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Organic Compounds Evaluation from Fumes Generated in Laboratory by Bio-recycled Asphalt Mixtures

Reference

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ABSTRACT

Using bio-binder and bio-additives as recycling agents for asphalt mixtures with high-content of reclaimed asphalt (RA) is proving to be feasible. It is still not clear whether this combination might provide new known hazardous emissions from airborne binder fumes. The health hazard related to airborne bitumen fume generation is primarily relevant for paving crews, whereas there is little opportunity for exposure for asphalt plant workers. In this study, measurements of gaseous organic compounds from airborne binder fumes of selected bio-asphalt mixtures have been measured during the laboratory mixing process by using a thermo-mixer equipped with a chimney at University Gustave Eiffel. Parameters studied are the binder nature, mix formula, and mixing temperatures. Results show that generally combining bio-based materials and RA is as safe as using conventional bitumen and RA; however, thanks to this approach, it was possible to identify a strong link between bituminous materials' composition and their emission potential.

Keywords

bio-materials, reclaimed asphalt, organic compounds, fumes, test

Background

The new Constructions Products Regulation (CPR, 305/2011/EU) puts emphasis on a life cycle perspective and on sustainability in a way that is comparable with the Re-Road project.^{1,2} As previous studies on fumes and mixtures incorporated reclaimed asphalt (RA),^{3–12} CPR also stresses the importance of evaluating emissions of particles, toxic gases, and volatile organic compounds to outdoor air and the working environment. Test methods

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developed to measure these emissions related to the life cycle of asphalt can thus be of great value in relation to declaring the performance of RA (e.g., EPD, Environmental Product Declarations). Emissions to air might be an important issue in relation to the design of multi-recycled materials. Depending on the performance of the “RA product,” alternative actions are available, e.g., burning, landfill, low-temperature, or high-temperature recycling.

A fume generation system has been developed in the laboratory that allows eliminating the fume condensation risk in the stack and in the total organic compounds (TOC) emitted sampling line by adding heating devices.¹¹ The goal of this asphalt fume generator is to be used as a predictive test so as to forecast the amounts and nature of fumes generated by bituminous mixtures in different emissions scenarios. To achieve this purpose, the experimental principle is to mimic the different steps of bituminous mixture production (including reclaimed asphalt, noted RA) emissions from the manufacture to laying on road sites.

The aim of this paper is to show the research program and the results dedicated to the assessment of mixes carried out during the BioRePavation project^{13,14} on fumes emissions during mixing in the laboratory.

Experimental Set

BITUMINOUS MIXTURE DEVICE AND FUME GENERATION, SAMPLING, AND ANALYSIS

The prototype was composed of an asphalt mixer, which allows preparation of 80 kg of asphalt mixtures according to EN 12697-35, *Bituminous Mixtures – Test Methods – Part 35: Laboratory Mixing*.

Aggregates and bitumen are mixed at the required temperature at a defined stirring speed during a specific time. During the entire mixing process, the mixer thermoregulating system allows keeping temperature constant. In the case of bituminous mixtures fumes, it can be assumed that high-temperature mixing allows bitumen stirring and thus fume emissions. In order to collect fumes, a stainless steel stack is linked to the mixer. One opening at the top of the stack allows the positioning of the TOC sampling probe. As emissions are generated, they are fed into the stack. To avoid condensation phenomenon, heated cables have been added. As in the stack, a heated probe and a heated line between the probe and the TOC analyzer are used to eliminate any condensation. The probe and the flame ionization detector (FID) line are heated to the fume temperature measured just above the asphalt material in the mixer.

The continuous sampling and analysis of TOC are carried out by a piece of portable and automatic total hydrocarbon measuring equipment. The device is calibrated by using propane gas. This TOC continuous measurement allows for deriving a curve plotting the mass concentration of the emitted TOCs in the case of a mix with RA, according to time. Then, by adding up the instantaneous masses, the final curve of cumulative mass of TOC according to time is determined. This methodology has already been applied successfully for addressing fume emission with asphalt mix containing RA and recycling agent.¹⁵

EXPERIMENTAL PROTOCOL

A specific protocol was developed to generate fumes from asphalt, from asphalt production to its laying on road sites. The focus is on the processing of asphalt mix from the plant to the road site, and following are four steps when asphalt is set in motion and able to generate fumes: mix manufacture, mix transfer from the plant silo to the truck, mix transfer from the truck to the paver, and mix spread on the paver screw. Therefore, to mimic these different

steps on a laboratory scale, the aforementioned fume generation protocol is divided into four mixing periods. Each mixing period lasts for four minutes, interspersed with 10-minute periods of time off. However, the protocol is not calibrated to actual real emissions but is meant to ensure detectable emissions. As with the fume generation protocol, a sequential sampling process is also used. The aim is to compare the emission potential of the different fume generation steps. TOCs are analyzed continuously without sequences, and mixing periods are marked on the TOC graph. From these initial data, a cumulative mass is calculated for each sequence.

