

Table S1. LOD in ng m⁻³ for each analyzed element with ED-XRF for Quartz and Teflon Filters.

Element	LOD (ng m ⁻³) Quartz	LOD (ng m ⁻³) Teflon	Element	LOD (ng m ⁻³) Quartz	LOD (ng m ⁻³) Teflon
Na	12.6	9.5	Fe	0.9	0.7
Mg	15.0	4.3	Co	0.4	0.4
Al	43.2	5.6	Ni	0.7	0.5
Si	-	5.8	Cu	0.8	0.6
S	1.9	1.5	Zn	0.9	0.7
Cl	0.7	0.7	Br	1.5	1.2
K	0.4	0.5	Rb	1.4	1.0
Ca	1.6	1.1	Sr	1.2	1.0
Ti	1.1	0.9	Cs	8.1	8.0
V	0.2	0.1	Ba	11.0	9.0
Cr	0.3	0.3	Pb	2.8	2.1
Mn	0.9	0.8			

Table S2. LOD in ng m⁻³ for each analyzed element with Near Real Time XRF spectrometer.

Element	LOD (ng m ⁻³)
Al	3.18
Si	0.50
S	0.18
K	0.27
Ca	0.04
Ti	0.14
Mn	0.06
Fe	0.39
Ni	0.05
Cu	0.23
Zn	0.16
Pb	0.06

Table S3. LOD in ng m⁻³ for each analyzed element for ICP-MS.

Element	LOD (ng m ⁻³)
Al	3.4
Ca	5.0
Ti	0.2
V	0.1
Cr	0.4
Mn	0.5
Fe	1.4
Co	0.1
Ni	0.7
Cu	1.7
Zn	5.5
Pb	0.2

Table S4. LOD in ng m⁻³ for the major water-soluble inorganic ions determined in PM_{2.5} samples.

Species	LOD (µg m ⁻³)
Na ⁺	0.07–1.17
NH ₄ ⁺	0.01–0.03
K ⁺	0.03–0.06
Ca ²⁺	0.07–0.17
Mg ²⁺	0.07–0.17
Cl ⁻	0.03–0.08
NO ₃ ⁻	0.02–0.05
SO ₄ ²⁻	0.02–0.05

Table S5. Seasonal mean concentrations ($\pm$ standard deviation) of PM_{2.5} ($\mu\text{g m}^{-3}$) and analyzed chemical species (ng m⁻³) during the warm and cold periods at ATH.DEM-UB, ATH.THIS-UB, and IOA-UB. “NA” indicates species that were not analyzed, or below the detection limit.

	ATH.DEM-UB		ATH.THIS-UB		IOA-UB	
Species	Warm	Cold	Warm	Cold	Warm	Cold
PM _{2.5}	12.4 $\pm$ 3.6	9.7 $\pm$ 4.3	14.5 $\pm$ 5.9	26.1 $\pm$ 17.6	13.8 $\pm$ 3.8	58.4 $\pm$ 36.9
OC	2847 $\pm$ 1374	2738 $\pm$ 862	4171 $\pm$ 2928	8675 $\pm$ 5873	2624 $\pm$ 880	26396 $\pm$ 17373
EC	271 $\pm$ 118	491 $\pm$ 128	527 $\pm$ 215	2131 $\pm$ 2232	408 $\pm$ 199	2646 $\pm$ 1738
Na ⁺	122 $\pm$ 55	188 $\pm$ 132	214 $\pm$ 619	354 $\pm$ 260	74 $\pm$ 95	167 $\pm$ 104
NH ₄ ⁺	883 $\pm$ 373	383 $\pm$ 357	1465 $\pm$ 496	835 $\pm$ 447	938 $\pm$ 354	1038 $\pm$ 740
K ⁺	123 $\pm$ 76	147 $\pm$ 89	94 $\pm$ 62	388 $\pm$ 238	166 $\pm$ 130	1341 $\pm$ 905
Mg ²⁺	12 $\pm$ 12	26 $\pm$ 20	57 $\pm$ 17	96 $\pm$ 29	38 $\pm$ 17	31 $\pm$ 17
Ca ²⁺	158 $\pm$ 70	117 $\pm$ 159	221 $\pm$ 201	783 $\pm$ 497	521 $\pm$ 211	851 $\pm$ 706
Cl ⁻	52.1 $\pm$ 21.2	91.2 $\pm$ 100.0	397.1 $\pm$ 123.2	414.3 $\pm$ 289.1	124 $\pm$ 57	558 $\pm$ 341
NO ₃ ⁻	104 $\pm$ 64	255 $\pm$ 198	153 $\pm$ 96	1384 $\pm$ 816	114 $\pm$ 67	3336 $\pm$ 2471
SO ₄ ²⁻	3219 $\pm$ 1176	1710 $\pm$ 1090	4423 $\pm$ 1588	2503 $\pm$ 1112	3520 $\pm$ 1552	2567 $\pm$ 1296
Na	74 $\pm$ 75	136 $\pm$ 156	NA	NA	NA	NA
Mg	29 $\pm$ 45	31 $\pm$ 125	NA	NA	NA	NA
Al	119 $\pm$ 105	59.1 $\pm$ 208	150 $\pm$ 93	92.2 $\pm$ 57.1	NA	NA
Si	215 $\pm$ 195	131 $\pm$ 520	NA	NA	NA	NA
S	1042 $\pm$ 348	534 $\pm$ 288	NA	NA	607 $\pm$ 212	473 $\pm$ 285
Cl	3.0 $\pm$ 5.0	33.0 $\pm$ 83.0	NA	NA	1.0 $\pm$ 1.0	96.0 $\pm$ 104.0
K	131 $\pm$ 99	169 $\pm$ 85	NA	NA	137 $\pm$ 95	735 $\pm$ 492
Ca	167 $\pm$ 86	75 $\pm$ 164	NA	NA	427 $\pm$ 207	600 $\pm$ 489
Ti	8.0 $\pm$ 7.0	5.0 $\pm$ 14.0	5.0 $\pm$ 3.0	3.0 $\pm$ 2.0	7.0 $\pm$ 3.0	6.0 $\pm$ 16.0
V	1.4 $\pm$ 1.8	0.9 $\pm$ 1.3	NA	NA	0.4 $\pm$ 0.3	0.3 $\pm$ 0.3
Cr	1.0 $\pm$ 1.0	1.0 $\pm$ 1.0	NA	NA	0.3 $\pm$ 0.1	0.5 $\pm$ 0.6
Mn	2.0 $\pm$ 2.0	1.0 $\pm$ 2.0	1.1 $\pm$ 0.8	12.3 $\pm$ 22.9	2.4 $\pm$ 1.4	3.2 $\pm$ 2.6
Fe	123 $\pm$ 65	97 $\pm$ 139	49 $\pm$ 33	285 $\pm$ 189	96 $\pm$ 37	135 $\pm$ 152
Co	NA	NA	NA	NA	0.5 $\pm$ 0.1	0.5 $\pm$ 0.2
Ni	1.8 $\pm$ 1.9	1.6 $\pm$ 1.9	0.9 $\pm$ 1.0	2.7 $\pm$ 1.4	1.3 $\pm$ 1.4	2.7 $\pm$ 3.4
Cu	6.8 $\pm$ 26.2	5.0 $\pm$ 6.1	1.5 $\pm$ 0.8	7.4 $\pm$ 5.1	3.2 $\pm$ 3.4	3.6 $\pm$ 3.8
Zn	13.7 $\pm$ 13.4	12.9 $\pm$ 8.8	7.5 $\pm$ 4.6	35.3 $\pm$ 23.7	8.9 $\pm$ 11.4	16.1 $\pm$ 13.4
Br	1.8 $\pm$ 1.4	2.7 $\pm$ 2.0	NA	NA	2.0 $\pm$ 1.0	3.7 $\pm$ 2.5
Rb	NA	NA	NA	NA	1.0 $\pm$ 0.0	2.0 $\pm$ 2.0
Sr	NA	NA	NA	NA	0.8 $\pm$ 0.5	1.7 $\pm$ 2.3
Cs	NA	NA	NA	NA	8.0 $\pm$ 0.9	9.0 $\pm$ 3.5
Ba	8.1 $\pm$ 5.4	11.4 $\pm$ 5.7	NA	NA	NA	NA
Pb	3.7 $\pm$ 5.3	3.6 $\pm$ 3.5	1.3 $\pm$ 1.0	5.3 $\pm$ 2.6	2.5 $\pm$ 2.1	4.7 $\pm$ 4.3

Table S6. Seasonal mean concentrations ($\pm$ standard deviation) of PM_{2.5} ($\mu\text{g m}^{-3}$) and analyzed chemical species (ng m⁻³) during the warm and cold periods at VOL-URB, PAT, and XAN-RUR. “NA” indicates species that were not analyzed or below the detection limit.

