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# Evaluation of Reductions in Fume Emissions (VOCs and SVOCs) from Warm Mix Asphalt Incorporating Natural Zeolite and Reclaimed Asphalt Pavement for Sustainable Pavements

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**Abstract:** Conventional asphalt mixtures used for road paving require high manufacturing temperatures and therefore high energy expenditure, which has a negative environmental impact and creates risk in the workplace owing to high emissions of pollutants, greenhouse gases, and toxic fumes. Reducing energy consumption and emissions is a continuous challenge for the asphalt industry. Previous studies have focused on the reduction of emissions without characterizing their composition, and detailed characterization of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in asphalt fumes is scarce. This communication describes the characterization and evaluation of VOCs and SVOCs from asphalt mixtures prepared at lower production temperatures using natural zeolite; in some cases, reclaimed asphalt pavement (RAP) was used. Fumes were extracted from different asphalt mix preparations using a gas syringe and then injected into hermetic gas sample bags. The compounds present in the fumes were sampled with a fiber and analyzed by gas-liquid chromatography coupled to mass spectrometry (GC/MS). In general, the preparation of warm mix asphalts (WMA) using RAP and natural zeolite as aggregates showed beneficial effects, reducing VOCs and SVOCs compared to hot mix asphalts (HMA). The fumes captured presented a similar composition to those from HMA, consisting principally of saturated and unsaturated aliphatic hydrocarbons and aromatic compounds but with few halogenated compounds and no polycyclic aromatic hydrocarbons. Thus, the paving mixtures described here are a friendlier alternative for the environment and for the health of road workers, in addition to permitting the re-use of RAP.

**Keywords:** warm mix asphalt; natural zeolite; fumes; VOCs and SVOCs; hydrocarbons

## 1. Introduction

The most widely used construction material in the world for constructing the surface courses of road pavement structures is hot mix asphalt (HMA); however, the construction and rehabilitation of paved asphalt roads produce a negative environmental impact. Pavement rehabilitation projects generate residues from milling the upper layers of asphalt-paved roads, called reclaimed asphalt pavement (RAP). These residues consist of aggregates and asphalt binder, which can be used as raw

material for new asphalt mixtures. The use of RAP is nowadays a common sustainable practice in the pavement industry; it saves on virgin construction materials and construction costs [1], and it also reduces the environmental impacts related to residue accumulation and the use of virgin raw materials [2]. Generally, there are three methods of pavement recycling: cold recycling, hot recycling, and full-depth reclamation, depending on whether pavement damage is structural or not [3].

On the other hand, the manufacture and laying of asphalt paving require high temperatures (between 150–180 °C) and therefore high energy consumption. In the process, the environment and workers are exposed to anthropogenic greenhouse gases and the massive toxic fumes emitted when asphalt mixtures are manufactured, transported, laid, and compacted at high temperatures [4–7]. Thus, the reduction of asphalt emissions related to production, mixing, transportation, and paving is a continuous issue and a challenge for the asphalt industry [8]. Growing international pressure to reduce fossil fuel consumption and greenhouse gas emissions has led the scientific and technical communities to develop a number of cleaner and more sustainable new technologies for asphalt materials [9,10].

One alternative method to reduce energy consumption and the emission of greenhouse gases and toxic fumes is to decrease the production temperature of asphalt mixtures by the development of warm mix asphalt (WMA) [9,11,12]. WMA is generally produced at between 110 and 140 °C, thirty degrees cooler than HMA [8]. Asphalt mixes with lower production and compaction temperatures are more environmentally friendly and economical [13]. One of the most commonly used processes for temperature-reduction is the incorporation of waxes [8,11,14,15] and synthetic or natural zeolites into asphalt mixes [16]. The temperature-reduction mechanism of zeolites is associated with the addition of water to WMA. Due to their honeycomb microstructure, crystallized zeolites can preserve water within their micropores and release it gradually when heated to above boiling point, when it creates foam. This reduces the viscosity of the asphalt mixture, increases its workability, and facilitates coating at lower temperatures [17–19]. Moreover, the quantity and mode of water release from zeolite are affected by the structure of the zeolite, its textural properties, and its crystallo-chemical characteristics [20]. Synthetic zeolite is prepared hydro-thermally by crystallizing a finely powdered hydrated sodium aluminum silicate; it retains from 18% up to 22% (by mass) of its water content, which is released when the temperature is increased above 85 °C. Natural zeolites are microporous, hydrated aluminosilicates generally used as commercial adsorbents. Clinoptilolite and phillipsite are the natural zeolites more commonly found in nature. In the synthetic mineral group, ZSM-5, X, Y, A, and NaP1 zeolite types are those most frequently found [21,22]. Both natural zeolites (clinoptilolite-type) and Na-P1 (GIS-gismondine zeolite minerals) and Linde A (LTA) structure-type synthetic zeolites are used to reduce the manufacture temperatures of mineral-asphalt mix [13,18,19].

The manufacture of bitumens involves oxidation of residue from the vacuum distillation of petroleum. During the vacuum distillation to produce the raw material for bitumen, as well as the oxidation process with hot air, the bitumen material deposited on heating parts undergoes partial thermal cracking; this results in the formation of unsaturated and aromatic compounds such as carbonyl sulfide, carbon disulfide, hydrogen sulfide, water vapor, etc. [23]. These compounds undergo further transformations, yielding different volatile compounds as well as ketones, aldehydes, organic acids, phenols and phenol derivatives, and organosulfur and organonitrogen compounds. A part of the produced volatile compounds is removed from the reactor using hot air, yielding exhaust gases, which undergo depuration in an alkaline aqueous solution or absorption in wash oil [24,25]. The residual volatile organic compounds (VOCs) in the bitumen material are emitted during storage [26–29], transport [30], manufacture of mineral-bitumen mixtures [31–36], roof impregnation [33,37–41], and road paving [42–54]. They can also be released from the post-oxidative effluents [55].

