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Source apportionment of volatile organic compounds in the northwest Indo-Gangetic Plain using a positive matrix factorization model

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Supplementary text:

Description of the PMF model: PMF is a multivariate factor analysis tool which decomposes the data matrix x_{ij} into two matrices, the factor contribution matrix g_{ik} and the factor profiles matrix f_{kj} both of which are established from the existing intrinsic variability in the dataset leaving behind a matrix of residuals e_{ij}.

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (1)$$

The PMF aims at finding non-negative values of g_{ik} and f_{kj} for a given p that best reproduce x_{ij} while minimizing e_{ij}. The uncertainty weighted residuals are minimized using the parameter Q

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right)^2 \quad (2)$$

wherein u_{ij} represents the matrix of measurement uncertainties for each data point and each species. Here, n and m represents the number of samples and number of species respectively. This method is described in more detail in Paatero & Tapper (1994)[1]; Paatero (1997)[2]. It is extensively employed in environmental air quality studies for source apportionment and air quality management.

Identification of the optimum number of factors: It is clear from Figure 2 in the main text and figure S4 that traffic emissions and photochemistry appear as separate sources even in a 3 Factor solution thanks to strong plumes from the urban sector and a distinct diurnal profile, respectively. Other combustion sources continue to be mixed till the model is run with a 6 Factor solution. A very distinct source, the wheat residue burning, which can be verified using MODIS fire counts appears first in the 6 Factor solution, indicating that at least 6 Factors are required to properly resolve the sources present. When the number of Factors is increased further to 7, the percentage contribution of all previously identified factors remains almost constant and an 'Unresolved Factor' accounting for only 2.5% of the total VOC mass appears. Since this factor could not be matched against any known VOC source, had no distinct diurnal

patterns and its contribution to the overall VOC burden was small we decided to retain the 6 Factor solution. The Q/Qexp plot Figure S4 also shows little improvement beyond 6 factors. Figure S5a shows how the concentration of different species in different factor profiles changes with increasing number of factors, while Figure S5b shows how the percentage of each species explained by each of the different factors changes with increasing number of factors. Figure S5c shows the evolution of the factor contribution time series with increasing number of factors.

Application of the constraint mode: Since wheat residue burning emits large quantities of oxygenated VOCs including methanol and acetic acid, clear separation of combustion derived and photochemically formed oxygenated compounds during daylight hours was an issue with some biomass burning emissions were attributed to the mixed daytime factor in the original solution. To improve the separation between photochemical formation and primary emissions, marked by compounds such as benzene, toluene, xylenes and trimethylbenzene, acetonitrile and styrene (which cannot be formed photochemically), these compounds were pulled down in the mixed daytime factor. In addition, the source contribution of the mixed daytime factor was pulled down between 2am and 4am at night. For a better separation of different combustion sources, strong plumes which represented the emission signature of the respective source were pulled up for the wheat residue burning, biofuel use and waste disposal, industrial and four wheeler source as detailed in supplementary table S3.

Normalization of factor and source profiles:

To facilitate the comparison, factor profiles comprising of the concentration of different species in µg/m³ and emission factors reported in g/kg of fuel were normalized using the following equation:

$$x' = \frac{x}{\max(x)}$$

Table S1. For each m/z used in PMF model, the table lists the major compound identifications and the references supporting such assignments from previous works along with detection limits and sensitivities.

Proto-nated mass (m/z)	Compound assignment (most likely)	Chemical formula	References	Sensitivity (ncps/ppb)	Detection limit (µg/m^3)	Average mixing ratio (stddev) (µg/m^3)
31	Formaldehyde	HCHO	[7-9]	16.3	0.472	3.414 (0.906)
33	Methanol	CH_3OH	[10, 11]	10.1	0.514	37.163 (16.049)
41	Propyne	C_3H_4	[9, 12]	16.5	0.630	3.270 (2.307)
42	Acetonitrile	CH_3CN	[11, 13]	20.7	0.065	1.745 (1.015)
43	Propene and fragment of acetic acid [1]	C_3H_6	[9, 12, 14, 15]	16.6	0.661	14.082 (7.236)
44	Isocyanic acid	HNCO	[9, 16]	16.6	0.677	1.839 (0.405)
45	Acetaldehyde	CH_3CHO	[11, 17]	20.2	0.125	9.123 (4.730)
46	Formamide/Dimethylamine	CH_3NO/ $(CH_3)_2NH$	[9, 17, 18]	16.6	0.708	8.626 (2.612)
47	Formic acid and ethanol	HCOOH	[9, 10, 19]	16.6	0.724	10.262 (2.243)
57	Acrolein/Methylketene	C_3H_4O	[9, 12]	16.5	0.881	5.990 (4.419)
59	Acetone	C_3H_6O	[20]	22.8	0.109	10.447 (5.603)
60	Acetamide/Trimethylamine	C_2H_5NO/ C_3H_9N	[12, 14]	16.5	0.929	1.962 (0.664)
61	Acetic acid	CH_3COOH	[11]	16.4	0.944	18.453 (9.551)
63	Dimethyl sulfide	C_2H_6S	[11]	16.4	0.976	0.920 (0.296)
68	Pyrrole	C_4H_5N	[19, 21]	16.2	1.055	0.528 (0.231)
69	Isoprene and Furan	C_5H_8	[11]	9.0	0.278	4.004 (1.710)
71	Methyl vinyl ketone	C_4H_6O	[11, 12]	16.0	1.102	2.577 (1.395)
73	Methyl ethyl ketone	C_4H_8O	[11, 12]	15.9	1.133	3.159 (1.578)
74	Propanamide/Butylamine	C_3H_7NO/ $C_4H_{11}N$	[22]	15.9	1.149	1.091 (0.331)
75	Hydroxyacetone	$C_3H_6O_2$	[9, 10, 21]	15.8	1.165	4.523 (2.791)
79	Benzene	C_6H_6	[11, 19]	13.5	0.196	4.105 (3.320)
83	Assorted Hydrocarbons	C_6H_{10}	[21]	15.3	1.291	2.531 (1.423)
85	Assorted Hydrocarbons	C_6H_{12}	[21]	15.1	1.322	2.686 (1.571)
87	2,3-Butanedione, 2-methyl-Butanal or pentanone	$C_4H_6O_2$ $C_5H_{10}O$	[21, 22]	15.0	1.354	3.407 (2.025)
93	Toluene	C_7H_8	[11, 19]	14.3	0.261	7.805 (6.977)
95	Phenol	C_6H_5OH	[9, 19]	14.2	1.480	1.766 (1.167)
101	2,3-Pentanedione, acetyl acetone , 2-butenoic acid methyl ester or hexanal,	$C_5H_8O_2$ $C_6H_{12}O$	[22]	13.5	1.574	2.935 (1.273)
105	Styrene	C_8H_8	[11, 12, 21]	13.1	1.637	1.477 (1.112)
107	Ethyl benzene + p-xylene	C_8H_{10}	[11, 19]	13.8	0.501	6.724 (6.381)
121	1,2,4-Trimethylbenzene	C_9H_{12}	[11, 19]	11.2	0.453	4.677 (4.102)
137	Sum of Monoterpenes	$C_{10}H_{16}$	[11, 13]	7.9	2.141	3.779 (1.577)