Experimental Program

Two mixes were studied: both French mixtures called “Grave bitume” (GB) and “Enrobé à Module Elevé” (EME) are used for the base layer. The fresh total added binder content of the GB was 2.8 % and was 4.8 % for the EME. The addition of RA and content (50 % for GB and 20 % for EME) does not modify the initial grading curve.

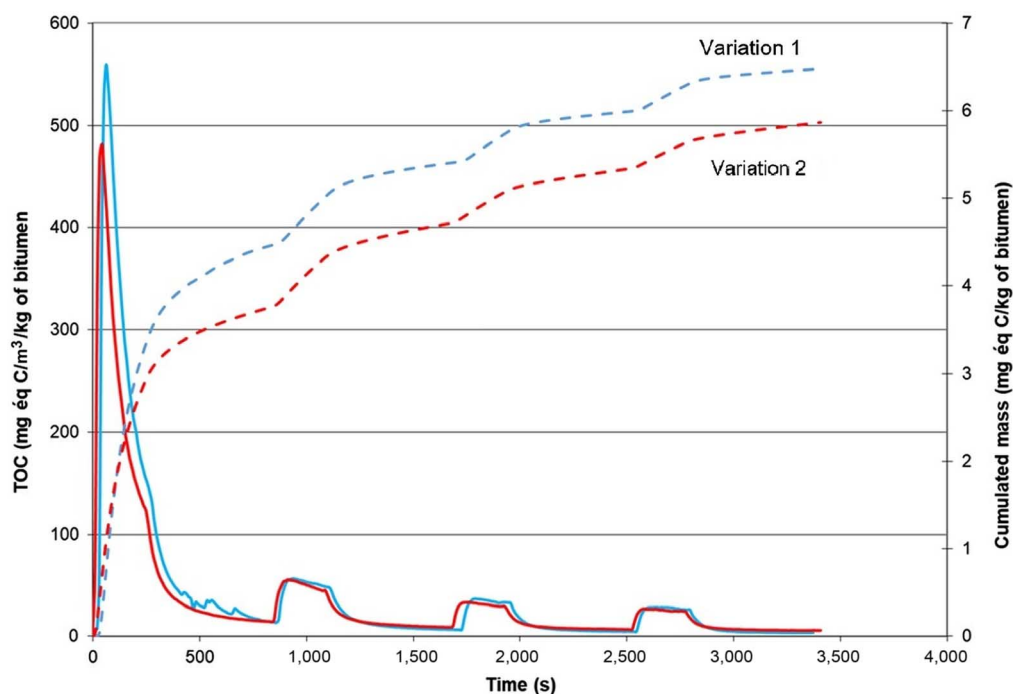
TABLE 1

Experimental plan for fume emissions evaluation

	Mix	Formula	Fresh Binder	Binder Content, M %	Additive Content, M %	Manufacturing Temperature, °C
Control	Mix A	EME (20 %RA)	French 20/30	4.80	0.000	175
	Mix A'	GB (50 %RA)	French 50/70	2.80	0.000	150
BioRePavation mix	Mix 1	GB (50 %RA + BM1)	French 50/70	2.70	0.100	120, 150, 180
	Mix 2	GB (50 %RA + BM2)	Modified binder	2.80	0.000	120, 150, 160, 180
	Mix 3	GB (50 %RA + BM3)	French 50/70	2.80	0.135	120, 150, 180

Note: According to pen-grade values, fresh binders were heated at different temperatures (from 130°C to 170°C). For mixes with RA incorporation (20 % and 50 %), RAs and virgin aggregates were heated at different temperatures over one night.

FIG. 1 TOC concentration (full line) and cumulated mass of TOC (dotted line) versus time for two Mix A' performed at 150°C.



The amount of fresh binder used in the mixes, which include RA, was calculated as a function of the binder content of the RA used. Mix components were heated to manufacture mixes from 120°C to 180°C for the GBs and at 175°C for EME (cf. [Table 1](#)).

