atmosphere

Supplementary Materials: Elucidating the Chemical Compositions and Source Apportionment of Multi-Size Atmospheric Particulate (PM_{10}, $PM_{2.5}$ and PM_1) in 2019–2020 Winter in Xinxiang, North China

Huanjia Liu [1,2,3,*], Mengke Jia [1], Ke You [4], Jingjing Wang [5], Jie Tao [5], Hengzhi Liu [1], Ruiqin Zhang [2], Lanqing Li [1], Mengyuan Xu [1], Yan Ren [1], Yijie Zhao [1], Yongli Liu [1], Ke Cheng [1], Yujuan Fan [1] and Juexiu Li [2,3,6]

[1] Key Laboratory of Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Key Laboratory for Environmental Pollution Control, School of Environment, Henan Normal University, Xinxiang 453007, China
[2] School of Ecology & Environment, Zhengzhou University, Zhengzhou 450001, China
[3] College of Chemistry, Zhengzhou University, Zhengzhou 450001, China
[4] Henan Environment Monitoring Center, Zhengzhou 450001, China
[5] Zhengzhou Ecological and Environmental Monitoring Center of Henan Province, Zhengzhou 450001, China
[6] School of Energy and Environment, Zhongyuan University of Technology, Zhengzhou 450007, China
* Correspondence: liuhuanjia@htu.edu.cn

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Table S1. Some nomenclature in this study.

Abbreviation	Interpretation
AMS	Aerosol Mass Spectrometer
BOM	Bureau of Meteorology Australia
BTH	Beijing–Tianjin–Hebei
CLP/CP	Clean Period
con	Concentration
EC	Element Carbon
EF	Enrichment Factor
HMs	Heavy Metals
HPP/HP	Heavy Pollution Period
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
MD	Mineral Dust
MDL	Method Detection Limit
MEEP	Ministry of Ecology and Environment Protection of China
NAAQS	National Ambient Air Standard
NCAR	National Center for Atmospheric Research
NCEP	National Centers for Environmental Prediction
NOAA ARL	US National Oceanic and Atmospheric Administration Air Resources Laboratory
NOR	Nitrogen Oxidation Ratio
NR–PM_1	Non–Refractory Submicron Aerosol
OC	Organic Carbon
OM	Organic Matter
PM	Particulate Matter
PM_{10}	Inhalable Particles(particulate matter with aerodynamic diameter smaller than 10 μm)
$PM_{2.5}$	Fine Particulate Matter(particulate matter with aerodynamic diameter smaller than 2.5 μm)
PM_1	Submicron Aerosols(particulate matter with aerodynamic diameter smaller than 1 μm)
PM_{chem}	Chemically Reconstructed PM Mass Concentration
PM_{grav}	Gravimetric PM Mass Concentration
PMF	Positive Matrix Factorization
POA	Primary Organic Aerosol
POC	Primary Organic Carbon
PSCF	Potential Source Contribution Function
PTFE	Polytetrafluoroethylene
QA/QC	Quality Assurance and Quality Control
SA	Secondary Aerosol
SNA	Sulfate, Nitrate, and Ammonium
SOA	Secondary Organic Aerosol
SOC	Secondary Organic Carbon
SOR	Sulfur Oxidation Ratio
SP	Slightly Pollution Period
SP-AMS	Single Particle Aerosol Mass Spectrometer
THMs	Total Heavy Metals
TOR	Thermal–Optical Reflectance
Unc	Uncertainty
US EPA	US Environmental Protection Agency
WPSCF	Weighted Potential Source Contribution Function
WSII	Water–Soluble Inorganic Ions

Table S2. Characteristics of research region.

Species	**GDP (10000 Yuan)**	**Consumption of Coal by Industrial Sector (10000 tons)**	**Consumption of Nitrogenous Fertilizer (ton)**	**Cultivated Land Area (1000 hectares)**	**VOCs Emission (ton)**
amount	29,181,771 [a]	1234.79 [a]	159,870 [a]	475.66 [b]	1389.0 [a]
species	Civil Vehicles (unit)	SO_2 Emission by industrial sector (ton)	NOx Emission by industrial sector (ton)	climate type	land uses
amount	1,057,602 [a]	3908.3 [a]	8596.1 [a]	Warm temperate continental monsoon climate	Arable land

[a] by the end of 2019. [b] by the end of 2018. Data source: Henan Statistical Yearbook 2020 and Xinxiang Statistical Yearbook 2020.

