Quantification and characterization of household air pollution exposure from the use of solid fuels;

Clues to the lung cancer epidemic in Xuanwei and Fuyuan, China

George Downward

Quantification and characterization of household air pollution exposure from the use of solid fuels; Clues to the lung cancer epidemic in Xuanwei and Fuyuan, China

George Downward
2015

George Downward, 2015
Quantification and characterization of household air pollution exposure from the use of solid fuels; Clues to the lung cancer epidemic in Xuanwei and Fuyuan, China
Thesis Utrecht University
ISBN: 978-90-393-6347-8

Cover design by: proefschrift-aio.nl
Printed by: dpp.nl

Quantification and characterization of household air pollution exposure from the use of solid fuels; Clues to the lung cancer epidemic in Xuanwei and Fuyuan, China

Karakterisering van binnenhuis luchtverontreiniging veroorzaakt door het gebruik van vaste brandstoffen, oorzaken voor de longkankerepidemie in Xuanwei en Fuyuan, China
(men een samenvatting in het Nederlands)

描述与量化家庭固体燃料产生的室内空气污染暴露；为中国云南省宣威市、富源县肺癌高发现象提供线索
(附中文简介)

Proefschrift

ter verkrijging van de graad van doctor aan de Universiteit Utrecht op gezag van de rector magnificus, prof.dr. G.J van der Zwaan, ingevolge het besluit van het college voor promoties in het openbaar te verdedigen op dinsdag 26 mei 2015 des middags te 2.30 uur

door

George Stanley Downward

geboren op 25 februari 1982
te Christchurch, Nieuw-Zeeland

Promotor: Prof. dr B. Brunekreef
Copromotor: Dr. R. C. H. Vermeulen

The studies described in this thesis were funded by the National Institutes of Health (USA) (HHSN261201400122P) intramural research program.

Contents

Chapter 1	General Introduction	1
Chapter 2	Heterogeneity in coal composition and implications for lung cancer risk in Xuanwei and Fuyuan, China	15
Chapter 3	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	47
Chapter 4	Polycyclic Aromatic Hydrocarbon exposure in household air pollution from solid fuel combustion among the female population of Xuanwei and Fuyuan counties, China	67
Chapter 5	Quartz in coal, ash, and air in a high lung cancer incidence are in China	107
Chapter 6	Outdoor, indoor, and personal black carbon exposure from cookstoves burning solid fuels	135
Chapter 7	General Discussion	157
	Summary	183
	Samenvatting	187
	总结	193
	Affiliation of contributors	197
	Acknowledgements	199
	About the author	201

Chapter 1

General Introduction

Solid fuels, household air pollution, and human health

Approximately 3 billion people world-wide, primarily from low and middle income countries, use solid fuels (wood, coal, animal dung, crop wastes etc.) for daily domestic tasks including cooking and heating, frequently using unventilated firepits or rudimentary stoves.[1] Household air pollution (HAP), caused by the emissions of solid fuel, is a major source of mortality and morbidity worldwide with up to 4 million deaths attributable annually to HAP exposure.[2] These 4 million deaths are attributable to a variety of communicable and non-communicable diseases including pneumonia, chronic obstructive pulmonary disease, cardiovascular disease, and lung cancer (Table 1).

Table 1 - Deaths attributable to HAP in 2012 (Source: WHO[3])

Cause of Death	Number of Deaths (%)
Stroke	1,462,000 (34%)
Ischaemic Heart Disease	1,096,000 (26%)
Chronic Obstructive Pulmonary Disease	928,000 (22%)
Acute lower respiratory disease (e.g. pneumonia)	534,000 (12%
Lung Cancer	272,000 (6%)

Lung cancer is an umbrella term which refers to malignancies of the bronchi, bronchioles and alveoli.[4] It is a major source of morbidity and mortality worldwide. According to the World Health Organization (WHO), there were 1.8 million new cases and 1.6 million deaths attributable to lung cancer in the year 2012, which represents nearly 20% of all cancer mortality.[5] Lung cancer mortality is very high, with the 5-year survival rate less than 10% in many countries, including high income nations[6,7] (for comparison, bowel cancer typically has a 5-year survival rate of greater than 50%, even in low income countries[8]). The most common cause of lung cancer is tobacco smoking,[9-11] however, up to 25% of lung cancer deaths occur among never-smokers (defined as having smoked less than 100 cigarettes in their lifetime[12]). The causes of lung cancer among never smokers are variable and include genetic factors, occupational exposures, infections with human papilloma virus or tuberculosis, and outdoor and household air pollution.[13,14]

It is estimated by the WHO that exposure to HAP, produced as a result of solid fuel combustion, accounts for 17% of the annual premature lung cancer deaths.[15] Case-control studies from a variety of nations, including China and India have independently demonstrated an increased risk of lung cancer associated with the domestic use of solid fuels (including after adjustment for potential confounders including smoking).[16] A recent meta-analysis has further established that the domestic use of solid fuels is associated with an overall increased risk of lung cancer, with a pooled odds ratio of 1.56 (95% CI 1.44-1.69).[17] The odds ratio of lung cancer for women (1.6, 95% CI 1.41-1.82) was higher than that for men (1.42, 95% CI 1.27-1.59), likely reflecting the increased exposure experienced by women as a consequence of their role in food preparation. Further, upon investigating the role that different solid fuels play, the risk of lung cancer is increased by a factor of two if coal is the primary solid fuel used (pooled odds ratio of 2.15, 95% CI 1.61-2.89) and is slightly higher among Asian (China and Taiwan) populations (pooled odds ratio:2.27, 95% CI 1.65-3.12).[17,18]

Xuanwei and Fuyuan

The role of solid fuel use and lung cancer risk is well illustrated in the Chinese counties of Xuanwei and Fuyuan. China has a population of over one billion and as a nation is rapidly urbanising. However, approximately half of the population still lives in rural environments[19] and are largely dependent upon solid fuels for heating and cooking.[20]

Xuanwei and Fuyuan counties are located in North-East Yunnan province and have a combined population of approximately 2 million. The bulk of the population is rural, operating mainly as subsistence farmers living in small villages throughout the region. Solid fuels represent the main source of energy for heating and cooking of which coal is the most common, being abundant in the region and produced by multiple active coal mines. During the 1970s the Chinese government carried out a nationwide cancer survey, which showed that the age adjusted lung cancer mortality rate was 6.8 and 3.2 per 100,000 for males and females respectively. The lung cancer rates in Yunnan province overall were lower than the national average for both men and women (4.3 and 1.5 per 100,000) with the exception of Xuanwei, where the lung cancer mortality rate was 27.7 per 100,000 for men and 25.3 per 100,000 for women.[21,22] The neighbouring county of Fuyuan had lung cancer rates of approximately a half to three quarters as high as those in Xuanwei (Figure 1).[22,23]

It was unlikely that tobacco smoking was the cause of this high lung cancer rate because the smoking rate at the time was approximately 40% for men, but less than 0.1% in women, while observed lung cancer rates for men and women were similar.[21] Like other rural areas in China, Xuanwei and Fuyuan were dependent upon solid fuels for their daily domestic cooking and heating. There are two main solid fuel groups available for use in Xuanwei and Fuyuan: coal and biofuels (plants). Plants used for combustion are typically wood, corn cobs (corn is a commonly grown crop in the area), and tobacco stems. There are two

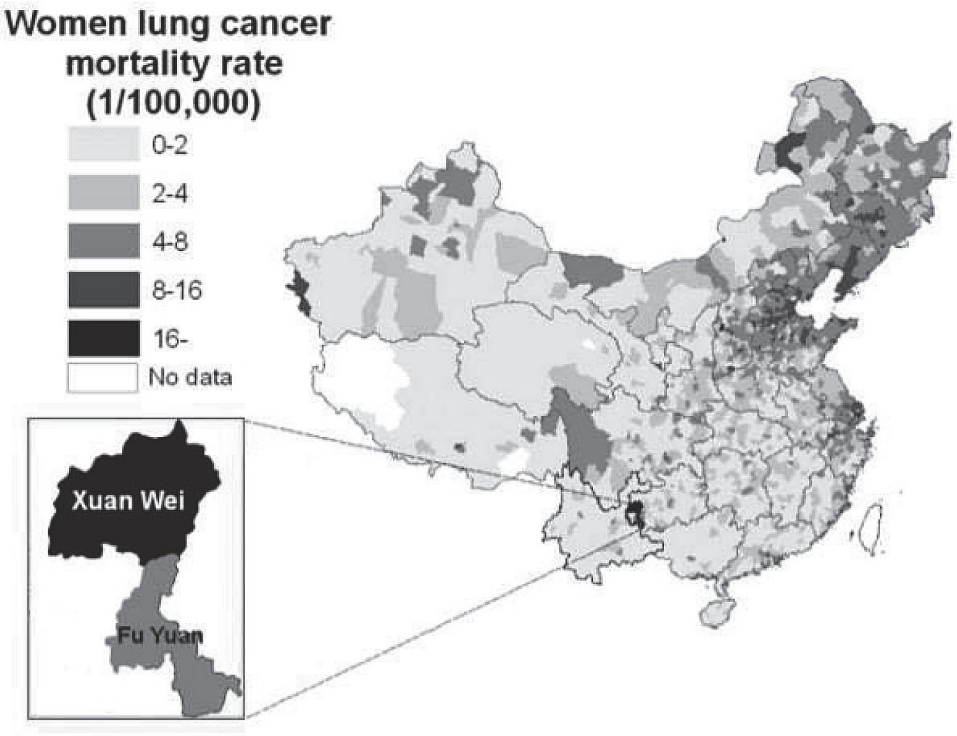

Figure 1 - Location of Xuanwei and Fuyuan within China and their associated lung cancer mortality rates (1973-1975). Figure adapted from Tian et.al.[23]

broadly identified types of coal used in the area, referred to locally as “smoky” and “smokeless” coal. The names relate to the amount of visible smoke emitted upon combustion but geologically refer to bituminous and anthracite coal, respectively. Early epidemiological studies, primarily focussing upon Xuanwei, identified that the use of smoky coal was strongly linked to lung cancer rates.[21,24,25] The initial evidence to suggest that smoky coal use was related to lung cancer was the observations that areas which used smoky coal more than other fuel types had higher lung cancer rates (in some cases in excess of a hundred-fold when compared to areas with zero usage of smoky coal [Table 2]).

Table 2 - Percentage of households burning smoky coal before 1958 and unadjusted lung cancer mortality between 1973 and 1975 in 11 Xuanwei communes. Table adapted from Mumford et.al.[21]

Commune	Smoky coal use (%)	Lung cancer mortality (per 100,000)
ChengGuan	100	151.8
LaiBin	89.7	109.3
RongCheng	81.9	93
LongTan	78	32.1
LongChang	76.1	33.2
HaiDai	49.7	10.8
PuLi	35.2	2.8
BanQiao	34	16.7
LuoShui	2.7	1.8
ReShui	0	2.3
XiZe	0	0.7

A subsequent case-control study provided further evidence that the lung cancer rates in the area were related to solid fuel use. This study, which primarily investigated the effect of smoking upon lung cancer risk found that smoking had a minimal effect upon lung cancer risk and that instead the age that someone started cooking and the total number of years spent cooking were strongly associated with lung cancer risk.[26] A further study, directly investigating the type of fuel used confirmed what had originally been suggested in these previous studies, that the use of smoky coal was directly related to lung cancer risk. In this study, an adjusted odds ratio of 7.53 (95% CI 3.31-17.17) was shown between the use of smoky coal and the risk of lung cancer (when compared to using any other fuel type).[27] Additionally, a recent retrospective cohort study, focussing upon only a few communes within Xuanwei county reported an adjusted hazard ratio of 98.8 (95% CI 36.8-265.6) for lung cancer mortality associated with the use of smoky coal (compared to using smokeless coal).[28]

Historically, solid fuels in Xuanwei and Fuyuan were burnt in unvented firepits (Figure 2). After the identification of the link between smoky coal use and lung cancer, a process of improving stoves was carried out. The focus of these stove improvements was to replace unvented firepits with stoves which were directly vented outdoors by chimneys. The purpose of these new stoves was twofold. First, by venting smoky emissions outdoors, they would reduce indoor exposure to carcinogenic emissions. Second, by improving airflow and oxygen supply, they would allow for a more efficient combustion process, resulting in a reduced demand for fuel. Internationally, improved stoves are advocated as methods to improve burning efficiency, reduce the amount of fuel used, and to reduce exposure to harmful emissions. Epidemiological studies assessing the effect of the stove improvements in Xuanwei and Fuyuan revealed that after the improved stoves were in place for at least

ten years, lung cancer rates reduced by over 50%.[29] Additionally, research investigating the effect of using portable stoves, which are designed to be lit outdoors and later brought inside for use (no ventilation is available for these stoves indoors), also showed a similar reduction in lung cancer rates.[30] These findings indicate that exposure to carcinogenic product(s) in the emissions of smoky coal use is mitigated to a degree by the use of stoves with improved ventilation.

In addition to the difference in lung cancer rates between smoky and smokeless coal users, geographic variation in lung cancer rates within smoky coal users has also been observed.[24-26,31] This suggests variation in the constitutional makeup of the coal between areas. Geologically, smoky coal and smokeless coal were formed during different time periods. Smoky coal is a bituminous coal which was formed during the Permian-Triassic boundary, approximately 252 million years ago.[23] This coincides with the Permian extinction event, which is the largest known extinction event in the history of our planet. During this event up to 96% of all marine species and 70% of terrestrial vertebrate species became extinct.[32] Additionally, this is a period during which very little coal was produced globally.[33] Despite this, smoky coal is the dominant coal type present in Xuanwei and Fuyuan and is available from many coal mines throughout both counties. Xuanwei and Fuyuan are both coal-rich areas, with multiple coal mines in operation throughout both counties. The Chinese State Standard Coal Classification, a body which standardizes coal classifications across the nation, divides smoky coal into at least four geochemically distinct subtypes: coking coal, 1/3 coking coal, meagre lean coal, and gas fat coal.[34] There is geographic variation in which smoky coal subtypes are produced by which areas, which parallels the geographic variation in lung cancer rates (Figure 3). However, the relationship between the variation in lung

Figure 2 - Photograph of typical firepit from Xuanwei, China

cancer rates and the identified smoky coal subtypes has never been directly investigated. Smokeless coal is an anthracite coal from the Carboniferous period.[35] It is only mined in a few locations in Xuanwei and Fuyuan and access is generally limited to those who live within geographical proximity to smokeless coal producing mines.

Fuel contents and emissions

Polycyclic Aromatic Hydrocarbons

Investigations of the potentially carcinogenic constituents of smoky coal emissions very rapidly identified that smoky coal emissions contained much higher levels of PAH than smokeless coal. Work by Mumford et.al[24] in 1989 studying emissions during peak burning periods identified Benzo[a]Pyrene (BaP) concentrations of 14.7μg/m^3 among homes burning smoky coal in unvented firepits, which was approximately 25 times higher than homes burning smokeless coal (0.6μg/m^3). Reported PAH measurements also show some similarities to observed lung cancer rates. For example, a moderate to strong correlation between BaP measurements and lung cancer rates has been reported. In 2005 Tian[35] reported a spearman coefficient of 0.45 ($p=0.125$) between lung cancer rates and BaP measurements gained via controlled burning experiments. Research by Lan et. al[31] in 2008, reported a stronger correlation (spearman correlation coefficient 0.93, $p<0.01$) between the odds ratios of lung cancer in various Xuanwei regions and indoor measurements of BaP.

Research investigating the role of stove design in PAH exposure has found that the reduction in lung cancer following stove improvements is paralleled by a reduction in PAH exposure. For example, Tian et. al[36] in 2009 reported that BaP emissions were 6 times lower when using a ventilated stove (143.0ng/m^3) than an unventilated stove (901.3ng/m^3), however these changes in exposures have not been formally matched to lung cancer rates.

Genetic research has found that Xuanwei residents with mutations (single nucleotide polymorphisms) in genes responsible for PAH metabolism (specifically, the GSTM1 genotype) had an odds ratio of 2.3 (95% CI 1.3-4.2) for development of lung cancer compared to those without the mutation.[37,38] Furthermore, the KRAS and P53 mutation profiles of lung tumours from Xuanwei and Fuyuan have been found to be consistent with high PAH exposure and showed different mutation profiles to tumours collected from smokers.[39]

Together, these collective findings have led to the formulation of the "PAH hypothesis" which postulates that the lung cancer epidemic in Xuanwei and Fuyuan can largely be explained by exposure to PAHs. However, there are currently multiple limitations to the evidence base collected and reported upon thus far. Firstly, the sample sizes in these studies has generally been extremely limited (max n=48) and while regional variation in BaP emissions has been observed, it has never been established whether that variation was matched to specific smoky coal subtypes or specific coal mines. Additionally, in many cases, the data collected was purely exploratory in nature, with no attempt made to match observed measurements with lung cancer epidemiology, and when efforts have been made to match exposure to lung cancer risk (as with the examples above), inconsistent results have been found. All-together, this makes the association between PAH exposure and lung cancer in the area inconclusive, albeit highly suggestive.

Quartz

Research has also been published which has identified that quartz (i.e. crystalline silica) is present in relatively high quantities in smoky coal from Xuanwei when compared to other

coals of similar rank. In 2009, Large et.al. reported free silica levels in Xuanwei smoky coal of 174,000ppm, which is many times higher than bituminous coal sourced from other areas in China (18,000ppm) and the USA (18,865ppm).[40] There has also been work attempting to identify airborne quartz in the emissions of smoky and smokeless coal. This work has relied upon estimating quartz content on the basis of an assumed ratio of silicon to aluminium[35] and found that the amount of estimated quartz in smoky coal emissions (average value approximately 0.5mg/meal) was several times lower than smokeless coal emissions (2mg/meal) but that there was variation in estimated quartz content between smoky coals sourced from different locations (range: 0.1-2.04 mg/meal). This work also found that that the estimated quartz in smoky coal emissions correlated strongly with lung cancer rates in Xuanwei (Spearman coefficient 0.97, $p<0.0001$). Additionally, investigation of lung tumours from Xuanwei found silica particles embedded within them.[35,41]

These findings, in combination with the classification of quartz as carcinogenic to humans by the International Agency for Research on Cancer (IARC)[42] led to the formulation of the "quartz hypothesis", which considers exposure to quartz as contributing factor in the lung cancer epidemic. However, as with the PAH hypothesis above, there are multiple limitations in the evidence base behind this hypothesis. The high correlation between estimated quartz emissions and lung cancer rates is restricted to 15 samples and the positive correlation between quartz and cancer only exists if the smokeless coal emission values are excluded (if included, the correlation becomes 0.25). An additional limitation of the use of this estimation is that it seems contradictory for the estimated quartz emissions of smokeless coal to be higher than smoky coal, while uncombusted smoky coal had been identified to have higher amounts of quartz than smokeless coal. This would suggest that either the assumptions underlying the estimation of quartz in coal emissions is unreliable in this setting (leading to an under-estimation of quartz in smoky coal emissions) or that the excess quartz in smoky coal fails to become airborne during the combustion process. This means that it may go on to form a part of the coal ash, which may provide an additional route of exposure, however, this possibility has never been explored. Recent research has also suggested that the positive correlation between coal-derived quartz and lung cancer risk may be restricted to coals sourced from Xuanwei. In 2012, He et. al. investigated the quartz content in coal (but not its emissions) collected from both Xuanwei and Fuyuan and found high levels of quartz in coal from areas of Xuanwei with high rates of lung cancer but also found negligible amounts of quartz in Fuyuan coals from areas with similar lung cancer rates, suggesting that quartz content may not play a significant role in lung cancer risk.[43]

A further limitation, pertaining to both the PAH and the Quartz hypotheses is that most of these studies have relied upon using indoor measurements, with little knowledge how they pertained to personal exposure.

The current study

As a consequence of the multiple limitations of the previous studies, there was a clear need for further research to be performed in order to both establish a better understanding of the constituents of solid fuel emissions and to establish a link between those emissions and lung cancer risk a clearer identification of the carcinogenic constituents of smoky coal may

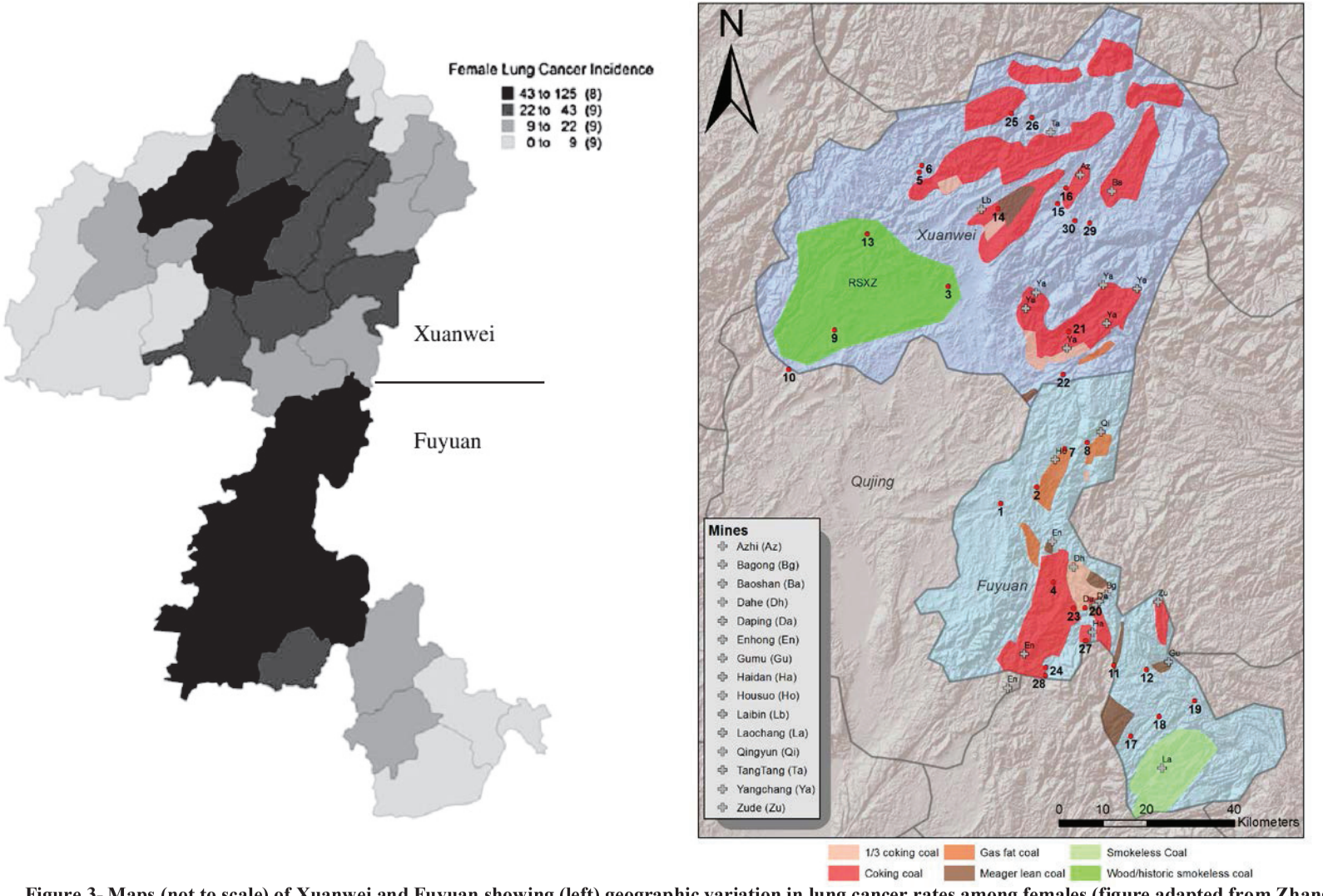

Figure 3- Maps (not to scale) of Xuanwei and Fuyuan showing (left) geographic variation in lung cancer rates among females (figure adapted from Zhang et.al[44]) and (right) villages selected for study, coal deposit types and mines reported by study participants. Figure produced by Beekhuizen & Wang, IRAS

allow for targeted public health interventions and assist in the most efficient use of available resources. It will also assist in understanding the potential carcinogenic risks of coals used in other domestic settings.