[1] Correction applied to the input concentration data for propene being the potential fragment of acetic acid with ~68% contribution.

Table S2. Input data statistics for PMF Model runs.

VOC Species	Category	S/N	Min	25th	Median	75th	Max
Isoprene/Furan	Weak	3.89	1.25	2.78	3.48	4.82	11.48
Benzene	Strong	3.87	0.57	1.83	3.21	5.15	24.64
Toluene	Strong	3.93	0.82	3.48	5.54	9.07	49.95
Ethyl benzene + p-xylene	Strong	3.72	0.80	2.99	4.72	8.07	62.51
1,2,4-Trimethylbenzene	Strong	3.61	0.54	2.31	3.38	5.53	31.45
Methyl vinyl ketone/hydrocarbon fragments	Weak	2.10	0.56	1.53	2.13	3.44	8.01
Methyl ethyl ketone/butanal	Weak	2.43	0.88	1.88	2.77	4.02	9.54
Acetic acid	Strong	3.97	5.54	18.64	28.18	38.53	107.72
Dimethyl sulfide	Weak	0.74	0.32	0.67	0.95	1.10	2.41
Pyrrole	Weak	0.14	0.09	0.37	0.54	0.66	2.50
Propanamide/Butylamine	Weak	0.75	0.37	0.86	1.07	1.24	2.32
Hydroxyacetone	Strong	2.81	0.98	2.50	3.91	5.75	16.24
Assorted Hydrocarbons	Weak	1.79	0.66	1.38	2.20	3.19	8.82
Assorted Hydrocarbons	Weak	1.85	0.55	1.50	2.32	3.37	9.36
$C_4H_6O_2$	Weak	2.18	0.77	1.90	2.95	4.34	11.88
Phenol	Strong	1.02	0.54	1.21	1.54	2.06	16.50
$C_5H_8O_2$	Weak	1.83	1.13	2.08	2.64	3.39	11.64
Styrene	Strong	0.62	0.20	0.92	1.21	1.65	9.73
Methanol	Strong	4.00	14.98	24.28	33.86	45.96	129.91
Acetonitrile	Strong	3.95	0.51	0.97	1.50	2.27	7.23
Acetaldehyde	Strong	3.99	2.30	5.13	7.83	12.16	24.69
Acetone	Strong	4.00	3.58	6.74	9.14	12.54	54.48
Monoterpenes	Weak	1.73	0.72	2.63	3.88	4.62	10.35
Formaldehyde	Strong	3.68	1.68	2.69	3.21	4.07	6.28
Propyne	Strong	3.11	0.70	1.63	2.63	3.98	16.63
Propene	Weak	3.56	0.94	2.92	4.71	6.79	17.32
Isocyanic acid	Weak	2.61	0.98	1.57	1.79	2.04	3.21
Formamide/Dimethylamine	Weak	3.87	3.01	6.91	8.42	9.90	21.52
Formic acid	Weak	3.91	5.22	8.74	9.99	11.58	18.55
Acrolein/Methylketene	Weak	3.29	1.07	2.63	4.90	7.63	32.31
Acetamide/Trimethylamine	Weak	2.10	0.66	1.52	1.82	2.25	4.78
Total VOC	Weak	4.00	64.00	124.77	171.23	230.51	515.52

Table S3. List of constraints applied to the wheat residue burning, biofuel use and waste disposal, industrial and four wheeler source.

