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# **Polycyclic Aromatic Hydrocarbons emitted from a hot-mix drum, asphalt plant: Study of the influence from use of recycled bitumen**

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**Abstract :** Asphalt mixing is an industrial activity of which energy consumption can reach 60% of the total energy consumed by the construction and maintenance of a road over a 30-year service life. Hot mix asphalt plant represents the most common process found in the road sector. Hot bitumen fumes however contain Polycyclic Aromatic Compounds (PAH), and, moreover, the use of recycled bitumen can lead to generating various emissions. PAH may also be emitted from the process itself, a step that requires warming and drying aggregate through combustion. In the aim of minimizing emissions, it has become necessary to identify the set of major influential parameters. A joint research program involving several institutions has been laid out to conduct an experimental campaign on the Blois Hot Mix Asphalt plant, with quantification of the 16 PAH listed by the US-EPA. Variations in asphalt recycling rate favour emissions of heavy molecular weight PAH, among those analysed.

*Key words*

Reclaimed Asphalt Pavement, airborne emissions, process study.

**Résumé :** La production d'enrobé bitumineux peut contribuer à 60% de la consommation d'énergie totale de la construction et de l'entretien d'une route pendant 30 ans. Le mélange à chaud est le procédé le plus courant. Cependant, les fumées du bitume chauffé contiennent des HAP, et l'utilisation de bitume recyclé est susceptible de modifier les émissions. Les HAP peuvent également être émis par le procédé lui-même qui requiert une combustion afin de sécher et chauffer les granulats. Dans une perspective de minimisation des émissions, il devient nécessaire d'identifier les paramètres les plus influents. Une collaboration a été montée entre plusieurs instituts, pour mener une campagne de mesures sur le site de la centrale d'enrobage à chaud de Blois, et les 16 HAP de la liste EPA ont été quantifiés. Des variations à la fois de la teneur en eau des granulats et du taux de recyclage d'enrobé, favorise l'émission des HAP à plus forte masse moléculaire, parmi ceux analysés.

### *Mots Clés*

Recyclage d'enrobé bitumineux, émissions atmosphériques, étude procédé.

# 1 INTRODUCTION

The energy consumed during asphalt can reach 60% of the total energy required for the construction and the maintenance of a road over a 30-year service life (Hoang et al. 2005).

Among the various asphalt production processes, hot mix is the most common and consists of warming and drying aggregate before mixing it with hot bitumen.

Hot bitumen (Landa and Wit 1996) and the fumes it releases (Kitto et al. 1997, Bonnet et al. 2000, Burstyn et al. 2001) however contain Polycyclic Aromatic Compounds (PAH), which have been gaining increasing attention due to their toxicity (Burstyn et al. 2000), (Blomberg et al. 1999) and (Brandt et al. 2000). Even though a sizable body of literature is available on PAH emitted by bitumen alone, only two studies can be found that focus on the PAH emissions generated during asphalt mix processes. One report on asphalt plants emissions examines PAH emissions factors (US-EPA 2004), while another article has been published on PAH emissions from a hot mix asphalt plant (Lee et al. 2004). The context of this targeted process is a batch mix plant, with PAH collected from various point sources and measures sought for the removal efficiency of installed air pollution control devices. Both of these previous studies have proven valuable in providing general emission factors, in association with plant production rates, in order to achieve regulatory compliance. Yet, neither study allows distinguishing the influences of process operations materials used. From the standpoint of the industrial decision-maker however, minimizing emissions is initially expressed by means of choosing the appropriate materials and controlling the process. The distinction between PAH issued from combustion reaction and from bitumen is hence one of the big issue of the study of asphalt mix processes. It thus becomes necessary to better understand the major influential parameters; in particular, asphalt-mixing industries

commonly recycle asphalt waste stemming from road demolition. In France, this practice has been promoted by the July 1992 waste management law. This type of material influences PAH emissions, in a way that remains unknown. Furthermore, the quantity of PAH emitted due to bitumen alone, in comparison with process operations, is also unknown. The hot mix drum process requires heat (to both warm and dry aggregate) to be produced by fuel combustion, even though many studies (not all of which have been referenced herein) show that PAH are emitted by any pyrolysis or incomplete combustion process, i.e. (D'Anna and Kent 2003) for methane combustion.

To better understand the correlation between PAH emissions, recycled bitumen, and process operations, a joint research project was undertaken between the SETRA Highway Engineering Agency, the Loir et Cher Departmental Public Works Office (DDE 41), the SEMR Road Materials Design Center and the Ponts et Chaussées laboratory (LCPC) to collect data on PAH emissions and several other environmental attributes (Ventura et al. 2005; Nouvion et al. 2005). In this aim, an experimental campaign was conducted at an industrial site in the French city of Blois: the hot-mix drum asphalt plant run by DDE 41. This plant is fuelled by a natural gas containing methane as the prime component.

