atmosphere

MDPI

Article

Physicochemical Characteristics of Individual Indoor Airborne Particles in the High Lung Cancer Rate Area in Xuanwei, China

Ying Hu [1,2], Longyi Shao [2,*], Kelly BéruBé [3], Ningping Wang [2], Cong Hou [4], Jingsen Fan [5] and Tim Jones [6]

[1] Radiation Environment Monitoring Center of Guangdong Nuclear Geology Bureau, Guangzhou 510800, China
[2] State Key Laboratory for Fine Exploration and Intelligent Development of Coal Resources, School of Geoscience and Surveying Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China
[3] School of Biosciences, Cardiff University, Cardiff CF10 3AX, UK
[4] School of Tourism, Hebei University of Economics and Business, Shijiazhuang 050061, China
[5] The Resources Surveying and Researching Laboratory of Hebei Province, Hebei University of Engineering, Handan 056038, China
[6] School of Earth and Ocean Sciences, Cardiff University, Cardiff CF10 3AT, UK
* Correspondence: shaol@cumtb.edu.cn

Abstract: Emissions from domestic coal burning are generally recognized as the cause of the lung cancer epidemic in Xuanwei City, Yunnan Province, China. To examine the physicochemical characteristics of airborne particles emitted from burning this locally sourced coal, $PM_{2.5}$ samples were collected from Hutou village which has high levels of lung cancer, and Xize village located approximately 30 km from Hutou without lung cancer cases. Transmission Electron Microscopy-Energy Dispersive X-ray (TEM-EDX) analysis was employed to study the physiochemical features and chemistry of individual particles. Sulfur and silica are the most abundant elements found in the airborne particles in both of the two villages. Fewer elements in aerosol particles were found in Xize village compared with Hutou village. Based on the morphologies and chemical compositions, the particles in Xuanwei can be classified into five types including composite particles (38.6%); organic, soot, tar balls, and biologicals (28.3%); sulfate (14.1%); fly ash (9.8%); and minerals (9.2%). The particles in Hutou village are abundant in the size range of 0.4–0.8 μm while that in Xize is 0.7–0.8 μm. Composite particles are the most common types in all the size ranges. The percentage of composite particles shows two peaks in the small size range (0.1–0.2 μm) and the large size ranges (2–2.3 μm) in Hutou village while that shows an even distribution in all size ranges in Xize village. Core-shell particles are typical types of composite particles, with the solid 'core' consisting of materials such as fly ash or mineral grains, and the shell or surface layer being an adhering soluble compound such as sulfates or organics. The heterogeneous reactions of particles with acidic liquid layers produce the core-shell structures. Typically, the equivalent diameter of the core-shell particles is in the range of 0.5–2.5 μm, averaging 1.6 μm, and the core-shell ratio is usually between 0.4 and 0.8, with an average of 0.6. Regardless of the sizes of the particles, the relatively high core-shell ratios imply a less aging state, which suggests that the core-shell particles were relatively recently formed. Once the coal-burning particles are inhaled into the human deep lung, they can cause damage to lung cells and harm to human health.

Keywords: individual particle analysis; lung cancer; Xuanwei; TEM-EDX (Transmission Electron Microscopy-Energy Dispersive X-Ray); domestic coal combustion

Academic Editor: Daniele Contini

Received: 31 December 2024
Revised: 22 January 2025
Accepted: 3 February 2025
Published: 6 February 2025

Citation: Hu, Y.; Shao, L.; BéruBé, K.; Wang, N.; Hou, C.; Fan, J.; Jones, T. Physicochemical Characteristics of Individual Indoor Airborne Particles in the High Lung Cancer Rate Area in Xuanwei, China. *Atmosphere* **2025**, *16*, 187. https://doi.org/10.3390/atmos16020187

1. Introduction

Xuanwei City, a county-level city in Yunnan Province, is not only an area with rich coal resources but also the most serious area of lung cancer in China [1]. The annual lung cancer rate in Xuanwei City is among the highest in China; especially in women (27.95/100,000) compared to men (24.49/100,000) [2]. The incidence rate and mortality of lung cancer rank first in the world [3]. According to the results of a nationwide retrospective mortality survey from 1973 to 2005, the standardized male-to-female ratio of lung cancer mortality in the Xuanwei region is close to 1.22, significantly lower than the Asian and global average ratios [4]. There are significant regional differences in the mortality rate of lung cancer in Xuanwei, with the Hutou village having the highest lung cancer mortality rates, being above 100/100,000 [5], and the Xize village having no reported lung cancer cases [1]. In Xuanwei, most men and very few women smoke tobacco. A large proportion of farming families cook food for themselves and their animals, mostly pigs, using their household coal-burning stove [6]; however, some use an electric induction cooker. The preparation of food is typically undertaken by the women; therefore, they are the family members most exposed to coal combustion emissions. Several studies have shown that lung cancer mortality in Xuanwei was highly associated with the domestic use of bituminous coals [7–9]. Large numbers of particles are produced during coal combustion depending on the coal quality and burning conditions, and a significant number of toxic substances are associated with those combustion particles [10–12] potentially harmful to human health. Toxicological studies have shown that the combustion products from the Xuanwei bituminous coal are more tumorigenic and mutagenic than combustion products from other solid fuels such as anthracite coal and wood products [7,13,14]. The indoor air emission of crystalline silica from coal burning has been interpreted as the critical exposure variable associated with the lung cancer epidemic in Xuanwei.. Therefore, elevated levels of respiration of combustion particles in a confined space, with the source being released from mineral grains from the high-ash coal burning at relatively low temperatures. It is noteworthy that the resulting disease in Xuanwei is lung cancer, rather than the non-cancer fibrotic disease silicosis that is commonly associated with respirable crystalline silica [15]. The high silica content in Xuanwei coal is regarded as interacting with toxic volatiles in the coal to cause unusually high rates of lung cancer [11]. A study by Lu et al. (2014) found that ambient particles from the local coal combustion in the Xuanwei atmosphere had the ability to produce free radicals, which potentially are harmful to human health [16].

A knowledge of the chemistry of individual particles is crucial to understanding the hygroscopic and optical properties of particles and to provide information about their atmospheric history [17,18]. Individual particle analysis can provide direct microscopic information about the state of these non-refractory particles and explain the heterogeneous reactions on the particle surfaces during air pollution episodes [19–27].

The aim of this research was to elucidate the physicochemistry and properties of respirable individual atmospheric particles in the Xuanwei lung cancer areas. TEM-EDX was used to investigate the structure of individual particles, including measuring their size ranges, core-shell diameter ratios, and elemental compositions. A classification of particle types is proposed. The relationship between particle physicochemical properties and the high incidence of localized lung cancer is discussed.

2. Sampling and Experiments

2.1. Sampling

Hutou village, the highest lung cancer mortality rate, is located in the southeast of Xuanwei, Yunnan Province, China (Figure 1). Yantang mine is the nearest coal mine, about 1.4 km away from the village and the main coal source for Hutou. Xize village, having low or no reported lung cancer cases, is located in the west of Xuanwei, and is a mountainous agricultural community. The Xize residents usually use biomass as fuel for cooking and preparing pigwash (AKA, Pigswill a viscous liquid pig food). Since 1973, many Xuanwei residents have used portable stoves or stoves with ventilation through an underground chimney pipe [14]. Almost every family in Xuanwei raises pigs, so people from Hutou and Xize villages cook a large amount of pigwash every day (Figure 2).

