Electronic Supplementary Material (ESI) for Faraday Discussions.
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Supplement to “Sources of non-methane hydrocarbons in surface air in Delhi, India”

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ESI1 – Air quality index in Delhi

Plot created with air quality information data downloaded from the US embassy, New Delhi, for 2018 using US EPA method for calculation of air quality index (AQI). [1]

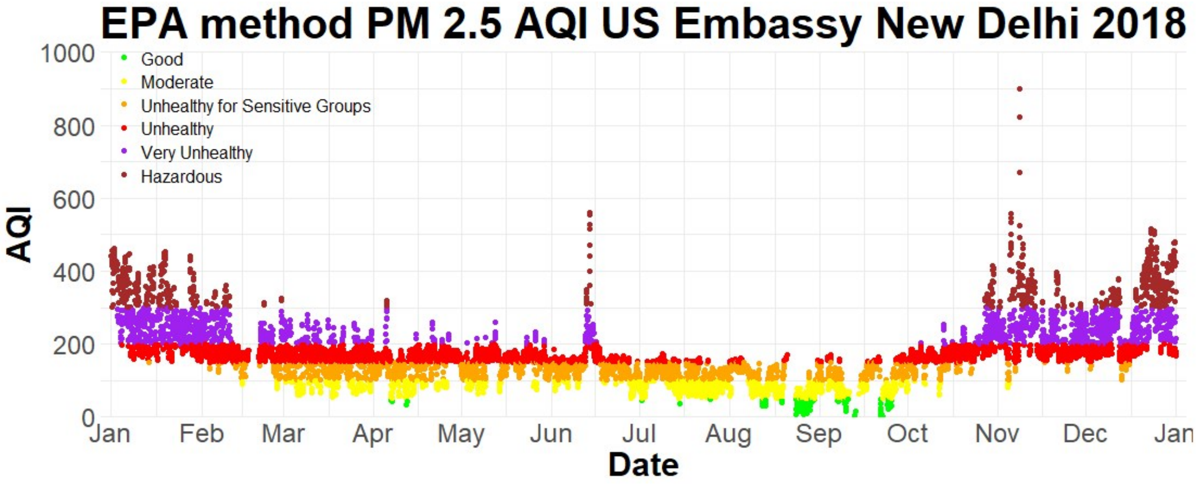


Figure S1. AQI for New Delhi measured at the US embassy during 2018.

ESI2 – Mean, minimum and maximum mixing ratios

Calculated over sample periods where both DC-GC-FID and GCxGC-FID were measuring (29/05/18 20:00 to 05/06/18 11:00 and 11/10/2018 22:00 to 27/10/18 17:00). Instrumental limits of detection (LOD) are provided elsewhere. [2]

Table S1. Mean, maximum and minimum mixing ratios (ppbv) of NMHC measured in Delhi during post- and pre-monsoon campaigns (based on hourly measurements with DC-GC-FID sample collection times of 20 minutes and GCxGC-FID sample collection times of 30 minutes).

NMHC	**Pre**	**Pre max**	**Pre min**	**Post**	**Post max**	**Post min**
Alkanes						
Ethane	6.15	18.28	2.64	32.02	159.10	1.21
Propane	19.91	598.07	1.81	43.15	172.78	0.62
i-Butane	5.62	115.21	0.78	20.77	79.71	0.19
n-Butane	7.89	135.32	<LOD	39.74	153.99	<LOD
Cyclopentane	0.26	3.83	0.04	0.89	4.01	<LOD
i-Pentane	4.39	16.39	0.52	17.54	77.10	0.24
n-Pentane	1.55	5.94	0.21	6.76	28.78	0.10
n-Hexane	0.36	1.42	0.02	1.86	7.97	0.023
n-Heptane	0.25	0.92	0.05	1.36	6.57	0.02
n-Octane	0.14	0.53	<LOD	0.74	3.78	0.03
C_8 aliphatics	1.42	4.13	<LOD	5.79	29.36	0.54
n-Nonane	0.16	0.59	0.04	1.07	5.09	0.07
C_9 aliphatics	0.99	3.16	<LOD	3.74	15.76	0.38
n-Decane	0.15	0.60	0.04	0.87	4.17	0.10
C_{10} aliphatics	0.55	2.06	0.12	3.37	16.31	0.29
n-Undecane	0.11	0.51	0.01	0.45	2.14	0.05
C_{11} aliphatics	0.33	1.59	0.09	2.08	8.58	0.13
n-Dodecane	0.03	0.36	<LOD	0.93	3.59	0.05
C_{12} aliphatics	0.10	0.75	0.01	4.09	17.57	0.25
n-Tridecane	0.04	0.13	0.01	2.66	8.98	0.29
C_{13} aliphatics	0.08	0.67	0.01	3.89	14.86	0.27
n-Tetradecane	<LOD	<LOD	<LOD	1.28	3.17	0.15
C_{14} aliphatics	0.11	0.59	0.01	1.83	4.70	0.05
Aromatics						
Benzene	1.36	5.13	0.35	6.67	41.24	0.51
Toluene	2.55	16.39	<LOD	18.38	120.89	1.02
Ethylbenzene	0.33	1.92	<LOD	2.64	14.52	0.21
m/*p*-Xylene	0.70	3.90	<LOD	4.93	29.92	0.31
o-Xylene	0.33	1.67	<LOD	2.42	13.93	0.08
Styrene	0.19	0.83	0.06	0.76	5.74	0.02
*i*Pr-benzene	0.02	0.11	<LOD	0.23	1.27	0.01

Pr-benzene	0.04	0.18	<LOD	0.32	1.58	0.02
3/4-Ethyltoluene	0.46	2.33	0.07	1.46	7.48	0.07
1,3,5-TMB	0.07	0.34	0.01	0.50	2.97	0.02
2-Ethyltoluene	0.08	0.39	0.01	0.53	2.70	0.03
1,2,4-TMB	0.27	1.40	0.05	1.53	8.13	0.06
*t*Bu-Benzene	<LOD	<LOD	<LOD	0.29	1.47	0.01
1,2,3-TMB	0.05	0.35	<LOD	0.51	2.84	0.02
Indan	0.01	0.08	<LOD	0.12	0.68	<LOD
C_4 aromatics	0.21	1.26	0.01	3.04	15.22	0.17
Indene	<LOD!	<LOD	<LOD	0.00	0.05	<LOD
2-Methylpropylbenzene	0.01	0.03	<LOD	0.12	0.64	<LOD
1-Methylpropylbenzene	0.01	0.05	<LOD	0.14	0.64	0.01
m/*p*-Cymene	0.03	0.22	0.01	0.42	2.10	0.02
o-Cymene	<LOD	<LOD	<LOD	0.02	0.26	<LOD
1-Methyl-3-propybenzene	0.01	0.03	<LOD	0.08	0.40	<LOD
1,3-Diethylbenzene	0.02	0.12	<LOD	0.16	0.85	<LOD
n-Butylbenzene/1,4-Diethylbenzene	0.04	0.20	<LOD	0.41	2.09	0.01
1,2-Diethylbenzene	0.01	0.07	<LOD	0.14	0.72	0.01
1-Methyl-4-propylbenzene	0.01	0.05	<LOD	0.11	0.61	<LOD
1-ethyl-2,4-dimethylbenzene	0.02	0.12	<LOD	0.14	0.73	0.01
4-Ethyl-1,2-dimethylbenzene	0.02	0.17	<LOD	0.27	1.51	0.01
1-Ethyl-2,3-dimethylbenzene	0.00	0.03	<LOD	0.07	0.42	<LOD
2-Ethyl-1,3-dimethylbenzene	0.00	0.02	<LOD	0.08	0.40	<LOD
1,2,4,5-Tetramethylbenzene	0.00	0.06	<LOD	0.13	0.55	<LOD
1,2,3,5-Tetramethylbenzene	0.01	0.13	<LOD	0.21	1.15	<LOD
1,1/1,3-Dimethylindan	<LOD	0.02	<LOD	0.03	0.17	<LOD
1,2,3,4-Tetramethylbenzene	0.01	0.09	<LOD	0.15	0.98	<LOD
1,1/1,3-Dimethylindan	<LOD	<LOD	<LOD	0.05	0.25	<LOD
1,2,3,4-Tetrahydronapthalene	0.00	0.01	<LOD	0.03	0.23	<LOD
C_5 aromatics	0.04	0.29	<LOD	0.83	3.95	<LOD
Monoterpenes						
a-Pinene	0.03	0.08	0.01	0.08	0.48	<LOD
Camphene	0.01	0.07	0.00	0.07	0.39	<LOD
Sabinene	<LOD	<LOD	<LOD	0.01	0.25	<LOD
B-pinene	0.01	0.05	<LOD	0.04	0.20	<LOD
Myrecene	<LOD	<LOD	<LOD	0.03	0.20	<LOD
a-Phalledrene	0.02	0.06	<LOD	0.07	0.35	<LOD
3-Carene	0.01	0.05	<LOD	0.06	0.39	<LOD
a-Terpinene	<LOD	<LOD	<LOD	0.02	0.12	<LOD
Limonene	0.01	0.19	<LOD	0.32	2.01	0.00
B-Ocimene	0.03	0.14	<LOD	0.22	1.71	<LOD
g-Terpinene	<LOD	0.05	<LOD	0.02	0.14	<LOD
Terpinolonene	<LOD	0.02	<LOD	0.04	0.29	<LOD
Sum monoterpenes	0.12	0.65	0.03	0.98	5.99	0.01

Alkenes						
Ethene	4.25	15.11	0.89	21.62	96.08	0.56
Propene	1.11	4.97	0.17	6.26	25.49	0.07
t-2-Butene	0.15	0.90	0.03	1.28	6.19	0.01
1-Butene	0.31	1.18	0.07	1.74	6.57	<LOD
i-Butene	0.47	1.72	0.15	2.59	10.05	0.02
c-2-Butene	0.16	0.77	0.04	1.21	5.42	0.01
1,3-Butadiene	0.12	0.67	<LOD	0.82	4.64	0.01
t-2-Pentene	0.14	0.60	0.01	0.60	3.20	0.01
1-Pentene	0.07	0.25	<LOD	0.39	1.83	0.01
Isoprene	1.10	4.62	0.01	0.90	3.92	0.05
1,2-Butadiene	0.13	0.39	0.06	0.31	1.09	0.01
Alkynes						
Acetylene	2.41	6.85	0.53	10.40	45.57	0.28
Propyne	0.08	0.31	0.01	0.45	1.91	0.013
Oxygenates						
Methanol	26.95	62.37	4.91	60.08	1187.81	13.75
Acetone	6.30	12.04	3.58	14.30	45.23	3.87
Ethanol	27.38	101.52	8.41	56.47	216.40	0.001

ESI3- Breakthrough testing

Example breakthrough testing for GCxGC-FID. Breakthrough testing was conducted for *n* = 2 injections at 500 ml increments between 500 and 4000 ml for the most volatile NMVOCs using the same sample collection flow rates as ambient samples (70 ml min^{-1}), but for longer sample times to ensure a linear response at the sample volumes used for ambient measurements (2100 ml).

