



**HAL**  
open science

## Relationship between chemical composition and VOCs emission potential of similar paving grade road bitumen

Marie-Astrid Dutoit, Pierre Faure, Catherine Lorgeoux, Eddy Langlois,  
Raymond Michels

► **To cite this version:**

Marie-Astrid Dutoit, Pierre Faure, Catherine Lorgeoux, Eddy Langlois, Raymond Michels. Relationship between chemical composition and VOCs emission potential of similar paving grade road bitumen. *International Journal of Pavement Engineering*, 2024, 25 (1), pp.Article: 2378343. 10.1080/10298436.2024.2378343 . hal-04750577

**HAL Id: hal-04750577**

**<https://hal.science/hal-04750577v1>**

Submitted on 23 Oct 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## **Relationship between chemical composition and VOCs emission potential of similar paving grade road bitumen**

Marie-Astrid Dutoit <sup>a-b-c</sup>, Pierre Faure <sup>b</sup>, Catherine Lorgeoux <sup>c</sup>, Eddy Langlois <sup>a\*</sup>, Raymond Michels <sup>c</sup>

<sup>a</sup> *Pollutants Metrology Division, Institut National de Recherche et Sécurité (INRS), 1 rue du Morvan, Vandœuvre-lès-Nancy 54519, France*

<sup>b</sup> *Université de Lorraine, Laboratoire Interdisciplinaire des Environnements Continentaux (LIEC), UMR7360, Vandœuvre-lès-Nancy 54506, France*

<sup>c</sup> *Université de Lorraine, CNRS, GeoRessources, UMR7359, Vandœuvre-lès-Nancy 54506, France*

\* [eddy.langlois@inrs.fr](mailto:eddy.langlois@inrs.fr) corresponding author

### **Abstract**

Exposure to bitumen fumes of the workers during road pavement is a subject of interest in the field of industrial hygiene. Even if improvements have been made to technical means of prevention, recent studies have shown that exposures need to be reduced. In this sense, the development of early diagnosis method able to assess the volatile organic compounds (VOCs) emission potential would be useful. Therefore, the objective of this study was to outline a possible relationship between chemical composition of bitumen and volatile organic (VOCs) emission during heating using thirteen 35/50 paving grade bitumen samples used in France. The samples are similar regarding their physical properties, elemental and SARA compositions. GC-FID, GCxGC/TOF-MS and GPC-UV investigations show that they contain the same class of compounds but in different proportions. Thermal analyses revealed different capacities of volatiles release potential. Combination of these data allowed to establish a relationship between chemical composition and volatile emission, leading to the identification of two groups of samples. Thus, we suggest three parameters based on molecular weight distribution, thermogravimetric profile and hydrocarbon release capacity that may distinguish bitumen by their emission potential prior to road pavement application. They may contribute to a methodology aiming to prevent workers exposure to bitumen fumes during road paving operations.

**Keywords:** asphalt binder, bitumen fumes, colloidal index, total petroleum hydrocarbons, thermal behaviour.

## **Introduction**

Bitumen workers are exposed to fumes emitted by the hot bituminous mix during road paving operations. Multiple studies have been conducted to investigate this kind of occupational exposure. In 2013, the International Agency for Research on Cancer (IARC) classified bitumen fumes as 2B, “possibly carcinogenic to humans” (IARC, 2013). Their characterization is therefore of great interest. A number of analytical methods have already been developed to quantify occupational exposure to bitumen fumes (INRS, 2014, NIOSH, 1998, NIOSH, 2000). However, they lack specificity and sensitivity, and they provide insufficient information on the molecular composition of these fumes. To enhance the knowledge of road bitumen fumes composition, it is important to further understand the link between the physical and chemical characteristics of bitumen and the quantity and nature of fumes generated under road paving conditions. The present study focuses on road bitumen: a petroleum derivative transformed by refinery operations to reach the required physical properties for road paving. A broad vocabulary is used in describing and discussing this petroleum product. We use the usual European term “bitumen” in this study, although the material is also called “asphalt” outside Europe. Each bitumen has a paving grade defined by two parameters in compliance with European standards (EN 12591): penetrability (EN 1426) and ring and ball softening point (EN 1427). 35/50 grade is most widely used in France (Le Guern et al., 2010). Road bitumen is mainly manufactured using a distillation process. Additives can be included in the mix to fulfill physical requirements or improve resistance to pavement fatigue and aging.

Unlike grade, the chemical composition of bitumen is not regulated by European standards. Bitumen is a complex mixture made up of 80–88 wt% carbon atoms and 8–12 wt% hydrogen atoms. Among heteroatoms, sulfur is the most abundant (0-9 wt%), followed by nitrogen and oxygen (0–2 wt% each). Bitumen also contains traces of metals (Lesueur, 2009, Michalica et al., 2008). Furthermore, bitumen composition depends on its crude source and refinery treatment (Lesueur, 2009, Speight, 2014). SARA fractionation is a commonly adopted approach to describe its chemical matrix. This separates the organic compounds into four fractions based on their polarity: saturates, aromatics and resins, which together are termed maltenes and asphaltenes (Loeber et al., 1998, Sultana and Bhasin, 2014, Weigel and Stephan, 2018). Bitumen can be described as a colloidal system. The asphaltenes aggregate as micelles, which are dispersed in the maltene phase and surrounded by resins (Aguiar and Mansur, 2015, Lesueur, 2009, Merdrignac and Espinat, 2007). The stability of this system relies on the proportion of each fraction. It is estimated by the colloidal index, also called the Gaestel index  $I_c$ , which is calculated using the following equation (1) as proposed by Gaestel et al. (1971):

$$I_c = \frac{\text{Wt\% Saturates} + \text{Wt\% Asphaltens}}{\text{Wt\% Aromatics} + \text{Wt\% Resins}} \quad (1)$$

$I_c$  is a very common index in the literature dealing with road bitumens.  $I_c$  usually ranges from 0.2 to 2.7 for road bitumens (Gaestel et al., 1971, Oyekunle, 2006, Weigel and Stephan, 2018). It is proportional to the softening point and inversely proportional to the penetrability (Gaestel et al., 1971).  $I_c$  is also helpful in highlighting the effect of additives incorporated during the industrial process (Alam and Hossain, 2017, Gawel et al., 2016). However, further understanding of bitumen behavior may arise from the study of chemical composition at a molecular scale.

The literature dealing with the relationship between the physical properties and the chemical composition of bitumen focuses mainly on the binder design process (Paliukaite

et al., 2015; Merola et al., 2016; Weigel and Stephan, 2017; Kleiziene et al., 2019). There are few publications explaining how this relationship affects volatile organic compound (VOC) emission. Moreover, fume production depends not only on the bitumen characteristics but also on the experimental system (Kriech et al., 2007) and the parameters applied during generation (Bolliet et al., 2015, Kriech et al., 1999). Recent studies reveal that VOC emission can be modified by the addition of certain additives. It appears that activated carbon (Gasthauer et al., 2008), nanoclay (Li et al., 2017) or additives initially used to modify physical behavior inhibit VOC emission (Autelitano et al., 2017, Bolliet et al., 2015, Lei et al., 2018) whereas it is enhanced by addition of a bio-rejuvenating agent (Porot et al., 2016). However, correlation between bitumen chemical composition, binding properties and type of VOC emitted remains poorly understood. A number of studies reveal that bitumen which do not emit the same fume quantities differ by their grade (Boczka et al., 2014), asphaltene content (Autelitano et al., 2017) or naphthenic prevalence (Gasthauer et al., 2008). Brandt and De Groot (1999) have developed a relationship that predicts the fume quantity generated by a bitumen. This calculation relies on its true boiling point measurement and the heating temperature.

Experimentation study of bitumen VOC emission requires a first step of bitumen fine chemical characterization as to understand why bitumen of same grade may generate different VOC quantities. Responding to this issue would contribute to the identification of major parameters controlling VOC emission or to the development of processes aiming to emission reduction.

The above literature review does neither evidence a reliable method assessing the VOCs emission potential nor an experimental setup providing representative fumes. Therefore, the aim of this research is to improve the knowledge in this area by identifying chemical parameters useful for the development of an early diagnostic tool making this assessment

possible. Without standardized method available, we propose to use thermal analysis as a proxy to bitumen fumes emission. This shall allow classification of bitumen according to their relative emission potential. Combination with fine molecular characterization should contribute to understand to which extend chemical variability may be linked to VOCs emissions potential.

In this objective thirteen road bitumens with similar grade all refined in Europe and representative of the French market were studied. Their chemical characteristics were firstly inter-compared to investigate the composition variability within similar bitumen grade. Our work then focused on developing a thermal analysis methodology attempting to rank bitumen as a function of VOC emission potential. This shall help in suggesting solutions for reducing worker occupational exposure to bitumen fumes.

## **Materials and methods**

The global experimental and analytical strategy is presented in figure 1 which illustrates the combination of methods and their nature :physical, molecular or thermochemical, applied to total bitumen or its sub-fractions: maltenes, saturates, aromatics and resins.

### ***Road bitumen.***

The study was based on thirteen road bitumens of similar 35/50 grade used most commonly in France. These materials were supplied by Eurobitume and were identified by a reference letter. Three physical parameters were measured: penetrability according to EN 1426:2015, ring and ball softening point according to EN 1427:2015 and kinematic viscosity at 135 °C according to EN 12595:2014.

### ***Bitumen general chemical characteristics.***

The carbon, hydrogen, oxygen, nitrogen and sulfur contents were measured for all the bitumens except for those named P and Q.

In order to investigate their global composition, the bitumens were fractionated using the SARA procedure as follows. 100 mg of bitumen was dissolved in 5 mL of dichloromethane (DCM) and diluted in 100 mL of *n*-pentane. The mixture was stirred and heated under reflux at 35 °C for 30 minutes before it was filtered. The “maltenes” fraction remained in solution, while the asphaltenes were collected on a filter. The latter fraction was then recovered by dissolution in DCM. Each fraction was dried and weighed. The maltenes were split into three fractions according to the nature of their constituents: saturated hydrocarbons called “saturates”, aromatic hydrocarbons called “aromatics” and polar compounds called “resins”. Two successive fractionations were performed using an alumina and a silica column. 18 mg of maltenes were dissolved in 300 µL of DCM and placed at top of the alumina column. The first fraction was eluted with 3 mL of DCM, then the second fraction (the resins) with as much of a 50% DCM: 50% methanol v/v solvent mixture as required. The first fraction was dried, dissolved in 1 mL of *n*-hexane and transferred on the head of the silica column. The “saturates” were eluted with 2.5 mL of *n*-hexane. The “aromatics” were eluted with 3 mL of a 65% *n*-hexane: 35% DCM v/v solvent mixture. The “resins” were then eluted with as much of the 50% DCM: 50% methanol v/v solution as required and pooled with the resin fraction collected on the alumina column. All three fractions were dried and weighed. The variability of the SARA method was tested on bitumen A by repeating five times asphaltenes precipitation. SAR fractionation was subsequently performed on the five maltene solutions and one out of the five maltene solutions was replicated four times.

#### ***Bitumen molecular characterization.***

The samples were analyzed by Gel Permeation Chromatography or size exclusion chromatography coupled to UV detector (GPC-UV) as 1 mg/mL tetrahydrofuran (THF) solutions using an Agilent 1100 Series chain. This analytical method aims at classified the compounds of a mixture according to their molecular size and gives an idea of the hindered molecule distribution. 50  $\mu$ L of solution were injected into a PLGel 5  $\mu$ m pre-column connected to a PLGel MIXED-E 3  $\mu$ m column. The mobile phase was THF at a flow rate of 1 mL/min for 15 minutes. The UV detector was used at  $\lambda = 254.4$  nm. GPC-UV allowed to compare the distribution of constituents according to their molecular sizes.