The virgin fine and coarse aggregates, originating from the French “La Noubleau” quarry containing a petrographic type of diorite, were selected for this laboratory study. The virgin filler was a limestone aggregate. Three added fresh binders were chosen for the fume emissions assessment. The first one is a 20/30 pen-grade (for EME, Mix A). The second one is a 50/70 pen-grade for GB (Mix A’). The binder for Mix 1 was RA treated with an asphalt recycling additive, a bio-based additive from pine chemistry, noted BM1. The binder for Mix 3 was doped

FIG. 2 TOC concentration (full line) and cumulated mass of TOC (dotted line) versus time for Mix 2 at different manufacturing temperatures (120°C, 150°C, 160°C, and 180°C).

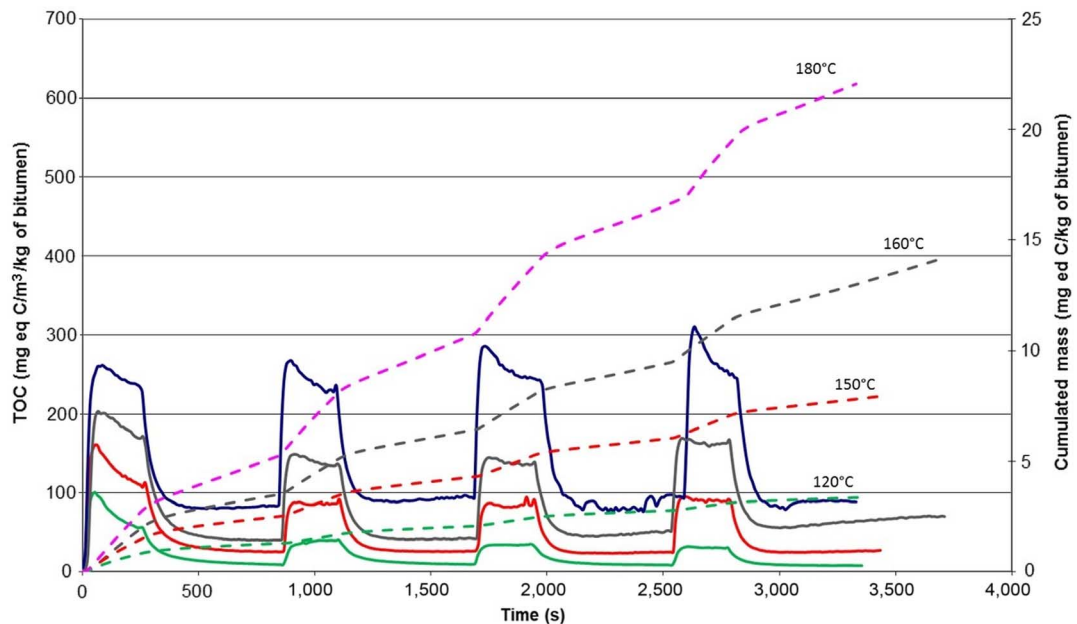
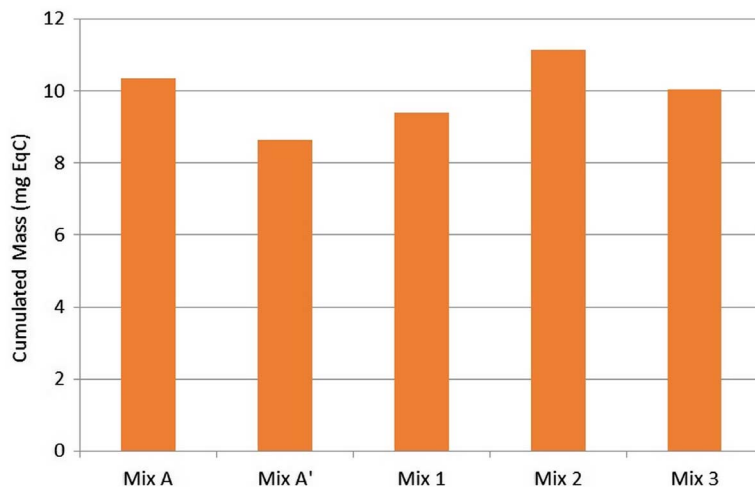


FIG. 3

Cumulated TOC mass after four mixing-rest periods for the Mix A at 175°C and Mix A’, Mix 1, Mix 2 and Mix 3 at 150°C.



by a bio-based additive, noted BM3, an epoxidized methyl soyate aimed to compatibilize fresh binder and aged binder from RA. In the case of Mix 2, the fresh binder was only made of bio-binder (more than 90 % composed of by-products from the pine industry) for total replacement of bituminous binder in recycling techniques. **Table 1** gathered the experimental program dedicated to the fume emissions from mixes made of different content of RAs and added fresh binders and additives.

