

Supplementary Material

Chemical Composition and Source Apportionment of Total Suspended Particulate in the Central Himalayan Region

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1. PMF Analysis

1.1. Data pre-processing

Missing concentration values were replaced by the geometric mean of the measured values (\hat{v}_{ij} ; for sample i , species j) and below detection limit (BDL) values were replaced by half of the detection limit for that species (MDL). The uncertainties for measured values (S_{ij}) are calculated as:

$$S_{ij} = 4(\hat{v}_{ij}) \quad \text{for missing values} \quad (1)$$

$$S_{ij} = x_{ij} + \frac{2}{3} MDL_j \quad \text{for } x_{ij} < MDL_j \quad (2)$$

$$S_{ij} = 0.2x_{ij} + \frac{2}{3} MLD_j \quad \text{for } MDL_j \leq x_{ij} < 3(MLD_j) \quad (3)$$

$$S_{ij} = 0.1x_{ij} + \frac{2}{3} MLD_j \quad \text{for } x_{ij} \geq 3(MLD_j) \quad (4)$$

where x_{ij} is the measured concentration for species j in the i^{th} sample and MDL_j is the detection limit for species j ; calculated as 3 times the standard deviation of values of 10 blank samples.

1.2. Model details

Species are classified as strong, weak or bad based on the signal to noise ratio (S/N) calculated as:

$$\left(\frac{S}{N}\right)_j = \sqrt{\frac{\sum_{i=1}^n (x_{ij} - S_{ij})^2}{\sum_{i=1}^n S_{ij}^2}} \quad (5)$$

Five samples (27-02-2005, 11-06-2006, 14-07-2006, 13-10-2007 and 12-02-2008) were excluded due to the exceptionally large value of the ratio of the estimated value of Q (Q_{robust}) to the expected value of Q ($Q_{\text{exp}} = (\text{Number of samples} - \text{Number of factors}) \times (\text{Number of strong species} - \text{Number of factors})$) for that sample. The Base model was run 20 times with different starting points to assess the robustness of the obtained solutions. Reduction in Q as the number of factors increased and $Q_{\text{robust}}/Q_{\text{theory}}$ ratio was utilized to identify the most likely sources (Figure S3).

To understand the uncertainty of a PMF solution, bootstrapping (BS), displacement (DISP), and bootstrapping with displacement (BS-DISP) error estimation methods were used. 100 BS runs were done to ensure reliable results. Each factor was mapped in >99% of BS runs. All strong species were displaced by DISP, with no factor swaps and the largest decrease in Q (dQ) being lower than 0.01%, implying that the solutions were free of rotational and random errors. In BS-DISP, five species NO_3^- , Na^+ , NH_4^+ , K^+ , and Ca^{2+} were displaced and 85% of BS-DISP runs were accepted with -0.52% dQ .

Table S1. Results of BS, DISP, and BS-DISP error estimates.

BS-DISP Diagnostics:						
# Of Cases Accepted:	85					
% Of Cases Accepted:	85%					
Largest Decrease in Q:	-1.50					
%dQ:	-0.52					
# Of Decreases in Q:	0					
# Of Swaps in Best Fit:	0					
# Of Swaps in DISP:	15					
Swaps by Factor:	1	0	1	0	0	
DISP Diagnostics:						
Error Code:	0					
Largest Decrease in Q:	-0.003					
%dQ:	-0.001					
Swaps by Factor:	0	0	0	0	0	
BS Mapping:						
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Unmapped
Boot Factor 1	100	0	0	0	0	0
Boot Factor 2	0	99	0	0	0	1
Boot Factor 3	0	0	100	0	0	0
Boot Factor 4	0	0	0	100	0	0
Boot Factor 5	0	0	0	0	100	0

Table S2. Percentage contributions of POC, SOC (estimated via EC-tracer, Percentile and MRS methods), and EC to total carbon (TC = OC + EC) mass at Nainital for the entire study period and four different seasons.

