Laboratory evaluation of emissions from asphalt binder and mixes using a bio-rejuvenating agent

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ABSTRACT

With the constant focus on health and safety, the paving industry is paying close attention to material emissions, particularly the fumes that are generated during the manufacture of Hot Mix Asphalt (HMA); this may impact occupational exposure limits. In recent years, a spotlight has been placed on bitumen fumes, and extensive studies have been published on this subject.

Concurrently, economic and environmental constraints require the development of new technologies that use new products in asphalt mixtures. These constraints drive the desire to incorporate high volumes of Reclaimed Asphalt (RA) in new pavement, which requires specific engineered rejuvenating agents. On the downside, questions may be raised regarding the impact of rejuvenating additives on emissions.

This paper describes the impact on fume emissions of a bio-based rejuvenating agent added to bitumen. An extensive laboratory analysis was conducted on both binder and HMA.

The binder evaluation was based on analytical testing using headspace analysis combined with Gas Chromatography/Mass Spectrometry (GC/MS). The static headspace of the binder was analysed and compared with the analyses of binder mixed with two levels of the rejuvenating agent. The headspace of the bitumen and bitumen/rejuvenator blends was evaluated over a range of temperatures typical of HMA production and use.

The asphalt mixture evaluation followed a methodology that involves mixing the aggregates and binder in a closed pug mill and collecting fume samples. The overall protocol includes four mixing sequences to mimic the entire process from mixing at the plant to paving the road. This testing enables the detection of emissions of Total Organic Compounds (TOC), which includes Polycyclic Aromatic Hydrocarbons (PAH).

The evaluations on the binders and mixes displayed similar trends and conclusions. The overall results show that the incorporation of the bio-based rejuvenating additive did not contribute to new components that affect occupational exposure limits, especially with regard to PAHs.

Keywords: Additives, Asphalt, Emissions, Fumes, Reclaimed asphalt pavement (RAP) Recycling

1 INTRODUCTION

With the constant focus on health and safety, the paving industry is paying more attention to material and processing emissions. During the manufacture of Hot Mix Asphalt (HMA) at elevated temperatures, controlling the emissions of Volatile Organic Compounds (VOCs) is one of the key focus areas [1], as it may impact occupational exposure limits. In previous years, extensive studies and research have been conducted and published to better monitor fume emissions and identify technologies that can reduce these emissions [2-8].
At the same time, economic and environmental constraints require the development of new technologies using new products in asphalt mixtures. Amongst other technologies, the reuse of Reclaimed Asphalt (RA) into new HMA is seen as a sustainable option to overcome these constraints. The incorporation of high volumes of RA in new pavement requires new technologies and specifically engineered products. A key part of this innovative process is testing to explore the impact of rejuvenating additives on emissions.
This study focused on the evaluation of the fume emissions of a bio-based rejuvenating agent added to bitumen through both binder and asphalt mixture assessment in the laboratory. These evaluations were conducted in addition to any mandatory health and safety evaluations including amongst other REACH registration, safety data sheets. The goal was to identify different compounds in fume emissions, specifically focusing on the ones that may affect occupational exposure, such as Polycyclic Aromatic Hydrocarbons (PAH). This paper describes the key outcomes of the study. In particular it:

- Describes the experimental plan and the materials used
- Presents the results of the binder evaluation
- Presents the results of the mix evaluation
- Draws specific conclusions and describes future steps

2 EXPERIMENTAL PLAN

2.1 Materials

In order to avoid uncontrolled emissions from an unknown source of Reclaimed Asphalt binder, testing was made using standard virgin binder 35/50 pen grade bitumen, according to EN 12591. This enables the comparison of the real impact of the additive alone with a reference binder.
The additive evaluated was a liquid pine-based additive designed specifically to be highly effective on aged asphalt binder. A dosage of 5 % restores the properties of an aged binder by 2 grades, causing it to behave more like virgin asphalt binder. The typical dosage is between 3 % and 7 % of the aged binder content, depending on its properties.
For the asphalt mixture, a standard French dense Asphalt Concrete mixture, for surface layer, was selected. Its composition is summarized in Table 1. The virgin aggregates came from the “La Noubleau” quarry in France, a diorite petrographic rock type.