Total Petroleum Hydrocarbons (TPH) of the bitumens was measured using a gas chromatograph coupled to a flame ionization detector (GC-FID Agilent 7890A). The bitumens were analyzed at 50 mg/mL in DCM except samples A, G, J and K, which were at 10 mg/mL. Quantities were measured using the method described in ISO 16703:2004. This method assesses the total quantity of “valuable” hydrocarbons in a bulk material, usually uses for soil or petroleum source rock. In the case of bitumen the result of this analysis could be a good first approach to the quantity of potential fumes. 1  $\mu$ L was injected in splitless mode with the injector set to 300  $^{\circ}$ C. An Agilent DB-5MS column (5%-phenyl)-methylpolysiloxane equivalent (60 m $\times$ 0.25 mm $\times$ 0.1  $\mu$ m) was used with helium as carrier gas at a constant flow of 1.5 mL/min. The oven was set to the following temperature program: 1 min at 40  $^{\circ}$ C, from 40  $^{\circ}$ C to 325  $^{\circ}$ C at 10  $^{\circ}$ C/min followed by a hold-time of 16 min at 325  $^{\circ}$ C. The FID was set to 300  $^{\circ}$ C while hydrogen, air and make-up (He) flows were 40 mL/min, 350 mL/min and 27 mL/min respectively.

Two-dimensional gas chromatography gives an accurate idea of the global hydrocarbon fingerprint in a complex mixture. Due to the huge separating power of this method, information provided is more complete and detailed than with a conventional one-dimensional gas chromatography method. All the complex mixture of maltenes were



therefore analyzed by comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry (GC×GC/TOF-MS) at a concentration of 57 mg/mL in DCM. An Agilent GC 7890B gas chromatograph fitted with a split/splitless injector and a normal-phase column system was used. This featured an apolar-polar combination enabling compounds to be separated first accordingly to their volatility and subsequently to their polarity. The first-dimensional column (1D) was a BPX5 (20 m×0.15 mm×0.2 μm), the second-dimensional column (2D) was a VF-17ms (7 m×0.25 mm×0.15 μm) and the bleed line was a capillary of deactivated fused silica (5 m×0.1 mm). The injector was set to 320 °C and 1 μL of sample was injected with a split ratio of 1:10. The GC oven was programmed from 60 °C to 330 °C at 4 °C/min and then held for 30 minutes. Helium was used as carrier gas with constant flows of 0.5 mL/min and 18 mL/min in the 1D and 2D columns respectively. The flow-modulation time was 6 seconds with a 10 cm×0.53 mm loop. Detection was ensured by a BenchTOF-Select MARKES International time-of-flight mass spectrometer with transfer line and ion source temperatures set to 320 °C and 325 °C respectively. Mass spectra were acquired from 38 to 500 amu by electronic impact mode set at -70 eV, frequency rate at 50 Hz and filament voltage at 1.6 V.

#### ***Bitumen thermochemical analysis.***

In order to investigate the thermal behaviour of bitumen, which may in first approximation reflect the total VOCs release potential, thermogravimetric measurements were carried out with a METTLER TOLEDO TGA/DSC 1 analyzer. Approximately 10 mg of bitumen were placed in a crucible and heated from 25 °C to 600 °C at 10 °C/min. Nitrogen flow rates of protective and reactive gases were set at 10 mL/min and 25 mL/min respectively.

These thermodesorptions were performed using a Frontier Lab Multi-shot pyrolyzer EGA/PY-3030D and a Micro Jet Cryo-Trap MJT-1030Ex installed on an Agilent GC

7890B fitted with a column ZB-5MS (60 m×0.25 mm×0.25 μm) and coupled to a 5977A mass spectrometer. Approximately 0.3 – 0.7 mg of bitumen was weighed in a cup, placed in the thermodesorption oven and heated from 80 °C to 300 °C at 10 °C/min. The desorbed compounds were transferred at the head of the column through the injector set to 300 °C with a 1:5 split ratio. They were focused by the cryo-trap maintained at -180 °C until start of the GC analysis. The GC oven was set with the following temperature program: 40 °C to 315 °C at 5 °C/min and then held for 20 minutes. Helium was used as carrier gas at a constant flow rate of 1.4 mL/min. Transfer line, ion source, and MS quadrupole temperatures were set to 320 °C, 230 °C and 150 °C respectively. Mass spectra were acquired from 50 to 500 amu. Two other analyses were performed on completion of the GC run. Both featured the same cup and GC parameters but different thermodesorption oven programs were applied: from 300 °C to 450 °C and from 450 °C to 600 °C.

### ***Statistical analysis.***

Statistical tests were carried on experiment results to confirm hypothesis on the influence of some parameters on the VOCs emission. As two groups of bitumen were discriminated by data analysis, test of Student (or t-test) were performed. The statistical analysis was performed with the software Statgraphic centurion 18®.

## **Results**

### ***Bitumen general chemical characteristics.***

As far as the physical measurements are concerned, penetrability, ring and ball softening point were compared with the specifications provided in NF EN 12591 (Afnor, 2009) (Figure 2). This standard enables us to determine the grade of each bitumen.

Elemental analyses reveal that the bitumens were composed of  $83.4\pm 0.8$  wt% carbon,  $10.6\pm 0.3$  wt% hydrogen,  $4.7\pm 0.9$  wt% sulfur,  $0.9\pm 0.2$  wt% oxygen and  $0.6\pm 0.1$  wt% nitrogen (Table S1 in supplementary material). The sum of these weight percentages was not exactly 100% because of measurement uncertainty.

Results of SARA composition exhibit low variability. Coefficient of variability are under 5% for precipitation of asphaltenes on five replication of bitumen A and around 5% for 8 replications of SAR constitution as described in Table S2 and S3 in supplementary material. The bitumens contained on average  $18\pm 3$  wt% saturates,  $34\pm 4$  wt% aromatics,  $28\pm 3$  wt% resins and  $20\pm 3$  wt% asphaltenes (Table S1 in supplementary material) according to the SARA fractionation. We compared our results with those in the literature on road bitumens. The average elemental compositions of the thirteen samples matched those previously reported (Lesueur, 2009, Michalica et al., 2008). Comparing our SARA values proved more difficult because they depended on the protocol used and the bitumen crude source (Corbett, 1969, Gaestel et al., 1971, Lesueur, 2009). However, our aromatic and resin fractions always dominate, a result consistent with other studies (Autelitano et al., 2017; Le Guern et al., 2010; Lesueur, 2009). The combination of physical parameters and SARA proportions allowed the colloidal index  $I_c$  to be calculated.  $I_c$  ranged from 0.4 to 0.8 for the thirteen bitumen samples (Table S1 in supplementary material) which is in accordance with the literature on road bitumens. For instance, Gaestel et al., (1971), Oyekunle (2006) (Fernández-Gómez et al., 2014, Gaestel et al., 1971, Oyekunle, 2006, Weigel and Stephan, 2018) present  $I_c$  values ranging between 0.2 and 2.7 irrespective of bitumen grade.

Taking into account the evaluation of the variability of the SARA fractionation carried out with the replication on the same bitumen, the differences observed in the SARA

composition of different investigated bitumens do not allow distinguish specific groups (Table S5 in supplementary material).

### ***Bitumen molecular characterization.***

With GPC-UV analyses, the bitumens were eluted from 6 to 13 minutes under our analytical conditions. The aromatic, resin and asphaltene fractions were also analyzed as separate fractions. Their chromatogram intensities were displayed in proportion to their respective contributions in the bitumen as deduced from the SARA fractionation (Figure 3).

The SARA protocol quantifies all the compounds including aliphatic hydrocarbons not detected by UV spectroscopy. This may lead to a slight shift between the bitumen chromatograms and those reconstructed using the signals of aromatic, resin and asphaltene fractions. This representation allowed us to evaluate the contribution of each fraction to the shape of the total bitumen profile.

Whatever the bitumen, the first peak centered on 7 minutes corresponded to the asphaltenes contribution (the fraction of the highest molecular mass). The shape beyond 7.5 minutes and its apex centered on 9 minutes were mainly due to the aromatic and resin fractions. In order to classify our bitumen according to GPC-UV profiles we selected the apex retention time and the width at half height of the whole bitumen or the aromatic fraction chromatograms (figure 4). Two groups of bitumens can be distinguished accordingly: (i) A, G, J, K bitumens and (ii) nine other bitumens. The A, G, J, K bitumens displayed a chromatogram with a less intense apex which eluted later than the other samples. This shift was mainly due to the contribution of the aromatic fraction. It revealed that the A, G, J and K bitumens contained a higher proportion of low molecular size compounds than the others.

TPH determined by GC quantifies only the compounds from bitumen volatilized in the injector set at 300 °C and eluted on the gas chromatogram between *n*-decane and *n*-tetracontane. TPH values ranged from 111.2 to 135.0 mg/g of bitumen for the A, G, J, K samples and from 12.0 to 19.4 mg/g of bitumen for the nine other samples.

An intense unresolved complex mixture (UCM) occurred for the G and K samples (Figure 5) and also for the A and J samples. Moreover, the G and J samples were unique in possessing a distribution of *n*-alkanes from C<sub>17</sub>H<sub>36</sub> to C<sub>40</sub>H<sub>82</sub>. The nine other bitumen chromatograms (illustrated as C and I in Figure 5 and Figure S2 in supplementary material) displayed a slight increase of the baseline with a very limited UCM intensity, a distribution of resolved *n*-alkanes up to C<sub>40</sub>H<sub>82</sub> and an amount of volatile compounds that was 6 to 11 times lower than those in the A, G, J and K bitumen group.

For all samples, maltenes analyses based on two-dimensional GC separation provide information on several chemical families including saturated hydrocarbons consisting of *n*-alkanes or *iso*-alkanes ( $m/z = 57, 71, 85$ ) and hopanes ( $m/z = 191$ ), alkylbenzenes ( $m/z = 91, 105, 119, 123$ ), naphthalene, alkylnaphthalenes ( $m/z = 128, 142, 156, 170$ ), phenanthrene, alkylphenanthrenes and anthracene ( $m/z = 178, 192, 206$ ). Sulfur heterocyclic hydrocarbons were also detected including benzothiophenes ( $m/z = 134, 147, 161, 175$ ) and dibenzothiophenes ( $m/z = 184, 197, 211, 225$ ) (Figure 6).

The 2D- gas chromatogram of bitumen K, A, G and J (Figure 6 and Figure S3 in supplementary material) exhibited an intense UCM which is not present in the nine other bitumen fingerprint (Figure 6). In the first dimension, compounds were separated according to their ascending volatility and the UCM eluted between *n*-alkanes C<sub>26</sub>H<sub>54</sub> and C<sub>35</sub>H<sub>72</sub>. In the second dimension, compounds were separated according to their ascending polarity and the UCM eluted between *n*-alkanes and dibenzo(a,h)anthracene. The 2D-GC

analysis suggested that the UCM was mainly composed of apolar compounds including aromatic compounds containing less than five fused benzene rings.

#### ***Bitumen thermochemical analysis.***

The thermogravimetric and derivative thermogravimetric profiles of the different bitumens (Figure 7 and Figure S4 in supplemental material) highlight that the A, G, J and K bitumen group is characterized by a highest weight loss rate in the 25 °C to 450 °C range and the lowest weight loss rate in the 450 °C to 600 °C range.

The derivative thermogravimetric profiles revealed that weight loss was a single stage process. Every profile reached an apex between 470 °C and 475 °C. According to the literature, this indicates volatilization and/or the decomposition of several constituents from the samples (Idris et al., 2010, Varol et al., 2010). Between 78 wt% and 85 wt% of the bitumens were volatilized at the end of the temperature program, suggesting incomplete decomposition of the organic matrices.

Thermodesorption combined with GC-MS. Three thermodesorption temperature programs were used: 80 °C – 300 °C (1), 300 °C – 450 °C (2) and 450 °C – 600 °C (3). Representative bitumens (C, I, G and K) were selected to depict the two previously identified sample groups.

(1) 80 °C – 300 °C. In this first temperature range, the G and K bitumen chromatograms displayed an intense UCM with an elution time between 30 and 40 minutes respectively. The chromatograms also exhibited resolved organic compounds (Figure 8). Several chemical families were identified, especially parent and alkyl-substituted aromatic hydrocarbons, specifically alkylbenzenes ( $m/z$  91, 105, 119) and linear alkyl-benzene ( $m/z$  91), naphthalene and alkyl-naphthalenes ( $m/z$  128, 142, 156, 170, 184, 198), and acenaphthene ( $m/z$  154). Saturate hydrocarbons were also detected including *n*-alkanes and *iso*-alkanes ( $m/z$  57, 71, 85, 99). Their quantities varied significantly depending on

the bitumen sample. Within this first thermodesorption range, the intensity of the chromatographic signal, including UCM and resolved molecules, revealed that the G and K bitumens generated more organic compounds than the C and I bitumens.