This thesis will report on the findings of the largest exposure assessment survey to date performed in Xuanwei and Fuyuan. This exposure survey was designed to catalogue the constituents of solid fuels and their emissions in Xuanwei and Fuyuan. These constituents will ultimately be applied to an ongoing case-control study of lung cancer among non-smoking women in the area. The specific goals of this thesis are as follows:

- Catalogue the constituents of the coals used in Xuanwei and Fuyuan
- Catalogue the constituents of household air pollution produced as a result of solid fuel combustion
- Explore variation in the constituents of coal and household air pollution between differing geographic locations.
- Explore the effect of stove design upon household air pollution.
- Present findings in a manner which can be meaningfully applied to ongoing epidemiological research in Xuanwei and Fuyuan

Study Population

Results of this exposure survey are intended to be assigned to another population (i.e. subjects in the ongoing case-control study), hence subject selection for the exposure survey was purposefully designed to mimic the population present in the case control study. For a household to be enrolled, there must be at least one female, between the ages of 20 and 60 residing there, who is primarily responsible for cooking and is in good health. The findings of this survey will be used to estimate previous exposure to fuel emissions for a period of up to several decades. Consequently, homes and stove types which could be reflective of those used historically were sought out and homes which were at least ten years old and contained stoves which had not been altered for at least the previous five years were preferentially enrolled. Due to the historical usage of firepits, any homes currently using firepits as their primary heating and cooking source were also preferentially enrolled. In order to explore geographic variation throughout Xuanwei and Fuyuan, subjects were enrolled from throughout both counties. In total, 30 villages were visited (15 from each county). The sampling goal was to enrol approximately 5 people from each village. Sampling took place during two time periods, August 2008 to February 2009 and March to June 2009. During the first sampling period 149 participants from all 30 villages were enrolled. During the second period, 16 of the original 30 villages were visited (8 from each county). Village selection during the second period was targeted towards those villages which best represented the overall population. During this second period, 15 new participants were enrolled and 53 subjects from the first period were re-sampled. In total, 163 subjects were enrolled. All study participants gave their written informed consent prior to being enrolled in the study and participation was voluntary. Ethical approval for this study was provided by the institutional review boards and the US National Cancer Institute and the China National Environmental Monitoring Centre. A map detailing the location of selected villages and the local coal mines and types is presented in Figure 3.

Data Collection

Each study participant completed a questionnaire which contained information relating to personal health, finances, marital history, historical fuel and stove use, employment, and

education. During each measurement period, participants also reported all of their fuel and stove usage. Participant's homes were measured and sketched. Pertinent features including stoves, doorways, stairways, windows and chimneys were documented. The details of sample analysis will be covered in the relevant thesis chapters, but briefly, sample collection was as follows: Fuel and ash samples were collected directly from the homes of study participants. In the case of coal samples, subjects would directly report whether they were using smoky or smokeless coal. They would also report which mine they purchased their coal from. This allowed for the smoky subtype to be characterised using the Chinese State Standard of coal classification.34 By examining the reported fuel usage by study participants, it was possible to establish which fuel(s) contributed to the collected ash. A variety of airborne samples were collected. All airborne contaminant measurements were collected over two consecutive 24 hours periods. Both personal and indoor measurements were collected. Personal measurements of particulate matter ($PM_{2.5}$) were taken by drawing air through a 37mm teflon filter mounted in a cyclone powered by a portable pump. The $PM_{2.5}$ measurements were analysed to provide $PM_{2.5}$ mass, particle bound PAHs, elemental and quartz composition, and black carbon measurements. Gaseous phase PAHs were collected through the use of XAD-2 sorbent tubes operated in parallel with the $PM_{2.5}$ measurements. The cyclone was attached near the breathing zone and overnight the sampling arrangement was placed by the study participant's bed. Indoor $PM_{2.5}$ measurements were also collected using the same equipment as for the personal measurements with devices placed approximately 1 - 2 metres from walls and stoves, as allowed by the size of the room. Passively diffusing OGAWA badges were also deployed to collect indoor measurements of NO_2 and SO_2 (results not presented in this thesis). Outdoor $PM_{2.5}$, NO_2 and SO_2 measurements were also collected at a central point in the village away from any obvious direct pollution sources. Outdoor measurements were collected using the same method detailed for indoor measurements. In addition, meteorological factors (temperature, humidity etc.) were recorded. All potential pollution sources (power plants, factories etc.) that may potentially contribute to outdoor air pollution within 5km of each village was documented. This information was gathered by asking inhabitants of each village of potential local sources and by driving through the area

Thesis outline

The findings of analysis performed upon coal samples collected from the homes of study participants will be presented in Chapter 2. In Chapter 3 we present the first of our findings of indoor and personal measurements with a presentation of $PM_{2.5}$ measurements. Indoor and personal measurements are further explored in Chapter 4 with a presentation of the findings of indoor and personal measurements of 16 priority PAHs and in Chapter 5 where we present the findings of quartz analysis, detailing the fate of quartz from coal to air and ash. As an appendix to this chapter we will present the findings of a small study further investigating quartz exposure and crystal morphology. The intersection between fuel emissions, human health and climate change will be explored in Chapter 6 where we present the findings of indoor, personal and outdoor black carbon measurements. Finally, in Chapter 7 we will provide a summary of the main findings of the previous chapters before entering into a general discussion of strengths, weaknesses and applications of the work presented in this thesis.

References

1. World Health Organization Fuel for Life: Household Energy And Health; World Health Organization: Geneva, 2006; .
2. Gordon, S. B.; Bruce, N. G.; Grigg, J.; Hibberd, P. L.; Kurmi, O. P.; Lam, K. H.; Mortimer, K.; Asante, K. P.; Balakrishnan, K.; Balmes, J.; Bar-Zeev, N.; Bates, M. N.; Breysse, P. N.; Buist, S.; Chen, Z.; Havens, D.; Jack, D.; Jindal, S.; Kan, H.; Mehta, S.; Moschovis, P.; Naeher, L.; Patel, A.; Perez-Padilla, R.; Pope, D.; Rylance, J.; Semple, S.; Martin, W. J. Respiratory risks from household air pollution in low and middle income countries. The Lancet Respiratory Medicine 2014.
3. World Health Organization Burden of disease from Household Air Pollution for 2012. http://www.who.int/phe/health_topics/outdoorair/databases/HAP_BoD_results_March2014.pdf (accessed 11/25/2014, 2014).
4. Horn, L.; Pao, W.; Johnson, D. H. In Chapter 89, Neoplasms of the Lung; Longo, D. L., Fauci, A. S., Kasper, D. L., Hauser, S. L., Jameson, L. and Loscalzo, J., Eds.; Harrison's Principles of Internal Medicine, 18th Edition; .
5. AnonymousGLOBOCAN Cancer Fact Sheets. http://globocan.iarc.fr/old/FactSheets/cancers/all-new.asp (accessed 11/13/2014, 2014).
6. Field, J. K.; Oudkerk, M.; Pedersen, J. H.; Duffy, S. W. Prospects for population screening and diagnosis of lung cancer. The Lancet 2013, 382, 732-741.
7. Wood, A. J. J.; Spira, A.; Ettinger, D. S. Multidisciplinary Management of Lung Cancer. N. Engl. J. Med. 2004, 350, 379-392.
8. Brenner, H.; Kloor, M.; Pox, C. P. Colorectal cancer. The Lancet 2014, 383, 1490-1502.
9. Doll, R.; Hill, A. B. The mortality of doctors in relation to their smoking habits; a preliminary report. Br. Med. J. 1954, 1, 1451-1455.
10. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 38, Tobacco Smoking. 1986.
11. Secretan, B.; Straif, K.; Baan, R.; Grosse, Y.; El Ghissassi, F.; Bouvard, V.; Benbrahim-Tallaa, L.; Guha, N.; Freeman, C.; Galichet, L.; Cogliano, V. A review of human carcinogens—Part E: tobacco, areca nut, alcohol, coal smoke, and salted fish. The Lancet Oncology 2009, 10, 1033-1034.
12. Sun, S.; Schiller, J. H.; Gazdar, A. F. Lung cancer in never smokers — a different disease. Nature Reviews Cancer 2007, 7, 778-790.
13. Couraud, S.; Zalcman, G.; Milleron, B.; Morin, F.; Souquet, P. J. Lung cancer in never smokers--a review. Eur. J. Cancer 2012, 48, 1299-1311.
14. Pallis, A. G.; Syrigos, K. N. Lung cancer in never smokers: disease characteristics and risk factors. Crit. Rev. Oncol. Hematol. 2013, 88, 494-503.
15. WHO Household air pollution and health. http://www.who.int/mediacentre/factsheets/fs292/en/ (accessed 12/3/2014, 2014).
16. IARC monographs on the evaluation of carcinogenic risks to humans. Volume 95, Household Use of Solid Fuels and High-temperature Frying. 2010.
17. Hosgood, H. D.,3rd; Boffetta, P.; Greenland, S.; Lee, Y. C.; McLaughlin, J.; Seow, A.; Duell, E. J.; Andrew, A. S.; Zaridze, D.; Szeszenia-Dabrowska, N.; Rudnai, P.; Lissowska, J.; Fabianova, E.; Mates, D.; Bencko, V.; Foretova, L.; Janout, V.; Morgenstern, H.; Rothman, N.; Hung, R. J.; Brennan, P.; Lan, Q. In-home coal and wood use and lung cancer risk: a pooled analysis of the International Lung Cancer Consortium. Environ. Health Perspect. 2010, 118, 1743-1747.
18. Hosgood, H. D.,3rd; Wei, H.; Sapkota, A.; Choudhury, I.; Bruce, N.; Smith, K. R.; Rothman, N.; Lan, Q. Household coal use and lung cancer: systematic review and meta-analysis of case-control studies, with an emphasis on geographic variation. Int. J. Epidemiol. 2011, 40, 719-728.
19. World Bank Rural population (% of total population). http://data.worldbank.org/indicator/SP.RUR.TOTL.ZS (accessed 11/13/2014, 2014).
20. Smith, K. R.; Mehta, S.; Maeusezahl-Feuz, M. In Indoor air pollution from household use of solid fuels; Ezzati, M., Lopez, A. D., Rodgers, A. and Murray, C. J. L., Eds.; Comparative

quantification of Health Risks: Global and Regional Burden of Disease due to Selected Major Risk Factors. World Healt Organization: Geneva, Switzerland, 2005; Vol. 2 of 3, .
21. Mumford, J. L.; He, X. Z.; Chapman, R. S.; Cao, S. R.; Harris, D. B.; Li, X. M.; Xian, Y. L.; Jiang, W. Z.; Xu, C. W.; Chuang, J. C. Lung cancer and indoor air pollution in Xuan Wei, China. Science 1987, 235, 217-220.
22. Editorial Committee for the Atlas of Cancer Mortality in the People's Republic of China Atlas of Cancer Mortality in the People's Republic of China; China Map Press: Shanghai, 1979; .
23. Tian, L.; Dai, S.; Wang, J.; Huang, Y.; Ho, S. C.; Zhou, Y.; Lucas, D.; Koshland, C. P. Nanoquartz in Late Permian C1 coal and the high incidence of female lung cancer in the Pearl River Origin area: a retrospective cohort study. BMC Public Health 2008, 8, 398.
24. Mumford, J. L.; Chapman, R. S.; Harris, D. B.; He, X. Z.; Cao, S. R.; Xian, Y. L.; Li, X. M. Indoor air exposure to coal and wood combustion emissions associated with a high lung cancer rate in Xuan Wei, China. Environ. Int. 1989, 15, 315-320.
25. Chapman, R. S.; Mumford, J. L.; Harris, D. B.; He, Z. Z.; Jiang, W. Z.; Yang, R. D. The epidemiology of lung cancer in Xuan Wei, China: current progress, issues, and research strategies. Arch. Environ. Health 1988, 43, 180-185.
26. He, X. Z.; Chen, W.; Liu, Z. Y.; Chapman, 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 Perspect. 1991, 94, 9-13.
27. Lan, Q.; Chen, W.; Chen, H.; He, X. Z. Risk factors for lung cancer in non-smokers in Xuanwei County of China. Biomed. Environ. Sci. 1993, 6, 112-118.
28. Barone-Adesi, F.; Chapman, R. S.; Silverman, D. T.; He, X.; Hu, W.; Vermeulen, R.; Ning, B.; Fraumeni, J. F.,Jr; Rothman, N.; Lan, Q. Risk of lung cancer associated with domestic use of coal in Xuanwei, China: retrospective cohort study. BMJ 2012, 345, e5414.
29. 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.
30. Hosgood, H. D.,3rd; Chapman, R.; Shen, M.; Blair, A.; Chen, E.; Zheng, T.; Lee, K. M.; He, X.; Lan, Q. Portable stove use is associated with lower lung cancer mortality risk in lifetime smoky coal users. Br. J. Cancer 2008, 99, 1934-1939.
31. Lan, Q.; He, X.; Shen, M.; Tian, L.; Liu, L. Z.; Lai, H.; Chen, W.; Berndt, S. I.; Hosgood, H. D.; Lee, K. M.; Zheng, T.; Blair, A.; Chapman, R. S. Variation in lung cancer risk by smoky coal subtype in Xuanwei, China. Int. J. Cancer 2008, 123, 2164-2169.
32. Sahney, S.; Benton, M. J. Recovery from the most profound mass extinction of all time. Proc. Biol. Sci. 2008, 275, 759-765.
33. Retallack, G.,J; Veevers, J.,J; Morante, R. Global coal gap between Permian-Triassic extinction and Middle Triassic recovery of pear-forming plants. Geol. Soc. Am. Bull. 1996, 108.
34. Chen, P. Study on integrated classification system for Chinese coal. Fuel Process Technol 2000, 62, 77-87.
35. Tian, L. Coal Combustion Emissions and Lung Cancer in Xuan Wei, China (PhD dissertation), University of California, Berkeley, California, 2005.
36. Tian, L.; Lan, Q.; Yang, D.; He, X.; Yu, I. T. S.; Hammond, S. K. Effect of chimneys on indoor air concentrations of PM10 and benzo[a]pyrene in Xuan Wei, China. Atmos. Environ. 2009, 43, 3352-3355.
37. Lan, Q.; He, X.; Costa, D. J.; Tian, L.; Rothman, N.; Hu, G.; Mumford, J. L. Indoor coal combustion emissions, GSTM1 and GSTT1 genotypes, and lung cancer risk: a case-control study in Xuan Wei, China. Cancer Epidemiol. Biomarkers Prev. 2000, 9, 605-608.
38. Lan, Q.; He, X. Molecular epidemiological studies on the relationship between indoor coal burning and lung cancer in Xuan Wei, China. Toxicology 2004, 198, 301-305.
39. DeMarini, D. M.; Landi, S.; Tian, D.; Hanley, N. M.; Li, X.; Hu, F.; Roop, B. C.; Mass, M. J.; Keohavong, P.; Gao, W.; Olivier, M.; Hainaut, P.; Mumford, J. L. Lung tumor KRAS and TP53 mutations in nonsmokers reflect exposure to PAH-rich coal combustion emissions. Cancer Res. 2001, 61, 6679-6681.

40. Large, D. J.; Kelly, S.; Spiro, B.; Tian, L.; Shao, L.; Finkelman, R.; Zhang, M.; Somerfield, C.; Plint, S.; Ali, Y.; Zhou, Y. Silica-volatile interaction and the geological cause of the Xuan Wei lung cancer epidemic. Environ. Sci. Technol. 2009, 43, 9016-9021.
41. Li, G. J.; Huang, Y. C.; Tian, L. W.; Liu, Y. J.; Guo, L.; Xiao, Y. Z.; Hou, W. J.; Yang, K.; Chen, Y.; Zhao, G. Q.; Lei, Y. J. Relationship between high incidence of lung cancer among non-smoking women and silica in C1 bituminous coal in Xuanwei, Yunnan Province, China [article in Chinese]. Zhonghua Lao Dong Wei Sheng Zhi Ye Bing Za Zhi 2013, 31, 30 - 6.
42. Straif, K.; Benbrahim-Tallaa, L.; Baan, R.; Grosse, Y.; Secretan, B.; El Ghissassi, F.; Bouvard, V.; Guha, N.; Freeman, C.; Galichet, L.; Cogliano, V. A review of human carcinogens - Part C: metals, arsenic, dusts, and fibres. Lancet Oncol. 2009, 10, 453-454.
43. He, J.; Cai, Y.; Lv, J.; Zhang, L. Primary investigation of quartz as a possible carcinogen in coals of Xuanwei and Fuyuan, high lung cancer incidence area in China. Environmental Earth Sciences 2012;, 67, 1679 - 1684.
44. Zhang, L.; Lv, J.; Sun, S. Elements in Lung Tissues of Patients from a High Lung Cancer Incidence Area of China. Biol. Trace Elem. Res. 2012, 148, 7-10.

Chapter 2

Heterogeneity in coal composition and implications for lung cancer risk in Xuanwei and Fuyuan counties, China.

George Downward
Wei Hu
David Large
Harry Veld
Jun Xu
Boris Reiss
Guoping Wu
Fusheng Wei
Robert S. Chapman
Nat Rothman
Lan Qing
Roel Vermeulen

(Environment International 2014, 68, July, 94-104)

Abstract

Background:

Xuanwei and Fuyuan Counties in Yunnan Province, China have among the highest lung cancer rates in the country. This has been associated with the domestic combustion of bituminous coal (referred to as "smoky" coal). Additionally, significant geographical variation in cancer rates among smoky coal users has been observed, suggesting heterogeneity in fuel source composition and/or combustion characteristics. Research thus far has indicated that smoky coal emits high levels of polycyclic aromatic hydrocarbons (PAHs) and contains high concentrations of fine grained crystalline quartz, however, much of this research is limited in terms of samples size and geographic scope. In order to more fully characterize geochemical and elemental composition of smoky and smokeless coal use in Xuanwei and Fuyuan, we carried out a large exposure assessment study in households in this region.

Methods:

Fuel samples representing smoky and "smokeless" (anthracite, the major alternative coal type in the region) coals were collected from 137 homes in Xuanwei and Fuyuan. Rock-eval, Leco-CS, XRF analysis and electron microscopy was used to establish hydrocarbon content (to represent volatile organic compounds), major and trace element composition and mineral composition respectively. Heterogeneity in coal characteristics between and within coal types was assessed by the Kruskal-Wallis test.

Results:

145 coal samples (116 smoky and 29 smokeless coal) were analysed. Statistically significant differences between smoky and smokeless coal with regard to hydrocarbon content, sulfur, trace elements and mineral composition were observed. Of note, smoky coal contained between 5 and 15 times the amount of volatile organic matter and twice the amount of quartz (including respirable quartz) than smokeless coal. Smoky coal generally had lower levels of trace elements (plus aluminium) than smokeless coal. Significant variation was also observed between smoky coal samples from different geographical areas with regard to hydrocarbon content and elemental composition (including aluminium and silicon).

Discussion:

This paper has identified compositional differences between and within smoky and smokeless coals sourced from Xuanwei and Fuyuan counties. A decreased ratio of aluminium to silicon in smoky coal suggests elevated free silica, a finding consistent with observed higher levels of quartz. Elevated volatile organic matter content in smoky coal (when compared to smokeless coal) is consistent with the geochemical expectations for smoky and smokeless coals. These findings also reflect previous observations of elevated volatile compound emissions (notably PAH's) from smoky coal in the area. The observed heterogeneity in coal composition between and within coal types may provide leads to the observed heterogeneity in cancer risk observed in this area.

Introduction

Xuanwei and its neighbouring county of Fuyuan, located in Yunnan Province, China, have some of the highest lung cancer rates in the nation among both males and females, irrespective of smoking status,[1-3] Previous research has linked this excess lung cancer rate with the domestic combustion of "smoky coal".[4,5] The term smoky coal refers to the locally available Late Permian bituminous coal,[6,7] referred to as “smoky” because of the large amounts of visible smoke released upon combustion. Coal is the primary fuel source for cooking and heating for residents in Xuanwei and Fuyuan and is available from many coal mines throughout the region. The majority of coal mines in the region produce bituminous coal while a small number produce anthracite coal (originating in the Carboniferous period[7] and referred to as "smokeless coal"), which is associated with a relatively lower cancer risk. For clarity, and consistency with previously published research related to lung cancer in Xuanwei and Fuyuan, we shall refer to these coals as smoky and smokeless, using the term “type” to differentiate between them.