	VOL-URB		PAT		XAN-RUR	
Species	Warm	Cold	Warm	Cold	Warm	Cold
PM _{2.5}	24.3 $\pm$ 14.3	41.6 $\pm$ 10.5	12.6 $\pm$ 3.9	25.3 $\pm$ 9.4	13.2 $\pm$ 4.4	12.8 $\pm$ 6.0
OC	3148 $\pm$ 684	11927 $\pm$ 3374	2883 $\pm$ 2144	9595 $\pm$ 4105	2794 $\pm$ 728	3774 $\pm$ 1870
EC	1077 $\pm$ 582	1464 $\pm$ 601	169 $\pm$ 146	1458 $\pm$ 693	151 $\pm$ 58	419 $\pm$ 232
Na ⁺	707 $\pm$ 587	99 $\pm$ 230	232 $\pm$ 198	283 $\pm$ 309	267 $\pm$ 369	78 $\pm$ 64
NH ₄ ⁺	950 $\pm$ 401	2319 $\pm$ 859	1074 $\pm$ 367	694 $\pm$ 428	1005 $\pm$ 376	755 $\pm$ 579
K ⁺	113 $\pm$ 129	908 $\pm$ 306	57 $\pm$ 29	715 $\pm$ 447	88 $\pm$ 102	294 $\pm$ 159
Mg ²⁺	104 $\pm$ 265	40 $\pm$ 18	30 $\pm$ 31	32 $\pm$ 35	21 $\pm$ 29	39 $\pm$ 13
Ca ²⁺	493 $\pm$ 315	665 $\pm$ 453	214 $\pm$ 178	335 $\pm$ 424	103 $\pm$ 97	164 $\pm$ 70
Cl ⁻	150 $\pm$ 511	576 $\pm$ 414	42.3 $\pm$ 48.1	238 $\pm$ 268	71 $\pm$ 224	379 $\pm$ 140
NO ₃ ⁻	306 $\pm$ 1074	4605 $\pm$ 2968	201 $\pm$ 173	1319 $\pm$ 808	84 $\pm$ 53	694 $\pm$ 581
SO ₄ ²⁻	6788 $\pm$ 6444	5001 $\pm$ 1942	4227 $\pm$ 1486	1920 $\pm$ 1046	1857 $\pm$ 1511	1896 $\pm$ 1374
Na	NA	NA	NA	NA	NA	NA
Mg	NA	NA	NA	NA	NA	NA
Al	NA	NA	NA	NA	NA	NA
Si	NA	NA	NA	NA	NA	NA
S	684 $\pm$ 188	637 $\pm$ 268	366 $\pm$ 283	403 $\pm$ 251	557 $\pm$ 229	225 $\pm$ 154
Cl	15.0 $\pm$ 32.0	51.0 $\pm$ 49.0	4.0 $\pm$ 3.0	65.0 $\pm$ 78.0	NA	3.0 $\pm$ 3.0
K	87 $\pm$ 33	366 $\pm$ 164	38 $\pm$ 42	602 $\pm$ 343	82 $\pm$ 48	122 $\pm$ 88
Ca	696 $\pm$ 389	469 $\pm$ 351	86 $\pm$ 99	97 $\pm$ 41	94 $\pm$ 53	70 $\pm$ 54
Ti	14.0 $\pm$ 7.0	3.0 $\pm$ 3.0	10.0 $\pm$ 12.0	5.0 $\pm$ 4.0	7.0 $\pm$ 6.0	3.0 $\pm$ 6.0
V	1.6 $\pm$ 1.8	0.4 $\pm$ 0.1	NA	NA	NA	NA
Cr	2.6 $\pm$ 1.9	0.3 $\pm$ 0.1	3.0 $\pm$ 2.4	3.0 $\pm$ 5.3	0.6 $\pm$ 0.4	0.6 $\pm$ 0.5
Mn	23.3 $\pm$ 21.0	19.0 $\pm$ 11.2	9.0 $\pm$ 8.0	4.0 $\pm$ 1.3	1.2 $\pm$ 1.3	1.0 $\pm$ 0.7
Fe	470 $\pm$ 478	299 $\pm$ 191	75 $\pm$ 96	32 $\pm$ 39	84 $\pm$ 66	39 $\pm$ 49
Co	0.9 $\pm$ 0.6	0.7 $\pm$ 0.2	NA	NA	NA	NA
Ni	2.2 $\pm$ 4.4	0.5 $\pm$ 0.6	4.3 $\pm$ 8.2	4.4 $\pm$ 6.3	2.2 $\pm$ 2.4	1.2 $\pm$ 1.6
Cu	16.0 $\pm$ 12.7	8.4 $\pm$ 7.9	32.0 $\pm$ 34.0	12.0 $\pm$ 18.0	1.1 $\pm$ 1.6	0.6 $\pm$ 1.3
Zn	215 $\pm$ 661	133 $\pm$ 78	11.0 $\pm$ 19.0	12.0 $\pm$ 18.0	13.2 $\pm$ 10.4	12.1 $\pm$ 8.1
Br	3.0 $\pm$ 1.3	5.0 $\pm$ 2.1	NA	NA	2.0 $\pm$ 1.5	2.7 $\pm$ 1.9
Rb	NA	NA	NA	NA	NA	NA
Sr	1.4 $\pm$ 1.5	1.0 $\pm$ 0.6	NA	NA	NA	NA
Cs	NA	NA	NA	NA	11.2 $\pm$ 5.0	8.7 $\pm$ 3.1
Ba	NA	NA	NA	NA	13.0 $\pm$ 8.5	11.5 $\pm$ 5.8
Pb	15.3 $\pm$ 8.7	16.2 $\pm$ 18.0	23.0 $\pm$ 21.0	23.0 $\pm$ 33.0	NA	NA

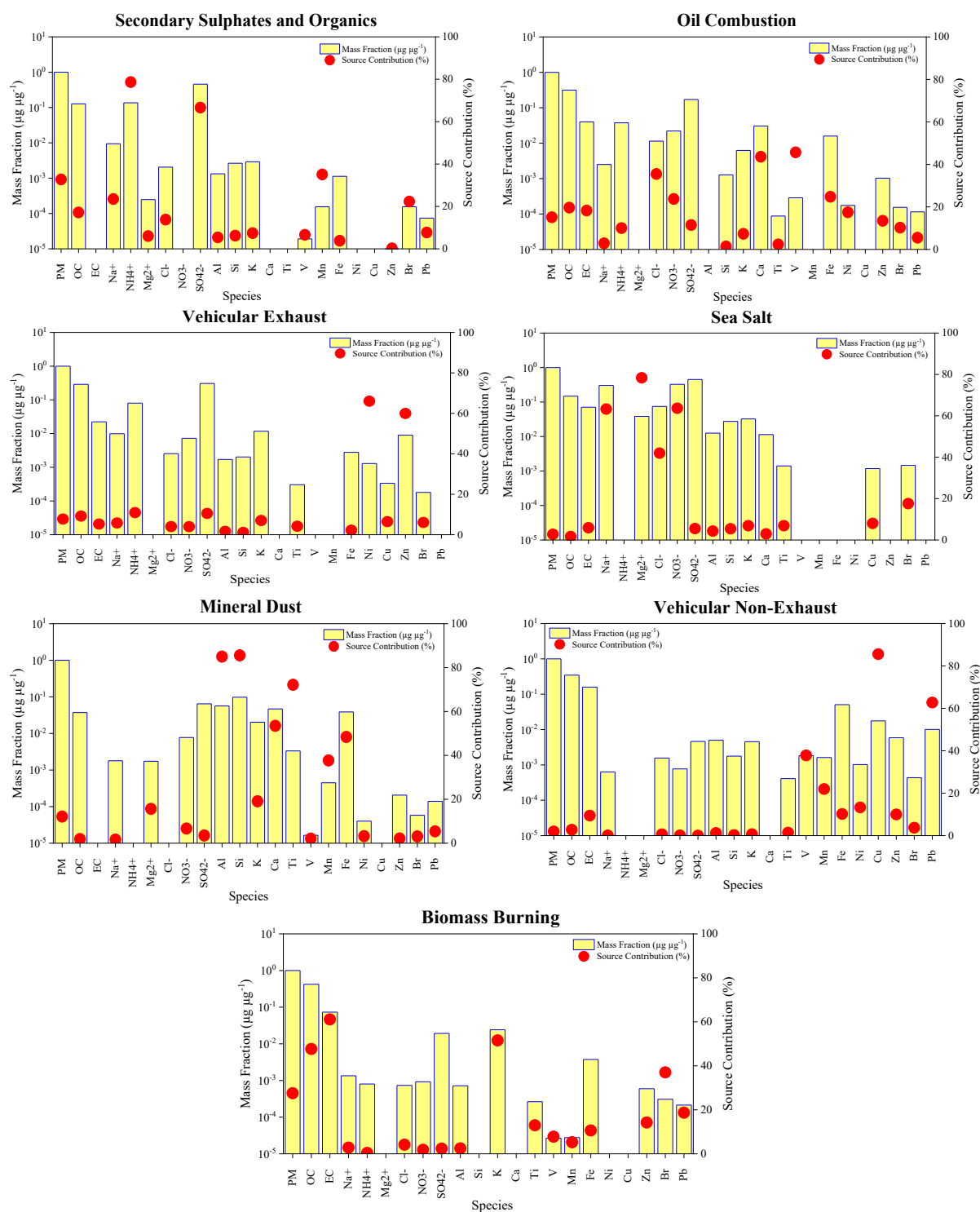


Figure S1: PM_{2.5} source profiles derived from PMF for the ATH.DEM-UB station. The bars represent the mass fractions of the species (in $\mu\text{g } \mu\text{g}^{-1}$), while the red circles display the relative amount of each species (%) apportioned to each factor/source.

