Supplementary Information: VOC Emissions by Fresh and Old Asphalt Pavements at Service Temperatures: Impacts on Urban Air Quality

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1. Analysis of STA and LTA Asphalt Mixture Samples

Figure S1 presents the visual aspect of the asphalt mixture samples collected. The fresh material (**Figure S1**, left) was collected in a loose state (that is to say, without prior compaction), while the old pavement specimen (**Figure S1**, right) was compacted after laying, and was in use for roughly 30 years before collection.

Figure S1: Left, a STA asphalt mixture sample; its diameter is roughly of 13 cm, and its thickness of 1.5 cm. Right, LTA asphalt mixture samples; their dimensions are 20 cm × 8.5 cm and 12 cm × 8.5 cm, respectively, and their thickness is of 1.3-1.7 cm.

To get a deeper understanding of the bituminous binders in our samples, we have extracted them from the asphalt mixtures.

1.1. Extraction of Binders from Fresh and Old Asphalt Mixture Samples

Extraction entails separating the asphalt binder from the mineral parts using a chlorinated solvent [Ziyani *et al.*, 2017], [Mikhailenko *et al.*, 2020]. In the present work, dichloromethane is used because the final step of solvent evaporation takes place at atmospheric pressure following a standard procedure [EN 12697-3+A1], [Mouillet *et al.*, 2011]. The asphalt mixtures are slowly heated at 130°C for 30 minutes to soften the bitumen film binding the aggregates. Then, dichloromethane is added to the mixture to dissolve bitumen. Centrifugation cycles allow removal of all mineral parts from the solution. Lastly, a simple distillation is conducted around 45°C and then up to 85°C to evaporate totally the dichloromethane. The bitumen sample collected can then be analyzed.

1.2. Infrared Analysis of Fresh and Old Binders

Bitumen aging can be assessed by measuring its oxidation state, via the formation of oxygen-bearing groups. Fourier Transform Infrared Spectroscopy (FTIR) is commonly used to assess the variations of the carbonyl and sulfoxide groups in bitumen [Marsac *et al.*, 2014]. We have characterized the extracted binders using a Nicolet™ iS™ 5 FTIR spectrometer. The Attenuated Total Reflection (ATR) mode is used, because little sample preparation is required. ATR spectra are recorded from 4000 to 400 cm^{-1} with 32 scans, at a resolution of 4 cm^{-1}. **Figure S2** shows the ATR spectra of binders extracted from old asphalt (red), and from fresh asphalt (black). The bitumen extracted from an old asphalt mixture displays more intense carbonyl (at 1698 cm^{-1}) and sulfoxide (at 1021 cm^{-1}) stretching modes than a bitumen extracted from a fresh asphalt mixture, highlighting the higher oxidation state of old bitumen. The other IR bands observed are assigned to: the CH_2 and CH_3 stretching modes, at 2920 cm^{-1} (asymmetric component) and 2850 cm^{-1} (symmetric component); the C=C stretching mode at 1600 cm^{-1}; the CH_2 and CH_3 deformation modes, at 1456 cm^{-1} and 1476 cm^{-1}; the SO_2 stretching mode at 1305 cm^{-1}; the CH deformation modes of aromatic carbons, at 875 cm^{-1}, 810 cm^{-1}, and 746 cm^{-1}; and the deformation mode of -$(CH_2)_n$- groups at 721 cm^{-1} [Lamontagne *et al.*, 2001], [Weigel and Stephan, 2018].

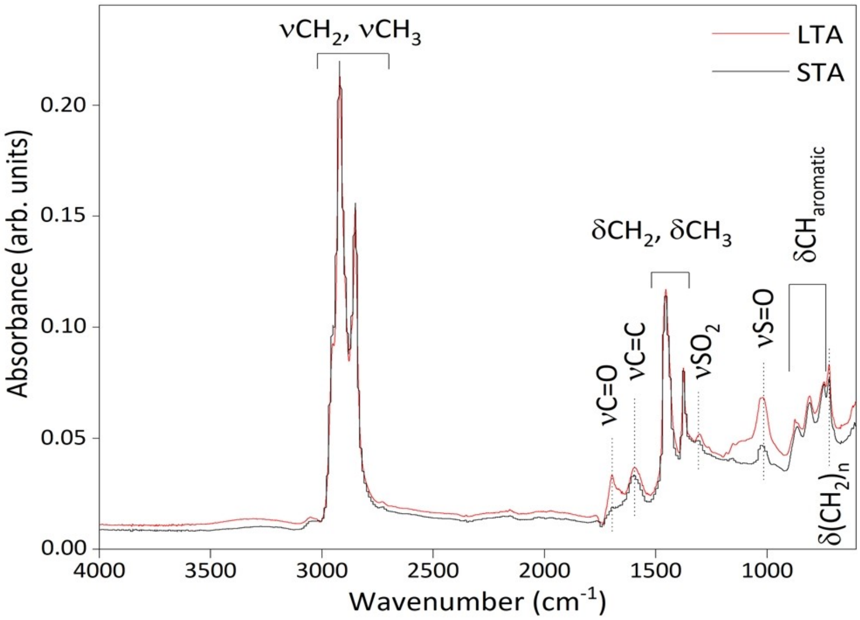


Figure S2: ATR spectra of binders extracted from the fresh asphalt mixture (STA) in black, and from the old asphalt mixture (LTA) in red. The spectra are recorded at room temperature, with a resolution of 4 cm^{-1}.

Integration of the peaks at 1698 cm^{-1} (νC=O) and 1025 cm^{-1} (νS=O) confirms the higher area of carbonyl and sulfoxide vibration bands in the old bitumen, compared to fresh bitumen. Therefore, the binder from the old asphalt mixture is more oxidized than the binder from the fresh asphalt mixture.

From this, we assume that VOCs present in the bitumen are different in fresh and old asphalt mixtures, leading to qualitatively and quantitatively different VOC emissions.

1.3. Simulated Distillation of Fresh and Old Binders

The extracted binders have also been characterized by simulated distillation; the experiments have been carried out by Intertek OCA France Caleb Brett. Simulated distillation is mostly used for the analysis of petroleum products and has been used here to determine the volatile fractions present in the bituminous binders of our samples. The boiling temperature range of petroleum products is determined by capillary gas chromatography using flame ionization detection, according to a standard procedure [EN 15199-2]. Experiments were carried out as follows: bitumen samples are dissolved in carbon disulfide (CS_2), the soluble part is injected in the column for analysis. The injector is heated to 400°C and subsequently to 750°C following a linear temperature ramp. Compounds of decreasing volatility are vaporized with increasing temperatures and are eluted with the carrier gas. The eluted products are detected by flame ionization.

Table S1 gathers the results of the simulated distillations for fresh and old binders. The initial boiling temperature of the fresh asphalt mixture binder is 382°C, 13°C lower than that of old asphalt mixture binder. 1% of the mass of the fresh binder has evaporated at 401°C whereas, this is achieved at 427°C for the old mix binder. At 750°C, the simulated distillation is stopped; the two bitumens are not completely eluted and the evaporated mass of fresh and old binders are 74.5% and 73.5%, respectively. The fresh binder therefore has a slightly higher concentration of light compounds.

Table S1: Results of the simulated distillation of binders extracted from fresh and old asphalt mixtures.

	Binder from fresh asphalt mixture	**Binder from old asphalt mixture**
Initial boiling point (°C)	382	395
1% mass	401	427

(°C)		
73% mass (°C)	729	745
Evaporated binder mass at the end of distillation (750°C) (% in mass)	74.5%	73.5%

Calibration of a gas chromatograph with various alkanes allows association of boiling points with elution times. The obtained chromatograms show the evolution of the mass of evaporated product as a function of retention time. They are displayed on **Figure S3** for fresh and old binders. The chromatograms show that fresh bitumen contains more low-carbon compounds (C20, C24, C32) than old bitumen (retention time between 10 and 20 minutes). At longer retention times (between 21 and 40 minutes), the old binder displays a larger concentration in high-carbon compounds (C40, C70, C120). Fresh and old asphalt mixtures' binders are composed of different fractions of light and heavy compounds with different volatilities. It certainly has an impact on the measured VOC emissions.

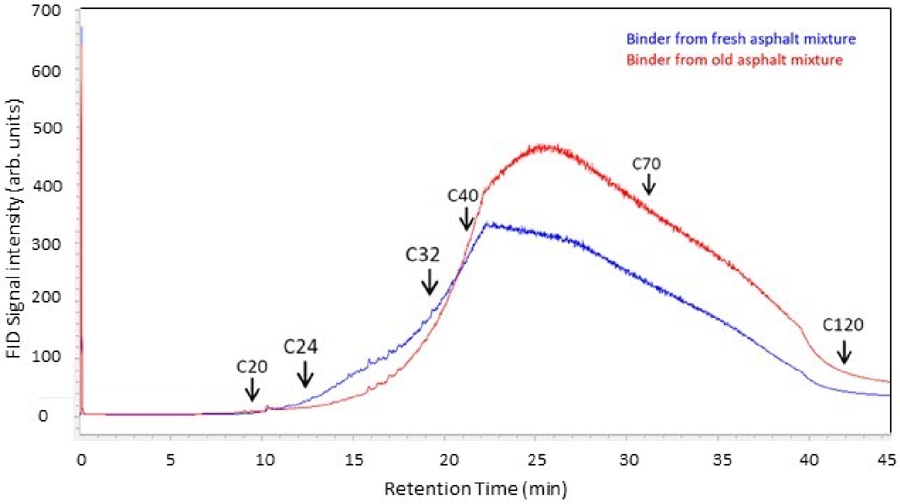


Figure S3: FID signal recorded as a function of retention time during the analysis of the binders extracted from the fresh asphalt mixture (blue) and from the old asphalt mixture (red).

