Elements in Fine Particulate Matter ($PM_{2.5}$) from Indoor Air during Household Stoves Coal Combustion at Xuanwei, China

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Abstract

The characteristics of elements in fine particulate matter ($PM_{2.5}$) emitted during indoor coal combustion in Xuanwei were investigated. Lead (Pb) emissions were high among the trace elements at all sampling locations. The average Pb concentrations in "Laibin" samples were ~1.5 time higher than "non-Laibin" samples and were statistically significantly difference (paired t-test).Concentration ratios normalized to total suspended particles for the elements were also characterized and compared between the two types of locations. Element ratio (Se/S) showed differences than in another study, possibly due to composition differences of the samples in Xuanwei compared with other regions in China. These findings provide information about concentrations of elements in different types of coal samples emission during household coal combustion. There is a need to address the health effects of environmentally relevant doses of elements in fine particulate matter, considering life-long exposure of people in indoor dwellings.

Keywords:

Xuanwei, Element, $PM_{2.5}$, Household coal combustion, Stove

1. Introduction

Coal utilization, such as coal combustion is an important energy source. China is considered to be a large energy consumer and the country's estimated coal reserve is the third largest in the world (> 100 Gt) with over 75% electricity supply comes from coal combustion (Dai et al., 2012; Liu et al., 2008). The country is facing severe carbonaceous aerosol pollution (~ 70% due to coal combustion) (Cooke et al., 1999) and suffering from deteriorated environmental quality.

Xuanwei County is located in the Yunnan Province of China with population approximately 1.2 million living in an area of 6,257 km^2. The county is renowned for exceptionally high lung cancer rate. The age-standardized mortality rate (ASMR) reached ~160 per 100,000 in 2011–2013. The high ASMR areas were in a range of ~80-160 per 100,000 and low ASMR areas fell below ~20 per 100,000. It was also noted that in the communities with the highest mortality rates (e.g., Laibin, 26°13.883′N, 26°13.883′E), the difference could be >20 times the rates in communities with the lowest mortality (Chen et al., 2015).

Past studies linked lung cancer mortality with coal combustion emissions in the area (Barone-Adesi et al., 2012; Kim et al., 2014; Mumford et al., 1993). Recent studies showed the rather high lung cancer rate could be attributed to indoor air emissions of crystalline silica and high silica content could interact with toxic volatiles in the coal (Large et al., 2009; Tian et al., 2008). The properties of paleogeography and geology of the coal setting were identified to be adjacent to the Permo-Triassic Boundary (PTB), which coincided with largest known mass extinction event that possibly have influences on the coal chemistry (Knoll et al., 2007).

Household coal combustion is usually for heating and cooking purpose at Xuanwei and other rural areas of China. During the combustion process, large amount of fine particulate matter ($PM_{2.5}$) can be released, along with the trace elements that co-exist at the particulate phase in

air. The more volatile elements can be enriched on the fine (submicron) particulate fraction (Nelson, 2007).

Past epidemiological studies and in vitro experiments have demonstrated toxicity of particulate matter (Li et al., 2003; McNeilly et al., 2004). A widely accepted hypothesis suggests that the bioavailable transition metals on particle surface can induce free radicals generation which are crucial in causing oxidative damage (Costa and Dreher, 1997; Donaldson et al., 1996). Many trace metals and metallic compounds in $PM_{2.5}$ can exacerbate health damage (Lu et al., 2014). According to the International Agency for Research on Cancer (IARC), arsenic and hexavalent chromium are Group 1 carcinogens. Water-soluble transition metals posed pro-inflammatory effects (McNeilly et al., 2004). Iron, vanadium and nickel were reported to be the primary determinant of acute inflammatory infection (Costa and Dreher, 1997). Studies in the past revealed household coal combustion could lead to different levels of metals poisoning (e.g. endemic fluorosis and arsenosis) (Belkin et al., 2008; Dai et al., 2004).

Characterization of trace elements in indoor condition is inevitable as people spend over 80% lifetime at indoor environment (Klepeis et al., 2001). The information about the fate of trace elements (e.g. partitioning, environmental impacts, emission controls and etc.) particularly in fine particles during the coal combustion at Xuanwei is still limited. The explicit circumstances could have dire consequences for the local inhabitants.

The aim of this study is to: 1) quantify concentrations of elements in different types of coal samples emission using household coal burning stoves; 2) provide an elements concentrations analysis and further develop a concentration profile for the local inhabitants and region.

2. Materials and Methods

2.1 Combustion Procedures

2.1.1 Indoor Environment Condition Mimics Common Occurrence of "Pre-1990" Kitchen Design

Seventeen types of coal were tested for emissions. The samples were labeled 1-17 and collected from different locations as noticed in Table 1. The samples collected from different coal seams and mines were denoted as mentioned in Table 1. Sample 10, 14 and 15 were classified without coal seams as the samples were re-processed from coal powders collected from the surface in the communities. The coal combustion experiment was conducted between 4th of November 2012 and 2nd of January 2013, in a separate kitchen area opposite a one story building in a village called Shangzuosuo (Latitude: 26.272255, Longitude: 104.131909) in Xuanwei. All doors and windows in the living room were closed during the experiment. The volume of the kitchen was ~42.6 m^3 (5.9 m long × 3.8 m wide × 1.9 m high). The air exchange rate in the kitchen was continuously monitored by measuring the first-order decay of carbon dioxide using a Q-Trak™ indoor air quality monitor (model 8550; TSI, Inc., Shoreview, MN, USA). The air change rate was set as 6.9 h^{-1}.