Table S3. MDL and error fraction used in calculating the uncertainties by EPA PMF.

	Cl^-	**SO_4^{2-}**	**NO_3^-**	**Na^+**	**NH_4^+**	**K^+**	**Mg^{2+}**	**Ca^{2+}**	
MDL (μg m^{-3})	0.019	0.019	0.019	0.009	0.009	0.009	0.009	0.009	
Error fraction%	10	10	10	10	10	10	10	10	
	Al	Fe	As	Ba	Cd	Co	Cr	Cu	Mn
MDL (μg m^{-3})	0.0004	0.0004	0.001	0.0001	0.0001	0.0004	0.0004	0.0004	0.0001
Error fraction%	10	10	10	10	10	10	10	10	10
	Ni	Pb	Sb	Ti	V	Zn	OC	EC	SUM
MDL (μg m^{-3})	0.0004	0.001	0.002	0.0001	0.001	0.0004	0.004	0.001	0.1
Error fraction%	10	10	10	10	10	10	10	10	10

Detail description about EPA PMF 5.0 as follows:

The US Environmental Protection Agency's PMF 5.0 receptor model was applied for PM source apportionment of Xinxiang area in this study. For a data matrix $\boldsymbol{x}$ with samples $\boldsymbol{i}$ by chemical species $\boldsymbol{j}$ dimensions, the goal of PMF is to identify the number factors $\boldsymbol{p}$, the species profile $\boldsymbol{f}$ of each source, the mass $\boldsymbol{g}$ contributed by each factor to each individual sample, and the residual e (Equation (S1)) [1,2]:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{S1}$$

According to EPA PMF 5.0 user guide, Q is a critical parameter. The species profile $\boldsymbol{f}$ and the mass contribution $\boldsymbol{g}$ are obtained in the case of the minimum the object function $\boldsymbol{Q}$, based upon the uncertainties (***Unc***) of each data (Equation (S2)) [1,2]:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{Unc_{ij}} \right]^2 \tag{S2}$$

The theoretical Q ($\boldsymbol{Q_{theoretical}}$) can be calculated as Equation (S3), and the best PMF solution should have $Q/Q_{theoretical}$ with the value of ~1 [1,2].

$$Q_{theoretical} = i \times j - p \times (i + j) \tag{S3}$$

When applied EPA PMF 5.0, a number of factors were selected after the evaluation of the following steps:

(1) Signal–to–noise. Signal–to–noise values less than 0.5 were recorded as bad, 0.5 to 1 were recorded as weak, and above 1 were recognize as strong [1]. Besides, a comparison between observed values (imput data) and predicted values (modeled) is used to evaluate the fitting results of the PMF model. Chemical components do not have a strong correlation between predicted values and observed values should be defined as week species or be removed from the simulation.

(2) The goodness–of–fit parameters, i.e., Q_{robust} and Q_{true}, were adjusted changing the number of factors, and compared with $Q_{theoretical}$. Q_{robust}, the goodness–of–fit parameter calculated excluding outliers, defined as samples for which the scaled residual was greater than 4 and Q_{true} was calculated including all points. Once a reasonable solution was found, the uncertainties in the modeled solution were estimated by using the bootstrapping technique.

(3) Residual. The scaled residuals were used to assess the performance of the modeled sources. The selected number of factors in both fractions led to solutions with 90–100% of the scaled residuals located between the optimal range −3 to +3.

(4) Ppeak function of PMF 5.0 was used to interpret the factor profile. The solution of model run should be rotated back to the real solution using the Ppeak function. Fpeak run was also performed in this study by using the strength of Fpeak rotation from −1 to +1. Moreover, Fpeak without rotation (Fpeak = 0) was also executed. We have considered all Fpeak rotations and physical meaning and PMF result without Fpeak rotation was selected (Fpeak = 0) to explain source profile and source contribution.

In general, the optimal number of factors of PM in Xinxiang were identified after the above steps were evaluated. The model was run 20 times with six factors. All runs converged and a global minimum was found. The number of factors ranged from 4 to 9 and was examined by checking the above parameters. The most optimal number of factors were selected in Xinxiang in North China.

Table S4. Average mass concentrations of chemical species in PM_{10}, $PM_{2.5}$, and PM_1 and SOR NOR during the various periods.