(2) 300 °C – 450 °C. The chromatograms for the 300 °C – 450 °C temperature range (Figure S5 in supplementary material) displayed the same profile for all the bitumens. They were dominated by *n*-alk-1-enes/*n*-alkanes doublets due to thermal cracking of the complex organic structure, especially Asphaltenes (Behar and Pelet, 1984). UCM at the end of the chromatogram was significantly more intense for G and K bitumens than for C and I. G and K bitumens yielded more organic compounds than the C and I.

(3) 450 °C – 600 °C. The chromatograms obtained by the analysis at the 450 °C - 600 °C temperature interval (Figure S6 in supplementary material) showed molecular distribution as well as quantities of generated compounds similar to those of the 300-450°C range. The *n*-alk-1-enes/*n*-alkanes doublet succession prevailed in all the chromatograms along with an UCM (apex at 55 minutes) due to thermal cracking of the bitumen constituents, especially asphaltenes.

### ***Statistical analysis.***

The two groups of bitumens were distinguished from advanced observation of the results from chemical characterization and thermochemistry analyses. To explore this observation further, a t-test or Student test was carried out with each individual measured parameter. The means of the two populations are calculated and their confidence interval are constructed. The width of the confidence interval determines the certainty of the difference in the means. Furthermore, the confidence interval for the difference between the two means is also constructed. This analysis highlights that SARA chemical characterization do not depend on the groups of bitumens, only two physical parameters are slightly dependent of the bitumen groups (kinematics viscosity and penetrability),

whereas GPC shape parameters and thermochemical parameter (TPH and P300) strongly depend on the two groups. (Table S4-S5 and S6 in supplementary material).

## Discussion

Geochemical differences between bitumen of similar grade.

Values of the conventional physical parameters such as penetrability, ring and ball softening point used to define bitumen grades confirmed that the thirteen bitumens used in our study were of the same grade, namely 35/50 (Figure 2). Elemental composition and SARA (Table S2 in supplementary material) of these bitumens were similar and in accordance with the values reported in the literature on road bitumens (Lesueur, 2009, Michalica *et al.*, 2008). Should a difference of fume emission be noted during heating, it would not be explained by these global composition parameters. Therefore, investigation at the molecular scale was needed.

Chromatograms provided by GPC-UV displayed a similar retention time range (6 - 13 minutes) for all the bitumen samples, suggesting a comparable molecular size distribution. However, two kinds of molecular distributions could be distinguished, for the whole bitumen and the aromatic GPC-UV chromatograms as for the resins to a lesser extent (Figure 3 and Figure S1 in supplementary material). The GPC-UV profiles could be characterized using two chromatographic parameters: the apex retention time ( $T_r$ ) and peak width at half height ( $\omega_{1/2}$ ). These parameters were expressed as the ratio  $\frac{\omega_{1/2}}{T_r}$  (Table 1).

These ratios were highest for the A, G, J and K bitumens and showed that they contained higher relative amounts of low molecular size constituents i.e. higher proportion of constituents eluted at higher retention times than the other nine samples (Figure 4). The



difference in contribution of lower molecular weight compounds as detected by GPC is therefore a first criterium useful to distinguish bitumen compositions.

Total Petroleum Hydrocarbons (TPH) measured by gas chromatography confirmed the existence of two distinct bitumen groups. TPH values for A, G, J and K bitumens are significantly greater than those measured for the nine others (Table 1). This difference might be explained by the fact that gas chromatography analysis in 1 or 2D for A, G, J and K exhibit a predominant UCM not present for other samples (Figures 5, 6 and Figures S2 and S3 in supplementary material). Characterization at molecular scale therefore distinguishes A, G, J and K bitumens from the others. This geochemical parameter (TPH) based on molecular distributions and proportions is another indicator that allows distinction of compositions between similar grade bitumens .

To evaluate whether these differences are in relationship to volatile compounds emission, the weight loss measurement obtained by ATG up to 300 °C (Figure 7 and Figure S4 in supplementary maerial) was expressed as the P<sub>300</sub> index calculated from the following equation:

$$P_{300} = \frac{W_{\text{Initial}} - W_{300^{\circ}\text{C}}}{W_{\text{Initial}}} \times 1000 \quad (2)$$

with:

$W_{\text{Initial}}$  = Weight of bitumen at start of analysis.

$W_{300^{\circ}\text{C}}$  = Weight of bitumen remaining at 300 °C.

The P<sub>300</sub> index values of A, G, J and K samples are significantly greater than for the nine others (Table 1). It may thus be used as a generic indicator to assess the total volatile emission potential of bitumen.

Combination of distinctive geochemical parameters.

The bitumen samples were characterized using chemical parameters  $\frac{\omega_{1/2}}{Tr}$  (GPC-UV),  $P_{300}$  (ATG), TPH (GC-FID). The combination of these parameters in figure 9 allows to distinguish A, G, J, K bitumens characterized by greater weight loss due to volatilization ( $P_{300}$ , ATG), higher relative contribution of low molecular size compounds in total bitumen GPC-UV chromatogram ( $\frac{\omega_{1/2}}{Tr}$ ) and the highest contribution of C<sub>10</sub>-C<sub>40</sub> hydrocarbons (TPH, GC-FID). Assuming that volatile content ( $P_{300}$ ) of bitumen is proportional to fumes emission capacity (Brandt and De Groot, 1999), a link with the chemical characteristics ( $\frac{\omega_{1/2}}{Tr}$  and TPH) of bitumen A, G, J, K can be suggested. The difference in volatile contents is however minor in regards to the entire weight of bitumen, which explains why global chemical characteristics (elemental and SARA compositions, Colloidal Index) failed in distinguishing these bitumen. Only a more discriminating analytical methods combination (GPC-UV, GC-FID, thermal analyses) were able to highlight the differences.

All bitumen of this study are of same grade (35/50) and would probably be used under similar conditions, especially application temperature, during road paving operations. However, according to our results, A, G, J and K bitumen would expose workers to more fumes than the nine others. The emission potential of bitumen must thus be evaluated before its application in order to counter occupational exposure risk at source. A combination of the analytical methods (GPC-UV, GC-FID and TGA) used in this study could contribute to a methodology able to preventively estimate the volatile emission potential. The identified parameters could also be helpful indicators to assess the efficiency of bitumen modifiers used to reduce volatile emission potential (Bolliet et al., 2015, Kriech et al., 1999, Xiao et al., 2017).

## Conclusion

Physical and chemical characterizations were performed on thirteen road bitumens of the same grade (35/50). All the investigated bitumens were similar in regards to penetrability, softening point, SARA fractionation and colloidal index. However, analyses at molecular scale revealed that some bitumens differ from the others with a higher proportion of low molecular size compounds (GPC-UV) and C<sub>10</sub>-C<sub>40</sub> hydrocarbons (GC-FID). Using complementary thermal analyses (TGA and thermodesorption-GC-MS), we suggest that three analytical parameters ( $\frac{\omega_{1/2}}{Tr}$ , P<sub>300</sub>, TPH) can be used to identify bitumen of higher fume emission potential. The classification of the bitumen according to these parameters was statistically validated through Student test. These parameters can be measured by standard laboratory methods such as gas chromatography, thermodesorption, gel permeation chromatography and may therefore contribute to a standardized methodology aiming to detect bitumen of higher emission potential prior to their use.

In order to relate these parameters to quantitative assessment of fumes emission, next step of development will be to perform laboratory fume generator experiments. This should validate the relationship between these parameters and fume emission capacity. Collection and molecular analysis of fumes will aim to establish genetic relationships between bitumen chemical composition and fumes emission. Ultimate goal is to validate the use of the  $\frac{\omega_{1/2}}{Tr}$ , P<sub>300</sub>, TPH as mere routine indicators for the assessment of workers exposure to bitumen fumes.

ASSOCIATED CONTENT

**Supplementary material.** File “Supplementary material”:

**Table S2.** Elemental analysis and SARA fractionation of A, B, C, E, F, G, I, J, K, L, M, P and Q bitumens.

**Figure S1.** GPC UV chromatograms of A, B, C, E, F, G, I, J, K, L and M bitumens.

**Figure S2 :** GC\_FID chromatograms of A, B, C, E, F, G, I, J, K, L, M, P and Q bitumens.

**Figure S3 :** Maltenes chromatogram of A, B, C, E, F, G, I, J, K, L and M bitumens with GCxGC/TOF-MS on apolar-polar columns set.

**Figure S4 :** Thermograms of A, B, C, E, F, G, I, J, K, L, M P and Q bitumens.

**Figure S5.** GC-MS chromatograms of C, G, I and K bitumens following the thermodesorption temperatures program 300 – 450 °C.

**Figure S6.** GC-MS chromatograms of C, G, I and K bitumens following the thermodesorption temperatures program 450 – 600 °C.

## **Author Contributions**

All authors have given approval to the final version of the manuscript.

## **Notes**

The authors declare no competing financial interest.

## **REFERENCES**

- AFNOR 2009. NF EN 12591 : 2009. *Bitumen and bituminous Binders - Specifications for paving grade bitumens*. Paris: AFNOR.
- AGUIAR, J. I. S. & MANSUR, C. R. E. 2015. Study of the interaction between asphaltenes and resins by microcalorimetry and ultraviolet–visible spectroscopy. *Fuel*, 140, 462-469.
- ALAM, S. & HOSSAIN, Z. 2017. Changes in fractional compositions of PPA and SBS modified asphalt binders. *Construction and Building Materials*, 152, 386-393.

- AUTELITANO, F., BIANCHI, F. & GIULIANI, F. 2017. Airborne emissions of asphalt/wax blends for warm mix asphalt production. *Journal of Cleaner Production*, 164, 749-756.
- BOCZKAJ, G., PRZYJAZNY, A. & KAMIŃSKI, M. 2014. Characteristics of volatile organic compounds emission profiles from hot road bitumens. *Chemosphere*, 107, 23-30.
- BOLLIET, C., KRIECH, A. J., JUERY, C., VAISSIERE, M., BRINTON, M. A. & OSBORN, L. V. 2015. Effect of temperature and process on quantity and composition of laboratory-generated Bitumen Emissions. *Journal of Occupational and Environmental Hygiene*, 12, 438-449.
- CORBETT, L. W. 1969. Composition of asphalt based on generic fractionation, using solvent deasphalting, elution-adsorption chromatography, and densimetric characterization. *Analytical Chemistry*, 41, 576-579.
- FERNÁNDEZ-GÓMEZ, W. D., RONDÓN QUINTANA, H. A., DAZA, C. E. & REYES LIZCANO, F. A. 2014. The effects of environmental aging on Colombian asphalts. *Fuel*, 115, 321-328.
- GAESTEL, C., SMADJA, R. & MLAMMINAN, K. 1971. Contribution à la connaissance des propriétés des bitumes routiers. *Revue Générale des routes Aérodrômes*, 466, 85-97.
- GASTHAUER, E., MAZÉ, M., MARCHAND, J. P. & AMOUROUX, J. 2008. Characterization of asphalt fume composition by GC/MS and effect of temperature. *Fuel*, 87, 1428-1434.
- GAWEL, I., CZECHOWSKI, F. & KOSNO, J. 2016. An environmental friendly anti-ageing additive to bitumen. *Construction and Building Materials*, 110, 42-47.
- IARC 2013. Bitumens and bitumen emissions, and some heterocyclic polycyclic aromatic hydrocarbons. In: IARC (ed.) *IARC monographs on the evaluation of carcinogenic risks to humans*. Lyon, France: International Agency for Research on Cancer
- IDRIS, S. S., RAHMAN, N. A., ISMAIL, K., ALIAS, A. B., RASHID, Z. A. & ARIS, M. J. 2010. Investigation on thermochemical behaviour of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA). *Bioresource Technology*, 101, 4584-4592.
- INRS. 2014. *MétoPol* [Online]. Available: [www.inrs.fr](http://www.inrs.fr) [Accessed].
- KRIECH, A. J., KUREK, J. T. & WISSEL, H. L. 1999. Effects of mode of generation on the composition of asphalt fumes. *Polycyclic Aromatic Compounds*, 14, 179-188.
- KRIECH, A. J., OSBORN, L. V., WISSEL, H. L., REDMAN, A. P., SMITH, L. A. & DOBBS, T. E. 2007. Generation of bitumen fumes using two fume generation protocols and comparison to worker industrial hygiene exposures. *Journal of Occupational and Environmental Hygiene*, 4, 6-19.
- LE GUERN, M., CHAILLEUX, E., FARCAS, F., DREESSEN, S. & MABILLE, I. 2010. Physico-chemical analysis of five hard bitumens: Identification of chemical species and molecular organization before and after artificial aging. *Fuel*, 89, 3330-3339.
- LEI, M., WU, S., LIU, G. & AMIRKHANIAN, S. 2018. VOCs characteristics and their relation with rheological properties of base and modified bitumens at different temperatures. *Construction and Building Materials*, 160, 794-801.
- LESUEUR, D. 2009. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Advances in Colloid and Interface Science*, 145, 42-82.