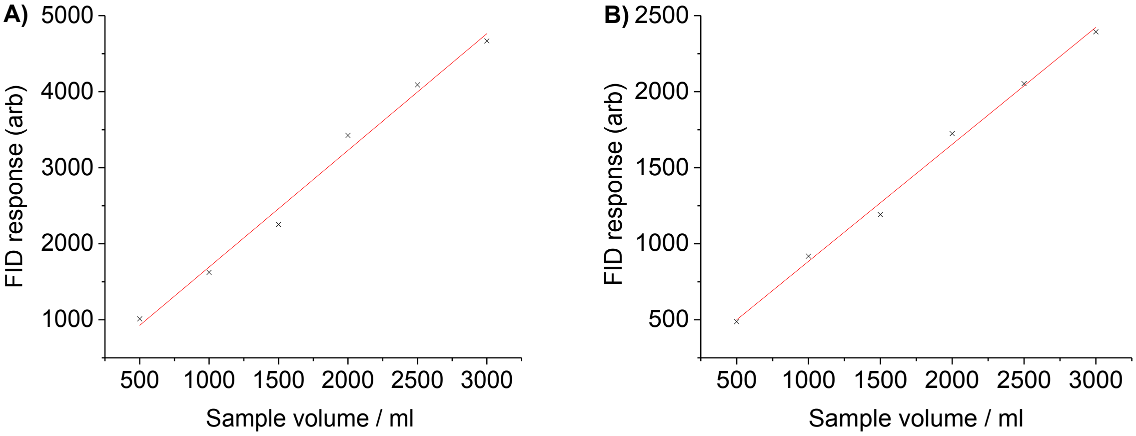


Figure S2. Breakthrough testing for GCxGC-FID for (A) benzene and (B) *n*-octane.

ESI4 – Linearity of detector response

A standard containing 4.85 ppmv benzene (National Physical Laboratory, UK) diluted in purified air to a range of concentrations 0-300 ppbv to test the linearity of the detector response for the DC-GC-FID (Figure S3A) and GCxGC-FID (Figure S3B).

The DC-GC-FID detector response was assessed with injections at 0 ppbv (n = 10), 10 ppbv (n = 17), 100 ppbv (n = 3) and 300 ppbv (n = 13).

The GCxGC-FID detector response was assessed with n = 3 injections each at 5 ppbv, 24 ppbv, 53 ppbv, 97 ppbv, 150 ppbv, 190 ppbv and 250 ppbv.

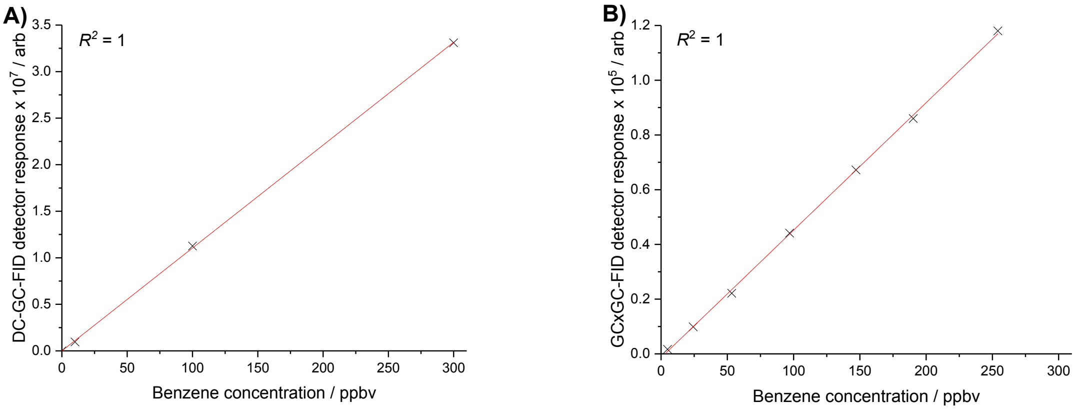


Figure S3. High concentration calibrations of DC-GC-FID and GCxGC-FID instruments to benzene.

ESI5 – Monoterpene quantification and qualification

Many components in ambient samples were not available in gas-phase standards from the NPL, either due to cost (monoterpenes) or stability in the gas phase (C_{12}-C_{14} alkanes, C_4/C_5-substituted monoaromatics). Monoterpenes are traditionally considered biogenic emissions and α-pinene and limonene have been qualified previously using the GCxGC-FID instrument, [2] however a much greater range of species are present in ambient air (see Figure S4).

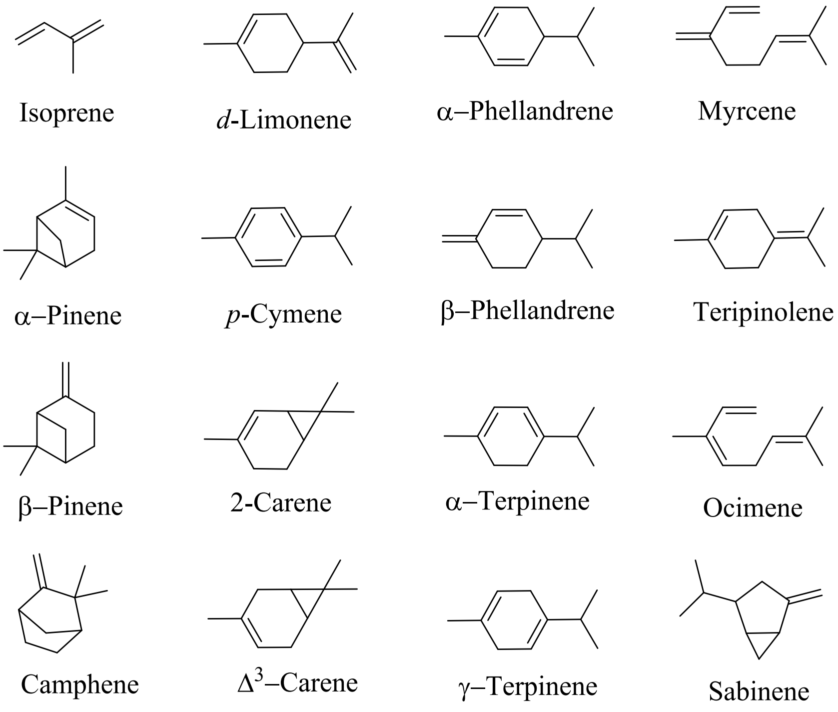


Figure S4. Common biogenic NMVOC. [3]

Monoterpenes present in the ambient air of Delhi have been qualified through stepwise addition (see Figure S5). Kovats retention indices (I) have been calculated for offline liquid injections, an ambient sample from 27/10/2018 at 08:13 and compared to literature to assist with peak qualification (see Table S2). The Kovats retention index allows unidentified eluents to be identified by comparing their position in the chromatogram relative to n-alkanes,

$$I = 100 \times \left[n + (N - n) \frac{t_{\mathrm{r(unknown)}} - t_{\mathrm{r}(n)}}{t_{\mathrm{r(N)}} - t_{\mathrm{r}(n)}} \right] \qquad \text{E1}$$

where I = Kováts retention index, N = carbon number of n-alkane of higher boiling point than unidentified eluent, n = carbon number of n-alkane of lower boiling point than unidentified eluent, $t_{r(\mathrm{unknown})}$ = retention time of unidentified eluent, $t_{r(n)}$ = retention time of n-alkane of lower boiling point than unidentified eluent and $t_{r(N)}$ = retention time of *n*-alkane of higher boiling point than unidentified eluent.

Quantification has been carried out by measuring the response of a known quantity of these components to a known quantity of toluene in solution which was then used to develop a detector response factor. Standards were prepared by dissolving 0.1 g into 10 ml EtOAC to give a stock solution concentration of 10000 µg ml^{-1}. This was diluted to give a concentration of 500 µg ml^{-1} by dissolving 0.5 ml of stock solution into 9.5 ml EtOAc. This solution was diluted to 100 µg ml^{-1} prior to analysis by dissolving 0.2 ml into 0.8 ml of EtOAc.

A 1 µL sample was injected split (100:1) into a liner held a 170 ^{o}C connected to a non-polar BP5 held at 50 psi (15 m x 0.25 µm x 0.25 mm) which was connected to a polar BPX50 (30 psi; 2 m x 0.25 µm x 0.25 mm) via. a modulator held at 180 ^{o}C (5 s modulation, Analytical Flow Products ELDV2-MT). The oven was held at 35 ^{o}C for 2 minutes then ramped at 2.5 ^{o}C min^{-1} to 130 ^{o}C and held 1 minute then ramped 10 ^{o}C min^{-1} to 180 ^{o}C with a final hold of 8 minutes. The syringe was cleaned prior to injection with EtOAC by 3 × pre/post injection washes in two different solvent wash bottles.