The typical compounds found in asphalt fumes include VOCs, polycyclic aromatic hydrocarbons (PAHs), volatile organosulfur and organonitrogen compounds (VSCs and VNCs), nitrogen oxides (NO<sub>x</sub>), sulfur oxides (SO<sub>x</sub>), CO<sub>2</sub> and carbon monoxide (CO), particulates, aliphatic and aromatic hydrocarbons, and oxygenated volatile organic compounds (O-VOCs). O-VOCs, involving alcohols,

ketones, aldehydes, esters, ethers, phenols, carboxylic acids, and their derivatives are very malodorous and toxic [23,56,57].

Strict environmental regulations imposed on refineries have led to a rising number of analytical procedures, allowing detailed identification of groups of compounds released into the atmosphere [56]. However, relatively little is known in detail about the presence of VOCs and semi-volatile organic compounds (SVOCs) in asphalt fumes because their content depends on crude oil and asphalt composition [23]. Furthermore, there is no standardized methodology for capturing and analyzing VOCs and SVOCs in asphalt fumes.

Classical analysis techniques have been used for compound identification, such as gas-liquid chromatography coupled to mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC), depending on the analyte. Kitto et al. [58] evaluated the emission of VOCs and SVOCs from hot asphalt mixtures by HPLC and GC/MS. HPLC analysis indicated the presence of naphthalene, acenaphthene, fluorene, phenanthrene, and anthracene as the most prevalent compounds. Benzene, toluene, ethylbenzene, and saturated carbon chains from 10 to 18 atoms were identified by gas-liquid chromatography (GC). Tang et al. [59] captured toxic fumes from asphalt preparations by solid-phase microextraction (SPME) and later identified the compounds desorbed by GC/MS, such as PAHs, fluorene (5.8 ng/ $\mu$ L), phenanthrene (12.9 ng/ $\mu$ L), 2-methyl-phenanthrene (10.1 ng/ $\mu$ L), and 9-methylphenanthrene (10.4 ng/ $\mu$ L), etc. Gasthauer et al. [34] characterized toxic fumes by GC/MS and evaluated the effect of the emission temperature. The authors tracked characteristic fragments of compound families, reporting naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, fluorene, phenanthrene, and anthracene, among others. Additionally, Wang et al. [60] identified PAHs in asphalt fumes by GC/MS, such as naphthalene (1.15 ng/ $m^3$ ), acenaphthylene (6.93 ng/ $m^3$ ), and 2-bromonaphthalene (22.02 ng/ $m^3$ ), etc. A recent study reported the reduction of airborne emissions and the identification of more than 200 volatile compounds by headspace-gas chromatography-mass spectrometry (HS-GC/MS) from WMA manufactured using organic waxes [8]. During the production of bitumens, large volumes of strongly toxic post-oxidative effluents are generated; these have to be treated and the content of individual groups of pollutants monitored to evaluate the effectiveness of treatment [55]. The determination of concentrations and concentration changes of VOCs [25], O-VOCs [55,56], VSCs [61], VNCs [62], carboxylic acids [63], and monoaromatic and PAHs [64] in wastewater has been described.

According to the above publications, efforts to produce new asphalt mixtures that are friendlier to the environment and to workers are being intensified. In this communication, we characterize and evaluate VOCs and SVOCs in fumes emitted from asphalt mixtures prepared at reduced production temperatures using clinoptilolite-modernite natural zeolite as an additive and RAP for partial replacement of natural aggregates (fluvial aggregates).

## 2. Materials and Methods

### 2.1. Asphalt Mixture Preparation and Fume Capture

Asphalt mixtures were designed in the laboratory according to the Marshall Method [65], following the approach for a surface layer, to obtain the optimum proportion of asphalt mix components. The mixtures were not compacted because this is not necessary for fume capture. Raw materials were mixed in a sealed cylindrical reactor (6 L) coupled to a manual stirring system to prevent fumes from leaking. Fluvial aggregates, mainly composed of dolomite, basalt, andesite, rhyolites, sandstone, quartz, and quartzite (12.5 mm sieve size; semi-dense type IV-A-12 aggregate gradation); conventional asphalt binder (CA-24), with absolute viscosity of 3077 P (60 °C, 300 mm Hg) and a density of 1.04 kg/ $m^3$ ; and natural clinoptilolite-modernite zeolite (Chemical composition: SiO<sub>2</sub>: 64.19%, TiO<sub>2</sub>: 0.51%, Al<sub>2</sub>O<sub>3</sub>: 11.65%, Fe<sub>2</sub>O<sub>3</sub>: 2.53%, MnO: 0.03%, MgO: 0.66%, CaO: 3.42%, Na<sub>2</sub>O: 0.75%, K<sub>2</sub>O: 1.60%, P<sub>2</sub>O<sub>5</sub>: 0.03%, PxC: 14.64%) were added to the reactor and treated according to the conditions provided in Table 1. Each asphalt mixture was prepared in triplicate. The RAP used came from milling works of surface course. In order to reduce the heterogeneity of the recycled mixtures, they were fabricated with two

fractions of RAP, as recommended by Solaimanian and Tahmoressi [66]. The RAP fractions used were 0/5 mm and 5/20 mm. The RAP gradation, the bitumen content for both RAP fractions and the characteristics of binder recovered from the RAP before fractioning, details of the fluvial aggregates, the asphalt binder used, and the mix design properties have all been published previously [67], and the research concluded that these warm mix asphalt and recycled warm mix asphalt performed well in rutting, cracking resistance, fatigue, and moisture damage tests.