- LI, L., WU, S., LIU, G., CAO, T. & AMIRKHANIAN, S. 2017. Effect of organo-montmorillonite nanoclay on VOCs inhibition of bitumen. *Construction and Building Materials*, 146, 429-435.
- LOEBER, L., MULLER, G., MOREL, J. & SUTTON, O. 1998. Bitumen in colloid science: a chemical, structural and rheological approach. *Fuel*, 77, 1443-1450.
- MERDRIGNAC, I. & ESPINAT, D. 2007. Physicochemical characterization of petroleum fractions: the state of the art. *Oil & Gas Science and Technology – Revue d'IFP Energies nouvelles*, 62, 7-32.
- MICHALICA, P., KAZATCHKOV, I. B., STASTNA, J. & ZANZOTTO, L. 2008. Relationship between chemical and rheological properties of two asphalts of different origins. *Fuel*, 87, 3247-3253.
- NIOSH 1998. Method 5042 : Benzene-soluble fraction and total particulate (asphalte fume). In: CASSINELLI, P. E. A. M. (ed.) *NIOSH Manual of Analytical Methods*. Cincinnati, us: National Institute of Occupational Health and Safety, DHHS (NIOSH): .
- NIOSH 2000. Health Effects of Occupational Exposure to Asphalt. In: MARY ANN BUTLER ET AL (ed.) *Hazard review*. Cincinnati, us: National Institute of Occupational Health and Safety, DHHS (NIOSH): .
- OYEKUNLE, L. O. 2006. Certain relationships between chemical composition and properties of petroleum asphalts from different origin. *Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles*, 61, 433-441.
- POROT, L., SCOTT, D. & GAUDEFROY, V. Laboratory evaluation of emissions from asphalt binder and mixes using a bio-rejuvenating agent. In: UNIVERSITY, C. T., ed. Euroasphalt and Eurobitume congress, 2016 Prague.
- SPEIGHT, J. G. 2014. *The Chemistry and Technology of Petroleum*, 5th ed., CRC Press.
- SULTANA, S. & BHASIN, A. 2014. Effect of chemical composition on rheology and mechanical properties of asphalt binder. *Construction and Building Materials*, 72, 293-300.
- VAROL, M., ATIMTAY, A. T., BAY, B. & OLGUN, H. 2010. Investigation of co-combustion characteristics of low quality lignite coals and biomass with thermogravimetric analysis. *Thermochimica Acta*, 510, 195-201.
- WEIGEL, S. & STEPHAN, D. 2018. Relationships between the chemistry and the physical properties of bitumen. *Road Materials and Pavement Design*, 19, 1636-1650.

Bitumen	$T_r$ (min)	$\omega_{1/2}$ (min)	$\frac{\omega_{1/2}}{T_r}$	$P_{300}$ (‰)	$TPH$ (mg/g)
A	9.19	2.13	0.232	18.5	126.0
B	8.96	1.64	0.183	5.2	12.0
C	8.96	1.64	0.183	4.8	12.0
E	9.07	1.66	0.184	4.6	17.1
F	9.02	1.72	0.190	0.2	15.2
G	9.05	2.28	0.252	29.7	119.8
I	9.00	1.72	0.191	3.3	16.0
J	9.12	2.14	0.234	30.3	135.0
K	9.19	2.14	0.233	21.6	111.2
L	8.98	1.72	0.191	2.1	13.8
M	8.99	1.70	0.190	0.6	12.6
P	8.97	1.64	0.182	3.2	15.0
Q	9.04	1.71	0.189	2.1	19.4

**Table 1.** Parameters values used to describe bitumens:

$\frac{\omega_{1/2}}{T_r}$  calculated with GPC-UV of bitumen.  $P_{300}$  (TGA

measurements in ‰) and  $TPH$  (Total Petroleum

Hydrocarbons in mg/g of bitumen).

## FIGURES

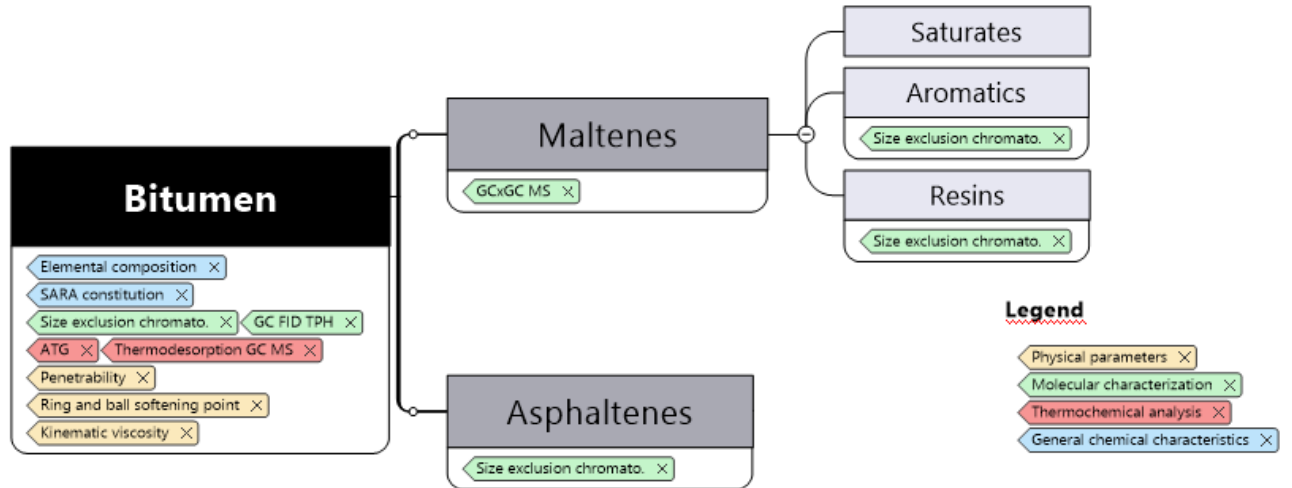


Figure 1. Mind map of the global experimental strategy of the study.

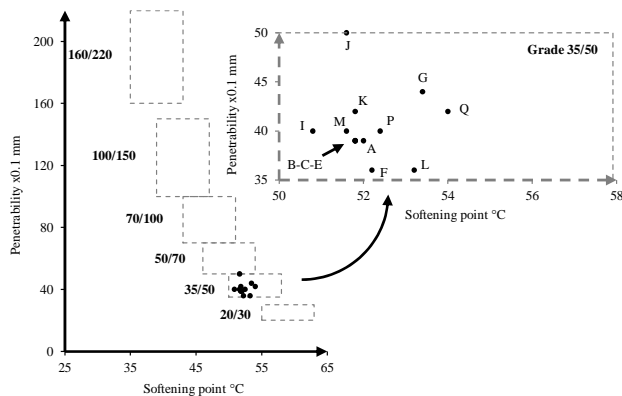


Figure 2. Comparison between the physical measurements (circles) and the grade specifications of road bitumen according to European standard EN 12591 (dashed rectangles). A single measurement is displayed but reproducibility was checked by the laboratory.



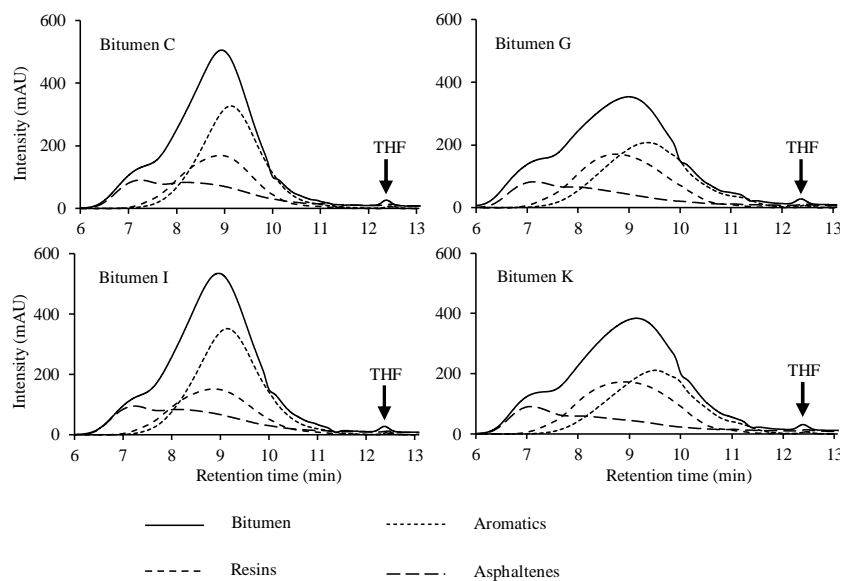


Figure 3. GPC-UV chromatograms of C, G, I, K bitumens, aromatic, resin and asphaltene fractions. Signal intensity of every fraction is represented proportionally to the SARA composition in bitumen, saturates excluded.

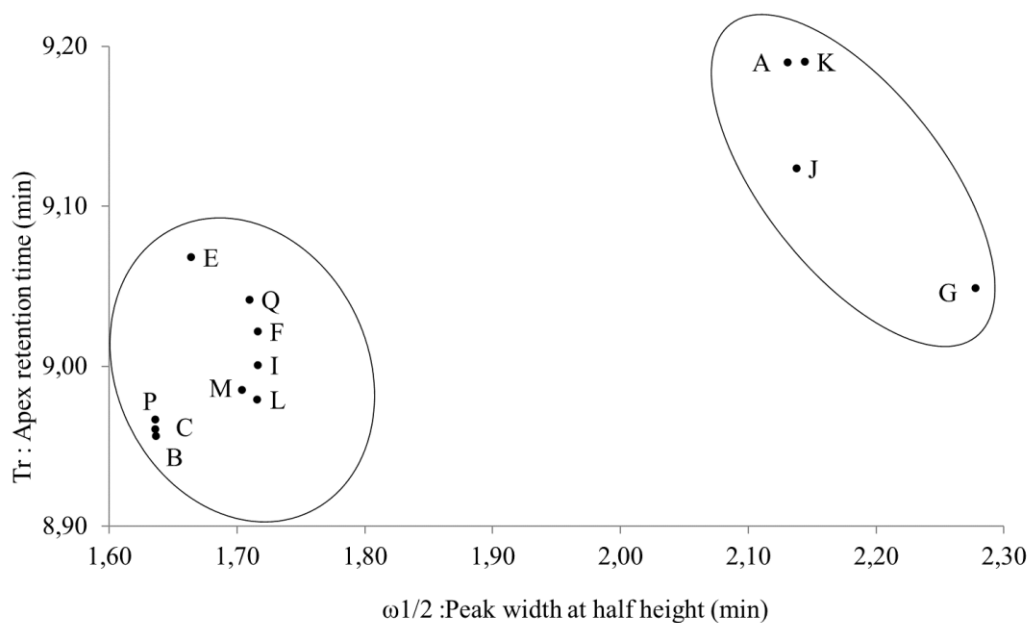


Figure 4. Correlation between the apex retention time  $T_r$  (min) and the peak width at half height  $\omega_{1/2}$  (min). These parameters were calculated for each bitumen from its GPC-UV chromatogram.