As an initial approach, and with the objective of strengthening the correlation of results with potential environmental impacts, the PAH selected for analysis were restricted to the 16 suspected or known carcinogens listed by US-EPA. In the absence of any precise regulation, the total mass of these 16 molecules yields a commonly-used PAH toxicity indicator. Among these PAH, benzo[a]pyrene gets frequently employed as a toxicity indicator by virtue of a European directive concerning indoor air quality (2004/107/CE 2004).

It should be remarked that, for such an experiment, the number of fixed parameters is high, with some of these parameters being measurable but yet not controllable, e.g. meteorology, aggregate water content. Such an observation has two main consequences. First, in order to

maintain good comparability between the studied protocols, the smallest possible time interval needs to be ensured when performing experiments. Second, none of the experiment can be strictly repeated.

Moreover, since the experimental campaign was being held on an industrial site, measurements had to satisfy manufacturer's logistical constraints and imperatives. In particular, the asphalt was produced for a customer and not for the needs of this experimental set-up, meaning that the quantity produced exactly matched the quantity sold; in addition, just 4 different protocols using the controlled materials and operating conditions could be accommodated within the given timetable.

The goal of this paper is to determine whether or not the use of recycled asphalt aggregate influences PAH emissions, as regards actual process operations.

## **2 MATERIALS AND METHODS**

### **2.1 Some Definitions**

Let's begin by recalling a number of basic definitions in the field of road engineering.

*Aggregate* : an assembly of differently-dimensioned grains, spanning the range 0 - 125 mm.

*Asphalt* : a mix of aggregate and sand (and filler included as an option), with a bitumen binder.

*Asphalt aggregate or Reclaimed Asphalt Pavement (RAP)* : granular material coming from the milling or demolition of asphalt and recycled in a new asphalt composition.

*Asphalt formulation* : description of a mix design, including the mass composition and origin of components, a size distribution curve of aggregate, and results obtained from the formulation test conducted on a representative sample according to the Standard NF P 98-149.

*Binder content* : bitumen mass as a ratio of dried aggregate mass, expressed in percentage terms (NF P 98-149 standard).

*Grading span  $d/D$*  : interval characterizing the smallest ( $d$ ) and the largest ( $D$ ) diameter in mm, of an aggregate fraction.

*Recycling rate* : proportion of recycled aggregate mass within the produced asphalt sample.

*Total water content* : mass of water contained in the aggregate as a ratio of dry aggregate mass, expressed in percentage terms.

## **2.2 Choice of experimental conditions**

The experimental campaigns were performed on an industrial site. Measurement conditions therefore had to conform to production priorities. The various protocols tested were chosen in order to minimize disturbances; the ultimate selection is presented in table 1. To compare the influence of using older bitumen, three recycling rates were applied (0%, 10% and 20% for protocols 0, 10 and 20 respectively) for an identical asphalt formulation using a 0/10 grading range. For the purpose of evaluating the influence of material parameters in the 10w protocol (also with a 10% recycling rate), the total aggregate water content was artificially increased by wetting the sand.

## **2.3 Process description**

The hot-mix plant in the city of Blois (see Fig. 1) of a hot-mix drum (HMD) with a parallel flow; this set-up allows aggregate particles to circulate in the same direction as gas flow. The plant features a TSM17 stationary process from Ermont (the Fayat Group), and is fuelled by natural gas.



## *Technology*

Aggregate is warmed and dried by introducing aggregate particles into the upper part of the drum (Fig. 1), using the main conveyor belt. Each grading range is stored in a separate hopper, which feeds the main conveyor belt by means of secondary belts. The RAP is stored in a specific hopper and then introduced into the middle part of the drum. The bitumen is entered into the second half part of the drum.

## *Process operations*

The process is semi-automated. The various operating parameters are presented in Table 2. An automaton sets both the production rate and the corresponding flows of granular materials for each hopper, as a function of: i) the nominal asphalt formulation, ii) the potential use of recycled asphalt aggregate, and iii) the water content of granular (natural and recycled) materials. An operator is assigned to check the system to ensure a couple of parameters are held constant: i) the asphalt temperature, to track product stability, and ii) the vacuum pressure at the head of the burner to monitor the successful discharge of gas from the burner flame and water vapour from the dried aggregate.

Some variations occur during actual operations; these would mainly be due to differences in aggregate temperature and water content as well as in outdoor temperature. Such variations influence the required drying energy and total gas volume flow; for the most part, they depend on external conditions and are only minimally controllable. In order to mitigate variations, the operator can open or close two valves, which when opened wider accentuate two phenomena: the natural gas feed valve for burner consumption, and the exhaust gas valve for gas volume discharge.

## 2.4 Description of materials

The input materials are natural aggregate, bitumen and asphalt aggregate, with constituting the sole output material. Each material may be characterized by a different set of parameters, as detailed in Table 3, used by the automaton to calculate mass flows from the asphalt formulation.

