The Indoor and Outdoor Chemical Components of PM$_{2.5}$ in Rural Area of Northwestern China-Case Study

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ABSTRACT

A case study of indoor and outdoor fine particles (PM$_{2.5}$) was undertaken for rural areas in northwestern China. Quantitative information was obtained on the chemical compositions (including carbon fractions, water soluble ions, and elements). OM (organic matter), sulfate, and geological material dominated PM$_{2.5}$, followed by nitrate and ammonium, which accounted to 78–85% of the mass for indoor and outdoor environments. The variations of the carbon fractions indicated that four OC factions and EC1 were more abundant in winter than those in summer. SO$_4^{2-}$ contributions were the highest of the ionic species for indoor and outdoor environment (about 40% for winter and 53% for summer of total ions), followed by NO$_3^-$ (about 23% for winter and 14% for summer). The integrated results from the ratios of K$^+$/OC, K$^+$/EC and as well as the EF (enrichment factor) values for K, Cl, S and Pb indicated that the biofuel contributions were significant in the rural area. The indoor/outdoor ratios and correlations of the components were also investigated. The results of indoor and outdoor PM$_{2.5}$ sources showed that biomass burning in summer was the dominant primary source (31% for indoor and 44% for outdoor), and those for winter were coal combustion (21% for indoor and 29% for outdoor) and biomass burning (24% for indoor and 16% for outdoor). Due to the local patterns of energy consumption, the discussion could give implications for the future strategies and implementation of rural air quality improvement.

Keywords: Fine particles; Rural area; Chemical components; Northwestern China.

INTRODUCTION

The usage of biomass and coal for cooking and heating is common in rural area in northwestern China. In reality, the emissions from the local 'kang stove' heating largely contribute to the chemical components of particulates. The variations of these components are due to the types and qualities of stoves and fuels, cooking and heating methods, and as well as the seasons. The previous studies showed that the chemical species can affect the roles of aerosol in many aspects, such as its impacts on climate, health and visibility reduction (Laden *et al*., 2000; Jacobson, 2002; Watson, 2002; Lohmann and Feichter, 2005; Chakraborty *et al.*, 2010;

Shakya *et al.*, 2010; Kim *et al.*, 2011). So understanding the composition and sources of airborne particulate matter in indoor and outdoor for the rural area is essential.

Up to now, the chemical composition for particulates has been investigated in various sites in China (eg., He *et al*., 2001; Cao *et al*., 2003; Zhang *et al*., 2003; Cao *et al*., 2004, 2005; Wang *et al*., 2006; Cao *et al*., 2007; Zhang *et al*., 2008, 2009; Shen *et al*., 2010). The government has also implemented a variety of programs to control urban air pollution and protect the atmospheric environment (He *et al*., 2002). Nevertheless, those for rural area were less concerned, and the previous studies for rural area just focused on some characteristics (eg., Yan *et al*., 2008; Zhu *et al*., 2010b). The results for rural area also exhibited differently with those of urban areas. At present, the integrated study of indoor and outdoor PM$_{2.5}$ for rural area was much scarce in northwestern China.

The study here presented the levels of indoor and outdoor carbonaceous fractions, ions and elemental compositions in winter and summer. The examinations of I/O (indoor/ outdoor) ratios and correlations for these species were also conducted. By using PMF (Positive Matrix Factorization)

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method, the indoor and outdoor source contributions were determined for winter and summer, respectively. The knowledge of the compositions and sources of $PM_{2.5}$ is critical for understanding and then for ameliorating the rural atmospheric environments.

METHODS

Sampling Sites

The observation campaigns were conducted in three rural sites in Lintong, Huxian and Weinan county, respectively (namely, LT, HX and WN) (Fig. 1). In the research area it was common for residents to use straw and corn stake burning for cooking and heating in winter. The indoor sites (three houses without smoking) for LT and HX are in the living room while the WN site is in an aisle, and the outdoor sites are on the rooftop of the house, at 3 meter above ground level. The frequency of cooking was three times daily during the sampling period.

Sample Collection and Analysis

Indoor and outdoor $PM_{2.5}$ samples were collected simultaneously from Nov. 11 to Dec. 12 of 2007 (winter) and Jun. 7 to Jun. 29 of 2008 (summer) by using mini-volume samplers (Airmetrics, USA) operating with a flow rate of 5 L/min for 24 hours. All samples were collected on 47 mm Whatman quartz microfibre filters (QM/A). The filters were pre-heated before sampling at 800°C for 3 hours. After collection, the filters were stored in a refrigerator before chemical analysis.