The number of moles of solute and EtOAc was calculated as:

$$\text{moles} = \frac{\text{mass}}{\text{molar mass}} \tag{E2}$$

and the number of molecules of each calculated by multiplying by Avogadro's constant. The ratio of solute to EtOAc was used to calculate the eventual concentration which was around 100 ppmv and a detector response factor for the solute was developed by (area ppmv^{-1}).

$$\text{monoterp area}_{(g)} \text{ at 3.9ppbv} = \frac{\text{monoterpene}_{(l)}}{\text{toluene}_{(l)}} \text{ x toluene signal at 3.9ppbv} \tag{E3}$$

where monoterpene$_{(l)}$ = response of the monoterpene per ppmv in solution and toluene$_{(l)}$ = toluene response per ppmv of toluene in solution and monoterpene area$_{(g)}$ has then been treated as though it was from the gas standard.

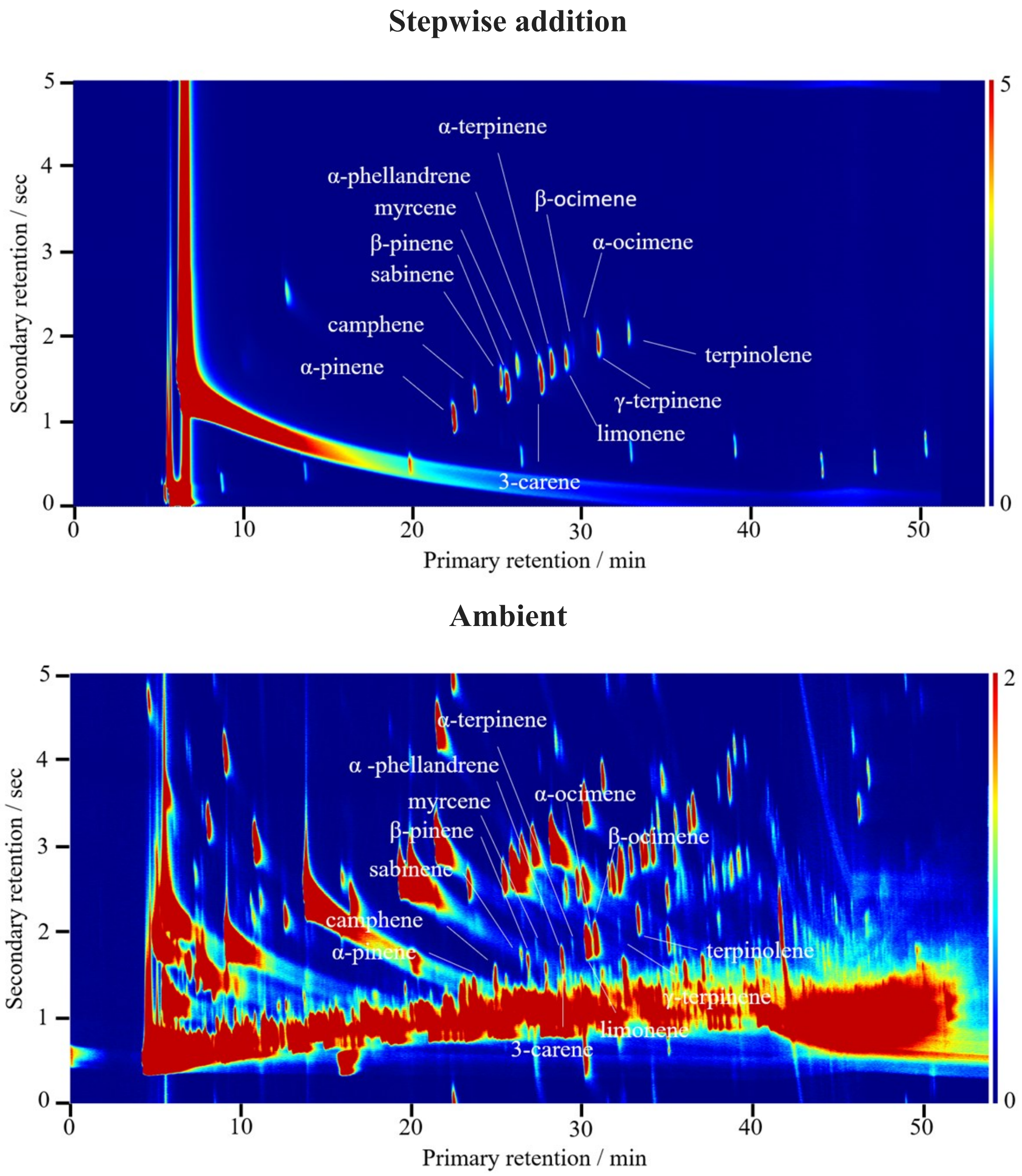


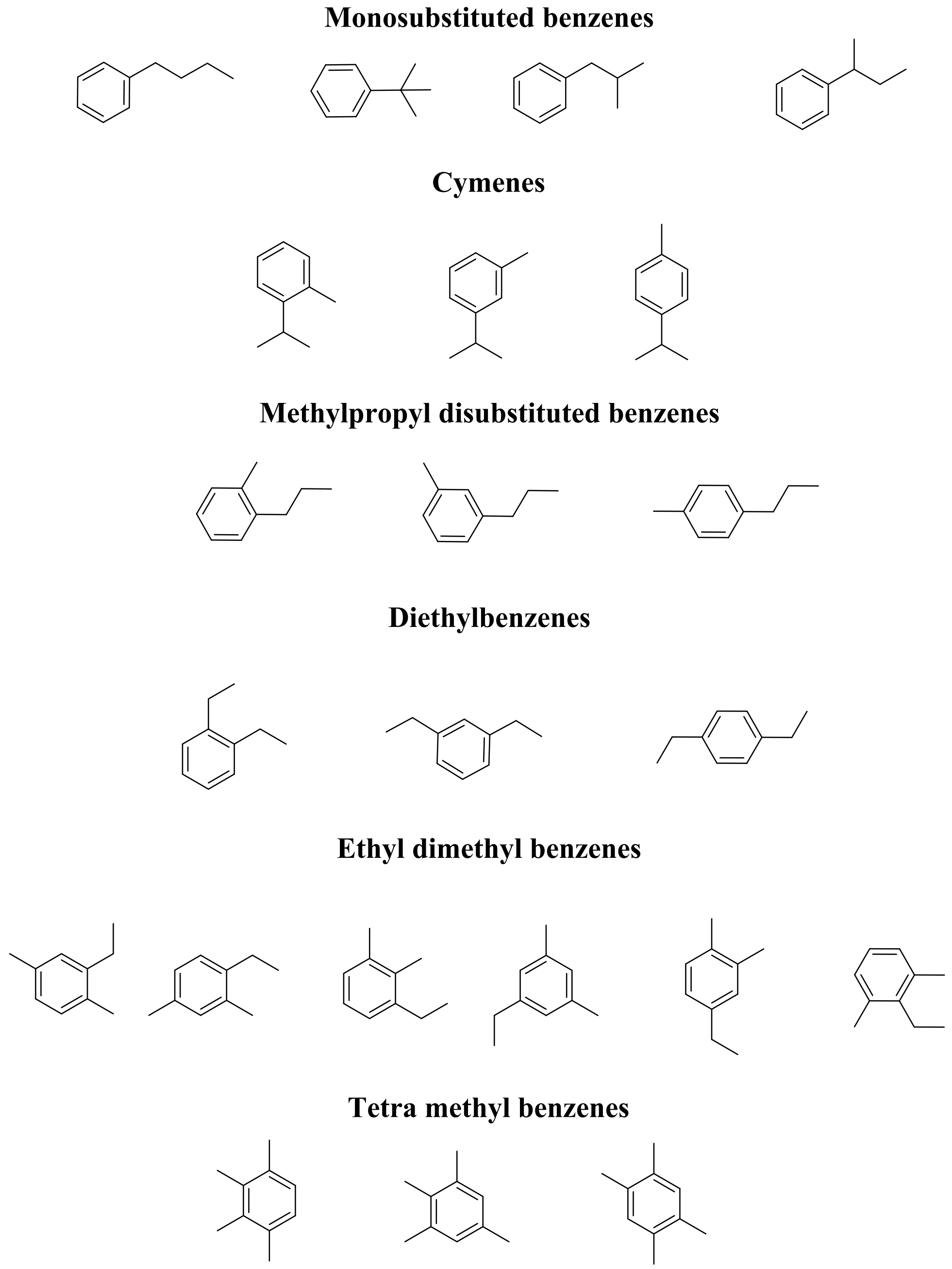
Figure S5. Stepwise qualification of monoterpenes.

Table S2. Qualification of monoterpenes through Kovats retention indices.

VOC	Kovat$_{liquid}$	Kovat$_{ambient}$	Kovat$_{literature}$	Ref
α -Pinene	940.7	940.5	941	[4]
Camphene	959.3	959.5	958	[4]
Sabinene	981.5	982.3	983	[4]
β-Pinene	985.3	988.6	990	[4]
Myrcene	996.3	996.2	995	[4]
α -Phellandrene	1017.9	1018.0	1017	[4]
3-Carene	1017.9	1018.0	1022	[5]
α -Terpinene	1027.0	1028.2	-	-
Limonene	1039.8	1041.1	1040	[4]
β-Ocimene	1047.5	1048.8	1051	[6]
α-Ocimene	1055.2	-	-	-
γ-Terpinene	1069.2	1070.5	1069	[5]
Terpinolonene	1097.4	1097.3	1096	[7]

ESI6 – Tentative C_4 substituted monoaromatic qualification

Figure S6 shows examples of some C_4 substituted monoaromatics. Previously, four C_4 alkyl-substituted monoaromatic species were qualified in London, with a grouped analysis providing information on the remaining species present. [2] Concentrations in Delhi in the post monsoon were much higher and thus these species are potentially more important than in previous studies. The large number of isomers of C_4 aromatics meant that their total contribution could be significant.