PMF SOURCE FACTOR	DATE (May2012)	TIME	CONSTRAINT APPLIED
Wheat residue burning	12	19:00-20:59	Pull up
	13	22:00-23:59	Pull up
	18	3:00-3:59, 6:00-7:59	Pull up
	19	2:00-2:59	Pull up
Cars	1	20:00-21:59	Pull up
	4	19:00-21:59	Pull up
Industrial emissions and solvent use	6	4:00-5:59	Pull up
	7	8:00-8:59	Pull up
Biofuel use and waste disposal	22	22:00-22:59	Pull up
	23	12:00-12:59, 6:00-6:59, 22:00-23:59	Pull up
	24	2:00-4:59, 21:00-22:59	Pull up
	25	7:00-7:59	Pull up

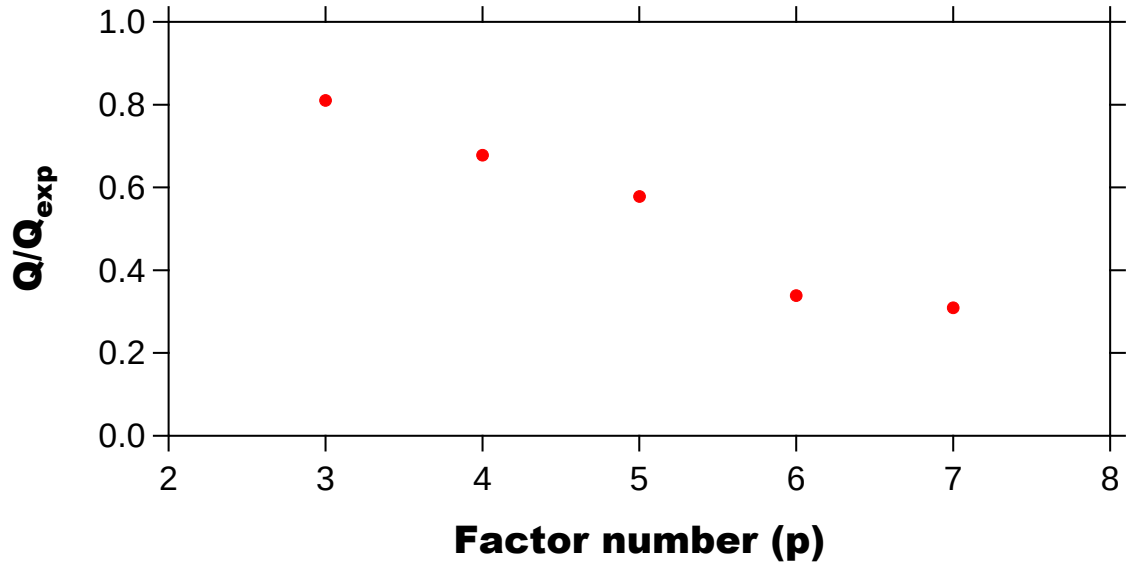

Figure S4 Q/Q_{exp} plot with increasing number of factor. The absolute Q is relatively low indicating that it may be more appropriate to only consider the 10% precision error of the PTR-MS instead of including the accuracy error while specifying the uncertainty in the PMF input. However, since equal uncertainty was applied to all strong m/z this only affects the absolute Q value and not the model output.