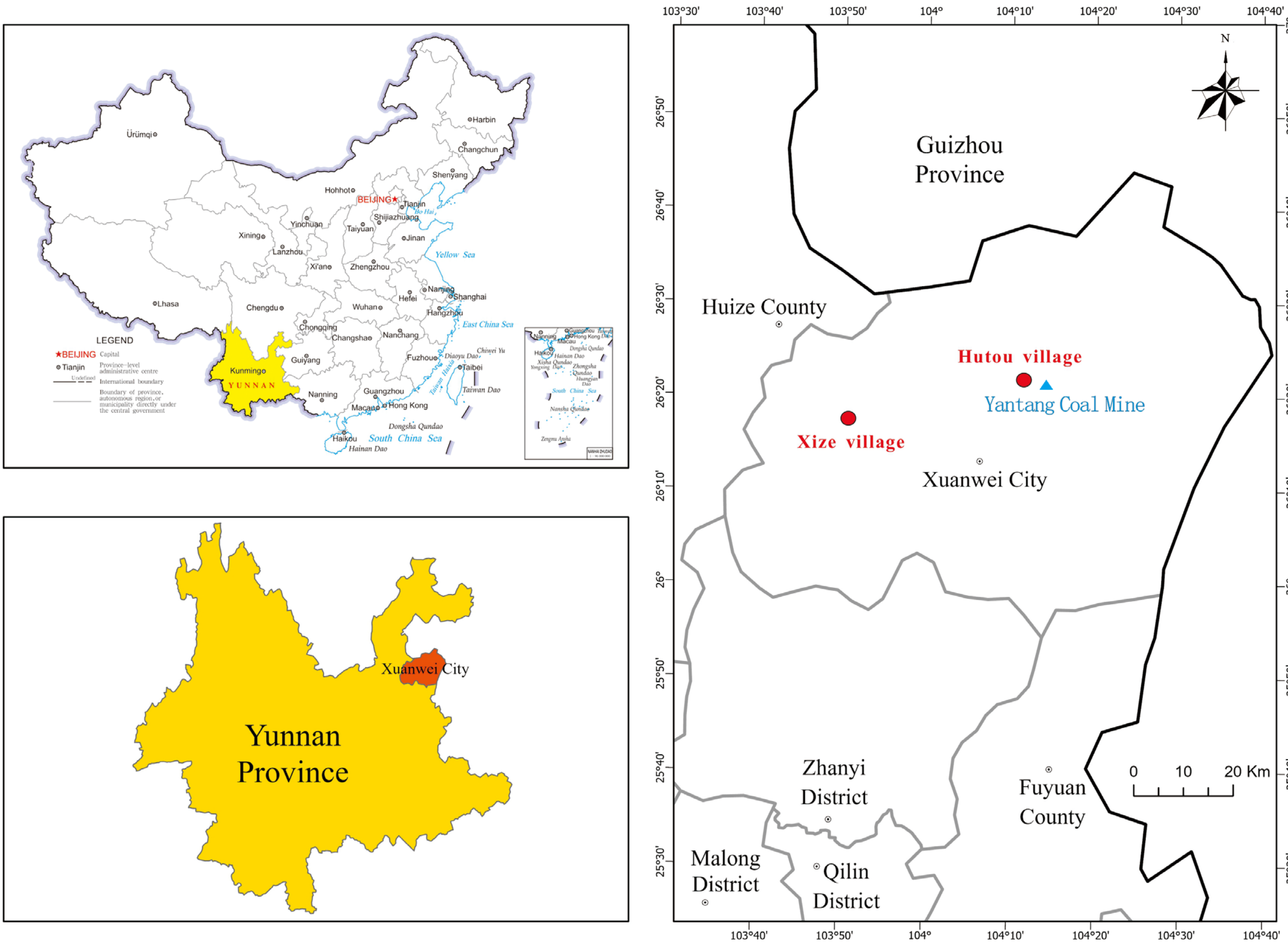

Figure 1. Maps showing sampling localities Hutou and Xize villages in Xuanwei City. (In the images on the left, yellow area represents Yunnan Province, red area represents Xuanwei city; In the image on the right, red font represents villages, blue font represents coal mine in Xuanwei city).

Figure 2. Pigwash cooking in the Hutou village of Xuanwei. (Photo by Ying Hu).

The indoor and outdoor atmospheric particles were collected from Hutou and Xize villages from 16th to 26th November 2013 (Table 1). Hutou village has high lung cancer mortality rates, and Xize village has low lung cancer mortality rates, with these two villages located around 30 km apart (Figure 1). At Hutou village, atmospheric particles were collected inside two houses; one in which the family used bituminous coal from the Yantang mine in a ventilated fixed stove for cooking, and the other used an electromagnetic oven for cooking. In Xize village, atmospheric particles were collected inside two houses, one in which the family used biomass as fuel for cooking pigwash, and the other where an electromagnetic oven was used for cooking. Outdoor air atmospheric particles were also collected just outside the four houses.

Table 1. Information of analyzed samples from Xuanwei (HT-Hutou village, XZ-Xize village, T—temperature, RH—relative humidity, P—barometric pressure).

Sample NO.	TEM NO.	T/℃	RH /%	P/hPa	Duration/s	Date and Start Time	Sampling Site	Fuel	Status
1	A1	12	75.4	810.1	60	2013.11.16 8:50	HT	coal	
2	A3	12.2	70.7	810.5	60	2013.11.16 9:49	HT	electricity	
3	B5	15.4	83.1	808.8	60	2013.11.17 9:04	HT	coal	cooking
4	D5	15.9	76.7	809.3	40	2013.11.18 9:36	HT	coal	cooking
5	F3	13.7	80.1	807.7	40	2013.11.19 9:30	HT	electricity	cooking
6	K5	9.3	85.6	804.4	90	2013.11.22 10:00	HT outdoor		Sunny
7	P5	18.8	45.6	817.3	60	2013.11.24 16:00	XZ	biomass	cooking
8	T1	11.1	72.8	815.1	60	2013.11.26 9:45	XZ outdoor		Sunny

The individual airborne particles ($PM_{2.5}$) were directly collected on copper TEM grids coated with a carbon film (300-mesh copper, Model T10023, Beijing XinXingBaiRui Technology Co., LTD., Beijing, China) using an individual-stage cascade impactor (l L/min, Model KB-2F, Qingdao instrument Co., LTD., Qingdao, China). The sampling time ranged from 10–90 s depending on the particle loading, which was estimated from different indoor conditions, such as a visual assessment of cooking emissions inside the house, the sampling distances between cookers and sampler ranged from 1 to 5 m. The meteorological parameters during sampling were automatically recorded by a Kestral 4000 weather and environmental meter (Boothwyn, PA, USA) (Table 1). The samples were stored in an air dryer at a constant humidity of 20 ± 3% before analysis. A total of 717 individual particles were analyzed from the 4 different samples. In addition, PM_{10} and $PM_{2.5}$ were collected, respectively, on a 90 mm quartz filter using the medium flow TSP-PM_{10}-$PM_{2.5}$ sampler (100 L/min, Model KB-120E, Qingdao instrument Co., LTD., Qingdao, China).

2.2. TEM-EDX

The aerosol samples were analyzed by TEM-EDX (AMETEK, Inc.) at the China University of Petroleum in Beijing. The elemental composition was determined by Energy Dispersive X-ray spectroscopy (EDX) with 200 kV and a 30 s spectral acquisition time. As the TEM grids were made of Cu this element was excluded from the analysis. The distribution of aerosol particles on the TEM grids was not uniform, with coarser particles typically near the center and finer particles on the periphery. Therefore, to ensure a representative particle analysis, five areas were chosen from the center to the periphery of the sampling spot on each grid. All the particles larger than 0.1 μm in the selected areas were analyzed [28,29]. Images were taken of all the different particle types seen during the analysis.

3. Results

3.1. Element Frequency in Individual Particles of Different Sizes

The aerosol particles in Xuanwei showed complex physicochemical compositions. The EDX detected 39 elements in addition to C, including Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Fe, P, Zn, and Mn. Figure 3 shows the percentage of element presence in the analyzed particles from the two villages. Overall, S and Si are the most abundant elements in both villages. In Hutou village, Si and S are the most common (20%), followed by Fe (16%), Na (8%), Al (6%), Ca (6%) and Zn (5%), the percentages of Cr, K, Cl, P, Ni, Mg, Ti, Co, Cd, Mg, Mn, Ta, Cu, and V are less than 5%. For particles from Xize village, S is the most abundant element (51%), followed by Si (27%), K (7%), and Ca (6%), the percentage of other elements is below 5% including Al, Fe, Na, Mn, Co, Mg, Ti, As, and P. In Xize village, fewer elements were found compared with Hutou village, and As was not detected in Hutou village particles. A positive correlation exists between the heavy metal element compositions and the hemolysis of human red blood cells of PM_{10} particles [30,31]. In the Hutou samples, heavy metals such as Zn showed a higher percentage than in the Xize samples. Therefore, the heavy metal elements in particles could be hazards for the local residents.

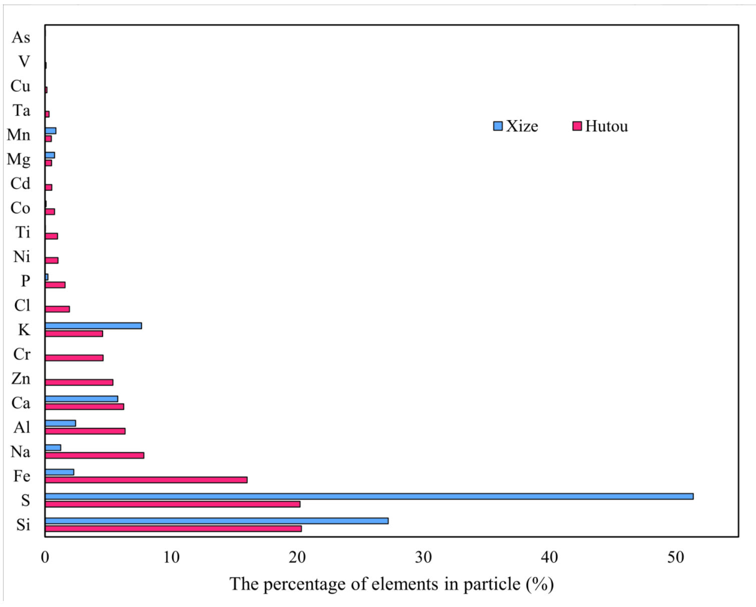

Figure 3. Percentage of elements in particles from the Hutou and Xize villages. XZ is for Xize village and HT is for Hutou village.