The water content of granular materials (natural and asphalt aggregate) is measured at the beginning of the day, and the values get initially transmitted to the automaton. They are not tracked on a continuous basis and their variability due to storage heterogeneity remains unknown. The new bitumen is classified as a 35/50 grade; the previous bitumen in the asphalt aggregate was also characterized as a 35/50 grade from the penetrability test (Shell Bitumes 1991). The asphalt aggregate stock (see Fig. 2) for recycling is highly heterogeneous and composed of asphalt from multiple origins. Before use in the drum, stock samples are calibrated to a homogeneous size distribution. Materials masses are measured after manufacturing, and the results obtained have been displayed, along with water content, in Table 4.

## 2.5 Determination of PAH mass flows

### *Calculation of PAH mass flows*

After desorption and analysis, the sampled PAH mass flow can be expressed as a function of the sample volume inside the stack, as written in equation (1), below:

$$C_s = \frac{m_s}{V_s} \quad (1)$$

with :

- $m_s$  : mass of PAH sampled in the filter and cartridge (g)

- $C_s$  : mass concentration of PAH (g/m<sup>3</sup>), and
- $V_s$  : sampled dry volume measured at the pump (m<sup>3</sup>).

The sampled volume is indeed dry since the condensation flask has been positioned upstream of the filter and cartridge. This volume is measured at temperature and pressure different from those occurring inside the stack and thus converted in normal conditions according to equation (2):

$$C_s^0 = \frac{m_s}{V_s \cdot \frac{T^0}{T_s} \cdot \frac{P_s}{P^0}} \quad (2)$$

with :

- $C_s^0$  : mass concentration of PAH in normal conditions (g/Nm<sup>3</sup>),
- $T^0$  : normal temperature (273 K),
- $P^0$  : normal pressure (1.013 x 10<sup>5</sup> Pa),
- $T_s$  : sampling temperature (K), and
- $P_s$  : sampling pressure (Pa).

The mass flow of PAH circulating inside the stack is calculated as follows:

$$M_{stack} = C_s^0 \cdot Q_{dry}^0 \quad (3)$$

with :

- $M_{stack}$  : mass flow of PAH inside the stack (g/h), and
- $Q_{dry}^0$  : normal dry volume inside the stack (Nm<sup>3</sup>/h).

The normal dry volume flow was then obtained by measuring the gas velocity, and stack gas density. The gas density was itself derived by measuring O<sub>2</sub>, CO<sub>2</sub> concentrations plus the water vapour H<sub>2</sub>O<sub>vap</sub> inside the stack.

## *Sampling and analytical methods*

The sampling and analysing procedures of PAH were implemented by a COFRAC-certified contractor.

According to the ISO 10-780 standard, a gas velocity map was produced inside the stack prior to sampling using a double Pitot tube linked to a micro-manometer. Knowing the gas velocity allowed setting the gas sampling flow at  $1.91 \text{ m}^3/\text{hr}$ , in order to perform an isokinetic sampling of the gas effluent, in conformance with Standard EN 1948-1.

The sampling time was set at 30 minutes, which corresponds to a short period of time (EN 1948 standard recommends 4 hours). This value was imposed due to the asphalt plant constraints: the total required asphalt production on that day amounted 400 tons, with a 100 tons/hr production rate capacity. This constraint allowed just 4 hours for operations, hence 1 hour for each protocol. PAH sampling started up several minutes following the beginning of asphalt production and stopped after 30 min in order to avoid unstable processing periods occurring at the beginning and end of the process.

The PAH sampling apparatus is described in Figure 3. The probe and its nozzle are both made of titanium. The probe is cooled with water and contains a glass tube with fumes circulating inside. The probe and nozzle were purchased from Paul Gothe Bochum and the glass tube from Willers. The absorption line is composed of one fritted glass cartridge filled with quartz wool and a plan filter, and a second glass cartridge filled with XAD-2 polymer (GF-10-HY, purchased from Schleicher & Schüll). The pump is a Picolino VTE-6 purchased from Werner Rietschle GmbH. The gas counter is a BK/G4 type produced by Krom Schröder. Cooling the probe entails entrapping both particulates PAH and gaseous phase PAH within the plan filter and cartridge.

An analysis has been performed on the total PAH extracted from both filter and cartridge, resulting in a total PAH mass without distinction between particulates and gaseous phases.

Condensates were extracted using a Soxhlet process, with toluene, during 2 hours. The solution was then concentrated by means of solvent evaporation and re-diluted in a smaller volume of toluene. PAH were separated by gas chromatography, identified and quantified by mass spectrometry.

Temperature and pressure were measured inside the stack as well as in ambient air.

Concentrations of O<sub>2</sub> and CO<sub>2</sub> were measured using paramagnetic (Rosemount Oxynos 100) and infrared (Maihak) analyzers respectively, in compliance with Standards NF X 43-300, Fd 20-377 and X 43-012. The water vapour mass was weighed after condensation in a glass flask, during the sampling procedure (see Fig. 3).