The lung cancer rate among those who routinely use smoky coal has shown considerable heterogeneity between geographic locations.[5,8] This likely reflects different styles of coal preparation (such as making coal briquettes, or packing coal dust with local clay/soil) and/or compositional differences in coal between geographic sources. These compositional differences, which may in turn reflect geological differences in coalification or depositional environment, are indicated also by the sub categorization of smoky coal by the State Standard of China Coal Classification[9] into: coking coal, 1/3 coking coal, gas fat coal and meagre lean coal. The factors which drive this sub-categorization are the combination of the degree of coalification (which is measured as the dry ash free volatile matter - V_{daf}) and the caking property of the coal (represented as a combination of the caking index, the maximum thickness of the plastic layer and the Audibert-Arnu dilation - see Table 1).[9]

Research on coal samples collected from mines has indicated that smoky coal contains high amounts of quartz (classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans[10]) when compared to locally sourced anthracite coal and bituminous coal sourced from other areas in China and from the USA.[6,7,11] However, much of this previous research has been restricted to small sample sizes and has focussed upon the region in Xuanwei with the highest lung cancer rate (i.e. Laibin commune) with very limited comparison to alternative fuel types (e.g. smokeless coal), making it unsuitable for examination of heterogeneity in lung cancer rates and coal composition. A further limitation of analysing fuel collected directly from coal mines is that it may not accurately

Table 1 - Characteristics of smoky coal subtypes

Coal sub-type	V_{daf} (%)	Caking Index	Maximum thickness of plastic layer (mm)	Audibert-Arnu dilatation (%)
Coking coal	17.87	73	10	-1
1/3 Coking Coal	30.16	75	13	22
Gas-fat Coal	44.27	100	36	246
Meagre-lean Coal	16.14	16	4	N/A

V_{daf} :dry ash free volatile matter
Maximum thickness of plastic layer: A representation of coal rank and petrographic composition
Audibert-Arnu dilatation: A measure of expansion and contraction characteristics of coal

represent the fuel to which residents are exposed if modifications are made by residents prior to combustion, for example by making mixtures of coal and clay in order to conserve fuel by extending its burning life. Research focusing upon the combustion products of smoky coal have revealed that smoky coal (when compared to smokeless coal) emits relatively high amounts of particulate matter, nanomaterials[12] and organic compounds, specifically polycyclic aromatic hydrocarbons (PAHs), most notably Benzo[a]Pyrene (BaP)[1], classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans.[13]

This paper presents the results of the largest analysis to date of coal samples collected directly from homes of residents of Xuanwei and Fuyuan counties. The objective of this paper is to catalogue the geochemical and elemental composition of the smoky and smokeless coal that is currently used by the populations of Xuanwei and Fuyuan. Emphasis is placed upon differences between smoky and smokeless coal as well as geographic variation in the composition of smoky coal.

Methods

Study design

This paper forms part of a large lung cancer case-control and cross-sectional molecular epidemiology study aimed at comprehensively cataloguing the constituents and associated burning products of solid fuels used in the Xuanwei and Fuyuan counties, and ultimately linking those constituents to specific lung cancer risks. 30 villages were selected from Xuanwei and Fuyuan (15 from each). Villages were selected to provide a representative overview of the local population and a variety of coal sources. Approximately five households were selected from each village. Selection was intended to represent the case-control study population in regards to both age and gender (all participants in the case-control study are female) as well as the typical variety of living arrangements, stove types and ventilation characteristics. The selection criteria for households were:

- At least one female between the ages of 20 and 60 residing there at the time of the study
- Stove type and configuration not changed for at least the past five years
- The house is at least ten years old.

One eligible female in each household was enrolled for personal monitoring of airborne pollutants and provided biographical information (including medical histories), biological samples (blood, sputum, urine etc.) and logged their activities during the monitoring periods. Data was collected over 2 time periods - the first being from August 2008 to February 2009 and the second being from March to June 2009. In the first time period, 149 participants, from all 30 villages were recruited. In the second, 16 of the initial 30 villages were re-visited. Villages were selected for revisiting such that a representative set of the overall fuel usage in Xuanwei and Fuyuan was represented. 53 subjects were re-sampled and 15 new subjects were recruited. During each visit, indoor and outdoor air pollution was measured and questionnaires covering personal activities and fuel usage during each measurement period were collected. Participants who reported the use of coal were also asked whether it was smoky or smokeless coal, and the mine from which it came (residents will typically purchase their coal in bulk once or twice a year). Smoky coal subtypes were established by matching the reported mines to their official coal classification as defined by

the State Standard of China Coal Classification (coking coal, 1/3 coking coal, gas fat coal or meagre lean coal[9]).

Fuel Sample collection

Fuel samples were collected from the homes of study participants. The type of fuel used (e.g. coal, wood) was recorded and, if applicable, the type (smoky/smokeless), and source of coal were recorded. 275 fuel samples were collected in total, 195 coal based samples, 64 wood and 16 "other" plant products (corn cobs, bamboo and/or tobacco stems). The coal based samples comprised solid coal, fragmented coal and manufactured coal briquettes. Only solid and fragmented coal samples were analysed for this paper. Participants did not differentiate between solid and fragmented samples and would refer to them both as “coal”. Manufactured briquettes (n=18) were not analysed as we could not determine the origin of the coal. The total number of coal samples (solid and fragmented) analysed was 177.

Coal sample selection for analysis

Of the 177 coal samples, 137 were from unique homes. 40 homes provided 2 coal samples, 31 of which were duplicate with regards to coal type and visitation period to those already collected from their respective homes and were not analysed. Of the remaining 9 homes, 2 reported burning 2 different types of coal and 7 provided coal samples during both the first and second data collection periods (4 used the same coal type during each period while the remaining 3 had changed coal types). In these cases all coal samples were analysed. The total number of samples analysed was 146.

Samples were analysed to assess the bulk organic geochemical composition, carbon and sulfur content and major and trace element composition.

Bulk organic geochemical analysis

The bulk organic geochemical analysis (Rock Eval), indicating hydrocarbon generation in an inert atmosphere at 300 degrees Celsius (S1), hydrocarbon generation during a programmed pyrolysis from 300 to 650 degrees Celsius at a heating rate of 25 degrees Celsius per minute (S2) and the temperature at which maximal hydrocarbon generation (Tmax) occurs was carried out via standard Rock-Eval VI process [14]. Coal samples were finely ground under constant pressure using a Herzog HM grinding machine but were otherwise analysed as received. S1 and S2 were used to broadly approximate volatile organic compounds and cracked hydrocarbons, respectively and were measured in milligrams of hydrocarbon per gram of coal (mg HC/g coal). Tmax was measured in degrees Celsius.

Carbon-Sulfur analysis

Total carbon and sulfur are measured with a LECO SC 632 using finely ground coal samples in an as received state. The total carbon content was analysed by means of total combustion of 0.1 grams of each sample at 1350 degrees Celsius and subsequently measuring the CO_2 and SO_2 release by means of an infra-red detector. The amount of CO_2 and SO_2 is calibrated with a pure calcite and Ag_2SO_4 standard, respectively. For accuracy, in-house geological standards are measured every 10 samples. The total inorganic carbon content is determined by a second analysis on a sample from which the organic carbon is removed by heating the material at 550 degrees Celsius. The total organic carbon content is calculated as the difference between the total carbon content and the total inorganic carbon content.

Ash Yield

Ash was obtained from a standard thermogravimetric analysis (TGA) using a temperature program from 105 to 1000 degrees Celsius. The ash yield is displayed as a percentage of each coal specimen.

Elemental Composition

Elemental composition was established through X-ray fluorescence (XRF) on glass beads prepared from the dry ash obtained as detailed above. Results of XRF analysis were corrected for the loss of ignition (LOI) after adjustment for moisture. In order to fully explore constitutional differences between smoky and smokeless coal a wide range of elements were measured. These were: Silicon (Si), Aluminium (Al) Titanium (Ti), Iron (Fe), Manganese (Mn), Calcium (Ca), Magnesium (Mg), Sodium (Na) Potassium (K), Phosphorus (P), Chromium (Cr), Nickel (Ni), Strontium (Sr), Barium (Ba) and Zirconium (Zr). Elements were initially reported as a percentage of coal when bound to oxygen (i.e. SiO_2). Levels of the individual elements were calculated using their respective atomic masses and converted to parts per million (ppm).

Quartz content (as a percentage of coal) was estimated by use of the following formula:[7]

Estimated Quartz = $(SiO_2)_{total} - 1.5 \times Al_2O_3$

Mineralogical analysis

25 coal samples, (approximately one per village), representing 19 smoky coals (11 from Xuanwei, 8 from Fuyuan) and 6 smokeless coals (2 from Xuanwei and 4 from Fuyuan) underwent scanning electron microscopy (SEM) to assess quartz and other mineral content of the coal samples. The physical size of quartz grains were measured and grains less than 9.6 micrometers were considered to be part of the "respirable fraction" (of a size that, if inhaled, could theoretically reach the end alveoli[15]). Results are presented as a percentage (%) of measured coal. Crystal structure was not included in analysis.

Quality assurance

Reliability of results in the full dataset was established by in-house testing of ISE921 standard reference samples. This indicated consistent functioning of the analytical devices. A subsample of the coal samples (n=7 [5%] – 5 smoky and 2 smokeless) was also re-analysed, showing consistency of measurements for all tests.

Statistical Analysis

Normal probability plots indicated that the results of the Rock Eval evaluation, carbon-sulfur analysis and SEM were not normally or log-normally distributed. The results of XRF analysis showed a log-normal distribution. Descriptive statistics are presented as medians. Wilcoxon-ranked tests were performed to assess differences between smoky and smokeless coals and Kruskal-Wallis tests were performed to assess for heterogeneity between and within designated smoky coal sub-types. Variation within smoky coal sub-types was assessed by specifying the coal mine that each coal sample was sourced from and assessing for variation between those coal mines. In testing for variation between coal types and sources, only coal types which were consistent with their reported region were included (n=140 [96%]). Where possible, results were broadly compared to equivalent average values for coals from throughout China and the USA[11,16] (see Table 2).

Within the XRF results, multi-correlate testing and exploratory factor analysis were carried out on the log-transformed values to identify underlying latent structures. Factor analysis

was performed with varimax rotation. Factors with eigenvalues greater than one were retained. Individual variables with loading values of greater than 0.5 were considered to significantly contribute to that factor. Identified factors underwent further Kruskal-Wallis testing to assess variation in the latent structures between coal sources.

The primary focus of this paper is to assess the constituents of the whole coal samples as this is what is used by the inhabitants of Xuanwei and Fuyuan. However, to ensure that the ash yield of the coal samples was not contributing to any observed differences between coal samples (for example, if a coal specimen contained a relatively high ash yield then that may result in an under-reporting of the other coal constituents), statistical testing was repeated following standardising for ash yield (i.e. measurements per unit ash).

In all statistical tests, a p value of less that 0.05 was used to indicate statistical significance. Statistical testing was carried out in R version 2.14,[17] utilising the Hmisc, reshape2, lattice and corrgram packages.[18-21]

Table 2 - Average Carbon, Sulfur and Trace element levels for coals from USA and China[11,16]

	USA coals	China coals
Total Carbon (%)	70	-
Sulfur (%)	2.2	-
Si	23,900	39,700
Al	14,110	32,000
Ti	796	2,218
Fe	15,103	40,400
Mn	33	124
Ca	2,637	10,000
Mg	632	1,500
Na	377	1,320
K	1,847	1,742
P	203	410
Cr	16	15
Ni	17	14
Sr	109	140
Ba	101	159
Zr	23	89
Zn	72	42
Pb	11	15
Co	7	7
Cu	17	18

Unless specified otherwise, values are in ppm

Results

Overview

146 coal samples were analysed. One sample was excluded after analysis revealed highly spurious results, indicative of analytical failure. Of the samples retained for analysis, 72 were from Xuanwei and 73 were from Fuyuan county, of which 68 Xuanwei samples and 66 Fuyuan samples could be matched to specific coal mines. In Xuanwei, all identified smoky coal mines were of the coking subtype (i.e. Azhi, Baoshan, Laibin, Tangtang and Yangchang). In Xuanwei, there is a region which historically produced smokeless coal (although now many residents burn wood as their primary solid fuel), referred to as "RSXZ" which is an amalgamation of the ReShui and XiZe areas. Fuyuan mines produce a variety of smoky coal subtypes. Coking coal is produced by the Daping, Enhong, Haidan and Zude mines. Bagong and Dahe produce 1/3 coking coal, Housuo and Qingyun produce gas fat coal and Gumu produces meagre lean coal. There is one smokeless coal mine in Fuyuan called LaoChang. The geographical positions of these mines and their corresponding coal types are shown in Figure 1.

Coal Reclassification

Coal subtypes (smoky or smokeless) were reported by the study participants. This reporting gave 26 smokeless, 114 smoky and 5 unspecified coal types. Rock Eval analysis indicated that the "Tmax" measurement showed a clear demarcation of coals into two groups, one above and the other below a Tmax value of 510 degrees. This demarcation predicted 107 of the 114 (94%) coals designated smoky and 22 of the 26 (85%) coals designated smokeless and indicated that all of the unspecified coals were of the smoky coal variety. Based on this clear demarcation, and the consistency with other reported Tmax values for equivalent coals from other sources [22], coals were reclassified as smoky or smokeless on the basis of their Tmax measurement. In order to ensure that results were not unduly influenced by this imputation, all statistical analyses were re-performed using only coal samples which matched with their original reported sub-type (n=129). Results were consistent with those presented here (Tables S4 and S5 in the supplement).

Ash Yield

Analysis of ash yield (Table 3) revealed variation between the smoky coal subtypes sourced from Fuyuan, but no significant difference between smoky and smokeless coal or within designated smoky coal subtypes. The median ash yield for all coal samples was 32%, which is the same as the median ash yield for both smoky and smokeless coal. Some variation was observed in the median values within smoky coal subtypes, for example, ash yield within Fuyuan coking coals ranged from 23% to 51% and within Xuanwei coking coals from 23% to 36%, however this difference did not reach statistical significance.

Rock Eval analysis

Rock Eval analysis revealed several (expected) differences between smoky and smokeless coals (Table 3). As stated, smokeless coal has a significantly higher Tmax than smoky coal (median value 581°C vs. 460°C respectively, $p<0.001$). The median values for S1 and S2 in smoky coal (2.15mgHC/g coal and 71.5mgHC/g coal respectively) are significantly higher (by up to a factor of 10) than those for smokeless coal (0.29mgHC/g coal and 8.39mgHC/g coal, $p<0.001$). On investigating for geo-spatial variation, we observe that there is significant variation among the five coal mines in Xuanwei designated "coking coal" in the

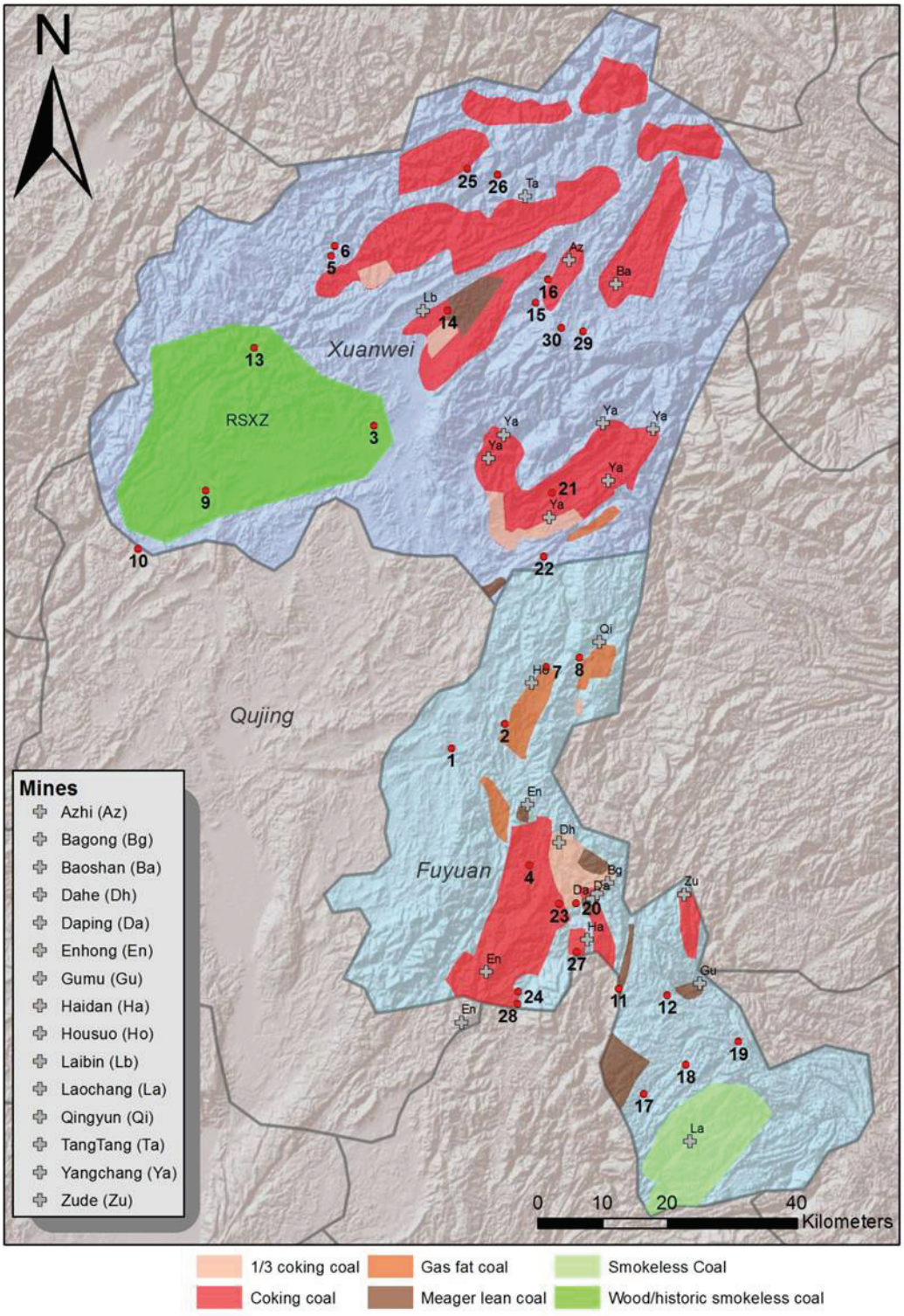

Figure 1:Map of Xuanwei and Fuyuan counties showing approximate locations of study villages, reported coal mines and coal sub-types

Villages enrolled in the study are marked numerically 1 to 30

Mine locations indicate functioning mine entrances, therefore, some mines may be indicated more than once.

Only mines reported by study participants are indicated.

values of Tmax (ranging from 443 to 463 degrees Celsius), S1 (1.62 - 4.03mgHC/g coal) and S2 (61.59 - 138.69mgHC/g coal). In Fuyuan, significant variation between the four smoky coal subtypes produced in the region for the values of S2 (43.96 - 131.87mgHC/g coal) and Tmax (433 - 467 degrees Celsius) was observed. Within the two coal mines producing 1/3 coking coal, a significant difference between the Tmax scores was observed (445 vs. 465 degrees Celsius). Significant variation between the two smokeless coal areas was observed for the S2 measurement (6.49 vs. 9.47mgHC/g coal). Standardizing values by ash yield (Table S6 in the supplement) did not alter the relative differences between smoky and smokeless coal.

Carbon-Sulfur

Carbon-sulfur analysis revealed internal variation within coal types (Table 3). The median values for total (59.4%), organic (58.8%) and inorganic carbon (0.5%) for smoky coal are slightly higher than those for smokeless coal (57.4%, 56.9% and 0.3% respectively), although these differences are not statistically significant. The median value for sulfur in smoky coal (0.2%) is significantly lower than that of smokeless coal (1.0%, $p<0.001$). On investigation for geo-spatial variation, statistically significant variation within the Xuanwei coking coals for total (range 55.76-70.12%), inorganic (0.19-0.92%) and organic (54.17-69.77%) carbon was observed. In Fuyuan, significant variation between smoky coal subtypes for total (50.83-64.34%), inorganic (0.2-1.4%) and organic carbon (53.3-63.7%) was observed. A significant difference between the two 1/3 coking coal regions in Fuyuan was observed for sulfur content (1.88 vs. 0.16%). In the smokeless coal samples there was significant variation between the two smokeless coal producing mines for total (57.41 vs. 46.17%) and organic (45.81 vs. 57.33%) carbon and sulfur (1.03 vs. 2.83%). Both smoky and smokeless coal have lower levels of total carbon and sulfur than the general USA and China coal values (Table 3). Adjusting for ash yield (Table S6 in the supplement) results in the loss of the previously observed statistically significant variation within Xuanwei coals and Fuyuan coking coals (implying that the ash free coal components have similar carbon contents).

Elemental composition

XRF revealed multiple differences between smoky and smokeless coal (Table 4). Median values of silicon for smoky (92,100 ppm) and smokeless (84,000 ppm) coal were both higher than that observed for China in general (39,700 ppm) and the USA (23,900 ppm). While the median level of silicon among smoky coal was observed to be higher than smokeless, this difference did not reach statistical significance ($p=0.21$).

In general, smoky coal was observed to have lower levels of trace and major elements than smokeless coal. Elements for which smoky coal had significantly lower levels were: Al (19,750ppm vs. 43,800ppm, $p<0.001$), Ti (1,400ppmvs. 5,100ppm, $p<0.001$), Na (200ppm vs. 600ppm, $p<0.001$), K (700ppm vs. 4,100ppm, $p<0.001$), P (100ppmvs. 300ppm $p<0.01$), Cr (20.4ppm vs. 35.1ppm, $p<0.01$), Ba (36.8ppm vs. 108.8ppm, $p<0.001$) and Zr (66.5ppm vs.156.7ppm, $p<0.01$).