Seasons	TSP	OC	EC	WSOC	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Winter	64.40 (±43.86)	11.46 (±5.49)	1.71 (±0.84)	6.54 (±3.01)	0.02 (±0.03)	0.41 (±0.42)	5.21 (±3.88)	0.43 (±0.39)	0.92 (±0.88)	0.54 (±0.28)	0.17 (±0.09)	1.19 (±0.68)
Spring	92.90 (±48.46)	8.46 (±4.21)	1.23 (±0.67)	4.02 (±1.91)	0.03 (±0.02)	0.84 (±0.67)	3.91 (±1.93)	0.67 (±0.39)	0.24 (±0.17)	0.52 (±0.40)	0.17 (±0.07)	1.94 (±0.99)
Summer	64.76 (±73.40)	4.42 (±2.36)	0.48 (±0.24)	2.08 (±0.89)	0.07 (±0.12)	0.63 (±1.02)	3.17 (±1.53)	0.57 (±0.53)	0.32 (±0.38)	0.16 (±0.14)	0.11 (±0.08)	1.07 (±0.94)
Autumn	60.13 (±32.42)	9.58 (±5.04)	1.26 (±0.66)	6.40 (±3.60)	0.02 (±0.03)	0.48 (±0.77)	6.25 (±3.78)	0.45 (±0.49)	0.88 (±0.90)	0.60 (±0.44)	0.16 (±0.08)	1.50 (±1.19)

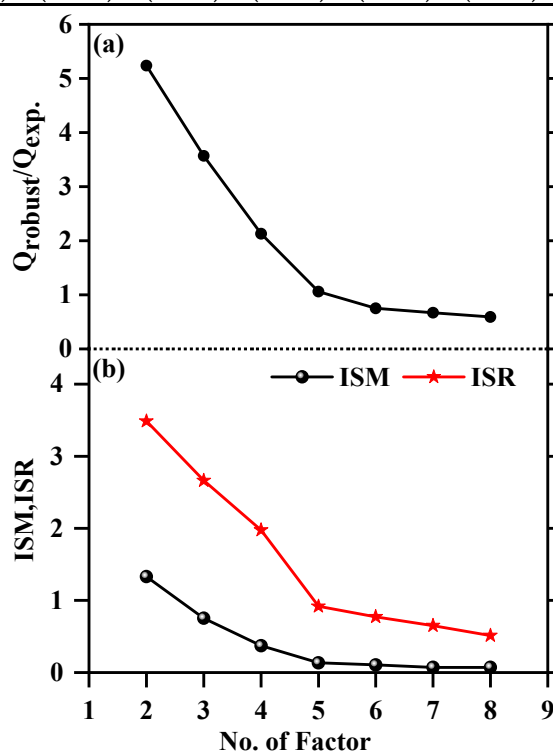


Figure S1. Plot of (a) the $Q_{\text{robust}}/Q_{\text{expected}}$ ratio against the number of factors, (b) the maximum individual mean (ISM), and maximum individual standard deviation (ISR) of scaled residuals, against the number of factors. These figures were prepared by Origin 2021 software.

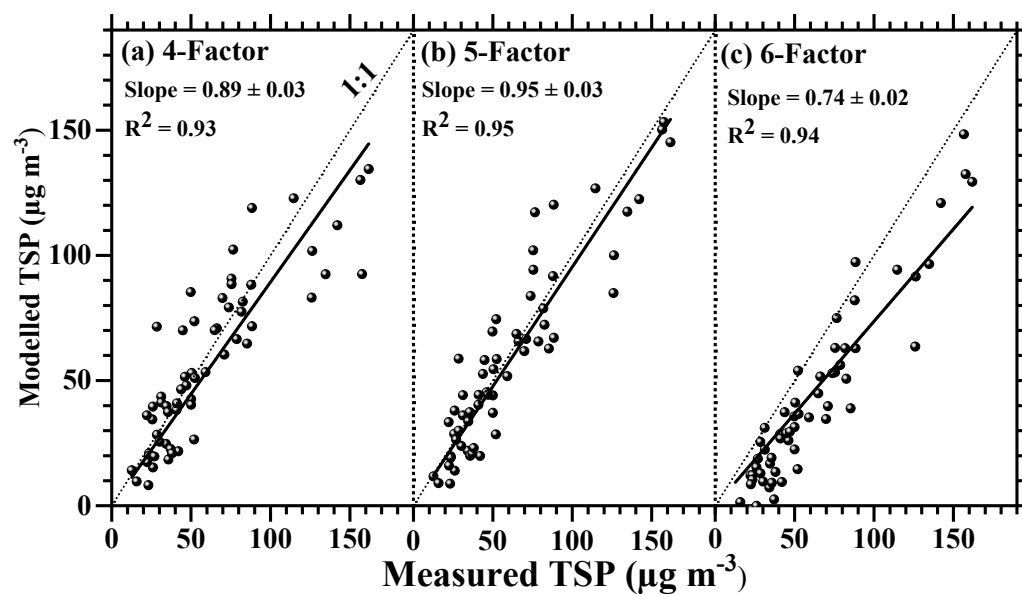


Figure S2. Scatter plot between PMF modeled and measured TSP concentrations for the (a) 4-factor solution, (b) 5-factor solution, and (c) 6-factor solution. These figures were prepared by Origin 2021 software.