		2019–2020 Winter					
		PP1	**PP2**	**PP3**	**PP**	**CP**	**Average**
PM_{10}	PM_{10}	217.39	199.06	171.63	185.55	74.36	155.53
	Cl^-	6.97	7.95	3.57	5.29	1.63	4.25
	SO_4^{2-}	39.75	16.44	32.00	29.23	6.56	23.03
	NO_3^-	48.72	42.07	42.12	43.27	12.36	35.49
	Na^+	0.75	0.81	0.51	0.63	0.32	0.54
	NH_4^+	27.30	15.79	20.60	20.90	4.47	16.68
	OC	22.70	31.27	15.63	20.36	10.37	17.59
	EC	9.80	10.46	8.02	8.71	4.91	7.72
	POC	12.08	12.89	9.89	10.74	6.06	9.51
	SOC	10.62	18.38	5.75	9.62	4.31	8.07
	MD	27.43	52.29	28.47	31.95	23.01	28.80
	SOR	0.63	0.32	0.62	0.55	0.26	0.47
	NOR	0.33	0.28	0.34	0.32	0.18	0.29
	Al	1.65	3.19	1.67	1.92	1.62	1.79
	Fe	2.52	3.46	1.94	2.36	1.50	2.09
	K	1.55	2.34	1.12	1.46	0.81	1.27
	As	0.02	0.02	0.01	0.01	0.01	0.01
	Ba	0.06	0.09	0.05	0.06	0.03	0.05
	Cd	0.01	0.02	0.01	0.01	0.01	0.01
	Co	0.01	0.01	0.003	0.005	0.002	0.004
	Cr	0.02	0.03	0.02	0.02	0.02	0.02

	Cu	0.04	0.08	0.03	0.04	0.01	0.04
	Mn	0.12	0.15	0.08	0.10	0.05	0.09
	Ni	0.03	0.03	0.01	0.02	0.01	0.02
	Pb	0.15	0.16	0.11	0.12	0.05	0.10
	Sb	0.01	0.02	0.01	0.01	0.005	0.01
	Se	0.002	0.001	0.001	0.001	0.001	0.001
	Ti	0.11	0.21	0.13	0.14	0.11	0.13
	V	0.003	0.005	0.003	0.004	0.003	0.003
	Zn	0.43	0.37	0.29	0.33	0.09	0.26
	TEs	12.04	22.02	12.46	13.78	8.39	12.06
$PM_{2.5}$	$PM_{2.5}$	171.34	144.15	136.31	143.58	52.91	120.07
	Cl^-	6.33	6.58	3.08	4.59	1.29	3.73
	SO_4^{2-}	31.97	12.02	25.91	23.53	5.19	18.77
	NO_3^-	44.73	35.16	38.38	38.87	10.39	31.49
	Na^+	0.51	0.45	0.31	0.40	0.18	0.34
	NH_4^+	24.54	14.04	19.95	19.49	4.63	15.64
	OC	22.00	27.78	14.30	18.61	8.46	15.98
	EC	10.61	8.66	7.62	8.20	3.85	7.08
	POC	15.49	12.65	11.12	11.98	5.63	10.33
	SOC	6.51	15.13	3.18	6.63	2.84	5.65
	MD	7.72	14.75	6.29	8.14	7.23	7.90
	SOR	0.58	0.26	0.57	0.50	0.22	0.43
	NOR	0.31	0.25	0.32	0.30	0.16	0.26
	Al	0.42	0.79	0.35	0.44	0.48	0.45
	Fe	1.06	1.72	0.66	0.97	0.55	0.86
	K	1.08	1.46	0.70	0.94	0.46	0.82
	As	0.02	0.01	0.01	0.01	0.005	0.01
	Ba	0.02	0.03	0.01	0.02	0.02	0.02
	Cd	0.01	0.01	0.003	0.01	0.003	0.005
	Co	0.001	0.002	0.001	0.001	0.001	0.001
	Cr	0.02	0.03	0.01	0.02	0.01	0.01
	Cu	0.03	0.05	0.02	0.03	0.01	0.02
	Mn	0.07	0.09	0.04	0.06	0.03	0.05
	Ni	0.01	0.03	0.004	0.01	0.004	0.01
	Pb	0.12	0.11	0.08	0.09	0.03	0.08
	Sb	0.01	0.01	0.01	0.01	0.004	0.01
	Se	0.001	0.001	0.001	0.001	0.001	0.001
	Ti	0.03	0.06	0.04	0.04	0.04	0.04
	V	0.001	0.002	0.001	0.001	0.001	0.001
	Zn	0.33	0.27	0.20	0.24	0.08	0.20
	TEs	4.03	7.23	3.16	4.11	2.90	3.79
PM_1	PM_1	139.28	100.98	95.15	102.97	36.24	85.64
	Cl^-	4.55	4.97	2.09	3.22	1.22	2.64
	SO_4^{2-}	19.73	7.21	14.29	13.55	4.09	11.05
	NO_3^-	32.22	25.20	25.68	26.82	9.00	22.61
	Na^+	0.33	0.28	0.20	0.25	0.15	0.23
	NH_4^+	19.63	12.23	14.19	14.71	4.53	12.16
	OC	16.12	19.27	8.52	12.45	6.54	10.76
	EC	7.78	6.05	5.32	5.98	3.00	5.17
	POC	8.35	6.49	5.71	6.41	3.21	5.54
	SOC	7.77	12.79	2.81	6.04	3.32	5.22