**Table 1.** Raw materials and manufacturing temperatures for asphalt mixtures samples.

Mixture	Composition (g)				Natural Aggregates Temperature (°C)	Asphalt Binder Temperature (°C)	RAP Temperature (°C)	Production Temperature of Mixes (°C)
	Natural Aggregates	Asphalt Binder Added	Natural Zeolite	Reclaimed Asphalt Pavement (RAP)				
P-155	4.000	216	0	0	155	155	-	155
Z0.3-135	4.000	216	12	0	135	155	-	135
Z0.6-135	4.000	216	24	0	135	155	-	135
PR10-155	3600	207.6	0	400 (10% of the aggregates)	142	155	25	155
Z0.6-R10-125	3600	207.6	24	400 (10% of the aggregates)	142	155	25	125
PR20-155	3200	199.2	0	800 (20% of the aggregates)	169	155	25	155
Z0.6-R20-135	3200	199.2	24	800 (20% of the aggregates)	169	155	25	135
PR30-155	2800	194.4	0	1200 (30% of the aggregates)	202	155	25	155
Z0.6-R30-145	2800	194.4	24	1200 (30% of the aggregates)	202	155	25	145

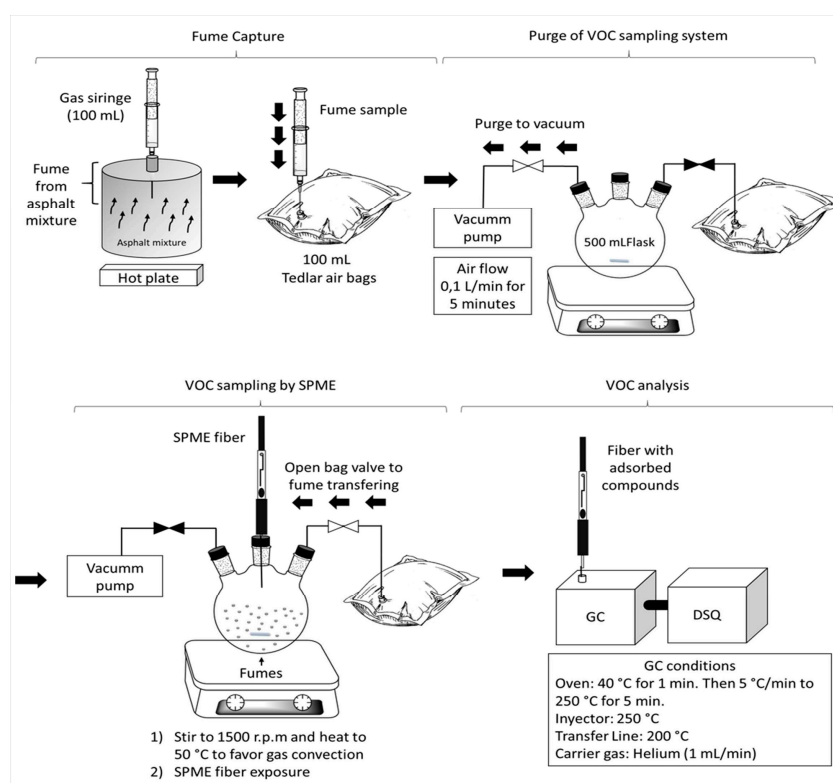
The mixtures were stirred and heated on a magnetic hot plate stirrer for 5 min and allowed to rest for 2 min before fume capture. The fumes (100 mL) were captured using a gas syringe and transferred to hermetic Tedlar gas sampling bags (SKC Inc., Pittsburgh, PA, USA) with a polypropylene valve (Figure 1). Three fume samples were collected from each asphalt mixture.

The mixtures presented in Table 1 are as follows: P-155: hot mix asphalt produced at 155 °C; Z0.3-135: warm mix asphalt with 0.3% natural zeolite produced at 135 °C; Z0.6-135: warm mix asphalt with 0.6% natural zeolite produced at 135 °C; PR10-155: hot mix asphalt with 10% RAP, produced at 155 °C; Z0.6-R10-125: recycled warm mix asphalt with 0.6% natural zeolite and 10% RAP, produced at 125 °C; PR20-155: hot mix asphalt with 20% RAP, produced at 155 °C; Z0.6-R20-135: recycled warm mix asphalt with 0.6% natural zeolite and 20% RAP, produced at 135 °C; PR30-155: hot mix asphalt with 30% RAP, produced at 155 °C; Z0.6-R30-145: recycled warm mix asphalt with 0.6% natural zeolite and 30% RAP, produced at 145 °C. For all mixes, the asphalt binder was added at 155 °C and the RAP at ambient temperature (25 °C). For mixes with RAP, overheating of the natural aggregates was necessary. Contact between the RAP and the overheated natural aggregates produced the desired mixing temperature.

## 2.2. Sampling of VOCs and SVOCs from Asphalt Mixture Fumes by SPME

The chemical contents of the asphalt mixture fumes were sampled using the system shown in Figure 1. A side valve on a 500-mL three-neck round-bottom flask containing a magnetic bar was linked to an air pump by a Teflon hose. The central neck was fitted with an exchangeable screw-cap and Teflon septum. The other side valve was connected by a Teflon hose to a Tedlar gas sampling bag containing a sample of fumes. The three-neck round-bottom flask was purged to vacuum using the pump. The valve connected to the fume sample bag was then opened, transferring the fume sample to the evacuated round-bottom flask. The fume was stirred (1500 rpm) using a

magnetic stirrer bar and heated to 50 °C to favor convection. Sampling was carried out with a divinylbenzene/polydimethylsiloxane (DVB-PDMS)-coated fiber (65 µm) and a manual SPME holder (Supelco Analytical, Bellefonte, PA, USA). This fiber is suitable for applications of SPME for non-polar organic compounds, such as benzene, toluene, ethylbenzene and xylenes, and polycyclic aromatic hydrocarbons (PAHs), etc. [68]. The SPME fiber was exposed to the fume sample for 30 min by manual insertion through the central neck septum of the round-bottom flask. Finally, the SPME fiber was inserted into the CG injection port for 1 min at 250 °C for sample desorption. The process was repeated three times for each fume sample.



**Figure 1.** Diagram of fume capture and volatile organic compound (VOC) and semi-volatile organic compound (SVOC) sampling system.