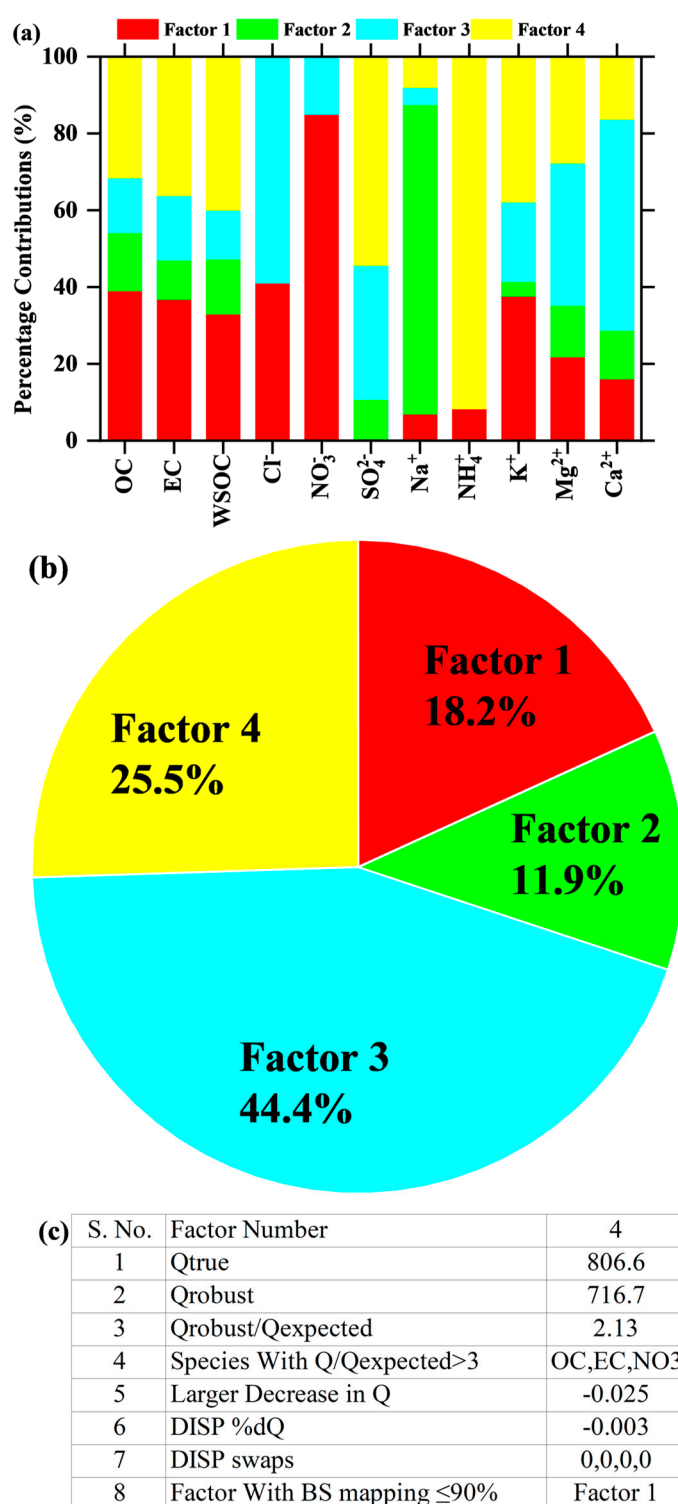


Figure S3. Emission sources identified by PMF analysis for 4 factors: (a) stacked bar chart of percentage concentration of each chemical species along with missing mass contributing to each of the factors that represent the chemical profile of each source identified in the PMF model; (b) Pie chart representing the contribution of the four sources to TSP mass; (c) the details of the PMF solution. These figures were prepared by Origin 2021 software.