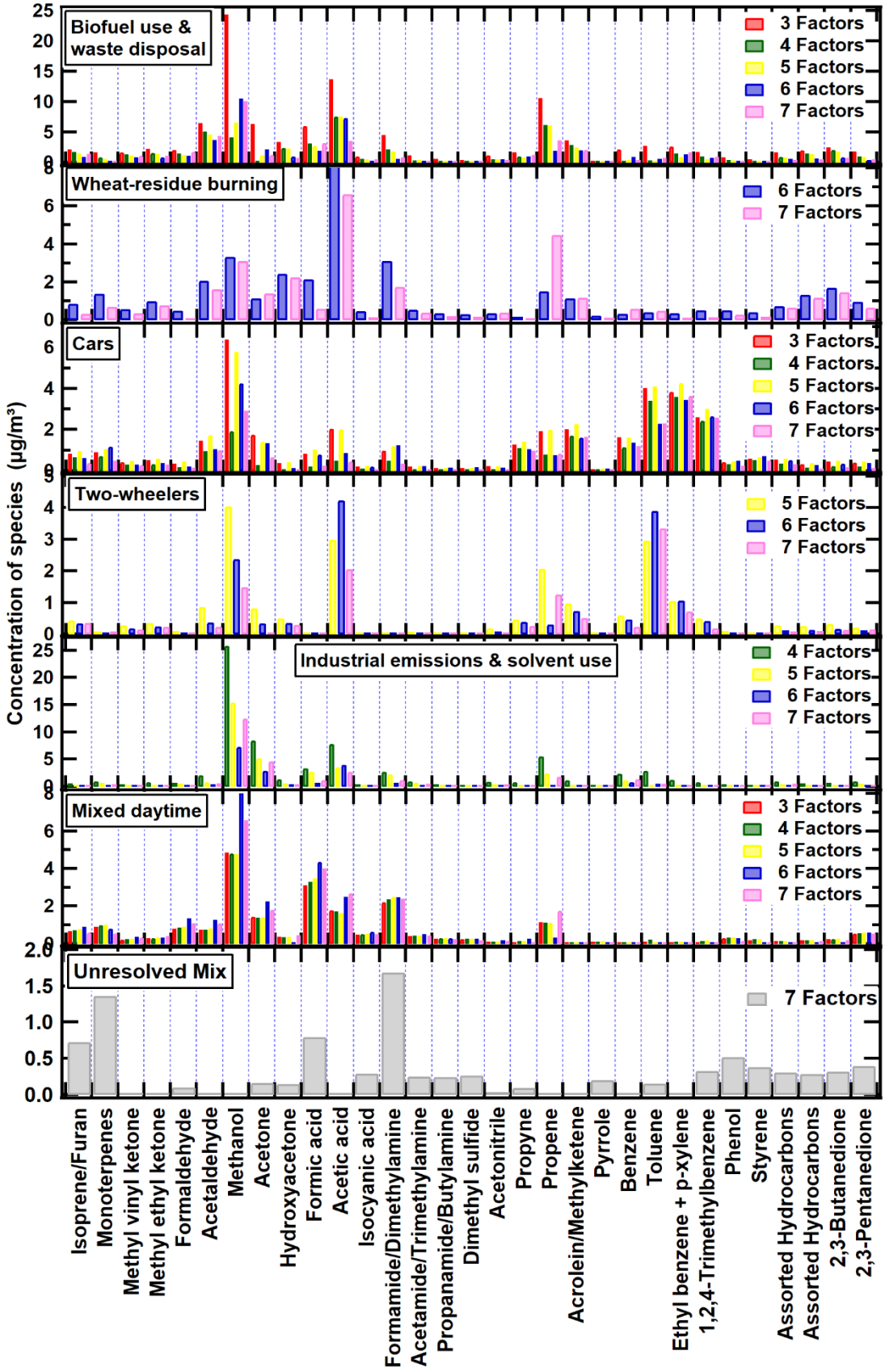

Figure S5a. Evolution of PMF factor profiles from 3 to 7 factor number solutions.

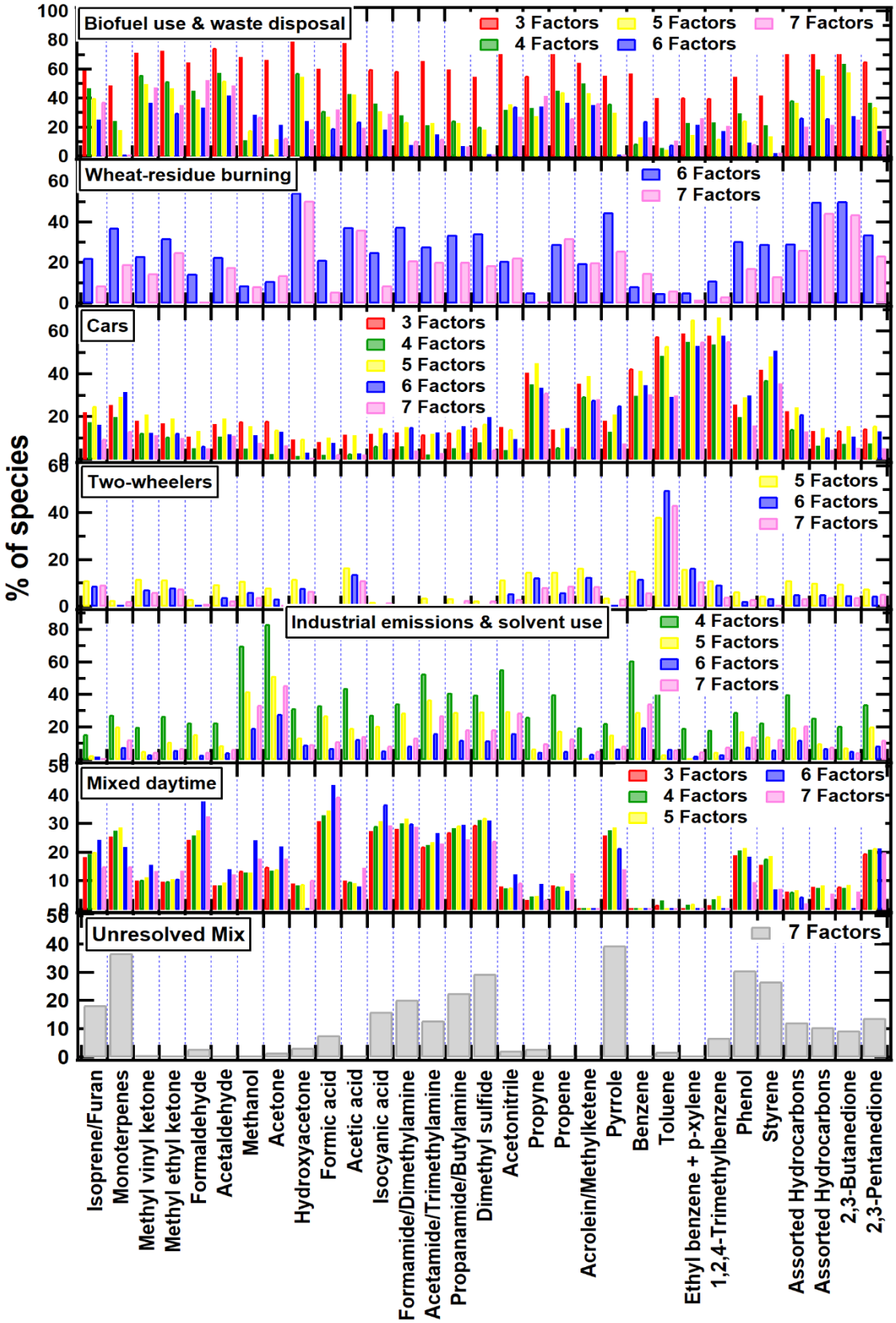

Figure S5b. Evolution of percentage contribution of different VOC species from 3 to 7 PMF factor solutions.