MD	3.31	6.63	1.84	3.16	2.41	2.93
SOR	0.47	0.19	0.43	0.38	0.18	0.33
NOR	0.24	0.20	0.24	0.23	0.14	0.21
Al	0.14	0.40	0.06	0.15	0.13	0.14
Fe	0.60	0.67	0.30	0.44	0.22	0.38
K	0.81	1.02	0.51	0.67	0.37	0.59
As	0.01	0.01	0.01	0.008	0.004	0.01
Ba	0.01	0.02	0.005	0.008	0.005	0.01
Cd	0.003	0.01	0.002	0.003	0.002	0.003
Co	0.0004	0.001	0.0003	0.0004	0.0003	0.0004
Cr	0.01	0.01	0.003	0.006	0.001	0.005
Cu	0.02	0.03	0.01	0.02	0.008	0.01
Mn	0.05	0.06	0.03	0.04	0.02	0.03
Ni	0.004	0.01	0.003	0.004	0.002	0.004
Pb	0.08	0.08	0.06	0.06	0.03	0.05
Sb	0.01	0.01	0.006	0.01	0.003	0.006
Se	0.001	0.001	0.001	0.001	0.001	0.001
Ti	0.01	0.02	0.01	0.01	0.01	0.01
V	0.001	0.0004	0.0003	0.0004	0.0003	0.0004
Zn	0.21	0.18	0.14	0.16	0.07	0.13
TEs	2.10	3.08	1.31	1.84	1.23	1.65

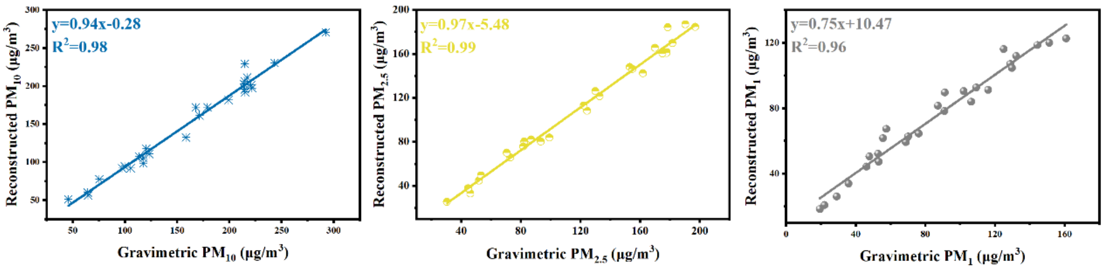

Figure S1. Correlation of reconstructed PM_{10}, $PM_{2.5}$, and PM_1 and gravimetric mass concentration in 2019–2020 winter for Xinxiang.