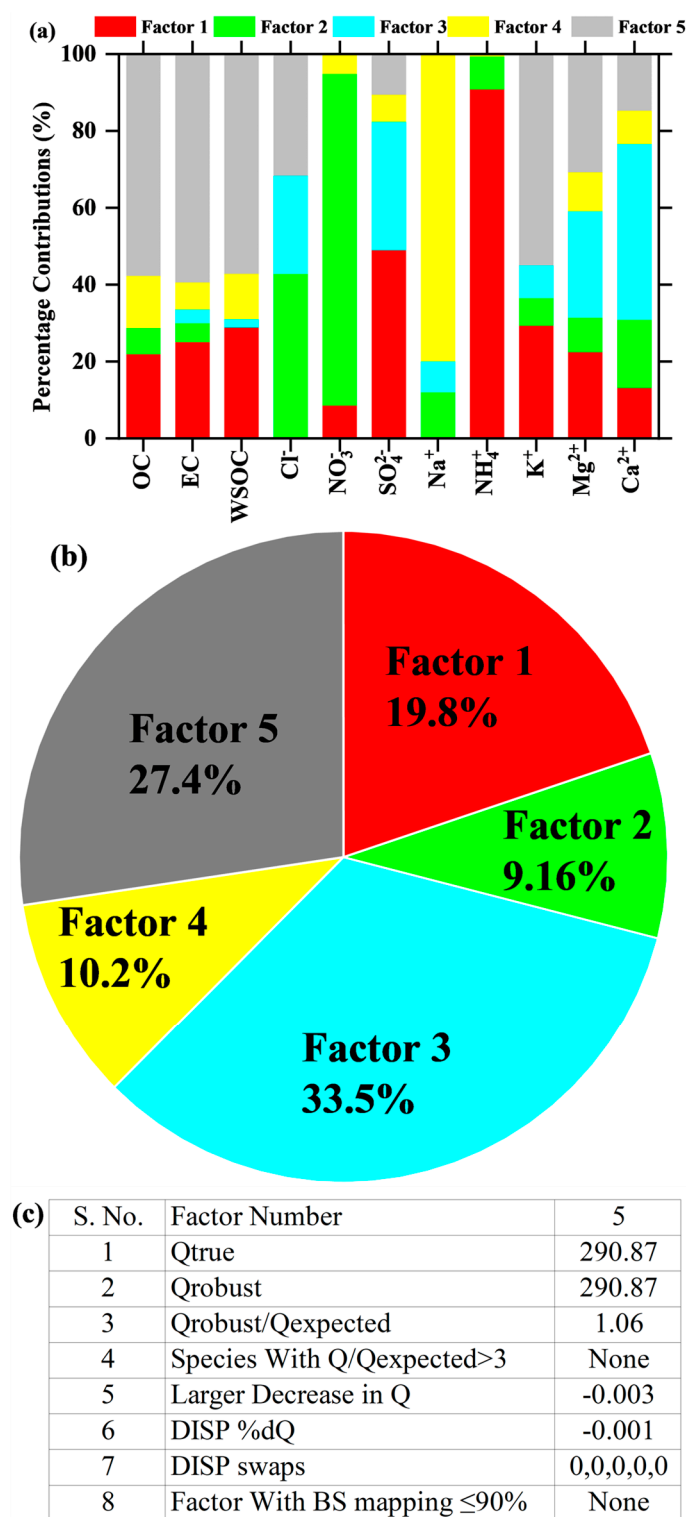


Figure S4. Emission sources identified by PMF analysis for 5 factors: (a) stacked bar chart of percentage concentration of each chemical species along with missing mass contributing to each of the factors that represent the chemical profile of each source identified in the PMF model; (b) Pie chart representing the contribution of the four sources to TSP mass; (c) the details of the PMF solution. These figures were prepared by Origin 2021 software.