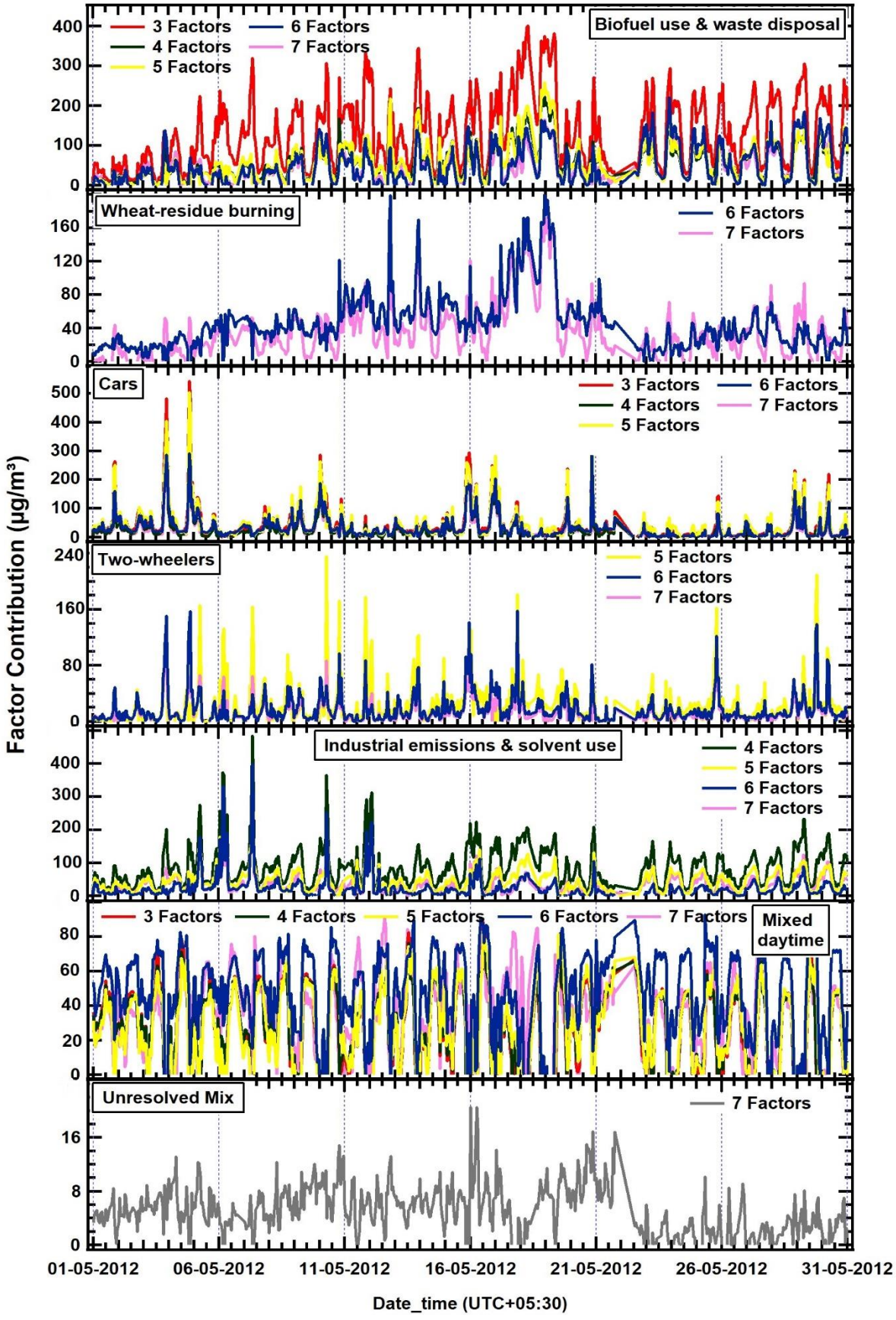

Figure S5c. Evolution of PMF factor contributions from 3 to 7 factor solutions.