2. Calibration of the GC-MS/FID

To calibrate the quantitative response of the GC-MS/FID instrument used to study the emissions of asphalt mixtures, Carbotrap 202 tubes are doped with 1 µL of three solutions containing 9 hydrocarbons of interest with known concentrations: toluene, octanal, decanal, dodecane, tridecane, tetradecane, pentadecane, 2-ethyl-1-hexanol, and 1-octene. Concentrations of these species used for calibration are displayed in **Table S2**; the three solutions are studied in triplicate. The response factors of the FID to the species of the calibration are determined from the slope of the peak area vs. concentration plot; each datapoint represents the average value of a triplicate. The response factors of the compounds absent from the calibration are estimated using on the Effective Carbon Number method [Szujelko *et al.*, 2013].

Table S2: Mass (ng) of the nine compounds in the three 1 µL solutions used for calibration of the GC-MS/FID.

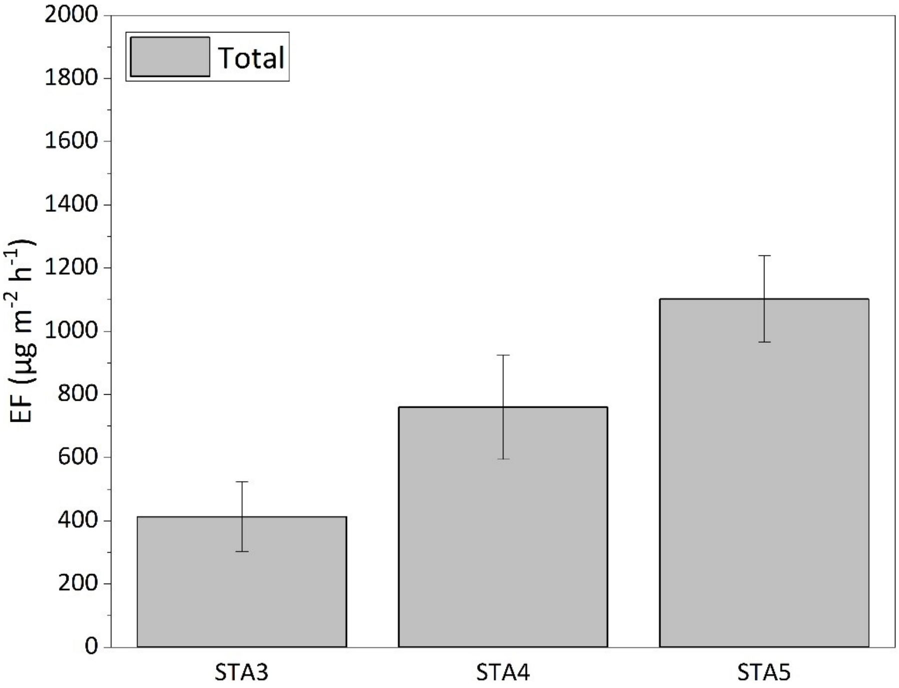
Solution # **Compound**	1	2	3
Toluene	5.58	90.38	140.59
Octanal	6.33	102.60	159.61
Decanal	4.75	76.97	119.73
Dodecane	4.72	76.42	118.89
Tridecane	4.79	77.69	120.85
Tetradecane	4.74	76.77	119.42

Pentadecane	4.70	76.21	118.56
1-Hexanol, 2-ethyl	5.21	84.50	131.45
1-Octene	4.65	75.34	117.20

3. Repeatability of Total VOC EF measurements of STA and LTA samples at 50°C

To investigate the repeatability of our results, we studied the total VOC emissions of three STA and three LTA asphalt mixtures at 50°C, under dry (RH = 0.1%) and dark conditions. The results obtained with PTR-ToFMS and GC-MS/FID are presented on **Figures S4** and **S5**, respectively.

Figure S4 shows the dispersion of total VOC EFs recorded with PTR-ToFMS during experiments with three different samples. Note that the samples have the same origin, described in **section 2.1.1**. The total VOC EF of STA samples (top) varies by a factor of 2.7, and of LTA samples (bottom), by a factor of 3.4.



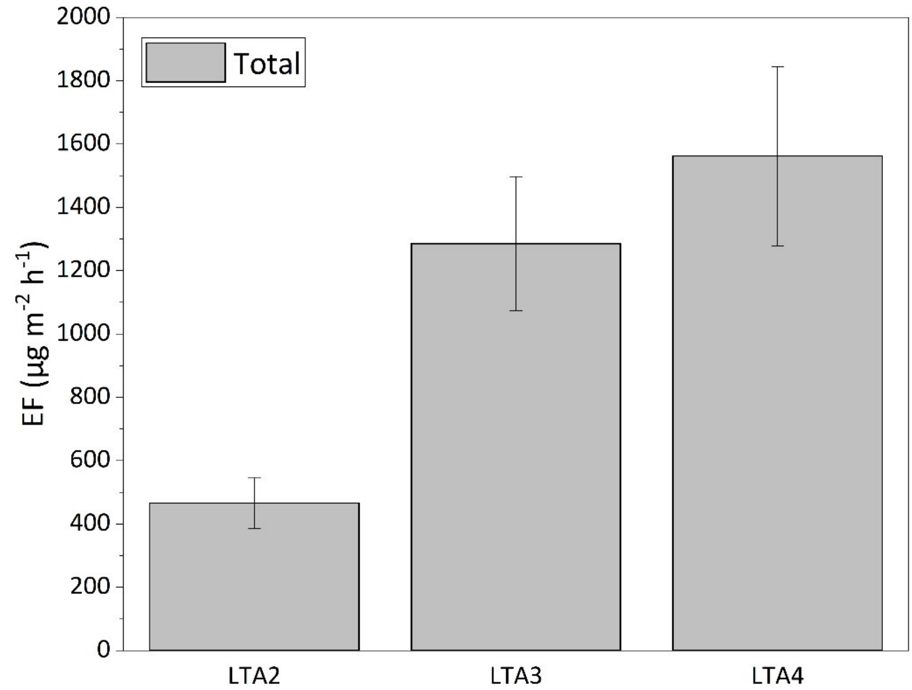


Figure S4: Total VOC EF measured with the PTR-ToFMS at 50°C, under dry (RH = 0.1%) and dark conditions, for three STA (top) and three LTA (bottom) asphalt mixtures.

Dispersion is also observed between GC-MS/FID measurements of total VOC emissions, as shown on **Figure S5**. For STA samples, total EFs vary by a factor of 1.5. For LTA samples, the measurements of total VOC emissions are consistent within a factor of 2.3. Although originating from the same sources, the asphalt mixtures are “real-life” samples and in our opinion such a large heterogeneity of total VOC emissions is not unreasonable.