### 2.3. Analysis of Asphalt Mixture Fumes

Fume samples were analyzed by GC and GC/MS using a Thermo Electron Model Focus GC (Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled to a DSQ Thermo Electron quadrupole mass spectrometer with an integrated data system (Xcalibur 2.0, Thermo Fisher Scientific Inc., Waltham, MA, USA). A BPX-5 capillary column of 30 m length (0.25 µm film thickness × 0.25 mm i.d., SGE Forte, Trajan Scientific and Medical, Ringwood, VIC, Australia) was used for compound separation. The operating conditions were as follows: on-column injection; temperature of the injector, transfer line, and detector, 250 °C; oven temperature program: hold at 40 °C for 2 min, increase to 250 °C at 5 °C min<sup>-1</sup>, and next hold at 250 °C for 5 min. He at 1.00 mL min<sup>-1</sup> was the carrier gas. The mass detector employed an ionization energy of 70 eV. Recording conditions employed a scan time of 1.5 s and a mass range of 30 up to 400 amu. The compounds were identified by comparison of their mass spectra with those in the NIST ver. 2.0 library database (NIST, Gaithersburg, MD, USA) and by comparison of their calculated retention index with those reported in the literature [69] for the same type of stationary phase. Calculated retention indices were determined by means of the retention time of C9–26 n-alkane standards (100 µg/mL in hexane) (Sigma-Aldrich, St. Louis, MO, USA) using the equation described by Kovats and Keulemans [70].

#### 2.4. Statistical Analysis

The statistical software Statistix 10 (Tallahassee, FL, USA) was used to analyze the data. The Shapiro–Wilk Test was used to test whether data conform to a normal distribution. When data were normally distributed, the differences in the abundances of groups of VOCs and SVOCs emitted by different asphalt mixtures were analyzed using a one-way ANOVA test ( $p \leq 0.05$ ) with a post hoc Tukey HSD test. The results were expressed as means and their corresponding standard errors.

### 3. Results and Discussion

Volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) in fumes from warm mix asphalts produced using natural zeolite and RAP were characterized and evaluated. Between 57 and 81 compounds were identified in fumes captured from the asphalt mixtures, corresponding to 70.8%, 76.8%, 70.6%, 79.3%, 77.9%, 74.8%, 76.5%, 74.3%, and 73.3% of the compounds detected in P-155, Z0.3-135, Z0.6-135, PR10-155, Z0.6-R10-125, PR20-155, Z0.6-R20-135, PR30-155, and Z0.6-R30-145, respectively. The compound identification compiled in Table 2 was confirmed by comparing the calculated retention indices with those available in the literature [69]. In general, the chemical compounds identified in sample fumes were saturated and unsaturated aliphatic hydrocarbons, cyclic hydrocarbons, aromatic and chlorinated compounds, alcohols, aldehydes, and ketones. Saturated aliphatic hydrocarbons were the principal class of compound emitted in the fumes, representing over 43.7% of the total compounds detected in all samples, which is consistent with the literature concerning VOC formation from bitumen production [23]; they were followed by aromatic compounds (6.1% up to 10.5%) and alkenes (4.5% up to 8.1%), as shown in Figure 2. Heptane, 2-methylheptane, octane, 2,3-dimethylheptane, 4-methyloctane, nonane, 3-ethyl-2-methylheptane, decane, and undecane were the most abundant compounds among all samples, as also reported by Wang et al. [71]. The predominance of saturated aliphatic hydrocarbons could indicate fewer oxidized bitumens, considering the partial thermal cracking and further transformations when bitumen mass was deposited on heating elements [23].

The saturated and unsaturated aliphatic hydrocarbons were C5–C16 and C5–C11 linear and branched alkanes and alkenes, respectively. Aromatic compounds included methyl- and ethyl-substituted C6 compounds, such as toxic benzene [72], toluene [73], and xylene [74] derivatives. Cyclic compounds included methyl- and ethyl-substituted C4–C6 compounds and toxic chlorinated compounds, namely tri-chlorine and tetra-chlorine C1–C2 compounds [75] (Table 2). Chemical compounds in these fume profiles are similar to those described by Boczkaj et al. [23], in which VOCs from bitumens were analyzed by dynamic head-space gas chromatography coupled to mass spectrometry (DH-GC-MS). Boczkaj et al. [23] identified forty-four compounds at most, of which alkanes and aromatic compounds were the most abundant. Fifteen of those 44 compounds identified were VOCs and SVOCs identified in fumes in the present study, including C6–C14 saturated aliphatic hydrocarbons, toluene, and benzene derivatives. Based on studies of bitumen effluents, it is evident that very sensitive, selective detectors are required for detailed analysis of the VNCs and VSCs in asphalt fumes at low concentration levels by GC. For a large number of VNCs, detectors such as nitrogen-phosphorus detector (NPD) [76], chemiluminescent nitrogen detector (CLND) [77], or surface ionization detector (SID) [78] must be used; while flame photometric detector (FPD) [79,80], pulsed flame photometric detector [24,81], sulfur chemiluminescence detector [82], or atomic emission detector [83] must be used for sulfur compounds [61,62].