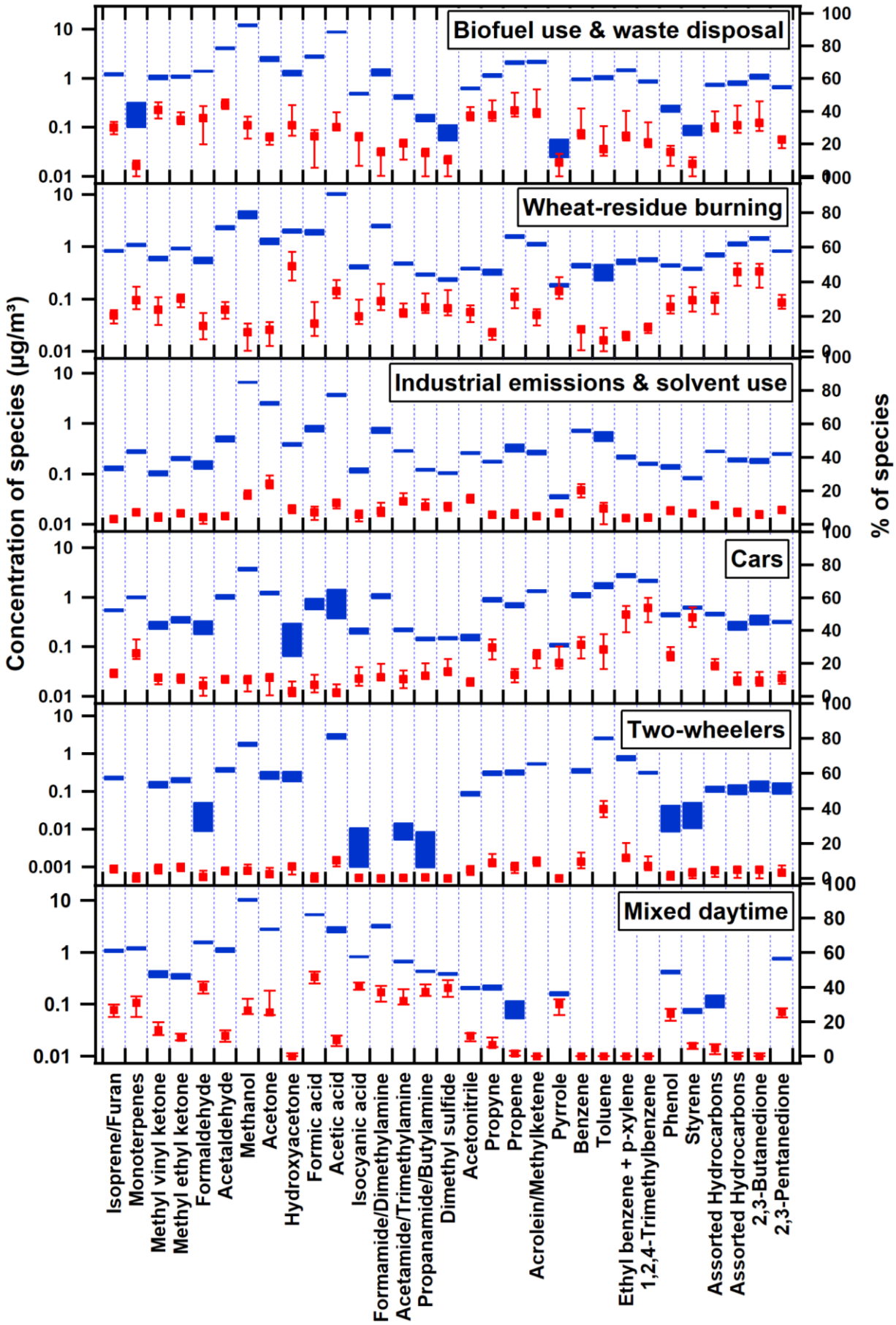

Figure S5d. Uncertainty assessment for the 6 factor solution using bootstrap runs.

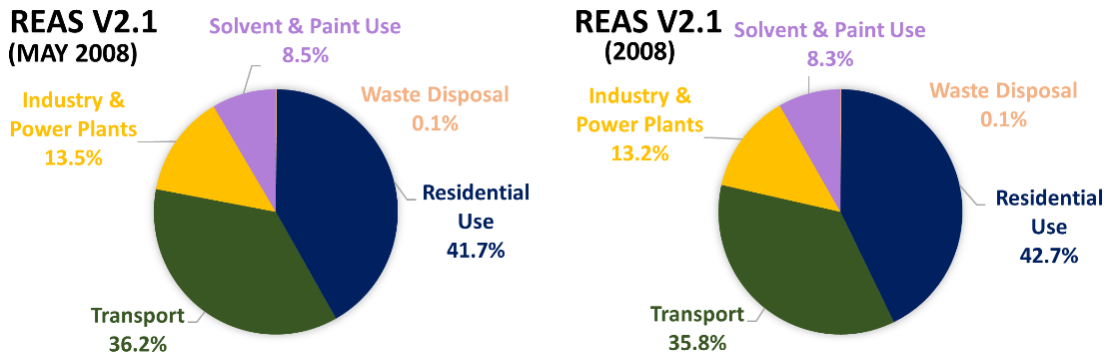

Figure S6. REAS database comparison to VOC source sectors on monthly and yearly resolution scales.

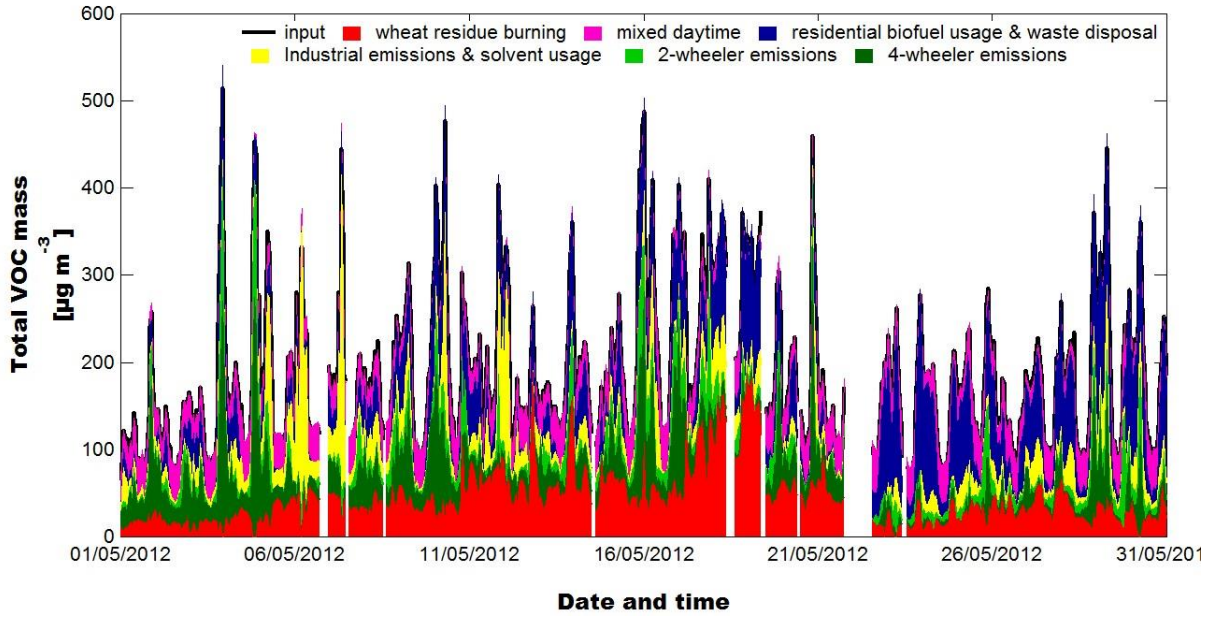

Figure S7. Time series of the total mass contributed by the different sources to the overall VOC mass