2.1.2 Preparation of Fuels

A laboratory stove (with internal diameter of 15 cm) and the experimental setup in the household indoor environment as shown in Figure S1 (Supplementary Material) was applied in this experiment to simulate fire pit being used for routine daily life coal burning activity. The stove mass, biomass (contained dried sugar cane and corn stock as combustion-supporting agents for kindling purpose) and coal sampling masses were measured to maintain consistency throughout the experiment. A biomass range of ~ 0.5-4 kg of the coal samples were used in each combustion process. Large coal samples were sieved to size range of 4-8 cm in diameter in order to facilitate combustion performance.

118

119 2.1.3 Burning Cycle

120 All types of coal sample were analyzed separately for combustion in order to collect air
121 particulate samples. Each type of samples was carried out for triplicate sampling analysis.
122 Small amount of biomass material was used to aid setting fire at outdoor environment along
123 with blower and chimney to ensure kindling. The air was purged through the stove inlet to
124 provide oxygen for combustion and the chimney was located on top of the stove enhancing
125 chimney effect. After full kindling occurred (~ 5 mins after initial ignition), ~ 2 kg of the coal
126 samples were further added to the stove for further fire setting. After reaching 10 minutes mark
127 from the initial ignition, all remaining coal samples were fully filled up the stove. The stove
128 was immediately transferred to the kitchen positioned above a balance. The weight of the stove
129 and coal samples were recorded altogether. All biomass materials were completely removed at
130 outdoor environment prior fire setting. A water pot containing 2 kg of water at room
131 temperature was placed above the stove. Coal lumps could melt and coagulate together during
132 combustion process which extinguished fire. To simulate the cooking practice, fire was stoked
133 and poked to assure air ventilating through coal lumps at beginning and every 20-minutes
134 during the combustion cycle. More coal was added to the stove in every 20-minutes cycle.
135 Water was heated up to boiling point during the heating process. The complete heating process
136 required 30-60 minutes depending on different fuel types. The remaining ashes were weighed
137 after each combustion cycle. The combustion cycle was in line with household coal burning
138 activities typically in Xuanwei (~ 1 hour). Fire was re-used for same type of coal burning
139 process or extinguished by water sprayer. The weight of coal and water was recorded in every
140 10 minutes interval during the experiment.

141

142 2.2 Samples Collection

143 All Teflon membranes were equilibrated at 21.5 ± 2 °C and relative humidity of 35 ± 5%, for
144 no less than 24 h before weighing. Sample weighing was performed on a microbalance (Mettler
145 Toledo MT5 with ±0.001 mg sensitivity). The charge on each filter was neutralized by exposure
146 to a ^{210}Po ionizing source for no less than 30 s before the filter was transferred to the balance
147 pan. The balance was calibrated to 200 mg and 100 mg Class 1 weights, and tare was set before
148 weighing the filters. The 200 mg Class 1 weight was used for re-calibration after weighing
149 every 10 filters. The balance performance was ensured not to deviate more than ±0.003 mg by
150 specification. Two Mini-volume portable air sampler (Mini-vol, Airmetrics, Eugene, OR, USA)
151 was used to collect air samples (TSP and $PM_{2.5}$ samples) at uniform flow rates of 5 L/min
152 during the combustion cycle. The samples were collected separately on 47 mm diameter Teflon
153 membranes filters. The air was purged through a TSP or $PM_{2.5}$ size cut impactor. Care was
154 taken that the filters were not overloaded with particles. The TSP and $PM_{2.5}$ particles were
155 deposited on the filters for further analysis.
156
157 2.3 Mass Analysis
158 The filters were weighed before and after sampling under equilibrium (> 24 hrs) a standard
159 controlled condition (temperature (20–23 °C) and relative humidity (35–45%)). Mass
160 concentrations were determined by a Sartorius ME 5-F electronic microbalance with sensitivity
161 of ±1 μg (Sartorius, Gottingen, Germany). The particles contained Teflon membranes filters
162 were weighed and subsequently transferred to clean plastic bags and stored in refrigerator (<
163 4 °C) prior chemical analysis. ~ 10% of the samples were submitted to replicate analysis with
164 absolute errors ≤ 0.015 mg for blank filters and ≤ 0.020 mg for filter samples.
165
166 2.4 Elemental Analysis
167 Energy Dispersive X-Ray Fluorescence (ED-XRF) spectrometry (Epsilon 5 ED-XRF,

PANalytical B. V., the Netherlands) was used to determine the concentrations of elements collected on the $PM_{2.5}$ Teflon membranes filters (Steinhoff et al., 2000; Wasson and Guo, 2002). A three-dimensional polarizing geometry contained eleven secondary targets (i.e., CeO_2, CsI, Ag, Mo, Zr, KBr, Ge, Zn, Fe, Ti, and Al) and a barkla target (Al_2O_3), along with good signal to background ratio and low detection limits were achieved. The X-ray source was a side window X-ray tube contained a gadolinium anode, operated at accelerating voltage of 25–100 kV and current of 0.5–24 mA (maximum power: 600 W). The characteristic of the X-ray radiation was detected by germanium detector (PAN 32). Each sample was analyzed for 30 mins to obtain a spectrum showing X-ray counts against photon energy. The individual peak energies were to match with specific elements and peak areas were referred to corresponding elemental concentrations (Brouwer, 2006). The ED-XRF spectrometer was calibrated with thin-film standards (MicroMatter Co., Arlington, WA, USA). A total of 16 elements (i.e., Na, Mg, Al, Si, K, Ca, Sc, Ti, Fe, Cr, Mn, Ni, Cu, Zn, Se, Pb, Cd) were determined and reported in the analysis. Elements such as Na, Ma, Al, Si, K, Ca, Ti and Fe were classified as major element, whereas elements such as Cr, Mn, Ni, Cu, Zn, Se, Pb and Cd were classified as trace element.