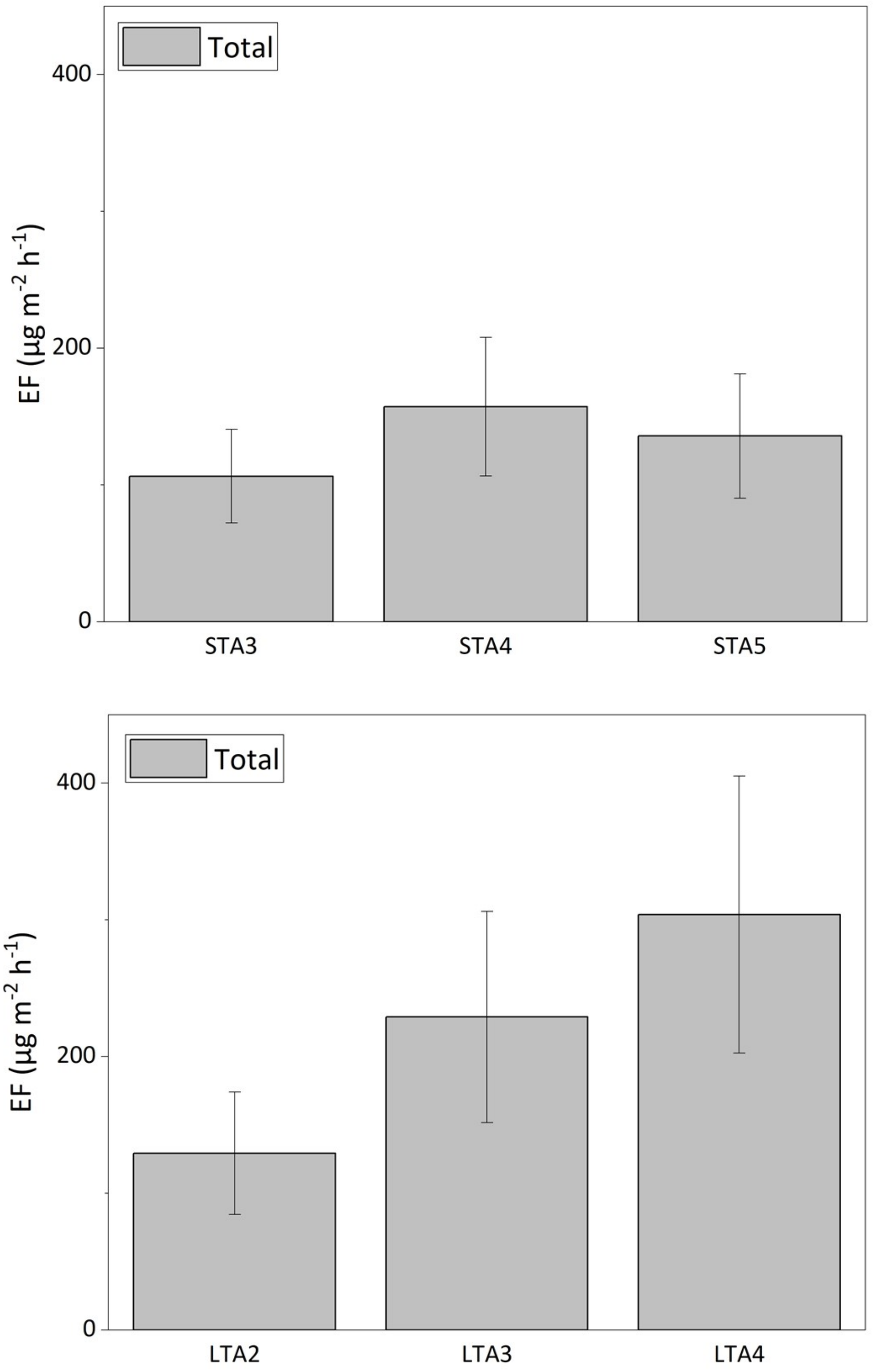


Figure S5: Total VOC EF of the compounds measured with the GC-MS/FID at 50°C, under dry (RH = 0.1%) and dark conditions, for three STA (top) and three LTA (bottom) asphalt mixtures.

In the present work, we only discuss in detail the emissions of STA3 and LTA2 asphalt mixtures, the samples having the largest surfaces. These samples have therefore the lowest VOC EFs, as seen on **Figures S4** and **S5**. The emission factors given is this work are therefore conservative lower limits of VOC emissions by asphalt mixtures.

4. Determination of the Uncertainties

4.1. PTR-ToFMS

The relative standard deviation (RSD) of the concentrations measured with PTR-ToFMS is calculated with Equation (S1).

$$RSD = \sqrt{\left(\frac{\sqrt{i(RH^+)_{norm} + i(RH^+)_{blank}}}{i(RH^+)_{signal} + i(RH^+)_{blank}}\right)^2 + \chi^2} \tag{S1}$$

where $i(RH^+)_{norm}$, $i(RH^+)_{signal}$, and $i(RH^+)_{blank}$ are, respectively, the normalized signal, the raw signal, and the signal in the blank for compound "R", and χ is the uncertainty from the calibration (5% for the compounds in the calibration and set at 30% for the compounds absent from in the calibration).

4.2. GC-MS/FID

The uncertainty on the VOC mass concentration adsorbed on the inner surface of a Carbotrap 202 tube, $\Delta[VOC]$, is calculated with Equation (S2). [VOC] is the product of the response factor of the GC-MS/FID, k_{VOC}, with the area of the peak measured on a chromatogram, A_{VOC}. We also consider the uncertainty on the volume of air sampled, $V_{sample} = Q_{sample} \times t$, where Q_{sample} is the flow in the sampler, and t the sampling time.

$$\Delta[VOC] = [VOC] \times \left(\frac{\Delta k_{VOC}}{k_{VOC}} + \frac{\Delta A_{VOC}}{A_{VOC}} + \frac{\Delta V_{sample}}{V_{sample}}\right) \tag{S2}$$

k_{VOC} is determined for the compounds of the calibration (listed in **section 2.2** of the manuscript, and indicated in **Table S3** of Supplementary Information) from the slope of the calibration plot (peak area vs. mass of VOC adsorbed in the Carbotrap 202 tube). We estimate $\Delta A_{VOC}/A_{VOC}$ = 15%, and $\Delta V_{sampling}/V_{sampling}$ = 5%.

4.3. Emission Factors

Now that the error on the concentrations measured with PTR-ToFMS or GC-MS/FID has been determined, the relative error on the emission factors can be calculated based on Equation (2). In addition to Δ[VOC], determined in the previous sections, uncertainties on molar mass of the VOC (M), temperature (T) and surface ($S_{asphalt}$) of the asphalt mixture, and air flow (Q_e) need to be considered.

- ΔM = ±0.01 g mol^{-1}. VOCs with masses ranging from 40 to 284 g mol^{-1} are detected. Therefore, ΔM/M = 0.0035% - 0.025%.

- ΔT = ±0.01°C. For temperatures between 23°C and 60°C, ΔT/T = 0.16% - 0.43%.

- ΔQ_e = ±2 sccm. Hence, $\Delta Q_e/Q_e$ = 0.2%.

- $\Delta S_{asphalt}$ = ±(0.5 cm × 0.5 cm) = ±0.25 cm^2. For STA3 and LTA2 samples, it corresponds to $\Delta S_{asphalt}/S_{asphalt}$ = 0.09% - 0.19%.

The overall uncertainty caused by these factors is < 0.85%. Other sources of uncertainty are much higher; this error can be neglected.

5. Determination of the Limits of Detection (LOD)

5.1. PTR-ToFMS

The LOD of the PTR-ToFMS, $LOD_{PTR\text{-}ToFMS}$, is calculated in ppb with equation (S3). The factor 150,000 accounts for instrumental sensitivity to H_3O^+. The signal of H_3O^+, $i(H_3O^+)$, is multiplied by 500 to account for the isotopic abundance of ^{18}O with respect to ^{16}O.

$$LOD_{PTR-ToF-MS} = 150{,}000 \times \left(\frac{3 \times \sqrt{i\left(RH^+\right)_{zero\ average}}}{i\left(H_3O^+\right)_{average} \times 500 \times s\left(RH^+\right)} \right) \qquad (S3)$$

$i(RH^+)_{zero\ average}$ represents the 10-minute average intensity of the signal of the PTR-ToFMS for compound “R” in zero air before each experiment, $i(H_3O^+)_{average}$ is the average intensity of the signal of the PTR-ToFMS for H_3O^+ and $s(RH^+)$ is the sensitivity of the instrument to the protonated form of compound “R” (in counts/ppb).

5.2. GC-MS/FID

The limit of detection of the GC-MS/FID, $LOD_{GC\text{-}MS/FID}$, is calculated in concentration units with equation (S4), then converted into EF with equation (2). σ represents the standard deviation of the six measurements performed with the calibration solution, and k the response factor of the instrument to a specific species.

$$LOD_{GC-MS/FID} = 3.3 \times \sigma \times k \qquad (S4)$$

5.3. Emission Factors

$LOD_{PTR-ToFMS}$ is initially determined in ppb, and $LOD_{GC-MS/FID}$ is initially determined in mass units. They are subsequently converted into EF (in µg m^{-2} h^{-1}) with equation (2), and displayed in **Table 4** ($LOD_{PTR-ToFMS}$) and **Table S4** ($LOD_{GC-MS/FID}$).

Note that LOD values in EF units, determined under otherwise similar experimental conditions, vary by a factor of roughly two between STA3 and LTA2. It reflects the difference of the areas of the two samples that are accounted for in the calculation of EF (see equation (2)).

6. Masses Monitored with PTR-ToFMS and Assignments

*Table S3: Masses (M+1, in Da) detected with the PTR-ToFMS Instrument and their possible assignment to parent VOC species. (fg): fragment. n.a.: not assigned. ^{PTR}: Reagent ions of the PTR-ToFMS; the mass displayed is that of the ion. * denotes a species present in the calibration. Lines shaded in orange represent masses excluded from the calculation of EF. Masses shaded in green represent the main emissions by STA asphalt at 60°C (EF > 22 µg m^{-2} h^{-1}). (1) [Holzinger et al., 2010]; (2) [Sekimoto and Koss, 2021]; (3) [Deuscher et al., 2019]; (4) [Bruns et al., 2017]; (5) [Loubet et al., 2022]. A comprehensive assignment of PTR-ToFMS masses can be found in [Yañez-Serrano et al., 2021].*

Mass detected with PTR-ToFMS ***M+1 (Da)***	**~~Assignment~~Possible assignment to the parent VOC species of mass M**						
15	CH_2 (fg)						

17	n.a.						
18	NH_3 (1) (2)						
19	H_3O^+ PTR						
20	n.a.						
23	n.a.						
28	CHN (1) (2)						
29	n.a.						
30	NO^+ PTR						
31	CH_2O (1) (2) (3)	CH_4N (fg) (3)	C_2H_6 (fg) (3)				
32	O_2^+ PTR	CH_5N (2)					
33	CH_4O* (2) (4)						
34	n.a.						
35	n.a.	H_2S (2)					
36	n.a. (1)						
37	$(H_2O)_2$						
38	n.a.						
39	n.a.						
41	C_3H_4 (fg) (3)						
42	C_2H_3N* (1) (2) (4)						
43	C_2H_2O (1) (3)	C_3H_6 (fg) (3) (4)					
44	CHNO (1) (2)	C_2H_5N (1) (2)	C_2H_3O (fg) (3)				
45	C_2H_4O* (1) (2) (4)	CO_2 (fg) (3)					