The quartz filters were analyzed for eight carbon fractions with a DRI Model 2001 Thermal and Optical Carbon

Analyzer (Atmoslytic Inc., Calabasas, CA, USA) following the IMPROVE-A (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol (Chow *et al.*, 1993, 2001; Fung *et al.*, 2002). Four anions (SO_4^{2-}, NO_3^-, Cl^-, and F^-) and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in aqueous extracts of the filters were analyzed using ion chromatography (IC). The elemental concentrations were determined using energy-dispersive X-ray fluorescence (ED-XRF), which provides a rapid and nondestructive method for the analysis of trace and major elements in samples. The Quality Assurance/Quality Control (QA/QC) procedures were described in Xu *et al.* (2012). A detailed description of the detection limits (MDLs) and methodology for the analyses can be found elsewhere (Cao *et al.*, 2011).

After excluding species that were frequently present at concentrations below the detection limit (BDL), 23 species were used for the PMF analysis: OC, EC, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-}, Mg, S, Cl, K, Ca, Ti, Mn, Fe, Zn, Br, Mo and Pb. In this data set, the data for species with BDL values were replaced with values corresponding to one-half of the appropriate analytical detection limit. PMF is a factor analytic technique that uses non-negativity constraints and allows non-orthogonal factors (Paatero, 1997; Oh *et al.*, 2011). PMF1.1 was used for the current analysis. The PMF program permits maximum use of available data and better treatment of missing and below detection limit values. PMF assumes that concentrations at receptor sites are impacted by the linear combinations of source emissions, which are derived as factors in the model. Uncertainty also plays an important role in the model because it reflects the quality and reliability of each data
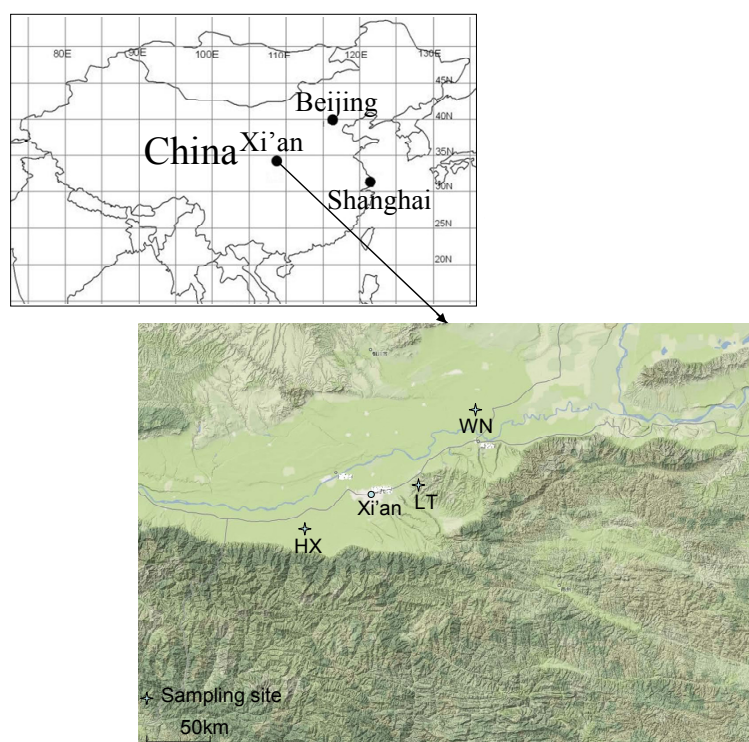

Fig. 1. Locations of sampling sites for the rural area.

point. The model solves the general receptor modeling problem using constrained, weighted, least-squares. The model determines signal-to-noise ratio (S/N) statistics for every input species and allows the user to downgrade the importance or remove species with small S/N values.

RESULTS AND DISCUSSION

Characterization of Carbon Fractions for Indoor and Outdoor

Table 1 showed the variations of indoor and outdoor mass and chemical components in winter and summer. The average indoor concentrations for mass, OC and EC in winter were 237.2, 61.1, and 6.2 $\mu g/m^3$, and those in summer were 96.7, 18.0, and 2.8 $\mu g/m^3$, respectively. Comparing with indoors, higher concentrations of mass and EC and lower OC were found for outdoor in the corresponding seasons (Table 1). The results indicated that there were some indoor sources for OC emission. The variations of carbon fractions among indoor and outdoor samples were shown in Fig. 2. The concentrations of all carbon fractions in winter were higher than those in summer for both indoor and outdoor.