3.2. Individual Particle Types

Based on their morphologies and chemical compositions, we classified the aerosol particles into five types: fly ash, organic (soot, tar balls, and biological), minerals, sulfate, and composite particles (Figure 4).

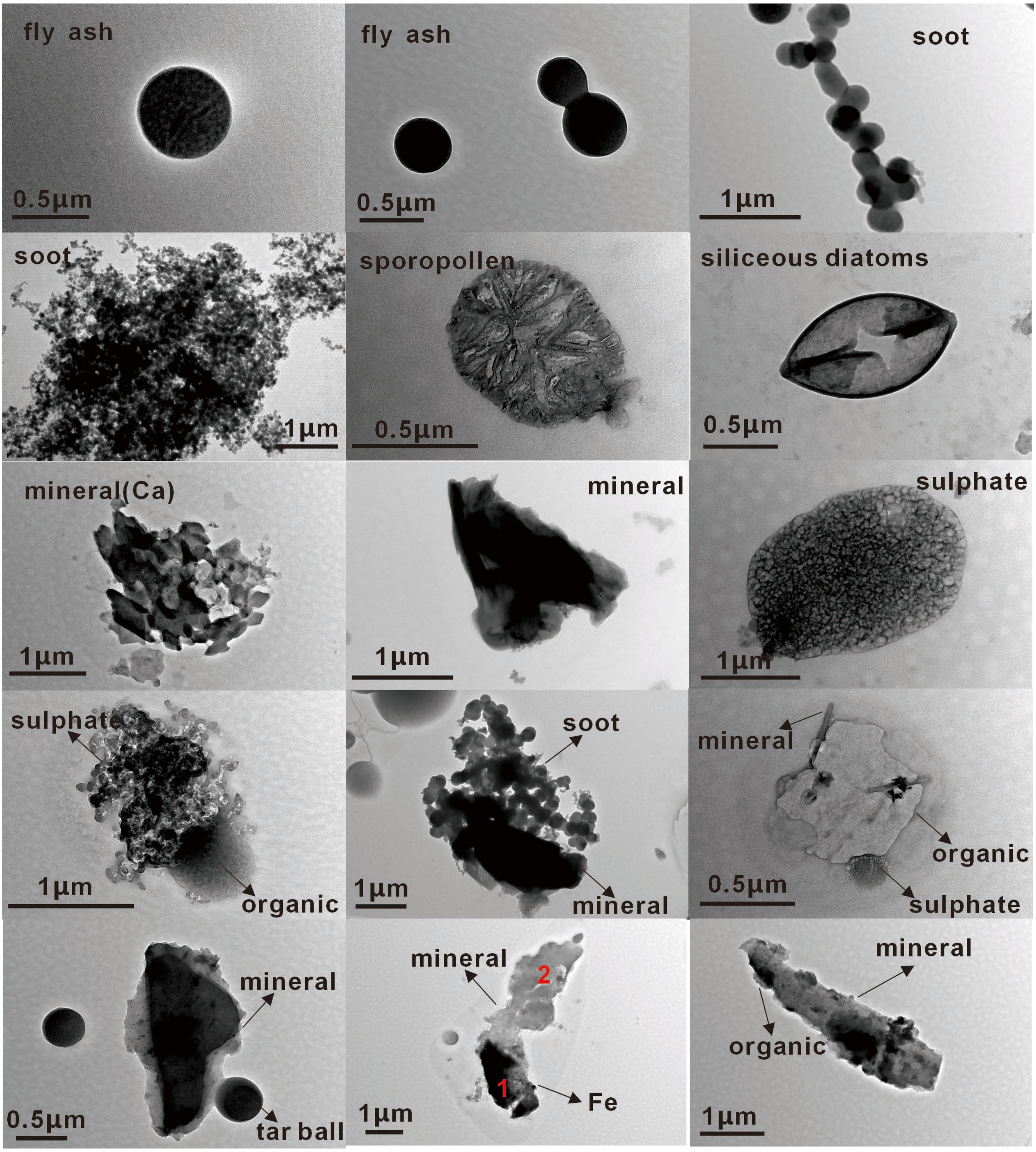

Figure 4. Different types of individual airborne particles in the Hutou and Xize villages. (The red numbers in the image shows an example of positions of spots when EDX analysis is performed).

The main components of fly ash are Si and O, and their morphology shows as small spheres. These are nanoparticles or fine particles of SiO_2, released into the air during coal combustion. It is probable that they represent melted and solidified spheres that are sourced from silicates in the mineral (ash) component of the coal. They are, therefore, effectively SiO_2 amorphous glass spheres that are contaminated by small amounts of other elements, typically non-combustible metals also found in coal ash. They have been considered as a possible cause of the lung cancer epidemic in Xuanwei area [14]. However, it is noted that most inhaled SiO_2 that has been linked to lung cancer is crystalline, not amorphous, and the carcinogenicity is believed to be caused by the charged crystalline surfaces with broken ionic bonds. There is still uncertainty about the carcinogenicity of glass amorphous products. The International Agency for Research on Cancer (IARC) concluded special purpose and refractory ceramic fibers are "possibly carcinogenic to humans". Insulation glass wool and filaments, rock and slag wool are "not classifiable as to their carcinogenicity to human." The National Toxicology Program (NTP)'s 12th report on carcinogens lists "certain glass wool fibers" as "reasonably anticipated to be a human carcinogen" [32].

Soot and tar balls are the results of incomplete fossil fuel combustion [33–36], in the Xuanwei particles the fossil fuel source will overwhelmingly be the local coal. Soot, a solid product, consists of nanoparticulate carbon spheres that form individually and then aggregate to form morphologically distinct chain-like or clusters that are considered individual particles. Residential firewood burning mainly emits pure carbonaceous particles (including organic matter (OM) and soot particles) [37,38]. Tar balls are microscopic droplets of highly viscous hydrocarbons and can be identified under electron microscopy by their unstable behavior under the electron beam, whereas the glass fly ash spheres are stable under the beam. In addition, biological particles such as sporopollen and siliceous diatoms showing excellent preserved structure were identified and are included in the 'organics' classification. Primary carbonaceous particles such as tar balls and soot warrant further attention due to their strong light-absorbing properties, presence of toxic organic constituents, and small size, which can impact human health [39].

Mineral particles show both regular and irregular morphologies. In most of the irregular mineral particles, TEM-EDX analysis showed that the main elements were Si, Al, Ca, S, K, and Fe, which is interpreted as the majority of the mineral particles were clays derived from natural sources such as crustal dust. However, it is possible that some mineral grains were released from the coal combustion as ash, with the domestic fire temperatures not reaching sufficient temperatures to melt the minerals converting them into fly ash. The regular-shaped minerals include gypsum, which can be formed by secondary reactions [40]; however, it is noted that gypsum is a common mineral naturally found in soil. In the atmosphere, mineral dust particles can act as cloud condensation nuclei, changing the reflectivity and duration of clouds. They react with trace atmospheric gases such as HNO_3 and SO_2, altering atmospheric trace gas composition, and thus influencing global climate [41–46].

Biomass combustion can cause a significant increase in the concentration of particulate matter, which could promote the formation of organic matter and secondary ions such as SO_4^{2-}, NO_3^- and NH_4^+ [47]. Sulfuric acid is rapidly neutralized by ammonia in the gas or aqueous phase after it is formed through homogeneous or heterogeneous reactions [48]. It was found that the interaction between organic and sulfuric acids promotes the efficient formation of organic and sulfate aerosols in the polluted atmosphere [49]. Sulfate formation is efficient on aluminosilicate-rich dust particles [45,50], which ties in with the identification of the majority of the airborne minerals as clays.

The composite particles in Xuanwei are mixtures of minerals, organics, sulfates, soot, compounds containing metals, and tar balls. These heterogeneous particles typically form around a solid nucleus of mineral or fly ash, with an outer layer or coating of secondary materials such as sulfates condensing on the surface. Composite particles are relatively chemically unstable compared to the other types, and the ongoing reactions can give an indication of the particle's formation age and primary sources. In addition, composite particles can be an agglomeration of smaller primary particles forming a larger 'composite of the different types. For the identification, even if the individual components of a composite can be identified, they are still classified as individual composite particles.

3.3. Size Distribution of Individual Particles in Xuanwei

A total of 717 particles from 8 samples were analyzed by TEM-EDX including 531 particles from Hutou and 186 particles from Xize village. Image J 1.48V software (Wayne Rasband, National Institutes of Health, Kesington, MA, USA) was used to measure the size and area of each of these particles. The equivalent diameter of the particles is divided into 26 size groups: <0.1 μm, 0.1 μm to 2.5 μm with 0.1 μm interval and >2.5 μm. The numbers at all these levels are recorded and shown as bar graphs (Figure 5 and Figure 6).