46	$NO_2^{+\text{ PTR}}$	CH_3NO (1) (2)	C_2H_7N (1) (2)				
47	CH_2O_2 (1) (2) (4)	H_2N_2O (1)	C_2H_6O (1) (2) (4)				
48	HNO_2 (1) (2)	n.a. (3)					
49	CH_4O_2 (1)	CH_4S (2) (3)					
50	n.a.						
51	n.a. (1)	CH_6O_2 (3)					
54	C_3H_3N (1) (2)						
55	$(H_2O)_3$	n.a. (1)	C_4H_6 (4)	C_3H_2O (1)			
56	CHN_3 (1)	n.a. (3)					
57	C_3H_4O (1) (2) (3) (4)	C_4H_8 (fg) (3)					
58	C_2H_3NO (1) (2)	n.a. (3)					
59	C_3H_6O* (1) (2) (4)	$C_2H_2O_2$ (2) (4)					
60	HN_3O (1)	C_2H_5NO (1) (2)	C_3H_9N (1)				
61	$C_2H_4O_2$ (1) (2) (3) (4)	C_3H_8O (3)					
62	$C_2H_4O_2$ (1)	CH_3NO_2 (2)	CHOS (1)				
64	HNO_3 (1)	CH_5NO_2 (1)					
65	CH_4O_3 (1)	C_5H_4 (fg) (3)	$C_2H_8O_2$ (3)				
66	n.a.						
67	$C_3H_2N_2$ (1)	C_5H_6 (1) (3)					
69	C_5H_8* (2) (4)	C_4H_4O (1) (2) (4)	C_5H_8 (3)				

70	C_3H_3NO (1)	C_4H_7N (2)					
71	C_4H_6O* (1) (2) (4)	C_5H_{10} (fg) (3) (4)					
72	C_2HNO_2 (1)	C_3H_5NO (1)					
73	C_4H_8O* (1) (2) (3) (4)	$C_3H_4O_2$ (1) (4)	C_3H_6NO (1) (3)	$(H_2O)_4$ (1)			
74	$C_2H_3NO_2$ (1)	C_3H_7NO (1)	$C_4H_{11}N$ (3)				
75	$C_2H_2O_3$ (1)	$C_3H_6O_2$ (1) (2) (3) (4)	$C_4H_{10}O$ (3)				
77	$C_3H_8O_2$ (1) (3)	N_2O_3 (1)					
79	C_6H_6* (2) (4)	$C_2H_6O_3$ (1)	C_5H_4N (fg) (3)				
81	C_5H_4O (1)	C_6H_8 (1) (3)					
82	n.a. (1)	C_5H_7N (2)					
83	$C_4H_2O_2$ (1)	C_5H_6O (1) (2) (3) (4)	C_6H_{10} (fg) (3)				
84	C_2HN_3O (1)	C_5H_9N (3)					
85	C_5H_8O (1) (4)	C_6H_{12} (fg) (3) (4)	$C_4H_4O_2$ (2)	C_4H_4S (2)			
86	C_4H_7NO (1)						
87	$C_4H_6O_2$ (1) (3) (4)	$C_5H_{10}O$ (1) (3)					
89	$C_4H_8O_2$ (1) (2) (3)	$C_5H_{12}O$ (3)					
90	$C_2H_3NO_3$ (1)						
91	$C_3H_6O_3$ (1)	$C_4H_{10}O_2$ (3)					
93	C_7H_8* (1) (2) (4)	C_3H_8OS (1) (3)					

95	C_6H_6O (1) (2) (4)	$CH_6N_2O_3$ (1)	C_7H_{10} (3)	$C_5H_6N_2$ (3)			
97	$C_5H_4O_2$ (1) (2) (3) (4)	C_6H_8O (1) (3) (4)	C_7H_{12} (fg) (3)				
98	$C_4H_3NO_2$ (1)	C_5H_7NO (1) (3)					
99	$C_4H_2O_3$ (1) (2) (3) (4)	$C_5H_6O_2$ (1) (2) (3)	$C_6H_{10}O$ (1) (3)	C_7H_{14} (3)	C_5H_6S (2)		
101	$C_4H_4O_3$ (1)	$C_5H_8O_2$ (1) (3)	$C_6H_{12}O$ (1) (3)				
103	$C_4H_6O_3$ (1)	$C_5H_{10}O_2$ (1) (3)	$C_6H_{14}O$ (3)	C_8H_6 (2)			
107	C_8H_{10}* (1) (4)	$C_3H_{10}N_2O_2$ (1)	C_7H_6O (2) (3) (4)				
109	$C_6H_4O_2$ (1) (2)	$C_3H_8O_2S$ (1)	C_7H_8O (1) (2) (3) (4)	C_8H_{12} (1) (3)	$C_6H_8N_2$ (3)		
111	$C_6H_6O_2$ (1) (3) (4)	$C_7H_{10}O$ (1) (3)	C_8H_{14} (fg) (3)				
113	$C_5H_4O_3$ (1) (2)	$C_6H_8O_2$ (1) (2) (3)	$C_7H_{12}O$ (1) (3)	C_8H_{16} (fg) (3)			
115	$C_5H_6O_3$ (1)	$C_6H_{10}O_2$ (1) (3)	$C_7H_{14}O$ (1) (3)				
119	n.a. (1)	$C_5H_{10}O_3$ (3)	$C_6H_{14}O_2$ (3)	C_9H_{10} (4)	C_8H_6O (2)		
120	C_7H_5NO (1)	C_4H_9NOS (1)					
121	C_8H_8O (1) (2) (3) (4)	$C_7H_8N_2$ (3)	C_9H_{12} (4)				
123	$C_7H_6O_2$ (1) (2)	$C_4H_{10}O_2S$ (1)	$C_8H_{10}O$ (1) (3) (4)	$C_3H_{10}N_2O_3$ (1)	C_9H_{14} (1) (3)		

125	$C_6H_4O_3$ (1)	$C_7H_8O_2$ (1) (2) (3) (4)	$C_8H_{12}O$ (1) (3)	C_9H_{16} (3)			
127	$C_6H_6O_3$ (1) (2) (4)	$C_7H_{10}O_2$ (1) (3)	$C_8H_{14}O$ (1) (3)	C_9H_{18} (3)			
129	$C_6H_8O_3$ (1) (2)	$C_7H_{12}O_2$ (1) (3)	$C_8H_{16}O$ (1) (3)	$C_{10}H_8$ (2) (4)			
131	$C_5H_6O_4$ (1)	$C_6H_{10}O_3$ (1) (3)	$C_{10}H_{10}$ (1) (2)	$C_5H_{10}N_2O_2$ (1)	$C_7H_{14}O_2$ (3)	$C_8H_{18}O$ (3)	
134	$C_5H_{11}NOS$ (1)	$C_6H_{15}NS$ (1)					
136	$C_4H_9NO_2S$ (1)	n.a. (3)	C_7H_5NS (5)				
137	$C_{10}H_{16}$ * (2)	$C_8H_8O_2$ (1) (2)	$C_5H_{12}O_2S$ (1)	$C_9H_{12}O$ (1)	$C_4H_{12}N_2O_3$ (1)	$C_{10}H_{16}$ (3)	$C_8H_{12}N_2$ (3)
139	$C_7H_6O_3$ (1)	$C_4H_{10}O_3S$ (1)	$C_8H_{10}O_2$ (1) (3) (4)	$C_3H_{10}N_2O_4$ (1)	$C_9H_{14}O$ (1) (3)	$C_8H_{14}N_2$ (3)	
141	$C_7H_8O_3$ (1)	$C_8H_{12}O_2$ (1)	$C_9H_{16}O$ (1) (3)				
143	$C_4H_6N_4S$ (1)	$C_7H_{10}O_3$ (1)	$C_8H_{14}O_2$ (1)	$C_9H_{18}O$ (3)	$C_{11}H_{10}$ (4)		
146	$C_4H_3NO_5$ (1)	C_9H_7NO (1)	$C_4H_7N_3O_3$ (1)				
147	$C_9H_6O_2$ (1) (4)	$C_6H_{10}O_2S$ (1)	$C_{10}H_{10}O$ (1) (3)	$C_5H_{10}N_2O_3$ (1)	$C_{11}H_{14}$ (1)	$C_6H_{14}N_2O_2$ (1)	
151	$C_8H_6O_3$ (1)	$C_5H_{10}O_3S$ (1)	$C_9H_{10}O_2$ (1) (3)	$C_{10}H_{14}O$ (1)	$C_5H_{14}N_2O_3$ (1)	$C_9H_{14}N_2$ (3)	
155	$C_8H_{10}O_3$ (1) (2) (4)	$C_{10}H_{18}O$ (1) (2) (3)	$C_{12}H_{10}$ (4)				
157	$C_7H_8O_4$ (1)	$C_8H_{12}O_3$ (1)	$C_{10}H_{20}O$ (3)	$C_{12}H_{12}$ (4)			