Monosubstituted benzenes

Cymenes

Methylpropyl disubstituted benzenes

Diethylbenzenes

Ethyl dimethyl benzenes

Tetra methyl benzenes

Figure S6. Examples of substituted C_4 substituted monoaromatics ($C_{12}H_{14}$).

It remained cost and time prohibitive to successfully qualify and quantify these species through liquid calibrations, however, several different approaches were used to tentatively qualify C_4 alkyl-substituted monoaromatics. These included previous liquid injections, [8] liquid injections of 6 available species, comparison to a setup in the literature with a similar primary dimension column (DB-5, 30 m, 0.25 mm, 1 µm) [9] and to a diesel fuel standard analysed by GCxGC-MS using a similar column (BPX5). Generally comparison between the Kovats retention indices of these systems with slightly different columns and chromatography offers a much poorer comparison, compared with those of exactly the same system shown in Table S2 and have not been used to qualify peaks. Peaks have been identified in groupings within the systems, based on their elution in the primary and secondary dimensional space, and peaks were identified relative to one another within these groups. Between the GCxGC-FID for ambient measurements and the GCxGC-MS for diesel there is a similar number of peaks with similar spacings.

The exact order of elution of C_4 substituted monoaromatics is not initially clear by comparing it to GCxGC-MS, due to many mis-qualified peaks being identified as cymenes. What is clear, however, is that general groupings can be identified (see Figure S7). Liquid injections in the supplement to Dunmore et al. (2015) [8] allow a relationship between the peaks in the system using MS and FID to be made. The thirteen C_4 aromatic peaks identified by Xu et al. (2003) [9] can also be related to these two systems, with the final missing peaks identified using a diesel liquid standard and GCxGC-MS and the suggested peak orders finally confirmed by liquid injection of 6 species.

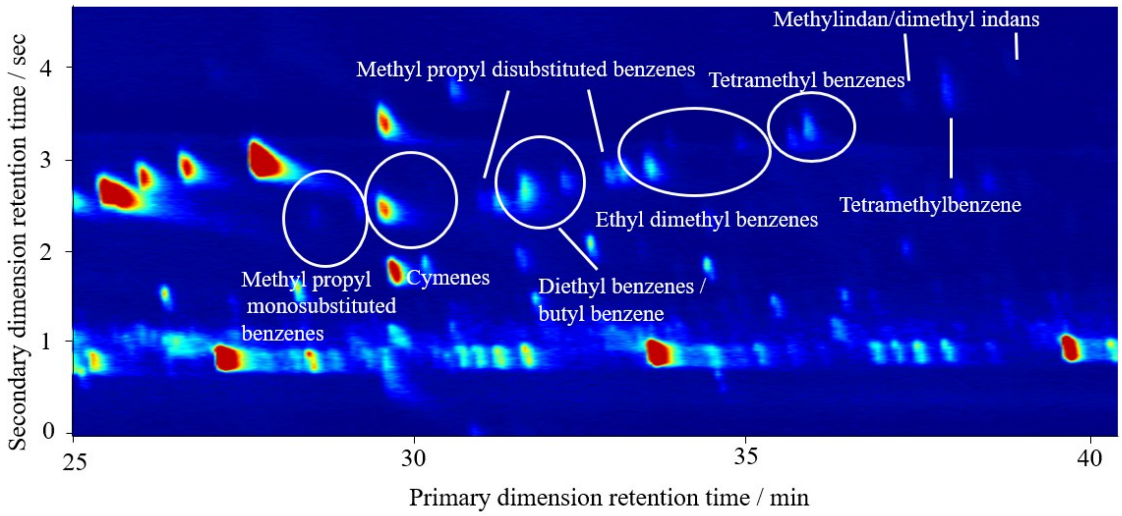


Figure S7. GCxGC-FID chromatogram with grouped identities of C_4 substituted monoaromatics determined by GCxGC-MS using diesel fuel.

The C_4 substituted monoaromatic region started at 2-methylpropylbenzene in Xu et al. (2003) [9] and our GCxGC-MS studies, so it is logical that the C_4 aromatics also start here for the GCxGC-FID. Benzene-tert butyl was determined as being slightly above the line of the C_4 monoaromatics, from the supplementary information in Dunmore et al. (2015), [8] where this peak was identified with a liquid standard. An additional peak was observed between the first cymene and 2-methylpropylbenzene when compared to Xu et al. (2003) [9] in the GC-FID and this was also found in the GCxGC-MS as Benzene, (1-methylpropyl)-. Next, 3 cymenes are observed in the GCxGC-MS, whilst in the GCxGC-FID this appeared to be closer to two peaks with the first peak being a coelution. It remained difficult to decide the order of these peaks, but the supplementary information in Dunmore et al. (2015) [8] showed the first peak as *p*-cymene. From Xu et al. (2003) [9] *m*/*p* cymene coeluted, which placed *o*-cymene separate to these. This elution order mimicked the xylenes which elute in the substitution order *m*-/*p*- then *o*- which seemed logical as these have highly similar substitutions, except instead of being dimethyl substituted they have methyl and isopropyl substitution.

Nothing was observed by Xu et al. (2003) [9] between the cymenes and diethyl benzenes, however there were 2 peaks in this region in the Delhi GCxGC-FID chromatogram. The first peak in this region was identified by comparison to GCxGC-MS as Benzene,1-methyl-3-propyl. The next two peaks were identified by comparison to the supplementary information in Dunmore et al. (2015), [8] as peaks 48/49 were identified as 1,3 and 1,4-diethylbenzenes. Liquid injection confirmed that 1,4-diethylbenzene and *n*-butyl benzene coelute (see Figure S8). In the GCxGC-MS chromatogram an additional diethyl benzene peak was present after this, which was concluded to be 1,2-diethyl benzene. This region was hard to assign as many peaks in the GCxGC-MS chromatogram were misidentified as *o*-cymene and generally peaks were coeluting in this region, which was also a problem when using Xu et al. (2003) [9] as 1,3- and 1,2–diethylbenzene coeluted.

The next 4 peaks were identified using the GCxGC-MS as ethyl dimethyl benzenes. It remained difficult to identify specific isomers from the GCxGC-MS comparison, but the order was given in the study of Xu et al. (2003) [9] and the same qualification was used in this analysis.

After the ethyl, dimethyl benzenes were peaks from tetramethylbenzenes, which appeared as a coelution in the GCxGC-MS studies and only one was identified in Xu et al. (2003) [9] but there were two very closely spaced peaks in the GCxGC-FID chromatogram, which resolved these two isomers. The order was confirmed through liquid injections as 1,2,4,5- then 1,2,3,5-tetramethyl benzene.

A dimethyl indan was observed next, and the GCxGC-MS gave two closely spaced hits for 1,1-dimethylindan and 1,3-dimethyl indan which meant that this study could not definitively say which of these isomers is present was the ambient chromatogram. The next peak was a tetramethyl benzene in the GCxGC-MS, which was concluded to be 1,2,3,4-tetramethyl benzene as the other two isomers had been identified. The next peak, which was only present in post monsoon data, was harder to identify but the GCxGC-MS gave a hit for 4-methylindan. The final peak was a strong hit for 1,2,3,4-tetrahydronapthalene which seemed logical that this eluted at the end of the C_4 monoaromatic grouping as it is similar to indan at the end of the C_3 monoaromatic grouping, just with an extra carbon in the unconjugated ring. This last peak sat slightly above 1,2,4,5-tetramethylbenzene in both the GCxGC-FID and GCxGC-MS chromatograms, which helped to confirm its identity as there were also poorer hits for substituted indans below this.

Figure S9 shows a comparison of chromatograms from C_4 substituted monoaromatics from diesel and an ambient sample, with the peak assignment given in Table S3. This approach seems to correctly identify specific regions of similarly substituted isomers when compared to the liquid injection in Figure S8, but may occasionally incorrectly assign the elution order of some of these isomers within this grouping.

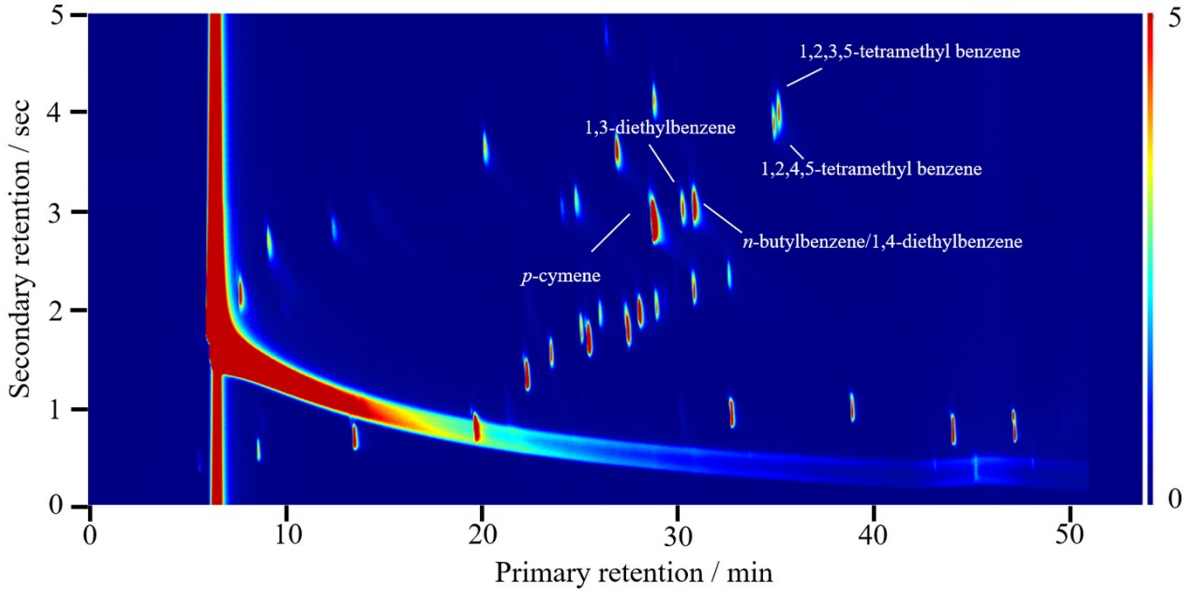


Figure S8. Liquid injections of C_4 substituted monoaromatics for peak identity confirmation.