On investigating for geospatial variation, we observed significant variation within the coking coal subtype in Xuanwei for Si, Fe, Mn, Ca, Mg, Na, Cr, Ni, and Sr. Among the Fuyuan coals, significant variation between the three smoky coal subtypes for Al, Ti, Fe, Mn, Ca, Mg, Na, K, P, Cr, Ni, Sr, Ba and Zr was observed. Variation was also observed within coals sourced from Fuyuan among: the coking coal regions for Na; the 1/3 coking

Table 3 - Geochemical analysis, Carbon sulfur content and Ash Yield, stratified by fuel type and source (median values)

Major Coal Type	County	Coal Sup-type	Coal Mine	N	S1 (mgHC/g coal)	S2 (mgHC/g coal)	Tmax (°C)	Total Carbon (%)	Inorganic Carbon (%)	Organic Carbon (%)	Total Sulfur (%)	Ash Yield (%)
Smoky				**116**	**2.15†**	**71. 5†**	**460†**	**59.39**	**0.5**	**58.81**	**0.24†**	**32**
	Xuanwei			*65*	*2.35*	*73.24*	*462*	*60.76*	*0.53*	*60.46*	*0.2*	32
		Coking Coal		63	2.34*	73.24*	462*	60.76*	0.52*	60.46*	0.2	33
			Azhi	15	2.52	75.62	462	65.53	0.92	64.6	0.23	30
			Baoshan	5	2.24	61.59	463	57.3	0.64	54.17	0.18	37
			Laibin	14	2.23	76.14	459.5	55.76	0.57	54.97	0.28	35
			Tangtang	22	1.62	61.98	464	55.7	0.19	55.22	0.18	38
			Yangchang	7	4.03	138.69	443	70.12	0.32	69.77	0.19	23
	Fuyuan			*51*	*1.95*	*68.86‡*	*452‡*	*57.28‡*	*0.43‡*	*55.79‡*	*0.34*	*29‡*
		Coking Coal		15	1.89	43.96	467	50.83	1.8	46.42	0.24	36
			Daping	4	2.34	33.9	458.5	43.58	0.8	42.74	0.29	40
			Enhong	4	1.73	40.53	469.5	50.23	5.56	42.26	0.74	51
			Haidan	6	1.78	46.75	468	46.29	3.01	43.28	0.19	32
			Zude	1	4.21	61.02	473	64.15	0.4	63.75	0.87	23
		1/3 Coking		8	1.98	52.35	459*	54.33	0.34	53.67	0.36*	29
			Bagong	5	1.7	47.19	465	53.32	0.13	52.14	1.88	29
			Dahe	3	3.08	80.18	445	65.46	0.43	64.89	0.16	25
		Gas Fat		23	1.97	131.87	433	64.34	0.2	63.7	0.39	24
			Housuo	20	2.03	138.44	433.5	63.98	0.24	63.6	0.4	25
			Qingyun	3	1.62	110.4	431	65.88	0.12	65.83	0.29	29
		Meagre Lean	Gumu	1	3.83	53.43	469	54.7	1.4	53.3	0.53	47
Smokeless				**29**	**0.29**	**8.39***	**581**	**57.41***	**0.3**	**56.92***	**1.03***	**32**
	Fuyuan		*LaoChang*	*19*	*0.28*	*9.47*	*571*	*57.41*	*0.22*	*57.33*	*1.03*	31
	Xuanwei		*RSXZ*	*5*	*0.29*	*6.49*	*572*	*46.17*	*0.15*	*45.81*	*2.83*	41

† : Statistically significant variation between smoky & smokeless coal types
‡ : Significant variation within smoky coal subtypes for that region
* : Significant variation between mines within that coal type in that region
S1: mg of hydrocarbons (per gram of coal) released under controlled burning at 300°C.
S2 : mg of hydrocarbons (per gram of coal) released during maximal release of hydrocarbons under controlled burning.
Tmax: temperature at which S2 occurs
Italics indicates overall value for each county

Table 4- Elemental composition (in parts per million) of coal samples, stratified by fuel type and source (median values)

Major Coal Type	County	Coal Sub-type	Coal Mine	N	Si	Al	Ti	Fe	Mn	Ca	Mg	Na	K	P	Cr	Ni	Sr	Ba	Zr
Smoky				**116**	**92,100**	**19,750†**	**1,400†**	**18,400**	**200**	**8,400**	**1,700†**	**200†**	**700†**	**100†**	**20†**	**29**	**53**	**37†**	**66†**
	Xuanwei			*65*	*102,100*	*16,600*	*1,000*	*19,100*	*500*	*14,400*	*1,800*	*200*	*500*	*100*	*15*	*29*	*45*	*28*	*45*
		Coking Coal		63	102,300*	16900	1000	19,100*	400*	13,000*	1,800*	200*	600	100	15*	29*	45*	29	45
			Azhi	15	80,800	13,000	600	10,300	700	27,900	1,500	200	400	100	8	22	83	25	32
			Baoshan	5	99,100	25,300	1,100	14,000	400	12,800	1,400	200	500	100	12	25	39	25	93
			Laibin	14	115,050	16,200	850	27,700	600	17,900	1,850	200	400	100	14	33	42	28	41
			Tangtang	22	115,750	22,500	1,750	27,800	200	3,950	2,050	250	1,100	100	32	34	31	35	71
			Yangchang	7	72,800	13,200	1,000	6,400	200	7,200	1,000	200	400	100	11	18	80	38	37
	Fuyuan			*51*	*85,100*	*30,400‡*	*3800‡*	*18,100‡*	*200‡*	*5,500‡*	*1,400‡*	*300‡*	*1,700‡*	*300‡*	*37‡*	*29‡*	*59‡*	*95‡*	*141‡*
		Coking Coal		15	121,100	49,700	7,400	30,200	300	8,600	3,200	1,100*	3,900	600	50	43	94	240	200
			Daping	4	112,100	54,050	7,950	34,750	250	9,550	2,850	750	4,900	850	64	39	95	215	218
			Enhong	4	97,650	41,650	6,700	27,900	300	10,750	5,150	850	2,950	450	60	35	108	207	191
			Haidan	6	121,150	55,000	10,500	30,850	400	5,100	3,000	1,350	5,100	750	60	48	92	418	276
			Zude	1	57,100	40,500	5,000	16,300	100	8,600	2,500	400	3,600	300	41	30	97	88	152
		1/3 Coking		8	79,750	41,550	5,850	27,900*	200	3,650*	800	300	1,700	250	60*	27	52*	95	208
			Bagong	5	79,800	43,900	6,500	36,100	200	1,000	600	300	1,700	300	63	26	36	95	238
			Dahe	3	79,700	22,000	1,700	5,900	200	8,200	900	200	1,200	200	14	28	83	95	73
		Gas Fat		23	77,100	14,900	900	12,500	0	2,400*	1,000	200	200	100	13	22	16*	29	46
			Housuo	20	79,000	13,600	950	12,200	0	2,600	850	200	250	100	13	23	24	28	45
			Qingyun	3	54,200	18,100	900	19,600	0	400	1,200	200	200	100	12	22	10	33	50
		Meagre Lean	Gumu	1	87,400	51,000	5,400	19,400	300	18,900	3,900	500	4,900	400	41	28	99	115	174
Smokeless				**29**	**84,000**	**43,800***	**5,100***	**22,100***	**200**	**7,800**	**2,000***	**600**	**4,100***	**300**	**35***	**25***	**69**	**109***	**157***
	Fuyuan		*LaoChang*	*19*	*85,700*	*36,800*	*4,700*	*17,700*	*200*	*7,800*	*2,500*	*700*	*4,900*	*300*	*29*	*22*	*74*	*130*	*148*
	Xuanwei		*RSXZ*	*5*	*77,900*	*71,000*	*7,500*	*47,500*	*200*	*6,000*	*1,400*	*300*	*2,500*	*300*	*75*	*31*	*19*	*65*	*223*

†: Statistically significant variation between smoky & smokeless coal types
‡ :Statistically significant variation within that smoky coal subtypes for that region
* :Statistically significant variation between mines within that coal type in that region
Italics indicates overall value for each county

regions for Fe, Ca, Cr and Sr; and among the gas fat regions for Ca and Sr. Significant variation between the two smokeless coal producing regions was observed for Al, Ti, Fe, Mg, K, Cr, Ni, Ba and Zr. Adjusting for ash yield (Table S7 in supplement) resulted in some loss of the previously observed statistically significant variation within some of the smoky coal subtypes. Of note, the significant variation on Si levels within Xuanwei coking coals was lost. However, in general the observed differences between smoky and smokeless coal remains largely unchanged.

Estimated quartz content, based on the aluminium and silica content, revealed that smoky coal had a significantly higher proportion of estimated quartz than smokeless coal (median value 11% versus 5.8%, $p<0.001$). Significant variation within the Xuanwei coking coals, ranging from 9.6% for coals from Yangchang to 17.5% for coals from Tangtang, was observed ($p<0.05$). A significant difference in estimated quartz between the two smokeless coal producing mines was also observed with coal from LaoChang containing 6.5% estimated quartz and coal from RSXZ containing 0% estimated quartz, $p<0.001$.

The results of factor analysis are presented in Table 5. Three factors were identified in smoky coal which together accounted for 77% of the observed variance. The first factor consisted of Al, Ti, Na, K, P, Cr, Ni, Ba and Zr, a combination suggesting that this factor represents lithophile elements. The second factor consisted of Mn, Ca, and Sr, which suggested that this factor might reflect carbonate. The third factor consisted of Fe, Mg and Ni, possibly suggesting a volcanic ash deposition during coal formation. Factor analyses on the smokeless coal samples identified five factors accounting for 86% of the observed variance. The first factor loaded heavily on Al, Ti, Fe, P, Cr and Zr, which similar as to smoky coal represents lithophile elements. The second factor loaded onto Na, Sr and Ba, which may partly represent a marine influence on the coal during deposition. The third

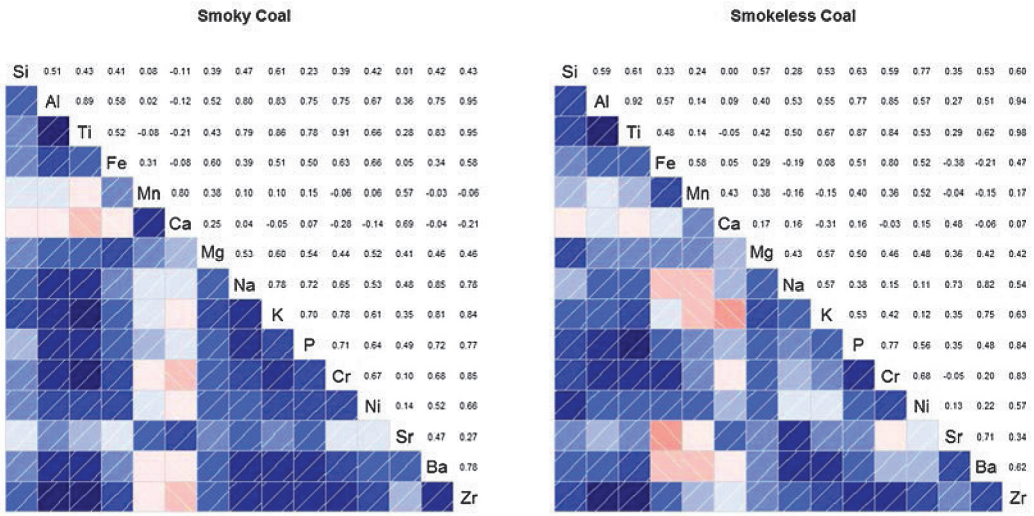

Figure 2: Correlogram for elemental analysis by smoky and smokeless coal

Blue colour and upward sloping lines indicates positive correlation, red and downward sloping lines indicates negative correlations.

Colour intensity indicates strength of correlation

factor loaded onto Si, and Ni, the fourth on Ca and the fifth on Mg and K. It is presently unclear what the third, fourth and fifth smokeless coal factors represent. Factor analysis following adjusting for ash yield resulted in the same factors being identified as those presented here (see Table S8 in supplement)

Scatter plot matrices of the factors are presented in Figures 3 and 4. Among smoky coals, the differing smoky coal subtypes (coking coals from Xuanwei and Fuyuan are displayed separately) have been indicated. Among smoky coal, variation in factor loadings can be observed between coking coal and gas fat coal. Furthermore, variation in the factor loadings between coking coal from Fuyuan and that from Xuanwei were observed. Statistical testing revealed significant variation in factor loadings ($p<0.05$) between the smoky coal subtypes for all three factors. In the smokeless coal samples, variation in loadings of factors was observed between the two smokeless coal producing areas. Statistical testing indicated significant variation ($p<0.05$) in the loading patterns of factors 1, 2 and 5 (but not 3 or 4) between the two areas.

Table 5 – Findings of exploratory factor analysis on elemental composition

	Smoky Coal			Smokeless Coal				
Trace elements	Factor1	Factor2	Factor3	Factor1	Factor2	Factor3	Factor4	Factor5
EVs (% variance explained)	6.6 (44%)	2.5(17%)	2.4(16%)	5.1(34%)	3.4(22%)	1.8(12%)	1.6(10%)	1.3(8%)
Si	0.37	-0.03	0.36	0.39	0.30	**0.65**	-0.06	0.33
Al	**0.86**	0.02	0.37	**0.89**	0.25	0.20	0.05	0.08
Ti	**0.92**	-0.09	0.30	**0.90**	0.34	0.17	-0.10	0.10
Fe	0.29	0.05	**0.90**	**0.68**	-0.52	0.21	0.13	0.25
Mn	-0.12	**0.86**	0.33	0.19	-0.26	0.40	0.47	0.27
Ca	-0.11	**0.93**	-0.09	0.00	0.16	0.02	**0.98**	0.00
Mg	0.38	0.37	**0.50**	0.24	0.26	0.33	0.12	**0.78**
Na	**0.84**	0.18	0.16	0.27	**0.81**	-0.02	0.04	0.13
K	**0.83**	0.08	0.33	0.46	0.54	-0.07	-0.40	**0.50**
P	**0.77**	0.20	0.29	**0.78**	0.25	0.22	0.12	0.23
Cr	**0.76**	-0.17	0.47	**0.89**	-0.14	0.32	-0.02	0.22
Ni	**0.53**	-0.03	**0.55**	0.43	-0.01	**0.89**	0.13	0.09
Sr	0.43	**0.79**	-0.14	0.02	0.84	0.09	0.35	0.09
Ba	**0.88**	0.09	0.07	0.29	**0.89**	0.13	-0.20	0.14
Zr	**0.90**	-0.09	0.36	**0.90**	0.37	0.21	0.00	0.06

Factor: Latent variable comprising of multiple correlated variables which assists in explaining overall variance in dataset.
Variables in bold are considered to be contributory to that factor.
Factor analysis performed under varimax rotation

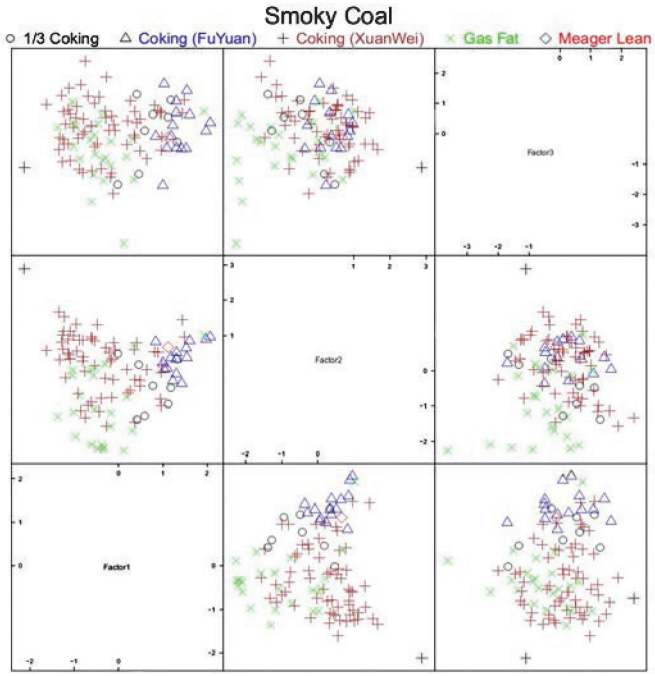

Figure 3 - Scatter plot matrix of smoky coal factors (n=3) by smoky coal subtype

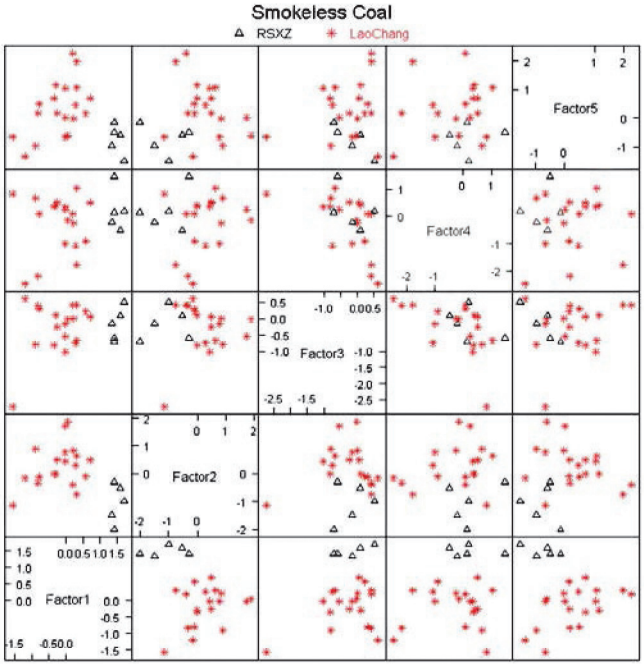

Figure 4 - Scatter plot matrix of smokeless coal factors (n=5) by coal producing region

Mineralogical analysis

Mineralogical composition was established on a subset of coal samples via the use of SEM (n=25). Smoky coal was found to have significantly higher amounts of total quartz (4.6%) than smokeless coal (2.2%, p=0.03, table 6). This extended to quartz within the respirable fraction (1.9% versus 0.6%, p<0.01). Among other minerals, carbonate (2.2% versus 0.2%, p=0.04), and albite (0.4% versus 0.2%, p=0.05) were present in significantly higher levels in smoky coal than smokeless. Full results for the mineralogical analysis are available in the supplement (Tables S9 and S10).

Discussion

The lung cancer rate in Xuanwei and Fuyuan Counties are among the highest in China. This excess risk has been linked to the domestic usage of locally sourced smoky coal [3], with additional geographic variation in lung cancer rates observed among smoky coal users [5,8]. The primary aetiological factor(s) present in smoky coal have not yet been identified. At present, the primary hypotheses implicate the emission of hydrocarbons, in particular PAHs [23], as the major carcinogenic factor, with the possibility of mineralogical agents (specifically silica/quartz) being involved [6]. Previous research investigating coal samples from the region acquired coal directly from mines [6,11]. This procedure, while giving highly detailed information regarding coal seam, type and precise location is limited when trying to apply these findings to an exposure assessment context. This limitation arises because in

Table 6 - Total and Respirable Quartz levels as measured from Scanning Electron Microscopy (SEM)

Major Coal Type	County	Coal Sub-type	Coal Mine	N	Total Quartz (% of coal)	Respirable Quartz* (% of coal)
Smoky				**19**	**4.58†**	**1.93†**
	Xuanwei			*11*	*6.77*	*3.1*
		Coking		10	7.52	3.39
			Azhi	2	4.11	2.33
			Baoshan	1	6.4	3.83
			Laibin	2	10.48	5.69
			Tangtang	4	7.52	3.39
			Yangchang	1	11.97	1.28
	Fuyuan			*8*	*3.24*	*1.14*
		Coking		3	4.58	1.87
			Daping	1	3.82	0.93
			Enhong	1	7.39	2.46
			Haidan	1	4.58	1.87
		1/3 Coking		2	1.87	0.98
			Bagong	1	1.08	0.63
			Dahe	1	2.66	1.33
		Gas Fat	Housuo	2	16.5	9.83
		Meagre Lean	Gumu	1	2	0.96
Smokeless				**6**	**2.24**	**0.60**
	Fuyuan		*LaoChang*	*4*	*2.41*	*0.85*
	Xuanwei		*RSXZ*	*2*	*1.77*	*0.27*

† : Statistically significant variation between smoky & smokeless coal types
*: Respirable quartz represents quartz grains of size less than 9.6 micrometers
Italics indicates overall value for each county

order to accurately portray individual exposure patterns no alteration (e.g. briquetting, blending with clay, weathering) must have been made to the coal product between mining and domestic use. Our observation that residents had a broad definition of coal, which extended to both whole and fragmented coal (which, upon gross visual inspection of selected samples showed evidence of being mixed with local dirt/clay to make a coal cake or briquette) would lend considerable uncertainty to that assumption. By collecting fuel samples directly from homes we are able to accurately collect, analyse and characterize the fuel currently being used.

Many of the observed differences between smoky and smokeless coals are to be expected given the generally known differences between bituminous and anthracite coals. However, these findings support the assertions that: smoky and smokeless coal are fundamentally different; heterogeneity within smoky and smokeless coal exist; and add plausibility to the current consensus that the elevated lung cancer risk in the region can be attributed to smoky coal.

Rock Eval analysis and the role of volatiles

The finding of higher hydrocarbon availability in smoky coal (as indicated by the hydrocarbon release at 300 degrees Celsius (S1) and during a programmed pyrolysis from 300 to 650 degrees Celsius (S2) compared to that of smokeless coal is consistent with the expectation that bituminous coal would, consequently to its being a less mature coal than anthracite, have a higher potential hydrocarbon release (as indicated by S2). The relative differences in S1 measurements between coal samples is broadly consistent with the stipulations for volatile matter set by the Chinese standard of coal classification (V_{daf}, see table 1), with the exception that the volatile matter in coking coal would be expected to be lower than that of 1/3 coking coal, but instead appears to be approximately equivalent. The hydrocarbon content in smoky coal is between 5 and 15 times that for smokeless, which reflects previous research observing an approximately 25 fold difference in indoor BaP levels between smoky and smokeless coal [23]. This would lend some support to the hypothesis that the organic fraction including PAHs are at least in part responsible for the excess cancer risk in the region. It must be noted though, that the classes of hydrocarbons measured in the geochemical analysis are not known and that there are multiple types of organic compounds that could be represented by these values.

The Tmax measurements (temperature at which maximal hydrocarbon generation occurs) made it apparent that some (n=11) coal types had been misclassified and needed reclassification. This decision is supported by similar Tmax measurements for equivalent coals [22] and by our own internal sensitivity analyses where we established that the results from the updated coal types is consistent with that which would have been obtained had we excluded those coal samples.