166	$C_5H_3N_5S$ (1)	$C_5H_{11}NO_3S$ (1)					
169	$C_5H_{12}O_4S$ (1)	$C_9H_{12}O_3$ (1) (4)	$C_4H_{12}N_2O_5$ (1)	$C_{10}H_{16}O_2$ (1)	$C_{11}H_{20}O$ (1)		
178	$C_5H_{11}N_3O_4$ (1)						
179	$C_7H_6N_4S$ (1)	$C_{14}H_{10}$ (1) (4)	$C_{11}H_{14}S$ (1)				
182	$C_7H_3NO_5$ (1)	$C_6H_{15}NO_5$ (1)					
183	$C_{13}H_{10}O$ (1)	$C_{10}H_{14}OS$ (1)	$C_{12}H_{22}O$ (1)	$C_9H_{10}O_4$ (4)	$C_{10}H_{14}O_3$ (4)		
195	$C_9H_{10}N_2O_3$ (1)	$C_{11}H_{14}O_3$ (1) (4)					
199	$C_{16}H_6$ (1)	$C_{11}H_6N_2O_2$ (1)	$C_{10}H_{14}O_4$ (1)				
211	$C_{14}H_{10}O_2$ (1)	$C_{11}H_{14}O_2S$ (1)	$C_{14}H_{26}O$ (1)				
225	$C_9H_8N_2O_5$ (1)	$C_{12}H_{16}O_4$ (1)	$C_9H_{20}O_4S$ (1)	$C_{13}H_{20}O_3$ (1)			

7. Compounds Identified with GC-MS/FID and Their Masses (M+1)

*Table S4: Emission Factors (EF) of the compounds detected with GC-MS/FID (masses are indicated as M+1, where M is the molar mass of the species in Da) for STA3 and LTA2 asphalt samples at 23°C, 35°C, 50°C, and 60°C. Alkanes are shown in deep blue, aromatics in light blue, alkenes in grey, carbonyls in purple, alcohols in yellow, and other compounds in red. * denotes a species present in the calibration. nd denotes a species that is not detected, but present in the calibration, hence LODs are calculated: it is the case for toluene, and 1-octene (lines shaded in gray). Lines shaded in green show compounds which masses (M+1) participate in the highest*

EFs as determined with PTR-ToFMS, and with proton affinities higher than that of H_2O, so that they can be observed with PTR-ToFMS. The Limit Of Detection (LOD) is only calculated for the compounds of the calibration; we add the label "< LOD" for undetected compounds absent from the calibration.

	STA3 EF (µg m^{-2} h^{-1})				**LTA2 EF** (µg m^{-2} h^{-1})			
Temperature (°C) / **Species** (M+1, Da)	23	35	50	60	23	35	50	60
	Alkanes							
Octane (115)	< LOD	0.006 ±0.002	0.032 ±0.009	< LOD	< LOD	< LOD	< LOD	< LOD
Nonane (129)	< LOD	< LOD	0.820 ±0.220	2.191 ±0.589	2.294 ±0.614	1.804 ±0.483	2.849 ±0.762	4.642 ±1.242
Octane, 2,2-dimethyl (143)	< LOD	0.109 ±0.040	0.401 ±0.148	0.513 ±0.189	1.939 ±0.714	1.558 ±0.574	2.569 ±0.946	3.281 ±1.209
Heptane, 3-ethyl, 2-methyl (143)	< LOD	< LOD	0.330 ±0.122	0.576 ±0.213	0.454 ±0.167	0.394 ±0.145	0.757 ±0.279	1.016 ±0.374
Nonane, 2-methyl (143)	< LOD	< LOD	0.244 ±0.090	0.547 ±0.202	1.909 ±0.703	1.349 ±0.497	2.354 ±0.867	3.635 ±1.339
Nonane, 3-methyl (143)	< LOD	< LOD	0.085 ±0.031	0.433 ±0.160	1.843 ±0.679	1.407 ±0.519	1.928 ±0.710	2.601 ±0.958
Cyclohexane, 1-methyl, x-propyl (141)	< LOD	< LOD	< LOD	< LOD	1.141 ±0.420	0.528 ±0.195	1.070 ±0.394	1.764 ±0.650
Octane, 3-ethyl (143)	0.010 ±0.004	< LOD	0.208 ±0.077	< LOD	0.187 ±0.069	< LOD	< LOD	< LOD
Decane (143)	< LOD	0.213 ±0.079	0.816 ±0.301	1.585 ±0.586	7.101 ±2.616	6.383 ±2.351	10.724 ±3.951	14.401 ±5.305
Decane, x-methyl	0.325	< LOD	0.839	2.020	6.174	5.993	12.323	16.059

(157)	±0.115		±0.297	±0.715	±1.814	±2.117	±4.352	±5.672
Cyclohexane, butyl (141)	< LOD	< LOD	0.175 ±0.065	< LOD	0.726 ±0.268	0.645 ±0.238	1.257 ±0.463	1.501 ±0.553
Undecane (157)	0.227 ±0.080	0.465 ±0.165	1.660 ±0.588	3.491 ±1.237	6.082 ±2.148	6.466 ±2.284	14.482 ±5.115	19.250 ±6.799
Decane, 4-ethyl (171)	0.092 ±0.031	< LOD	< LOD	< LOD	< LOD	< LOD	0.838 ±0.285	1.393 ±0.474
Undecane, x-methyl (171)	< LOD	0.233 ±0.079	1.254 ±0.428	3.030 ±1.035	1.707 ±0.581	2.344 ±0.798	7.269 ±2.475	10.280 ±3.500
Dodecane* (171)	< 0.919	< 0.883	1.750 ±0.597	3.183 ±1.087	5.413 ±1.843	6.791 ±2.312	18.483 ±6.293	23.400 ±7.967
Undecane, 2,6-dimethyl (185)	< LOD	< LOD	0.590 ±0.195	1.002 ±0.331	1.242 ±0.410	1.742 ±0.574	5.452 ±1.798	6.806 ±2.244
Cyclohexane, hexyl (169)	< LOD	< LOD	< LOD	< LOD	0.376 ±0.128	0.425 ±0.145	1.709 ±0.582	2.140 ±0.729
Dodecane, x-methyl (185)	0.188 ±0.064	0.199 ±0.068	3.619 ±1.235	3.266 ±1.115	2.499 ±0.850	1.701 ±0.579	3.298 ±1.122	4.474 ±1.522
Tridecane, 7-methyl (199)	< LOD	< LOD	< LOD	< LOD	0.935 ±0.302	0.692 ±0.224	1.683 ±0.544	2.425 ±0.784
Tridecane* (185)	< 0.965	< 0.928	3.157 ±1.077	5.440 ±1.856	1.992 ±0.678	2.683 ±0.913	9.308 ±3.167	13.075 ±4.448
Hexadecane, 2,6,10,14-tetramethyl (284)	< LOD	< LOD	1.528 ±0.453	3.188 ±0.947	< LOD	0.225 ±0.067	1.087 ±0.322	1.763 ±0.522
Tetradecane* (199)	< 0.845	1.146 ±0.372	4.481 ±1.570	8.230 ±2.670	< 0.406	0.512 ±0.166	2.043 ±0.661	2.977 ±0.963
Pentadecane* (213)	< 1.350	< 1.298	3.847 ±1.384	7.392 ±2.659	< 0.649	< 0.624	1.073 ±0.385	2.039 ±0.731
Decane, 5,6-	< LOD	1.220	4.610	8.339	< LOD	< LOD	< LOD	< LOD

dipropyl (227)		±0.391	±1.479	±2.676				
Hexadecane (227)	< LOD	0.799 ±0.256	2.814 ±0.903	6.338 ±2.033	< LOD	< LOD	0.480 ±0.154	1.059 ±0.339
	Aromatics							
Toluene^{*,nd} (93)	< 0.836	< 0.803	< 0.766	< 0.743	< 0.402	< 0.386	< 0.368	< 0.357
o/p-xylene (107)	< LOD	0.022 ±0.006	0.140 ±0.039	0.317 ±0.088	0.136 ±0.037	0.104 ±0.029	< LOD	0.156 ±0.043
Benzene, x,y,z-trimethyl (121)	0.028 ±0.008	0.067 ±0.018	0.829 ±0.223	0.612 ±0.164	0.610 ±0.163	< LOD	< LOD	0.247 ±0.066
Benzene, 1,2-diethyl (135)	< LOD	0.100 ±0.037	0.484 ±0.179	< LOD	0.873 ±0.322	0.919 ±0.338	1.199 ±0.442	1.709 ±0.630
Benzene, x-methyl, y-propyl (135)	< LOD	< LOD	0.461 ±0.170	0.640 ±0.237	0.343 ±0.126	< LOD	0.569 ±0.209	0.661 ±0.243
Benzene, x-ethyl, y,z-dimethyl (135)	< LOD	< LOD	0.130 ±0.048	1.217 ±0.450	0.779 ±0.287	0.172 ±0.063	1.678 ±0.618	1.941 ±0.715
Benzene, 1,2,4,5-tetramethyl (135)	< LOD	< LOD	0.383 ±0.142	0.843 ±0.311	0.104 ±0.038	0.126 ±0.046	0.483 ±0.178	0.647 ±0.238
Naphthalene, x-methyl (143)	0.156 ±0.040	0.393 ±0.101	5.560 ±1.436	7.366 ±1.889	0.516 ±0.132	0.603 ±0.154	3.322 ±0.848	4.231 ±1.081
Naphthalene, 1-ethyl (157)	< LOD	< LOD	1.222 ±0.308	3.630 ±0.914	< LOD	< LOD	0.168 ±0.042	0.761 ±0.191
Naphthalene, x,y-dimethyl (157)	0.751 ±0.189	0.342 ±0.086	6.949 ±1.751	15.004 ±3.780	0.727 ±0.182	0.703 ±0.176	3.419 ±0.858	7.706 ±1.933
Acenaphthene (155)	0.429 ±0.108	1.918 ±0.483	7.948 ±2.002	16.376 ±4.125	< LOD	< LOD	0.742 ±0.186	0.966 ±0.242
1,1'-Biphenyl, x-methyl (169)	< LOD	< LOD	1.977 ±0.490	2.667 ±0.662	< LOD	< LOD	< LOD	< LOD
Naphthalene, x,y,z-trimethyl (171)	< LOD	< LOD	3.872 ±1.273	6.325 ±2.078	< LOD	0.483 ±0.159	1.453 ±0.475	4.381 ±1.435