Table 1. Gradation and binder content of the asphalt mix (BBSG 0/14)

Sieve (mm)									Binder content
0,063	0,250	0,5	2	4	8	10	14	16	4,76 %
6,4 %	11,7 %	16,4 %	33,1 %	42,6 %	61,8 %	72,3 %	96,5 %	100,0 %	

In this study, a higher dosage than normally recommended was used in order to enhance emissions and clearly highlight any negative impact. For the binder assessment, two levels, 5 % and 10 %, were used per weight of asphalt binder. On the asphalt mixture, a dosage of 10 % per weight of bituminous binder was selected. It has to be bear in mind that this dosage level was not in line to what will be used in the field. In a case of 50 % RA recused in the mix with 5 % of additive by weight of the RA binder, the theoretical dosage should be 50 % RA x 5 % dosage = 2,5 % of total weight of binder in the final mix. The dosage was artificially inflated to insure adequately laboratory respond.

2.2 Fumes emission evaluation on binder

The analysis of fume emissions on the bituminous binder alone was conducted through headspace analysis combined with Gas Chromatography / Mass Spectrometry (GC/MS). This technique facilitates the characterisation and relative comparison of the volatile compounds emitted by bitumen over a range of temperatures. This approach has previously been used successfully by the asphalt industry [9]. Each test sample was sealed in a vial with a PFTE-lined septum. The sample vial was allowed to equilibrate at a chosen temperature for 30 minutes. After the equilibration step, a fixed aliquot of the emissions was transferred and analysed by GC/MS. The analysis allows the identification and relative comparison of emission levels from the samples tested.

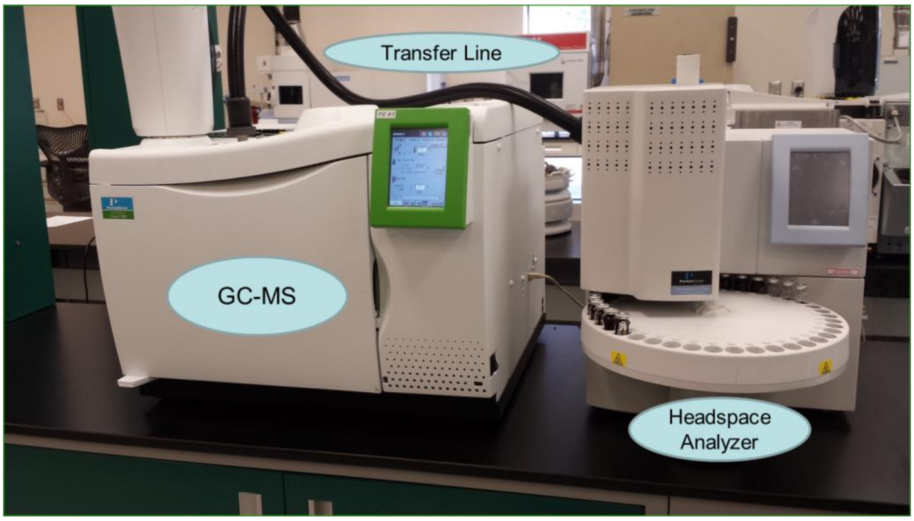

Figure 1. Headspace with Gas Chromatography equipment

The amount of volatile compounds emitted clearly depends on the temperature at which the binder is heated. Four temperatures were considered: 120 °C, 140 °C, 160 °C covering the normal range of manufacturing temperatures and 180 °C representing an extreme condition outside the normal temperature range. Three samples of asphalt binders were evaluated: neat bitumen (35/50 pen grade), and blends made with 5 % and 10 % dosage per weight of bitumen. A total of twelve samples were evaluated to explore the matrix of four temperatures and three blends.
The effect of the rejuvenating additive was assessed through the intensity and/or compositional change of the emissions with regards to relative levels of Volatile Organic Compounds (VOCs), and Polycyclic Aromatic Hydrocarbons (PAHs).

2.3 Fumes emission evaluation on asphalt mixture

Fumes emissions from the asphalt mixture were assessed through a specific protocol during the mixing process in the laboratory [6]. The protocol involved mixing sequences of aggregates and bituminous binder in a closed thermos-regulated asphalt mixer. In order to collect the fumes emitted from the mixture, a stainless steel stack was connected to the mixer. As the emissions were generated, they were fed into the stack and collected into two probes. The first one was dedicated to recording TOC levels and the second one to PAH analysis.