The indoor four organic carbon fractions ranged from 8.41 to 12.87 $\mu g/m^3$ in winter and 0.8 to 5.21 $\mu g/m^3$ in summer, respectively. Correspondingly, those for outdoor were lower than those for indoor in winter (from 6.79 to 10.84 $\mu g/m^3$) and comparable in summer (from 0.79 to 5.19 $\mu g/m^3$). The variations of three EC fractions were similar for indoor and outdoor. EC1 was the dominant contributor to EC in both

seasons. The concentrations of EC1 were 21.7 $\mu g/m^3$ for indoor and 23.78 $\mu g/m^3$ for outdoor in winter, which were higher than those in summer samples for indoors (5.41 $\mu g/m^3$) and outdoors (5.97 $\mu g/m^3$), respectively. The levels of EC2 for indoor samples were 0.72 and 0.25 $\mu g/m^3$ in winter and summer, respectively. Those for outdoor were 0.69 $\mu g/m^3$ in winter and 0.3 $\mu g/m^3$ in summer, respectively. The concentrations of EC3 were 0.45 and 0.34 $\mu g/m^3$ in winter for indoor and outdoor, respectively, and those for summer samples were almost below the method detection level.

The percentages of OC to total carbon (TC) were comparable for indoor and outdoor, which accounted for ~90% in winter and ~85% in summer, respectively. The previous studies reported that the percentages of OC to TC for urban area in China (including Beijing, Shanghai, Hongkong, Guangzhou, Shenzhen and Zhouhai) ranged from 67% to 73% (He *et al.*, 2001; Cao *et al.*, 2003; Dan *et al.*, 2004; Duan *et al.*, 2004; Ye *et al.*, 2004). And the percentages for urban area at Xi'an were 75% and 80% in autumn and winter, respectively (Cao *et al.*, 2005). Comparing with the results from urban area, the higher contribution of OC to TC in our study reflected the presence of richer OC in rural area. The variations of the carbon fractions indicated that four OC factions and EC1 were more abundant in winter than those in summer. In northwestern China, the traditional 'kang stove' is commonly used in rural areas. Considering the simple burning equipment and low burning efficient, more emissions of low-temperature carbon fractions were reasonable.

Table 1. The concentrations of mass and chemical species ($\mu g/m^3$).

	Indoor Sum. (n = 23)			Indoor Win. (n = 30)			Outdoor Sum. (n = 23)			Outdoor Win. (n = 30)		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
mass	96.72	160.97	29.38	237.19	471.18	61.48	115.75	226.78	67.92	267.47	495.65	68.73
OC	18.04	32.71	9.75	61.07	187.53	15.14	17.62	30.82	10.58	58.58	122.04	18.18
EC	2.80	5.50	1.64	6.15	11.71	2.66	3.23	6.03	1.99	6.59	11.58	2.89
Char	2.55	5.28	1.48	4.98	10.57	2.14	2.89	5.69	1.83	5.21	9.72	0.65
Soot	0.25	0.47	0.12	1.17	2.13	0.36	0.34	0.76	0.13	1.09	2.19	0.31
Na^+	3.62	5.00	2.59	3.08	6.94	1.46	4.04	7.45	2.16	3.33	5.56	2.12
NH_4^+	5.63	14.47	0.05	15.02	38.38	0.67	6.53	16.00	0.08	20.48	49.32	0.78
K^+	2.22	6.16	0.51	7.95	21.95	1.50	2.47	4.38	0.70	7.96	15.34	1.32
Mg^{2+}	0.16	0.40	0.05	0.70	1.32	0.48	0.21	0.41	0.09	0.75	1.26	0.55
Ca^{2+}	0.99	2.72	0.06	1.05	4.76	0.14	1.67	3.40	0.50	0.71	4.27	0.07
Cl^-	2.00	4.57	0.38	7.35	17.51	1.40	2.08	6.53	0.62	8.61	16.43	2.23
NO_3^-	5.70	17.36	0.56	23.58	61.26	3.04	7.36	21.15	1.75	28.23	66.89	2.74
SO_4^{2-}	23.26	46.24	3.21	39.72	89.14	8.02	27.04	48.90	5.77	48.34	107.52	5.39
Mg	0.31	0.63	0.03	0.43	1.85	0.11	0.32	0.79	0.03	0.44	1.64	0.13
S	4.19	8.61	0.39	6.71	13.86	1.53	4.28	8.29	0.95	6.62	14.90	1.37
Ca	0.84	2.39	0.20	1.21	7.71	0.11	1.46	5.67	0.25	1.17	6.30	0.19
Ti	0.06	0.20	0.02	0.07	0.49	0.01	0.09	0.32	0.02	0.08	0.42	0.01
Cr	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.00
Mn	0.04	0.07	0.01	0.08	0.17	0.04	0.06	0.11	0.03	0.10	0.22	0.02
Fe	0.64	1.98	0.24	0.96	1.96	0.20	1.05	3.70	0.22	1.10	4.76	0.11
Zn	0.52	2.93	0.10	0.81	1.49	0.30	0.61	2.99	0.12	1.04	2.94	0.28
Br	0.01	0.03	0.00	0.05	0.10	0.00	0.01	0.03	0.00	0.06	0.14	0.01
Mo	0.04	0.07	0.01	0.05	0.14	0.04	0.05	0.08	0.01	0.06	0.20	0.02
Cd	0.01	0.04	0.00	0.03	0.07	0.00	0.02	0.07	0.00	0.03	0.10	0.00
Pb	0.17	0.39	0.02	0.63	1.12	0.13	0.19	0.36	0.06	0.74	1.48	0.02