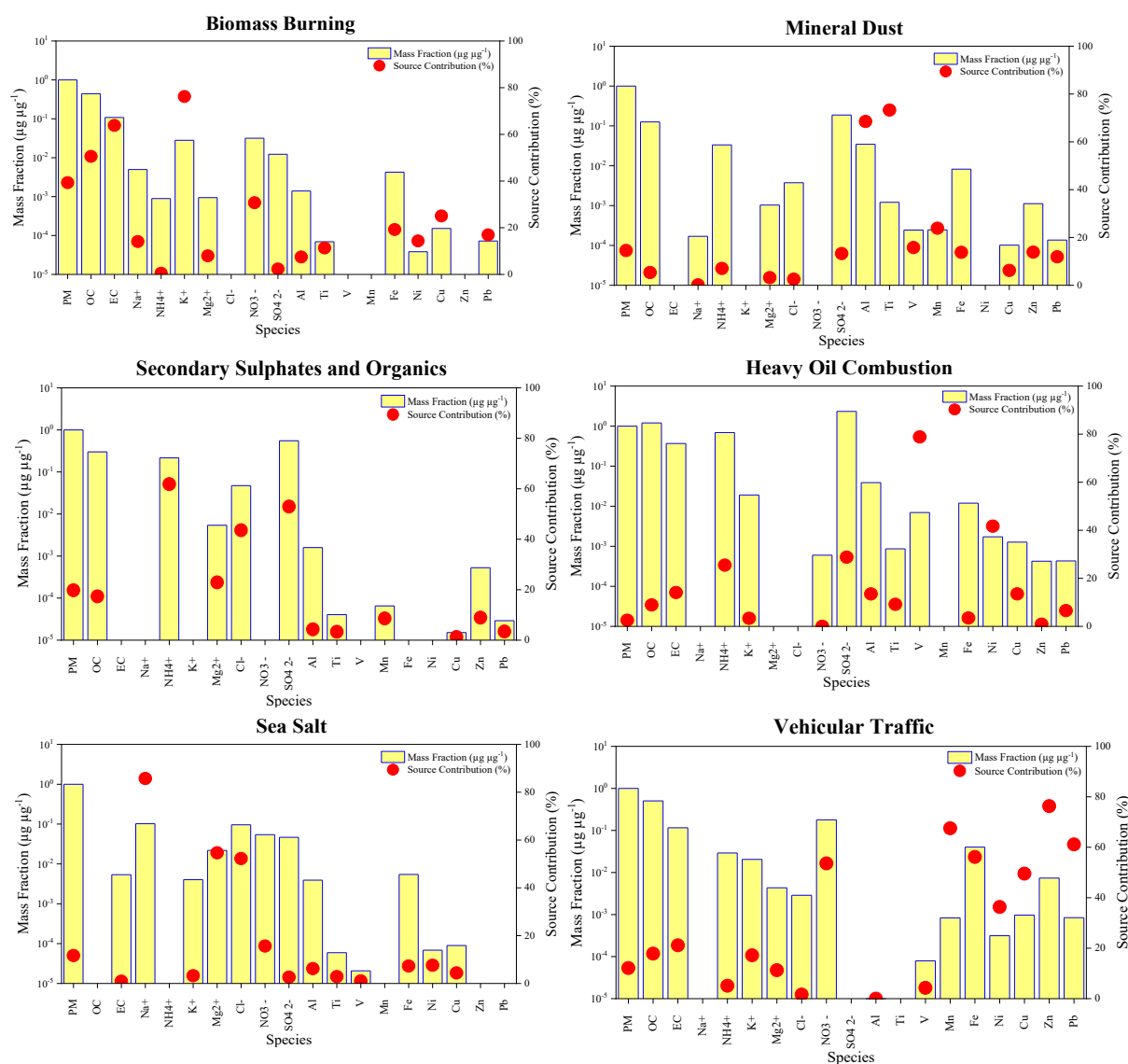


Figure S2. PM_{2.5} source profiles derived from PMF for the ATH.THIS-UB station. The bars represent the mass fractions of the species (in $\mu\text{g } \mu\text{g}^{-1}$), while the red circles display the relative amount of each species (%) apportioned to each factor/source.

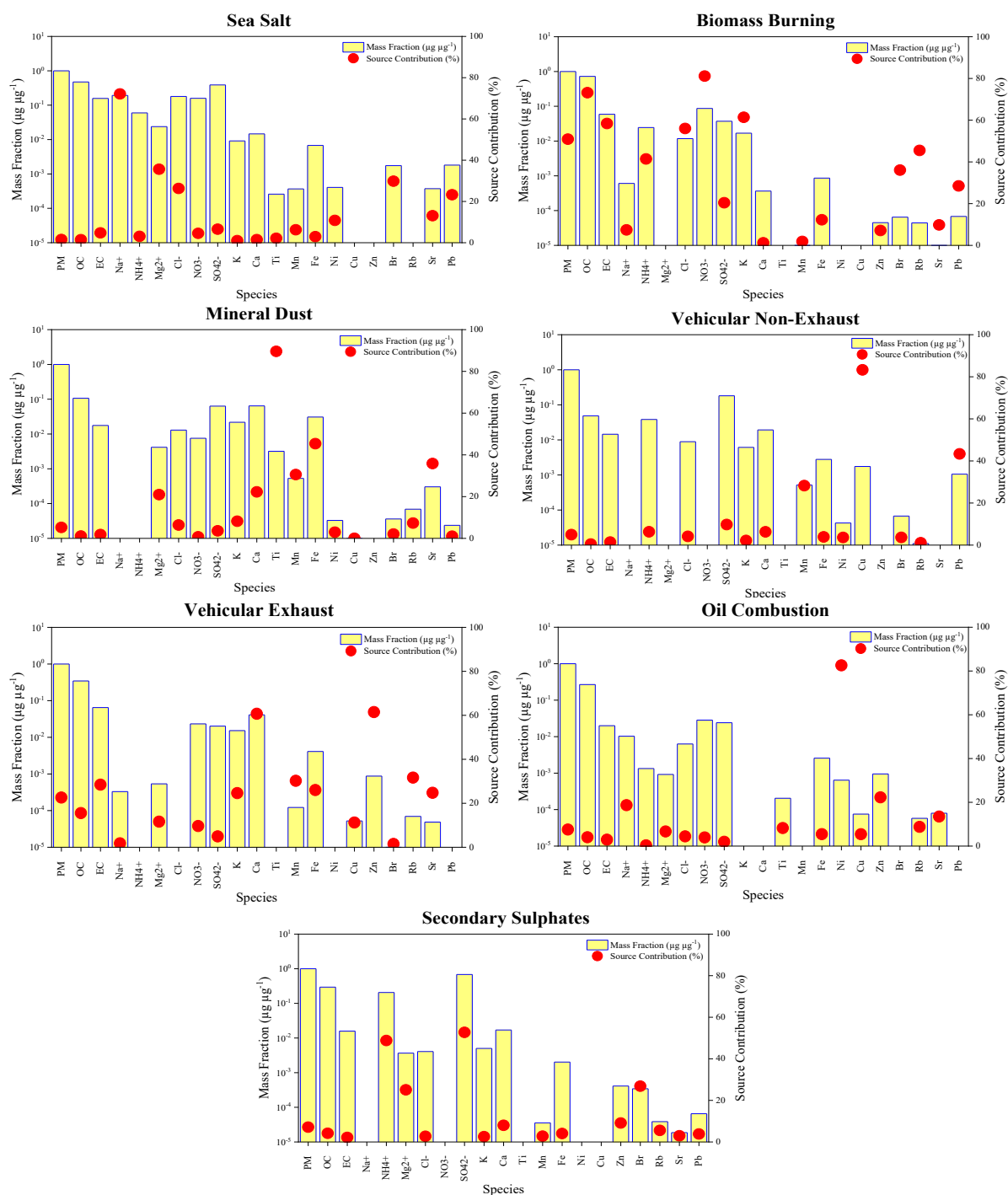


Figure S2: PM_{2.5} source profiles derived from PMF for the IOA-UB station. The bars represent the mass fractions of the species (in $\mu\text{g } \mu\text{g}^{-1}$), while the red circles display the relative amount of each species (%) apportioned to each factor/source.