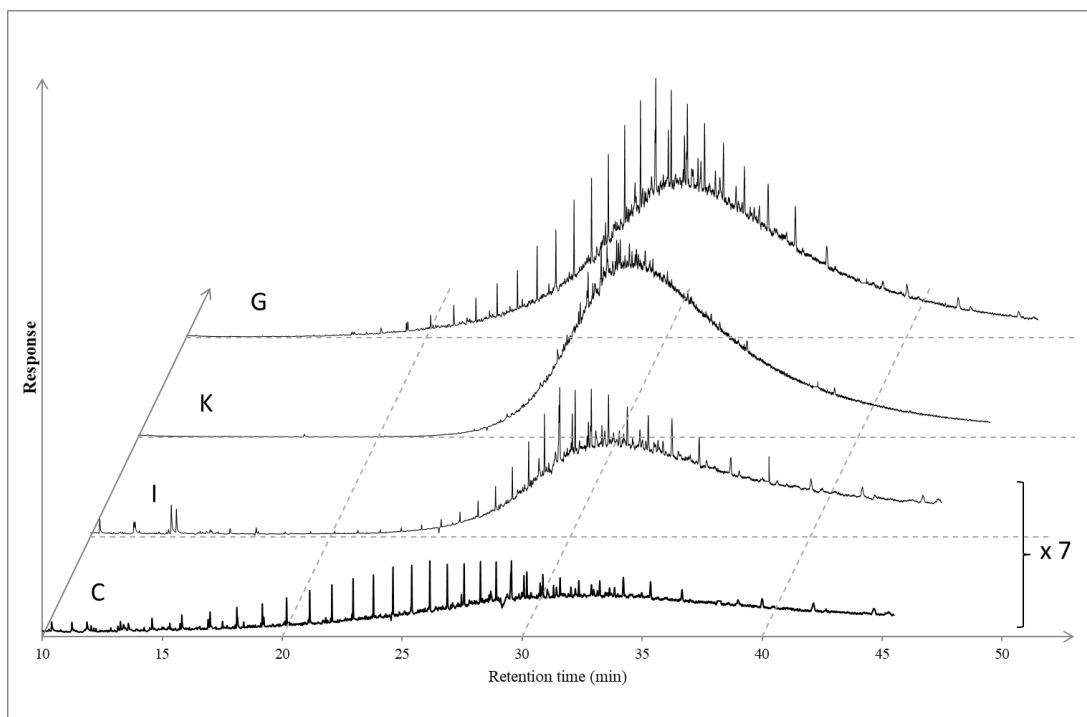


Figure 5. GC-FID chromatograms of C, G, I and K bitumens. Samples were injected at same concentration and chromatograms are displayed using the same scale Determination of the Total Petroleum Hydrocarbons (TPH) in mg/g of bitumen.

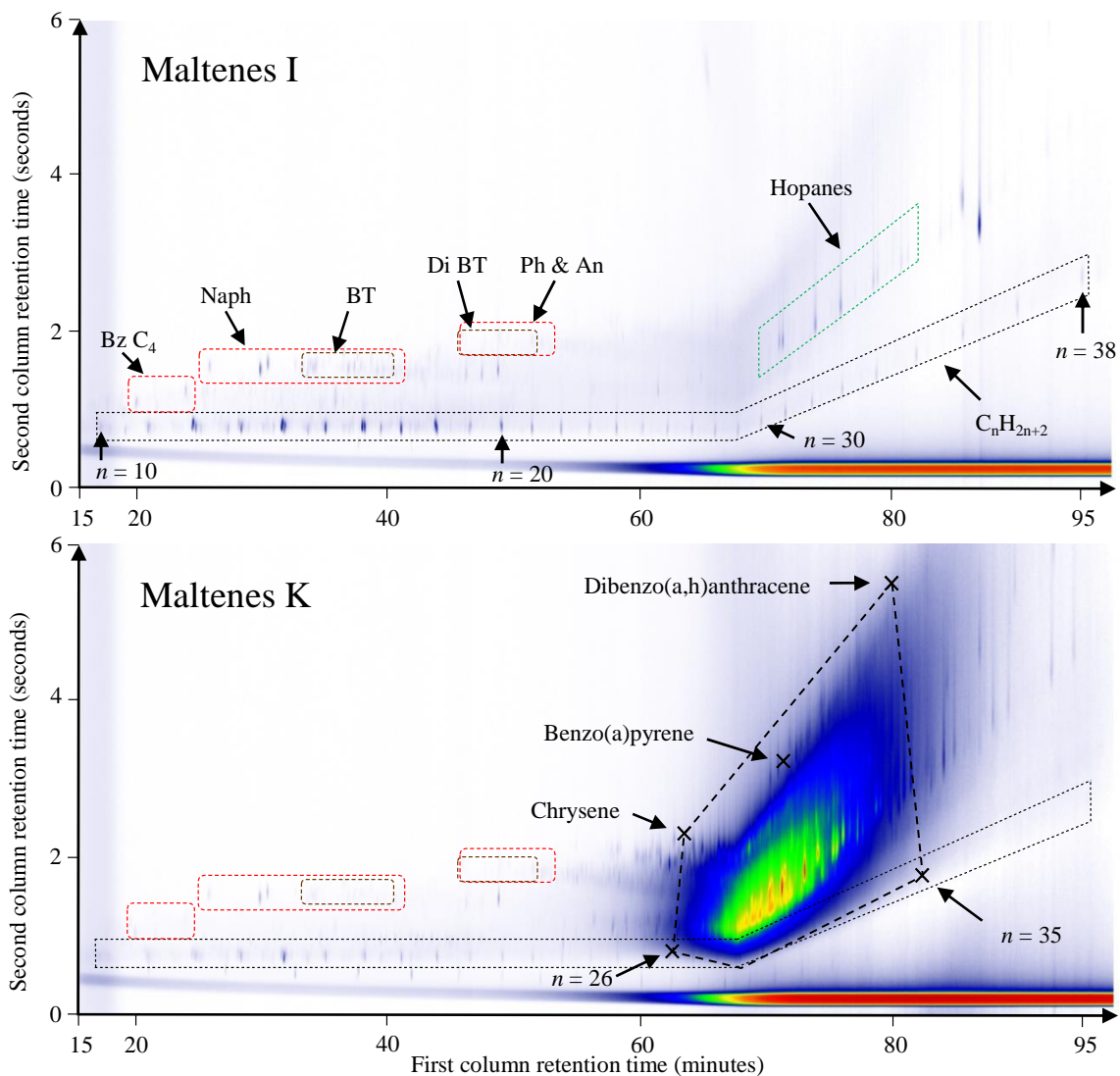


Figure 6. Maltene chromatogram of I (top) and K (bottom) bitumens with GCxGC/TOF-MS on apolar-polar columns set. BT: C<sub>2</sub>/C<sub>3</sub>/C<sub>4</sub> alkybenzothiophenes; Bz C<sub>4</sub>: tetramethylbenzenes; Di BT: dibenzothiophene and C<sub>2</sub>/C<sub>3</sub> alkyl-substituted; Naph: naphthalene and C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub> alkyl-substituted; Ph&An: Phenanthrene, anthracene and C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub> alkyl-substituted.

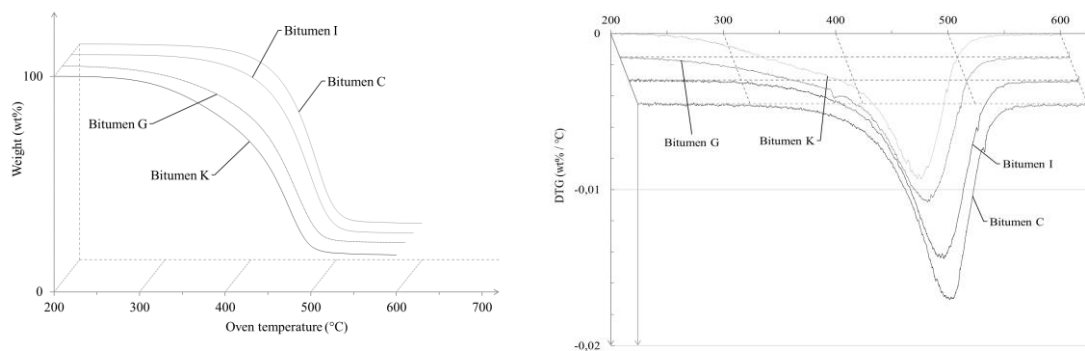


Figure 7. Thermograms (left) and derivatives (right) of C, G, I and K bitumens. The dashed lines separate the three zones of interest common to all our thermal analyses.

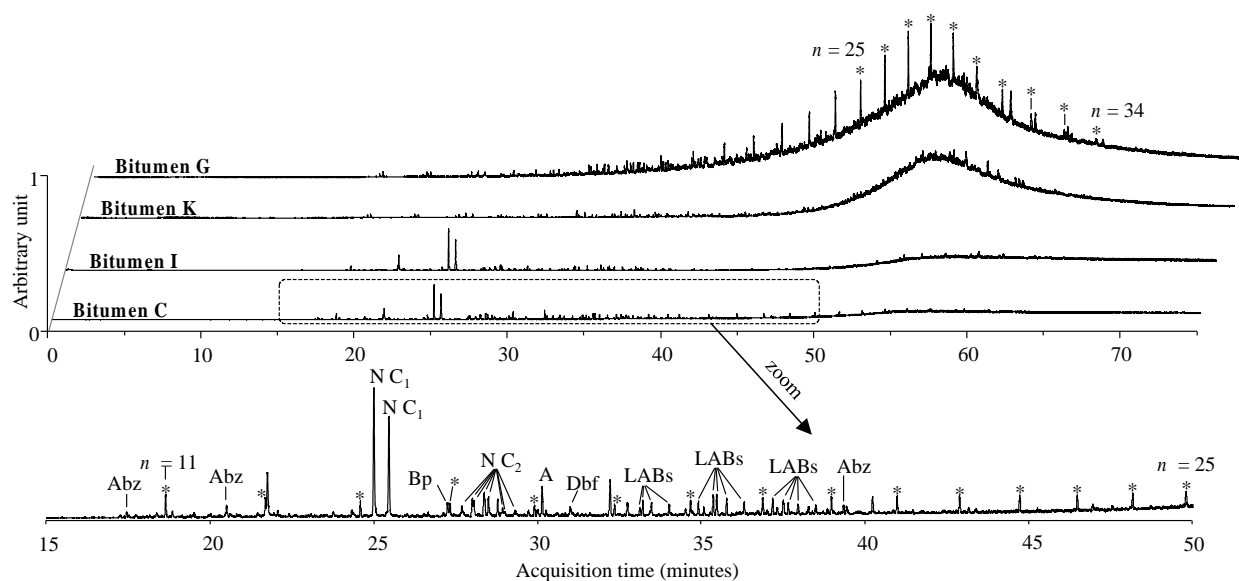


Figure 8. GC-MS chromatograms of C, G, I and K bitumens following the thermodesorption temperatures program 80 – 300 °C. \*: *n*-alkanes; A: Acenaphthene; Abz: Alkylbenzenes; Bp: Biphenyl; Dbf: Dibenzofuran; LABs: Linear alkylbenzenes; N C<sub>i</sub>: Naphtalene and C<sub>1</sub>/C<sub>2</sub> alkyl-substituted.