**Table 2.** Chemical composition of fumes from WMA and HMA by GC/MS.

N°	RT	RI calc	Compound	Concentration in Mixtures (ppm)								
				P-155	Z0.3-135	Z0.6-135	PR10-155	Z0.6-R10-125	PR20-155	Z0.6-R20-135	PR-30-155	Z0.6-R30-145
1	1.38	-	Pentane	-	-	-	-	3.86	-	2.86	-	2.41
2	1.66	-	2-Methylpentane	-	1.28	2.97	-	-	1.38	2.24	1.40	1.25
3	1.73	-	3-Methylpentane	-	-	1.09	-	0.47	-	0.63	-	0.53
4	1.75	-	2-Methyl-1-pentene	-	2.56	2.51	-	1.33	-	-	1.56	-
5	1.79	-	<i>cis</i> -1-Ethyl-2-methyl cyclopropane	-	-	-	-	-	2.62	1.40	1.83	-
6	1.84	-	Hexane	6.28	8.66	8.14	3.94	7.79	5.49	6.00	6.38	4.68
7	1.88	-	Trichloromethane	10.06	5.99	12.12	5.15	23.00	2.55	4.27	7.77	9.43
8	2.45	-	2-Methylhexane	3.99	2.60	5.50	12.55	2.29	6.29	8.47	2.48	2.57
9	2.58	-	3-Methylhexane	5.80	3.68	4.77	6.56	4.06	4.71	3.88	5.62	2.75
10	2.75	-	1-Heptene	6.09	4.55	5.77	3.88	4.92	4.71	4.40	5.00	3.09
11	2.91	-	Heptane	18.92	12.64	16.44	10.98	13.46	13.43	12.35	14.53	11.03
12	2.99	-	2-Heptene	-	2.26	1.39	-	2.34	-	1.24	2.15	1.68
13	3.12	-	3-Heptene	-	0.57	0.59	-	0.53	0.21	0.44	0.59	0.43
14	3.22	-	Methylcyclohexane	2.38	1.80	2.07	1.54	1.83	2.00	1.64	2.13	1.57
15	3.29	-	Methyl isobutyl ketone	1.06	1.20	1.24	-	0.63	0.39	0.44	0.66	0.35
16	3.57	-	1,2,4-Trimethyl cyclopentane	-	0.06	-	-	-	4.06	3.86	-	-
17	3.77	-	3-Methylpentanal	7.25	4.78	4.44	-	4.46	5.49	3.67	-	-
18	3.87	-	Toluene	6.20	6.05	4.48	5.62	5.59	3.89	3.43	6.95	3.40
19	3.99	-	3-Ethyl-2-methyl pentane	4.41	4.55	4.96	4.23	4.06	4.63	3.76	5.38	4.16
20	4.10	-	2-Methylheptane	16.47	12.21	14.25	10.52	12.18	13.47	11.72	14.65	11.23
21	4.26	-	3-Methylheptane	9.62	7.51	7.97	2.46	7.22	8.20	5.70	9.60	6.97
22	4.40	-	Hexanal	4.03	1.85	1.35	5.89	2.19	1.98	1.36	4.16	1.23
23	4.50	-	2-Methyl-1-heptene	3.19	2.66	2.40	2.01	2.59	2.35	2.03	3.44	2.00
24	4.60	-	1-Octene	7.89	6.34	5.65	5.29	6.21	5.58	4.77	6.90	4.52
25	4.82	-	Tetrachloroethylene	-	130.40	18.63	-	-	0.66	0.56	-	-
26	4.87	-	Octane	33.63	22.23	24.74	24.05	27.88	23.25	19.63	29.48	18.97
27	5.02	-	3-Octene	-	-	-	-	3.40	2.94	2.23	-	2.34
28	5.15	-	2-Octene	1.79	1.44	1.04	-	1.19	1.18	0.83	1.56	0.94
29	5.32	-	4-Hydroxy-4-methyl-2-pentanone	4.79	4.16	3.82	5.99	11.48	3.04	7.06	3.48	5.39
30	5.44	-	2,4-Dimethylheptane	2.22	1.64	1.72	-	1.70	1.91	1.72	2.12	1.82
31	5.60	-	2,6-Dimethylheptane	7.90	2.90	2.76	-	3.14	2.98	2.71	3.48	2.55
32	5.70	-	1,1,3-Trimethyl cyclohexane	5.64	4.56	3.54	-	3.53	3.73	2.78	4.85	3.39
33	5.81	-	3,5-Dimethylheptane	-	1.09	-	-	0.96	1.16	0.91	1.19	1.03
34	6.31	-	2,3-Dimethylheptane	23.27	19.55	13.21	19.39	17.64	14.84	12.12	22.24	12.53

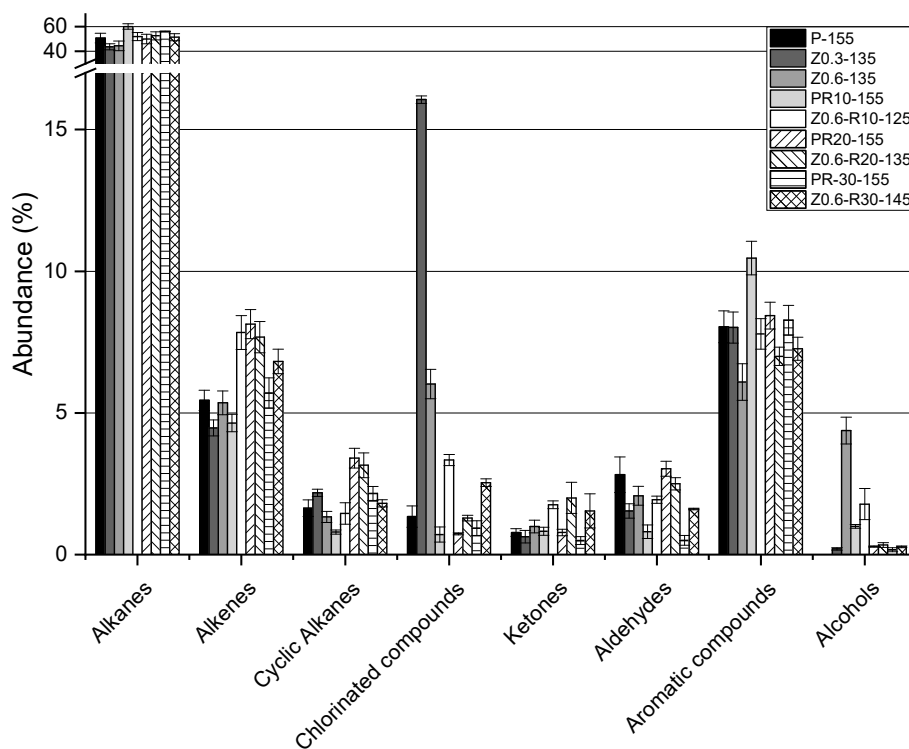
Table 2. Cont.