### **3 RESULTS**

#### ***3.1 Control of sampling parameters and operating conditions***

The several parameters required for calculating PAH mass flows as well as for checking process stability are shown in Table 5. According to standard deviation values, almost all parameters are found to be very stable from one protocol to the next, with the exception of dynamic pressure. Since the asphalt temperature remains stable across protocols, its influence on PAH emission is not expected to differ. The stack gas temperature, which is expected to influence the gas/particle partitioning of PAH, does not vary between protocols either.

The only major variations involved concern the stack gas dynamic pressure and water vapour concentration.

- The stack gas dynamic pressure is correlated with gas velocity; its variations may be explained by working the bag fabric collector (see Fig. 1). This equipment has been intended to filter particles downstream of the drum and is requires in pumping ambient air, which means that air is being irregularly introduced inside the stack. Variations may

also be caused by changes in aggregate water content. An increase in water content induces an increase in water vapour, hence an increase in total gas volume. The gas velocity therefore also increases. Table 5 reveals that wide variations in gas velocity, despite being used to calculate the gas volume flow, do not considerably affect gas volume flow stability.

- The stack gas water vapour concentration is directly and primarily correlated with the aggregate water content: it was found to increase with recycling rate given that the asphalt aggregate displays a high water content (3.2%), which influences the total water content of the aggregate mix.

### **3.2 Parameters influencing PAH total mass flow**

The PAH total mass flow is presented in Figure 4, along with the total recycled bitumen mass and the total water content of granular materials (natural and asphalt aggregate). All three of these parameters increase with recycling rate. Between 10 and 10w protocols, with the same recycling rate and the same previous and new bitumen masses, an increase of around 14% (from 2.1 to 2.4 g/hr) of PAH total mass flow has been observed. For an identical bitumen mass and composition of both old and new bitumen, total mass flow also depends therefore on total water content.

### **3.3 Parameters influencing PAH molar composition**

Molar flows and compositions are given in Figure 5 for each studied protocols.

### *Influence of total water content: Protocols 10 and 10w*

The evolution of PAH molar flow between 10 and 10w protocols may be viewed on Figure 5. A slight increase of around 3.4% of the total molar flow can be observed, which is smaller than the increase observed in total mass flow (Fig. 4). The details of each PAH flow are given in Table 6. Molar composition differs slightly between these protocols: the naphthalene, acenaphthylene, and acenaphthene proportions decrease in the 10w protocol, while fluorene, phenanthrene, fluoranthene and pyrene proportions rise. The previously observed changes in total PAH mass (Fig. 4) are thus due to a slight change in PAH molar composition: the PAH of higher molecular mass are being emitted. **Since the water content of aggregate is the only parameter that actually varies among protocols, the slight change in molar composition could be explained by a steam distillation process. The increase in aggregate water content does cause an increase of water vapour volume inside the drum. This finding is confirmed by the humidity value measurements (see Table 5). The heavier PAH compounds contained inside bitumen, can thus be vaporised by a steam distillation process, which occurs by means of vapour water making contact with bitumen inside the drum.**

### *Influence of recycling rate : Protocols 0, 10 and 20*

As opposed to the mass flows presented above (Fig. 4), Figure 5 shows that the molar flow is nearly constant across all protocols. The total mass previously observed is therefore correlated with a change in molecular composition of the PAH mix; but not with an increase in the number of molecules emitted. Among the 16 analyzed PAH, only 8 show significant flow levels. The “other PAH from US-EPA list” (benz[a]anthracene, chrysene, benzo[b,j]fluoranthene, benzo[k,j]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene,

benzo[g,h,i]perylene, et indeno[1,2,3-cd]pyrene) merely represents 0.22% to 0.65% of the total.

Naphtalene accounts for more than half of the total molar flow. Both the naphthalene and anthracene flows decrease with recycling rate, whereas acenaphtylene, phenanthrene, fluoranthene and pyrene flows all increase. Acenaphtene and fluorene seem to be entirely independent of recycling rate.

## 4 DISCUSSION

For variations in water content (protocols 10 and 10w) the PAH total mass flow increases with just a slight change in molar composition: the proportion of lower molecular weight PAH (naphthalene, anthracene, acenaphthene) decreases, whereas that of higher molecular weight PAH (fluorene, phenanthrene, fluoranthene and pyrene) increases. **This compositional change may be explained by a steam distillation process, as a result of the increase in water vapour (Table 5).**

The same type of results has been also observed when using older bitumen from recycled aggregate; such material modifies the molar PAH composition by favoring the emission of heavier compounds, without changing total mass flow. The lower molecular weight PAH (naphthalene and anthracene) decrease, whereas the higher molecular weight PAH (acenaphtylene, phenanthrene, fluoranthene and pyrene) increase. **Two reasons might explain this increase in higher molecular weight PAH:**

- recycled asphalt aggregate contains older bitumen, which is capable of modifying the emissions of organic compounds into the atmosphere, given that (Chambrion 1993; Durand 1997) accounted for a link between bitumen aging and a smaller proportion of lighter molecules; and



- a steam distillation process may also occur, since the increase in recycling rate induces an increase in total water content of the aggregate (see Fig. 4) and water vapour (Table 5).