Elemental composition and quartz

XRF analyses of the coal samples reveals that smoky coal, in general, contains lower levels of elements when compared to smokeless coal. It is possible that the levels of several elements (e.g. Na, P, Sr) may have been under-reported due to volatization during the ashing process at 1000 degrees. However, we would not expect this to alter the relative differences between smoky and smokeless coals. The difference in elemental composition also extends to identifying latent variables through the use of factor analysis, which identified 3 factors in smoky and 5 in smokeless coal. Both coal types appeared to have lithophile elements (i.e. those elements which predominantly occur in silicate minerals and

are concentrated in the crust) contributing to their first (and highest loading) factor, however the subsequent factors appear to be different between the coal types. Of the remaining four factors for smokeless coal, one potentially represents previous marine influence while the remaining three have no presently known geological meaning. The remaining two smoky coal factors appear to represent carbonate and volcanic influence respectively. These factors appear to be consistent with the observed geology of the area, as previous research carried out upon coal samples collected from mines in Yunnan has indicated the presence of carbonate layers and volcanic influence in the formation of coal in the area.[11,24]

Previous research has indicated that the levels of silicon in smoky coal are higher than those observed in similar coals in the USA and other Chinese sources.[6,11] Our study has confirmed this assertion, but has also shown that silicon in smokeless coal is at a similar level as smoky coal. If we assume that all silicon detected exists in a mineralogical capacity (i.e. as silica) and consider the relative difference in aluminium levels between smoky and smokeless coal, we would predict that there are marked differences in the mineralogical state of silica between smoky and smokeless coal. Mineralogically, silica either exists as "free" (i.e. as SiO_2 crystals – of which quartz is the most common) or combined with metals – of which aluminium is the most common (aluminosilicates). It has been postulated that the "expected" ratio between silica and aluminium in these aluminosilicates is 1:1.5, with the excess silica representing "free" silica and thus being an indicator of quartz content[6]. Using this premise we predicted quartz levels for the entire dataset and found significantly higher levels of estimated quartz among the smoky coal samples. This was reflected by the finding of higher quartz identified at the surface of smoky coal via SEM. While these results are numerically different from each other (estimated values are approximately double that measured by SEM) they each show a similar relative difference in quartz levels between smoky and smokeless coal (approximately double). Furthermore, correlate testing indicates that the estimated and measured quartz values are positively correlated with a Spearman correlation coefficient of 0.6. This would indicate that, in addition to confirming previous assertions of elevated quartz content in smoky coal,[6,11] the use of the relative difference between silicon and aluminium provides a reasonable method for comparing relative differences in quartz between smoky and smokeless coal in this region.

Quartz is categorized as carcinogenic to humans by IARC[13] and so this finding has implications for a potential aetiological factor for the lung cancer epidemic in the region, either alone (Tian 2005), or in combination with hydrocarbons/volatiles [6]. However it has been pointed out that the attributed degree of carcinogenicity to quartz is insufficient to fully explain the degree of cancer risk observed.[25] Furthermore, these assessments are restricted to the analysis of uncombusted coal samples. As yet, no published articles investigating quartz in combustion related indoor air pollution are available. Thus, we are unable to state whether or not these elevated levels of quartz become aerosolized during the combustion process or in the clean-up of ash.

Variability within coal types

Variation in constituents between designated smoky coal subtypes (coking coal, 1/3 coking etc.) is to be expected to a degree as the geochemical properties defining the smoky coal subtypes are represented by some of the measurements presented in this paper. However, these findings provide support for previous observations of varying cancer rates between regions [8], which implies a relationship between coal area and carcinogenicity. A finding of

variation between mines producing the same coal subtype (as seen for coking coal from Xuanwei) would imply either regional differences in coal preparation or further heterogeneity in coal generation within designated coal subtypes, which may assist in further identifying variation in carcinogenic constituents between locations. However, how this observed heterogeneity in coal constitution relates to personal exposure and specific cancer risks is not yet known and needs to be investigated further before drawing any aetiological conclusions.

While this paper is the most comprehensive analysis of coal from Xuanwei and Fuyuan to date, some limitations relating to sample size exist. Coal samples were taken throughout the whole of the Xuanwei and Fuyuan, providing a wide variety of coal samples but a limited number of samples from each region. Additionally, while attention has been given to the variation in coal composition between mines (changes in the horizontal plane), this paper is unable to ascertain whether compositional changes in coal have occurred as a result of decades of mining (changes in the vertical plane). Given the long latency period of lung cancer,[26] there may have been variations in carcinogenic exposures over these previous decades. However, there is some evidence to suggest that there has been no major compositional change within at least the last 2 decades as research that has compared Xuanwei coal mined 20 years ago with recently excavated coal[6] has indicated little compositional difference between the two specimens.

Summary and conclusion

The excess lung cancer risk in Xuanwei and Fuyuan has previously been linked to the domestic combustion of smoky coal with a strong geographic heterogeneity within homes that regularly use smoky coal. This paper has identified a clear difference in coal composition between smoky and smokeless coals among the aspects of hydrocarbon content (i.e. potential hydrocarbon emissions), elemental composition and quartz content. Variation is also observed within coal type (samples) dependent upon their geographical source. These results parallel heterogeneity in cancer risk resulting from the use of coal in this region.

Acknowledgements

This project was supported by the National Institutes of Health intramural research program. The content of this publication does not necessarily reflect the views or policies of the Department of Health and Human Services, nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government. The authors would like to acknowledge Johan Beekhuizen and Meng Wang from the Institute for Risk Assessment Sciences, Utrecht University for their support in the production of figure 1.

Conflict of interest statement

The authors state no conflict of interest in the planning, analysis or publication of this research.

References

1. Mumford, J. L.; He, X. Z.; Chapman, R. S.; Cao, S. R.; Harris, D. B.; Li, X. M.; Xian, Y. L.; Jiang, W. Z.; Xu, C. W.; Chuang, J. C. Lung cancer and indoor air pollution in Xuan Wei, China. Science 1987, 235, 217-220.
2. He, X. Z.; Chen, W.; Liu, Z. Y.; Chapman, 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 Perspect 1991, 94, 9-13.
3. Barone-Adesi, F.; Chapman, R. S.; Silverman, D. T.; He, X.; Hu, W.; Vermeulen, R.; Ning, B.; Fraumeni, J. F.,Jr; Rothman, N.; Lan, Q. Risk of lung cancer associated with domestic use of coal in Xuanwei, China: retrospective cohort study. BMJ. 2012, 345, e5414.
4. Chapman, R. S.; Mumford, J. L.; Harris, D. B.; He, Z. Z.; Jiang, W. Z.; Yang, R. D. The epidemiology of lung cancer in Xuan Wei, China: current progress, issues, and research strategies. Arch. Environ. Health. 1988, 43, 180-185.
5. Lan, Q.; He, X.; Shen, M.; Tian, L.; Liu, L. Z.; Lai, H.; Chen, W.; Berndt, S. I.; Hosgood, H. D.; Lee, K. M.; Zheng, T.; Blair, A.; Chapman, R. S. Variation in lung cancer risk by smoky coal subtype in Xuanwei, China. Int. J. Cancer. 2008, 123, 2164-2169.
6. Large, D. J.; Kelly, S.; Spiro, B.; Tian, L.; Shao, L.; Finkelman, R.; Zhang, M.; Somerfield, C.; Plint, S.; Ali, Y.; Zhou, Y. Silica-volatile interaction and the geological cause of the Xuan Wei lung cancer epidemic. Environ. Sci. Technol. 2009, 43, 9016-9021.
7. Tian, L. Coal Combustion Emissions and Lung Cancer in Xuan Wei, China (PhD dissertation), University of California, Berkeley, California. 2005.
8. Lin, H.; Ning, B.; Li, J.; Ho, S. C.; Huss, A.; Vermeulen, R.; Tian, L. Lung Cancer Mortality Among Women in Xuan Wei, China: A Comparison of Spatial Clustering Detection Methods. Asia. Pac. J. Public. Health. 2012.
9. Chen, P. Study on integrated classification system for Chinese coal. Fuel Process Technol. 2000, 62, 77-87.
10. Straif, K.; Benbrahim-Tallaa, L.; Baan, R.; Grosse, Y.; Secretan, B.; El Ghissassi, F.; Bouvard, V.; Guha, N.; Freeman, C.; Galichet, L.; Cogliano, V. A review of human carcinogens - Part C: metals, arsenic, dusts, and fibres. Lancet Oncol. 2009, 10, 453-454.
11. Dai, S.; Tian, L.; Chou, C.; Zhou, Y.; Zhang, M.; Zhao, L.; Wang, J.; Yang, Z.; Cao, H.; Ren, D. Mineralogical and compositional characteristics of Late Permian coals from an area of high lung cancer rate in Xuan Wei, Yunnan, China: Occurrence and origin of quartz and chamosite. International Journal of Coal Geology. 2008, 76, 318-327.
12. Hosgood, H. D.; Lan, Q.; Vermeulen, R.; Wei, H.; Reiss, B.; Coble, J.; Wei, F.; Jun, X.; Wu, G.; Rothman, N. Combustion-derived nanoparticle exposure and household solid fuel use in Xuanwei and Fuyuan, China. Int. J. Environ. Health Res. 2012, 22, 571-581.
13. Baan, R.; Grosse, Y.; Straif, K.; Secretan, B.; El Ghissassi, F.; Bouvard, V.; Benbrahim-Tallaa, L.; Guha, N.; Freeman, C.; Galichet, L.; Cogliano, V. A review of human carcinogens - Part F: Chemical agents and related occupations. Lancet Oncol. 2009, 10, 1143-1144.
14. Behar, F.; Beaumont, V.; De B. Penteado, H. L. Technologie Rock-Eval 6 : performances et d\'eveloppements. Oil \& Gas Science and Technology - Rev.IFP. 2001, 56, 111-134.
15. World Health Organization Hazard prevention and control in the work environment: Airborne dust. 1999.
16. Bragg, L.; Oman, J.; Tewalt, S.; Oman, C.; Rega, N.; Washington, P.; Finkelman, R. U.S. Geological Survey Coal Quality(COALQUAL) Database: Version 2.0. 1998.
17. R Development Core Team R: A Language and Environment for Statistical Computing. 2014.
18. Harrell, F. E. J. Hmisc: Harrell Miscellaneous. 2012.
19. Wickham, H. Reshaping Data with the reshape Package. Journal of Statistical Software. 2007, 21, 1-20.
20. Sarkar, D. Lattice: Multivariate Data Visualization with R. 2008.
21. Wright, K. corrgram: Plot a correlogram. 2013.

22. Laumann, S.; Micic, V.; Kruge, M. A.; Achten, C.; Sachsenhofer, R. F.; Schwarzbauer, J.; Hofmann, T. Variations in concentrations and compositions of polycyclic aromatic hydrocarbons (PAHs) in coals related to the coal rank and origin. Environ. Pollut. 2011, 159, 2690-2697.
23. Mumford, J. L.; Chapman, R. S.; Harris, D. B.; He, X. Z.; Cao, S. R.; Xian, Y. L.; Li, X. M. Indoor air exposure to coal and wood combustion emissions associated with a high lung cancer rate in Xuan Wei, China. Environ. Int. 1989, 15, 315-320.
24. Dai, S.; Ren, D.; Zhou, Y.; Chou, C.; Wang, X.; Zhao, L.; Zhu, X. Mineralogy and geochemistry of a superhigh-organic-sulfur coal, Yanshan Coalfield, Yunnan, China: Evidence for a volcanic ash component and influence by submarine exhalation. Chem. Geol. 2008, 255, 182-194.
25. Vermeulen, R.; Rothman, N.; Lan, Q. Coal combustion and lung cancer risk in XuanWei: a possible role of silica? Med. Lav. 2011, 102, 362-367.
26. Pass, H. I.; David P Carbone; Johnson, D. J.; Minna, J. D.; Giorgio V Scagliotti Principles and Practice of Lung Cancer: The Official Reference Text of the International Association for the Study of Lung Cancer (IASLC) (Pass, Lung Cancer); Lippincott Williams & Wilkins: .

Chapter 2

Appendix - Supplementary information: Heterogeneity in coal composition and implications for lung cancer risk in Xuanwei and Fuyuan counties, China.

(Online: http://dx.doi.org/10.1016/j.envint.2014.03.019)

Table S1 – Quality Control testing: Rock eval

	Tmax		S1		S2	
Sample Identifier	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest
A	443	441	4.27	5.23	170.47	165.73
B	464	470	5.48	4.76	69.23	88.94
C	446	444	3.08	3.96	80.18	108.72
D	459	465	2.15	2.31	94.75	117.59
E	464	460	2.2	2.01	70.36	67.8

Table S2 – Quality Control testing: Carbon-Sulphur

	Total Carbon		Inorganic Carbon		Organic Carbon		Total Sulfur	
Sample Identifier	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest
A	64.46	68.53	1.76	2.59	62.71	65.94	0.15	0.19
B	66.01	69.32	0.26	0.45	65.75	68.87	0.23	0.28
C	64.14	66	0.15	0.19	63.99	65.81	0.15	0.2
D	65.53	68.13	0.93	1.34	64.6	66.79	0.23	0.22
E	48.13	51.03	2.32	2.02	45.81	49.01	3.44	3.55
F	62.6	66.22	0.19	0.9	62.41	65.32	0.4	0.43
G	30.39	30.94	0.34	0.71	30.05	30.23	0.08	0.08

Table S3 – Quality Control testing: XRF

	Si		Al		Ti		Fe		Mn	
Sample Identifier	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest
A	79827	79736	71633	70635	8696	8357	49688	49657	236	243
B	60990	60779	32419	32063	2548	2515	14719	14590	202	203
C	44502	44347	13172	13208	1004	1012	3301	3304	97	97
D	49662	48961	8818	8524	421	408	10201	10099	1764	1777
E	66601	66482	21915	21877	1688	1703	5924	5864	182	177
F	115908	117618	13050	13102	815	813	12395	12371	134	143
G	88737	87138	11344	11202	631	630	5179	5118	674	664
	Ca		Mg		Na		K		P	
	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest
A	7262	7861	1394	1333	310	353	2497	2249	262	258
B	7324	7445	3313	3316	944	987	2778	2967	176	179
C	5262	5425	501	501	203	186	107	129	65	66
D	60708	62073	1527	1549	167	124	137	131	44	41
E	8210	8116	872	881	197	214	1191	1276	221	216
F	3324	3335	691	717	153	185	358	365	20	21
G	28763	29103	753	723	140	175	371	391	49	51
	Cr		Ni		Sr		Ba		Zr	
	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest	Original	Blind Retest
A	74	92	46	71	19	22	65	87	292	293
B	29	28	26	27	49	49	84	87	99	100
C	11	12	15	17	56	59	26	28	36	38
D	6	8	26	28	99	101	15	12	20	25
E	14	14	28	28	72	73	95	96	73	74
F	15	15	22	23	22	22	25	27	26	30
G	5	8	19	19	69	71	26	24	32	32

Table S4 – Geochemical analysis and Carbon-sulfur content using only coal samples which have Tmax matching their reported coal type

Major Coal Type	County	Coal Sub-type	Coal Mine	N	S1 (mgHC/g coal)	S2 (mgHC/g coal)	Tmax (°C)	Total Carbon (%)	Inorganic Carbon (%)	Organic Carbon (%)	Total Sulfur(%)
Smoky				**107**	**2.24†**	**73.24†**	**460†**	**60.12**	**0.49**	**59.38**	**0.24†**
	Xuanwei			*60*	*2.48*	*74.43*	*461.5*	*61.74*	*0.55*	*61.54*	*0.2*
			Azhi	15	2.52	75.62	462	65.53	0.92	64.6	0.23
			Baoshan	5	2.24	61.59	463	57.3	0.64	54.17	0.18
			Laibin	13	2.31	76.26	459	56.7	0.57	56.17	0.27
			Tangtang	19	1.68	65.07	464	56.88	0.23	56.08	0.19
			Yangchang	7	4.03	138.69	443	70.12	0.32	69.77	0.19
	Fuyuan			*47*	*2.03*	*72.35‡*	*446‡*	*57.87‡*	*0.42‡*	*57.16‡*	*0.34*
		Coking Coal		15	1.89	43.96	467	50.83	1.8	46.42	0.24
			Daping	4	2.34	33.9	458.5	43.58	0.8	42.74	0.29
			Enhong	4	1.73	40.53	469.5	50.23	5.56	42.26	0.74
			Haidan	6	1.78	46.75	468	46.29	3.01	43.28	0.19
			Zude	1	4.21	61.02	473	64.15	0.4	63.75	0.87
		1/3 Coking		6	2.54	58.02	450	57.13	0.2	57.02	0.29
			Bagong	3	1.7	47.19	465	55.33	0.11	55.2	1.88
			Dahe	3	3.08	80.18	445	65.46	0.43	64.89	0.16
		Gas Fat		23	1.97	131.87	433	64.34	0.2	63.7	0.39
			Housuo	20	2.03	138.44	433.5	63.98	0.24	63.6	0.4
			Qingyun	3	1.62	110.4	431	65.88	0.12	65.83	0.29
		Meagre Lean	Gumu	1	3.83	53.43	469	54.7	1.4	53.3	0.53
Smokeless				**22**	**0.28**	**8.77***	**576**	**57.24***	**0.26**	**56.87***	**1.22**
	Fuyuan	*LaoChang*		*18*	*0.29*	*9.58*	*569.5*	*57.24*	*0.22*	*57.12*	*1.22*
	Xuanwei	*RSXZ*		*2*	*0.28*	*3.41*	*586*	*40.81*	*1.55*	*39.26*	*1.86*

† : Statistically significant variation between smoky & smokeless coal types
‡ : Significant variation within smoky coal subtypes for that region
* : Significant variation between mines within that coal type in that region
S1: mg of hydrocarbons (per gram of coal) released under controlled burning at 300°C.
S2 : mg of hydrocarbons (per gram of coal) released during maximal release of hydrocarbons under controlled burning.
Tmax: temperature at which S2 occurs
Italics indicate overall value for each county

Table S6 – Geochemical analysis and Carbon-sulfur content adjusted for ash yield

Major Coal Type	County	Coal Sup-type	Coal Mine	N	S1 (mgHC/g coal)	S2 (mgHC/g coal)	Total Carbon (%)	Inorganic Carbon (%)	Organic Carbon (%)	Total S ulfur(%)
Smoky				**116**	**0.06†**	**2.3†**	**1.81**	**0.02**	**1.78**	**0.01†**
	Xuanwei			*65*	*0.08**	*2.35**	*1.86**	*0.02*	*1.78*	*0.01*
		Coking Coal		63	0.07	2.35	1.81	0.02*	1.78*	0.01
			Azhi	15	0.1	2.74	2.25	0.03	2.19	0.01
			Baoshan	5	0.07	1.7	1.57	0.03	1.46	0.01
			Laibin	14	0.06	2.13	1.77	0.02	1.75	0.01
			Tangtang	22	0.04	1.89	1.46	0.01	1.46	0.01
			Yangchang	7	0.2	6.65	2.9	0.02	2.87	0.01
	Fuyuan			*51*	*0.06*	*1.9‡*	*1.75‡*	*0.02‡*	*1.75‡*	*0.01*
		Coking Coal		15	0.05	1.21	1.2	0.06	1.09	0.01
			Daping	4	0.05	0.79	0.93	0.02	0.93	0.01
			Enhong	4	0.04	1.01	1.17	0.13	1.04	0.01
			Haidan	6	0.05	1.22	1.4	0.08	1.32	0.01
			Zude	1	0.19	2.69	2.83	0.02	2.82	0.04
		1/3 Coking		8	0.06	1.46	1.72	0.01	1.71	0.01*
			Bagong	5	0.05	1.44	1.68	0.00	1.68	0.06
			Dahe	3	0.14	3.77	2.64	0.01	2.62	0.01
		Gas Fat		23	0.08	6.07	2.52	0.01	2.51	0.02
			Housuo	20	0.09	6.07	2.62	0.01	2.6	0.02
			Qingyun	3	0.06	3.8	2.27	0.01	2.27	0.02
		Meagre Lean	Gumu	1	0.08	1.13	1.15	0.03	1.13	0.01
Smokeless				**29**	**0.01**	**0.28**	**1.96**	**0.01**	**1.93**	**0.04***
	Fuyuan		*LaoChang*	*19*	*0.01*	*0.3*	*1.96*	*0.01*	*1.95*	*0.04*
	Xuanwei		*RSXZ*	*5*	*0.01*	*0.16*	*1.13*	*0.00*	*1.13*	*0.07*

† : Statistically significant variation between smoky & smokeless coal types
‡ : Significant variation within smoky coal subtypes for that region
* : Significant variation between mines within that coal type in that region
S1: mg of hydrocarbons (per gram of coal) released under controlled burning at 300°C.
S2 : mg of hydrocarbons (per gram of coal) released during maximal release of hydrocarbons under controlled burning.
Italics indicate overall value for each county