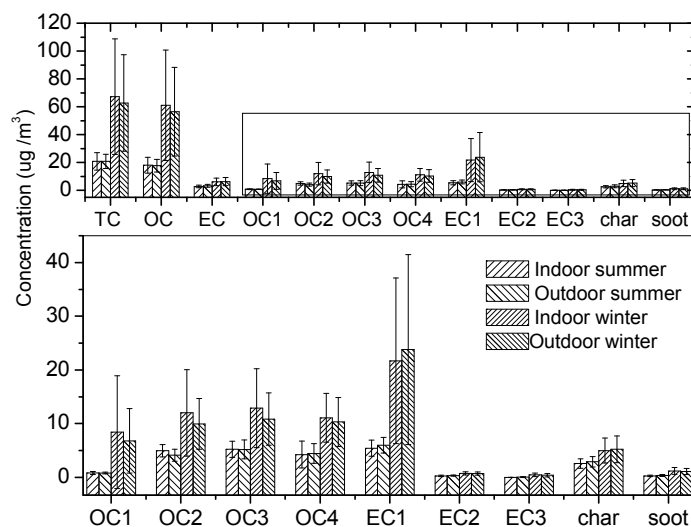**Fig. 2.** The average concentrations and Stdev. of carbon fractions.

The average concentrations of char and soot in summer were 2.55 and 0.25 µg/m³ for indoor and 2.89 and 0.34 µg/m³ for outdoor, respectively. And higher concentrations of char and soot were found in winter than those in summer. The levels of char and soot were 4.98 and 1.17 µg/m³ for indoor and 5.21 and 1.09 µg/m³ for outdoor, respectively. The previous study reported the average char and soot concentrations of $PM_{2.5}$ for the fourteen cities in China were 8.7 and 1.26 µg/m³ in winter; 2.4 and 1.21 µg/m³ in summer, respectively. The variations of char and soot mainly attributed to the different fuel consumption (Han *et al.*, 2009). Compared with the level of urban areas, lower concentrations of soot in rural area were observed, which indicated that there was less vehicle emission in rural area than those for urban area.

Distributions of Water Soluble Inorganic Ions

The average concentrations of inorganic species were presented in Table 1. In general, the major cations were: NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, and those for anions were:

SO_4^{2-}, NO_3^- and Cl^-. The indoor concentrations of SO_4^{2-} were 39.72 and 23.26 µg/m³ in winter and summer, respectively, and those for outdoor were 48.34 and 27.04 µg/m³, respectively. The concentrations of NO_3^- were much higher in winter (23.58 µg/m³ for indoor and 28.23 µg/m³ for outdoor) than those in summer (5.70 µg/m³ for indoor and 7.36 µg/m³ for outdoor). The comparable trends were also found for K^+ and NH_4^+. The concentrations of K^+ gave 7.95 and 7.96 µg/m³ in winter for indoor and outdoor, respectively, which for NH_4^+ in winter were 15.02 and 20.48 µg/m³ for indoor and outdoor, respectively. The levels of K^+ and NH_4^+ in winter were about 3 times of those in summer. Fig. 3 showed the comparisons of water soluble ions for indoor and outdoor in both seasons. It was seen that the SO_4^{2-} is the most abundant ionic species for indoor and outdoor environment (about 40 % for winter and 53% for summer of total ions), followed by NO_3^- (about 23% for winter and 14% for summer) and NH_4^+ (about 16% for winter and 13% for summer). The levels of NO_3^-, K^+ and Cl^- in winter were more abundant than those in summer. The
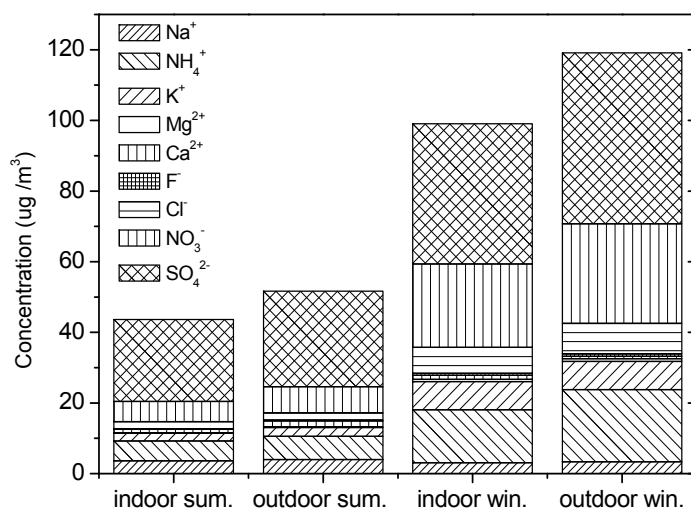