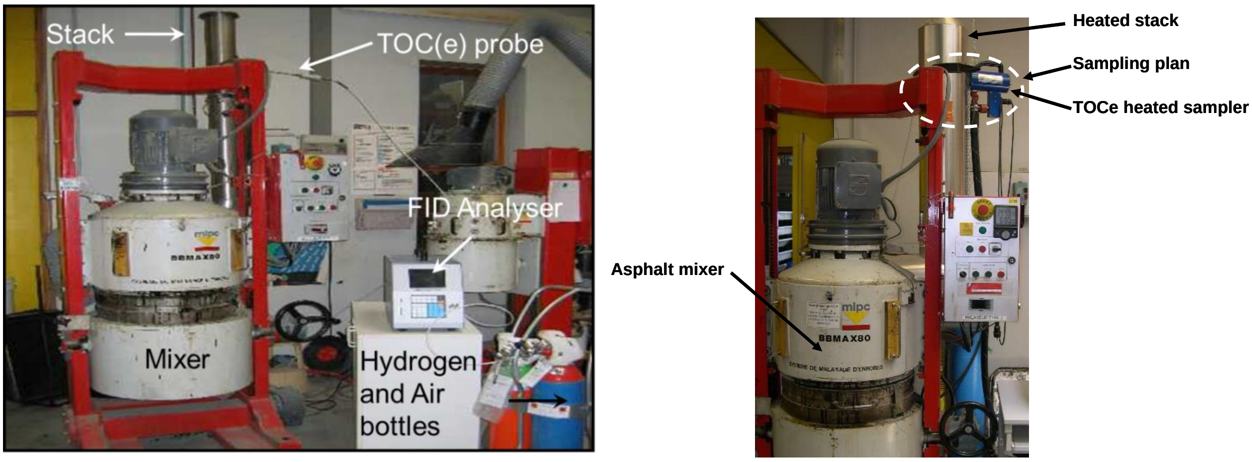

Figure 2. Asphalt mixer with fume collection equipment

The four mixing sequences were designed to mimic the asphalt journey from the plant to the road site.

- a) Mix manufacture
- b) Mix transfer from the plant silo to the truck
- c) Mix transfer from the truck to the paver
- d) Mix dispersion on the paver screw

Each mixing period lasted four minutes, with a 10-minute rest period between mixing periods, as illustrated in Figure 3.

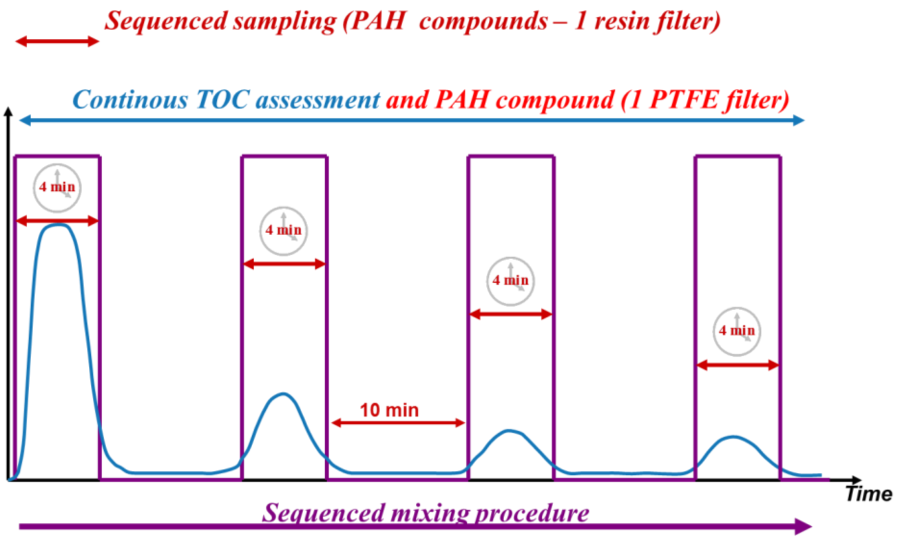

Figure 3. Diagram of the sequential mixing protocol

Two asphalt mixtures were assessed, a standard mix with neat bitumen and a mixture of bitumen treated with 10 % rejuvenated additive per weight of binder. All mixes were prepared and tested at the same temperature of 160 °C; for each mix, two replicates were made. Normally as the bio-based additive reduces the viscosity of the binder, a lower mixing temperature should have been applied to compare mix at equi-viscosity. But for the purpose of the experiment and to enhance the effect of the additive, the experiment was done at equi mixing temperature.

3 RESULTS ON BINDER

Binder evaluation was performed on a blend of 35/50 pen grade bituminous binder dosed with the bio-based additive at 0 % (neat binder, as a control sample), 5 % and 10 %.
Comparison of the chromatograms of each sample, exhibited, as expected, a rise in concentration as the temperature increases. Similar to the increase in temperature, the headspace chromatograms showed a rise in concentration when the dosage increased.
It has to be noted here that one effect of the bio-based additive is to change the properties of the bituminous binder with a decrease in viscosity at elevated temperatures. Logically, decreasing the viscosity has similar effect than increasing the temperature. A dosage of 5 % corresponds to a Temperature decrease of 10 °C at equal viscosity. Figure 4 displays the levels of headspace volatiles as a function of temperature for each dosage.