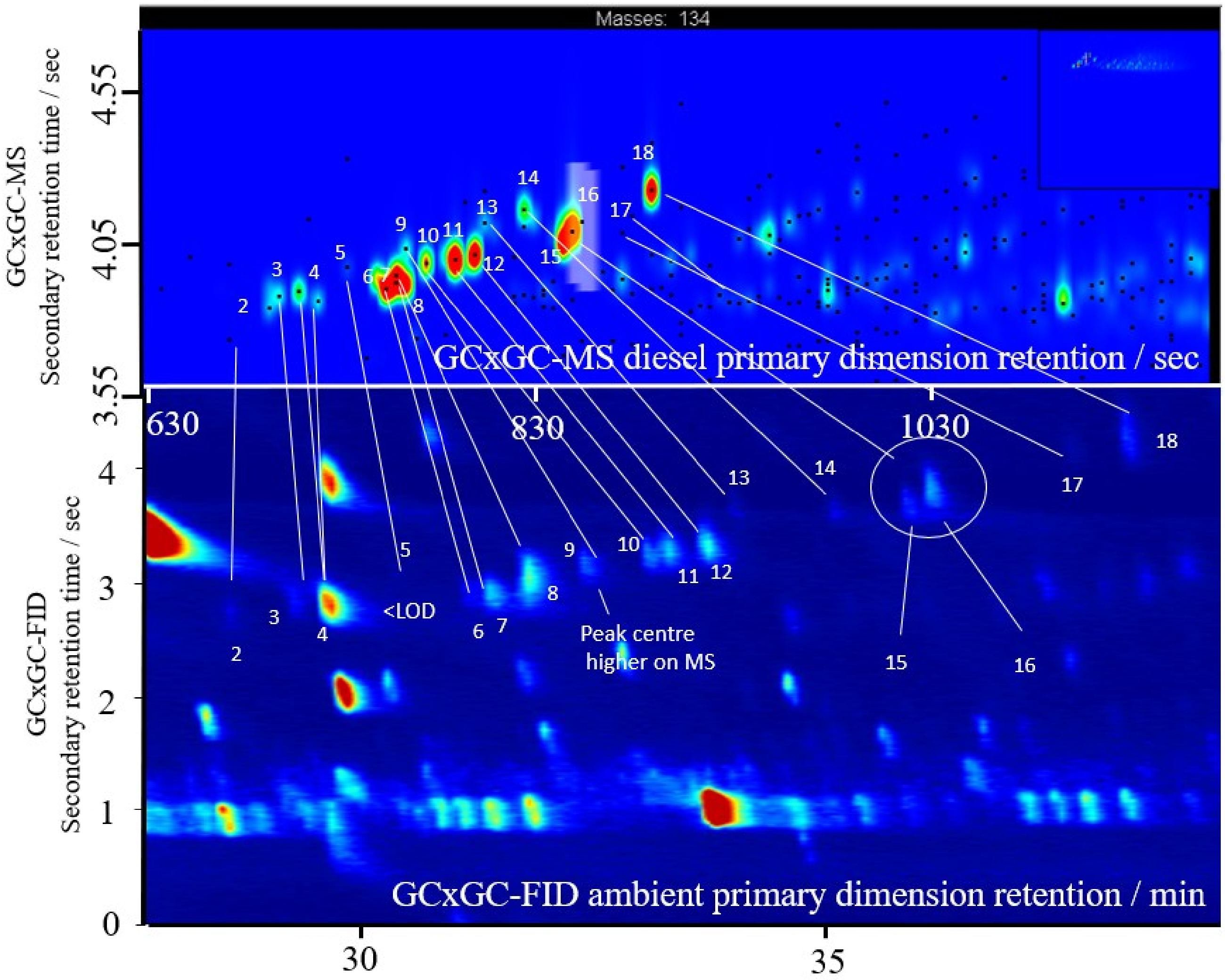


Figure S9. C_4 substituted monoaromatics elution order from diesel and petrol where numbers correspond to peaks in Table S3.

Table S3. Tentative C_4 aromatic identifications where Rt_1 and Rt_2 are from GCxGC-MS, RI_a = Kovats retention index from GCxGC-FID, R_{ib} = Kovats retention index from GCxGC-MS of diesel, RI_c = Kovats retention index from Xu et al. (2003) [9] and RI_d = Kovats retention index from literature with refs in Xu et al. (2003). [9] Confirmed via: a = standards in Dunmore et al. (2015), b = elution order from diesel GCxGC-MS and c = elution order from Xu et al. (2003). [9]

VOC	**Peak number**	**Rt_1 /s**	**Rt_2 / m**	**Similarity**	**Reverse**	**Probability**	**RI_a**	**RI_b**	**RI_c**	**RI_d**	**Confirmed via**
Benzene-tert butyl	1										*a*
Benzene, (2-methylpropyl)	2	695	3.835	905	905	7319	1021	1007.4	1015	1008	*b, c*
Benzene, (1-methylpropyl)-	3	700	3.875	883	883	2737	1031.7	1011.1			*b*
m-Cymene	4	710	3.890	951	952	5952	1037.9	1019	1027	1023	*a, b, c*
p-Cymene	4	720	3.860	903	903	1449	1037.9	1026	1029	1034	*a, b, c*
o-Cymene	5	735	3.970	860	860	3135	1050.6	1037			*b*
Benzene,1-methyl-3-propyl	6	755	3.900	921	923	4394	1060.7	1052			*b*
1,3-Diethylbenzene	7	760	3.945				1070.9	1056	1055	1053	*a ,c*
Benzene-butyl	8	760	3.920	877	877	3780	1064.5	1055			*b*
1,4-Diethylbenzene	8	760	3.945	882	883	4694	1079.8	1059	1070.1	1051	*a ,c*
1,2-Diethylbenzene	9	760	4.030				1070.9	1056	1057	1061	*c*
Benzene,1-methyl-4-propyl	10	775	3.985	934	934	5816	1090.0	1066			*b*
1-Ethyl-2,4-dimethylbenzene	11	790	3.995	921	924	1263	1092.4	1077	1087	1075	*b, c*
4-Ethyl-1,2-dimethylbenzene	12	800	4.115	908	912	1003	1098.78	1085	1093	1086.7	*b, c*
1-Ethyl-2,3-dimethylbenzene	13	805	4.115	840	840	944	1104	1089	1094	1106.9	*b, c*
2-Ethyl-1,3-dimethylbenzene	14	825	4.175	921	921	1263	1120	1103.8	1100	1091	*b, c*
1,2,3,5-Tetramethylbenzene	15	845	4.065	917	917	1332	1133.28	1123			*b*
1,2,3,4-Tetramethylbenzene	16	850	4.090	930	930	2233	1137.28	1123			*b*
1,1/1,3-Dimethylindan	17	875/880	4.085/4.140	912/913	912/913	3091/9874	1163	1142/1146			*b*
1,2,4,5-Tetramethylbenzene	18	890	4.225	911	911	1243	1170	1153			*b*

ESI7 – PTR GCxGC-FID toluene time series comparison

Figure S10 shows a comparison of concentration-time series for toluene for the post-monsoon campaign between the PTR-QiTOF-MS (red) and the GCxGC-FID instrument (blue). Generally good agreement is found between the instruments, with the PTR-QiTOF-MS measuring higher values on some of the night-time spikes. This has been attributed to the PTR-QiTOF-MS measuring for the full 60 minutes per hour and the GCxGC-FID only making measurements for 30 minute samples windows in an hour period.

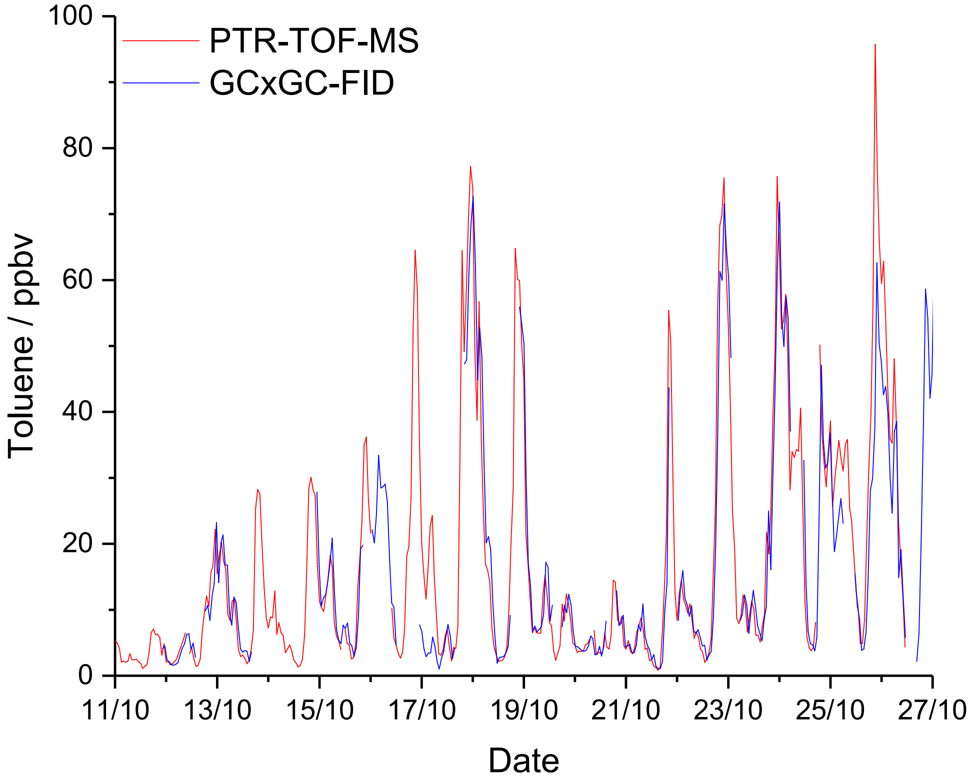


Figure S10. Concentration-time series comparison of PTR-QiTOF-MS (red) and GCxGC-FID (blue) for the post monsoon campaign.