Fig. 3. The comparisons of water soluble ions concentrations.

results of water soluble ions indicated that biomass burning and secondary aerosols make a significant contribution to fine particulate in rural area.

The emissions from biomass burning contribute significantly to the atmospheric concentrations of K^+ and carbonaceous species (OC and EC). Likewise, fossil fuel and vehicle emissions are also the dominant sources of OC and EC, however, K^+ concentration is insignificant. Thus, K^+/OC and K^+/EC ratios can be used to characterize the emission sources. The K^+/OC ratios in winter were 0.13 and 0.14 for indoor and outdoor, respectively. And those for summer were 0.12 and 0.14, respectively. Minor variations were found for K^+/OC ratios in the present study. The results were comparable with those of previous studies, which exhibited that the K^+/OC ratios were in the range of 0.08 to 0.10 for savanna burning and 0.04 to 0.13 for agricultural waste burning (Echalar *et al.*, 1995; Andreae *et al.*, 2001). Similarly, K^+/EC ratios in winter for the rural area were 1.29 and 1.26 for indoor and outdoor, respectively. And those were 0.79 and 0.77 in summer for indoor and outdoor, respectively. The present results were higher than those from the previous studies, which reported the ratios were from 0.20 to as high as 0.69 for biomass burning aerosols (Andreae *et al.*, 1983; Ram *et al.*, 2010). On the other hand, Ram *et al.* (2010) has pointed out that fossil fuel emissions have characteristically low K^+/EC ratios. The high ratios of K^+/OC and K^+/EC in the present study showed that the biomass burning were significant in the rural area, especially in wintertime.

The Variations of Elemental Compositions

The indoor and outdoor concentrations of elements were given in Table 1 for winter and summer, respectively. The interesting elements were divided into two groups: major (Mg, Ca, Fe) and sub-major elements (S, Zn, Mn, Pb, Cr, Cd, Mo, Br and Ti). During the sampling period, the mean concentrations of the major elements were in the range of 0.31–0.44 μg/m³ for Mg, 0.84–1.46 μg/m³ for Ca and 0.64–1.10 μg/m³ for Fe, respectively. The concentrations for sub-major elements were 0.0–1.1 μg/m³, whereas the concentrations of S were as high as 4.19–6.71 μg/m³.

In the present study, the enrichment factor method was applied to discriminate natural and anthropogenic origin of the elements. The measured elements, showing high values of the enrichment factor, suggested a prevailing anthropogenic origin. The enrichment factor (EF) for the i-th sampling day (with I = 1,…, n; n = number of observations) and for a generic element X in comparison with a crustal reference element Y is defined as:

$$EF_X^i = \frac{(X^i / Y^i)_{air}}{(X / Y)_{crust}} \qquad (1)$$

in which $(X_i/Y_i)_{air}$ is the concentration ratio calculated starting from X_i-concentration and Y_i-concentration measured in the i-th aerosol sample, and $(X/Y)_{crust}$ is the concentration ratio in the crust. In this study, Ti was used as the crustal reference element based on chemical composition of the Earth's crust (Taylor and McLennan, 1985). EF_X values ≌ 1 indicate that crustal soils are likely the predominant source for element X, while EF_X values > 5 suggest that the element X has mainly non-crustal origin.

The sources of these elements were investigated by EFs shown in Fig. 4. Elements, including Si, Al, Fe, Ca and Mn had EFs of < 5, indicating that these elements were mostly from crustal dust. The indoor and outdoor EFs of Pb, Zn, S, and Cl in $PM_{2.5}$ for winter and summer were greater than 10 and even greater than 100, which indicated these elements were mainly from the pollution source. In general, the EF values of K, Cl and Pb in winter were much higher than those in summer, which showed the significant contribution of anthropogenic sources in winter. The results indicated that K was mostly from local biomass burning and Pb from coal combustion in heating seasons.