2.5 Statistical Analysis

All the data were analyzed using SPSS statistic 21.0 (IBM ®, New York, NY) or GraphPad Prism software (Version 5 for Windows) for the analysis.

3. Results and Discussion

3.1 Major and Trace Elements Profile in $PM_{2.5}$

Table 2 summarizes the results of elemental analysis in $PM_{2.5}$. The concentrations of major and trace elements are classified as from “Laibin” (sample 1-7) and “non-Laibin” (sample 8-17)

192 area for comparison. The corresponding results of elemental analysis in total suspended
193 particles (TSP) can be referred to Table S1 (Supplementary Material). “Laibin” is the location
194 that has been, since 1990, and remains, the community with the highest mortality from lung
195 cancer (Chen et al., 2015). Pb (2074.6-5970.2 ng m^{-3}) shows high concentration in trace
196 element at all sampling locations. A study showed Pb emissions were ~1-2 order of magnitude
197 higher than Cr and Ni in $PM_{2.5}$ during domestic coal combustion (Ge et al., 2004). The result
198 in this study is also consistent with the above findings. However, Ti (0.2-1.0 μg m^{-3}) and Cr
199 (605.1-968.1 ng m^{-3}) are the elements with low concentrations, demonstrating ~1-3 orders of
200 magnitude lower than the high elements. Major elements show minimal concentration variation
201 in “Laibin” and “non-Laibin” samples (sample 1-17, concentration range in same order of
202 magnitude for all elements). The concentrations of trace elements are also in same order of
203 magnitude between the two types of samples (sample 1-7 and 8-17). The average
204 concentrations of major and trace elements show no statistically significant differences
205 between “Laibin” and “non-Laibin” samples except for the lead (Pb) element (paired t-test; Pb
206 ($p < 0.05$)). The average concentration of Pb in “Laibin” (average concentration of sample 1-
207 7) and “non-Laibin” (average concentration of sample 8-17) are 4261.9±970.5 and
208 2842.7±636.8 ng m^{-3}, respectively. The “Laibin” samples are ~1.5 times higher than the “non-
209 Laibin” samples. Home metals pollutants exposure may result in retarded growth, learning
210 disabilities and nervous system damage. Indoor pollution such as Pb poisoning can pose a
211 significant environmental risk to children, adults, and pets in house (Charney et al., 1983;
212 Meyer et al., 1999; Roberts and Dickey, 1995). The result shows “Laibin” samples can evaluate
213 different concentration of Pb than the “non-Laibin” samples. The findings suggest that safety
214 of “Laibin” coal users can possibly be put in jeopardy.
215

3.2 Concentrations and Environmental Implications of Elements between Sample Locations

The results of elemental analysis present in ratio of concentration of a given element determined in $PM_{2.5}$ relative to TSP in order to normalize anomalies of sampled air volume. Concentration ratios, taken account with standard deviation altogether (>1) are considered as outliers. The outliers with observations remote from values in the random sampling population were removed prior presentation as shown in Figure 1-4. Further information can be referred to Table S2 (Supplementary Material).

The overall concentration ratios of major elements (Figure 1-2) share similar variation distributions (except for Na and Ti) between "Laibin" and "non-Laibin" samples, suggesting possible composition and structural resemblance between the two locations. Na and Mg are the most abundant inorganic elements in the major elements with average concentration ratios of 0.70±0.33 and 0.71±0.19 in "Laibin" area, whereas, the concentration ratios are in a range of 0.88±0.23 and 0.74±0.15 for the "non-Laibin" area. High ratios indicate greater proportions of source contributing to $PM_{2.5}$ fraction with respect to the TSP.

Among the trace elements, Cr, Cd and Pb demonstrate different concentration ratios variation between "non-Laibin" and "Laibin" area, suggesting possible composition and structural differences of the coals between the two types of locations. However, element ratios such as Mn, Ni, Cu, Zn and Se share similar ratio distributions. The combination and contents of trace elements vary among coal types possibly due to different coalification processes (Xu et al., 2004). The above trace elements were listed as key toxic and priority trace elements under prime concern by different environmental organizations (US Congress, 1990; Swaine, 2000; Tian et al., 2013). Cd, Ni, Pb and Cr were also classified as the U.S. EPA hazardous air pollutants (French et al., 1998). Coal burning with high hazardous trace element contents could

cause surge of hazardous trace element concentrations in ambient air and pose threat to human health and environment. The above concentration ratios suggest samples from "Laibin" could have different emission characteristics of hazardous airborne trace elements (Cr, Pb and Cd in this situation) in fine particulate matter to the atmosphere than the "non-Laibin" samples. Airborne contaminants could cause symptoms such as pulmonary dysfunction, cardiovascular dysfunction and cancer (Liu et al., 2012; Shraim et al., 2003). Household coal combustion has been identified to cause endemic arsenosis in southwest Guizhou at China in previous studies (Wei et al., 2012; Zheng et al., 1999). The combustion process associated with boiling can lead to ultrafine particles to the atmospheres (Varshney et al., 2016). Metals such as Pb, Mn, Al, Cu, and Fe are widely distributed in particulate matter and suspected to be an important source of particulate matter toxicity (Varshney et al., 2016). Oxidative stress and impaired lung functions were shown to be more susceptible towards elements bound in fine than coarse particulate matter (Allen et al., 2001).