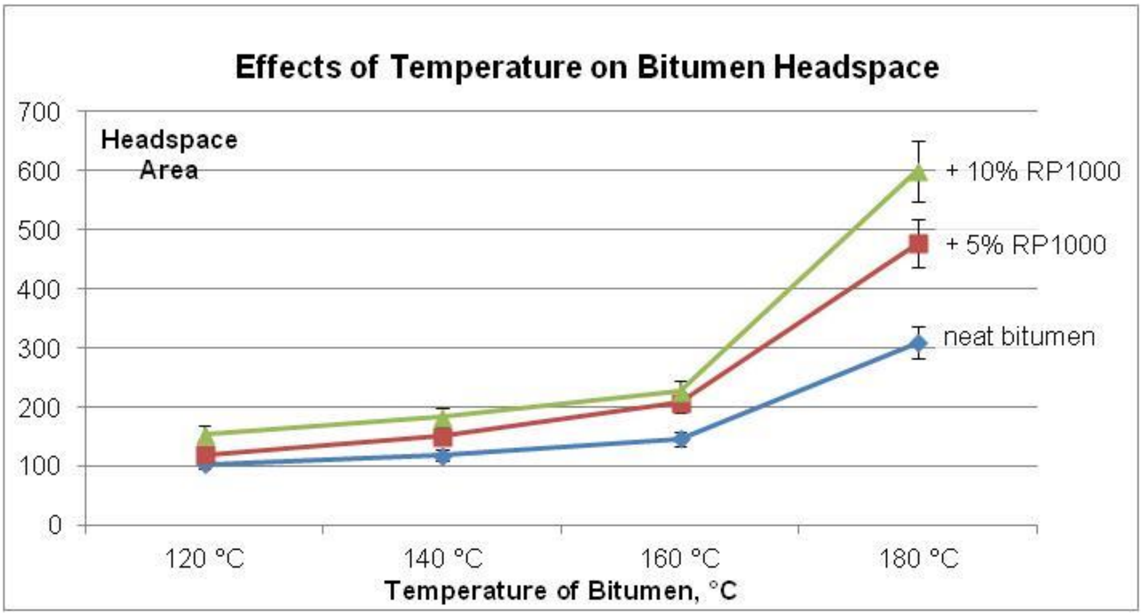

Figure 4. Effects of temperature and dosage on headspace

Modern GC/MS analysis not only provides component separation and identification, but also allows the isolation and plotting of a specific ion, a fragment that will target a specific compound or group of compounds. The analysis uses both specific ion(s) and chromatographic retention times to identify specific chemicals. The area of these specific ion plots can provide a relative comparison of classes of compounds like straight-chain hydrocarbons, aromatic compounds or PAH [9]. Figure 5 focuses on aromatic compounds. The aromatic compounds in bitumen increase with temperature, but the increase from the dosage effect is within the range of measurement variation.