The aggregate water content and stack gas water vapour of the 10w protocol have been increased by 50% and 32% respectively, in comparison with the 10 protocol. These differences only lead to slight changes in PAH molecular composition between both protocols. When protocol 20 is compared to protocol 10, the aggregate water content and stack gas water vapour are increased of 17% and 21% respectively, even though this yields a significant change in composition. The influence of old bitumen composition can thus be considered stronger than that of the steam distillation process.

This steam distillation assumption could be verified by maintaining the total aggregate water content strictly constant, while increasing the recycling rate. With the current process under study (drum mix), such a verification would not be possible, because RAP have a higher water content than natural aggregate; moreover, this process is not adapted to drying the aggregate prior to placement inside the drum. An identical experiment could be instructive if carried out on a batch mix asphalt plant, where aggregates are dried separately previous to being mixed with bitumen.

Improved knowledge of the bitumen chemical composition would certainly prove relevant to the correlation with emitted PAH. It would also be useful to seek more specific PAH within the bitumen. Some sulfured or methyled forms of PAH were strongly detected in bitumen fumes (US-EPA 2004, Mc Carthy et al. 1999), since for sulfuric forms, the bitumen refining process does not include a desulfuration step (US-Energy 1998).

## 5 CONCLUSION

Measurements of the 16 HAP from the US-EPA list have been carried on the chimney of the hot-mix asphalt plant in the city of Blois; this facility uses a hot-mix drum with parallel flow, and is fuelled with natural gas. Four protocols have been compared using different asphalt recycling rates, and varying aggregate water content, in order to distinguish combustion effects from material effects in PAH emissions.

In the end, the analysis restricted to PAH from the US-EPA list is not apparently sufficient to clearly distinguish process and material effects.

Variations in aggregate water content could exert an influence, and this influence could be manifested through a steam distillation process that incites the emission of higher molecular weight PAH. The use of recycled bitumen from asphalt aggregate is also found to favor emission of higher molecular weight PAH. Similar tests with other batch mix processes may be developed since this process dries aggregate separately from bitumen mixing.

The study of PAH produced exclusively by means of combustion reactions must still be considered. It is not altogether excluded that burner operating conditions are indirectly modified by increasing aggregate water content. The energy required to dry aggregate is indeed increased (Nouvion et al. 2005), and can thus modify burner efficiency. The development of a benchmark protocol, i.e. without bitumen, would be useful in evaluating both the nature and quantity of PAH produced by combustion reactions. Since fuel consumption is tightly correlated with process parameters (production rate, asphalt temperature), varying these parameters could serve to identify the role of the combustion reactions as well as emission variability. The influence of spent fuel could also be investigated by means of a series of tests performed on identical materials and process, using fuel oil instead of natural gas. A PAH combustion marker is still being sought (Siegmann and

Sattler 2000, Siegmann et al. 2002) because PAH emitted by combustion processes may vary with their chemical group (Jenkins et al. 1996).

The search for more specific markers of combustion and materials could contribute to a better understanding of the entire process. A chemical characterization of bitumen might also help in predicting PAH emissions and could be tied to the Nickel/Vanadium ratio, which is commonly used as an indicator for the origin of crude oil (Lewan 1984).

Lastly, in the aim of determining the process components primarily responsible for PAH emissions, the total mass flow has not provided a satisfactory indicator. The chemical composition analysis yields additional information about the origin of PAH emissions.

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## **6 REFERENCES**

Blomberg J., de Groot P.C., Brandt H.C.A., van der Does J.J.B., Schoenmakers P.J. 1999.

Development of an on-line coupling of liquid–liquid extraction, normal-phase liquid chromatography and high-resolution gas chromatography producing an analytical marker for the prediction of mutagenicity and carcinogenicity of bitumen and bitumen fumes.

Journal of Chromatography A **849** : 483–494.

Bonnet P., Binet S., Brandt H., Kriech A.J., Lafontaine M., Nunge H., Morele Y., de Groot P.,

Wissel H., Castegnaro M. 2000. Inhalation Study on Exposure to Bitumen Fumes - Part 1:

Development and Validation of the Equipment. Ann. occup. Hyg. **44** (1) : 15-29.