The behavior of trace elements during coal combustion depends further on volatilities and volatilization trends. Elements such as Cu, Zn, Cd and Pb are more volatile than Mn or Fe, but less than Se (Danihelka et al., 2003). The trends can be determined by mode of occurrence, combustion conditions and coal ranks (Nelson, 2007; Tian et al., 2013). The mode of occurrence of an element decides how the element is chemically bound and physically distributed throughout the coal usage (Nelson, 2007). This also determines the toxicity and behavior of an element during coal combustion process (Tian et al., 2013). The above mentioned conditions could all affect the outcome of the present analysis. Further characterization (e.g. maturity) of the samples to quantify the composition differences associated with human health implication is essential in future analysis.

Transition metals such as iron could have contributed to the production of hydroxyl radicals through Fenton reaction (Winterbourn, 1995). The average concentration ratios of Fe in

265 "Laibin" and "non-Laibin" are 0.30±0.06 and 0.33±0.08, respectively. The production of
266 radicals by soluble elements and their mediated Fenton chemical reaction is the primary
267 pathway to generate oxidants, in addition particle size plays an important role in element
268 bioavailability and toxicity (Allen et al., 2001). The concentration ratios in $PM_{2.5}$ can be
269 extrapolated to toxicological analysis for the local inhabitants in future.

270 According to air quality guidelines from the World Health Organization, the lowest estimate
271 of the critical cumulative exposure to airborne cadmium is 100 μg/m^3 per year, which is
272 equivalent to continuous lifetime permissible exposure concentration of 300 ng/m^3. At an air
273 concentration of chromium (VI) of 1 μg/m^3 (total chromium in present samples: 0.61-0.97
274 μg/m^3), the lifetime risk is estimated to be 4 x 10^{-2}. For every 1 μg/m^3 lead in air (lead in present
275 samples: 2.1-6.0 μg/m^3) could contribute 50 μg/litre of blood and the critical level of lead in
276 blood is set to be 100 μg/litre (WHO, 2000). The present analysis suggests that the emissions
277 can be posed for different adverse human health impacts due to the present of these metals,
278 although further possible relations between the two require further studies in future.

279

280 3.3 Element Ratios

281 Element ratios can be used as markers to trace profiles of the samples and the origin of air
282 masses (Cheng et al., 2000; Voutsa et al., 2002; Weckwerth, 2001). Diagnostic ratio is a binary
283 ratio for source identification which uses ratios of frequently appeared compounds in emissions
284 to distinguish between various sources (Abdullahi et al., 2013). Selenium (Se) is regarded as
285 an important tracer for coal combustion. A past study showed Selenium against Sulphur (Se/S)
286 ratio was 0.0027 for residential coal combustion emissions (Watson and Chow, 2001). The
287 Se/S ratios were in a range of 0.73-1.75 for "Laibin" samples and 0.68-2.66 for the "non-
288 Laibin" samples. "non-Laibin" samples showed wider range of the ratios, implying possible

289 similar origins of the “Laibin” samples. The present concentration ratios are ~2 orders of
290 magnitude higher than the previous study, possibly due to lower sulphur content in the coal
291 samples (Mumford et al., 1987).

292 Other element ratios referred coal combustion were also determined and listed with other
293 studies (Table 2). The diagnostic ratios are compared with other studies, the results show that
294 Pb/Br and Cu/Sb ratios at both locations are consistent with a similar study at Northwestern
295 Colorado (Gatari et al., 2005; Van Duong et al., 1995; Watson et al., 2001). Elemental
296 diagnostic ratios can be used to compare inter-source similarity. However, caution should be
297 taken when used for sources diagnosis as the values can vary during the environmental fate of
298 these elements. The chosen pairs of compounds are often highly reactive and bias is inevitable
299 (Abdullahi et al., 2013). More than one diagnostic ratio should be used to confirm the analysis
300 and molecular markers can further be employed to warrant the results.

301

302 3.4 Elements Emissions Overview

303 Many studies targeted characterizing elements in different circumstances (Supplementary
304 Materials: Table S3). Past studies showed ambient concentrations of elements and different
305 elemental concentrations in coal samples at Xuanwei (Lu et al., 2013; Lv et al., 2013). Potential
306 toxic elements are mainly confined to particulate phase can show enhanced release to the
307 environment as a result of preferential condensation on the surface of submicron particulate
308 matter (Senior et al., 2000). A study in Puertollano, Spain demonstrated that Sb and Pb were
309 markers linked with local coal deposits (Moreno et al., 2007). A previous study reported mass
310 concentrations of Pb, Zn, Cd, Cu, Ni and Mn in $PM_{2.5}$ for household coal combustion in rural
311 Henan Province in China. The results indicated that the measured elements in the kitchen area
312 were in a range of 1.94-609.7 pg m^{-3} during two seasons (autumn and winter), which was

highest compared to sitting area and outdoor in the study (Wu et al., 2015). A past study found that fine particles were the major component of the Xuanwei ambient particulate matters and trace elements (Cr, Mn, Ni, Cu, Zn and Pb) dominated in fine particle fraction, accounted for ~6-8% in composition in two seasons (spring and winter) (Lu et al., 2014). A study showed honeycomb coal could have higher Cd and Ni emissions in $PM_{2.5}$ than coal cake (Ge et al., 2004). A previous experiment demonstrated that less than 5% of the total Cd and Pb contents in coal were released at 500 °C, but at 30-60% in 1000 °C (Guo et al., 2003). All of the above conditions could possibly be used to understand further about the elemental emissions in household coal combustion and served as additional information with present study.