N°	RT	RI calc	Compound	Concentration in Mixtures (ppm)								
				P-155	Z0.3-135	Z0.6-135	PR10-155	Z0.6-R10-125	PR20-155	Z0.6-R20-135	PR-30-155	Z0.6-R30-145
35	6.54	-	4-Methyloctane	15.06	11.52	8.96	6.31	10.51	9.93	8.14	12.89	8.37
36	6.74	-	3-Methyloctane	12.70	8.51	7.45	9.71	9.16	8.55	6.82	11.59	7.13
37	6.90	-	p-Xylene	5.31	4.63	2.64	5.00	4.49	2.84	2.13	5.49	2.25
38	7.07	-	Heptanal	9.88	6.45	4.83	-	6.70	5.80	4.34	-	4.75
39	7.21	-	1-Nonene	9.25	7.24	4.74	7.04	7.88	5.55	4.55	8.84	4.48
40	7.36	-	2-Butoxyethanol	-	1.68	22.34	7.25	12.29	1.24	1.27	1.46	1.02
41	7.55	900	Nonane	44.14	30.57	21.98	28.07	30.83	23.21	20.67	42.23	22.32
42	7.65	904	4-Nonene	4.58	2.70	1.63	-	2.91	2.05	1.81	4.40	2.25
43	7.83	911	3,7-Dimethyl-1-octene	1.54	-	-	1.55	1.27	1.00	1.88	1.09	-
44	8.26	928	Propylcyclohexane	2.47	2.88	1.19	-	1.64	1.18	1.02	2.83	1.10
45	8.31	930	3,5-Dimethyloctane	2.82	2.03	1.37	-	2.07	1.69	1.36	3.12	1.41
46	8.56	939	2,6-Dimethyloctane	12.73	9.60	6.90	10.51	9.62	7.66	6.16	14.37	6.59
47	8.76	946	3-Ethyl-2-methyl heptane	16.58	13.42	8.90	12.88	13.45	9.94	8.02	18.03	8.62
48	8.88	950	4-Methyl-1-octene	3.67	3.04	1.82	3.89	3.15	2.06	1.67	4.17	1.81
49	8.93	952	1-Ethyl-3-methyl benzene	3.42	10.97	1.42	6.09	3.96	1.37	1.21	3.89	1.33
50	9.04	955	1-Ethyl-2-methyl benzene	10.03	2.80	2.02	10.95	2.92	2.04	1.65	5.38	1.91
51	9.37	966	4-Methylnonane	11.69	12.11	5.71	11.96	10.88	5.16	3.55	14.52	4.00
52	9.47	970	2-Methylnonane	10.76	10.44	5.82	11.22	10.42	5.84	5.05	11.85	4.87
53	9.65	975	3-Methylnonane	6.69	6.92	3.15	6.32	6.13	3.35	2.77	8.49	2.69
54	9.89	983	1-Ethyl-2-methyl benzene	7.49	10.43	5.13	13.01	9.15	4.08	3.53	14.44	2.62
55	10.15	991	2-Methyl-1-nonene	-	-	-	-	3.17	2.07	1.26	-	-
56	10.16	991	1-Decene	3.72	5.18	1.50	6.18	4.58	1.71	1.33	4.35	1.35
57	10.29	995	1-Methyl-2-propyl cyclohexane	-	5.29	-	-	1.31	0.69	0.55	2.56	0.61
58	10.41	999	cis-3-Decene	-	-	-	4.20	2.98	1.32	1.14	4.23	1.08
59	10.54	1003	Decane	38.29	37.00	19.42	42.08	38.18	16.47	14.80	57.26	14.48
60	10.73	1011	1,2,3-Trimethyl benzene	2.81	-	-	1.27	0.84	0.72	3.54	0.69	-
61	11.24	1029	2,6-Dimethylnonane	11.31	11.11	6.02	12.30	10.02	4.45	3.59	22.17	4.59
62	11.46	1037	Pentylcyclopentane	1.52	2.91	-	3.60	1.33	0.50	0.46	2.98	0.00
63	11.67	1044	3,7-Dimethylnonane	2.24	3.65	1.10	6.24	2.19	-	0.69	5.73	0.68
64	12.26	1064	5-Methyldecane	4.41	5.75	1.04	7.19	4.78	1.61	1.32	7.98	1.45

Table 2. Cont.

N°	RT	RI calc	Compound	Concentration in Mixtures (ppm)								
				P-155	Z0.3-135	Z0.6-135	PR10-155	Z0.6-R10-125	PR20-155	Z0.6-R20-135	PR-30-155	Z0.6-R30-145
65	12.35	1067	2,3-Dimethylnonane	4.53	6.68	1.75	8.98	5.30	1.54	1.25	8.48	1.38
66	12.46	1070	2-Methyldecane	5.94	8.58	1.96	11.39	6.65	1.97	1.21	11.37	1.81
67	12.64	1076	3-Methyldecane	5.58	7.59	2.29	10.16	5.99	2.18	1.70	9.77	1.79
68	13.30	1096	1-Undecene	-	-	-	-	5.82	1.85	1.08	-	-
69	13.51	1103	Undecane	24.91	35.09	7.14	49.90	27.63	9.31	7.48	41.81	7.79
70	14.37	1135	2,3-Dimethyldecane	-	-	-	11.16	5.47	1.54	1.25	7.50	1.13
71	14.51	1140	1,2,4,5-Tetramethyl benzene	2.28	5.77	1.10	6.12	2.86	0.98	0.69	3.77	0.52
72	15.17	1163	2,6-Dimethyl undecane	-	-	-	6.44	2.83	-	0.48	-	0.42
73	15.26	1166	4-Methylundecane	-	3.39	-	5.97	2.76	0.75	0.64	2.45	0.40
74	15.37	1169	2-Methylundecane	1.87	3.25	0.79	5.01	2.17	0.67	0.50	2.40	0.37
75	16.05	1191	2,3-Dimethyl undecane	-	3.82	-	3.32	1.63	0.73	0.53	-	-
76	16.21	1197	1,2-Benzisothiazole	-	1.27	0.10	4.94	2.95	4.15	-	-	0.85
77	16.43	1204	Dodecane	9.02	13.71	2.29	23.43	10.79	1.00	3.43	10.23	3.14
78	16.77	1218	2,6-Dimethyl undecane	3.06	5.38	2.69	5.58	3.73	-	0.63	0.98	0.60
79	18.43	1278	2-Butyl-1-octanol	1.59	0.61	3.08	1.33	0.59	0.23	0.49	0.21	-
80	19.09	1301	Tridecane	2.41	2.98	0.83	5.52	2.38	1.17	0.73	1.19	0.47
81	21.66	1400	Tetradecane	0.33	0.35	0.26	0.86	0.46	-	0.25	0.13	0.06
82	24.11	1500	Pentadecane	-	0.12	0.17	0.37	0.20	-	0.28	-	0.34
83	26.38	1597	Hexadecane	-	-	-	-	0.08	-	-	-	0.24
Identified compounds (%)				70.79	76.76	70.63	79.32	77.86	74.76	76.52	74.34	73.29