Table S7 – Elemental composition (in ppm) adjusted for ash yield

Major Coal Type	County	Coal Sub-type	Coal Mine	N	Si	Al	Ti	Fe	Mn	Ca	Mg	Na	K	P	Cr	Ni	Sr	Ba	Zr
Smoky				**116**	**2998**	**709†**	**50†**	**560**	**7**	**287**	**53**	**8†**	**22†**	**4†**	**0.7†**	**0.9**	**1.5**	**1.4†**	**2.5†**
	Xuanwei			*65*	*3065*	*545*	*31*	*530*	*13*	*477*	*52*	*7*	*18*	*3*	*0.5*	*0.9*	*1.4*	*0.9*	*1.5*
		Coking Coal		63	3065	558	32	522*	12*	471*	51	7	19	3	0.5*	0.9	1.4*	0.9	1.5
			Azhi	15	2407	444	24	424	23	1039	50	6	16	2	0.3	0.7	2.8	0.9	1.2
			Baoshan	5	2725	611	46	386	16	534	50	7	22	3	0.5	0.7	1.4	1.0	2.3
			Laibin	14	3252	531	23	747	15	529	57	7	13	3	0.4	1.0	1.7	0.8	1.3
			Tangtang	22	3074	638	45	730	7	107	50	8	23	4	0.9	1.0	0.7	1.0	2.0
			Yangchang	7	3545	539	39	331	8	314	52	8	23	5	0.5	0.7	4.0	1.6	1.5
	Fuyuan			*51*	*2836*	*1047‡*	*113‡*	*605*	*4‡*	*162*	*58‡*	*12‡*	*44‡*	*7‡*	*1.1‡*	*1.0*	*1.7‡*	*2.7‡*	*3.7‡*
		Coking Coal		15	2618	1487	220	777	7	209	80	26*	139	14	1.5	1.2	2.4	5.9*	6.7
			Daping	4	2745	1542	188	866	6	198	68	15	129	22	1.6	0.9	2.0	5.1	5.8
			Enhong	4	1799	779	125	564	5	263	128	11	55	9	1.1	0.7	1.9	3.8	3.6
			Haidan	6	3112	1528	295	815	11	200	99	52	144	22	1.5	1.4	3.7	1.4	7.4
			Zude	1	2523	1788	220	721	4	382	112	19	159	14	1.8	1.3	4.3	3.9	6.7
		1/3 Coking		8	2732	1230	174	897*	6	109*	29	9	57	8	1.7*	0.9	1.8*	3.7	5.9
			Bagong	5	2046	1347	181	947	5	34	17	9	58	7	2.2	0.8	1.1	3.3	7.9
			Dahe	3	3139	1031	79	279	8	387	41	9	56	10	0.7	1.3	3.3	4.5	3.4
		Gas Fat		23	3413	656	48	504	2	97*	40	8	11	3	0.7	1.0	1.1	1.4	2.0
			Housuo	20	3263	702	49	469	3	134	39	8	11	4	0.7	1.1	1.2	1.4	2.0
			Qingyun	3	3624	624	45	637	1	13	42	6	8	2	0.9	0.8	0.4	1.3	3.6
		Meagre Lean	Gumu	1	1845	1077	114	409	6	398	81	11	104	8	0.9	0.6	2.1	2.4	3.7
Smokeless				**29**	**2495**	**1489***	**154**	**654***	**5**	**268**	**88**	**22**	**145**	**9**	**1.2***	**0.7**	**2.3**	**4.3**	**4.8**
	Fuyuan		*LaoChang*	*19*	*2568*	*1365*	*146*	*606*	*5*	*253*	*97*	*28*	*162*	*8*	*1.1*	*0.7*	*2.5*	*4.4*	*4.8*
	Xuanwe		*RSXZ*	*5*	*2049*	*1741*	*182*	*1171*	*4*	*148*	*37*	*12*	*66*	*13*	*2.0*	*0.8*	*1.0*	*1.8*	*5.4*

†: Statistically significant variation between smoky & smokeless coal types
‡ :Statistically significant variation within that smoky coal subtypes for that region
* :Statistically significant variation between mines within that coal type in that region
Italics indicate overall value for each county

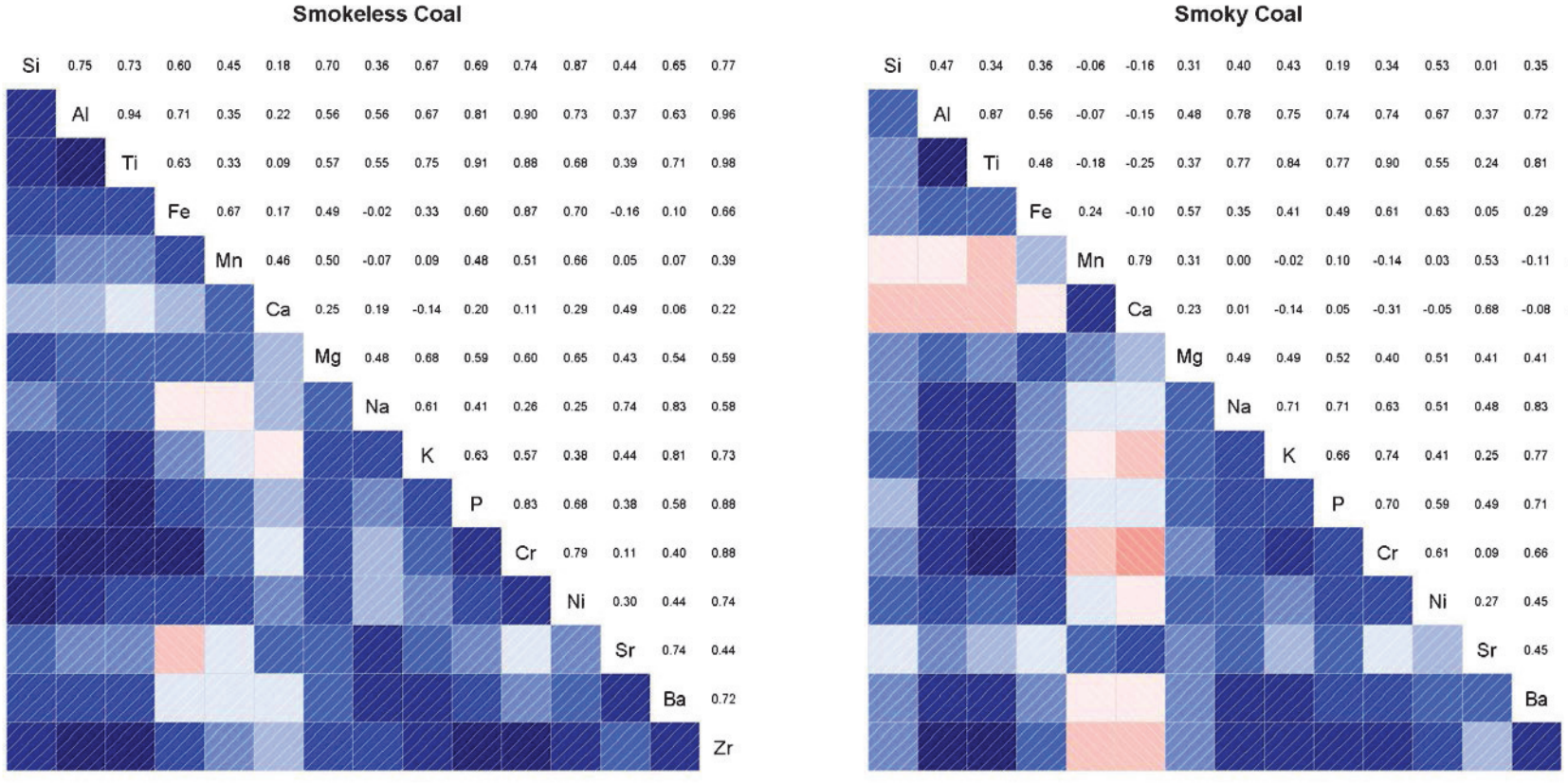

Figure S1 – Correlogram for elemental analysis, adjusted for ash yield, by smoky and smokeless coal

Blue colour indicates positive correlation, red indicates negative correlations.
Colour intensity indicates strength of correlation

Table S8 - Factor analysis among XRF results standardized for ash yield

	Smoky Coal			Smokeless Coal				
Trace elements	Factor1	Factor2	Factor3	Factor1	Factor2	Factor3	Factor4	Factor5
EVs (% variance explained)	6.4(43%)	2.4(16%)	2.3(15%)	5.3(35%)	3.5(23%)	2.4(16%)	1.4(9%)	0.9(6%)
Si	0.32	-0.09	0.3	0.47	0.37	**0.69**	0	0.26
Al	**0.86**	0.01	0.36	**0.86**	0.35	0.26	0.09	0.12
Ti	**0.93**	-0.12	0.26	**0.87**	0.42	0.19	-0.04	0.13
Fe	0.24	0.02	**0.97**	**0.76**	-0.28	0.41	0.14	0.2
Mn	-0.18	**0.82**	0.27	0.32	-0.16	**0.57**	0.41	0.11
Ca	-0.14	**0.94**	-0.09	0.05	0.16	0.14	**0.97**	-0.04
Mg	0.34	0.35	0.5	0.31	0.31	**0.52**	0.14	**0.54**
Na	**0.83**	0.17	0.15	0.25	**0.82**	-0.03	0.05	0.09
K	**0.81**	-0.01	0.22	0.47	**0.56**	0.11	-0.25	**0.62**
P	0.76	0.21	0.3	**0.78**	0.32	0.25	0.08	0.13
Cr	**0.76**	-0.19	0.44	**0.89**	0.03	0.39	0.01	0.15
Ni	0.49	0.07	**0.53**	**0.53**	0.17	**0.82**	0.12	-0.03
Sr	0.4	**0.79**	-0.07	0.01	**0.86**	0.13	0.34	0.05
Ba	**0.86**	0.07	0.08	0.32	**0.88**	0.17	-0.12	0.19
Zr	**0.9**	-0.11	0.34	**0.84**	0.44	0.25	0.07	0.12

Factor: Latent variable comprising of multiple correlated variables which assists in explaining overall variance in dataset
Variables in bold are considered to be contributory to that factor
Factor analysis carried out under varimax rotation

Table S9 – Mineralogical analysis (% of coal)

Major Coal Type	County	Coal Sub-type	Coal Mine	N	Quartz	Respirable Quartz	Carbonate	Albite	Chamosite	Other Sheet Silicates	Apatite	Goethite	Gypsum	Ilmenite
Smoky Coal				**19**	**4.6†**	**1.9†**	**2.2†**	**0.43†**	**2.7**	**8.9**	**0†**	**0.08**	**0.01†**	**0**
	Xuanwei			*11*	*6.8*	*3.1*	*2.0*	*0.43*	*2.8*	*5.6*	*0*	*0.01*	*0*	*0*
		Coking		10	7.5	3.4	2.2	0.43	3.4	5.6	0	0.01	0	0
			Azhi	2	4.1	2.3	4.5	0.63	1.1	3.4	0	0	0	0
			Baoshan	1	6.4	3.8	15.4	0.42	11.0	16.2	0.16	0.09	0.01	0.05
			Laibin	2	10.5	5.7	1.3	0.38	3.4	2.9	0.01	0.05	0	0
			Tangtang	4	7.5	3.4	0.5	0.43	4.4	7.1	0.05	0.02	0.17	0.01
			Yangchang	1	12.0	1.3	2.4	2.19	2.6	24.0	0	0.01	0	0
	Fuyuan			*8*	*3.2*	*1.1*	*2.4*	*0.48*	*2.4*	*11.7*	*0.01*	*0.3*	*0.02*	*0.01*
		Coking		3	4.6	1.9	2.6	0.62	2.7	27.0	0.01	0.3	0.02	0.05
			Daping	1	3.8	1.0	3.0	0.62	2.7	43.5	0.01	0.3	0.04	0
			Enhong	1	7.4	2.5	1.8	0.88	2.1	13.4	0	0.3	0.02	0.05
			Haidan	1	4.6	1.9	2.6	0.57	3.3	27.0	0.07	1.2	0.01	0.12
		1/3 Coking		2	1.9	1.0	1.8	0.37	4.1	11.4	0	0.2	0.2	0.01
			Bagong	1	1.1	0.6	0.1	0.39	8	13.3	0	0.2	0.01	0.01
			Dahe	1	2.7	1.3	3.4	0.35	0.2	9.5	0	0.2	0.47	0.01
		Gas Fat	Housuo	2	16.5	9.8	14.4	0.58	4.1	5.6	0	3.1	0.5	0
		Meagre Lean	Gumu	1	2	1.0	1.7	0.23	0.7	8.9	0.01	0.1	0	0.01
Smokeless Coal				**6**	**2.2**	**0.6**	**0.2**	**0.23**	**4.0**	**14.5**	**0**	**0.2**	**0.2**	**0.01**
	Fuyuan		*LaoChang*	*2*	*2.4*	*0.9*	*0.1*	*0.23*	*1.1*	*8.8*	*0*	*0.2*	*0.2*	*0*
	Xuanwei		*RSXZ*	*4*	*1.8*	*0.3*	*0.7*	*0.23*	*9.6*	*24.5*	*0*	*0.2*	*0.2*	*0.2*

†: Statistically significant variation between smoky & smokeless coal types
*Respirable quartz represents quartz grains of size less than 9.6 micrometers
Italics indicate overall value for each county

S10 – Mineralogical analysis continued (% of coal)

Major Coal Type	County	Coal Sub-type	Coal Mine	N	Melanterite	Pyrite	Titanite	Bauxite	Melanterite clay	Rutile	Titanium magnetite
Smoky Coal				**19**	**0**	**0.02**	**0.04**	**0**	**0.33**	**0.01**	**0**
	Xuanwei			*11*	*0*	*0.02*	*0.07*	*0*	*0.17*	*0.01*	*0*
		Coking		10	0	0.01	0.05	0	0.14	0.01	0
			Azhi	2	0	0.01	0.02	0	0.02	0	0
			Baoshan	1	0.01	2.7	0.31	0.02	1.34	0.01	0
			Laibin	2	0	0.02	0.04	0	0.09	0.02	0
			Tangtang	4	0.04	0.01	0.05	0	0.66	0.02	0.01
			Yangchang	1	0	0	0.15	0	0.06	0	0
	Fuyuan			*8*	*0*	*0.03*	*0.03*	*0*	*0.54*	*0.01*	*0.01*
		Coking		3	0.01	0	0.07	0	0.21	0.03	0.03
			Daping	1	0.01	0	0.07	0	0.56	0.01	0
			Enhong	1	0.01	0.4	0.04	0.01	0.21	0.03	0.03
			Haidan	1	0	0	0.6	0	0.13	0.08	0.11
		1/3 Coking		2	0	0	0.02	0	1.42	0.03	0.01
			Bagong	1	0	0	0.02	0	2.31	0.05	0.01
			Dahe	1	0	0	0.03	0	0.52	0.01	0.01
		Gas Fat	Housuo	2	0.1	3.75	0.22	0	2.06	0.01	0.33
		Meagre Lean	Gumu	1	0	0.06	0.02	0	0.09	0.01	0
Smokeless Coal				**6**	**0.04**	**0.1**	**0.02**	**0**	**0.85**	**0.01**	**0.01**
	Fuyuan		*LaoChang*	*2*	*0.03*	*0.01*	*0.01*	*0*	*0.63*	*0.01*	*0*
	Xuanwei		*RSXZ*	*4*	*0.09*	*1.3*	*0.04*	*0.01*	*2.14*	*0.02*	*0.16*

†: Statistically significant variation between smoky & smokeless coal types
*Respirable quartz represents quartz grains of size less than 9.6 micrometers
Italics indicate overall value for each county

Chapter 3

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

George S. Downward*
Wei Hu*
Boris Reiss
Jun Xu
Bryan A. Bassig
H. Dean Hosgood
Linlin Zhang
Wei Jie Seow
Guoping Wu
Robert S. Chapman
Linwei Tian
Fusheng Wei
Roel Vermeulen
Lan Qing

(Environmental Science and Technology, 2014 Aug 5, 48 (15), 8456-64)
*: Equal co-authors

Abstract

The combustion of biomass and coal is the dominant source of household air pollution (HAP) in China, and contributes significantly to the total burden of disease in the Chinese population. To characterize HAP exposure related to solid fuel use and ventilation patterns, an exposure assessment study of 163 non-smoking female heads of households enrolled from 30 villages was conducted in Xuanwei and Fuyuan, two neighbouring rural counties with high incidence of lung cancer due to the burning of smoky coal (a bituminous coal, which in health evaluations is usually compared to smokeless coal(an anthracite coal available in some parts of the area).Personal and indoor 24-h $PM_{2.5}$ samples were collected over two consecutive days in each household, with approximately one-third of measurements retaken in a second season. The overall geometric means (GM) of personal $PM_{2.5}$ concentrations in Xuanwei and Fuyuan were 166 [Geometric Standard Deviation (GSD):2.0] and 146 (GSD:1.9) $\mu g/m^3$, respectively, which were similar to the indoor $PM_{2.5}$ air concentrations [GM(GSD):162 (2.1) and 136 (2.0) $\mu g/m^3$, respectively]. Personal $PM_{2.5}$ was moderately highly correlated with indoor $PM_{2.5}$ (Spearman $r = 0.70$, $p < 0.0001$). Burning wood or plant materials (tobacco stems, corncobs etc.) resulted in the highest personal $PM_{2.5}$ concentrations (GM:289 and 225 $\mu g/m^3$, respectively), followed by smoky coal, and smokeless coal (GM:148 and 115 $\mu g/m^3$, respectively). $PM_{2.5}$ levels of vented stoves were 34−80% lower than unvented stoves and firepits across fuel types. Mixed effect models indicated that fuel type, ventilation, number of windows, season, and burning time per stove were the main factors related to personal $PM_{2.5}$ exposure. Lower $PM_{2.5}$ among vented stoves compared with unvented stoves and firepits is of interest as it parallels the observation of reduced risks of malignant and non-malignant lung diseases in the region.

Background

More than 60% of the population in China is rural. Nearly all of this population use biomass and coal fuels for their day to day cooking and heating, the combustion of which is the dominant source of household air pollution (HAP) in China and contributes significantly to the total burden of ill health in the Chinese population.[1] Particulate matter with an aerodynamic diameter smaller than 2.5μm ($PM_{2.5}$) is one of the main pollutants in solid fuel smoke and is closely associated with many of the adverse health effects associated with HAP.[2–9]

Xuanwei and Fuyuan, two neighbouring counties in Yunnan province, China have a mostly rural population, and have increased rates of non-malignant and malignant lung disease associated with HAP from solid fuel combustion.[6,10] In particular, the lung cancer rates in this region are among China's highest in both males and females regardless of smoking status.[11] Previous epidemiological studies have shown that the excess lung cancer risk could be mainly attributed to the domestic combustion of "smoky" coal in poorly ventilated homes for heating and cooking.[11–13] Coal is the major domestic fuel in this region and depending upon the source (residents typically purchased coal from their nearest mines) is either referred to as smoky or smokeless coal, terms which relate to the amount of visible smoke produced on combustion. Smoky coal is further divided into subtypes based upon the underlying geochemical properties and geographic location.[14,15] These subtypes may have varying carcinogenic potentials as a wide variation in lung cancer risk (up to 25-fold) has been observed between geographic locations in Xuanwei.[16] Additionally, stove improvement programs have resulted in a reduction in HAP and a decreased burden of non-malignant and malignant lung disease in this region,[12,17,18] thus suggesting that HAP is important in the aetiology of malignant and non- malignant respiratory disease in the study area.

There have been few systematic indoor air quality studies in Xuanwei and Fuyuan to date, and these have mainly focused on the quantification of airborne benzo[a]pyrene (BaP).[13,19] Moreover, these studies focused on indoor air measurements, and it is unclear how these relate to personal exposure. This work presents our findings from personal and indoor $PM_{2.5}$ measurements collected from 30 villages throughout the Xuanwei and Fuyuan counties. Particular attention will be paid to differences between solid fuels (especially differences between smoky and smokeless coal), differences between stove designs (e.g., vented and unvented), and variation between smoky coal subtypes. This study also provides an opportunity to characterize the relationship between indoor and personal measurements, which may have an influence on costs, participation, and other logistical concerns for long-term studies[18,20] and provides information on the efficiency of stove improvement programs.

Methods

Study Design

This exposure assessment study was designed to provide a comprehensive characterization of air contaminants and exposures related to the use of solid fuels for cooking and heating, coordinating with an ongoing large case- control study of lung cancer, and a cross-sectional molecular epidemiology study of lung cancer in the same area.

A total of 30 villages were selected to represent the major geographical regions in Xuanwei and Fuyuan (Figure 1). In each selected village, up to 5 households were selected according

to the following criteria, which was intended to allow for eventual comparability to the larger case-control study: (i) having a stove that used solid fuel; (ii) the residence was more than 10 years old; (iii) use of the same cooking/ heating equipment for the past 5 years; and (iv) presence of a non-smoking healthy female aged 20−80 who was primarily responsible for cooking. The exposure survey was carried out in two phases. Phase I was carried out from August 2008 to February 2009 with all 30 villages visited and 148 subjects enrolled. Phase II was carried out between March and June of 2009. Sixteen of the initial 30 villages, chosen to represent the geographical spread, fuel use, and stove type distribution to phase I were revisited (Figure 1). In the second phase, 15 new subjects were enrolled and 53 of the enrolees from phase I were revisited allowing estimation of seasonal effects. Each sampling phase consisted of two sequential 24-h air measurements during which indoor and personal measurements were taken.

$PM_{2.5}$ Measurement

$PM_{2.5}$ measurements for 24-h were collected on preweighed 37 mm Teflon filters using a cyclone with an aerodynamic cut-off of 2.5μm (model BGI, GK 2.05SH) at a flow rate of 3.5 L/min (±20%). Pumps were calibrated prior to all measurements and flow rates were recorded pre and post sampling. Data were not accepted for further analysis if the post sampling flow was not within 10% of the presampling flow. For personal measurements, the pump was packed in a hip bag and the cyclone was attached near the breathing zone. At night, the sampling bag was put next to the subject's bed.

Most houses had a single living/cooking area. Measurements of 24-h indoor $PM_{2.5}$ were collected in the main living area using the same methods as described for the personal measurements. The samplers were placed at least 0.25m from the walls and between 1 and 2m from the stove. Placement varied somewhat because of limited available space in some households. If a subject had a separate room with an additional stove for cooking or heating, then a second stationary measurement was taken (this represents 6% of indoor measurements).

Exposed filters were packed individually in Petri slides sealed in zipped amber plastic bags and stored at −80 °C before post weighing. Particulate mass was assessed by pre- and post-weighing of the filters in an environmentally controlled weighing room using a microbalance at 1 μg accuracy. Each filter was pre- and post-weighed in duplicate. If the duplicate measurements differed by more than 5 μg, then the filter was reweighed. Weights were divided by the volume of air drawn through the filters to calculate $PM_{2.5}$ concentrations ($\mu g/m^3$).

For quality control purposes, approximately 10% of households were randomly selected to have duplicate $PM_{2.5}$measurements collected. The coefficient of variation of this quality control was 13%, based on 26 pairs of collocated indoor $PM_{2.5}$ samples.