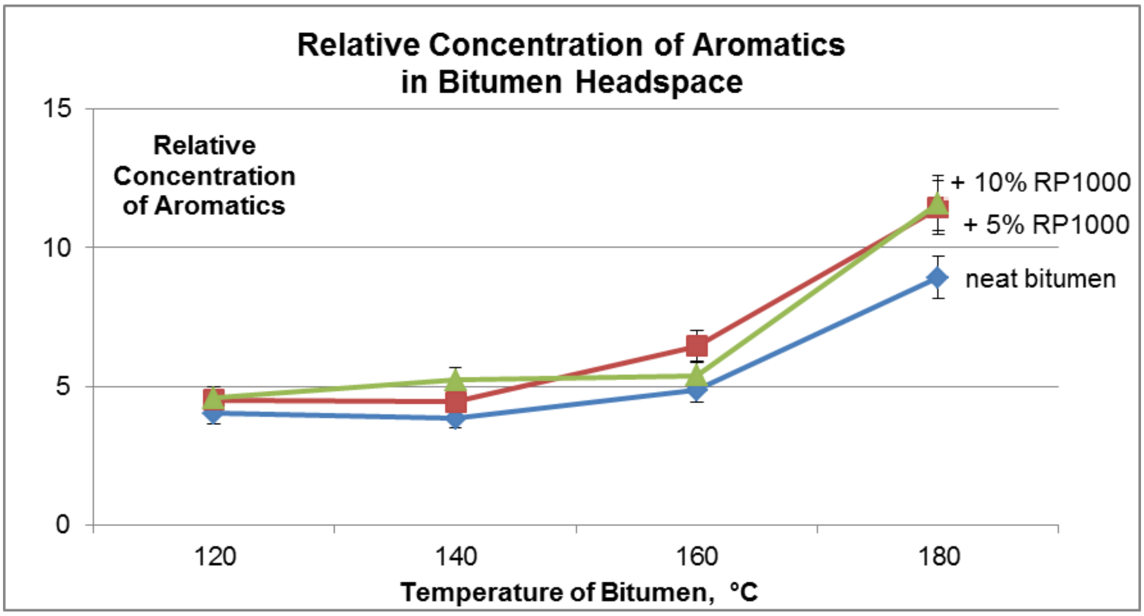

Figure 5. **Relative Concentration of Aromatics in bitumen headspace, ppm**

Table 2 displays the relative concentrations of PAH. The concentrations shown are based on external calibration of benzene, toluene, xylene and naphthalene in highly purified vacuum oil. The term "relative concentration" is used because the calibration matrix is different from the samples. Considering the effect of the dosage, the changes are in the magnitude of the precision of the method. The effect of temperature is more prominent than that of dosage.

Table 2. Relative concentration of PAH in ppm

Temperature, °C	Neat bitumen	Dosage at 5 %	Dosage at 10 %
120	Not detectable	Not detectable	Not detectable
140	Not detectable	Not detectable	Not detectable
160	77	135	87
180	267	168	143

4 RESULTS FROM LAB ASPHALT MIX EVALUATION

Two asphalt mixtures were evaluated: one without the additive and one with 10 % per weight of asphalt binder. Both were processed at the same mixing temperature of 160 °C. and for each the test was duplicated.

4.1 Additive influence on Total Organic Compounds emitted from bituminous mixture

Figure 6 shows the Total Organic Compounds, TOC, concentration and cumulated TOC mass versus time for the different mixtures without and with the bio-based additive. The values are given as equivalent for 1 t of produced asphalt mix. At the end of the first mixing sequence, the maximum concentration and the cumulated TOC mass were similar for both mixes. After the four successive mixing sequences, the TOC concentrations and mass significantly decreased. Based on the results obtained, TOC curves display good repeatability. The curves for the mix with the additive showed a passive ability to emit more TOC than the mix without additive.