Indoor/Outdoor Ratios and Correlations for the Species

The seasonal variations of the components were evaluated by using the winter/summer concentration ratios shown in Table 2 for indoor and outdoor. The winter/summer ratios of OC, soot, K^+, Mg^{2+}, Cl^-, NO_3^- and Pb were more than 3.0 for both indoor and outdoor, indicating the emissions of
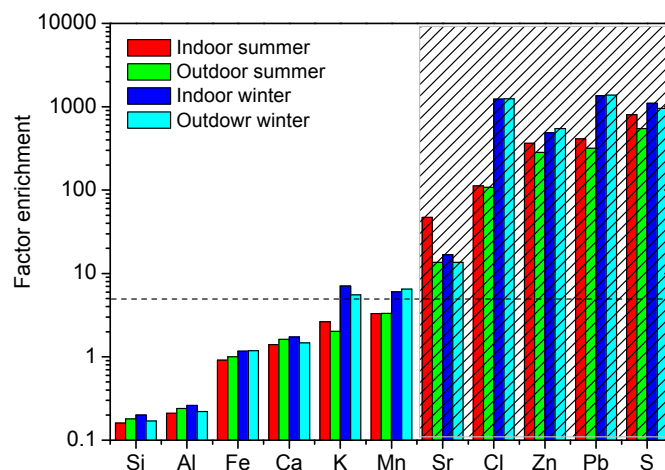

Fig. 4. Enrichment factors of elements against average crustal composition.

Table 2. The ratios of winter/summer and indoor/outdoor for major components as well as the correlation coefficients of indoor/outdoor.

	Indoor	Outdoor	Winter		Summer	
	Win./Sum.[a]	Win./Sum.[a]	I/O[b]	I/O Corr.[c]	I/O[b]	I/O Corr.[c]
$PM_{2.5}$	2.45	2.31	0.89	0.74	0.84	0.55
OC	3.38	3.32	1.04	0.73	1.02	0.47
EC	2.20	2.04	0.93	0.75	0.87	0.78
char	1.90	1.80	0.96	0.69	0.89	0.79
soot	4.60	3.20	1.08	0.38	0.74	0.37
Na^+	0.85	0.83	0.92	0.53	0.90	0.77
NH_4^+	2.67	3.14	0.73	0.58	0.86	0.92
K^+	3.58	3.22	1.00	0.85	0.90	0.90
Mg^{2+}	4.42	3.52	0.94	0.69	0.75	0.40
Ca^{2+}	1.07	0.43	1.48	0.90	0.59	0.33
Cl^-	3.68	4.15	0.85	0.60	0.96	0.53
NO_3^-	4.14	3.84	0.84	0.73	0.77	0.89
SO_4^{2-}	1.71	1.79	0.82	0.76	0.86	0.94
crustal	1.50	1.05	0.87	0.55	0.61	0.85
Pb	3.83	3.84	0.86	0.65	0.86	0.89

[a] Winter/Summer concentration ratios; [b] Indoor/Outdoor concentration ratios; [c] Indoor/Outdoor correlation coefficient.

carbonaceous fractions and these components are much higher in winter than in summer. More abundant of these components could be attributed to several factors, such as increasing fossil fuel combustion and biomass burning for residential heating, high atmospheric stability, and low mixing height conditions during winter. The winter/summer ratios of Na^+ were lower than 1.0 in both indoor and outdoor, which was also found for Ca^{2+} in outdoor. As shown in Table 2, the winter/summer ratios of EC, soot, K^+, Mg^{2+}, Ca^{2+}, NO_3^-, and major elements for indoor were higher than those for outdoor, which indicated that there was significant contribution from indoor sources in winter.

I/O ratios and related correlation coefficients (r) (Table 2) were computed for the target components measured in rural area to determine the relationship between indoor and outdoor pollutants. The I/O ratio was first calculated for each sample, and then the average ratio was computed. The I/O ratios for mass, carbon fractions, ions, crustal and Pb varied between 0.59–1.02 in summer and 0.73–1.48 in winter. The I/O ratio is an indicator of whether indoor levels are influenced by significant indoor sources of particulates or if indoor levels are the result of outdoor particle concentrations. The ratios were lower than 1.0 for most components measured in winter and summer, respectively. For both winter and summer sampling periods, the mean concentrations of NH_4^+, NO_3^-, SO_4^{2-}, crustal and Pb for outdoor were significantly higher than those for indoor. These results indicated a considerable contribution from outdoor sources. On the contrary, the ratios of I/O were higher than 1.0 for OC, soot, K^+ and Ca^{2+} in winter, and which was only for OC in summer. The results suggested that there were significant contributions for these components from indoor sources.

The relationship between indoor and outdoor datasets was evaluated by correlation coefficients (r) for each season. In general, EC, char, NH_4^+, K^+, NO_3^-, SO_4^{2-}, crustal and Pb showed higher correlations in summer than those in winter.