Household Interview and Measurement

Household interviews were conducted by two trained interviewers. House dimensions were recorded and a sketch of each household was made detailing the position and dimensions of stoves, windows, chimneys, doors, and stairways. Subjects' activities during the sampling periods were recorded by administering a short activity questionnaire. The activity survey included information on cooking activities, heating practices, fuel usage, outdoor activities,

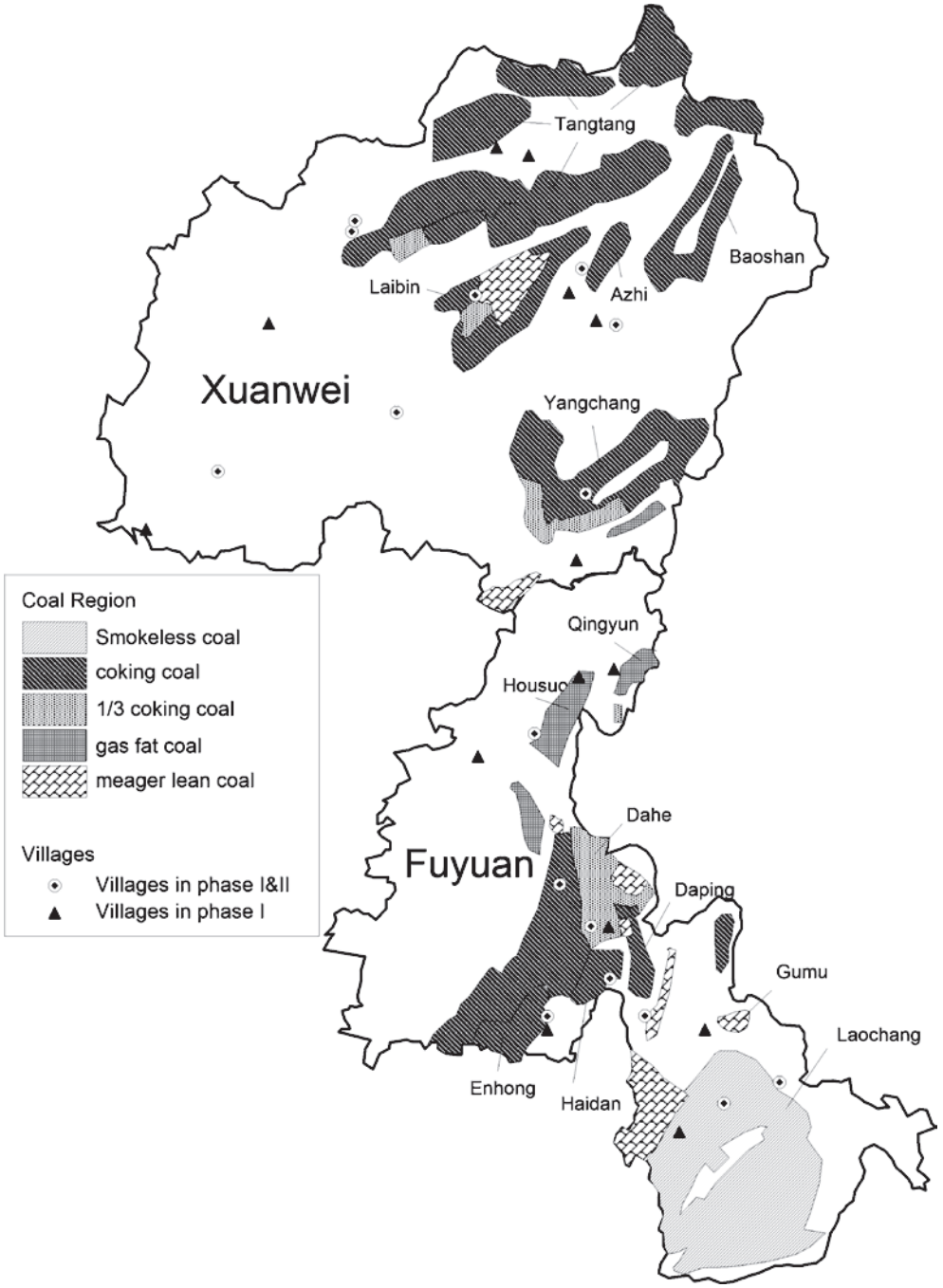

Figure 1 - Villages selected for the exposure survey and coal mines in Xuanwei and Fuyuan counties. Classification of coal regions based on the State Standard of China Coal Classification (GB5751-86); 1/3 coking, coking, gas fat, and meagre lean coals are subtypes f smoky coal

and sleeping habits. Stove details were recorded with a particular focus upon the ventilation aspect of their design. Traditionally, fuel has been burned in unvented firepits, but in recent decades a variety of stove types have been utilized throughout the area, not all of which include a functioning chimney. The major stove designs encountered were as follows: vented stoves, unvented stoves, firepits, portable stoves (a stove design intended to be lit outdoors and then carried indoors for use) and a combination of these stove designs. The other major sources of ventilation recorded were the numbers of doors, windows, and the presence or absence of a stairway in the main cooking area.

Fuel types were reported by respondents. Coal was generally reported as either "smoky" or "smokeless". Coal types were confirmed by petrochemical analysis of collected coal samples and in 11 cases the classification of coal type was changed to match petrochemical analysis (7 samples were reclassified as smoky coal and 4 samples were reclassified as smokeless coal).[14] Other categories identified were as follows: wood, plant products (which included the burning of corn cobs and tobacco stems−sometimes also in combination with wood), "mixed" coal (which represented the burning of manufactured coal briquettes and combinations of briquettes, smoky and smoke- less coal), and "mixed" fuel (which represented the burning of combinations of wood, plant materials and coal). The coal mines supplying coal were ascertained at interviews during household visits. Smoky coal burned during the exposure measurements came from 5 coal mines in Xuanwei and 8 mines in Fuyuan. Smoky coal was divided into subtypes according to the parameters of the State Standard of China Coal Classification (GB5751-86).[15] These smoky coal subtypes, based upon the parameters of volatile matter on a dry ash free basis and caking index, are referred to as coking, 1/3 coking, gas fat, and meagre lean coals.

On each measuring day, weather parameters including outside temperature, humidity, rainfall, wind speed, and direction were monitored by a portable weather station set up in the centre of each village.

Statistical Analysis

Normal probability plots indicated that exposures could best be described by a log-normal distribution. Therefore, natural logarithms of exposure concentrations were used in the statistical analyses. Exposure levels were summarized as arithmetic means (AM), geometric means (GM), and geometric standard deviations (GSD). Analysis of variance (ANOVA) testing was performed to test for differences in $PM_{2.5}$ exposure between differing stove and fuel configurations and for variation within the designated smoky coal subtypes. Tukey Honestly Significant Difference (HSD) testing was performed to assess pairwise differences within each combination of two levels of the various fuel and stove configurations.

A linear mixed effect model was constructed to identify variables that contributed to personal $PM_{2.5}$ exposure. Subjects and villages were assigned as random effects with a scalar (variance component) covariance structure. Multiple variables were considered for inclusion as fixed effects including: stove design, fuel type (including both broad fuel categories and the inclusion of smoky coal subtypes), fuel source, weight of fuel used, meteorological conditions, room size, number of owned stoves, number of doors, windows and the presence or absence of a stairway in the main cooking room, hours of using stoves, and the season during which measurements were taken. A full list of the 32 considered variables is available in Supporting Information (SI) Table S1. The variables selected for inclusion in the final model were those which best contributed to the prediction of $PM_{2.5}$

measurements and contributed to the lowest Akaike information criterion (AIC) score. The model can be summarized using the following formula:

$yijf = \mu + \beta1x1 + \beta2x2...\beta nxn + bIi + b\,Jij + \varepsilon ijf$

where yijf represents the natural log transformed value of personal $PM_{2.5}$exposure being modelled for village i, person j on day f; μ represents the intercept value (i.e., the log transformed $PM_{2.5}$ value for the reference group); β1 through to βn represent the fixed effect variable coefficients for variables x1 through xn; bIi represents the random effect coefficient for village i, while bJij represents the random effect coefficient for subject j from village i; and εijf represents the error for subject j in village i on day f.

Spearman correlation was calculated between personal and indoor $PM_{2.5}$ measurements collected on the same day and a linear mixed effect model was constructed to identify which variables best explained any differences in the association between personal and indoor $PM_{2.5}$ measurements.

Results

A total of 163 subjects participated in the exposure survey and 216 household visits were conducted. An overview of the characteristics of the study population is available in Table 1. Smoky coal was the main fuel type used during the measurement in both counties (45.8%), followed by "mixed" fuels (25.9%), and smokeless coal (8.8%). The most commonly used stove design was vented stoves (34.7%) followed by the use of multiple stoves with differing ventilation designs [which we refer to as "mixed ventilation" (28.2%)]. The average age of the subjects in the exposure survey was 56 years. The distribution of the villages visited is shown in Figure 1.

The overall GM of personal $PM_{2.5}$ concentrations in Xuanwei and Fuyuan were 166 (GSD:2.0) and 146 (GSD:1.9) $\mu g/m^3$, respectively. These levels were similar to the overall indoor $PM_{2.5}$ concentration [GM(GSD):162 (2.1) and 136 (2.0) $\mu g/m^3$ for Xuanwei and Fuyuan, respectively]. Personal and indoor $PM_{2.5}$ measurements correlated well, with Spearman correlation analysis indicating a moderately high coefficient between personal and indoor $PM_{2.5}$ ($r = 0.70$, $P < 0.0001$). Personal measurements were generally higher than indoor measurements (median percentage difference 6.5%). Linear mixed effect models were constructed, using the same approach as detailed above in order to assess which variables contributed to the observed differences between the log of the personal and indoor measurements. They observed that colder temperatures and the use of more fuel (as measured by weight) contributed to higher personal measurements, relative to indoor measurements (SI Table S2).

Descriptive statistics showed variations of $PM_{2.5}$ measurements between the various fuel types and stove designs (Table 2). In general, burning wood [GM(GSD):289 (2.1) and 327(1.9) $\mu g/m^3$] or plant materials [GM(GSD):225 (2.1) and 276(2.6) $\mu g/m^3$] resulted in the highest personal and indoor $PM_{2.5}$ levels, respectively. Significantly higher indoor $PM_{2.5}$ concentrations were observed among smoky coal burning homes compared to homes using smokeless coal [GM(GSD):144 (2.0) versus 96 (1.6) $\mu g/m^3$, $p < 0.05$]. Personal $PM_{2.5}$ exposure attributable to people using smoky coal was also higher than those using smokeless coal [GM(GSD):148(1.9) versus 115(1.9) $\mu g/m^3$], although the exposure did not differ significantly.

When assessing the role of stove design, we observed that measurements from homes and individuals using vented stoves were generally lower than if an unvented stove or firepit was used. Notably, among smoky coal burning homes, vented stoves had significantly lower personal and indoor $PM_{2.5}$ exposures as compared with firepits [personal values: GM (GSD):134 (1.6) versus 277 (1.6) $\mu g/m^3$, $p < 0.05$; indoor values: 127(1.7) versus 350(1.4) $\mu g/m^3$, $p < 0.05$]. Vented stoves were also observed to have significantly lower $PM_{2.5}$ levels than unvented stoves for homes burning "mixed" fuels [personal measurements: 104 (1.8) versus 250 (2.2) $\mu g/m^3$, $p < 0.05$; indoor measurements: 98(2.3) versus 220(2.5) $\mu g/m^3$,$p < 0.05$].

An assessment of variation in $PM_{2.5}$ levels between and within designated smoky coal subtypes is presented in Table 3. Only households that exclusively burned smoky coal were included in the analysis (199 personal and 210 indoor measurements). ANOVA analysis revealed little variation between the coking coal mines from Xuanwei but showed significant variation between the four designated smoky coal subtypes for both personal and indoor measurements (coking coal, 1/3 coking coal, gas fat coal, and meagre lean coal) in Fuyuan. Furthermore, significant variation in personal $PM_{2.5}$ levels was observed for coal

Table 1 - Characteristics of the study population in Xuanwei and Fuyuan

	Phase I		Phase II		All
	Xuanwei	Fuyuan	Xuanwei	Fuyuan	
Subjects, n	74	74	31	37	163[a]
Villages, n	15	15	8	8	30
Age (in 2009), mean ± SD	54.0 ± 14.9	56.7 ± 13.7	62.0 ± 11.3	58.9 ± 12.2	56.0 ± 14.4
Stove type, n(%)					
Vented stove	34(45.9)	19(25.7)	12(38.7)	10(27.0)	75(34.7)
High stove with chimney	13(17.6)	5(6.8)	6(19.4)	1(2.7)	25(11.6)
Low stove with chimney	8(10.8)	11(14.9)	2(6.5)	6(16.2)	27(12.5)
Multiple stoves with chimneys	13(17.6)	3(4.1)	4(12.9)	3(8.1)	23(10.6)
Unvented stove	4(5.4)	12(16.2)	0(0.0)	11(29.7)	27(12.5)
High stove without chimney	0(0.0)	6(8.1)	0(0.0)	2(5.4)	8(3.7)
Low stove without chimney	0(0.0)	0(0.0)	0(0.0)	1(2.7)	1(0.5)
Multiple stoves without any chimney	4(5.4)	6(8.1)	0(0.0)	8(21.6)	18(8.3)
Portable stove	2(2.7)	19(25.7)	1(3.2)	8(21.6)	30(13.9)
Firepit	3(4.1)	7(9.5)	3(9.7)	3(8.1)	16(7.4)
Mixed ventilation stoves[b]	30(40.5)	13(17.6)	13(41.9)	5(13.5)	61(28.2)
Unknown ventilation stove	1(1.4)	4(5.4)	2(6.5)	0(0.0)	7(3.2)
Solid fuel type, n(%)					
Smoky coal	42(56.8)	32(43.2)	19(61.3)	6(16.2)	99(45.8)
Smokeless coal	0(0.0)	13(17.6)	1(3.2)	5(13.5)	19(8.8)
"Mixed" coal[c]	9(12.2)	5(6.8)	1(3.2)	4(10.8)	19(8.8)
Wood	3(4.1)	1(1.4)	2(6.5)	6(16.2)	11(5.1)
Plant materials[d]	4(5.4)	3(4.1)	1(3.2)	0(0.0)	9(4.2)
"Mixed" fuel[e]	16(21.6)	18(24.3)	6(19.4)	16(43.2)	56(25.9)
Unknown	0(0.0)	2(2.7)	1(3.2)	0(0.0)	3(1.4)
Median length of stove operation, hours per day	4	3.3	8	13	5.1

[a]There were 216 visits to the households in total: of the 148 subjects visited in phase I, 53 were revisited the second time, and 15 new subjects were enrolled in phase II.
[b]Refers to the use of vented stove and unvented stove/portable stove simultaneously.
[c]Refers to the use of combinations of smoky and smokeless coal and also to the use of prepared coal briquettes.
[d]Plant materials include combinations of wood, tobacco stem and corncob.
[e]Refers to combinations of wood, plant materials and coal

Table 2 - Personal and Indoor $PM_{2.5}$ (μg/m^3) Exposure Related to Different Stove Ventilation Configurations and Fuel Types

		Personal				Indoor			
Fuel Type	Stove Design	N[a]	AM[b]	GM[b]	GSD[b]	N[a]	AM[b]	GM[b]	GSD[b]
Smoky coal		206	180	148[c]	1.9	210	185	144[c]	2.0
	Vented stove	110	150	134	1.6	114	149	127	1.7
	Unvented stove[d]	8	252	233	1.6	8	221	183	2.0
	Portable stove	22	178	143	1.9	20	168	135	2.0
	Firepit	15	307	277[e]	1.6	15	371	350[e]	1.4
	Mixed ventilation stove	44	219	164	2.3	45	232	166	2.1
Smokeless coal		47	152	115	1.9	45	104	96[f]	1.6
	Vented stove	5	151	126	2.0	5	117	104	1.7
	Unvented stove[d]	18	167	109	2.1	17	107	103	1.4
	Portable stove	19	150	123	1.9	18	101	89	1.8
	Firepit	3	104	102	1.3	3	91	90	1.3
	Mixed ventilation stove	2	97	95	1.3	2	85	83	1.4
"Mixed" coal[g]		38	183	161	1.7	42	164	130	2.0
	Vented stove	13	152	137	1.7	14	151	123	1.9
	Unvented stove[d]	0	-	-	-	0	-	-	-
	Portable stove	14	209	180	1.8	14	173	121	2.4
	Firepit	2	156	150	1.5	2	157	154	1.3
	Mixed ventilation stove	9	192	176	1.6	12	170	145	1.8
Wood		24	369	289[f]	2.1	24	393	327[f]	1.9
	Vented stove	8	226	183	1.9	8	339	257	2.2
	Unvented stove[d]	0	-	-	-	0	-	-	-
	Portable stove	6	327	320	1.3	5	247	244	1.2
	Firepit	10	508	392	2.4	10	520	467	1.7
	Mixed ventilation stove	0	-	-	-	0	-	-	-
Plant materials[h]		13	284	225[c]	2.1	13	417	276[f]	2.6
	Vented stove	3	123	109	1.8	3	80	76	1.4
	Unvented stove[d]	3	416	408	1.3	3	402	377	1.6
	Portable stove	2	439	439	1.0	2	422	407	1.5
	Firepit	4	146	138	1.5	4	617	382	3.0
	Mixed ventilation stove	1	605	605	-	1	658	658	-
"Mixed" fuel[i]		94	205	160[c]	2.0	113	210	152[c]	2.2
	Vented stove	19	121	104	1.8	22	140	98	2.3
	Unvented stove[d]	17	306	250[e]	2.2	26	316	220[e]	2.5
	Portable stove	7	219	203	1.5	7	204	196	1.3
	Firepit	0	-	-	-	0	-	-	-
	Mixed ventilation stove	47	207	165	1.9	54	196	153	1.9

[a]Data for unknown ventilation stoves or unknown fuel type are not shown.
[b]AM = Arithmetic Mean, GM = Geometric Mean, GSD = Geometric Standard Deviation.
[c]Significant ($p < 0.05$) variation between stove ventilation designs within designated fuel type via ANOVA testing.
[d]Refers to high and/or low stoves without any chimney.
[e]$p < 0.05$ when compared with vented stove in same fuel type via Tukey HSD test.
[f]$p < 0.05$ when compared with smoky coal via Tukey HSD test.
[g]Refers to the use of combinations of smoky, smokeless coal, and prepared coal briquettes.
[h]Plant materials include combinations of wood, tobacco stem, and corncob.
[i]Refers to combinations of wood, plant materials and coal.

sourced from within the coking coal, 1/3 coking coal and gas fat coal mines in Fuyuan (indoor measurements showed significant variation in the coking and gas-fat coal subtypes). Linear mixed effect modelling was carried out to identify variables that had a significant role in personal $PM_{2.5}$ exposures. Of the 32 variables considered, 5 were found to significantly impact personal $PM_{2.5}$. These determinants are the broad fuel types (smoky coal, smokeless coal, etc.), stove ventilation, the season of the year, the number of windows in the main cooking area, and the recorded number of hours burning a solid fuel standardized by the number of stoves used. Estimates (β), 95% confidence intervals, and geometric mean ratio [GMR = exp(β) = GM(estimate)/GM(reference)] are provided in Table 4. The linear mixed effect model of personal $PM_{2.5}$ explains 35% of the variance between subjects and 79% of the variance between villages (Table 4). Among the assessed fuel types, wood results in the highest modelled $PM_{2.5}$ exposure (GMR: 2.80). Among stove designs, unvented stoves were found to result in the highest predicted $PM_{2.5}$ exposure (GMR: 1.62) although the use of firepits resulted in similar predicted $PM_{2.5}$ exposure (GMR: 1.47). Homes with one window in their main cooking area were found to result in higher $PM_{2.5}$ exposure (GMR for one window: 1.25) than those with zero or two windows (GMR for two windows: 0.99). The season during which measurements were taken also played a role in $PM_{2.5}$ exposure, with measurements taken in summer resulting in the lowest predicted $PM_{2.5}$ exposure (GMR: 0.71) and measurements taken in winter resulted in the highest (GMR: 1.21). The amount of time burning fuels, standardized by the number of stoves used, also played a role in $PM_{2.5}$ exposure with every hour of stove operation

Table 3 - Personal and Indoor $PM_{2.5}$ (μg/m^3) Concentrations from Smoky Coal Burning Homes from Xuanwei and Fuyuan, by Coal Source

			Personal				Indoor			
County	Smoky coal subtype	Coal mine	N[a]	AM[b]	GM[b]	GSD[b]	N[a]	AM[b]	GM[b]	GSD[b]
Xuanwei	Coking coal		119	189	153	2.0	122	196	149	2.0
		Azhi	34	227	181	1.9	33	186	160	1.7
		Baoshan	12	210	168	2.2	12	246	193	2.1
		Laibin	28	153	132	2.1	30	220	152	2.2
		Tangtang	31	194	152	2	33	191	133	2.3
		Yangchang	14	142	125	1.6	14	135	124	1.5
Fuyuan	Overall		80	168	142[c]	1.8	88	169	138[c]	1.9
	Coking coal		23	213	175[d]	1.9	27	188	154[d]	1.9
		Daping	9	111	104	1.5	10	87	83	1.4
		Enhong	9	241	208	1.8	11	250	222	1.7
		Haidan	5	348	329	1.4	6	242	221	1.7
	1/3 coking coal		13	183	165[d]	1.6	12	271	245	1.7
		Bagong	10	207	194	1.4	9	274	262	1.4
		Dahe	3	104	96	1.6	3	263	200	2.8
	Gas fat coal		40	135	120[d]	1.6	39	117	107[d]	1.6
		Housuo	38	130	116	1.6	37	111	102	1.5
		Qingyun	2	237	237	1	2	236	235	1.1
	Meager lean coal	Gumu	4	138	96	2.8	4	196	149	2

[a]Number of measurements is from households which exclusively burn smoky coal and report a coal source consistent with reported coal type. [b]AM= Arithmetic Mean, GM = Geometric Mean, GSD = Geometric Standard Deviation.

[c]Significant ($p < 0.05$) variation between smoky coal subtypes sourced in Fuyuan via ANOVA test.