RT: Retention time (min); RIcalc: Calculated retention index; %: Relative abundance, considering only the compounds identified in each extract.

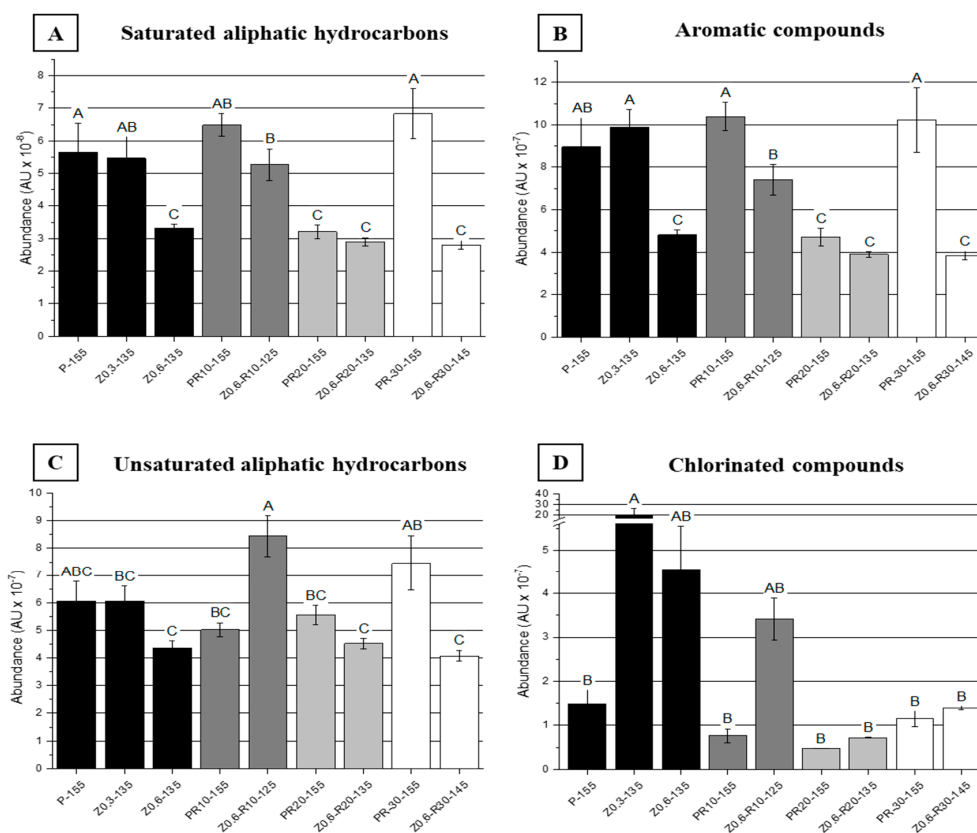


**Figure 2.** Abundance of chemical compounds present in fumes from warm mix asphalt. Values indicate mean + standard error (SE). %: Calculated considering compounds detected.

A similar study has been carried out to analyze VOCs in air from the paving and compaction stages of HMA; twenty-eight compounds were identified in the air samples, of which toluene, 4-ethyltoluene, xylene, 1,3,5-trimethylbenzene, and ethylbenzene were the most abundant [84]. All twenty-eight compounds were also identified in the asphalt mixture fumes analyzed in the present study. Additionally, Chong et al. [84] described the presence of chlorinated compounds such as tetrachloroethylene, chloromethane, and 1,2-dichloroethane, among many others, of which only tetrachloroethylene was identified in the present study. Moreover, Sharma and Lee [16] determined the presence of other chlorinated compounds such as di- and trichloroethane derivatives, chloroform, carbon tetrachloride, and tri- and tetrachloroethylene derivatives in atmospheric samples taken from HMA and WMA, of which only chloroform (trichloromethane) was identified in the present study.

Although polycyclic aromatic hydrocarbons (PAHs) are commonly present in hot mix asphalts [23,85], none were detected in the present study even though DVB/PDMS fibers were used to trap volatile compounds. Fibers containing DVB and PDMS layers have been found to be suitable for PAH analyses [59,67,86,87]. Quantification of PAHs is a complex, expensive, and time-consuming process due to the hydrophobicity and low water solubility of PAHs and their propensity for low recovery levels due to losses during sampling and sample preparation [87]. Gas-phase PAH sampling and sample preparation is usually performed by trapping on different types of sorbent materials and filters such as polyurethane foam (PUF) [88,89], XADs [90], Teflon [91], and Carboxypack C [92], and by subsequent extraction with organic solvents. Thermal desorption or solid phase microextraction (SPME) are widely used as an alternative to those methods [87]. Currently, SPME-based methods are used for sampling and quantitative analysis of PAHs in water [93], soil [94–97], and air [98]. The SPME-based method involves different PAH capturing methods followed by thermal extraction of analytes using a thermogravimetric analyzer to Tedlar bags and determination of concentration by SPME in a conventional exposed fiber coating mode [99], which is comparable to the methodology used in the present study (Figure 1). Exposed SPME fibers have been used for determining PAHs directly in tailpipes [98,100]. The absence of PAHs in the sample could indicate that the preparation method avoids production of these compounds.