4. Conclusions

Elements in fine particulate matter were characterized from emitted indoor coal combustion. Samples were collected in Xuanwei (Yunnan Province), a region in China with a high rate of lung cancer. Lead emissions were high in trace elements at all sampling locations. The Pb concentrations demonstrated statistically differences between "Laibin" and "non-Laibin" samples. Concentration ratios normalized to total suspended particles for the elements were also characterized the ratio distributions were also compared between the two types of locations. Element ratio (Se/S) was analyzed and showed ~2 orders of magnitude higher than the previous study, suggesting possible composition differences of the coal samples in Xuanwei compared to other regions in China.

Indoor air pollution due to household combustion is a serious health concerns for population in developing and underdeveloped countries. Women and infants are prone to this problem as they are more often involved in cooking activities (Begum et al., 2009; Jin et al., 2006). The results indicate the importance of addressing health effects of environmentally relevant doses

of elements in fine particulate matter, considering people spend most of time in indoor environment.

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507 in Xuanwei, Yunnan Province, China.

508 Figure 4 Ratios of Trace Element Concentrations in Fine Particulate Matter ($PM_{2.5}$) and
509 Total Suspended Particle (TSP) in Coal Emissions Sampled at "non-Laibin"
510 Areas in Xuanwei, Yunnan Province, China.

511

512 Table 1 Locations and Information of the Collected Coal Samples*

Sample Number	Sampling Location in Xuwanwei	Seam	Morphology
1	Laibin, Zhenxing	B4	coal lumps
2	Laibin, Zhenxing	B3	coal lumps
3	Laibin, Longdong	B2	coal lumps
4	Laibin, Changzheng	B5	coal lumps
5	Laibin, Zhenxing	B1 and B2	coal lumps
6	Laibin, Changzheng	B3	coal lumps
7	Laibin, Longdong	B1	coal lumps
8	Wenxing	M30	coal lumps
9	Huchang	K7	coal lumps
10	Reshui	N.A.[a]	coal powders
11	Haidai	K9	coal lumps
12	Haidai	K7	coal lumps
13	Wenxing	C1	coal lumps
14	Xize	N.A.	coal powders
15	Lehua	N.A.	coal powders
16	Heping	K2	coal lumps
17	Tianba	K7	coal lumps