Nevertheless, these were not for mass, OC, Mg^{2+} and Ca^{2+}. The correlation coefficients showed that the contribution of outdoor pollutants to indoor pollution is higher in summer than those in winter. This is consistent with the fact that well-ventilated conditions involving open windows were more prevalent in summer.

Material Balances of PM₂.₅ and Source Apportionment

The results of material balances were shown in Fig. 5. Fe is used to estimate the upper limit of geological material by the equation: geological material = $(1/0.035) \times$ Fe (Taylor and Mclennan, 1985). The amount of organic material (OM) can be determined by multiplying the amount of OC by 1.6 as expressed by the equation: organic material = $1.6 \times$ OC (Turpin *et al.*, 2001). The major contributions in winter ranged as the following: OM (36.0% for indoor and 30.7% for outdoor), sulfate (16.7% for indoor and 18.1% for outdoor), geological material (11.5% for indoor and 11.7% for outdoor), nitrate (9.9% for indoor and 10.6% for outdoor), and ammonium (6.3% for indoor and 7.7% for outdoor). Those for summer were: OM (26.0% for indoor and 21.4% for outdoor), sulfate (24.0% for indoor and 23.4% for outdoor), geological material (18.3% for indoor and 25.9% for outdoor), nitrate (5.9% for indoor and 6.4% for outdoor), and ammonium (5.8% for indoor and 5.6% for outdoor). The fraction unaccounted for by chemical analysis comprised on average 10% during wintertime and 7% during summertime (Fig. 5).

Seasonal variations of the contributions showed significantly high levels of OM, nitrate and ammonium in winter. The contributions of indoor OM were higher than those of outdoor in both winter and summer. There was large variation of OM between winter and summer, which was attributed to the biomass burning and coal combustion during the heating time. High percentage of sulfate in summer attributed to the accelerating transformation rate of SO_2 by stronger solar radiation (or photochemical reactions)
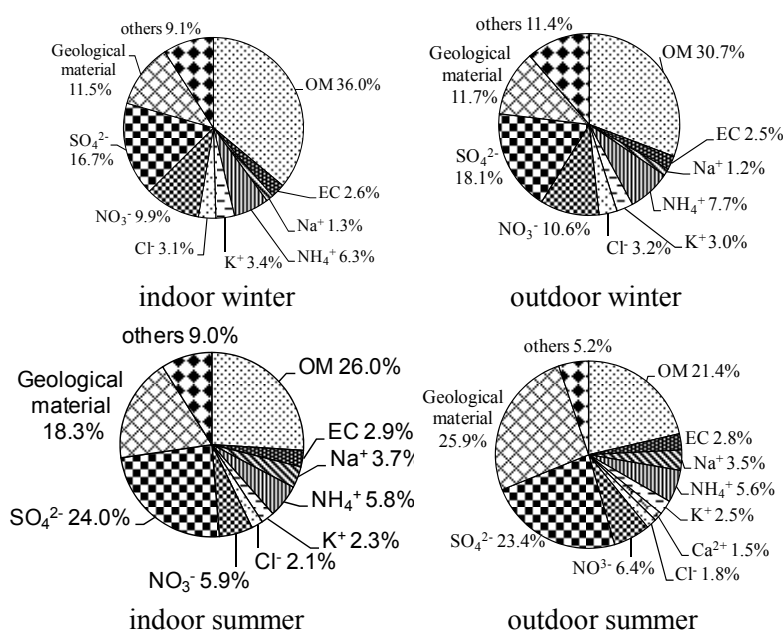
Fig. 5. The material balance for indoor and outdoor PM$_{2.5}$ in winter and summer.

The contribution of geological matter was considerably higher in summer than in winter for both indoor and outdoor. This result was due to the fact that the contributions of soil/road dust and construction dust were increased as the result of the intensive anthropogenic activities in summer. There was no clear difference for the percentage of nitrate between indoor and outdoor PM$_{2.5}$. Nitrate accounted for high percentage in winter than those in summer, which may be due to more particulate nitrate resided in particles under lower temperature in winter. The contributions of indoor and outdoor ammonium and EC kept stable in both winter and summer.

In this study, PMF was used with the indoor and outdoor data. The results of the source apportionment were presented in Fig. 6. Coal combustion, secondary aerosol and biomass burning contributed significantly to the detected PM$_{2.5}$ mass for indoor and outdoor in winter, those for summer were biomass burning and secondary aerosol. Coal combustion showed the largest contribution for outdoor particulates in winter (29% of the mass), and high percentage was also found for indoor (21%). The contributions of biomass burning to the measured indoor and outdoor mass ranged widely, across indoor and outdoor in both seasons. The average biomass burning contributions were 31% and 44% for indoor and outdoor in summer, respectively, which were higher than those in winter (24% for indoor and 16% for outdoor).