- Brandt H., Lafontaine M., Kriech A.J., De Groot J., Bonnet P., Binet S., Wissel H., Moreles Y., Nunge H. , Castegnaro M. 2000. Inhalation Study on Exposure to Bitumen Fumes - Part 2: Analytical Results at Two Exposure Levels, *Ann. occup. Hyg.* **44** (1) : 31-41.
- Burnstyn I., Kromhout H., Kauppinen T., Heikkilae P., Boffetta P. 2000. Statistical Modelling of the Determinants of Historical Exposure to Bitumen and Polycyclic Aromatic Hydrocarbons Among Paving Workers. *Ann. Occup. Hyg.* **44** (1) : pp. 43-56.
- Burnstyn I., Randem B., Lien J.E., Langard S., Kromhout H. 2001. Bitumen, Polycyclic Aromatic Hydrocarbons and vehicle exhaust : exposure levels and controls among norwegian asphalt workers. *Ann. Occup. Hyg.* **46** (1) : 79-87.
- Chambrion P. 1993. Influence d'adjuvants carbochimiques sur le comportement physicochimique d'un bitume pétrolier. Thèse de l'Université de Mulhouse.
- D'Anna A., Kent J.H. 2003. Aromatic formation pathways in non-premixed methane flames. *Combustion and Flame* **132** : 715–722.
- European Directive 2004/107/CE of parliament and council of déc. 15<sup>th</sup> 2004 concerning arsenic, cadmium, mercury, nickel and aromatic hydrocarbons in indoor air. Official Journal of European Union of January 26<sup>th</sup> 2005 n° L23/3, 14 p.
- Durand A. 1997. Relation entre la composition des bitumes et leurs propriétés physicochimiques - Application à la formulation des liants modifiés. Thèse de l'Université de Rouen.
- Hoang T., Jullien A., Ventura A. 2005. A global methodology for sustainable road - Application to the environmental assessment of French highway. 10DBMC International Conference On Durability of Building Materials and Components, Lyon (France), April 17-20, 10 p.

Jenkins B., Jones D., Turn S., Williams R.B. 1996. Particle concentrations, gas-particle partitioning, and species intercorrelations for polycyclic aromatic hydrocarbons emitted during biomass burning. *Atmospheric Environment* **30** (22) : 3825-3835.

Kitto, A.M., Pirbazari, M., Badriyha, B.N., Ravindran, V., Tyner, R. and Synolakis, C.E. (1997) Emissions of Volatile and Semi-Volatile Organic Compounds and Particulate Matter from Hot Asphalts. *Environmental Science and Technology* **18** (2) : 121-138.

Landa P., Wit W. 1996. Determination of PAH in asphalt mixtures by thin layer chromatography. Euraspalt and Eurobitume Congress, Strasbourg, paper No 2.028.

Lee WJ, Chao WH, Shih M, Tsai CH, Chen TJ, Tsai PJ. (2004) Emissions of polycyclic aromatic hydrocarbons from batch hot mix asphalt plants, *Environmental Science and Technology* **38** (20) : 5274-80.

Lewan M.D. 1984. Factors controlling the proportionality of vanadium to nickel in crude oils. *Geochimica et Cosmochimica Acta* **48** (11) : 2231-2238.

McCarthy B.M., Blackburn G.R., Kriech A.J., Kurek J.T., Wissel H.L., Osborn L.V. 1999. Comparison of Field versus Laboratory Generated Asphalt Fumes. Transportation Research record, paper No 1661, pp. 54-59.

Nouvion S., Ventura A., Jullien A., Monéron P., Schemid M. 2005. Émissions à l'atmosphère liées à l'élaboration d'enrobés en centrale d'enrobage à chaud. Colloque Européen Orgagec - Matériaux organiques pour la construction, risques sanitaires et environnementaux, Nantes 4-5 oct. 10 p.

Shell Bitumes 1991. Bitumes – Techniques et utilisation. Ouvrage de la Société des Pétroles Shell, éd. Génération (Paris) 147 p.

- Siegmann K. and Sattler K. 2000. Formation mechanism for polycyclic aromatic hydrocarbons in methane flames. *J. Chem. Phys.* **112** (2) : 698-709.
- Siegmann K., Sattler K., Siegmann H.C. 2002. Clustering at high temperatures: carbon formation in combustion. *J. Electron Spectrosc. Related Phenomena* **126** : 191–202.
- U.S. Environmental Protection Agency 2004. Emissions Factor Documentation for AP-42. Hot Mix Asphalt Plant. Final Report. Report from US-EPA Office of Air Quality Planning and Standards. Emission Measurement Center.
- US Department of Energy (1998) Energy and environmental profile of the US petroleum refining industry, Report of US department of Energy – Office of Industrial Technologies, dec. 1998, 124 p.
- Ventura A., Monéron P., Jullien A., Paranhos R., Schemid M. 2005. Approche multi-échelle de la collecte des données sur une centrale d'enrobage, Colloque Européen Orgagec - Matériaux organiques pour la construction, risques sanitaires et environnementaux, Nantes 4-5 oct., 9 p.

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**Table 2.** Process operating parameters.

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**Table 1.** Protocols description (RAP = Reclaimed Asphalt Pavement).