513 [a]N.A. = not available

514 *n = 3 for each type of coal
515

516 Table 2 Descriptive Analysis and Relative Abundances of Concentrations of Elements in $PM_{2.5}$*

Sample Number	Na	Mg	Al	Si	K	Ca	Ti	Fe	Cr	Mn	Ni	Cu	Zn	Se	Pb	Cd
	Major Element								Trace Element							
	μg/m³								ng/m³							
1	187.5±183.9.3	95.5±150.6	18.4±10.6	5.9±3.1	6.7±4.7	4.1±2.3	0.6±0.2	8.3±3.2	668.5±182.5	2645.1±779.5	507.1±56.5	1976.6±416.9	2074.6±508.6	2016.9±728.8	3146.4±1690.8	3457.6±977.7
2	177.9±131.4	28.8±6.9	17.6±9.3	7.8±2.1	3.3±3.1	4.0±1.4	0.5±0.2	6.3±1.0	847.1±270.6	2714.2±718.9	501.4±202.8	2074.6±338.2	2091.9±249.1	1936.3±1477.2	4131.9±1296.7	3232.9±1429.7
3	211.9±46.6	34.0±20.7	30.0±1.9	14.8±6.5	3.5±1.5	4.9±1.8	0.5±0.4	8.1±2.2	645.4±369.7	2097.6±139.7	242.0±0.0	1936.3±419.2	1855.6±698.7	1452.2±640.4	3146.4±242.0	1532.9±916.3
4	208.5±124.1	22.9±1.5	21.6±2.2	7.1±4.9	1.9±0.3	3.7±0.5	0.4±0.2	5.2±1.0	726.1±311.2	1936.3±119.8	242.0±59.9	1659.7±207.5	3595.9±1333.8	2282.0±548.9	4598.6±158.4	1383.0±666.9
5	169.2±67.8	42.1±17.9	27.3±2.1	9.7±4.8	5.3±1.9	3.5±1.0	0.2±0.2	6.6±1.3	847.1±209.6	3065.8±1333.0	605.1±121.0	2178.3±484.1	2783.4±1154.4	3065.8±978.2	4598.6±872.7	2985.1±139.7
6	275.0±86.6	37.6±10.6	26.9±5.5	5.2±5.1	3.2±1.3	4.7±2.6	1.0±1.4	7.5±2.7	806.8±369.7	1936.3±872.7	564.7±139.7	2501.0±503.8	2823.7±369.7	1855.6±1143.8	5970.2±1478.8	1613.6±2387.8
7	220.7±63.6	22.9±6.1	28.7±6.6	7.8±6.8	5.6±5.2	4.0±0.3	0.1±0.1	8.8±2.4	622.4±179.7	2189.8±818.5	530.2±254.9	2212.9±487.8	2097.6±609.1	3480.7±2164.9	4241.3±2264.5	2397.3±2385.8
8	220.4±25.5	30.5±10.3	18.0±8.7	13.4±6.5	16.0±33.7	4.5±1.7	0.4±0.4	8.9±2.0	847.1±524.7	2259.0±874.9	726.1±216.5	2339.7±395.2	2138.0±786.8	2259.0±586.2	2420.3±980.2	1290.8±1286.8
9	213.3±41.8	30.2±9.2	24.7±2.4	6.7±2.0	4.5±3.2	4.8±1.1	0.6±0.3	8.9±2.6	605.1±253.8	2198.5±751.5	403.4±250.0	2299.3±333.6	1835.4±585.0	1734.6±871.5	2460.7±728.8	2521.2±1453.0
10	269.7±77.1	34.7±16.8	18.3±4.3	11.6±4.7	11.5±6.1	5.6±2.3	1.0±0.8	10.1±0.8	726.1±242.0	3065.8±1478.8	322.7±369.7	2662.4±242.0	1855.6±139.7	2662.4±640.4	2501.0±279.5	2420.3±2110.0
11	362.9±16.6	40.7±13.2	34.8±6.4	7.7±7.9	9.1±9.1	4.5±0.8	0.8±1.0	12.2±6.1	726.1±242.0	1694.2±640.4	645.4±139.7	2501.0±279.5	2501.0±1242.0	2339.7±978.2	3872.5±2151.2	2823.7±2484.0
12	276.3±126.5	30.8±4.5	25.1±6.5	8.3±2.4	10.4±15.3	3.8±1.1	0.2±0.1	7.0±1.3	968.1±242.0	2823.7±559.0	605.1±320.2	2016.9±279.5	1492.5±805.8	2501.0±1242.0	2501.0±698.7	3670.8±1443.8
13	324.2±34.7	21.8±0.5	21.1±7.3	13.1±6.1	3.9±0.6	4.9±1.2	0.2±0.2	7.9±1.0	887.5±279.5	1936.3±1055.0	322.7±279.5	2016.9±559.0	1532.9±279.5	1936.3±1511.5	2339.7±739.4	2339.7±1458.9
14	242.0±28.9	36.3±6.3	22.0±0.5	8.2±3.8	7.5±2.9	3.3±0.7	1.0±0.8	6.3±1.3	622.4±207.5	2351.2±431.9	518.6±103.7	2282.0±904.3	4633.2±2475.0	5739.7±2914.3	3768.8±1482.8	2593.2±922.0
15	158.6±87.5	29.1±12.6	27.2±7.8	6.3±2.7	4.0±2.4	5.5±2.8	0.5±0.2	6.5±0.5	691.5±239.6	1452.2±548.9	484.1±119.8	2005.4±431.9	3388.5±3001.6	899.0±935.5	2074.6±359.3	1037.3±829.8
16	170.8±40.0	20.1±5.2	24.2±1.5	7.6±8.0	2.1±0.8	3.6±1.1	0.4±0.5	7.3±1.4	760.7±239.6	2282.0±548.9	345.8±119.8	2282.0±207.5	1936.3±431.9	2420.3±1764.4	3181.0±1064.6	2627.8±2129.2
17	271.3±139.5	24.2±3.6	21.0±7.9	12.8±9.5	3.3±2.2	4.3±1.7	0.4±0.3	7.9±2.4	887.5±503.8	2823.7±1611.5	968.1±0.0	2178.3±419.2	2016.9±369.7	2581.7±739.4	3307.8±1458.9	2662.4±1827.3

517 *n = 3 for each type of coal.
518

519 Table 3 Elemental Ratios at Sampling Locations and in Relevant Studies

Sampling Location	Se/S	Pb/Br	Cu/Sb	Zn/Pb	Zn/Cd	References
Laibin, China	0.73-1.75	0.80-2.92	0.31-1.07	0.54-1.21	0.37-2.27	This study
non-Laibin, China	0.68-2.66	0.80-1.78	0.54-1.34	0.53-1.61	0.37-2.27	This study
Northwestern Colorado, U.S.A.	$2.7x10^{-3}$	1.8	0.5	1.9	17	(Watson et al., 2001)
Pha Lai, Northeast of Hanoi, Vietnam	N.A.[a]	N.A.	N.A.	0.39	N.A.	(Van Duong et al., 1995)
Hanoi, Vietnam	N.A.	N.A.	N.A.	0.39	N.A.	(Gatari et al., 2005)