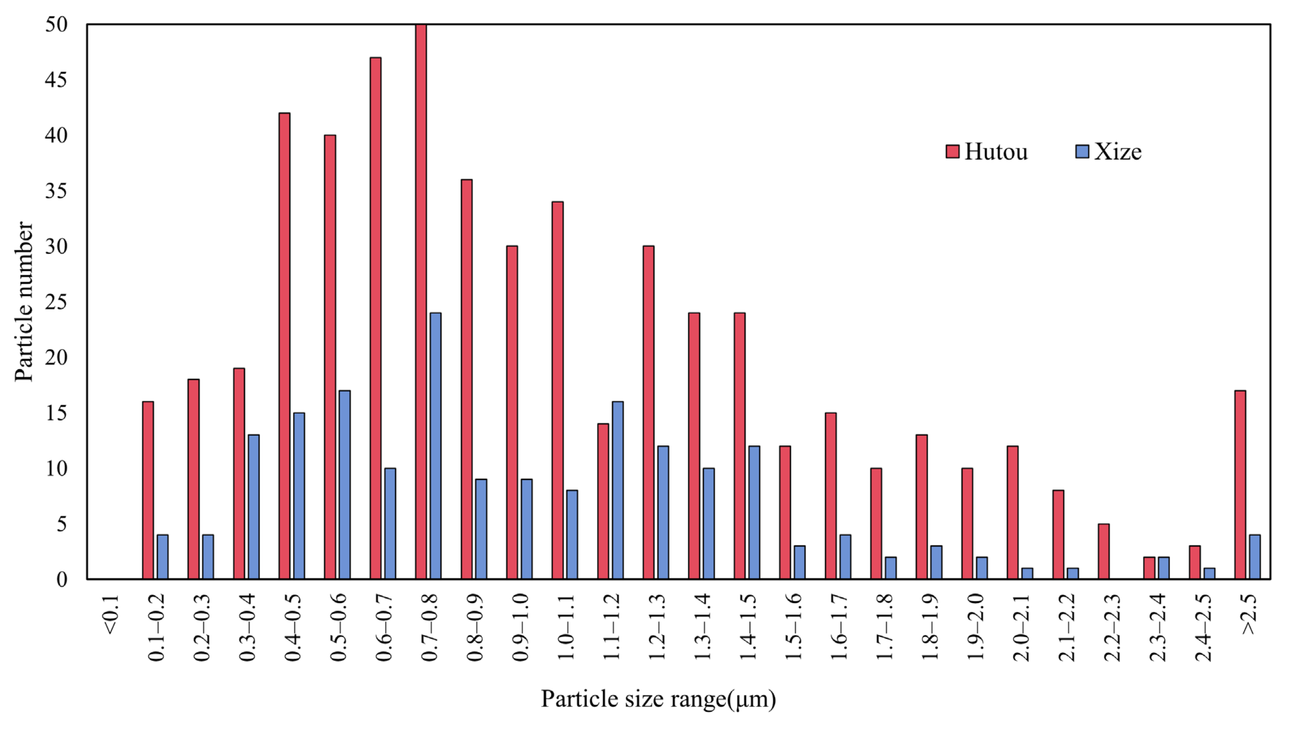

Figure 5. Number-size distribution of individual particles from the Hutou and Xize villages.

The particles in Hutou village are abundant in the size range of 0.4–0.8 μm, and the particles in Xize village are over the size range of 0.7–0.8 μm. Particles above 2 μm are rare in both villages. The size distributions in particles from the two villages show a very similar pattern. According to monitoring results, the mass concentration of PM_{10} in Hutou and Xize is around 189 μg/m^3 and 156 μg/m^3, respectively, and the mass concentration of $PM_{2.5}$ in Hutou and Xize is around 83 μg/m^3 and 41 μg/m^3, respectively. As the particle mass concentrations of Hutou village are higher than that of Xize, the particle mass in each size range is accordingly higher in Hutou.

In a comparison of particles from biomass-burning and coal-burning, the particles from coal-burning are abundant over the size range of 0.4–1.1 μm, and the number of particles from biomass-burning over the size range of 0.3–0.8 μm. Particles with sizes larger than 2 μm are rare from both fuels.

All of the collected particles are inhalable (PM_{10}), and the vast majority are respirable ($PM_{2.5}$), and thus able to reach the distal gas-exchange parts of the lung. Exposures to pollutants result in pollutant-specific oxidative/nitrative stress changes in the lungs and circulation [51]. Ambient air particles in the Xuanwei atmosphere have the ability to generate free radicals, and fine and ultrafine particles are hazardous to local residents [16].

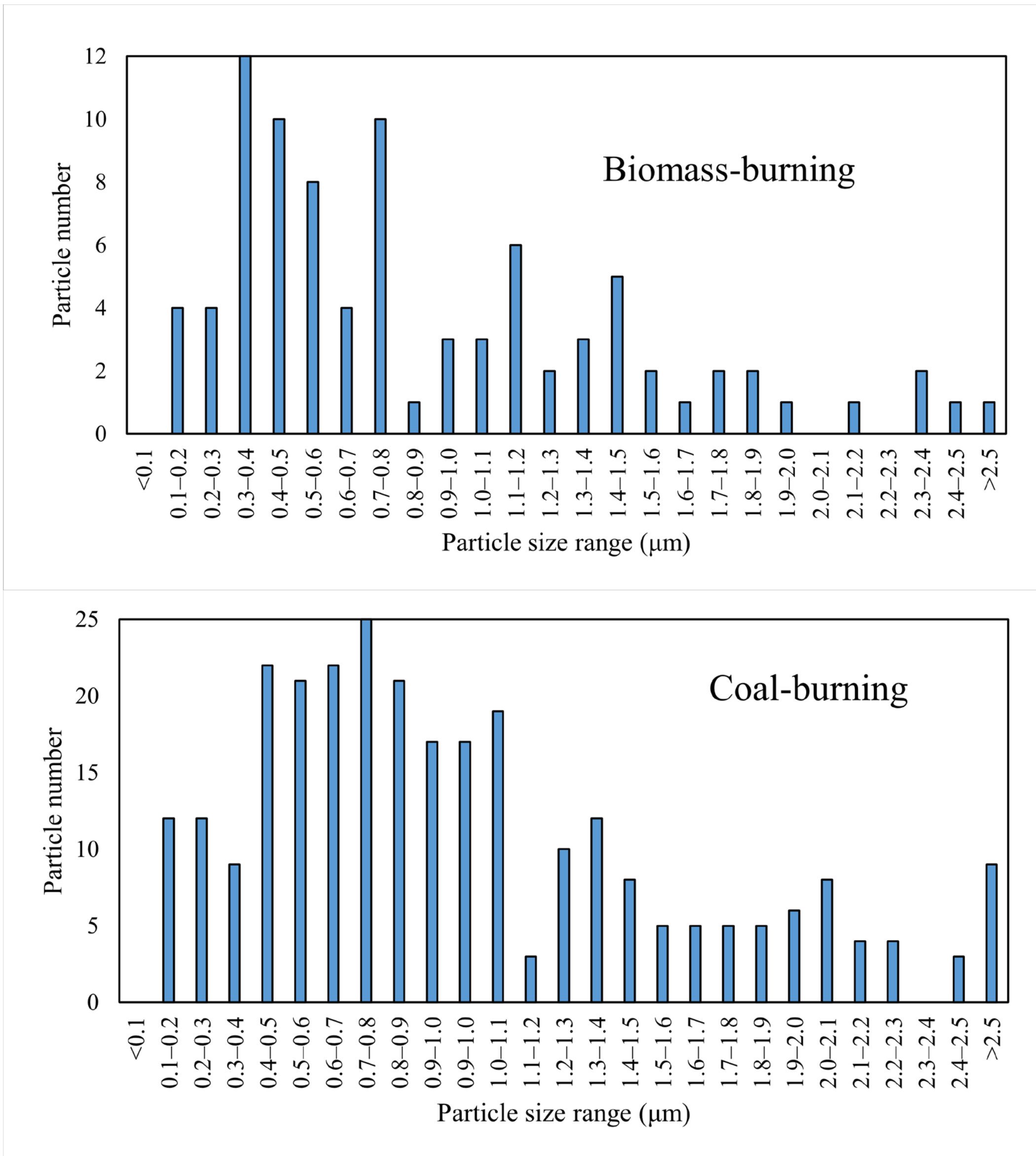

Figure 6. Number-size distribution of Hutou coal-burning and Xize biomass-burning individual particles.

3.4. Size Distribution of Different Individual Particle Types

All the particles are classified into 7 types and the distribution in the 26 size ranges is plotted (Figure 7). Composite particles were the most abundant in all size ranges in both villages. In Hutou village, the percentage of composite particles shows two peaks in the small size range (0.1–0.2 μm) and the large size range (2–2.3 μm). In Xize village, the percentage of composite particles shows an even distribution in all size ranges. Mineral particles in Xize were most abundant in almost every size range when compared to Hutou village.