<b><i>Protocols</i></b>	<b><i>Description</i></b>
0	<i>without RAP</i>
10	<i>10% RAP with low <math>\omega</math></i>
10w	<i>10% RAP with high <math>\omega</math></i>
20	<i>20% RAP</i>



**Table 2.** Process operating parameters.

<b><i>Initial settings of automaton</i></b>	<b><i>Operator's parameters</i></b>	<b><i>Followed parameters</i></b>
<i>Mass flows of initial materials</i>	<i>Natural gas feed opening valve</i>	<i>Asphalt temperature</i>
<i>Mass flow of asphalt</i>	<i>Exhaust gas opening valve</i>	<i>Exhaust gas temperature</i>
<i>Bitumen temperature</i>		<i>Vacuum at the head of the burner</i>

**Table 3.** Characterization of Materials.

<b>Materials</b>	<b>Parameters</b>	
	<b>known or measured</b>	<b>calculated</b>
<i>Asphalt</i>	<i>Total bitumen content</i>	
	<i>RAP recycling rate</i>	
	<i>Mass fractions of grading span</i>	
<i>Natural aggregate</i>	<i>Water content</i>	<i>Dry and total masses by grading span</i>
<i>Reclaimed Asphalt Pavement</i>	<i>Water content</i>	<i>Dry and total masses of RAP</i>
	<i>RAP bitumen content</i>	
<i>New bitumen</i>	<i>New bitumen class</i>	<i>New bitumen mass</i>

**Table 4.** Description of Materials for each studied Protocol (RAP = Reclaimed Asphalt Pavement).

<i>Protocols</i>	<i>Asphalt mass</i>	<i>Aggregate masses</i>		<i>Total water content <math>\omega</math></i>	<i>Bitumen masses</i>	
		<i>RAP</i>	<i>natural</i>		<i>RAP</i>	<i>new</i>
	tons	Tons	tons	mass %	tons	tons
<b>0</b>	114.70	0	114.70	0.9	0	6.01
<b>10</b>	113.50	11.35	102.15	1.2	0.45	5.21
<b>10w</b>	114.00	11.51	102.49	1.8	0.48	5.21
<b>20</b>	114.90	23.09	91.80	1.4	0.96	4.78

**Table 5.** PAH sampling conditions description.

<i>Protocols</i>	<i>Asphalt</i>		<i>Stack gas</i>				
	<i>Temp.</i>	<i>Water vapour</i>	<i>Temp.</i>	<i>Static pressure</i>	<i>Dynamic pressure</i>	<i>Dry volume flow</i>	<i>Sampled volume</i>
	(°C)	(% total vol.)	(°C)	(Pa)	(Pa)	(Nm <sup>3</sup> /hr)	(Nm <sup>3</sup> <sub>dry</sub> )
<b>0</b>	162	7.8	111	100,991	191	16,279	0.927
<b>10</b>	163	10.7	121	100,897	97	15,874	0.895
<b>10w</b>	169	14.1	121	100,920	120	14,722	0.879
<b>20</b>	167	12.9	119	100,895	95	15,567	1.018
<b>Mean</b>	<b>165</b>	<b>11.4</b>	<b>118</b>	<b>100,926</b>	<b>126</b>	<b>15,610</b>	<b>0.930</b>
<b>Stand. dev.</b>	<b>3</b>	<b>0.03</b>	<b>5</b>	<b>45</b>	<b>45</b>	<b>660</b>	<b>0.062</b>

**Table 6.** Evolution of PAH molar Flows emitted per hour for 10 and 10w protocols.

<i>PAH</i>	<i>Molar weight</i> (g/mol)	<b>10</b>		<b>10w</b>	
		(mmol/hr)	%	(mmol/hr)	%
TOTAL		29.61	99.2	30.54	98.7
naphtalene	128.16	17.71	59.3	17.23	55.7
acenaphthylene	152.20	0.76	2.5	0.58	1.9
acenaphthene	154.21	2.23	7.5	2.16	7.0
fluorene	166.20	2.93	9.8	3.10	10.0
phenanthrene	178.23	3.69	12.4	4.21	13.6
anthracene	178.23	0.34	1.2	0.34	1.1
fluoranthene	202.26	0.77	2.6	1.19	3.8
pyrene	202.26	1.18	3.9	1.73	5.6