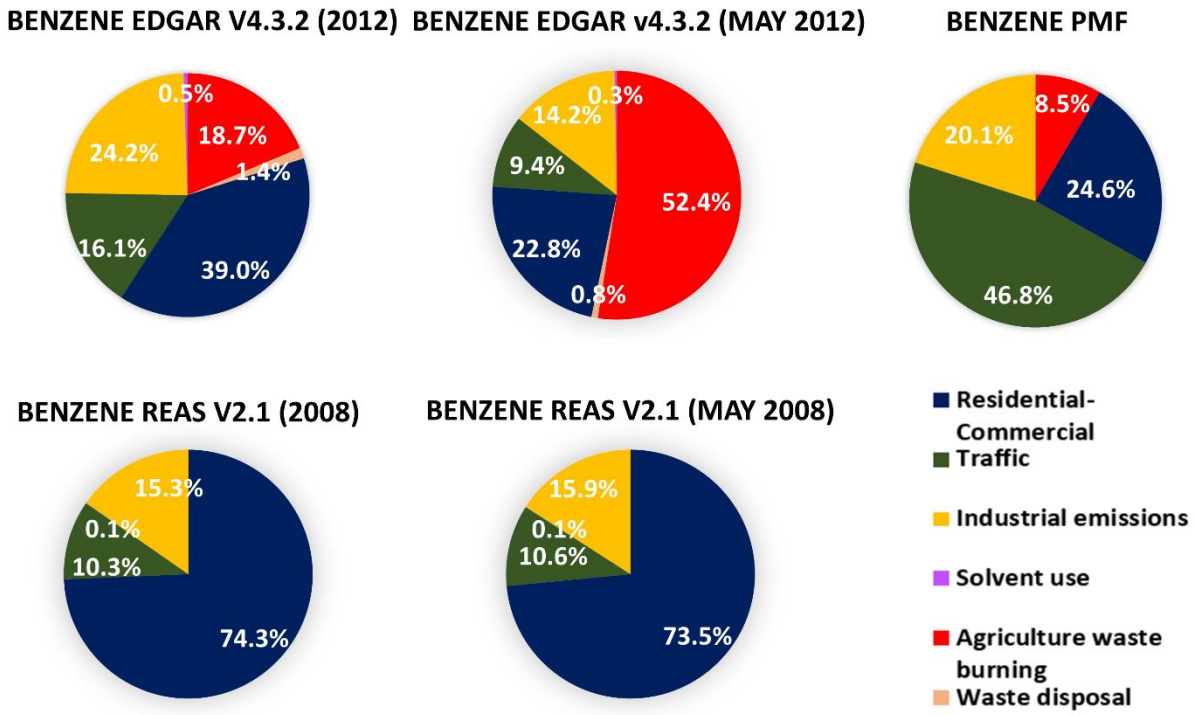

Figure S8a: Comparison of the PMF output with benzene emission inventories for the study region.

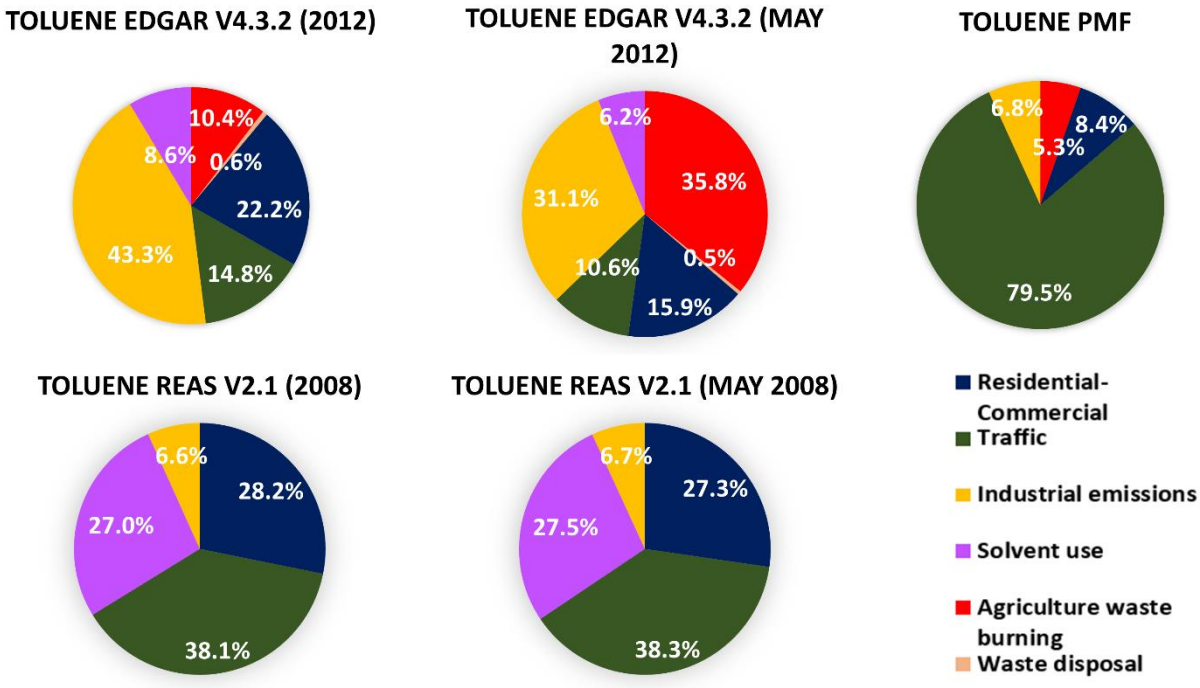

Figure S8b: Comparison of the PMF output with toluene emission inventories for the study region.