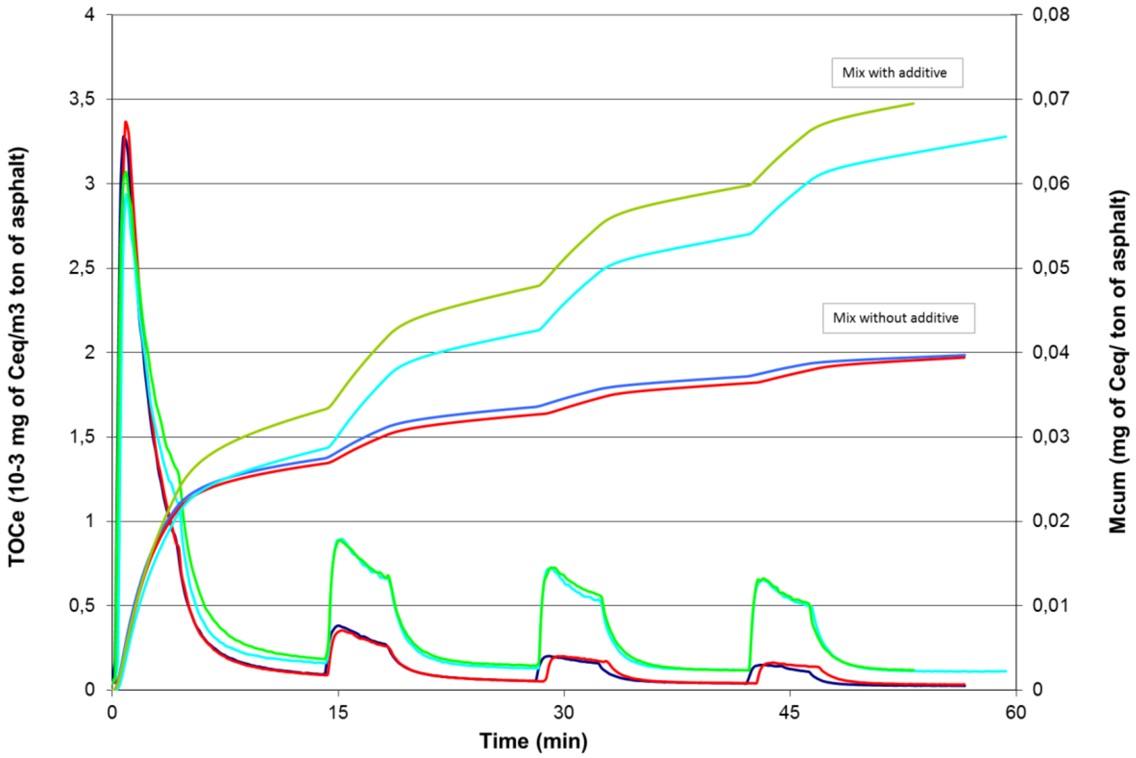

Figure 6. **TOC curves of mixes at 160°C (expressed in tons of asphalt)**

4.2 Additive influence on PAH compounds emitted from bituminous mixture

Figure 7 shows the total PAH concentration accumulated during the 1st and 4th sampling mixing sequences for the two mixes (without and with additive) at 160 °C. As can be seen, the mixture with the additive appeared to generate more PAHs than the one without additive.

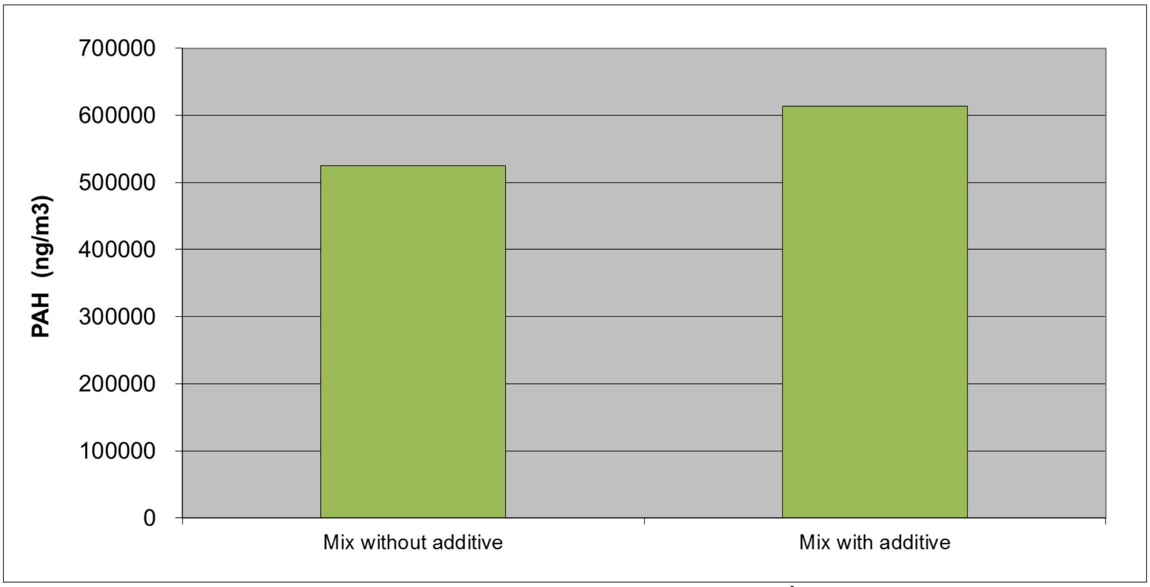

Figure 7. **Total PAH concentration cumulated during the 1st and 4th mixing sequences for mix with and without additive**

On closer analysis of the different components, the naphthalene appears to have mainly contributed to the PAH emission (around 95%, i.e. 0.5×10^6 to 0.6×10^6 ng/m^3) as seen in Figure 8. As an example, in France, the exposition limit threshold for naphthalene is equal to 50 mg/m^3 (50×10^6 ng/m^3).