	Alkenes							
2-Ethyl-1-hexene (113)	< LOD	0.125 ±0.035	0.613 ±0.172	< LOD	0.018 ±0.005	0.052 ±0.015	0.059 ±0.016	< LOD
1-Octene^{*,nd} (113)	< 0.587	< 0.564	< 0.538	< 0.521	< 0.282	< 0.271	< 0.259	< 0.251
2-Octene (113)	< LOD	0.067 ±0.019	0.201 ±0.056	0.052 ±0.015	0.212 ±0.059	0.396 ±0.111	0.353 ±0.099	0.560 ±0.157
2-Heptene, 3-methyl (113)	< LOD	0.070 ±0.020	0.252 ±0.071	< LOD	< LOD	0.038 ±0.011	0.015 ±0.004	< LOD
1-Nonene (127)	< LOD	< LOD	0.080 ±0.022	< LOD	0.107 ±0.029	0.101 ±0.027	0.394 ±0.107	0.424 ±0.115
Styrene (105)	< LOD	< LOD	0.132 ±0.037	0.133 ±0.037	0.103 ±0.029	0.055 ±0.015	0.178 ±0.050	0.182 ±0.051
α-pinene (137)	< LOD	< LOD	0.166 ±0.044	0.407 ±0.108	< LOD	< LOD	< LOD	< LOD
1-Tetradecene (197)	< LOD	0.323 ±0.080	1.277 ±0.315	2.677 ±0.660	< LOD	0.101 ±0.025	0.615 ±0.151	1.021 ±0.251
	Carbonyls							
3-Heptanone (115)	< LOD	< LOD	0.334 ±0.113	1.109 ±0.375	< LOD	< LOD	< LOD	< LOD
2H-Pyran-2-one, tetrahydro- (101)	< LOD	< LOD	0.036 ±0.037	0.229 ±0.233	0.050 ±0.051	0.066 ±0.067	0.189 ±0.192	0.246 ±0.250
2-Undecanone (171)	< LOD	0.310 ±0.120	1.001 ±0.388	2.307 ±0.893	< LOD	< LOD	< LOD	< LOD
2-Dodecanone (185)	< LOD	< LOD	2.189 ±0.810	4.042 ±1.496	< LOD	< LOD	< LOD	1.085 ±0.401
Pentanal (87)	< LOD	< LOD	< LOD	0.506 ±0.206	< LOD	< LOD	< LOD	< LOD
Hexanal (101)	< LOD	0.779 ±0.284	2.437 ±0.890	7.863 ±2.870	< LOD	0.341 ±0.124	< LOD	0.414 ±0.151

Hexanal, 2-ethyl (129)	0.640 ±0.204	0.784 ±0.250	0.495 ±0.158	6.483 ±2.065	< LOD	< LOD	< LOD	< LOD
Benzaldehyde (107)	< LOD	0.003 ±0.001	0.405 ±0.137	1.048 ±0.354	2.781 ±0.937	2.090 ±0.704	4.104 ±1.383	5.223 ±1.759
Octanal* (129)	< 1.638	< 1.574	2.220 ±0.707	5.636 ±1.795	< 0.788	< 0.757	< 0.722	0.798 ±0.253
Nonanal (143)	< LOD	< LOD	3.484 ±1.059	12.814 ±3.894	< LOD	< LOD	0.414 ±0.125	0.843 ±0.255
Decanal* (157)	< 2.925	< 2.811	3.522 ±1.363	12.324 ±4.770	< 1.407	< 1.352	2.568 ±0.991	4.454 ±1.719
Tridecanal (199)	< LOD	0.079 ±0.028	2.580 ±0.919	5.132 ±1.828	< LOD	< LOD	< LOD	< LOD
Tetradecanal (213)	< LOD	< LOD	0.379 ±0.130	3.168 ±1.091	< LOD	< LOD	< LOD	< LOD
	Alcohols							
1-Hexanol, 2-ethyl* (131)	< 0.820	2.682 ±0.816	18.677 ±5.686	35.251 ±10.731	< 0.394	< 0.379	0.579 ±0.176	1.177 ±0.357
1-Heptanol (118)	< LOD	< LOD	0.151 ±0.054	0.715 ±0.253	0.383 ±0.135	< LOD	0.374 ±0.132	0.493 ±0.173
Phenol (95)	< LOD	< LOD	0.353 ±0.132	0.684 ±0.256	0.563 ±0.210	0.304 ±0.114	0.591 ±0.221	1.392 ±0.520
1-Octanol (131)	< LOD	0.020 ±0.007	0.827 ±0.273	1.435 ±0.474	0.473 ±0.156	0.516 ±0.170	1.085 ±0.357	1.329 ±0.437
Menthol (157)	< LOD	0.224 ±0.067	0.836 ±0.252	1.315 ±0.396	< LOD	< LOD	1.113 ±0.334	1.565 ±0.470
3-Cyclohexene-1-ol, 4-methyl-1-(1-methylethyl)- (155)	< LOD	< LOD	0.272 ±0.081	0.498 ±0.148	< LOD	< LOD	< LOD	0.941 ±0.278
	Others							

Dibenzofuran (169)	< LOD	0.852 ±0.350	2.487 ±1.023	< LOD	< LOD	< LOD	< LOD	< LOD
Octane, 1,1'-oxybis- (243)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.335 ±0.133
Total	**2.846** **±0.843**	**13.550** **±4.260**	**108.621** **±34.259**	**221.589** **±69.946**	**52.792** **±17.902**	**50.812** **±17.529**	**128.700** **±43.821**	**185.869** **±62.871**
Temperature (°C)	23	35	50	60	23	35	50	60
	STA3 EF (µg m^{-2} h^{-1})				**LTA2 EF (µg m^{-2} h^{-1})**			

8. VOC Emissions by Chemical Family with GC-MS/FID

Individual EFs of **Table S4** are grouped by chemical family: alkanes, aromatics, alkenes, carbonyls (aldehydes and ketones), alcohols, and other compounds. **Figure S6** shows the evolution of the EFs of these six families as a function of temperature in the 23°C – 60°C range, under dry (RH = 0.1%) and dark conditions. Total VOC EF of STA asphalt is lower than LTA asphalt at 23°C and 35°C but similar at 50°C and 60°C. Most of the difference at 23°C comes from the stronger alkane emissions of the LTA sample. At 50°C and 60°C, STA asphalt lower alkanes emissions are compensated by stronger emissions of aromatics and carbonyls than in LTA asphalt. Specifically, carbonyl emissions by STA asphalt are 2.6 times higher than LTA asphalt at 50°C, and 4.8 times higher at 60°C. Aromatic emissions are roughly twice stronger in STA asphalt emissions than in LTA emissions at 50°C and 60°C. Emissions of alcohols by STA asphalt are higher than LTA asphalt by a factor of roughly 5.7 at 50°C and 60°C.