VOCs and SVOCs listed in Table 2 were classified on the basis of their chemical structure into seven groups of chemical compounds. The major groups of VOCs and SVOCs emitted by the prepared asphalt mixtures are compared in Figure 3.



**Figure 3.** Comparison of groups of VOCs and SVOCs emitted by warm mix asphalt. (A) Saturated aliphatic compounds; (B) Aromatic compounds; (C) Unsaturated aliphatic compounds; (D) Chlorinated compounds. Values indicate mean + SE. Different letters indicate significant differences based on the Tukey HSD test ( $p \leq 0.05$ ).

In general, asphalt mixtures prepared at lower temperatures emitted fewer saturated and unsaturated aliphatic hydrocarbons and aromatic compounds than asphalt mixtures produced at higher temperatures. The addition of zeolite allows lower manufacturing temperatures to be used [18,19,101], and asphalt mixtures containing 0.6% natural zeolite produced fewer saturated and unsaturated aliphatic hydrocarbons and aromatic compounds than mixtures containing 0–0.3% zeolite—although Z0.6-R10-125 emitted significantly more unsaturated aliphatic hydrocarbons than the standard mixture (zeolite-free PR10-155). Additionally, among the asphalt mixtures prepared with RAP, all mixtures containing 0.6% natural zeolite produced fewer saturated and unsaturated aliphatic hydrocarbons and aromatic compounds than hot mixtures, excepting the unsaturated aliphatic hydrocarbons emitted by Z0.6-R10-125. Compared to standard mixtures (P-155, PR10-155, PR20-155, and PR30-155), saturated aliphatic hydrocarbons and aromatic compounds emissions increased slightly when RAP was added at concentrations of 10% and 30% but significantly decreased when 20% RAP was added. However, the incorporation of 0.6% natural zeolite into the mixture with 10–30% RAP produced a substantial decrease in emissions. These results are consistent with the incorporation of synthetic zeolites into asphalt mixtures to decrease the production temperatures and thus produce fewer fumes; this agrees with Report FHWA/OH-2009/08 of the Ohio Research Institute for Transportation and the Environment [102], in which the production of VOCs from three WMAs were measured. The WMAs were prepared with the following different materials: Aspha-min (contains zeolite with 20–21%

of water), Sasobit (a sasol wax, commercially known as FT hard wax), and Evotherm (a chemical material not described by the authors). Aspha-min WMA, containing zeolite at 0.3% by mass of the mix, and Sasobit WMA both show substantial reductions in VOCs of 62.8% and 51.3%, respectively, compared to conventional HMA. On the other hand, Evotherm WMA shows a substantial increase in VOCs, over two and a half times compared to conventional HMA [102]. Similarly, Sharma and Lee [16] demonstrated that the VOCs identified in atmospheric samples taken from HMA and WMA decreased with the use of synthetic zeolites as additives, compared to VOC emissions from mixes without additives at 180, 140, and 120 °C. The reduction in VOC emissions increased continuously as the zeolite dosage was increased from 2% to 6%.

In the present study, emissions of saturated aliphatic hydrocarbons were reduced by 3.3% (Z0.3-135) up to 58.9% (Z0.6-R30-145); unsaturated aliphatic hydrocarbons by 0.1% (Z0.3-135) up to 45.3% (Z0.6-R30-145); and aromatic compounds by 17.5% (Z0.6-R20-135) up to 62.3% (Z0.6-R30-145) in warm mix asphalts and zeolite-amended WMAs. On the other hand, WMAs produced greater emissions of chlorinated compounds (Figure 3) than the hot mixtures, from 21.3% (Z0.6-R30-145) to 1256.0% (Z0.3-135), probably because the competitive adsorption of water significantly decreased the adsorption by zeolites of chlorinated compounds such as tetrachloroethylene [103,104]. However, all the asphalt mixtures studied produced fewer chlorinated compounds compared with the literature [16,84].

Thus, considering the lower production of toxic aromatic and chlorinated compounds compared with the literature, and the fact that PAHs were not detected, the WMAs prepared in the present study should be less harmful to paving workers and the environment than HMA.

#### 4. Conclusions

In this research, asphalt mixtures modified with clinoptilolite-modernite natural zeolite and RAP reduced the temperatures required for asphalt mixture production, as reported by Topal et al. [18] and Wozzuk and Franus [13,19], resulting in the decreased emanation of major VOCs and SVOCs, and thus toxic fumes. Emissions of saturated and unsaturated aliphatic hydrocarbons and aromatic compounds were reduced in warm mix asphalts and zeolite-amended WMAs. Specifically, Z0.6-R20-135 and Z0.6-R30-145 produced the lowest emissions of saturated and unsaturated aliphatic hydrocarbons and aromatic compounds. The absence of polycyclic aromatic hydrocarbons indicated that the preparation technique would avoid the production of these toxic compounds; however, further experiments are needed to establish this conclusion. Although WMAs produced greater emissions of chlorinated compounds than the hot mixtures, all the asphalt mixtures studied produced fewer chlorinated compounds compared with the literature [16,84]. This is one of the few reports showing the chemical composition released from asphalt fumes. All the results indicate that manufacturing warm mix asphalts using natural zeolite and RAP is a valuable alternative to hot mix asphalts because it is both more environmentally friendly and less harmful to the health of paving workers.

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