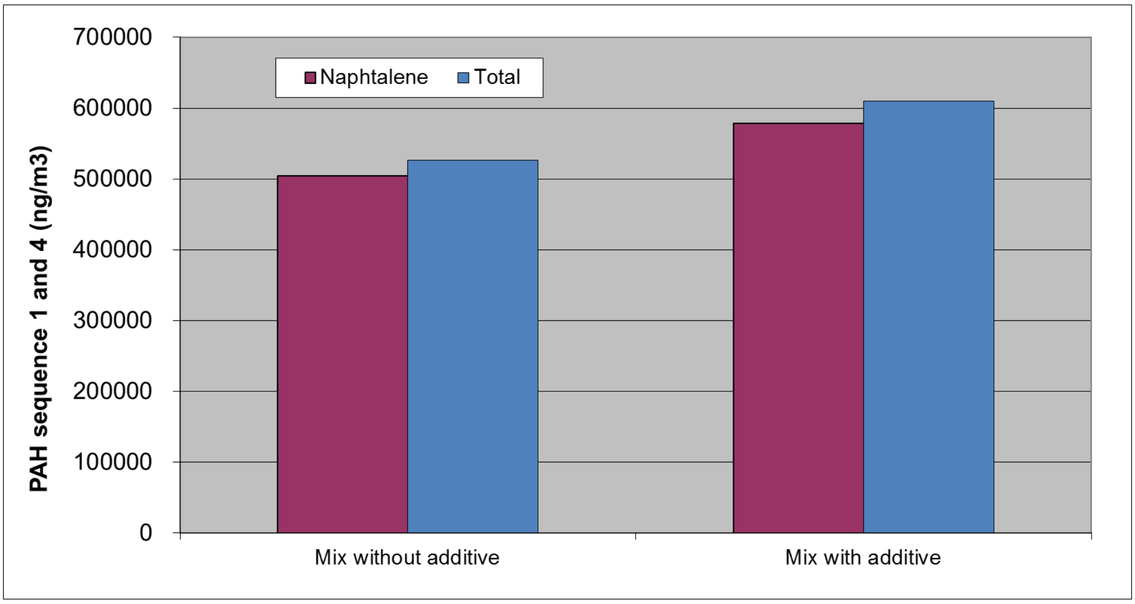

Figure 8. **Naphthalene and Total PAH concentration cumulated during the 1st and 4th mixing sequences**

Figure 9 shows the concentrations of other PAHs for the mixes without and with additive as collected during the 1st and the 4th sequence. It can be observed that all PAHs of the EPA-US list (except Acenaphthylene) [11] have been detected and quantified. The results show that while the mix with additive generated more PAHs overall, they were lighter PAHs than those generated by the mix without additive.

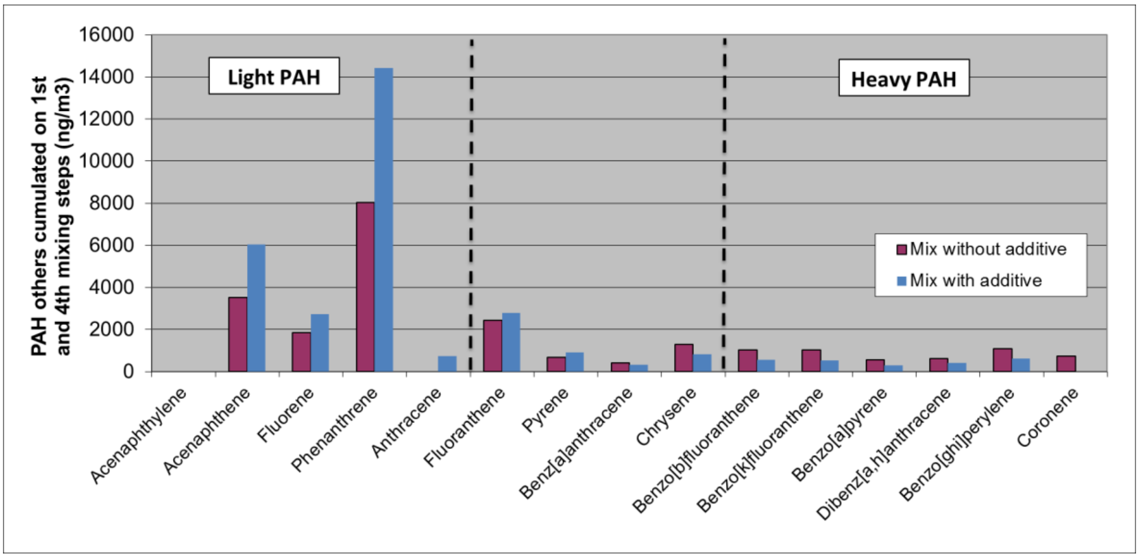

Figure 9. **PAH cumulated at 1st and 4th mixing sequence for mix without and with additive**

5 DISCUSSION

This study is aimed at determining the influence of a bio-based additive used as a rejuvenating agent for Reclaimed Asphalt on fumes emissions during the manufacturing of Hot Mixture Asphalt. This study was conducted in the laboratory on the binder itself using Headspace analysis combined with Gas Chromatography/Mass Spectrometry and on an asphalt mixture made in the lab, with the fumes being collected during the mixing process for further analysis.