## List of Figures

**Figure 1.** Hot-mix drum process.

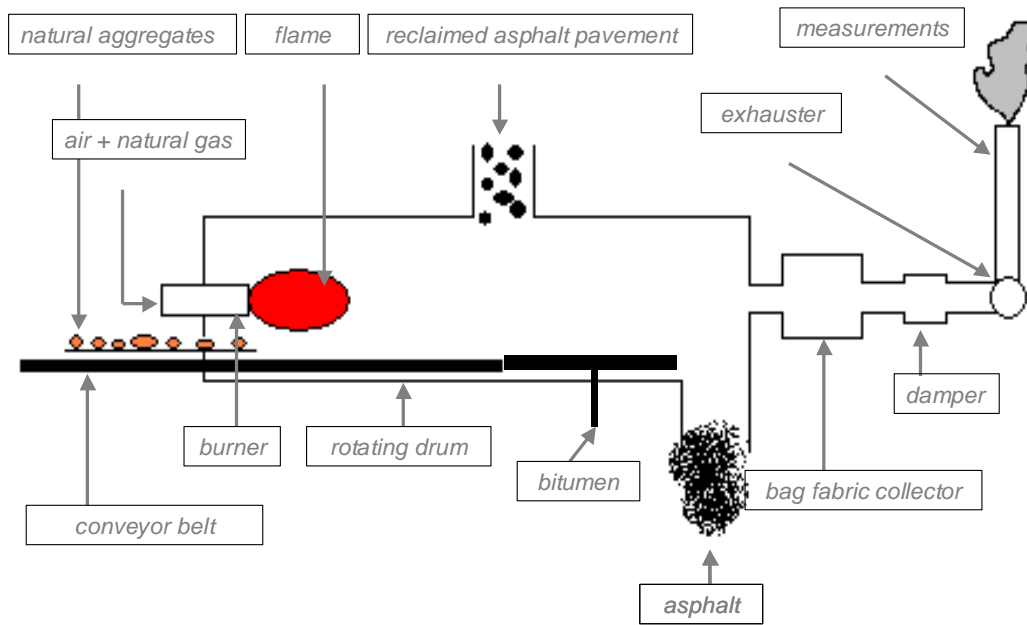
**Figure 2.** Reclaimed Asphalt Pavement (RAP), stockpile of Blois.

**Figure 3.** PAH isokinetic sampling system.

**Figure 4.** PAH total mass flow and water content as a function of RAP recycling rate.

**Figure 5.** PAH molar flows for each protocol.

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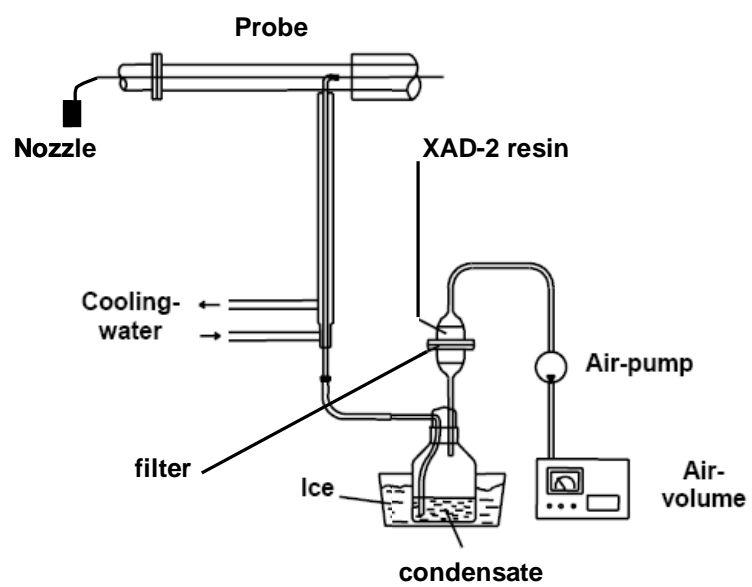


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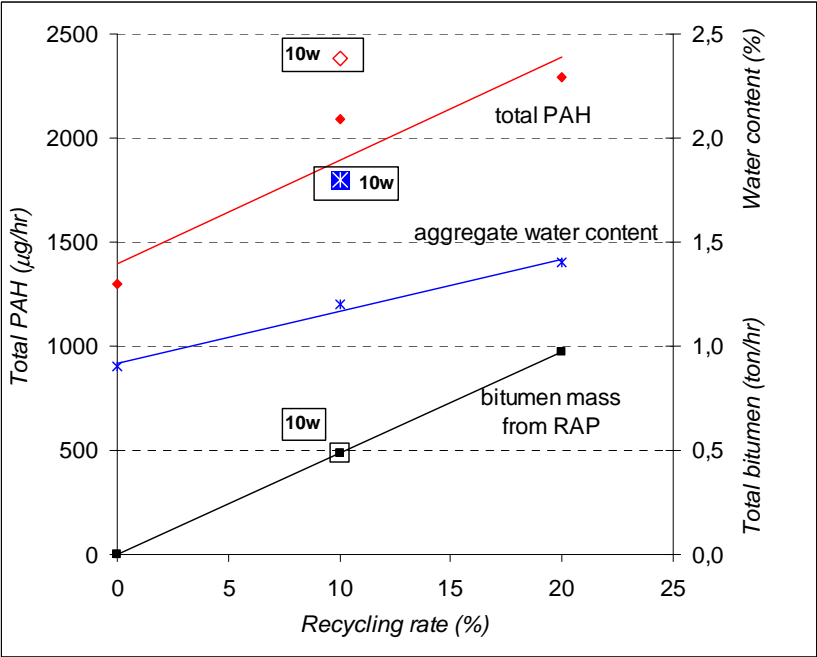




**Figure 3.** PAH isokinetic sampling system.



**Figure 4.** PAH total mass flow and water content as a function of RAP recycling rate.



**Figure 5.** PAH molar flows for each protocol.