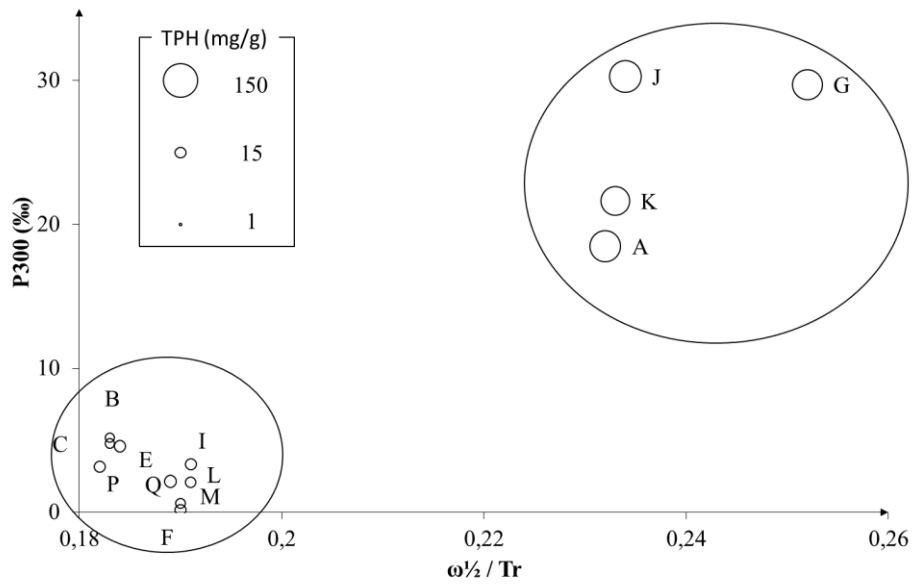


Figure 9. Representation of the three parameters used to describe bitumens:  $\frac{\omega_{1/2}}{Tr}$  (calculated with GPC-UV), P<sub>300</sub> (weight loss in ‰ due to volatilization at 300 °C) and TPH (Total Petroleum Hydrocarbons in mg/g of bitumen).

## FIGURE CAPTIONS

Figure 1. Mind map of the global experimental strategy of the study.

Figure 2. Comparison between the physical measurements (circles) and the grade specifications of road bitumen according to European standard EN 12591 (dashed rectangles). A single measurement is displayed but reproducibility was checked by the laboratory.

Figure 3. GPC-UV-UV chromatograms of C, G, I, K bitumens, aromatic, resin and asphaltene fractions. Signal intensity of every fraction is represented proportionally to the SARA composition in bitumen, saturates excluded.

Figure 4. Correlation between the apex retention time  $T_r$  (min) and the peak width at half height  $\omega_{1/2}$  (min). These parameters were calculated for each bitumen from its aromatic GPC-UV chromatogram.

Figure 5. GC-FID chromatograms of C, G, I and K bitumens. They are displayed at the same concentration. Determination of the Total Petroleum Hydrocarbons (TPH) in mg/g of bitumen.

Figure 6. Maltene chromatogram of I (top) and K (bottom) bitumens with GCxGC/TOF-MS on apolar-polar columns set. BT: C<sub>2</sub>/C<sub>3</sub>/C<sub>4</sub> alkylbenzothiophenes; Bz C<sub>4</sub>: tetramethylbenzenes; Di BT: dibenzothiophene and C<sub>2</sub>/C<sub>3</sub> alkyl-substituted; Naph: naphthalene and C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub> alkyl-substituted; Ph&An: Phenanthrene, anthracene and C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub> alkyl-substituted.

Figure 7. Thermograms (left) and derivatives (right) of C, G, I and K bitumens. The dashed lines separate the three zones of interest common to all our thermal analyses.

Figure 8. GC-MS chromatograms of C, G, I and K bitumens following the thermodesorption temperatures program 80 – 300 °C. \*: *n*-alkanes; A: Acenaphthene; Abz: Alkylbenzenes; Bp: Biphenyl; Dbf: Dibenzofuran; LABs: Linear alkylbenzenes; N C<sub>1</sub>: Naphthalene and C<sub>1</sub>/C<sub>2</sub> alkyl-substituted.

Figure 9. Representation of the three parameters used to describe bitumens:  $\frac{\omega^{1/2}}{Tr}$

(calculated with GPC-UV),  $P_{300}$  (weight loss in ‰ due to volatilization at 300 °C) and TPH (Total Petroleum Hydrocarbons in mg/g of bitumen).

# Relationship between chemical composition and VOCs emission potential of similar paving grade road bitumens

## Supplementary material

Marie-Astrid Dutoit <sup>a-b-c</sup>, Pierre Faure <sup>b</sup>, Catherine Lorgeoux <sup>c</sup>, Eddy Langlois <sup>a\*</sup>,  
Raymond Michels <sup>c</sup>

<sup>a</sup> *Pollutants Metrology Division, Institut National de Recherche et Sécurité (INRS), 1 rue du Morvan, Vandœuvre-lès-Nancy 54519, France*

<sup>b</sup> *Université de Lorraine, Laboratoire Interdisciplinaire des Environnements Continentaux (LIEC), UMR7360, Vandœuvre-lès-Nancy 54506, France*

<sup>c</sup> *Université de Lorraine, CNRS, GeoRessources, UMR7359, Vandœuvre-lès-Nancy 54506, France*

\* [eddy.langlois@inrs.fr](mailto:eddy.langlois@inrs.fr) corresponding author

Bitumen	Elemental analysis %wt					SARA fractionation %wt				
	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	Saturates	Aromatics	Resins	Asphaltenes	Colloidal index
A	83.6	10.3	0.6	1.5	3.5	20.8	30.9	26.6	21.7	0.74
B	83.9	10.1	0.3	0.8	4.7	20.1	34.2	24.7	21.1	0.70
C	82.8	10.5	0.5	1.0	4.8	21.8	32.3	25.7	20.1	0.72
E	83.9	10.7	0.6	1.0	3.9	18.0	33.3	27.0	21.8	0.66
F	83.2	11.1	0.6	0.8	4.6	20.1	36.1	25.6	18.2	0.62
G	82.2	10.8	0.7	1.2	6.1	12.5	34.9	30.2	22.5	0.54
I	82.7	10.9	0.5	0.7	5.6	17.3	39.5	23.8	19.4	0.58
J	82.3	10.8	0.6	1.0	5.7	15.5	31.5	29.0	24.1	0.65
K	84.4	10.9	0.6	1.0	3.5	22.5	29.9	29.2	18.5	0.69
L	83.7	10.4	0.5	0.8	4.6	20.8	26.7	33.3	19.2	0.67
M	84.2	10.2	0.4	0.7	4.6	15.8	39.8	28.6	15.8	0.46
P	Not determined					15.6	38.8	30.1	15.5	0.45
Q	Not determined					19.0	38.4	26.7	15.9	0.54
<b>Mean</b>	83.4	10.6	0.6	0.9	4.7	18.4	34.3	27.7	19.5	0.45 < I <sub>c</sub> < 0.74
<b>SD</b>	0.8	0.3	0.1	0.2	0.9	3.0	4.1	2.6	2.7	

**Table S1.** Elemental analysis and SARA fractionation of A, B, C, E, F, G, I, J, K, L, M, P and Q bitumens.



Bitumen	Asphaltenes	Maltenes	Losses
A#1	22,83	77,17	-0,38
A#2	20,92	76,81	2,28
A#3	21,95	78,05	-0,62
A#4	20,94	79,06	-1,07
A#5	22,18	77,82	-3,43
<b>Mean</b>	<b>21,8</b>	<b>77,8</b>	<b>-0,6</b>
<b>St. deviation</b>	<b>0,8</b>	<b>0,9</b>	<b>2,0</b>
<b>Coef.of variation</b>	<b>3,80%</b>	<b>1,12%</b>	

**Table S2.** Replicates of asphaltene precipitation for bitumen A.

Bitumen	Saturates	Aromatics	Resins
A#1a	29,3	36,8	33,9
A#1b	29,0	39,0	31,4
A#1c	28,7	38,9	32,3
A#1d	30,5	36,3	32,5
A#2	25,9	39,9	34,5
A#3	26,4	37,5	34,9
A#4	26,8	41,8	31,6
A#5	29,0	40,3	31,0
<b>Mean</b>	<b>28,2</b>	<b>38,8</b>	<b>32,8</b>
<b>St.deviation</b>	<b>1,63</b>	<b>1,85</b>	<b>1,48</b>
<b>Coef. of variation</b>	<b>5,8%</b>	<b>4,8%</b>	<b>4,5%</b>

**Table S3.** Replicates of SAR fractionation for bitumen A.

Bitumen name	Bitumen group	Penetrability 25°C	Ring and ball softening	Kinematic viscosity at 135°C
A	1	39	52	551
B	2	39	51,8	639
C	2	39	51,8	538
E	2	39	51,8	481
F	2	36	52,2	520
G	1	44	53,4	783
I	2	40	50,8	526
J	1	50	51,6	644
K	1	42	51,8	604
L	2	36	53,2	595
M	2	40	51,6	559
P	2	40	52,4	539
Q	2	42	54	495
Group 1 mean		43,75	52,2	645,5
Gr1 confidence interval		[36,3575; 51,1425]	[50,9008; 53,4992]	[487,546; 803,454]
Group 2 mean		39	52,1778	543,556
Gr2 confidence interval		[37,5115; 40,4885]	[51,4549; 52,9007]	[505,918; 581,193]
conf.int. between means		[0,8682; 8,6318]	[-1,1791; 1,2236]	[13,9023; 189,987]
t Value		2,69327	0,0407124	2,54854
P Value		0,020907	0,968255	0,0270656
difference		Slightly	No	Slightly

**Table S4.** Student test for the influence of the two groups on the bitumen physical parameters.

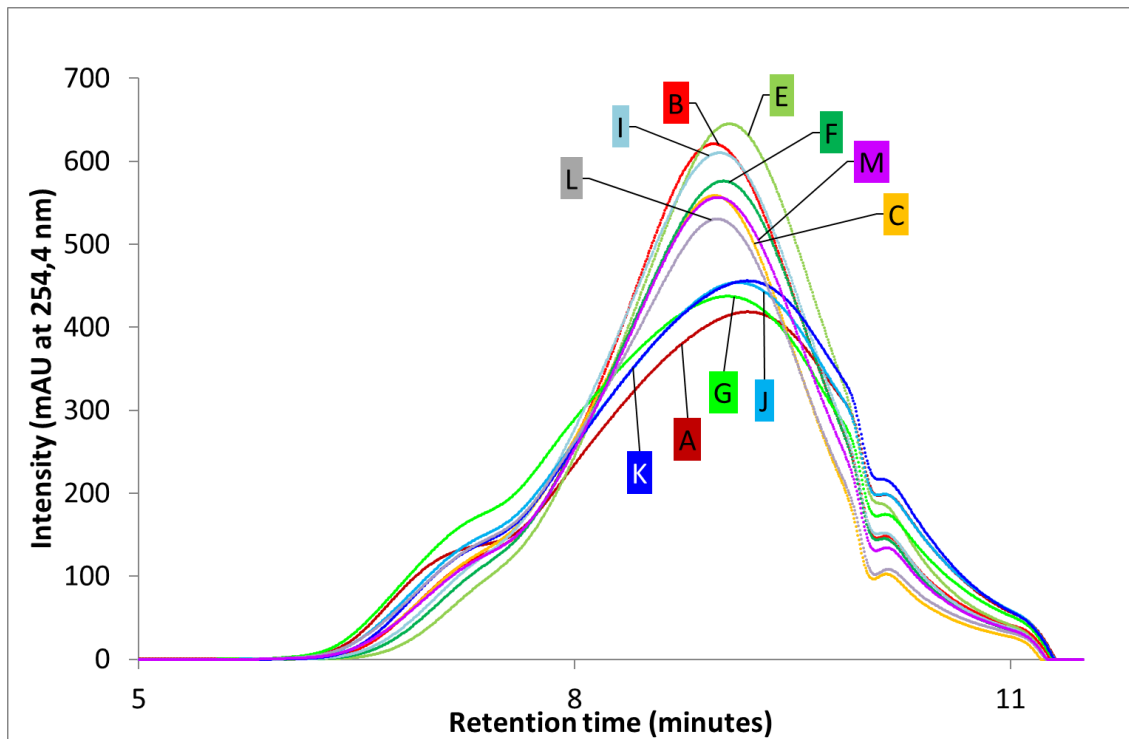
Bitumen name	Bitumen group	Saturates (m/m%)	Aromatics (m/m%)	Resins (m/m%)	Asphaltenes (m/m%)	Colloidal index
A	1	20,8	30,9	26,6	21,7	0,74
B	2	20,1	34,2	24,7	21,1	0,7
C	2	21,8	32,3	25,7	20,1	0,72
E	2	18	33,3	27	21,8	0,66
F	2	20,1	36,1	25,6	18,2	0,62
G	1	12,5	34,9	30,2	22,5	0,54
I	2	17,3	39,5	23,8	19,4	0,58
J	1	15,5	31,5	29	24,1	0,65
K	1	22,5	29,9	29,2	18,5	0,69
L	2	20,8	26,7	33,3	19,2	0,67
M	2	15,8	39,8	28,6	15,8	0,46
P	2	15,6	38,8	30,1	15,5	0,45
Q	2	19	38,4	26,7	15,9	0,54
Group 1 mean		17,825	31,8	28,75	21,7	0,655
Gr1 confidence interval		[10,4487; 25,2013]	[28,3479; 35,2521]	[26,3211; 31,1789]	[17,9524; 25,4476]	[0,5197; 0,7903]
Group 2 mean		18,7222	35,4556	27,2778	18,5556	0,6
Gr2 confidence interval		[17,0361; 20,4084]	[32,1456; 38,7656]	[24,997; 29,5586]	[16,7402; 20,3709]	[0,5234; 0,676578]
conf.int. between means		[-4,9437; 3,1493]	[-8,7385; 1,4274]	[-2,0368; 4,9812]	[0,02312; 6,2658]	[-0,0718; 0,1818]
t Value		-0,488017	-1,5829	0,923437	2,21729	0,954691
P Value		0,63512	0,141751	0,375592	0,048595	0,360244
difference		No	No	No	Slightly	No