ESI8 - Monthly wind rose plots from Indira Gandhi International Airport 2018

Data accessed from Indira Gandhi International Airport for 2018 using package worldmet from openair with data plotted as a wind rose. [10] Figure S11 shows that the lowest mean monthly wind speeds were during the post-monsoon/winter seasons from October, November and December (1.6/1.9/1.5 m s^{-1}) and the highest windspeeds were during the pre-monsoon from April – June (3.1/3.0/3.6 m s^{-1}). The largest % of calm periods with 0 m s^{-1} windspeed were from October-November (24.3-36.5 %), with a lower 3.1-10.0 % calm in the pre monsoon.

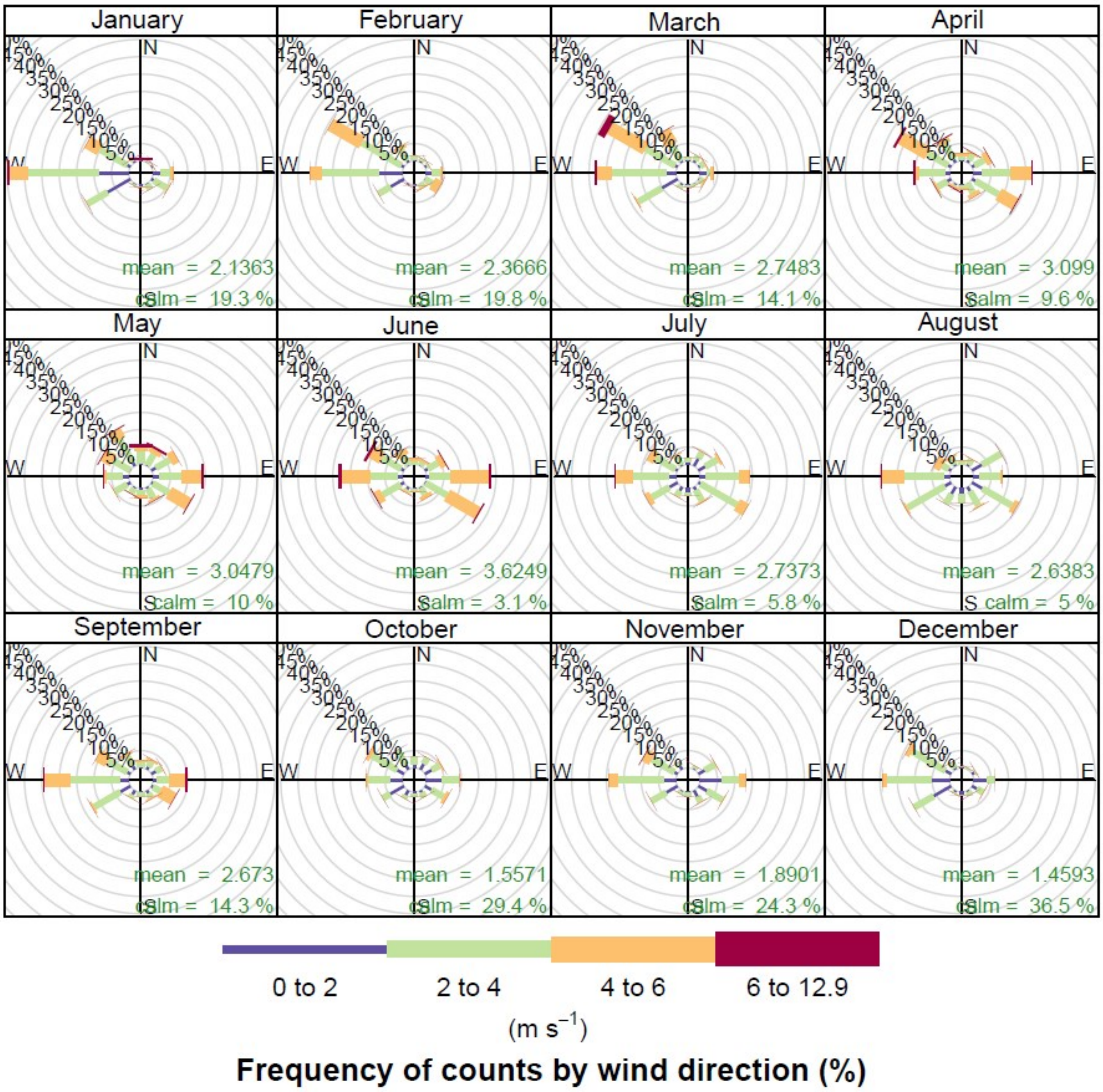


Figure S11. Monthly wind rose plots for Indira Gandhi International Airport for 2018.

ESI9 - Seasonal windspeed and planetary boundary layer variations over Delhi in 2018

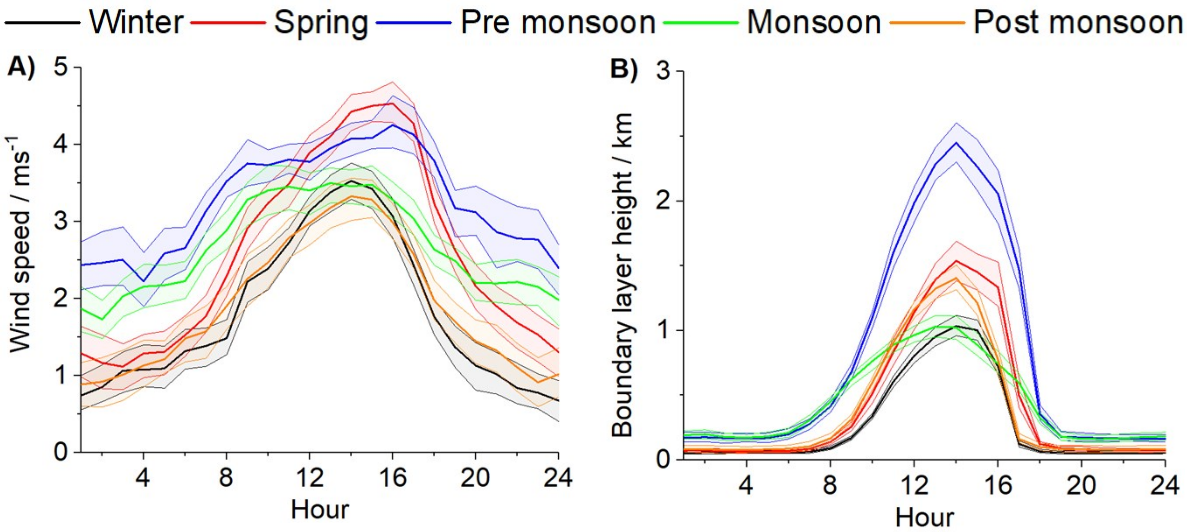


Figure S12. A: diurnal variation of windspeed at Indira Gandhi International Airport in 2018. B: diurnal variation of PBLH over Delhi in 2018.

ESI10 – Zoomed pre-monsoon NMHC, O_3, NO, NO_2 and CO timeseries

Data missing for large periods (> 6 hours) due to instrumental downtime in Figure 4 have been plotted as gaps in the data.

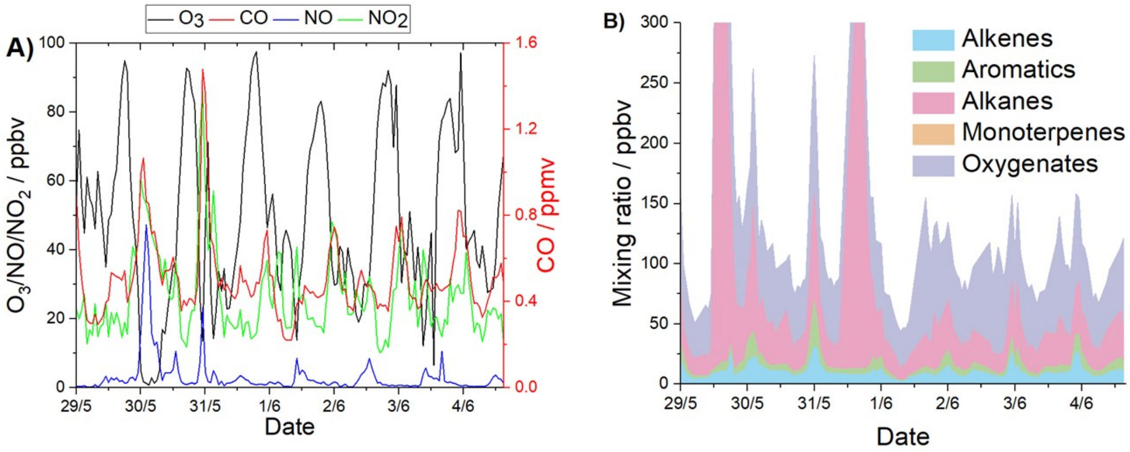


Figure S13. Zoomed-in timeseries of NMHCs, O_3, NO, NO_2 and CO timeseries during pre-monsoon campaign.

ESI11 - Pre- and post-monsoon diurnal profiles for selected NMVOC

Pre monsoon

DC-GC-FID sample window 28/05/18 21:00 – 05/06/18 12:00.

GCxGC-FID sample window 29/05/18 16:00 – 05/06/18 11:00.