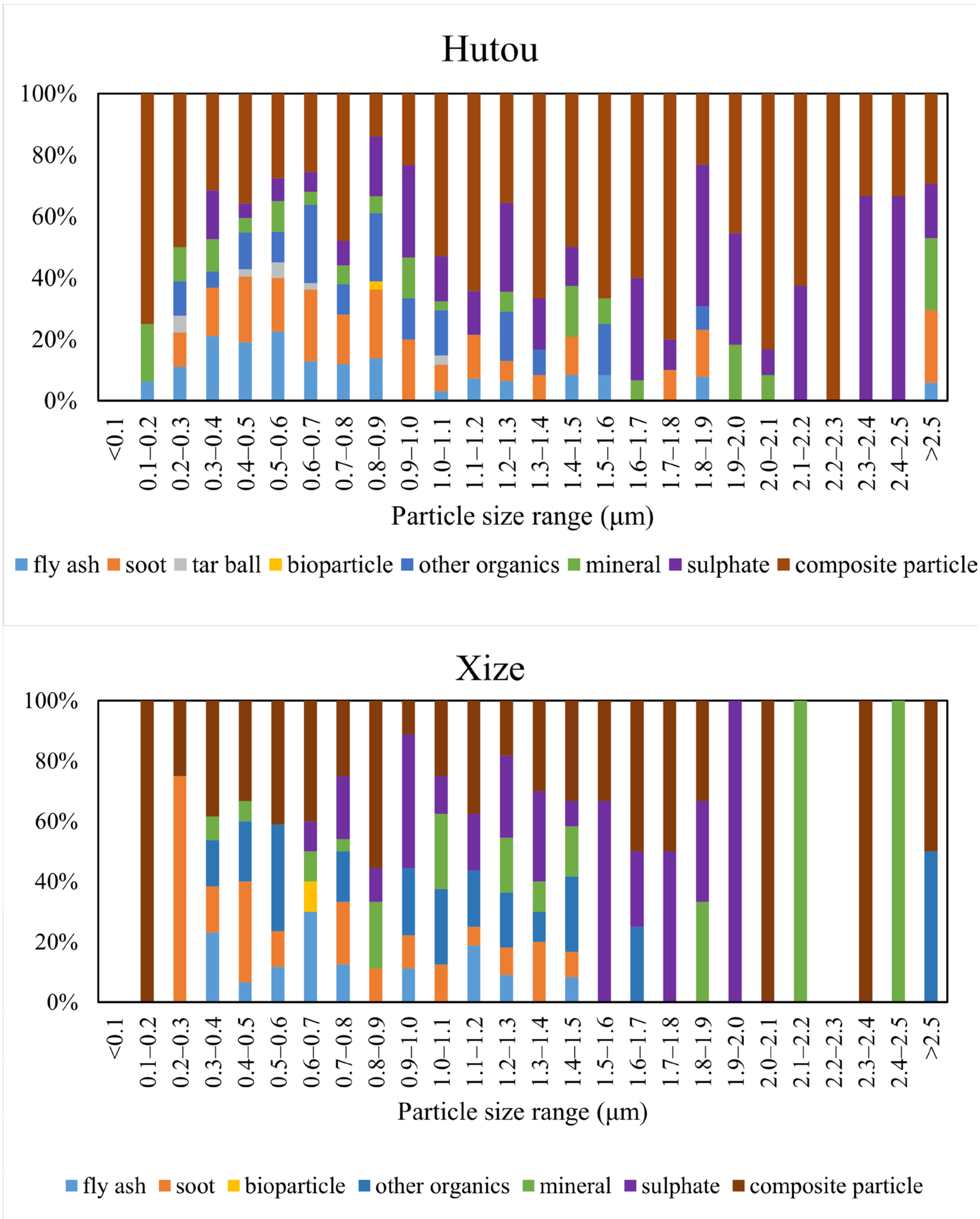

Figure 7. Relative percentages of different individual particle types in different size ranges in individual particles from Hutou and Xize villages.

3.5. The Core-Shell Structure of Airborne Particles in Xuanwei

Composite particles are the most common type of particles in Xuanwei. In composite particle classification, one kind of particle is referred to as a 'core-shell' particle. Of the 277 composite particles analyzed, 32 particles had core-shell structures (Figure 8). The 'core' of these composite particles consists of different materials such as fly ash or mineral grains, whereas the outer layer tends to be a soluble compound such as sulfates or organics.

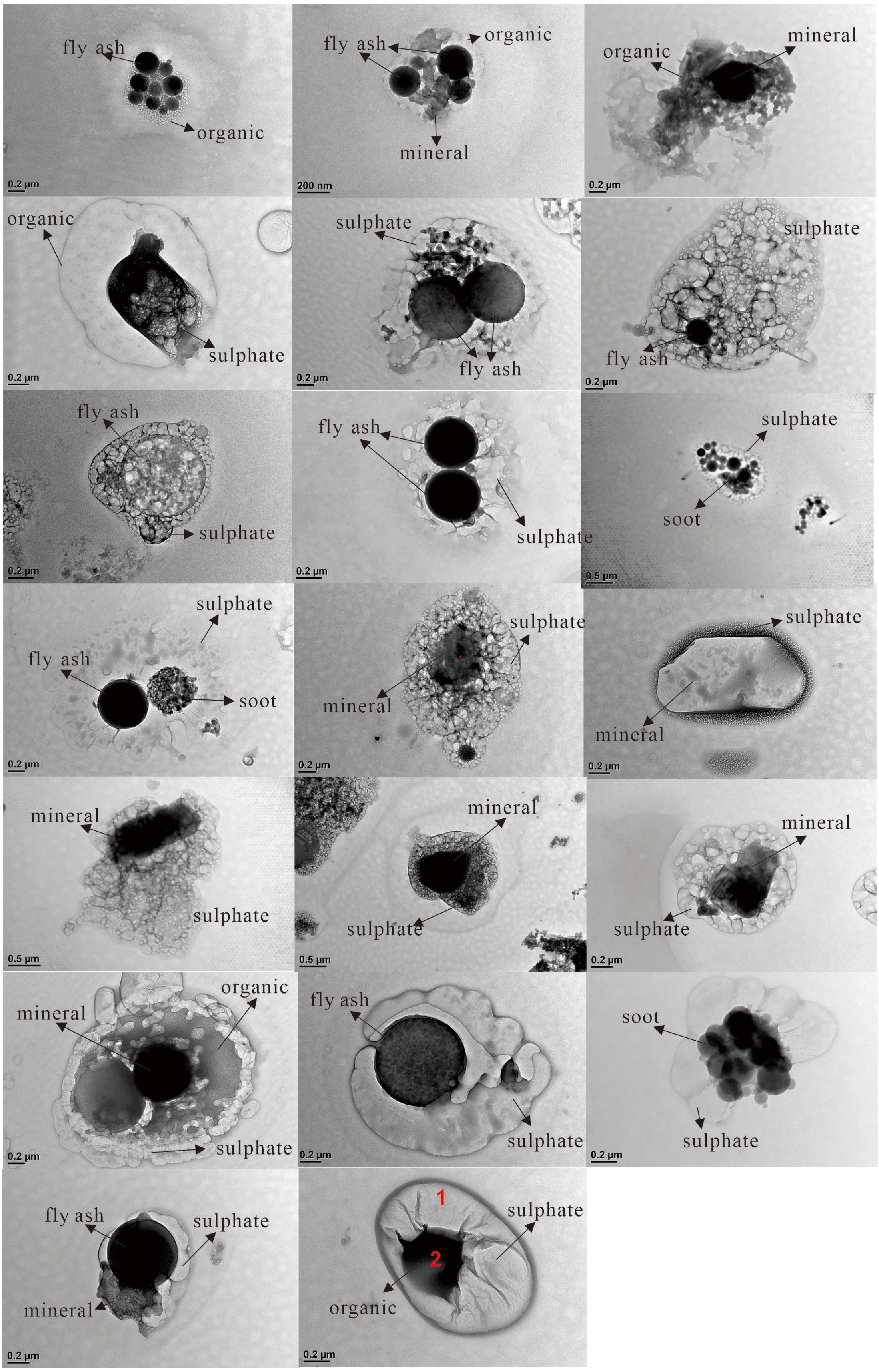

Figure 8. Individual particles with core-shell structures in individual particles from Hutou and Xize villages. (The red numbers in the image shows an example of positions of spots when EDX analysis is performed).

For composite particles, aerosols derived as secondary sulfates and nitrates are important compounds to envelope solid core particles such as minerals, metal-containing, fly ash, and soot [28,52–56]. The heterogeneous reactions of alkaline minerals and NaCl with SO_2, NO_x, and their acids (HNO_3 and H_2SO_4) can produce hygroscopic nitrates and sulfates [57,58]. Most composite particles are formed through condensation, coagulation, and cloud processing during atmospheric transports; only a small fraction are directly emitted from sources [17]. Soot aging mechanisms revealed that condensation dominates fresh soot aging when the particle diameter is <400 nm; coagulation leads to multi-soot cores in a particle with a diameter > 400 nm [59].