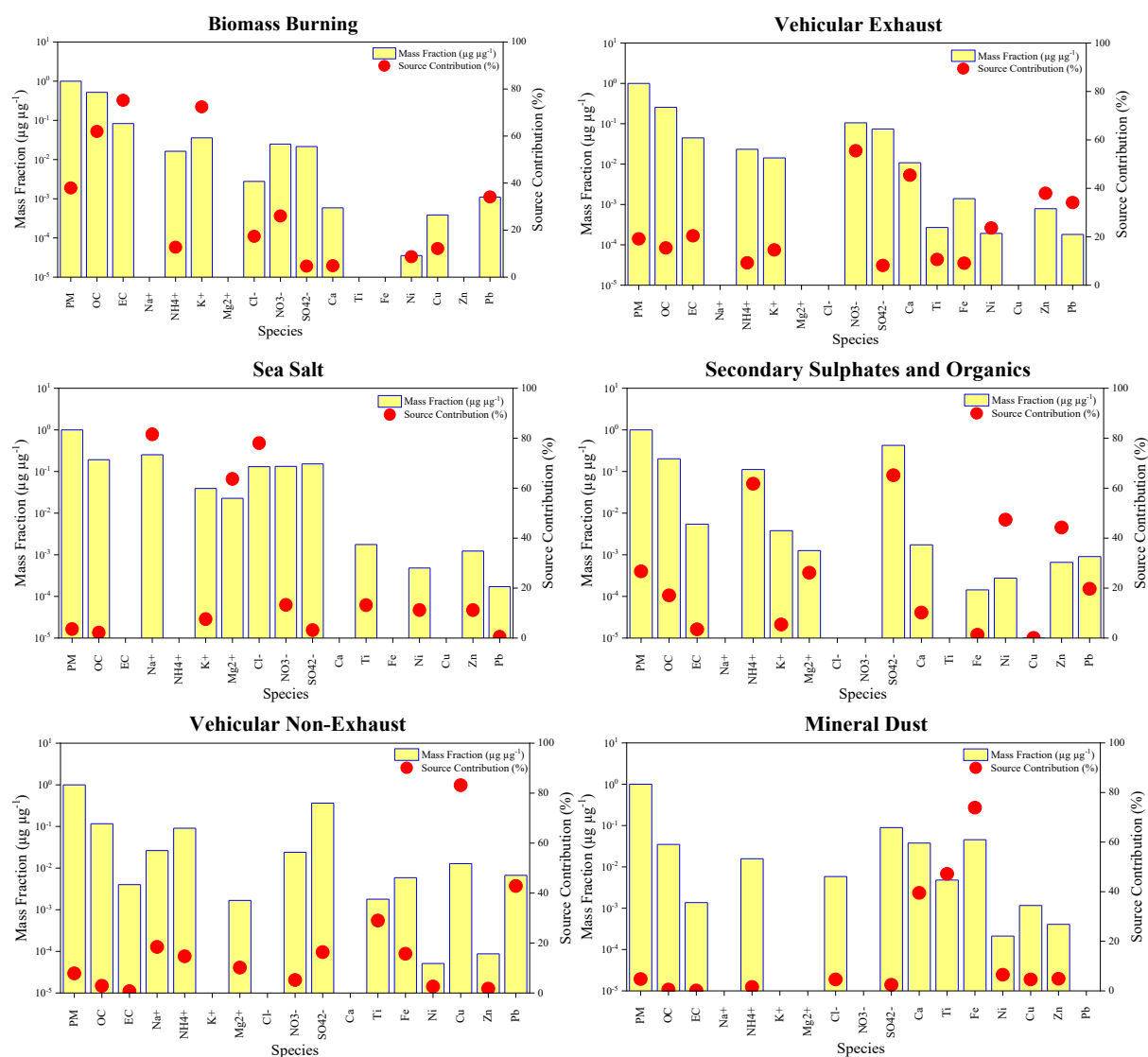


Figure S4: PM_{2.5} source profiles derived from PMF for the PAT stations. The bars represent the mass fractions of the species (in $\mu\text{g } \mu\text{g}^{-1}$), while the red circles display the relative amount of each species (%) apportioned to each factor/source.

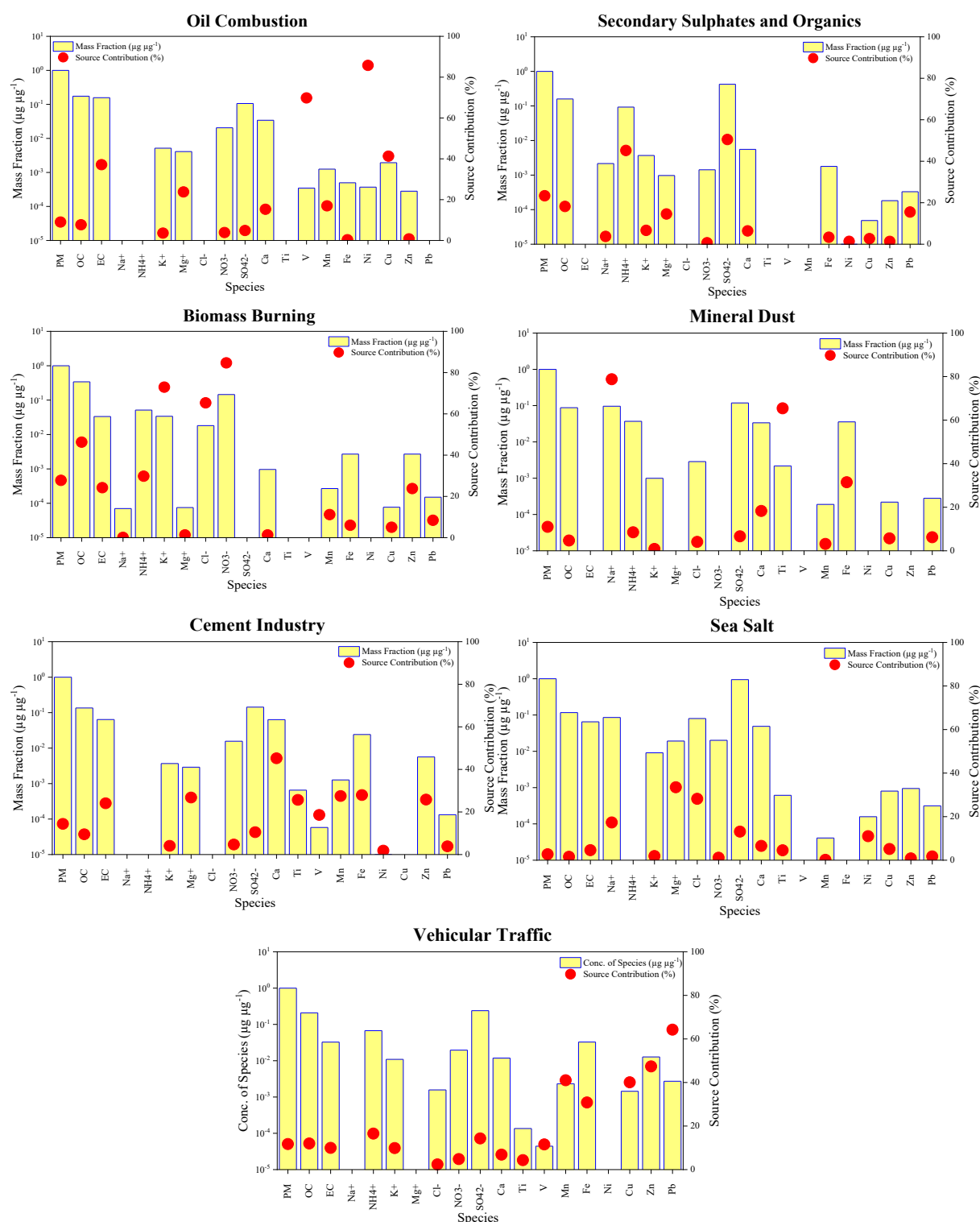


Figure S5: PM_{2.5} source profiles derived from PMF for the VOL-URB station. The bars represent the mass fractions of the species (in $\mu\text{g } \mu\text{g}^{-1}$), while the red circles display the relative amount of each species (%) apportioned to each factor/source.