Variability was investigated for Mix A'. As shown in **figure 1**, two tests were carried out and curves exhibited the same trend and appeared as repeatable for identical experimental conditions. These results highlight the limitations of the test carried out, but the observed scatter still allows one to discriminate the various parameters' effects.

First, the TOC curve and cumulated TOC mass of two Mix A' measured at 150°C by the FID analyzer are shown in **figure 1**. For this mixture, the outline of the TOC curve clearly displays the four mixing sequences by distinct "emission peaks." This behavior confirms the impact of mixing on fume generation: only mixed material generates fumes. It can also be observed that the bituminous mix behaves as if it were depleting its volatile TOC stock. This behavior is not well observed in the case of Mix 2 (made of bio-binder) (**fig. 2**). In this case, fumes at

FIG. 4

TOC max concentration during the first mixing for Mix A at 175°C and Mix A', Mix 1, Mix 2, and Mix 3 at 150°C.

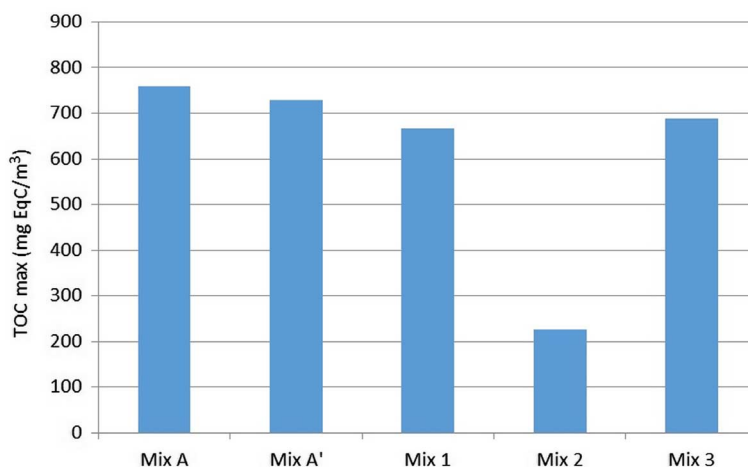
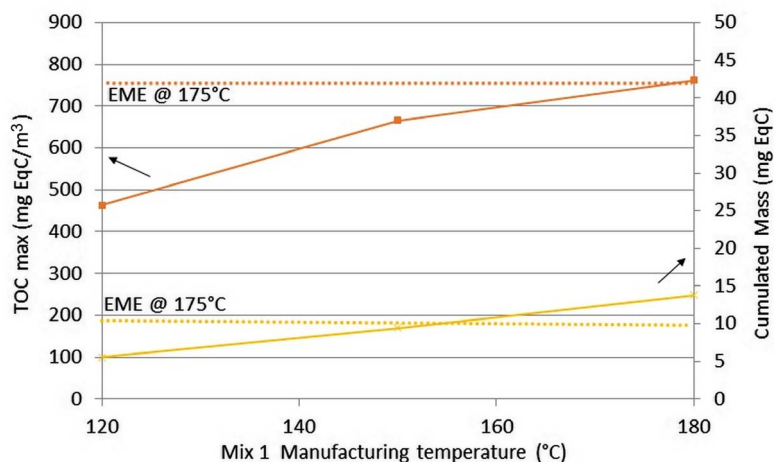


FIG. 5

TOC maximum concentration and cumulated mass versus temperature for Mix 1 (and EME at 175°C, dotted lines).



the first work mixing step are temperature dependent: increasing mixing temperature enhances fumes intensity and concentration. However, after a short time, only a low TOC was observed even at 180°C. Below 180°C, the fume level decreased with stirring as bitumen mixes, but the exhaustion kinetic was low in contrast to typical petroleum binders.

Now, by comparing the cumulated TOC mass curves of the mixes (with 50 % of RA at 150°C), it appeared that their emission levels were binder dependent (see [fig. 3](#)). The incorporation of bio-binder/bio-additive increased the cumulated TOC mass from 8.6 mg of carbon equivalent (eqC) (for 50 kg of asphalt) for reference material to a range of 9.4 up to 11.1 mg of eqC.