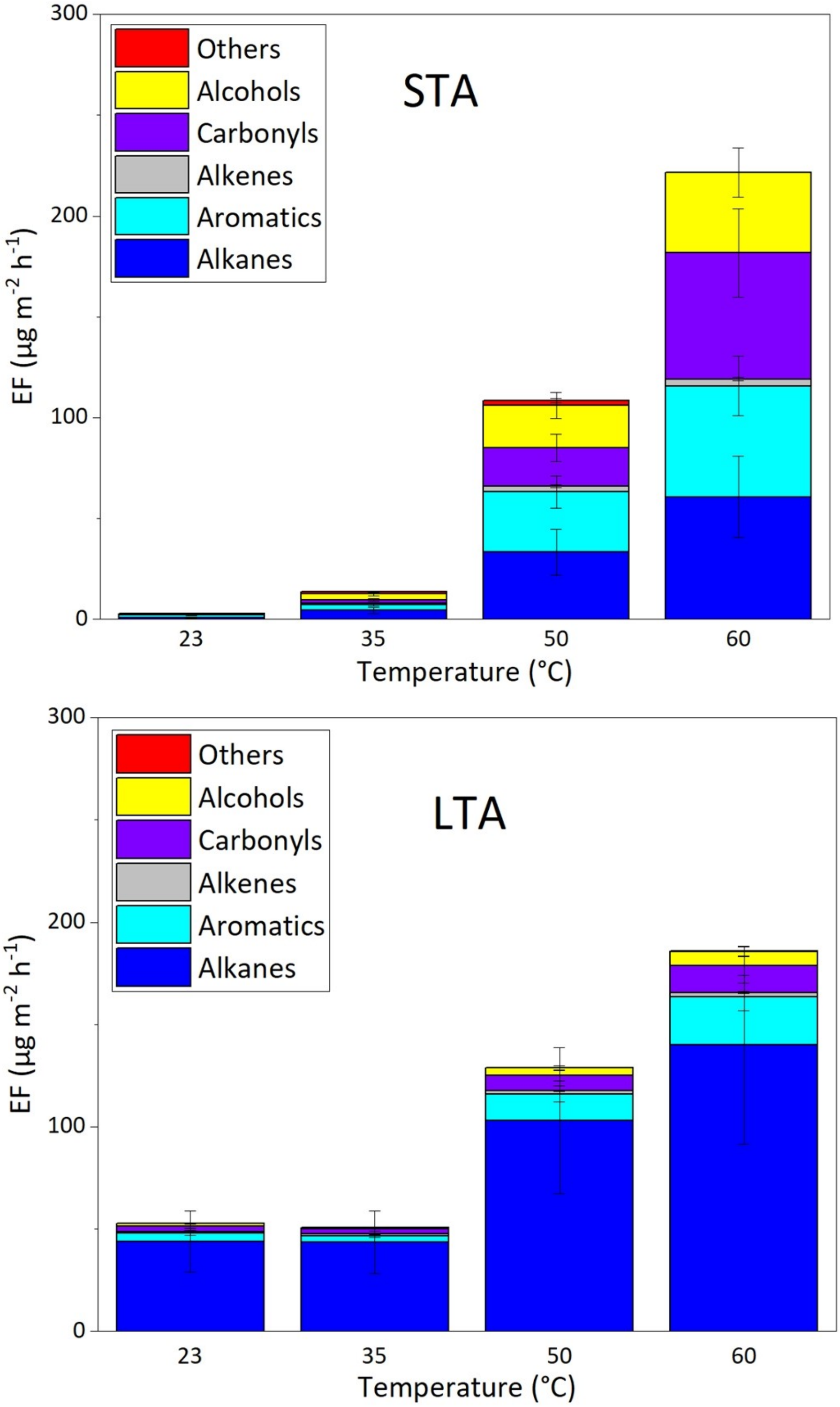


Figure S6: Evolution of VOC EFs as a function of temperature for STA3 (top) and LTA2 (bottom) asphalt samples, as determined with GC-MS/FID, under dry (RH = 0.1%) and dark conditions. The contribution of alkanes, aromatics, alkenes, carbonyl compounds (aldehydes and ketones), alcohols, and other species, is detailed.

Figure S7 shows the proportion of each family of compounds in total VOC emissions. VOCs emissions of STA and LTA asphalt are mostly composed of alkanes and aromatics at all temperatures investigated in the 23°C – 60°C range, confirming the observation with PTR-ToFMS of bitumen emissions at 120°C – 180°C by [Borinelli *et al.*, 2020].

In fresh STA asphalt, emissions are mostly composed of alkanes and aromatics at all temperatures. The contribution of alkanes remains stable at around 30%, whereas aromatics contribute for ≈ 50% of total emissions at 23°C, before decreasing to ≈ 25% at higher temperatures. The proportion of carbonyls emitted represents on average ≈ 20% of all VOCs, with a minimum of 14% at 35°C increasing to 28% at 60°C. Alcohols are not detected at 23°C but account for ≈ 20% of the total at 35°C and above. Alkenes represent less than 5% of VOCs emissions at all temperatures. Other compounds (dibenzofuran) are not detected in STA asphalt emissions at 23°C or 60°C; they become significant (6.3%) at 35°C but decrease to 2.3% at 50°C.

Old LTA asphalt exhibits a different emission pattern. Alkanes dominate the emissions at all temperatures, with an average of 80% of the total. The proportion of alkanes decreases from 35°C (84%) to 60°C (75%) but it is compensated by the increase of aromatics emissions, from 7.7% at 23°C, to 12.6% at 60°C. The proportion of carbonyl compounds oscillates between 5% and 7% of total emissions. The same holds for alcohols, about 2.7% of total VOC emissions, and for alkenes, close to 1% of total VOCs emissions. The contribution of other compounds is < 0.2% at all temperatures.

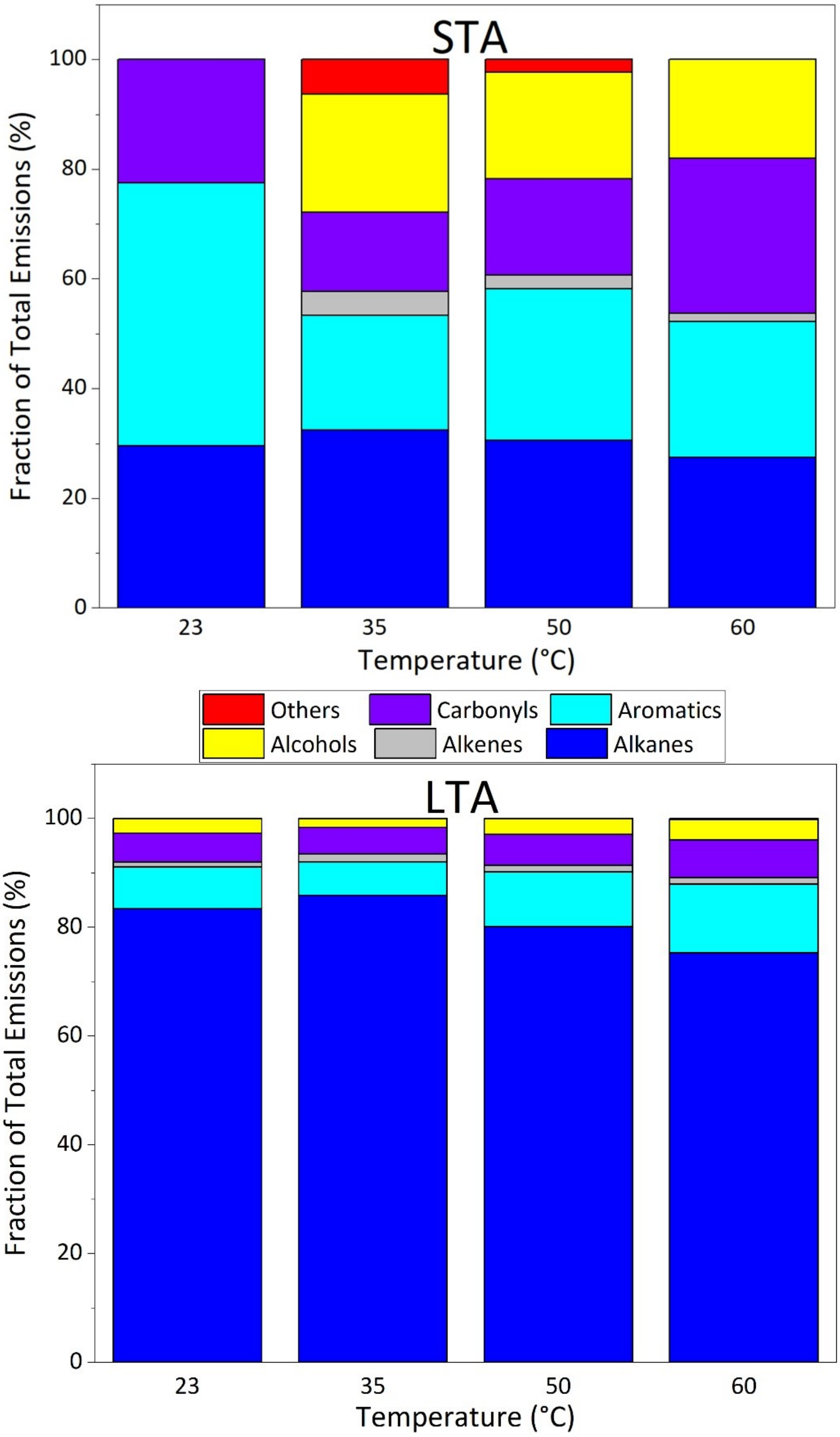


Figure S7: Composition of VOC emissions (in %) as a function of temperature for the STA3 (top) and LTA2 (bottom) asphalt samples, as determined with GC-MS/FID, under dry (RH = 0.1%) and dark conditions. The contribution of alkanes, aromatics, alkenes, carbonyl compounds (aldehydes and ketones), alcohols, and other species, is detailed.

9. POCP and SOAP indices

VOC POCP and SOAP indices used in this work are listed in **Table S5**. Most of them have been extracted from the literature (see caption of **Table S5**). SOAP indices of some alkanes and substituted naphthalenes are published here for the first time. They have been determined following the methodology described in [Derwent *et al.*, 2010b].

Table S5: POCP and SOAP indices of the VOCs detected in asphalt mixtures' emissions by GC-MS/FID.

[a] [Jenkin et al., 2017]; [b] [Passant, 2002]; [c] [Derwent et al., 2010b]; [d] this work; [EG] = Educated Guess; [e] [Gilman et al., 2015]. Lines shaded in blue (respectively gray/orange) indicate the species that dominate the emissions of STA asphalt (respectively LTA / both STA and LTA) measured by GC-MS/FID. -: no value available. [1] Average of seven x,y-dimethyloctane values. [2] Value for 1-methyl,1-propylcyclohexane. [3] Average of five x-methyldecane values. [4] Value for C_{12}-alkanes. [5] Average of four x-methylundecane values. [6] Value for C_{13}-alkanes. [7] Value for C_{14}-alkanes. [8] Value extrapolated from the linear fit to the data of [Passant, 2002] for alkanes vs. number of C atoms. [9] Value for C_{16}-alkanes. [10] Average of values for o- and p-xylene. [11] Average of values for 1,2,3-/1,2,4-/1,3,5-trimethylbenzene. [12] Average of values for 1,2-/1,3-/1,4-methylpropylbenzene. [13] Value for unspeciated aromatic hydrocarbons. [14] Value for C_{13}+ aromatic hydrocarbons. [15] Value for C_8-alkenes. [16] Value for cis-2-octene. [17] Value for unspeciated alkenes. [18] Value for unspeciated ketones. [19] Negative value. [20] Value for unspeciated alcohols. [21] Value for 1,4-diethylbenzene. [22] Value for the sum of two isomers of x-methylproplbenzene. [23] Value for naphthalene; the SOA precursor is a ring-opened secondary product of naphthalene oxidation, therefore the presence of methyl or ethyl groups attached to the rings are not expected to modify significantly the SOAP.