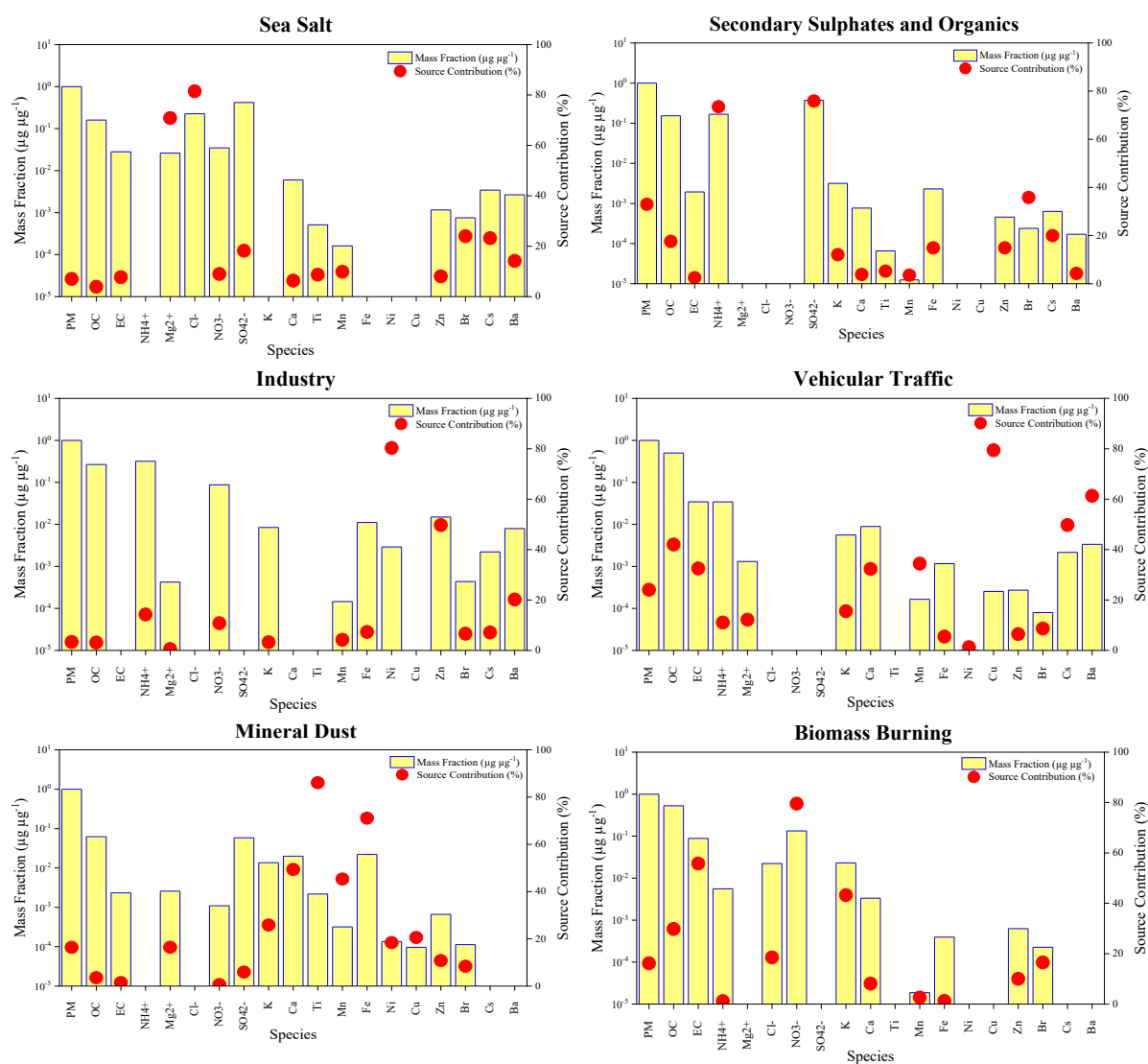


Figure S6: PM_{2.5} source profiles derived from PMF for the XAN-RUR station. The bars represent the mass fractions of the species (in $\mu\text{g } \mu\text{g}^{-1}$), while the red circles display the relative amount of each species (%) apportioned to each factor/source.

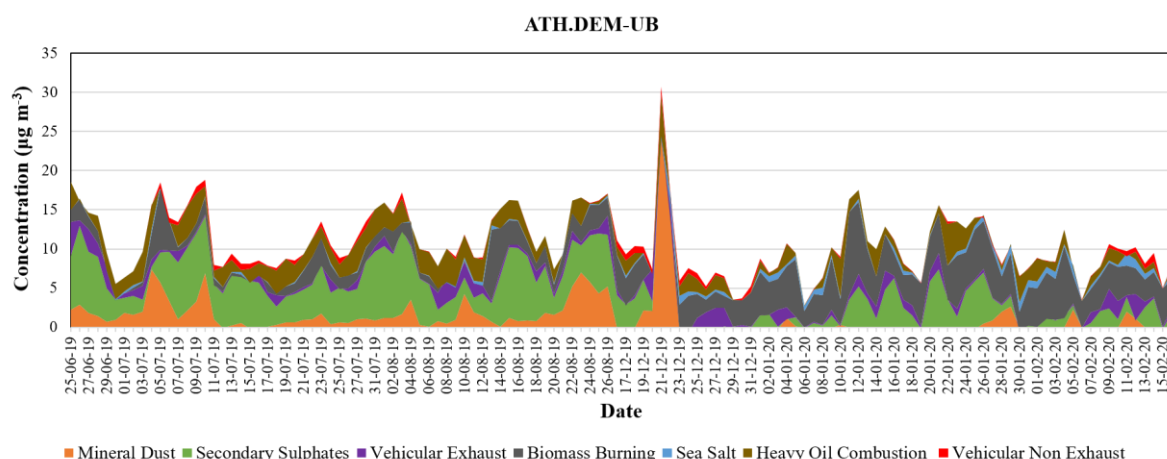


Figure S7. Daily source contributions ($\mu\text{g m}^{-3}$) to $\text{PM}_{2.5}$ resolved by PMF at ATH.DEM-UB. Stacked areas represent reconstructed $\text{PM}_{2.5}$ mass.

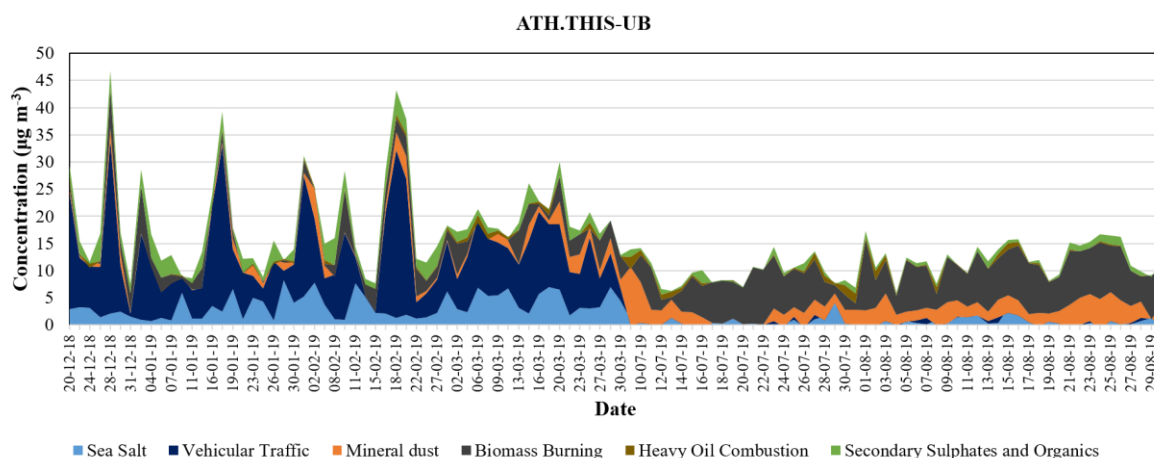


Figure S8: Daily source contributions ($\mu\text{g m}^{-3}$) to $\text{PM}_{2.5}$ resolved by PMF at ATH.THIS-UB. Stacked areas represent reconstructed $\text{PM}_{2.5}$ mass.

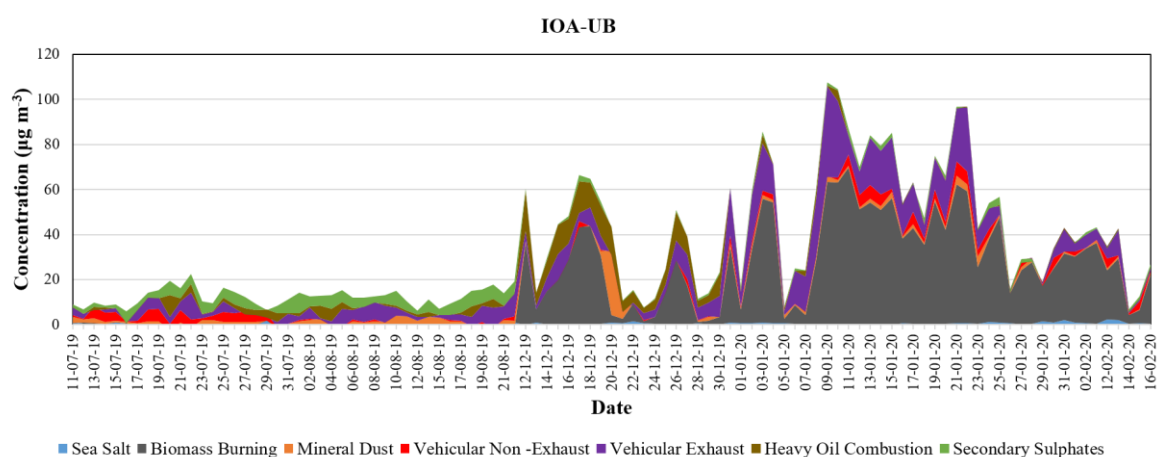


Figure S9: Figure S8. Daily source contributions ($\mu\text{g m}^{-3}$) to $\text{PM}_{2.5}$ resolved by PMF at IOA-UB. Stacked areas represent reconstructed $\text{PM}_{2.5}$ mass.