According to the TOC maximum concentration (at the first mixing step, see [fig. 4](#)), Mix 2 made of bio-binder was a low emissive mixture at 150°C. Mix 1 and Mix 3 (using 50/70 pen-grade bitumen and additive BM1 and additive BM3) generated fumes in a similar way to the Mix A' at the same temperature and Mix A at 175°C. In detail, the bio-based additives, even with a low dosage, did not affect or slightly reduced the total emission of the mix with standard bitumen, 50/70. There was a combined effect between mixing temperature, fresh binder, and RA content. This is in line with a previous study conducted on BM1.¹⁵

FIG. 6

TOC maximum concentration and cumulated mass versus temperature for Mix 2 (and EME at 175°C, dotted lines).

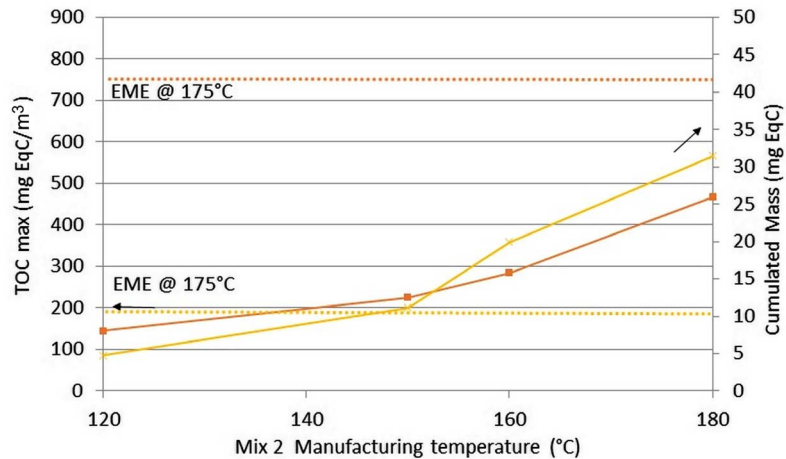
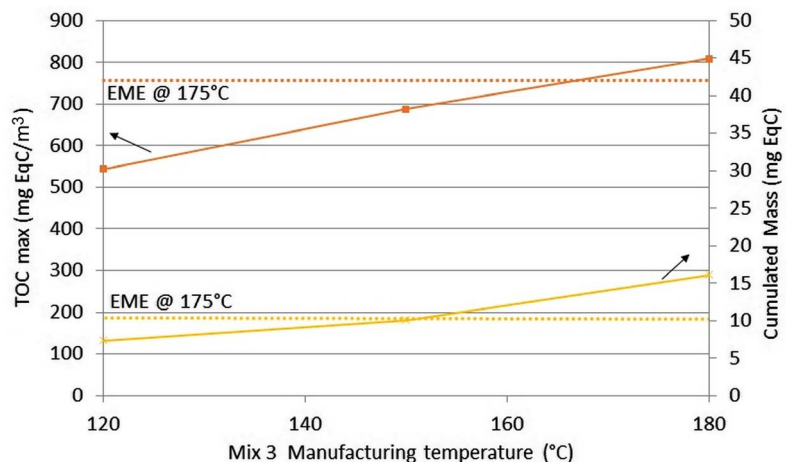


FIG. 7

TOC maximum concentration and cumulated mass versus manufacturing temperature for Mix 3 (and EME at 175°C, dotted lines).



As seen in **figures 5–7**, fumes from mixes made of 50/70 bitumen combined with additive BM1 for Mix 1 and additive BM3 for Mix 3 were temperature dependent, and mixtures behaved in the same way as the mix with pure bitumen. On the other hand, Mix 2 generated fumes in a different way from typical petroleum binders or other formulas after successive mixing-rest periods: a low TOC maximum concentration and no exhaustion kinetic. As a consequence, the TOC cumulated mass after four mixing-rest periods was higher for Mix 2 (see **fig. 3**). According to fume results, the bio-binder used significantly increased the fume emissions to higher than 150°C and thus it is not recommended to heat this binder above 150°C (**fig. 6**).

Conclusions

Measurements of fume emissions were performed on bituminous materials to characterize TOCs generated by asphalt material by temperature. Parameters studied are the binder nature and mix formula. The dispersion observed from the data obtained with the experimental device also makes it possible to discriminate the different effects of the parameters. This laboratory study shows a strong link between bituminous materials' composition and their emission potential. At the usual manufacturing temperature, 160°C, for Mix 1 with additive BM1, no additional fumes were observed in comparison with the reference mix or mix with no additive. At the usual manufacturing temperature, 160°C, for Mix 3 with additive BM3, no additional fumes were observed in comparison with the reference mix or mix with no additive. Concerningly, for Mix 2 with bio-binder BM2, the fume regime of this bio-binder mix is very different from bitumens, and the best emission performance in comparison with reference mixes is below 150°C.

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