Species (M+1, Da)	**POCP (O_3)** $POCP_{ethene} = 100$	**SOAP (SOA)** $SOAP_{toluene} = 100$
Octane (115)	34.0[a]	0.8[c]

Nonane (129)	34.0[a]	1.9[c]
Octane, 2,2-dimethyl (143)	39.6[b,1]	3.7[d]
Heptane, 3-ethyl, 2-methyl (143)	39.9[b]	3.7[d]
Nonane, 2-methyl (143)	39.9[b]	3.6[d]
Nonane, 3-methyl (143)	40.2[b]	3.7[d]
Cyclohexane, 1-methyl, x-propyl (141)	38.5[b,2]	-
Octane, 3-ethyl (143)	44.4[b]	-
Decane (143)	36.0[a]	7.0[c]
Decane, x-methyl (157)	37.6[b,3]	3.6[d]
Cyclohexane, butyl (141)	42.5[b]	-
Undecane (157)	36.0[a]	16.2[c]
Decane, 4-ethyl (171)	35.7[b,4]	-
Undecane, x-methyl (171)	35.1[b,5]	3.6[d]
Dodecane* (171)	33.0[a]	34.5[c]
Undecane, 2,6-dimethyl (185)	31.7[b]	3.6[d]
Cyclohexane, hexyl (169)	36.7[b]	-
Dodecane, x-methyl (185)	31.7[b,6]	3.6[EG]
Tridecane, 7-methyl (199)	30.7[b,7]	-
Tridecane* (185)	32.7[b]	3.5[d]
Hexadecane, 2,6,10,14-tetramethyl (284)	18.05[8]	-
Tetradecane* (199)	30.7[b]	3.5[d]
Pentadecane* (213)	28.4[b]	3.5[EG]
Decane, 5,6-dipropyl (227)	24.2[b,9]	3.5[EG]
Hexadecane (227)	26.0[b]	3.5[EG]
Toluene* (93)	44.0[a]	100.0[c]
o/p-xylene (107)	75.0[a,10]	81.3[c,10]

Benzene, x,y,z-trimethyl (121)	107.3[a,11]	26[c,11]
Benzene, 1,2-diethyl (135)	105.7[b]	90[e,21]
Benzene, x-methyl, y-propyl (135)	96.2[b,12]	95[e,22]
Benzene, x-ethyl, y,z-dimethyl (135)	104.0[a]	12.2[c]
Benzene, 1,2,4,5-tetramethyl (135)	114.6[b]	99.0[d]
Naphthalene, x-methyl (143)	125.2[b]	106.0[d,23]
Naphthalene, 1-ethyl (157)	95.4[b,13]	106.0[d,23]
Naphthalene, x,y-dimethyl (157)	95.4[b,13]	106.0[d,23]
Acenaphthene (155)	121.9[b]	106.0[EG]
1,1’-Biphenyl, x-methyl (169)	128.3[b,14]	106.0[EG]
Naphthalene, x,y,z-trimethyl (171)	128.3[b,14]	106.0[d,23]
2-Ethyl-1-hexene (113)	93.7[b,15]	-
2-Octene (113)	99.4[b,16]	-
2-Heptene, 3-methyl (113)	93.7[b,15]	-
1-Nonene (127)	95.6[b]	1.9[e]
Styrene (105)	5.0[a]	212.3[c]
α-pinene (137)	68.0[a]	17.4[c]
1-Tetradecene (197)	97.5[b,17]	-
3-Heptanone (115)	42.0[b,18]	-
2H-Pyran-2-one, tetrahydro- (101)	-	-
2-Undecanone (171)	42.0[b,18]	-
2-Dodecanone (185)	42.0[b,18]	-
Pentanal (87)	71.0[a]	0[c]
Hexanal (101)	100.0[b]	0[e]
Hexanal, 2-ethyl (129)	-	-
Benzaldehyde (107)	-19.0[a,19]	216.1[c]
Octanal* (129)	-	0[EG]
Nonanal (143)	-	0[EG]

Decanal* (157)	-	0[EG]
Tridecanal (199)	-	0[EG]
Tetradecanal (213)	-	0[EG]
1-Hexanol, 2-ethyl* (131)	63.2[b]	-
1-Heptanol (118)	36.4[b,20]	-
Phenol (95)	63.3[b]	150[e]
1-Octanol (131)	36.4[b,20]	-
Menthol (157)	36.4[b,20]	0[EG]
3-Cyclohexene-1-ol, 4-methyl-1-(1-methylethyl)- (155)	36.4[b,20]	-
Dibenzofuran (169)	95.4[b,13]	90[EG]
Octane, 1,1'-oxybis- (243)	-	-

Table S6 presents the major masses detected at 60°C under dark and dry conditions in emissions of fresh and old asphalt mixtures with PTR-ToFMS. Only species detected with PTR-ToFMS in the literature (see **Table S3**), and based on C, H, and O atoms, are considered; their chemical formulae are given. Possible species are then suggested, when values of their SOAP coefficient are available, the POCP coefficient is also indicated. The proton affinity of these compounds is given, to confirm that they may be observed with PTR-ToFMS; alkanes are therefore excluded from this list, because their proton affinity is lower than that of water. Lastly, we state whether the compounds can also be seen in our GC-MS/FID analysis (the case of naphthalene is discussed in the manuscript).

Table S6: Major masses contributing to the emissions of fresh and old asphalt mixtures measured with PTR-ToFMS. The chemical formula of compounds observed with PTR-ToFMS in the literature (see ***Table S2****) with C, H and O atoms only is given, together with the POCP and SOAP coefficients of these compounds, when available, and their proton affinity. In the last column, we state whether these species can be seen with our GC-MS/FID analysis.* [b] *[Passant, 2002];* [d] *this work;* [e] *[Gilman et al., 2015];* [f] *[Hunter and Lias, 1998].*

Mass M+1 (Da)	**Chemical formula**	**Possible species**	**POCP (O_3)** POCP$_{ethene}$ = 100	**SOAP (SOA)** SOAP$_{toluene}$ = 100	**Proton Affinity** PA(H_2O) = 691 kJ mol^{-1}	**Can be seen with our GC-MS/FID analysis?**
57	C_3H_4O	Propen-2-al (acrolein)	73[b]	1[e]	797[f]	**NO**
71	C_4H_6O	Buten-2-al (crotonaldehyde)	70[b]	1[e]	831[f]	**NO**
71	C_4H_6O	2-methylpropenal (methacrolein)	82.9[b]	1[e]	809[f]	**NO**
71	C_4H_6O	But-3-en-2-one (methylvinylketone)	-	1[e]	835[f]	**NO**
71	C_4H_6O	2,5-dihydrofuran	-	1[e]	823[f]	**NO**
85	C_5H_8O	Pentenone	-	1[e]	864[f] (for 3-penten-2-one)	**NO**
85	C_5H_8O	Cyclopentenone	-	1[e]	-	**NO**
85	C_5H_8O	2-methyl,2-butenal	-	1[e]	844[f] (for 2-butenal,2-methyl-(Z))	**NO**
85	$C_4H_4O_2$					
111	$C_6H_6O_2$	1,2- and 1,3-benzenediol (sum of 2 isomers)	-	200[e]	-	**NO**
111	$C_7H_{10}O$	-				
125	$C_6H_4O_3$	-				
125	$C_7H_8O_2$	-				
127	$C_6H_6O_3$	-				
127	$C_7H_{10}O_2$	-				
127	$C_8H_{14}O$	-				

129	$C_6H_8O_3$	-				
129	$C_7H_{12}O_2$	-				
129	$C_8H_{16}O$	-				
129	$C_{10}H_8$	Naphthalene	97.7[b]	106[d]	803[f]	**YES, but co-eluted with decanal**
139	$C_7H_6O_3$	-				
139	$C_8H_{10}O_2$	-				
139	$C_9H_{14}O$	-				
141	$C_7H_8O_3$	-				
141	$C_8H_{12}O_2$	-				
141	$C_9H_{16}O$	-				
143	$C_7H_{10}O_3$	-				
143	$C_8H_{14}O_2$	-				
143	$C_9H_{18}O$	-				
151	$C_8H_6O_3$	-				
151	$C_9H_{10}O_2$	-				
151	$C_{10}H_{14}O$	-				
155	$C_8H_{10}O_3$	-				
155	$C_{10}H_{18}O$	-				
157	$C_7H_8O_4$	-				
157	$C_8H_{12}O_3$	-				
157	$C_{10}H_{20}O$	-				
166	$C_8H_4O_4$	-				
169	$C_9H_{12}O_3$	-				
169	$C_{10}H_{16}O_2$	-				
169	$C_{11}H_{20}O$	-				

178	$C_{10}H_8O_3$	-				
179	n.a.	-				
182	n.a.	-				
183	$C_{13}H_{10}O$	-				
183	$C_{12}H_{22}O$	-				
183	$C_9H_{10}O_4$	-				
183	$C_{10}H_{14}O_3$	-				
195	$C_{11}H_{14}O_3$	-				

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