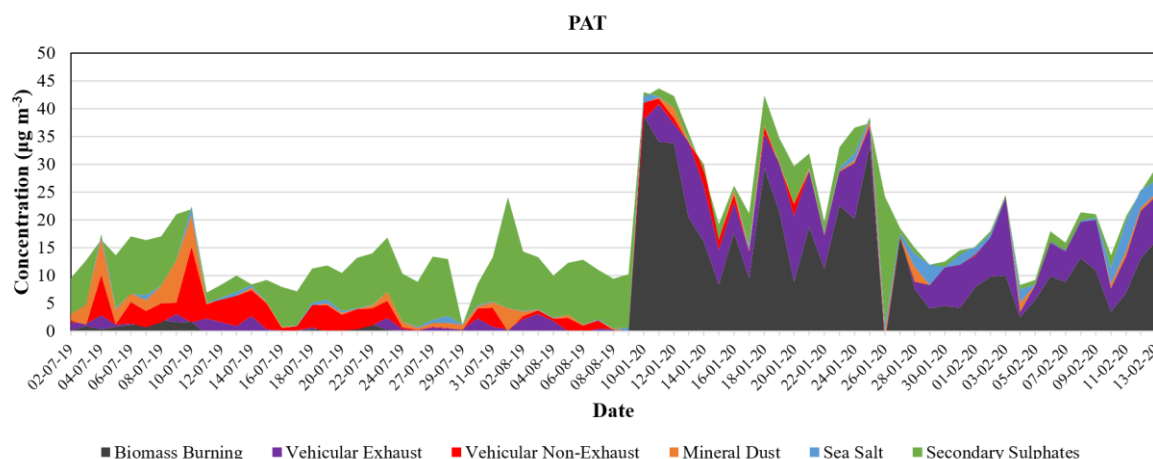


Figure S10: Daily source contributions ($\mu\text{g m}^{-3}$) to $\text{PM}_{2.5}$ resolved by PMF at PAT. Stacked areas represent reconstructed $\text{PM}_{2.5}$ mass.

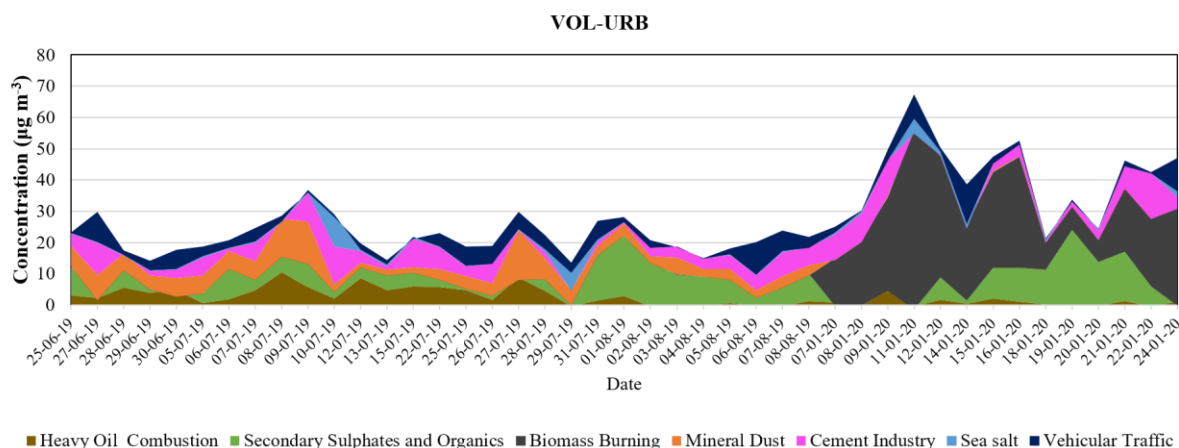


Figure S11: Daily source contributions ($\mu\text{g m}^{-3}$) to $\text{PM}_{2.5}$ resolved by PMF at VOL-URB. Stacked areas represent reconstructed $\text{PM}_{2.5}$ mass.

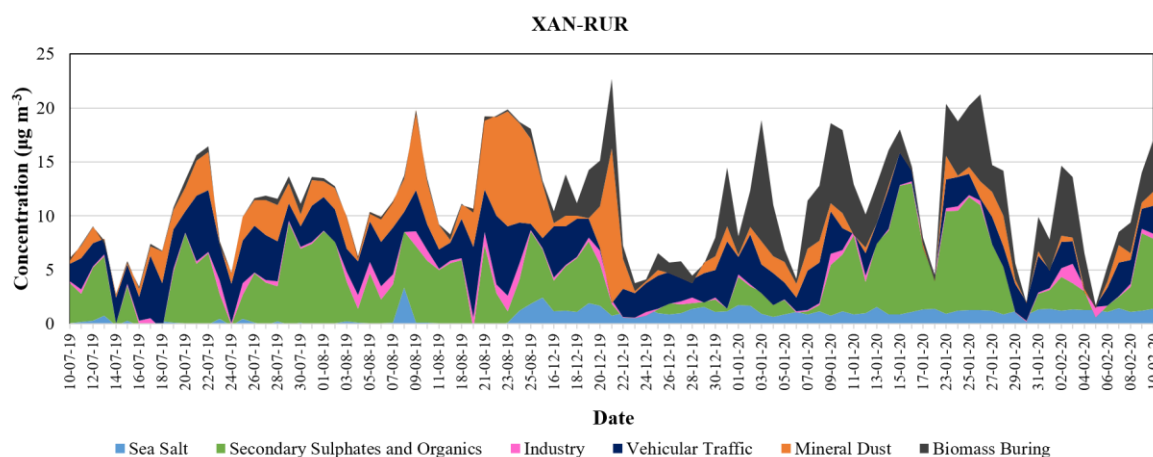
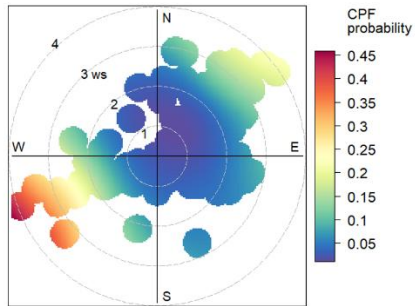


Figure S12: Daily source contributions ($\mu\text{g m}^{-3}$) to $\text{PM}_{2.5}$ resolved by PMF at XAN-RUR. Stacked areas represent reconstructed $\text{PM}_{2.5}$ mass.

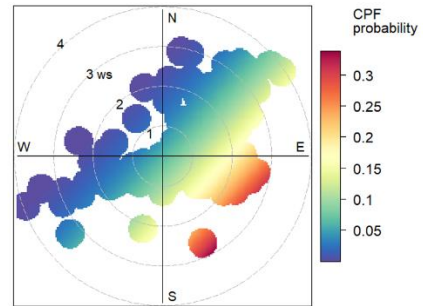
ATH.DEM-UB

Mineral Dust



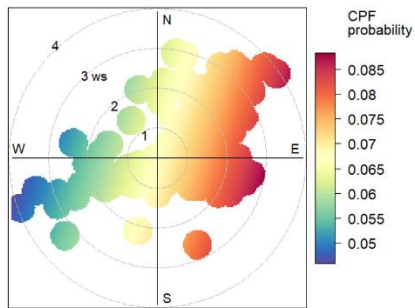
CPF at the 75th percentile (≈ 1.4)

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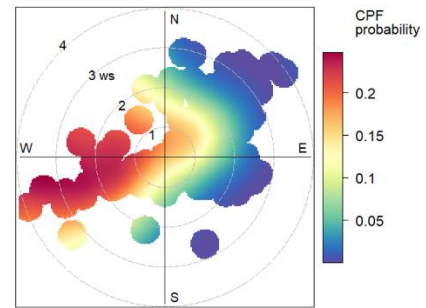
CPF at the 75th percentile (≈ 5.9)

Vehicular Exhaust



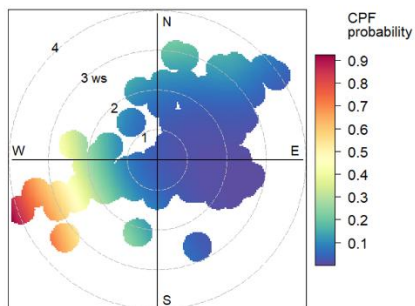
CPF at the 75th percentile (≈ 1.4)

