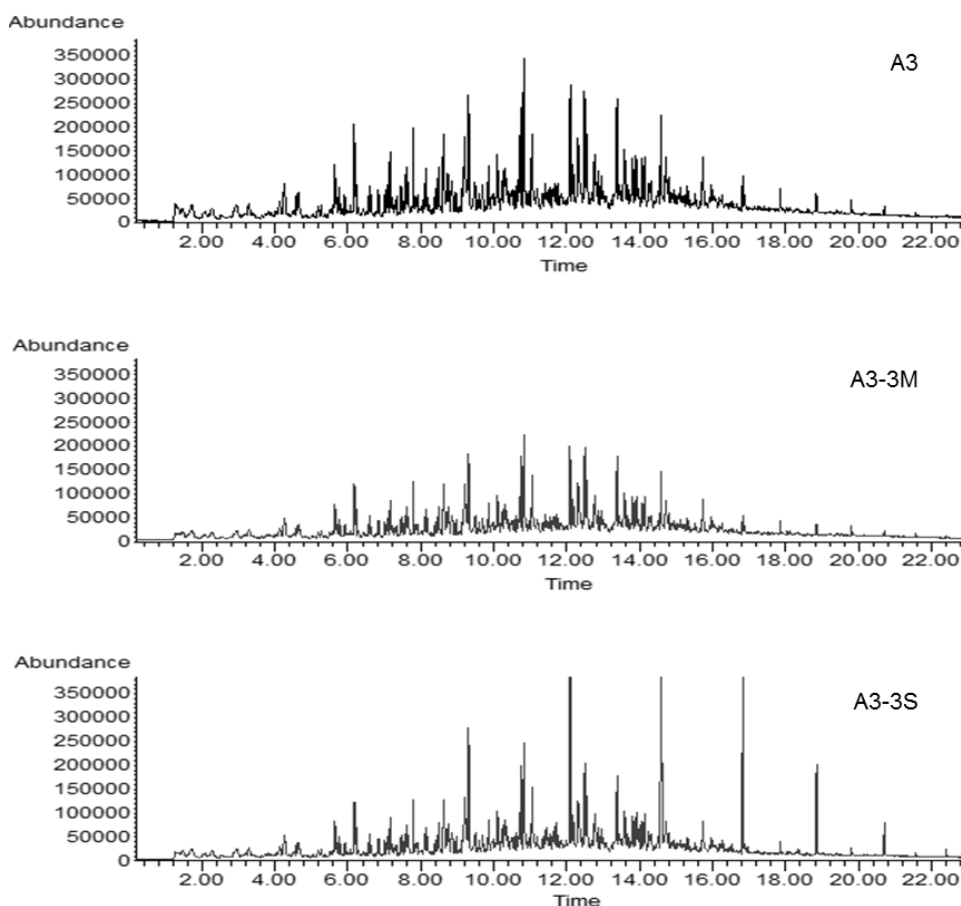


Figure 6 - HS-GC/MS chromatograms of asphalts A3, A3-3S and A3-3B heated at 160°C.

With regards to the PID responses, the addition of both waxes produced a reduction of asphalt emissions, especially at temperatures below the waxes melting point (110°C) with a reduction of VOCs concentration of about 80% at 90 °C (Fig. 7). This behavior can be explained taking into account that waxes form fully interconnected solid particles (micro- and macro-crystalline structures) with the asphalt, limiting the volatilization of the volatile compounds (Merusi et al., 2013; Lu et al., 2005; Rubio et al., 2012). To a lower extent, this phenomenon was also observed at higher temperatures, when the asphalts matrix becomes liquid: the wax crystals and the asphaltene micelles move and re-arrange forming a structured network (Polacco et al., 2012).