In Xuanwei indoor airborne solid particles include fly ash, organics, and minerals. Acidic gases such as SO_2 and NOx in the atmosphere dissolve into water vapor and form ions such as H^+, SO_4^{2-}, and NO_3^-. The acidic liquid forms an envelope around the solid particles and reacts with the particle compounds in the core. Some parts of the cores dissolve in the envelope, for example, parts of mineral cores become Ca^{2+}, Na^+, and M (other metals), then the $CaSO_4$, Na_2SO_4, and metal sulfates (MSO_4). The surface of some mineral particles can lead to further absorption of soluble acidic gases. This atmospheric process has been understood for many years, with famous pollution episodes including the "yellow smogs" of London in the 1950s [60].

When the core-shell particles are inhaled by humans into the lung, the soluble salts contact with the lung's defensive mechanisms such as the epithelial lining fluid, and metal ions such as Zn^{2+} and Fe^{2+} can be released. As a result, these particles can have a negative health impact on the human airway epithelial cells [61,62].

4. Discussion

4.1. The Features of Coal-Burning Particles in Xuanwei

S, Si, and Fe are the most abundant elements in the Hutou airborne particles, typically corresponding in Xuanwei to some individual particle types including, fly ash with the main elements Si and O, and sulfate, suggesting emissions from coal-burning. The coal-burning particles are abundant in the size range of 0.4–1.1 μm, over which size range soot and composite particles are dominant. The IARC classified quartz as a group 1 substance-carcinogen for humans (International Agency for Research on Cancer, 1996). The low-temperature domestic burning of the local coal will have resulted in the release of some airborne crystalline silica along with some melted minerals in the form of fly ash. It is noted, however, that these types of combustion emissions are common all around the world, and therefore assigning them as a possible cause of the cancer clusters in these Chinese villages is problematic as they do not appear to have a similar respiratory health impact elsewhere [63].

4.2. The Aging State of Core-Shell Particles in Xuanwei

The typical core-shell structure consists of a solid central core with an outer envelope or shell of secondary material that forms in an aqueous coating. The relative thickness of the outer layer compared to the core represents the time and extent of the chemical process that the particles took to form [64]. As such, aging is a function of change or additions to the particles, rather than time. Controlling factors will include the pH of the liquid envelope, the RH of the atmosphere, the chemistry of the atmospheric water-soluble gases, and the chemistry of the core. The equivalent spherical diameter of the core and the shell are defined as R1 and R2, respectively. The calculated R1/R2 ratio thus represents the aging state, the smaller the R1/R2 the greater the aging state. The R1/R2 ratios of the core-shell particles in Xuanwei are plotted against the equivalent spherical diameters of these particles (Figure 9). Typically, the equivalent spherical diameter of the core-shell particles ranges from 0.5–2.5 μm, averaging 1.6 μm; therefore, the R1/R2 of most core-shell particles is between 0.4 and 0.8, with an average of 0.6. Regardless of the sizes of the particles, the relatively high R1/R2 ratios imply a generally less aging state for the Xuanwei particles.

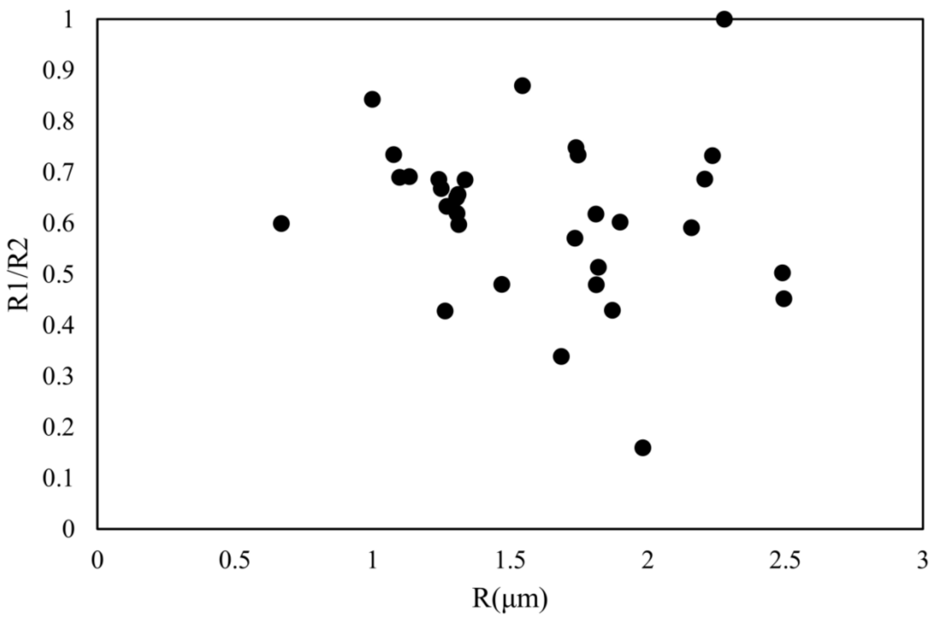

Figure 9. R1/R2 ratio of 32 individual particles with core (R1)-shell (R2) structure in the Hutou and Xize villages. (R represents the equivalent diameter of the core-shell particle).

5. Conclusions

S and Si are the most abundant elements found in the atmospheric particles in Xuanwei. Individual particles were analyzed by TEM-EDX and classified into five types: fly ash, organic (soot, tar balls, and biological), mineral, sulfate, and composite particles. Composite particles are the most common type, followed by organic, sulfate, and fly ash particles. Most composite particles were externally or internally mixed soot, organic, and mineral particles with sulfates or organics. The solid individual particles including fly ash, organics, and minerals can combine and react with acidic gases such as SO_2 and NO_x in the atmosphere to form aqueous liquid envelopes containing H^+, SO_4^{2-}, and NO_3^-. With further chemical reactions between the core and certain elements including metals in the liquid envelope, they can precipitate on the particles as salts as the liquid envelope evaporates, or be mobilized and bioavailable in the liquid envelope. The sizes of individual particles are almost always below 2 μm, which is respirable and thus they are able to reach the distal path of the human lung. Once the coal-burning particles are inhaled into the human deep lung, they can cause damage to lung cells and harm to human health.

Author Contributions: Conceptualization, L.S.; Methodology, L.S.; Formal analysis, Y.H.; Investigation, J.F.; Data curation, N.W.; Writing—original draft, Y.H.; Writing—review and editing, K.B., C.H. and T.J.; Supervision, L.S. All authors have read and agreed to the published version of the manuscript.