**Table S5.** Student test for the influence of the two groups on the SARA fractionation and the colloidal index

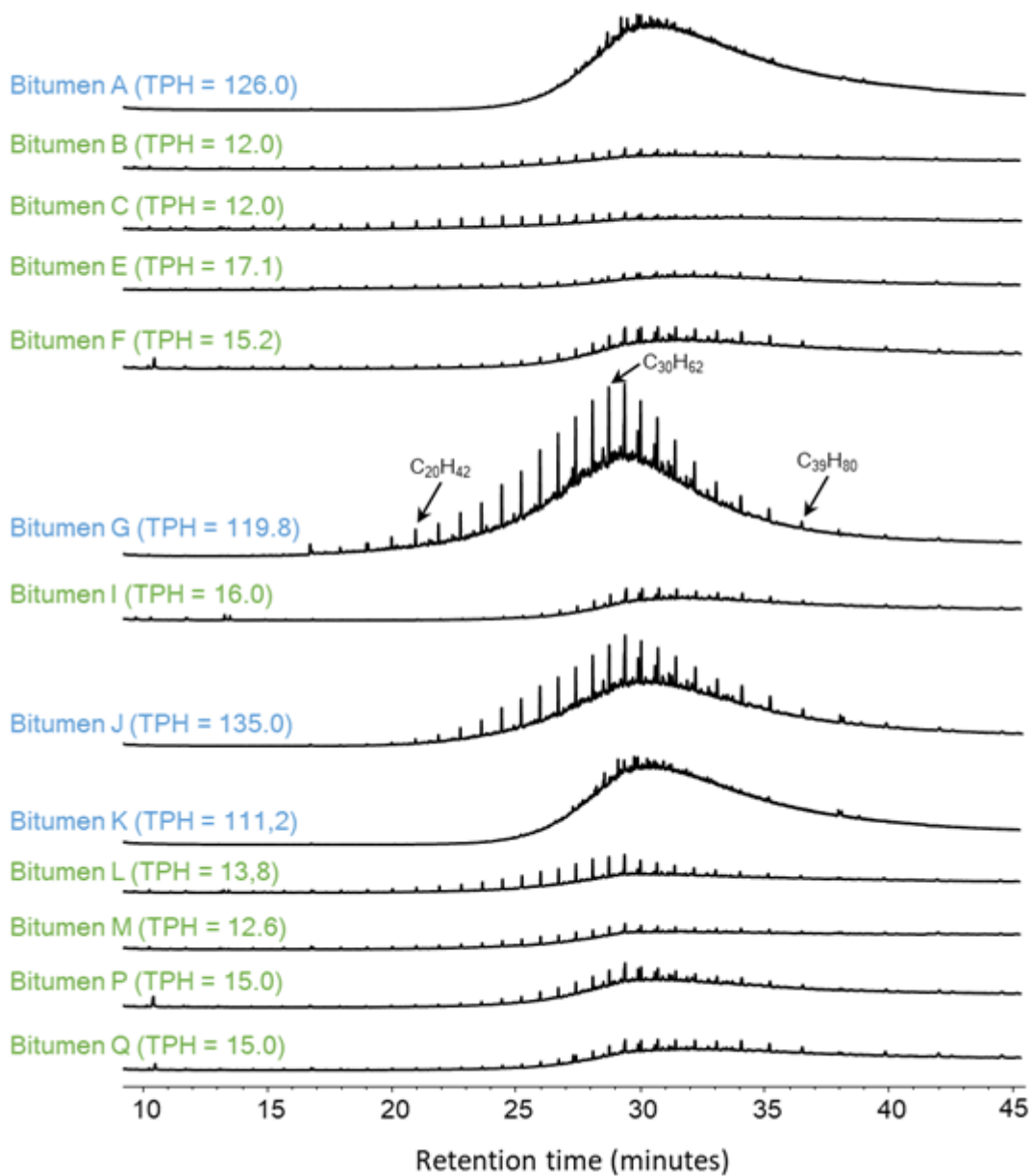
Bitumen name	Bitumen group	Tr Apex retention time (min)	w Peak width at half height	Tr/w (min)	P300 (‰)	TPH (mg/g)
A	1	9,19	2,13	0,232	18,5	126
B	2	8,96	1,64	0,183	5,2	12
C	2	8,96	1,64	0,183	4,8	12
E	2	9,07	1,66	0,184	4,6	17,1
F	2	9,02	1,72	0,19	0,2	15,2
G	1	9,05	2,28	0,252	29,7	119,8
I	2	9	1,72	0,191	3,3	16
J	1	9,12	2,14	0,234	30,3	135
K	1	9,19	2,14	0,233	21,6	111,2
L	2	8,98	1,72	0,191	2,1	13,8
M	2	8,99	1,7	0,19	0,6	12,6
P	2	8,97	1,64	0,182	3,2	15
Q	2	9,04	1,71	0,189	2,1	19,4
Group 1 mean		9,1375	2,1725	0,23775	25,025	123
Gr1 confidence interval		[9,0309; 9,2441]	[2,0582; 2,2868]	[0,2226; 0,2529]	[15,6567; 34,3933]	[107,022; 138,978]
Group 2 mean		8,99889	1,68333	0,187	2,9	14,7889
Gr2 confidence interval		[8,9698; 9,0280]	[1,6546; 1,7121]	[0,1840; 0,1900]	[1,5169; 4,2831]	[12,8747; 16,703]
conf.int. between means		[0,0756; 0,2016]	[0,4240; 0,5543]	[0,0428; 0,0587]	[17,5801; 26,6699]	[100,728; 115,694]
t Value		4,84192	16,5303	14,1336	10,7146	31,8289

P Value	0,0005174	4,08E-09	2,13E-08	3,69E-07	3,50E-12
difference	Strongly	Strongly	Strongly	Strongly	Strongly

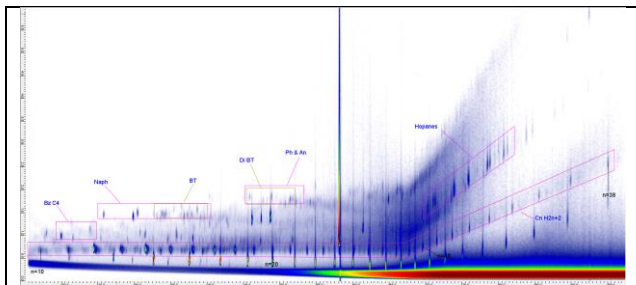
**Table S6.** Student test for the influence of the two groups on the bitumen GPC shape and thermochemical parameters.



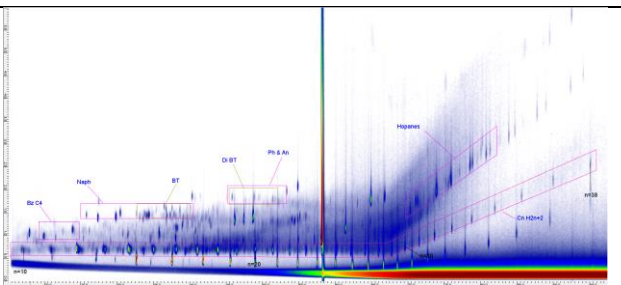
**Figure S1.** GPC UV chromatograms of A, B, C, E, F, G, I, J, K, L and M bitumens.



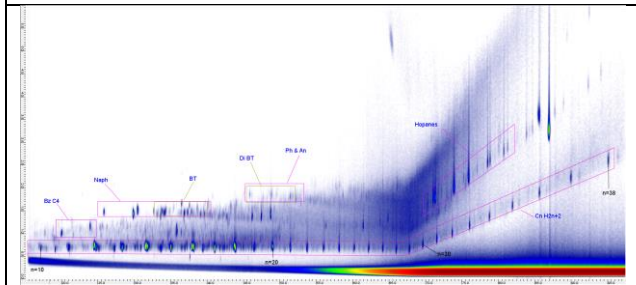
**Figure S2.** GC-FID chromatograms of A, B, C, E, F, G, I, J, K, L, M, P and Q bitumens. Samples were injected at the same concentration and chromatograms are displayed using the same scale. TPH: Total Petroleum Hydrocarbons in mg/g of bitumen.