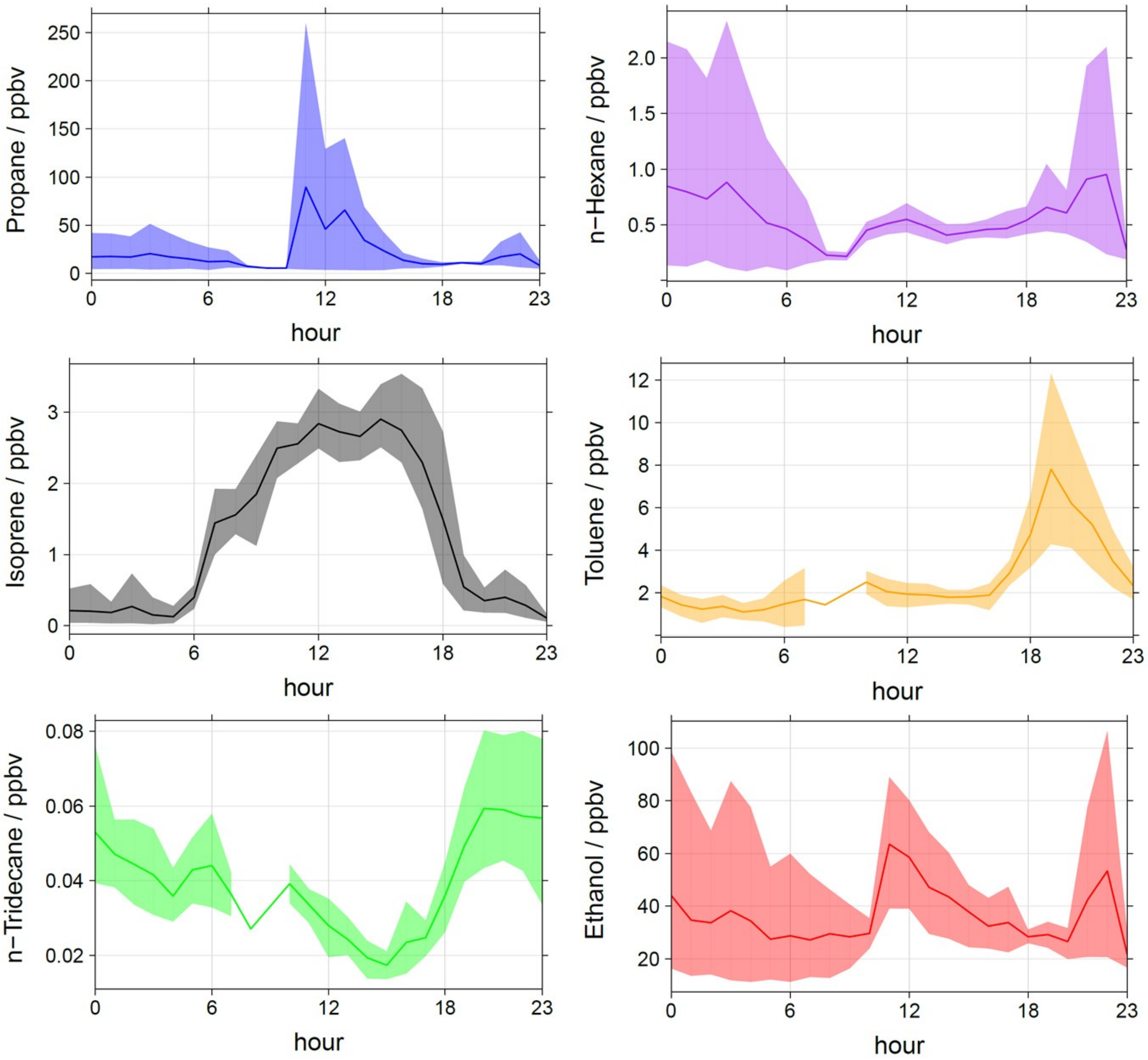


Figure S14. Diurnal profiles for propane, *n*-hexane, isoprene, toluene, *n*-tridecane and ethanol from the pre-monsoon campaign.

Post monsoon

DC-GC-FID sample window 05/10/18 00:00 – 27/10/18 17:00.

GCxGC-FID sample window 11/10/18 22:00 – 04/11/18 05:00.

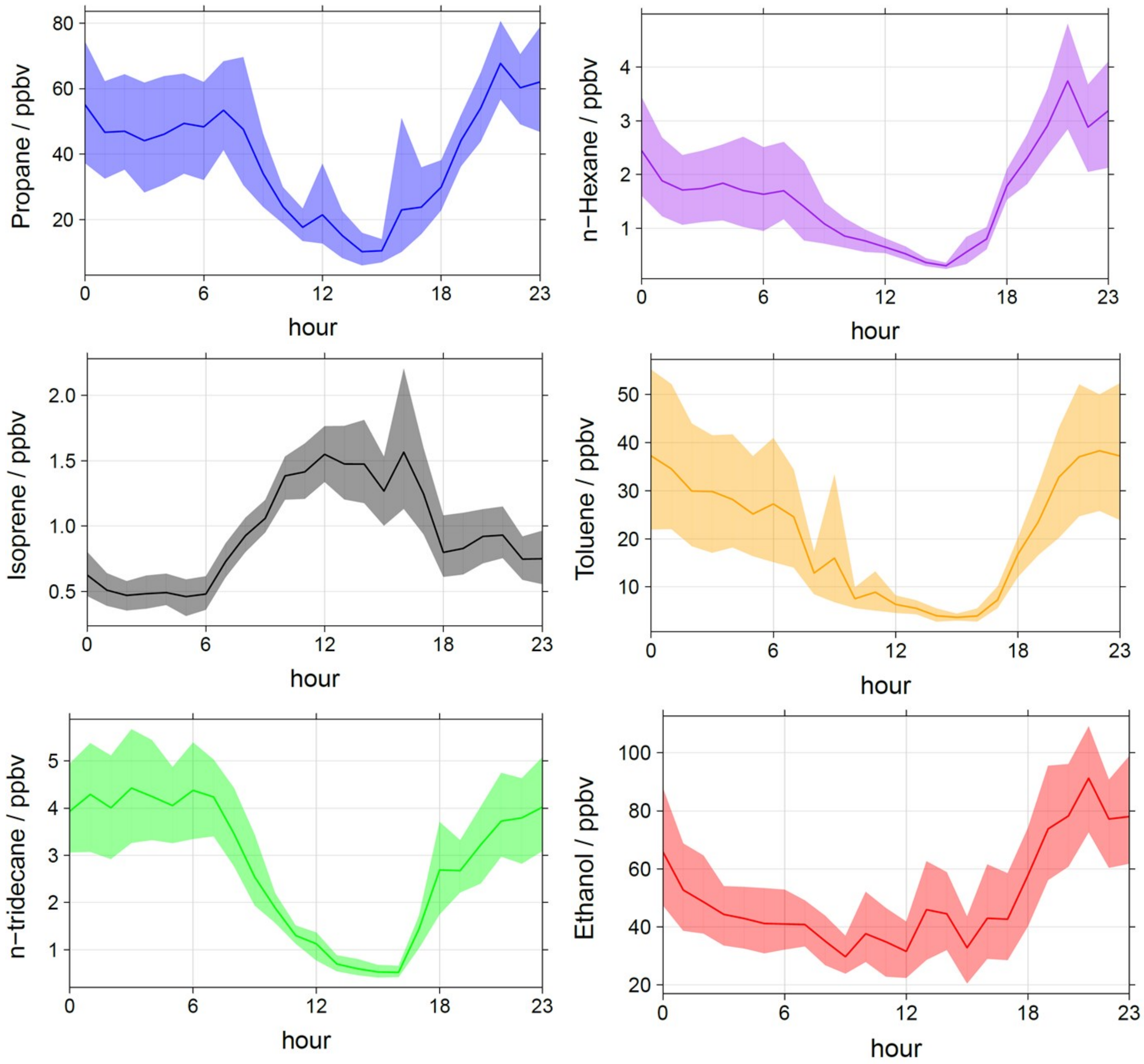


Figure S15. Diurnal profiles for propane, *n*-hexane, isoprene, toluene, *n*-tridecane and ethanol from the post-monsoon campaign.

ESI12 - Pre-monsoon stacked diurnals

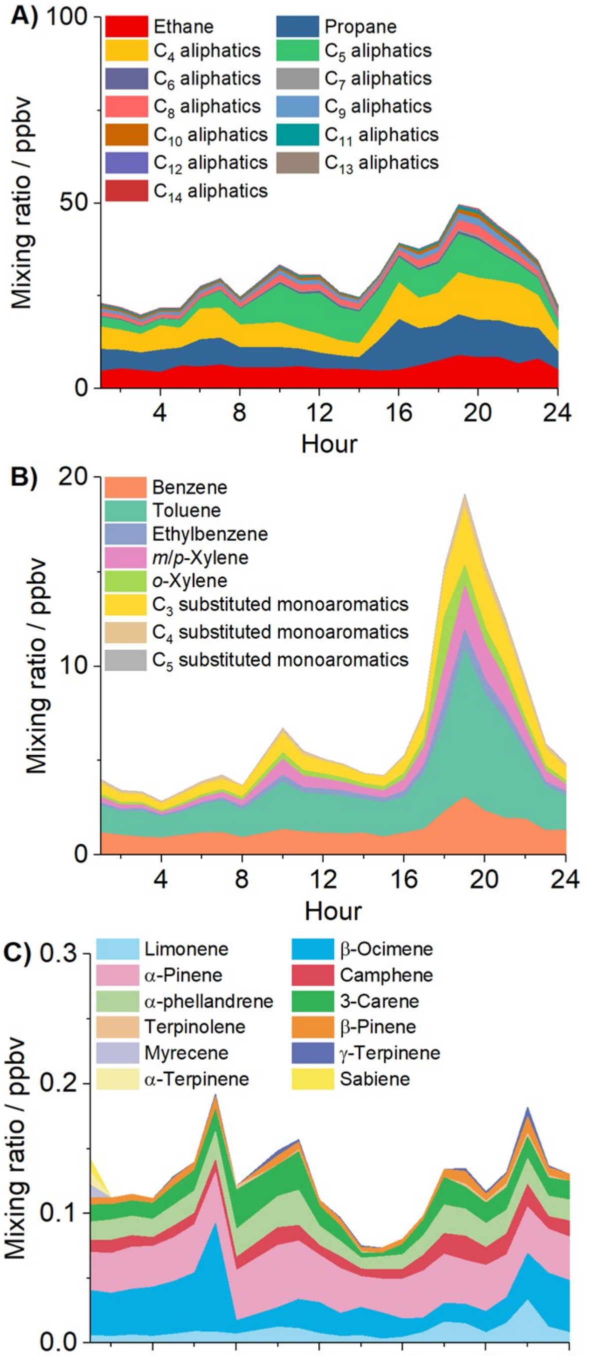


Figure S16. Zoomed stacked area diurnals for (A) alkanes excluding LPG spikes, (B) aromatics and (C) monoterpenes from the pre-monsoon campaign.