Funding: This study is supported by the National Natural Science Foundation of China (Grant No. 42475113, 42075107).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Shao, L.Y.; Zhang, M.Y.; Feng, X.L.; Jiao, J.W.; Wang, W.H.; Zhou, Y.P. The toxicology of particulate matter emitted from coal combustion and the geological origin of lung cancer epidemic in Xuanwei City, Yunan Province, China. *Coal Geol. Explor.* **2023**, *51*, 45–58. (In Chinese with English abstract). https://doi.org/10.12363/issn.1001-1986.22.12.0973.
2. Mumford, J.L.; He, X.Z.; Chapman, R.S.; Cao, S.R.; Harius, D.B.; Li, X.M.; Xia, Y.L.; Jiang, Y.L.; Xu, C.W.; Chuang, J.C.; et al. Lung cancer and indoor air pollution in Xuanwei, China. *Science* **1987**, *235*, 217–220. https://doi.org/10.1126/science.3798109.
3. Huang, Y.C.; Zhao, G.Q.; Xiao, Y.Z.; Chen, X.B.; Ma, Q.L.; Lei, Y.J.; Yang, K.Y. Trend analysis of lung cancer mortality from high incidence areas in Yunnan Province. *Cancer Res. Prev. Treat.* **2011**, *38*, 98–100. (In Chinese with English abstract)
4. Hao, J.H.; Huang, Y.C.; Ren, H.X.; Chen, Y.; Hao, X.; Shi, Q.P.; Xiao, Y.Z. Trend analysis of lung cancer mortality in area with high incidence from 1973 to 2005. *Chin. Gen. Pract.* **2009**, *12*, 2279–2282. (In Chinese with English abstract)
5. Liu, X.Y.; Liu, L.Q.; Zou, X.N.; Ma, X.Y.; Ning, B.F.; Ning, Y.F.; Wan, X. Epidemiological features of lung cancer mortality between 1990 and 2016 in Xuanwei City, Yunnan Province. *Acta Acad. Med. Sin.* **2019**, *41*, 338–343. (In Chinese with English abstract)
6. Lan, Q.; Chapman, R.S.; Schreinemachers, D.M.; Tian, L.; He, X. Household stove improvement and risk of lung cancer in Xuanwei, China. *J. Natl. Cancer Inst.* **2002**, *94*, 826–835.
7. Mumford, J.L.; Helmes, C.T.; Lee, X.; Seidenberg, J.; Nesnow, S. Mouse skin tumorigenicity studies of indoor coal and wood combustion emissions from homes of residents in Xuan Wei, China with high lung cancer mortality. *Carcinogenesis* **1990**, *11*, 397–403.
8. He, X.; Chen, W.; Liu, Z.; Chapmant, R.S. An epidemiological study of lung cancer in Xuan wei county, China: Current progress. Case-control study on lung cancer and cooking fuel. *Environ. Health Persp.* **1991**, *94*, 9–13.
9. Doenward, G.S.; Hu, W.; Large, D.; Veld, H.; Xu, J.; Reiss, B.; Wu, G.P.; Wei, F.S.; Chapman, R.S.; Rothman, N.; et al. Heterogeneity in coal composition and implications for lung cancer risk in Xuanwei and Fuyuan counties, China. *Environ. Int.* **2014**, *68*, 94–104.
10. BeruBe, K.A.; Sexton, K.J.; Jones, T.P.; Moreno, T.; Anderson, S.; Richards, R.J. The spatial and temporal variations in PM_{10} mass from six UK homes. *Sci. Total Environ.* **2004**, *324*, 41–53.
11. Large, D.J.; Kelly, S.; Spiro, B.; Tian, L.; Shao, L.; Finkelman, R.; Zhang, M.; Somerfield, C.; Plint, S.; Ali, Y.; et al. Silica-volatile interaction and the geological cause of the Xuan Wei lung cancer epidemic. *Environ. Sci. Technol.* **2009**, *43*, 9016–9021.
12. Hu, W.; Downward, G.S.; Reiss, B.; Xu, J.; Bassig, B.A.; Hosgood, H.D.; Zhang, L.L.; Seow, W.J.; Wu, G.P.; Chapman, R.S.; et al. Personal and Indoor $PM_{2.5}$ Exposure from Burning Solid Fuels in Vented and Unvented Stoves in a Rural Region of China with a High Incidence of Lung Cancer.*Environ. Sci. Technol.* **2014**, *48*, 8456–8464.
13. Tian, L. Coal combustion emissions and lung cancer in Xuan Wei, China. Ph.D. Thesis, University of California, Berkeley, the USA, 2005.
14. Tian, L.W.; Lucas, D.; Fischer, S.L.; Lee, S.C.; Hammond, S.K.; Koshland, C.P. Particle and gas emissions from a simulated coal-burning household fire pit. *Environ. Sci. Technol.* **2008**, *42*, 2503–2508.
15. Yang, L.T.; Liu, X.; Wu, G.H.; Chen, L.F. Association between tumor necrosis factor-α -308 Gauss/A polymorphism and risk of silicosis and coal workers pneumoconiosis in Chinese population. *Inhal. Toxicol.* **2018**, *30*, 213–217.
16. Lu, S.; Yi, F.; Hao, X.; Yu, S.; Ren, J.; Wu, M.; Feng, J.; Yonemochi, S.; Wang, Q. Physicochemical properties and ability to generate free radicals of ambient coarse, fine, and ultrafine particles in the atmosphere of Xuanwei, China, an area of high lung cancer incidence. *Atmos. Environ.* **2014**, *97*, 519–528.
17. Li, W.; Shao, L.; Zhang, D.; Ro, C.-U.; Hu, M.; Bi, X.; Geng, H.; Matsuki, A.; Niu, H.; Chen, J. A review of single aerosol particle studies in the atmosphere of East Asia: Morphology, mixing state, source, and heterogeneous reactions. *J. Clean Prod.* **2015**, *112*, 1330–1349.
18. Pósfai, M.; Buseck, P.R. Nature and climate effects of individual tropospheric aerosol particles. *Annu. Rev. Earth Planet Sci.* **2010**, *38*, 17–43.
19. Adachi, K.; Zaizen, Y.; Kajino, M.; Igarashi, Y. Mixing state of regionally transported soot particles and the coating effect on their size and shape at a mountain site in Japan. *J. Geophys. Res. Atmos.* **2014**, *119*, 5386–5396.
20. Fu, H.; Zhang, M.; Li, W.; Chen, J.; Wang, L.; Quan, X.; Wang, W. Morphology, composition and mixing state of individual carbonaceous aerosol in urban Shanghai. *Atmos. Chem. Phys.* **2012**, *12*, 693–707.

21. Geng, H.; Kang, S.; Jung, H.J.; Choël, M.; Kim, H.; Ro, C.U. Characterization of individual submicrometer aerosol particles collected in Incheon, Korea, by quantitative transmission electron microscopy energy-dispersive X-ray spectrometry. *J. Geophys. Res.Atmos.* **2010**, *115*, 2156–2202.
22. Li, W.J.; Shao, L.Y. observation of nitrate coatings on atmospheric mineral dust particles. *Atmos. Chem. Phys.* **2009**, *9*, 1863–1871.
23. Li, W.J.; Wang, Y.; Collett, J.L., Jr.; Chen, J.; Zhang, X.Y.; Wang, Z.F.; Wang, W.X. Microscopic evaluation of trace metals in cloud droplets in an acid precipitation region. *Environ. Sci. Technol.* **2013**, *47*, 4172–4180.
24. Niu, H.; Shao, L.; Zhang, D. Aged status of soot particles during the passage of a weak cyclone in Beijing. *Atmos. Environ.* **2011**, *45*, 2699–2703.
25. Shi, Z.B.; Zhang, D.Z.; Hayashi, M.; Ogata, H.; Ji, H.Z.; Fujiie, W. Influences of sulfate and nitrate on the hygroscopic behaviour of coarse dust particles. *Atmos. Environ.* **2008**, *42*, 822–827.
26. Yang, F.; Chen, H.; Du, J.; Yang, X.; Gao, S.; Chen, J.; Geng, F. Evolution of the mixing state of fine aerosols during haze events in Shanghai. *Atmos. Res.* **2012**, *104*, 193–201.
27. Zhang, G.; Bi, X.; Li, L.; Chan, L.Y.; Li, M.; Wang, X.; Sheng, G.; Fu, J.; Zhou, Z. Mixing state of individual submicron carbon-containing particles during spring and fall seasons in urban Guangzhou, China: A case study. *Atmos. Chem. Phys.* **2013**, *13*, 4723–4735.
28. Li, W.; Shao, L.; Shi, Z.; Chen, J.; Yang, L.; Yuan, Q.; Yan, C.; Zhang, X.; Wang, Y.; Sun, J.; et al. Mixing state and hygroscopicity of dust and haze particles before leaving Asian continent. *J. Geophys. Res. Atmos.* **2014**, *119*, 1044–1059.
29. Shao, L.Y.; Liu, P.J.; Jones, T.; Yang, S.S.; Wang, W.H.; Zhang, D.Z.; Li, Y.W.; Yang, C.X.; Xing, J.P.; Hou, C.; et al. A review of atmospheric individual particle analyses: Methodologies and applications in environmental research. *Gondwana Res.* **2022**, *110*, 347–369. https://doi.org/10.1016/j.gr.2022.01.007.
30. Zhang, M.Y.; Shao, L.Y.; Jones, T.; Hu, Y.; Adams, R.; BéruBé, K. Hemolysis of PM_{10} on RBCs in vitro: An indoor air study in a coal-burning lung cancer epidemic area. *Geosci. Front.* **2021**, *13*, 101176. https://doi.org/10.1016/j.gsf.2021.101176.
31. Feng, X.L.; Shao, L.Y.; Xi, C.X.; Jones, T.P.; Zhang, D.Z.; BéruBé, K.A. Particle-induced oxidative damage by indoor size-segregated particulate matter from coal-burning homes in the Xuanwei lung cancer epidemic area, Yunnan Province, China. *Chemosphere* **2020**, *256*, 127058.
32. Hesterberg, T.; Anderson, R.; Bernstein, D.M.; Bunn, W.B.; Chase, G.A.; Jankousky, A.L.; Marsh, G.M.; McClellan, R.O. Product stewardship and science: Safe manufacture and use of fiber glass. *Regul Toxicol Pharmacol.* **2012**, *62*, 257–277.
33. Toner, S.M.; Shields, L.G.; Sodeman, D.A.; Prather, K.A. Using mass spectral source signatures to apportion exhaust particles from gasoline and diesel powered vehicles in a freeway study using UF-ATOFMS. *Atmos. Environ.* **2008**, *42*, 568–581.
34. Li, Y.W.; Shao, L.Y.; Wang, X.M.; Wang, W.H.; Yang, C.X.; Li, W.J.; Fang, Z. Fresh organic and soot particles from crop straw burning: Morphology, composition and size distribution. *Geol. J.* **2023**, *58*, 12, 4299. https://doi.org/10.1002/gj.4861.
35. Wang, W.H.; Wang, M.Y.; Shao, L.Y.; Zhou, X.Y.; Zhao, Z.; Li, N.; Zhou, H.; Li, W.J. Morphology and elemental composition of individual solid dust particles: From different sources to the atmosphere. *Atmos. Environ.* **2024**, *338*, 120842.
36. Zhang, Y.; Li, W.; Zhang, J.; Ding, X.; Yuan, Q.; Liu, L.; Xu, L.; Wang, Y.; Jiang, X.; Ma, W.; et al. Morphological and elemental classification of freshly-emitted individual particles from field and laboratory residential biomass burning. *J. Geophys. Res. Atmos.* **2024**, 129, e2023JD040379. https://doi.org/10.1029/2023JD040379.
37. Niu, H.; Wu, C.; Schindler, M.; Silva, L. F. O.; Ma, B.; Ma, X.; Ji, X.; Tian, Y.; Zhu, H.; Bao, X.; Cheng, Y. Characterization of $PM_{2.5}$ carbonaceous components in a typical industrial city in China under continuous mitigation measures. Toxics **2024**, 12, 461. https://doi.org/10.3390/toxics12070461.
38. Li, W.; Riemer, N.; Xu, L.; Wang, Y.; Adachi, K.; Shi, Z.; Zhang, D.; Zheng, Z.; Laskin, A. Microphysical properties of atmospheric soot and organic particles: Measurements, modeling, and impacts. *NPJ Clim. Atmos. Sci.* **2024**, *7*, 65.
39. Zhang, D.Z.; Iwasaka, Y.; Shi, G.Y.; Zang, J.Y.; Hu, M.; Li, C.Y. Separated status of the natural dust plume and polluted air masses in an Asian dust storm event at coastal areas of China. *J. Geophys. Res. Atmos.* **2005**, *110*, D06302. https://doi.org/10.1029/2004JD005305.
40. Albrecht, B.A. Aerosols, cloud microphysics, and fractional cloudiness. *Science* **1989**, *245*, 1227–1230.
41. De Reus, M.; Fischer, H.; Sander, R.; Gros, V.; Kormann, R.; Salisbury, G.; Van Dingenen, R.; Williams, J.; Ollner, M.Z.; Lelieveld, J.Observations and model calculations of trace gas scavenging in a dense Saharan dust plume during MINATROC. *Atmos. Chem. Phys.* **2005**, *5*, 1787–1803.
42. Koehler, K.A.; Kreidenweis, S.M.; DeMott, P.J.; Petters, M.D.; Prenni, A.J.; Carrico, C.M. Hygroscopicity and cloud droplet activation of mineral dust aerosol. *Geophys. Res. Lett.* **2009**, *36*, L08805. https://doi.org/10.1029/2009GL037348.
43. Myhre, G.; Stordal, F. Global sensitivity experiments of the radiative forcing due to mineral aerosols. *J. Geophys. Res.* **2001**, *106*, 18193.
44. Sullivan, R.C.; Guazzotti, S.A.; Sodeman, D.A.; Prather, K.A. Direct observations of the atmospheric processing of Asian mineral dust. *Atmos. Chem. Phys.* **2007**, *7*, 1213–1236. https://doi.org/10.5194/acp-7-1213-2007.