520 [a]N.A. indicates not available.
521

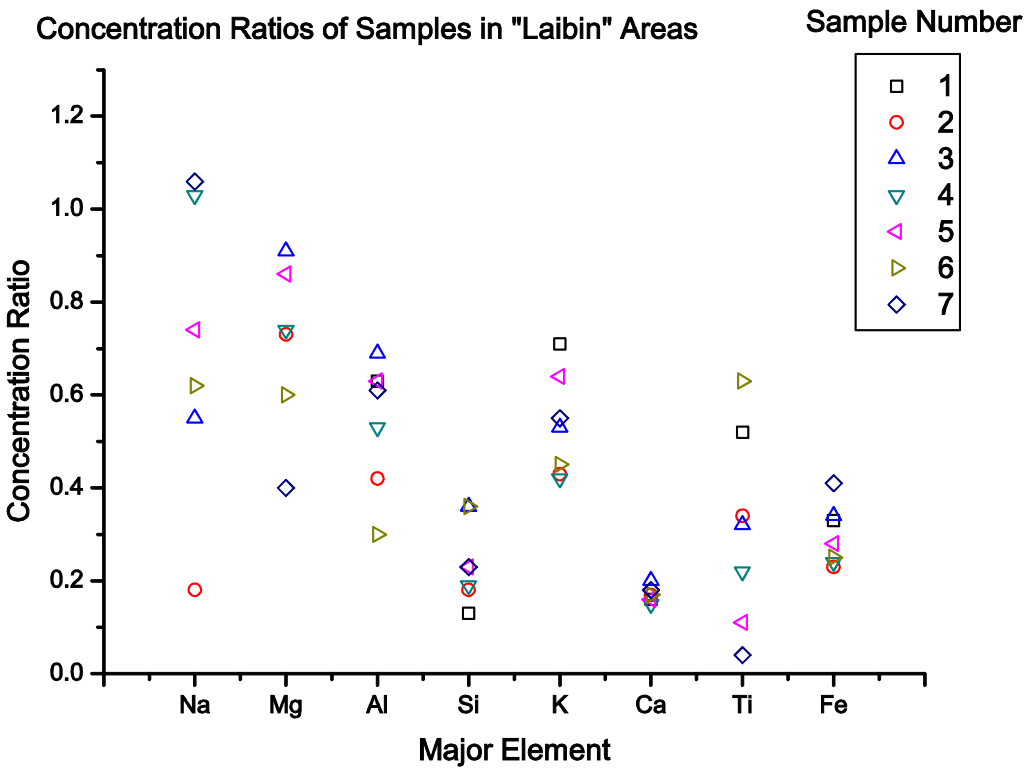
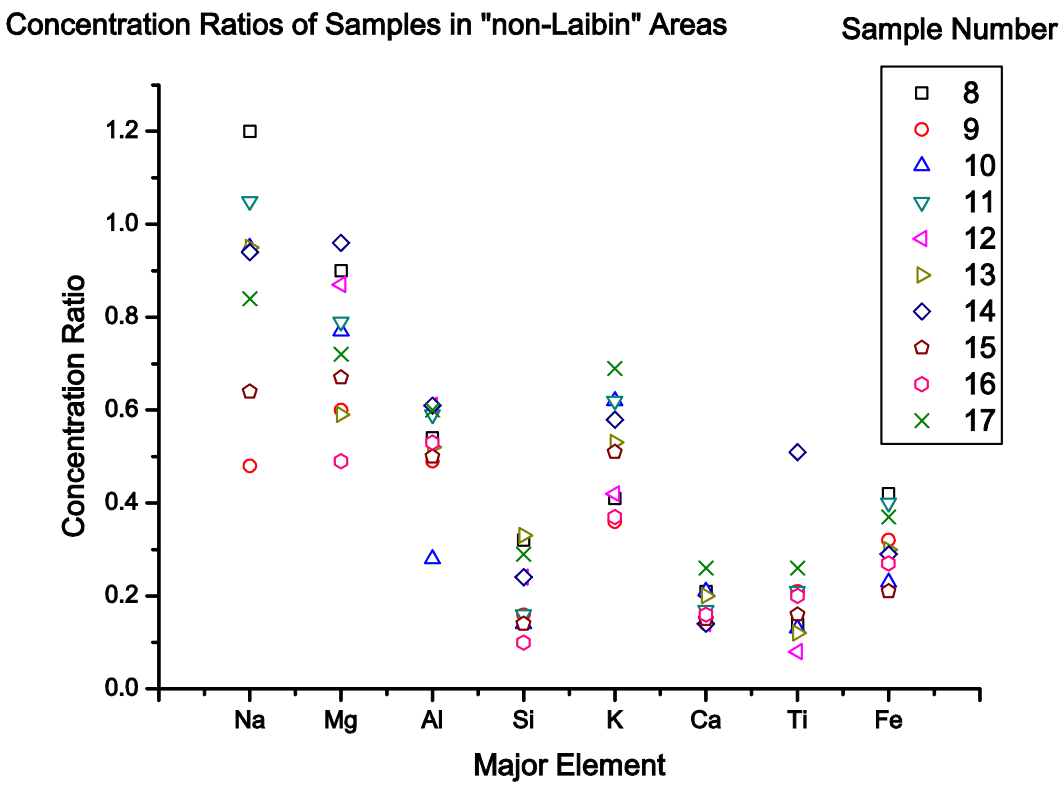