ESI13- Pre monsoon diurnal profile of toluene, PBLH and *ws* from 28/05/18-05/06/18

Figure S17 shows the diurnal profiles of toluene, PBLH and windspeed during the same sample period as the AQI data in Figure 7C. A longer sample period has been used than in Figure 7A using data from the PTR-MS from 26/05/18 16:00 to 09/06/18 08:00 to illustrate that the diurnal profiles of toluene of both campaigns are similar, but the concentrations different. This is better illustrated using the larger dataset collected by the PTR-MS (~ 2 weeks) vs. the GC dataset (~1 week).

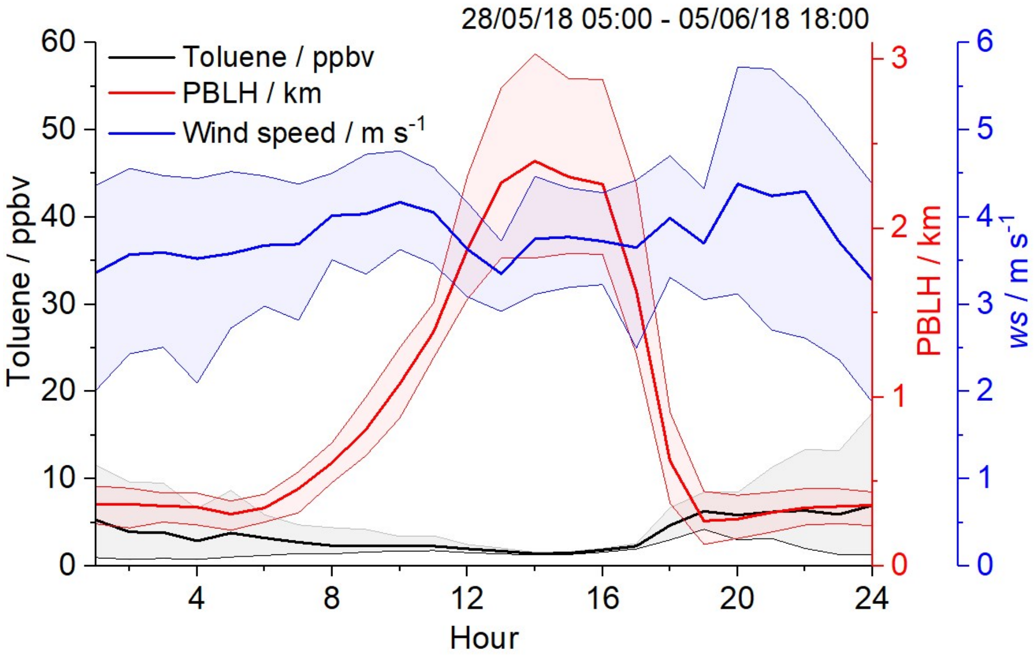


Figure S17. Diurnal profile of toluene, boundary layer height and windspeed during the same sample period as the AQI data during the pre-monsoon campaign.

ESI14 - PCA/APCS and EPA Unmix 6.0

Figure S18 and Figure S19 show the outputs of the Unmix 6.0 model and the combined mean output of PCA/APCS and Unmix 6.0 models. The results are relatively similar, but Unmix 6.0 showed slightly larger contributions of diesel to aromatics and heavier alkanes, and the differences between the two approaches may be caused by slight collinearity of sources.

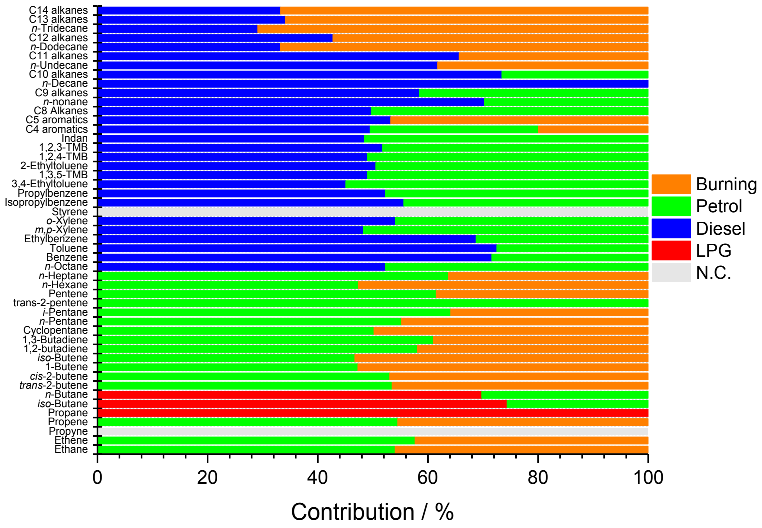


Figure S18. Mean contribution of sources to NMHC measured in Delhi by Unmix 6.0, where NC means that the model did not converge.

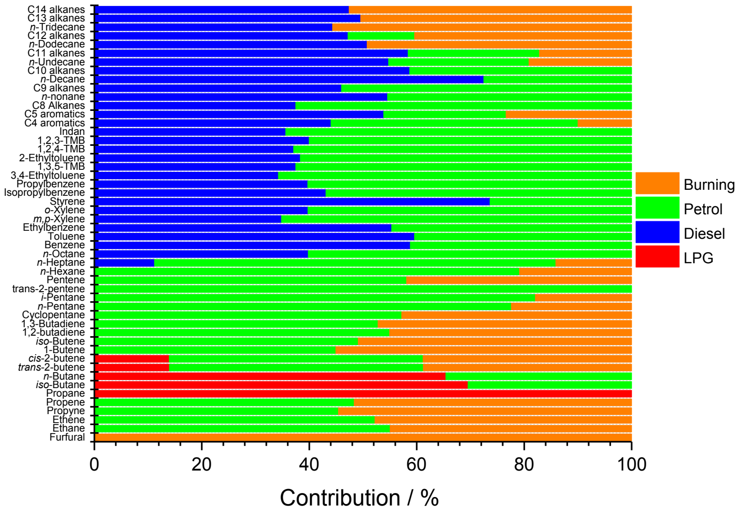
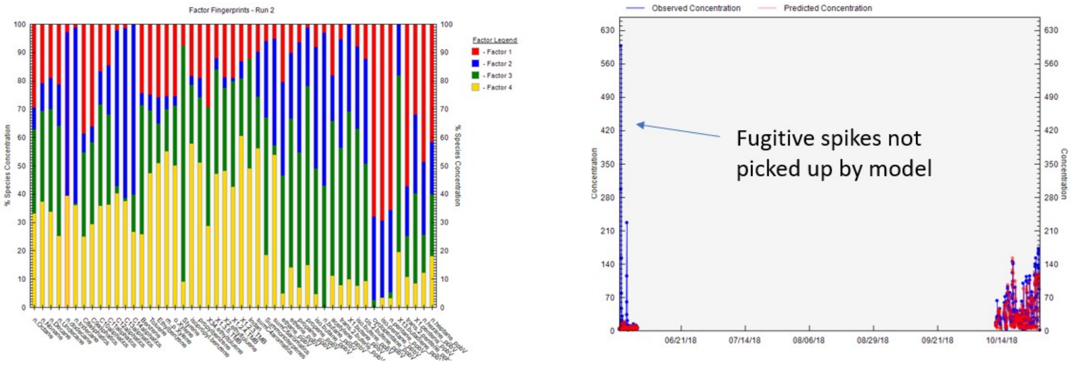


Figure S19. Mean contribution of sources to NMHC measured in Delhi by PCA/APCS and Unmix 6.0.

ESI15 – 4 factor PCA/APCS PMF comparison

Comparison of EPA PMF 5.0 (see Figure 20) vs. PCA/APCS (see Figure 21) models using the combined dataset for a 4-factor solution for propane. Inclusion of additional factors into the PMF model did not resolve into an LPG factor and multiple factors from one source type.



Fugitive spikes not picked up by model

Figure 20. EPA PMF 5.0 4 factor solution on combined dataset.

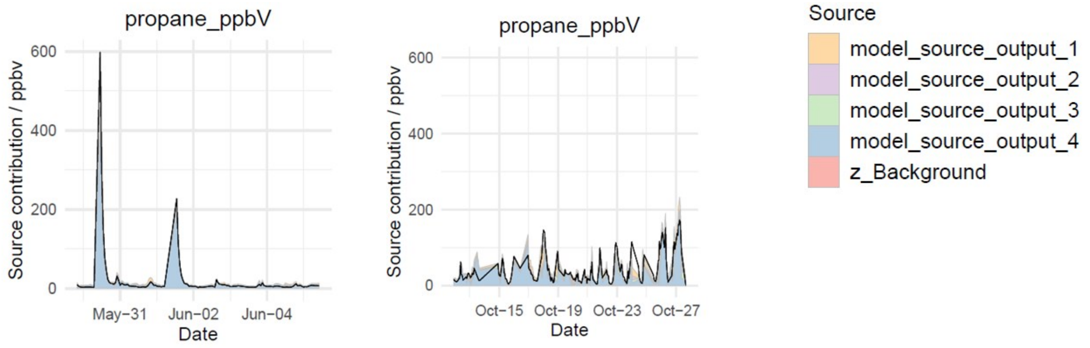


Figure 21. PCA/APCS 4 factor solution both datasets where model_source_output_4 = LPG source and the black line indicates the measured value.

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