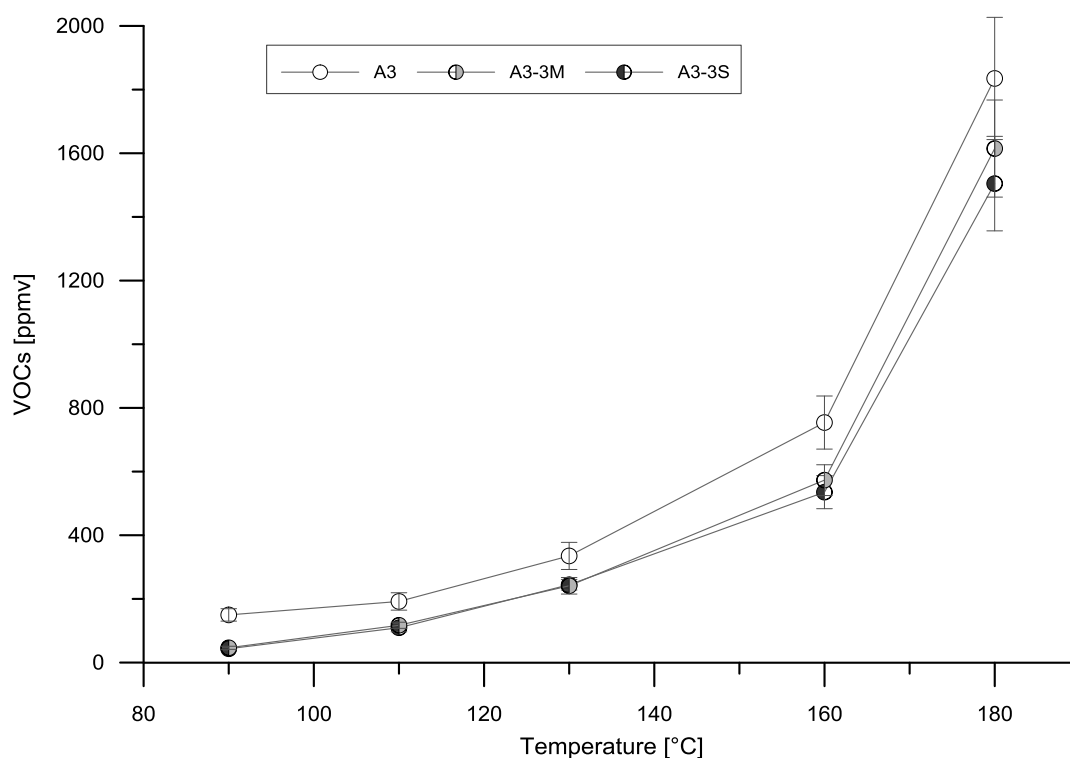


Figure 7 - PID responses (VOCs concentration) vs temperature in asphalts/wax blends headspaces (A3, A3-3M and A3-3S)

## 5. Conclusions

During the asphalt heating process in the various stages of road pavement construction a complex mixture of hydrocarbon aerosols, vapors and gases is emitted into the atmosphere. The gas chromatographic procedure has allowed the identification of more than 200 compounds, including linear and branched hydrocarbons, cyclic alkanes, aromatic hydrocarbons and heterocyclic compounds containing principally sulfur, highlighting at the same time a hierarchy of their appearance in relation to the temperature. Both techniques (HS-GC/MS and PID) used for the analysis of the asphalt headspace have confirmed as the temperature represents the major factor in the generation of such airborne substances. It is important to emphasize that the same results were obtained by using both an analytical instrumentation, that operates under strictly controlled conditions (HS-GC/MS), and a portable device (PID) that allows for greater flexibility of use also for field measurements. The comparison with the data emerging from asphalt macro-compositional analysis (SARA fractions) revealed that there were a negative correlation between the amount of

volatile organic compounds in the emissions and the content of the asphaltene fraction, characterized by high molecular weight, in the asphalt solid matrix.

The study of the binary asphalt/wax mixtures highlighted the twofold way in which the wax performs in reducing emissions. From a technological point of view, the introduction of such additives allows the production of WMA in road construction, with a temperature manufacturing and laying decrease of around 30 °C, in accordance with the findings of the literature. The data obtained in this experimental program showed a halving of the asphalt emission as a result of temperature reduction from 160 °C (typical HMA paving temperature) to 130 °C. At the same time, both at high temperatures and at those registered during the pavement service life, the wax crystals tend to interact with the asphalt molecules, forming crystalline and/or crosslinked structures, which generate macromolecules with higher molecular weight on the one hand and inhibit the release of lighter and more volatile compounds on the other.

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