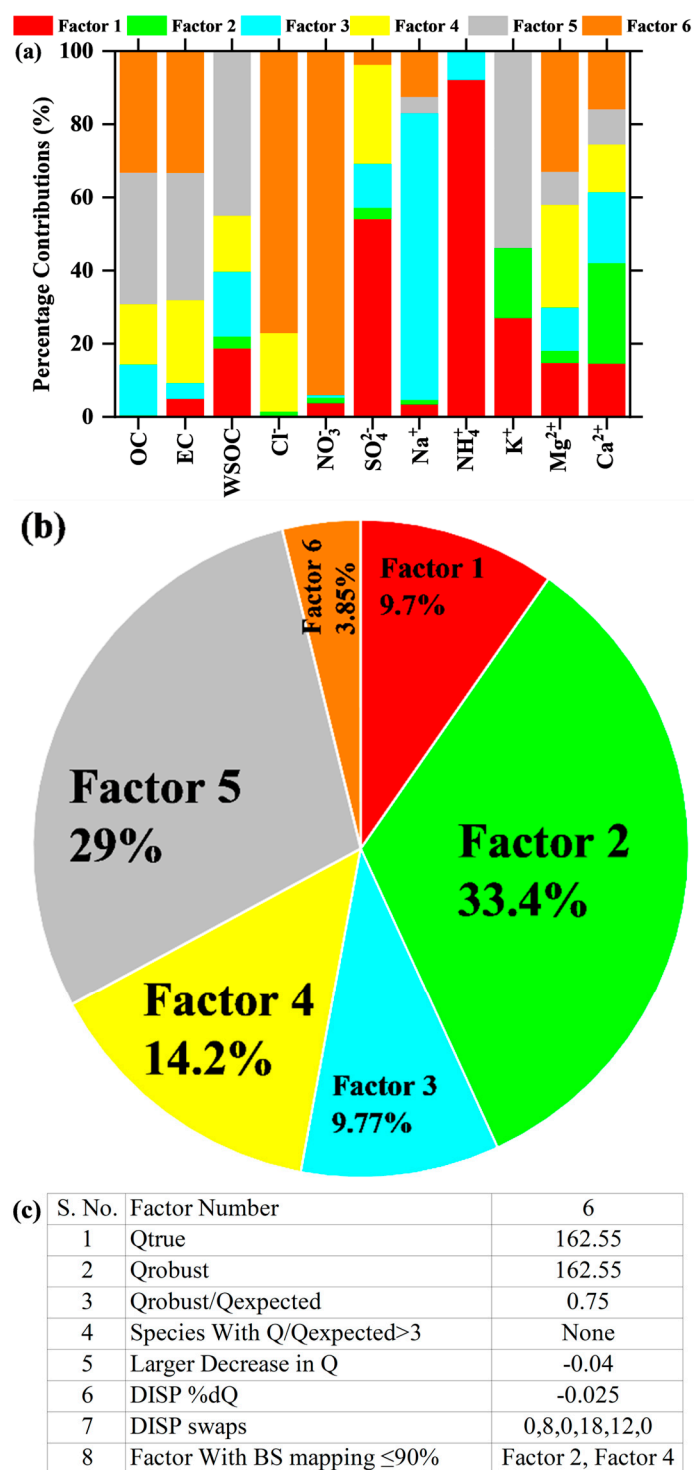


Figure S5. Emission sources identified by PMF analysis for 6 factors: (a) stacked bar chart of percentage concentration of each chemical species along with missing mass contributing to each of the factors that represent the chemical profile of each source identified in the PMF model; (b) Pie chart representing the contribution of the four sources to TSP mass; (c) the details of the PMF solution. These figures were prepared by Origin 2021 software.

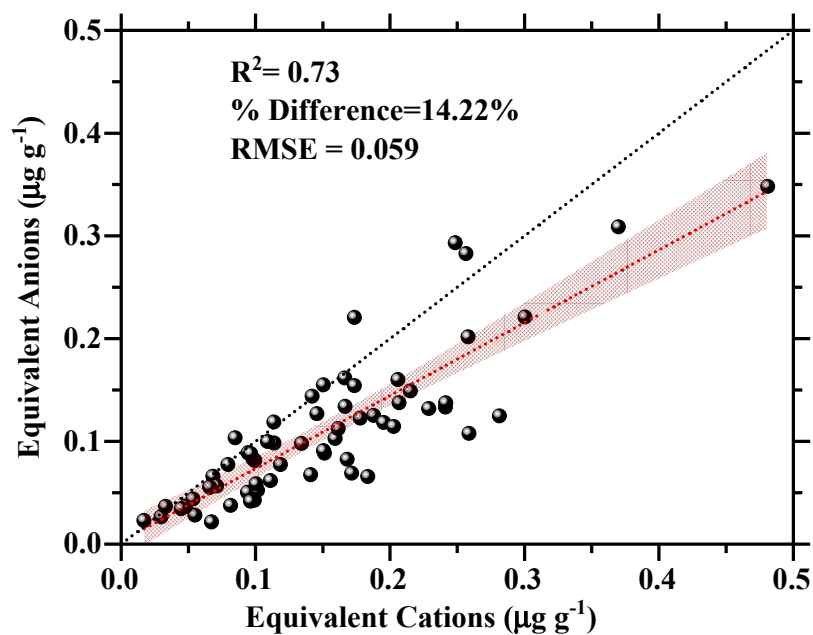


Figure S6. Correlation between measured Equivalent cation and Equivalent anion concentrations in Nainital during Feb. 2005 to Feb. 2008. The shaded area shows the lower and upper 95 % confidence levels of the linear regression. The red dotted line shows the linear least-square fit and the black dotted line shows the 1:1 line. This figure was prepared by Origin 2021 software.