Biomass Burning



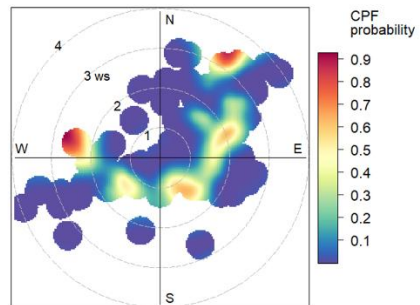
CPF at the 75th percentile (≈ 4.3)

Sea Salt



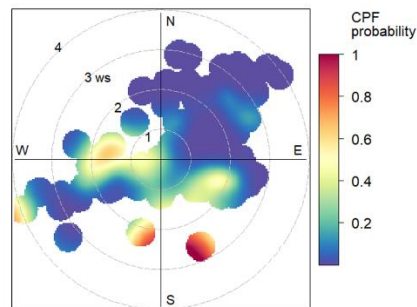
CPF at the 75th percentile (≈ 0.48)

Heavy Oil Combustion



CPF at the 75th percentile (≈ 2.6)

Vehicular Non-Exhaust

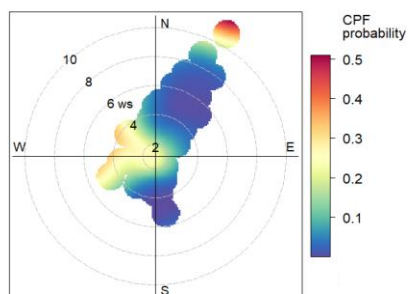


CPF at the 75th percentile (≈ 0.35)

Figure S13: CPF plots for source contribution for the ATH.DEM-UB station.

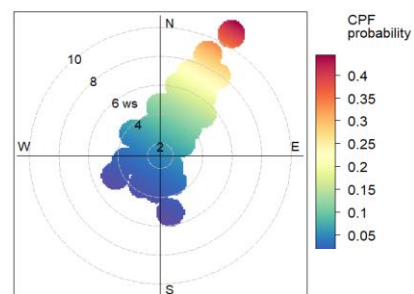
ATH.THIS-UB

Biomass Burning



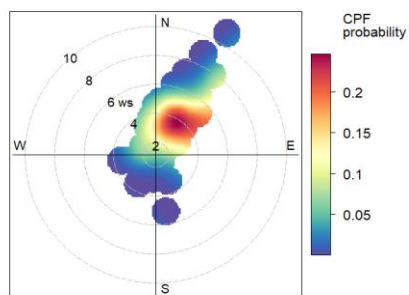
CPF at the 75th percentile (≈ 8.9)

Mineral Dust



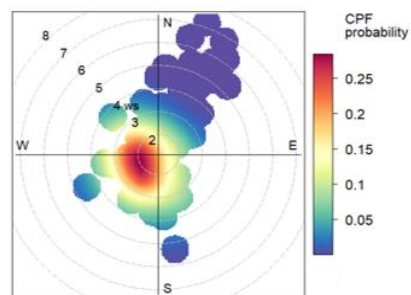
CPF at the 75th percentile (≈ 3.6)

Sec. Sulphates & Organics



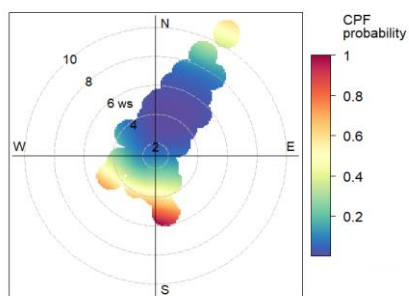
CPF at the 75th percentile (≈ 5.2)

Heavy Oil Combustion



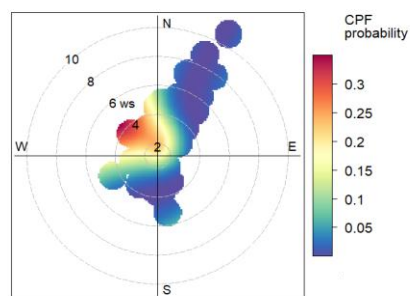
CPF at the 75th percentile (≈ 0.72)

Sea Salt



CPF at the 75th percentile (≈ 2.4)

Vehicular Traffic



CPF at the 75th percentile (≈ 4.3)

Figure S14: CPF plots for source contribution for the ATH.THIS-UB station.

IOA-UB

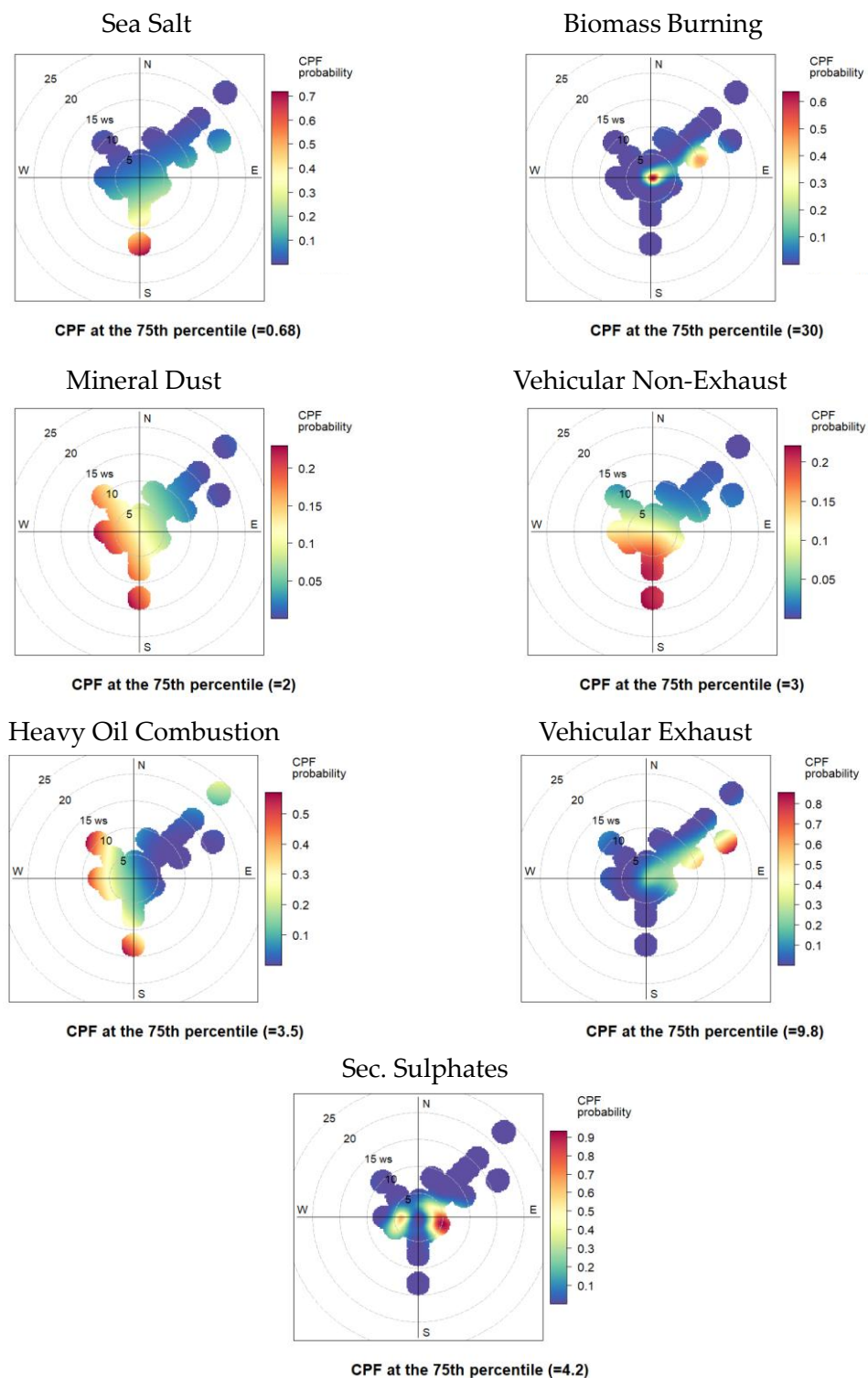
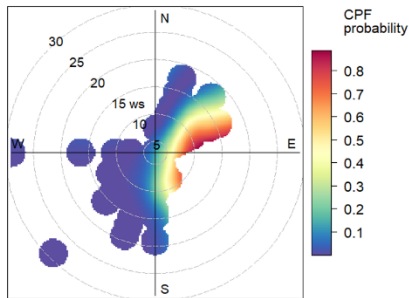


Figure S15: CPF plots for source contribution for the IOA-UB station.