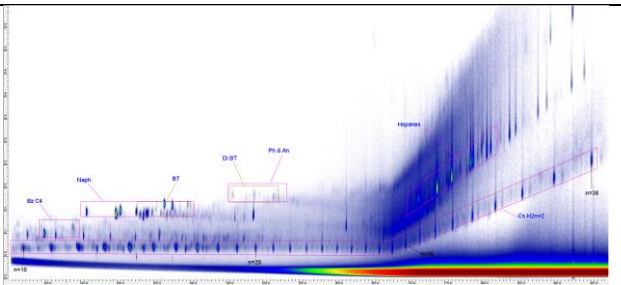
Maltene B



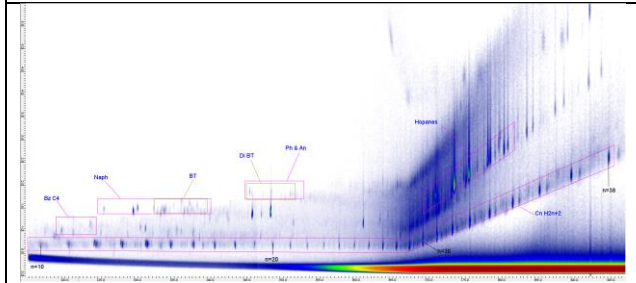
Maltene C



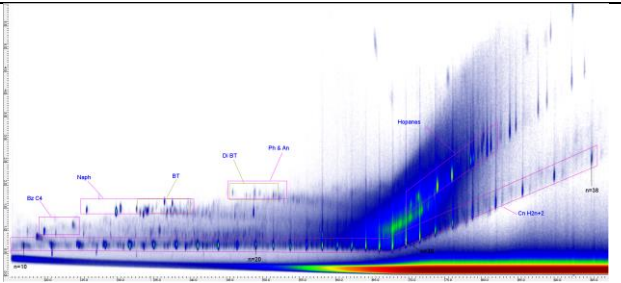
Maltene E



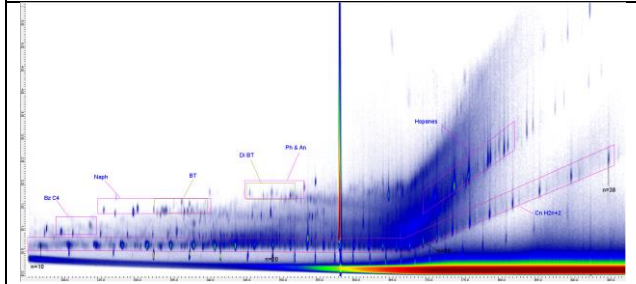
Maltene F



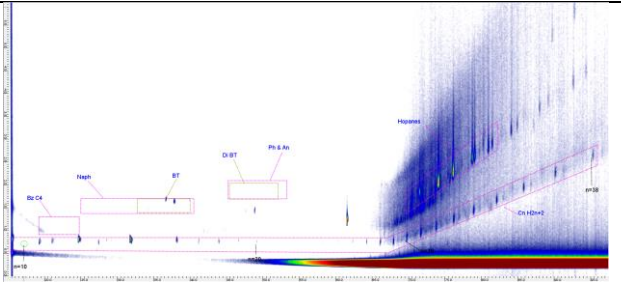
Maltene I



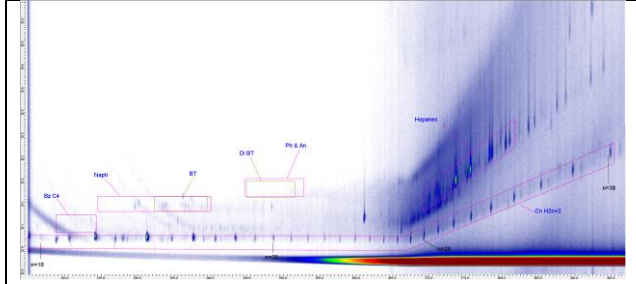
Maltene L



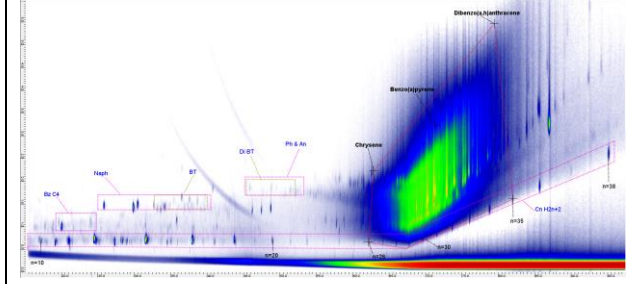
Maltene M



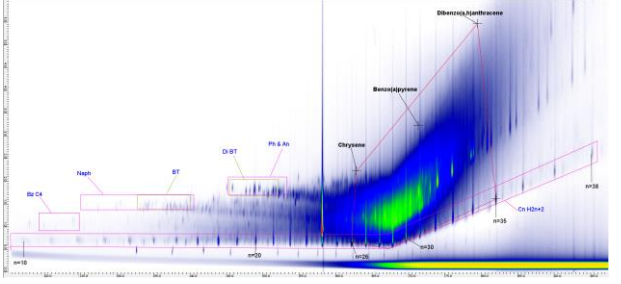
Maltene P



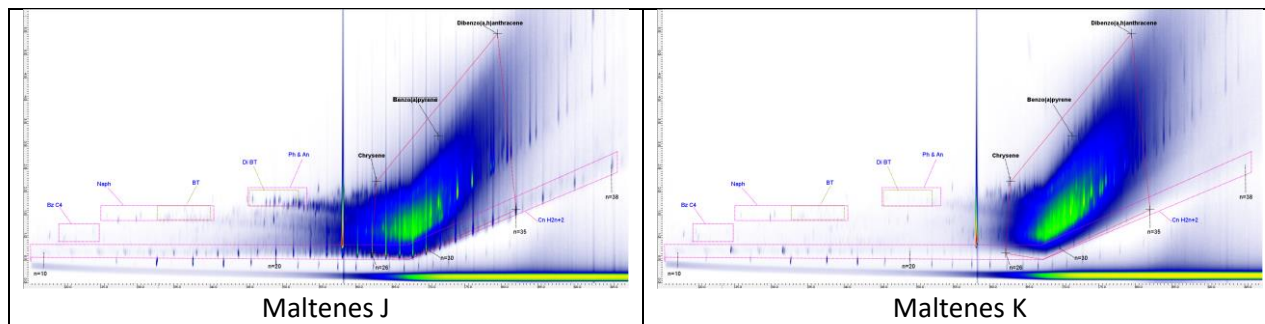
Maltene Q



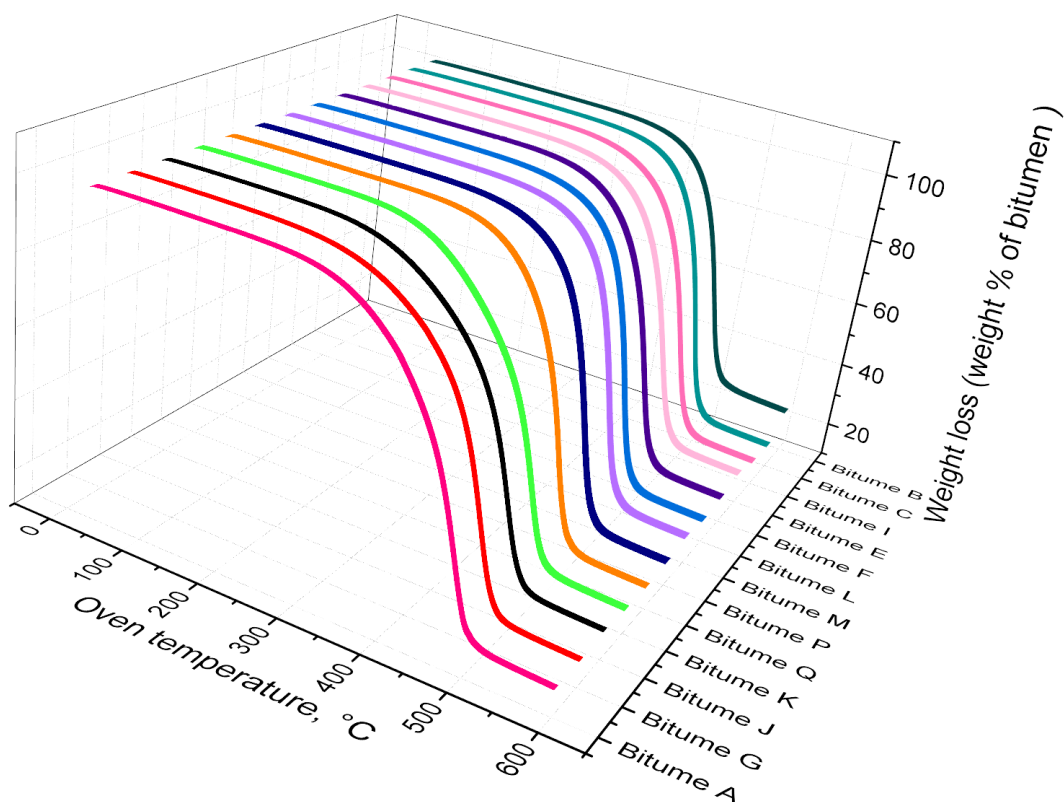
Maltene A



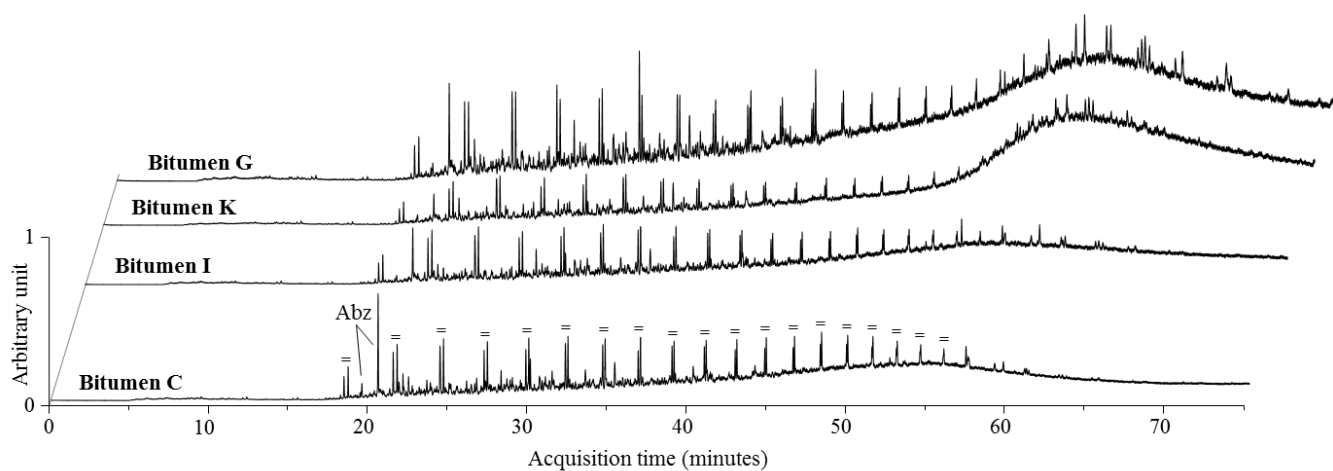
Maltene G



**Figure S3.** Maltenes chromatogram of A, B, C, E, F, G, I, J, K, L and M bitumens with GCxGC/TOF-MS on apolar-polar columns set. BT: C<sub>2</sub>/C<sub>3</sub>/C<sub>4</sub> alkylbenzothiophenes; Bz C<sub>4</sub>: tetramethylbenzenes; Di BT: dibenzothiophene and C<sub>2</sub>/C<sub>3</sub> alkyl-substituted; Naph: naphthalene and C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub> alkyl-substituted; Ph&An: Phenanthrene, anthracene and C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub> alkyl-substituted.

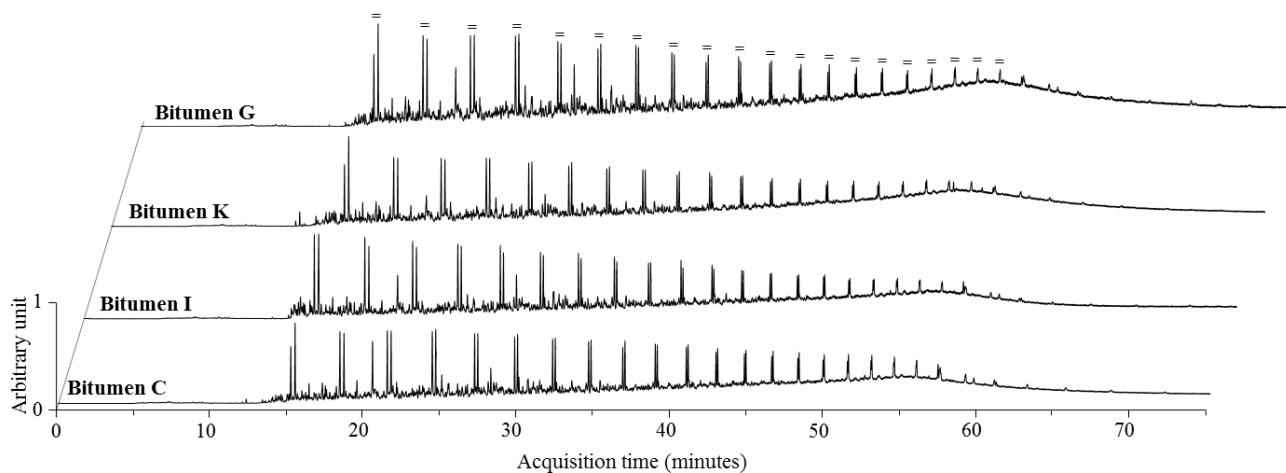


**Figure S4.** Thermograms of A, B, C, E, F, G, I, J, K, L, M P and Q bitumens.



**Figure S5.** GC-MS chromatograms of C, G, I and K bitumens following the thermodesorption temperatures program 300 – 450 °C.

= : *n*-alk-1-enes/*n*-alkanes doublet; Abz: alkylbenzenes.



**Figure S6.** GC-MS chromatograms of C, G, I and K bitumens following the thermodesorption temperatures program 450 – 600 °C.

= : *n*-alk-1-enes/*n*-alkanes doublet.