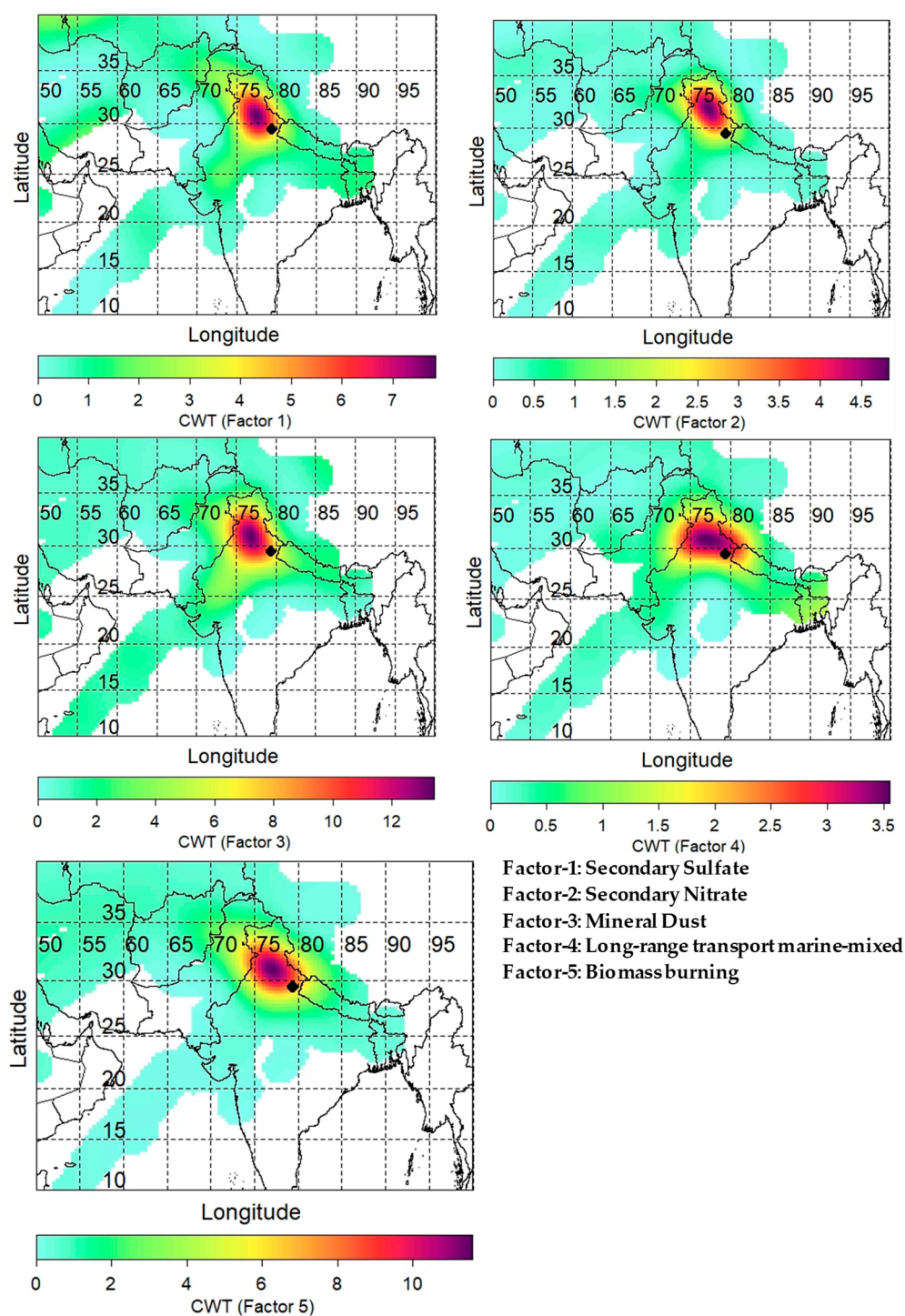


Figure S7. Potential locations of PMF identified aerosol sources resolved by Concentration Weighted Trajectory Analysis (CWT). The black dot shows the location of the measurement site. These figures were prepared by R-4.0.1 programming software.