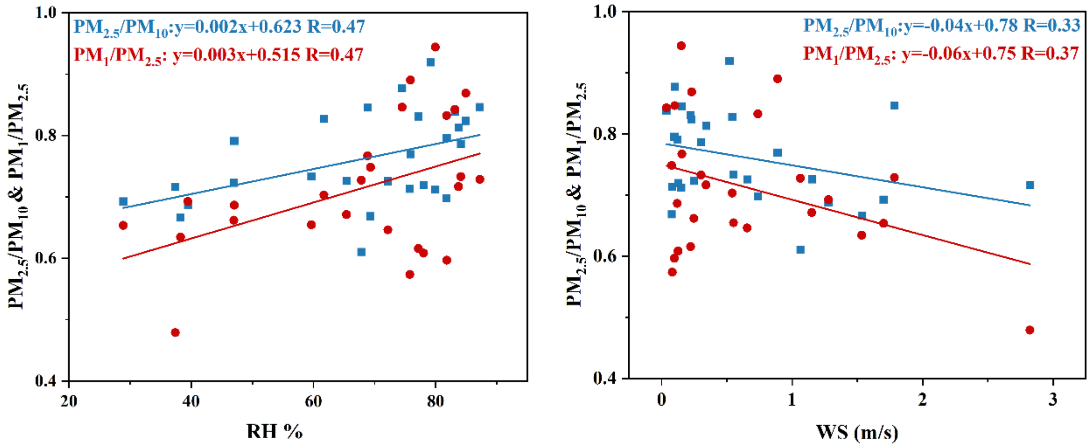

Figure S2. The correlation relation between the ratios of $PM_1/PM_{2.5}$ and $PM_{2.5}/PM_{10}$ with RH and WS.

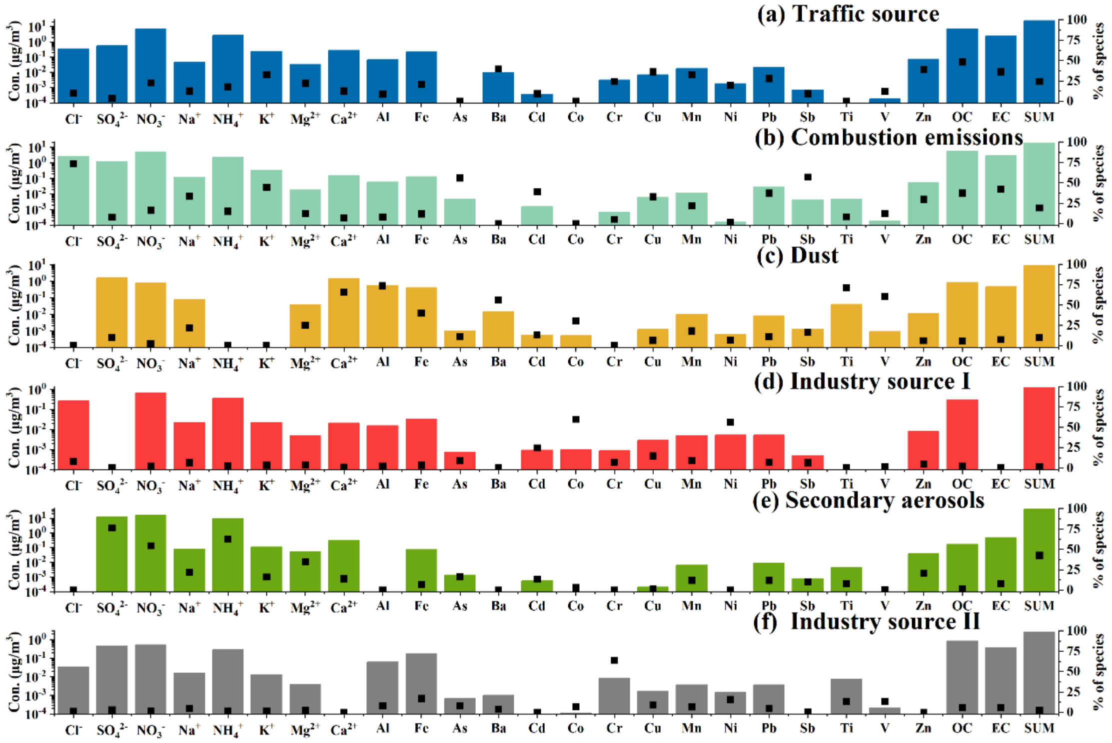

Figure S3. PMF source factor profiles for the PM samples through the entire study period in Xinxiang in terms of concentrations (μg m^{-3}) and percentages (%).

Reference

1. United States Environmental Protection Agency (USEPA). Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide, **2014**.
2. Liu, J.W.; Chen, Y.J.; Chao, S.H.; Chao, H.B.; Zhang, A.C.; Yang, Y. Emission control priority of $PM_{2.5}$-bound heavy metals in different seasons: A comprehensive analysis from health risk perspective. Sci. Total Environ. **2018**, 644, 20-30; DOI:10.1016/j.scitotenv.2018.06.226.