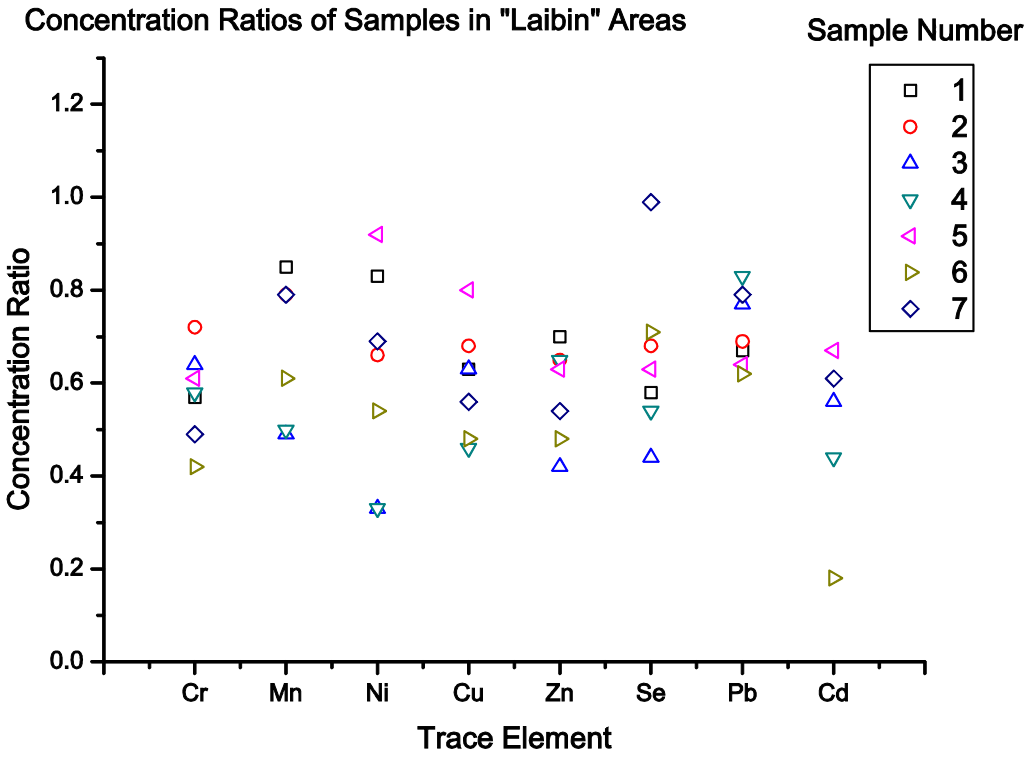
Figure 1 Ratios of Major Element Concentrations in Fine Particulate Matter ($PM_{2.5}$) and Total Suspended Particle (TSP) in Coal Emissions Sampled at “Laibin” Areas in Xuanwei, Yunnan Province, China.



528

529 Figure 2 Ratios of Major Element Concentrations in Fine Particulate Matter ($PM_{2.5}$) and
530 Total Suspended Particle (TSP) in Coal Emissions Sampled at “non-Laibin”
531 Areas in Xuanwei, Yunnan Province, China.

532



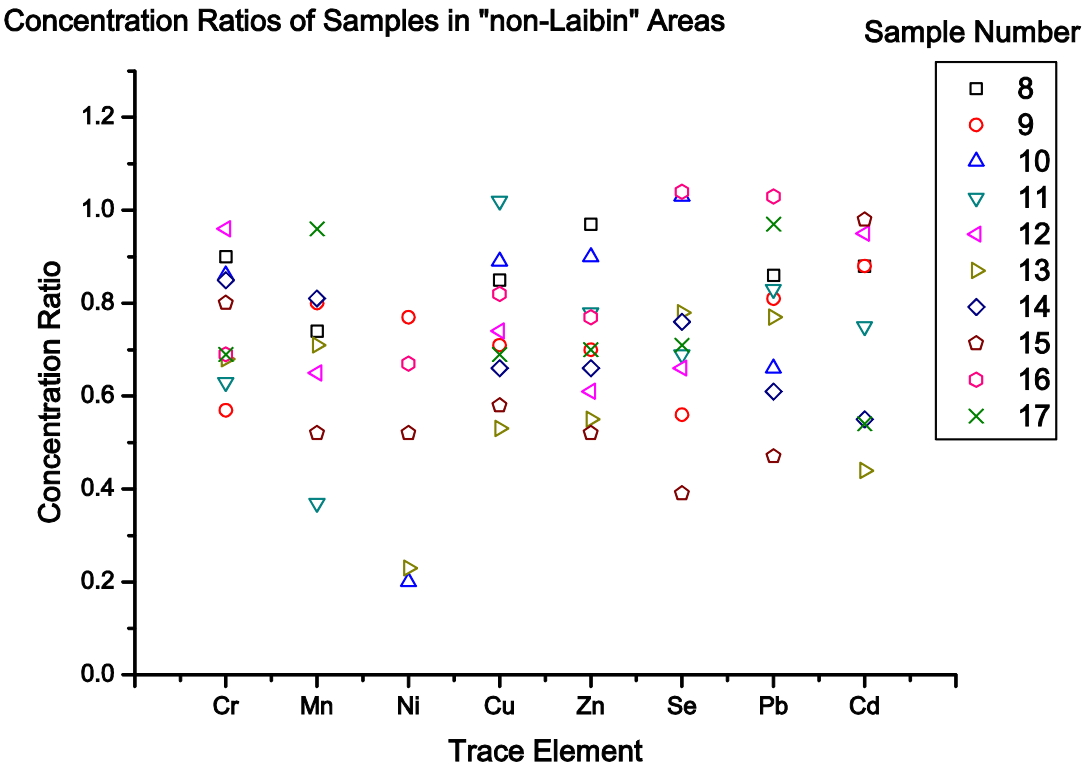
533

534 Figure 3 Ratios of Trace Element Concentrations in Fine Particulate Matter ($PM_{2.5}$) and

535 Total Suspended Particle (TSP) in Coal Emissions Sampled at “Laibin” Areas

536 in Xuanwei, Yunnan Province, China.

537



538

539 Figure 4 Ratios of Trace Element Concentrations in Fine Particulate Matter ($PM_{2.5}$) and

540 Total Suspended Particle (TSP) in Coal Emissions Sampled at “non-Laibin”

541 Areas in Xuanwei, Yunnan Province, China.

542