The binder assessment was made at different temperatures between 120 °C and 180 °C, with dosages of 0 %, as the reference neat binder, 5 % and 10 %. Both, increase of temperature and increase of dosage lead to an overall increase in emissions, with the 5 % dosage having an effect similar to that of a 10 °C increase. When considering aromatic compounds or PAH emissions, the variations with dosage were in the magnitude of the measurement accuracy, and temperature variation had a prominent effect on the increase of emissions. During this evaluation, a deeper analysis did not detect the presence of acrolein as compared to other vegetable oil.

The asphalt mix assessment was made on mix without additive and mix with a 10 % dosage of additive per weight of binder. Over the different sequences of the mixing process, the level of emission decreased; the 1st sequence generated the largest amount, as already shown in the bibliography [10]. The mixture with additive generated two times more TOCs in all four sequences of mixing; however, the increase in PAH levels in the fumes was only 20 % and mostly

composed of naphthalene but far away from the common exposure limit threshold. A more specific analysis of the PAHs has shown that, although the lower molecular weight PAHs increased, PAHs of higher molecular weight were found to decrease. This is a fundamental outcome as the heavy PAHs are considered potentially carcinogenic [11].
Both assessments are consistent and comparable in conclusion. One of the objectives of the bio-additive is to restore the properties of an aged binder similar to a virgin asphalt binder. As a consequence, the viscosity at elevated temperature is reduced; typically at equi-viscosity, the temperature is decreased by 20 °C for a dosage of 10 %. Under this condition, the mixing temperature of the asphalt mix should have been reduced by -20 °C compared to the mix without additive but the experiment was made at the same temperature.
The emission generated from the mixture with the additive could be favored by a lower viscosity of the bitumen film around the aggregate during the mixing steps. The interface between the binder and the air is modified by the additivation which allows for easier organic compounds emission. This phenomenon could be linked to a skin effect mentioned in a previous study on warm mix asphalt [12].
Additionally, in the case of a blend of two components, the boiling temperature of a liquid (reference) can be modified by the addition of another liquid (additive). This phenomenon is known as the azeotrope effect. It could most likely explain the increase in light fractions in emissions at high temperatures in the presence of the additive.
Nevertheless, these experiments used conditions more severe than any encountered during asphalt mix production. The dosage is usually 3 % –7 % per weight of binder from the RA, meaning that for a mix made with 50 % RA, and assuming constant binder content from RA and the final mixture, the end dosage per weight of the total binder content would be four times less than in the experiment. Assuming a linear effect on emission, the relative impact of the additive should be four times lower. On the other hands, the testing conditions collect emissions from a closed environment, while at the mix plant, mixing is made and used in an open environment. This means the concentration should be lower than that used in the experiment.
These outcomes can be further validated during full-scale manufacturing at an asphalt mix plant and during application comparing an asphalt mix made with 0 % RA with asphalt mixtures made with 50 % RA with and without the additive at the proper dosage level. However, the key outcomes displayed here show that the magnitude of the difference would be extremely low and difficult to detect.

6 CONCLUSION

The study presented hereby described the results of an extensive analysis of fumes emissions for the use of a bio-based additive for reclaimed asphalt. It was conducted on both binder and hot mix asphalt, in the laboratory. The conditions of testing in laboratory were more severe than any conditions at the manufacturing plant. In order to avoid uncontrolled emissions from an unknown source Reclaimed Asphalt binder, the testing was done using a standard virgin binder.
The binder evaluation was performed with headspace analysis combined with GC-MS (Gas Chromatography Mass Spectrometry) at different temperatures and for different dosage levels. It shows that there were no differences in the levels of aromatics and PAH’s**.** No new harmful substances relating to the addition of the bio-based additive, like acrolein, were released.
Asphalt mix fumes emissions were evaluated through a specific protocol consisting of mixing aggregates and binder in a close pug mill and collecting fumes samples in four mixing sequences that mimic the whole processes from mix plant to paving. The comparative experiment was performed at the same mixing temperature. Under these conditions, the mix with the bio-additive displayed more emissions as a result of lower binder viscosity. Normally the mixing temperature should have been reduced consequently and thus emissions reduced as well. So far, the results show that the asphalt mix with the bio-based additive emitted a higher content of light PAHs but a lower content of heavy PAHs, the latter being considered potentially carcinogenic.
The overall results of binder and mix evaluation display similar trends and conclusions. The bio-based additive does not generate new hazardous breakdown components that can affect occupational exposure, especially with regard to acrolein as compared to other vegetable oil or heavy PAHs.

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