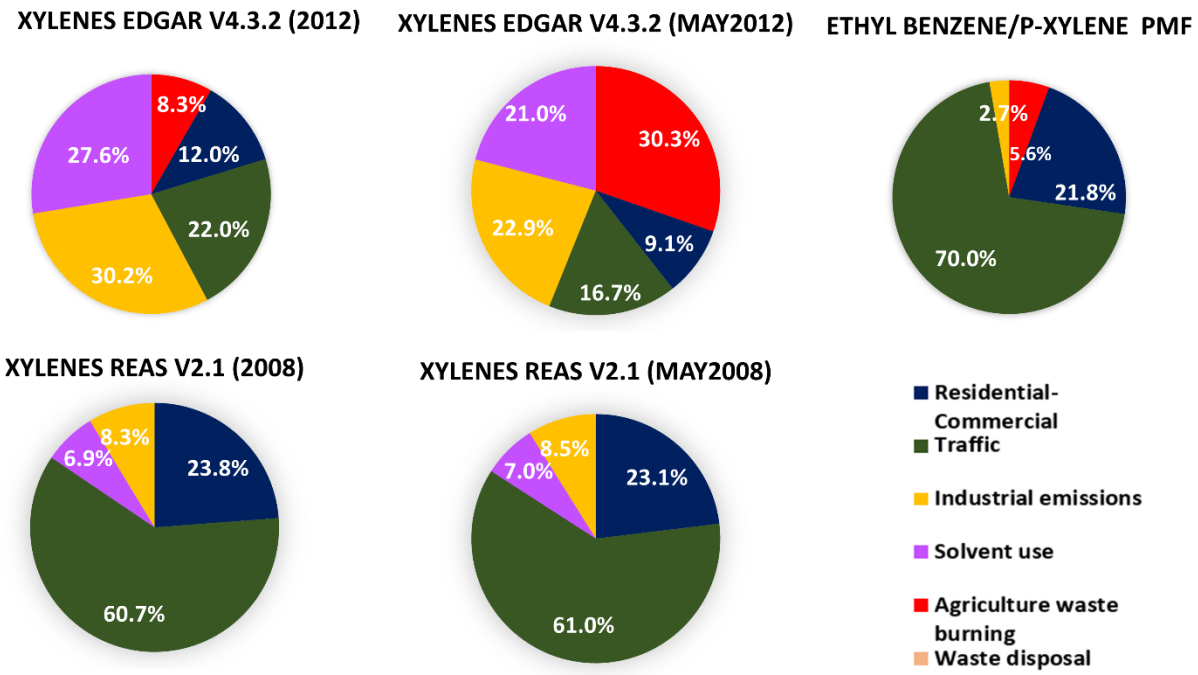

Figure S8c: Comparison of the PMF output with xylenes in the emission inventories for the study region.

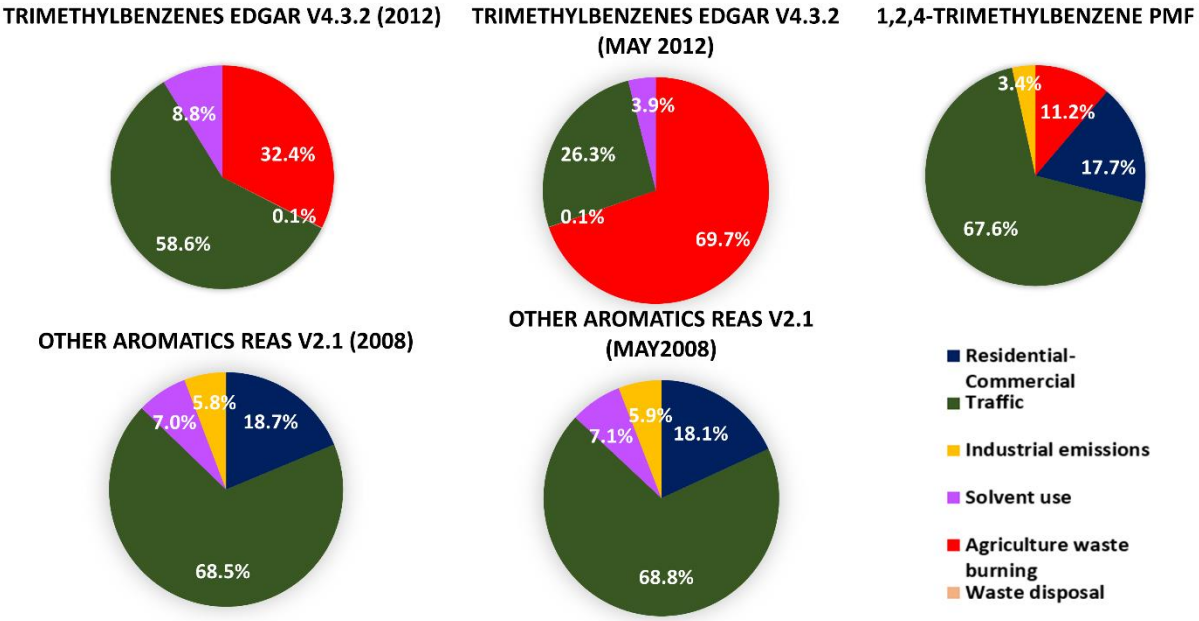

Figure S8d: Comparison of the PMF output of C-9 aromatic compounds with the class "other aromatic compounds" in the emission inventories for the study region.

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