45. Twomey, S. The influence of pollution on the shortwave Albedo of clouds. *J. Atmos. Sci.* **1977**, *34*, 1149–1152. https://doi.org/10.1175/1520-0469(1977)034<1149:TIOPOT>2.0.CO;2.
46. Tang, X.B. Biomass Burning Impacts on the Haze Weather and Its Emission Factorsand PM Chemical Composition. Ph.D. Thesis, East China University of Science and Technology, Shanghai, China, 2014. (In Chinese with English abstract)
47. Zhang, D.Z.; Shi, G.Y.; Iwasaka, Y.; Hu, M. Mixture of sulfate and nitrate in coastal atmospheric aerosols: Individual particle studies in Qingdao (36°04′N,120°21′E), China. *Atmos. Environ.* **2000**, *34*, 2669–2679.
48. Zhang, R.; Suh, I.; Zhao, J.; Zhang, D.; Fortner, E.C.; Tie, X.X.; Molina, L.T.; Molina, M.J. Atmospheric new particle formation enhanced by organic acids. *Science* **2004**, *304*, 1487–1490.
49. Shi, Z.B.; Zhang, D.Z.; Ji, H.Z.; Hasegawa, S.; Hayashi, M. Modification of soot by volatile species in an urban atmosphere. *Sci. Total Environ.* **2008**, *389*, 195–201.
50. Kumarathasan, P.; Blais, E.; Saravanamuthu, A.; Bielecki, A.; Mukherjee, B.; Bjarnason, S.; Guénette, J.; Goegan, P.; Vincent, R. Nitrative stress, oxidative stress and plasma endothelin levels after inhalation of particulate matter and ozone. *Part. Fibre Toxicol.* **2015**, *12*, 28. https://doi.org/10.1186/s12989-015-0103-7.
51. Adachi, K.; Buseck, P.R. Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City. *Atmos. Chem. Phys.* **2008**, *8*, 6469–6481. https://doi.org/10.5194/acp–8–6469–2008.
52. Healy, R.M.; Sciare, J.; Poulain, L.; Crippa, M.; Wiedensohler, A.; Prévôt, A.S.H.; Baltensperger, U.; Sarda-Estève, R.; McGuire, M.L.; Jeong, C.H.; et al. Quantitative determination of carbonaceous particle mixing state in Paris using single-particle mass spectrometer and aerosol mass spectrometer measurements. *Atmos. Chem. Phys.* **2013**, *13*, 9479–9496.
53. Li, W.; Shao, L. Mixing and water-soluble characteristics of particulate organic compounds in individual urban aerosol particles. *J. Geophys. Res.* **2010**, *115*, D02301. https://doi.org/10.1029/2009JD012575.
54. Ueda, S.; Osada, K.; Takami, A. Morphological features of soot-containing particles internally mixed with water-soluble materials in continental outflow observed at Cape Hedo, Okinawa, Japan. *J. Geophys. Res. Atmos.* **2011**, 116, D17207. https://doi.org/10.1029/2010JD015565.
55. Whiteaker, J.R.; Suess, D.T.; Prather, K.A. Effects of meteorological conditions on aerosol composition and mixing state in Bakersfield, CA. *Environ. Sci. Technol.* **2002**, *36*, 2345–2353.
56. Xing, J.P.; Shao, L.Y.; Chen, F.F.; Wang, W.H.; Zhang, D.Z. Characteristics and aging of traffic-emitted particles with sulfate and organic compound formation in Urban Air. *Atmosphere* **2022**, *13*, 608. https://doi.org/10.3390/atmos13040608.
57. Hwang, H.; Ro, C.-U. Direct observation of nitrate and sulfate formations from mineral dust and sea-salts using low-Z particle electron probe X-ray microanalysis. *Atmos. Environ.* **2006**, *40*, 3869–3880.
58. Wang, W.H.; Gao, Y.T.; Shao, L.Y.; Fan, C.; Li, X.; Li, Y.W.; Liu, M.Y.; Zhou, X.Y. Chemical compositions and possible transportation of $PM_{2.5}$ during two haze periods in a coastal city of the North China Plain. *Geol. J.* **2023**, *58*, 4417–4427. https://doi.org/10.1002/gj.4850.
59. Chen, X.; Ye, C.; Wang, Y.; Wu, Z.; Zhu, T.; Zhang, F.; Ding, X.; Shi, Z.; Zheng, Z.; Li, W. Quantifying evolution of soot mixing state from transboundary transport of biomass burning emissions. *iScience* **2023**, *26*, 108125. https://doi.org/10.1016/j.isci.2023.108125.
60. Whittaker, A.; BeruB, K.; Jones, T.; Maynardc, R.; Richardsa, R. Killer smog of London, 50 years on:particle properties and oxidative capacity. *Sci. Total Environ.* **2004**, *334–335*, 435–445.
61. Carter, J.D.; Ghio, A.J.; Samet, J.M.; Devlin, R.B. Cytokine production by human airway epithelial cells after exposure to an air pollution particle is metal-dependent. Toxicol. *Appl. Pharmacol.* **1997**, *146*, 180–188.
62. Kim, Y.M.; Reed, W.; Wu, W.; Bromberg, P.A.; Graves Lee, M.; Samet, J.M. Zn^{2+}induced IL-8 expression involves AP-1, JNK, and ERK activities in human airway epithelial cells. *Lung Cell Mol. Physiol.* **2005**, *290*, 1028–1035.
63. Wang, W.H.; Shao, L.Y.; Li, J.; Chang, L.L.; Zhang, D.Z.; Zhang, C.C.; Jiang, J.K. Characteristics of individual particles emitted from an experimental burning chamber with coal from the lung cancer area of Xuanwei, China. *Aerosol Air Qual. Res.* **2019**, *19*, 355–363. https://doi.org/10.4209/aaqr.2018.05.0187.
64. Liu, P.J.; Shao, L.Y.; Li, Y.W.; Wang, W.H.; Zhang, M.Y.; Yang, C.X.; Niu, H.Y.; Feng, X.L.; Zhang, D.Z. Compositions, sources, and aging processes of aerosol particles during winter hazes in an inland megacity of NW China. *Atmosphere* **2022**, *13*, 521. https://doi.org/10.3390/atmos13040521.