The indoor and outdoor dust (including soil, road and construction dust) contributions to PM$_{2.5}$ were low in both winter and summer, which corresponded to around 5–10% of the measured mass. Road dust and soil dust were the main indoor and outdoor sources of re-suspended dust in summer. Estimated indoor and outdoor gasoline vehicle contributions tracked each other in both winter and summer, suggesting that a substantial portion of indoors originates from outdoors.

Estimated secondary aerosol sources, including secondary sulfate, secondary nitrate and biomass secondary aerosol, accounted for 23–43% of the indoor and outdoor PM$_{2.5}$ in winter and summer. The estimated secondary aerosol contributions were higher indoors than outdoors in summer (up to approximately 1.5 times), which is partially because of the formation of secondary particles in indoor environments from reactions of household products with ozone and hydroxyl radicals (Weschler and Nazaroff, 2008). The average secondary aerosol contribution in summer was about 1.5 times higher than in winter.

CONCLUSIONS

This study presented the integrated investigation of indoor and outdoor chemical components for rural area in northwestern China during wintertime and summertime. The results showed that OM, sulfate, and geological material dominated PM$_{2.5}$, followed by nitrate and ammonium, which accounted to 78–85% of PM$_{2.5}$ mass for indoor and outdoor environments. Comparing with the results from urban area, the higher contributions of OC to TC were observed in rural area. The results from the ratios of K$^+$/OC, K$^+$/EC and the EF values for K, Cl and Pb indicated that local biomass burning and coal combustion were the significant contributors. The ratios of I/O for OC, soot, K and Ca were higher than 1.0 in winter, which suggested that there were significant contributions for these species of indoor sources. Biomass burning in summer was the most dominant source (31% for indoor and 44% for outdoor), and those for winter were coal combustion (21% for indoor and 29% for outdoor) and biomass burning (24% for indoor and 16% for outdoor). Considering the patterns of local energy consumption, effective control measures were proposed to reduce the emissions of biomass burning and coal combustion for residential heating and cooking.
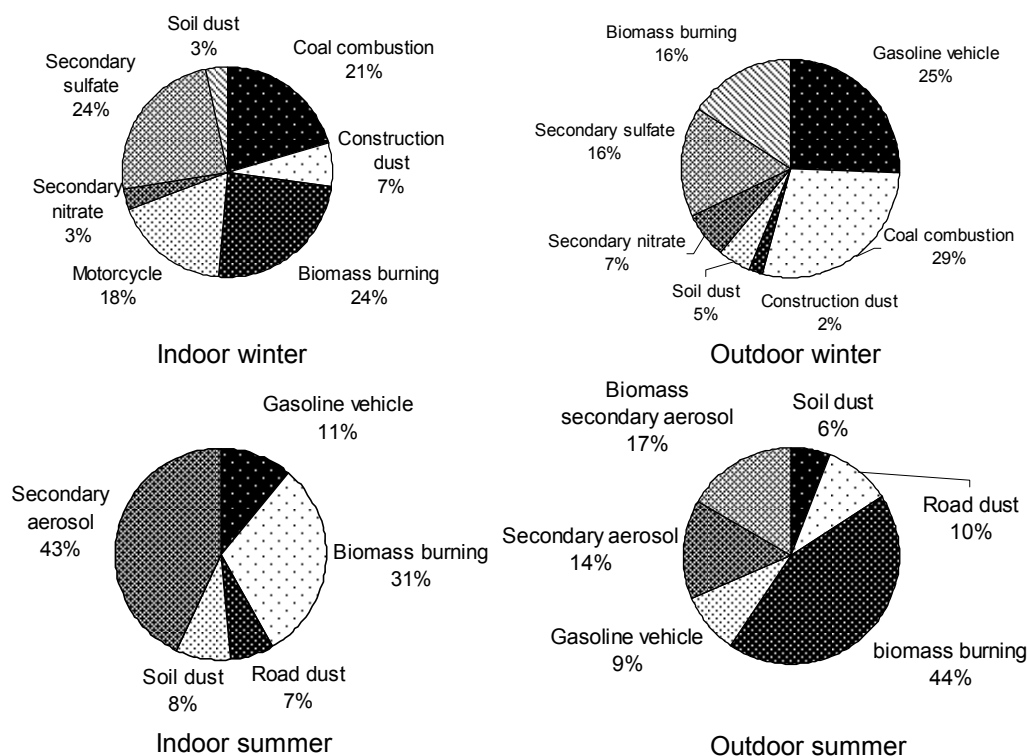
Fig. 6. The indoor and outdoor source apportionments for $PM_{2.5}$ in winter and summer.

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