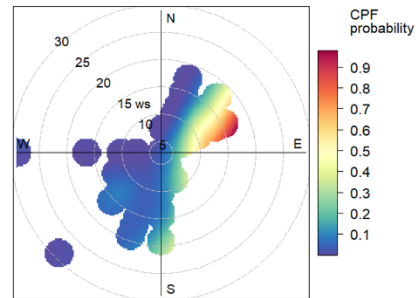
PAT

Biomass Burning



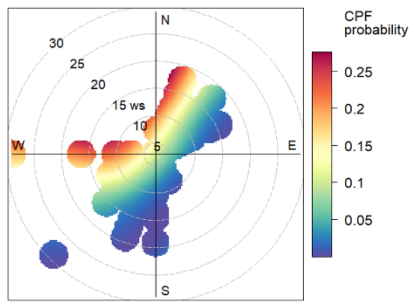
CPF at the 75th percentile (=10)

Vehicular Exhaust



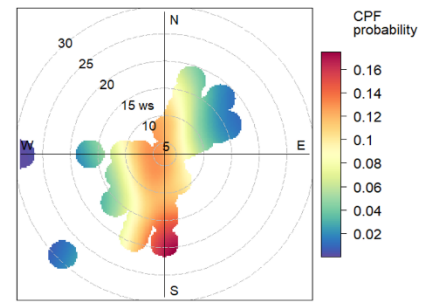
CPF at the 75th percentile (=6.2)

Vehicular Non-Exhaust



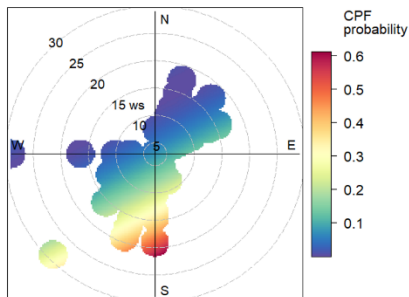
CPF at the 75th percentile (=2.4)

Mineral Dust



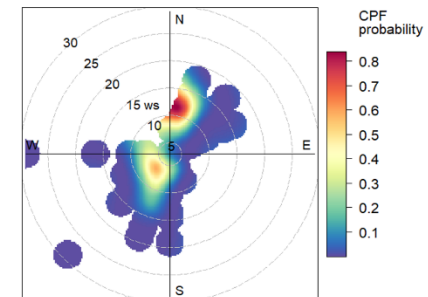
CPF at the 75th percentile (=0.91)

Sea Salt



CPF at the 75th percentile (=0.7)

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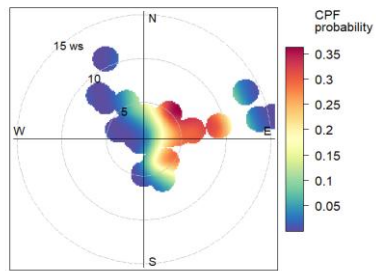


CPF at the 75th percentile (=8.6)

Figure S16: CPF plots for source contribution for the PAT stations.

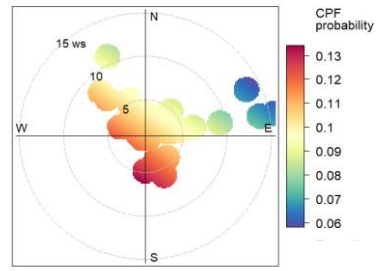
VOL-URB

Heavy Oil Combustion



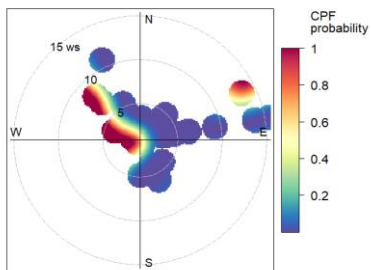
CPF at the 75th percentile (=4.6)

Sec. Sulphates & Organics



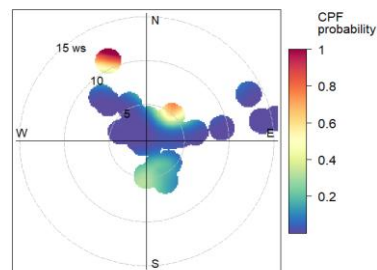
CPF at the 75th percentile (=9.4)

Biomass Burning



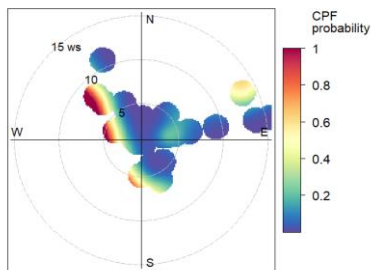
CPF at the 75th percentile (=12)

Mineral Dust



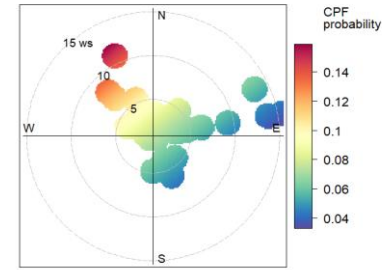
CPF at the 75th percentile (=5.4)

Cement Industry



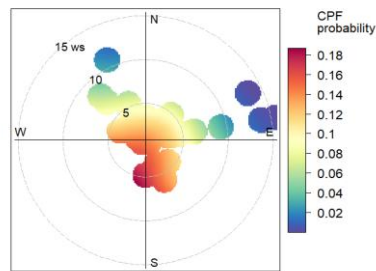
CPF at the 75th percentile (=6.5)

Sea Salt



CPF at the 75th percentile (=0.6)

Vehicular Traffic



CPF at the 75th percentile (=5)

Figure S17: CPF plots for source contribution for the VOL-URB station.

XAN-RUR

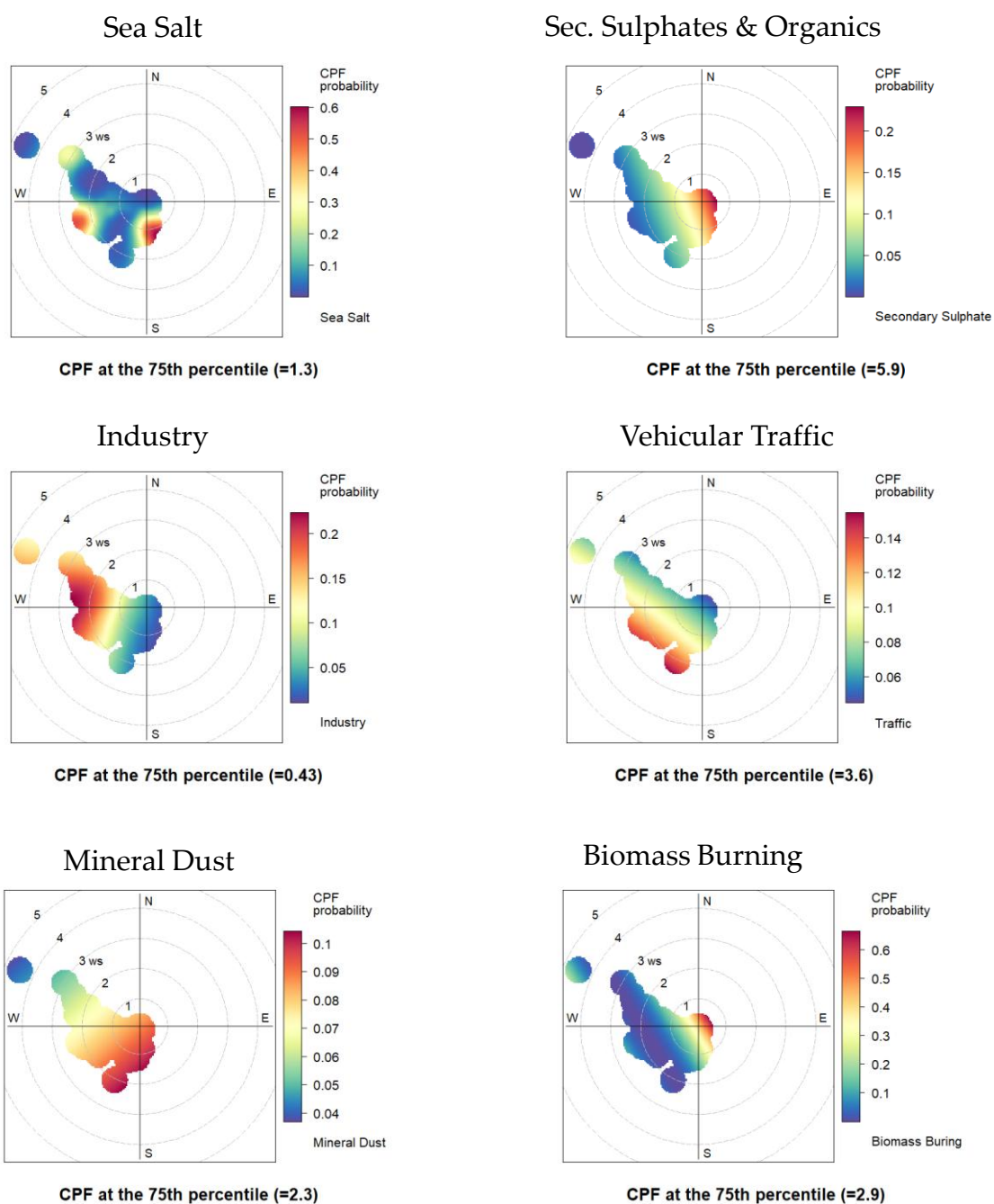


Figure S18: CPF plots for source contribution for the XAN-RUR station.