[d]Significant ($p < 0.05$) variation between coal mines within identified smoky coal subtype via ANOVA test

Table 4 - Linear Mixed Effect Modelling of ln-Transformed Personal $PM_{2.5}$ Exposure

		Estimate(β)	95%CI	GMR[a]
Fuel Type				
	Smokeless coal	ref.		1
	Smoky coal	0.27	0.02,0.52	1.31
	"Mixed" coal	0.35	0.06,0.64	1.42
	Wood	1.03	0.66,1.40	2.8
	Plant materials	0.43	0.02,0.84	1.54
	“Mixed” fuel	0.37	0.11,0.63	1.45
Stove design				
	Vented stove	ref.		1
	Unvented stove	0.48	0.22,0.74	1.62
	Portable stove	0.26	0.06,0.47	1.3
	Firepit	0.38	0.10,0.66	1.47
	Mixed ventilation	0.2	0.03,0.36	1.22
	Unknown ventilation	−0.34	−0.77,0.09	0.71
Number of windows in main cooking room				
	None	ref.	1	
	One	0.22	0.01,0.44	1.25
	Two	−0.01	−0.26,0.23	0.99
Season				
	Autumn	ref.	1	
	Winter	0.19	0.02,0.36	1.21
	Spring	−0.24	−0.41,-0.07	0.79
	Summer	−0.34	−0.68,0.00	0.71
Number of hours burning fuel standardized by number of used stoves[b]		0.01	0.003,0.03	1.01
Variation explained, %				
Between individual subjects			35	
Between villages			79	
Reference value[c], ln-μg/m^3			4.35	

[a]Geometric mean ratio = GM(estimate)/GM(reference) = Exp(β).
[b]Median period 4.3 h; IQR 2.2 to 9.6 h per stove.
[c]Reference value represents base value of log transformed $PM_{2.5}$ in model for reference group (smokeless coal burnt in a vented stove, during autumn in a room with no windows)

[median operating time 4.3 h; Interquartile Range (IQR) 2.2 to 9.6 h per stove] resulting in an incremental increase (GMR: 1.01) of $PM_{2.5}$ exposure. The model output for indoor measurements is very similar to personal measurement model, shown in SI Table S3.

Discussion

The combustion of biomass and coals is a significant contributor to HAP and exposure to $PM_{2.5}$ worldwide. Biomass burning may account for 74−87% total $PM_{2.5}$ in households with a single dominant cooking source.[21] A wide range of factors, including stove design, fuel type, activity patterns, weather conditions, and household room configuration, can contribute to HAP.[20] For example, fuel type and ventilation were found to be significant determinants of household $PM_{2.5}$ in a study based in India,[22] while a Chinese based stove emission study showed that honeycomb coal resulted in lower emissions of sulfur dioxide, nitrogen oxide, and total suspended particulate, but 2−3 fold higher $PM_{2.5}$ compared to coal cake.[23]

In our study on personal and indoor $PM_{2.5}$ exposure in a rural population in China with high lung cancer incidence, fuel type, ventilation, cooking room configuration, season, and burning time per stove were identified as main determinants of $PM_{2.5}$ exposure. Our study found that burning wood and other plant materials in unvented stoves resulted in the highest $PM_{2.5}$ measured both personally and indoors. These measurements are consistent with international research in similar settings for unvented stoves using wood [albeit our measurements are at the lower end of the exposure range (AM for indoor $PM_{2.5}$ air measurements 520μg/m^3)]. For example, the AM of 22-h $PM_{2.5}$ measurements of 9 households in kitchens with an open wood stove in Guatemala was 528±249 μg m^3.[24] The geometric mean 48-h $PM_{2.5}$of 53 households in kitchens using wood in an open fire without ventilation in rural Mexico was 615μg/m^3,[25] and the AM of 48-h $PM_{2.5}$ measurements of 63 households in the highlands of San Marcos, Guatemala using open wood fires was 900 ±700μg/m^3.[26]

$PM_{2.5}$ exposure levels among coal users in our study were similar to other studies studying coal combustion for cooking and heating in China. An indoor air pollution measurement study in four provinces in China observed indoor Respirable Particulate Matter (RPM) concentrations in the primary biomass fuel provinces of Inner Mongolia and Gansu of 719 and 661μg/m^3, respectively, while indoor RPM concentrations in the primarily coal-burning provinces of Guizhou (202−352μg/m^3) and Shanxi (187−361μg/m^3) were lower.[27] The Sino Dutch project including 150 households in five counties of three provinces monitored 24-h $PM_{2.5}$ levels averaging 290 μg/m^3 in households mainly burning coal.[28]

The observed differences between studies could be caused by several factors including differences in coal types. In our study, we observed differences in $PM_{2.5}$emissions between smoky and smokeless coal (GM for indoor measurements: 144μg/m^3 and 96μg/m^3 respectively). Furthermore, when investigating for variation in $PM_{2.5}$ measurements between smoky coal sources, we observed significant variation between smoky coal subtypes from Fuyuan. Variation was also observed between coal mines producing the same smoky coal subtypes for the coking, 1/3 coking and gas fat coal subtypes. This indicates that when comparing HAP exposure studies the exact fuel types need to be carefully considered. It also provides indications that the observed health effects may be differential within a particular solid fuel type (e.g., coals).[29]

Many of the previous exposure studies on HAP have focused on measuring indoor air concentrations with relatively few measuring personal exposure, resulting in uncertainty in

how these indoor measurements correspond to personal exposure.[20] Several studies have shown that indoor air measurements do not always accurately reflect personal exposure levels to HAP, possibly limiting the interpretation of these indoor measurements.[30,31] In our study, we found that personal and indoor $PM_{2.5}$ air measurements were quite similar and that the correlation coefficient between indoor air $PM_{2.5}$concentrations and personal $PM_{2.5}$ exposure levels was high (Spearman r =0.70,P< 0.0001). This association was modified primarily by the volume of fuel used and temperature (i.e., season) (SI Table S2), both likely proxies of residence time inside the home. This suggests that indoor air concentrations may be good proxies for personal exposure levels of non-smoking females in this study area. The generalizability of this observation may be limited as our enrolees were generally older women (mean age of 56 years) who were primarily responsible for cooking and housekeeping, meaning that they generally spent the majority of their days indoors. Men, and younger women, who may spend a greater portion of their time outdoors may have different exposure experiences and a weaker correlation between indoor and personal $PM_{2.5}$ exposure levels.

Mixed effect modelling showed that fuel type, ventilation, number of windows, and season are strong determinants of personal $PM_{2.5}$ exposure, which reflects some of the findings of the descriptive statistics (specifically fuel types and stove design). Ventilation has been shown to be effective in reducing HAP exposures[24,25,30,32] and in reducing malignant and non-malignant disease both internationally and in Xuanwei and Fuyuan. We observed a difference of 34−80% in $PM_{2.5}$ concentrations between vented stoves and unvented stoves/firepits burning smoky coal, wood, plant materials and combinations of coal/plant materials. These values are similar to the reduction reported by the Sino-Dutch project in China where a reduction of 40% was observed after implementation of stove improvements,[33]and slightly lower than what has been reported for stove improvement programs in Latin America where reduction levels ranging between 70% and 80% have been reported among primarily wood burning homes.[24,25,30,32] Additionally, although our study is using a cross-sectional design, our households were selected based on having no stove improvements in the last 5 years. As such the role of stove ventilation presented here represents designs that have been continually used for many years and have likely undergone some “wear and tear”. Therefore, this may result in somewhat lower decreases than observed in other studies that performed their evaluations shortly after the introduction of stove improvements. However, this also shows that stove improvement programs do not only result in a short-term reduction in HAP but one which seems to be sustained for a longer time. The finding of increased personal $PM_{2.5}$ in the colder seasons is consistent with expected behaviour, as people would spend a greater proportion of their time indoors.

The finding that having one window in the main cooking room presented higher modelled $PM_{2.5}$ measurements than those with zero or two windows seems counterintuitive to the logical expectation. A possible explanation for this observation may relate to home design. If we postulate based on field observations that homes with zero windows represent poorer households, then it is likely that they have poorer construction than homes with windows. This poorer construction may increase home ventilation due to imperfections in the structure of the home acting as ventilation conduits. The role of burning time, standardized by the number of stoves used in personal exposure to $PM_{2.5}$ is consistent with the expectation of increased exposure with increased burning time.

The findings of this work provide a valuable insight into potential etiological factors of the lung cancer epidemic in Xuanwei and Fuyuan. However, the high $PM_{2.5}$ measurements in

emissions from wood and plant burning homes (which do not have high lung cancer rates when compared to smoky coal burning homes) indicate that measurements of $PM_{2.5}$ exclusively will not be sufficient to explain the lung cancer epidemic in Xuanwei and Fuyuan. Future research will further investigate the constituents of fuel emissions and work toward associating those emissions with lung cancer epidemiology

Acknowledgements

This project was supported by the National Institutes of Health intramural research program. The content of this publication does not necessarily reflect the views or policies of the Department of Health and Human Services, nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government. The authors would like to acknowledge Jackie King from BioReliance and Peter Hui and Nathan Appel from Information Management Systems, Inc. for their support.

References

1. Zhang, J. J.; Smith, K. R. Household air pollution from coal and biomass fuels in China: Measurements, health impacts, and interventions. *Environ*. *Health Perspect*, 2007, 115, 848−855.
2. Hosgood, H. D., III; Menashe, I.; He, X. Z.; Chanock, S.; Lan, Q.PTEN identified as important risk factor of chronic obstructive pulmonary disease.Respir. Med, 2009, 103, 1866−1870
3. Zhang, J. J.; Hu, W.; Wei, F.; Wu, G.; Korn, L. R.; Chapman, R. S.Children's respiratory morbidity prevalence in relation to air pollution in four Chinese cities. Environ. Health Perspect, 2002, 110, 961−967.
4. Zhou, X.; Jin, Y.; He, X. Z. A study on the relationship between in-door air pollution and chronic obstructive pulmonary disease in Xuanwei County. Zhonghua Yu Fang Yi Xue Za Zhi 1995, 29,38−40.
5. Ezzati, M., World Health Organization. Comparative quantification of health risks: global and regional burden of disease attributable to selected major risk factors; World Health Organization; Geneva, 2004.
6. Chapman, R. S.; He, X. Z.; Blair, A. E.; Lan, Q. Improvement in household stoves and risk of chronic obstructive pulmonary disease in Xuanwei, China: Retrospective cohort study. BMJ. 2005, 331,1050.
7. Shen, M.; Vermeulen, R.; Chapman, R. S.; Berndt, S. I.; He, X. Z.;Chanock, S.; Caporaso, N.; Lan, Q. A report of cytokine polymorphisms and COPD risk in Xuan Wei, China.Int. J. Hyg. Environ.Health, 2008, 211, 352−356.
8. Smith, K. R.; McCracken, J. P.; Weber, M. W.; Hubbard, A.;Jenny, A.; Thompson, L. M.; Balmes, J.; Diaz, A.; Arana, B.; Bruce, N. Effect of reduction in household air pollution on childhood pneumonia in Guatemala (RESPIRE): A randomised controlled trial. Lancet, 2011, 378, 1717−1726.
9. Wu, C.; Hu, Z.; Yu, D.; Huang, L.; Jin, G.; Liang, J.; Guo, H.; Tan, W.; Zhang, M.; Qian, J.; Lu, D.; Wu, T.; Lin, D.; Shen, H. Genetic variants on chromosome 15q25 associated with lung cancer risk in Chinese populations. Cancer Res.2009, 69, 5065−5072.
10. Shen, M.; Chapman, R. S.; Vermeulen, R.; Tian, L.; Zheng, T.; Chen, B. E.; Engels, E. A.; He, X. Z.; Blair, A.; Lan, Q. Coal use, stove improvement, and adult pneumonia mortality in Xuanwei, China: A retrospective cohort study. Environ. Health Perspect.2009, 117, 261−266.
11. Mumford, J. L.; He, X. Z.; Chapman, R. S.; Cao, S. R.; Harris, D. B.; Li, X. M.; Xian, Y. L.; Jiang, W. Z.; Xu, C. W.; Chuang, J. C. Lung cancer and indoor air pollution in Xuan Wei, China. Science 1987, 235, 217−220.
12. Lan, Q.; Chapman, R. S.; Schreinemachers, D. M.; Tian, L.; He, X. Z. Household stove improvement and risk of lung cancer in Xuanwei, China.J. Natl. Cancer Inst 2002, 94, 826−835.
13. He, X. Z.; Chen, W.; Liu, Z. Y.; Chapman, 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 Perspect, 1991, 94,9−13.
14. Downward, G. S.; Hu, W.; Large, D.; Veld, H.; Xu, J.; Reiss, B.; Wu, G.; Wei, F.; Chapman, R. S.; Rothman, N.; Qing, L.; Vermeulen, R. Heterogeneity in coal composition and implications for lung cancer risk in Xuanwei and Fuyuan counties, China. Environ. Int.2014, 68C, 94−104.
15. Chen, P. Study on integrated classification system for Chinese coal. Fuel Process. Technol. 2000, 62,77−87.
16. Lan, Q.; He, X. Z.; Shen, M.; Tian, L.; Liu, L. Z.; Lai, H.; Chen, W.; Berndt, S. I.; Hosgood, H. D.; Lee, K. M.; Zheng, T.; Blair, A.; Chapman, R. S. Variation in lung cancer risk by smoky coal subtype in Xuanwei, China. Int. J. Cancer 2008, 123, 2164−2169.
17. Hosgood, H. D., III; Chapman, R.; Shen, M.; Blair, A.; Chen, E.; Zheng, T.; Lee, K. M.; He, X.; Lan, Q. Portable stove use is associated with lower lung cancer mortality risk in lifetime smoky coal users. Br. J. Cancer 2008, 99, 1934−1939.
18. Barone-Adesi, F.; Chapman, R. S.; Silverman, D. T.; He, X.; Hu, W.; Vermeulen, R.; Ning, B.; Fraumeni, J. F., Jr.; Rothman, N.; Lan, Q. Risk of lung cancer associated with domestic use of coal in Xuanwei, China: Retrospective cohort study. BMJ. 2012, 345, e5414.

19. Tian, L. W.; Lan, Q.; Yang, D.; He, X. Z.; Yu, I. T. S.; Hammond, S. K. Effect of chimneys on indoor air concentrations of PM10 and benzo[a]pyrene in Xuan Wei, China. Atmos. Environ. 2009, 43, 3352−3355.
20. Clark, M. L.; Peel, J. L.; Balakrishnan, K.; Breysse, P. N.; Chillrud, S. N.; Naeher, L. P.; Rodes, C. E.; Vette, A. F.; Balbus, J. M. Health and household air pollution from solid fuel use: the need for improved exposure assessment. Environ. Health Perspect. 2013, 121, 1120−1128.
21. Zhou, Z.; Dionisio, K. L.; Verissimo, T. G.; Kerr, A. S.; Coull, B.; Howie, S.; Arku, R. E.; Koutrakis, P.; Spengler, J. D.; Fornace, K.; Hughes, A. F.; Vallarino, J.; Agyei-Mensah, S.; Ezzati, M. Chemical characterization and source apportionment of household fine particulate matter in rural, peri-urban, and urban West Africa. Environ. Sci. Technol. 2014, 48, 1343−1351.
22. Balakrishnan, K.; Ghosh, S.; Ganguli, B.; Sambandam, S.; Bruce, N.; Barnes, D. F.; Smith, K. R. State and national household concentrations of $PM_{2.5}$ from solid cookfuel use: Results from measurements and modelling in India for estimation of the global burden of disease. Environ. Health, 2013, 12, 77.
23. Ge, S.; Xu, X.; Chow, J. C.; Watson, J.; Sheng, Q.; Liu, W.; Bai, Z.; Zhu, T.; Zhang, J. Emissions of air pollutants from household stoves: honeycomb coal versus coal cake. Environ. Sci. Technol.2004, 38, 4612−4618.
24. Naeher, L. P.; Smith, K. R.; Leaderer, B. P.; Neufeld, L.; Mage, D. T. Carbon monoxide as a tracer for assessing exposures to particulate matter in wood and gas cookstove households of highland Guatemala. *Environ*. *Sci*. *Technol*. 2001, 35, 575−581.
25. Zuk, M.; Rojas, L.; Blanco, S.; Serrano, P.; Cruz, J.; Angeles, F.; Tzintzun, G.; Armendariz, C.; Edwards, R. D.; Johnson, M.; Riojas Rodriguez, H.; Masera, O. The impact of improved wood-burning stoves on fine particulate matter concentrations in rural Mexican homes. *J*. *Expo Sci*. *Environ*. *Epidemiol*. 2007, 17, 224−232.
26. Northcross, A.; Chowdhury, Z.; McCracken, J.; Canuz, E.; Smith, K. R. Estimating personal $PM_{2.5}$ exposures using CO measurements in Guatemalan households cooking with wood fuel. J. Environ. Monit.2010, 12, 873−878.
27. Jin, Y.; Zhou, Z.; He, G.; Wei, H.; Liu, J.; Liu, F.; Tang, N.; Ying, B.; Liu, Y.; Hu, G.; Wang, H.; Balakrishnan, K.; Watson, K.; Baris, E.; Ezzati, M. Geographical, spatial, and temporal distributions of multiple indoor air pollutants in four Chinese provinces. Environ. Sci. Technol. 2005, 39, 9431−9439.
28. Wei, X. Influence on indoor air quality by using different type of stove and fuel. Trans. CSAE 2006, 22, 236−239.
29. Hosgood, H. D., III; Wei, H.; Sapkota, A.; Choudhury, I.; Bruce, N.; Smith, K. R.; Rothman, N.; Lan, Q. Household coal use and lung cancer: Systematic review and meta-analysis of case-control studies, with an emphasis on geographic variation. Int. J. Epidemiol, 2011, 40, 719−728.
30. Cynthia, A. A.; Edwards, R. D.; Johnson, M.; Zuk, M.; Rojas, L.; Jimenez, R. D.; Riojas-Rodriguez, H.; Masera, O. Reduction in personal exposures to particulate matter and carbon monoxide as a result of the installation of a Patsari improved cook stove in Michoacan Mexico. Indoor Air 2008, 18,93−105.
31. Van Vliet, E. D.; Asante, K.; Jack, D. W.; Kinney, P. L.; Whyatt, R. M.; Chillrud, S. N.; Abokyi, L.; Zandoh, C.; Owusu-Agyei, S. Personal exposures to fine particulate matter and black carbon in households cooking with biomass fuels in rural Ghana. Environ. Res. 2013, 127,40−48.
32. Albalak, R.; Bruce, N.; McCracken, J. P.; Smith, K. R.; De Gallardo, T. Indoor respirable particulate matter concentrations from an open fire, improved cookstove, and LPG/open fire combination in a rural Guatemalan community. Environ. Sci. Technol.2001, 35, 2650−2655.
33. Dong, R. Assessment of improvements in the Sino-Dutch rural renewable energy project. Chinese Agricultural University report to the Chinese Association of Rural Energy Industries; Chinese Agricultural University; Beijing, China, 2006.

Chapter 3

Appendix - Supplementary information: 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

(Online: http://pubs.acs.org/doi/suppl/10.1021/es502201s)

Table S1 - Variables considered for inclusion in mixed model creation

Broad Category	Detailed variables
Stove design	**Stove ventilation (ventilated, unventilated, mixed, portable stove or firepit)**
	Stove ventilated, unventilated or mixed ventilation*
	Stove ventilated, unventilated mixed or firepit
	Stove either firepit or other design (or mixed)
	Stove design as reported by study participant£
Fuel type/source	Major fuel type including smoky coal subtypes and county from which coal sourced (Fuyuan was divided into north/south)
	County from which fuel purchased
	Broad fuel types (smoky coal, smokeless coal, "mixed" coal, wood, plant materials, "mixed" fuels)
	Fuel type including smoky coal subtypes
	Fuel type including individual smoky coal mines
	Fuel type including smoky coal subtypes
	Weight of fuel used†
Meteorological conditions	**Season of measurement**
	Average daily temperature
	Average daily high temperature
	Average daily low temperature
	Average daily humidity
	Average daily wind speed
	Average daily maximum wind speed
	Average daily dew point
	Average daily rainfall
Other variables	Room size†
	Phase of study during visit
	Number of owned stoves
	Number of doors in main cooking room
	Number of windows in main cooking room
	Presence or absence of a stairway in the main cooking room
	Hours of stove use standardized by number of used stoves
	Hours of stove use per measurement period
	Age of participant
	Month of visit
	Administrative borders‡

*refers to the use of multiple stoves with different ventilation designs.
£categories are high stove, low stove (with or without ventilation), portable stove, firepit and multiple stoves.
†divided into quartiles.
‡townships/areas as defined by local administrative bodies.
Variables in bold were selected for model construction

Table S2 - Linear mixed effect model indicating variables which contribute to differences between indoor and personal measurements

		Estimate (β)	95%CI	GMR[‡]
Ln(indoor $PM_{2.5}$ measurement), ln-μg/m^3		0.59	0.53,0.66	1.80
Average daily high temperature		-0.01	-0.02,-0.01	0.99
Weight of fuel (in quartiles)				
	1	Ref.		1.00
	2	0.06	-0.07,0.20	1.06
	3	0.18	0.04,0.32	1.20
	4	0.15	0.00,0.29	1.16
	Unknown	0.20	0.03,0.36	1.22
Variance explained				
	Between subjects		73%	
	Between villages		100%[*]	
Reference value[†] (ln personal measurement), ln-μg/m^3			2.12	

[‡]Geometric mean ratio = GM(estimate)/GM(reference) = exp(β).
[†]Reference value represents base value of ln-transformed $PM_{2.5}$ in model for reference group [low weight fuel used coinciding with lowest ln-transformed indoor $PM_{2.5}$ (3.17) and temperature measurements (-0.4˚C)].
[*]Zero residual between village variance remained in the final model as a result of the high correlation between indoor and personal measurements.

Table S3 - Linear mixed effect modelling of ln-transformed indoor $PM_{2.5}$ exposure

		Estimate(β)	95% CI	GMR‡
Fuel type				
	Smokeless coal	Ref.		1.00
	Smoky coal	0.29	0.02,0.56	1.34
	"Mixed" coal	0.22	-0.08,0.52	1.24
	Wood	0.78	0.38,1.18	2.19
	Plant materials	0.55	0.13,0.97	1.73
	"Mixed" fuel	0.28	0.01,0.56	1.33
Stove design				
	Vented stove	Ref.		1.00
	Unvented stove	0.34	0.06,0.61	1.40
	Portable stove	0.15	-0.07,0.38	1.17
	Firepit	0.54	0.23,0.85	1.72
	Mixed ventilation stove	0.20	0.02,0.37	1.21
	Unknown ventilation stove	-0.30	-0.69,0.09	0.74
Number of windows in main cooking room				
	Zero	Ref.		1.00
	One	0.03	-0.22,0.27	1.03
	Two	-0.15	-0.43,0.12	0.86
Season				
	Autumn	Ref.		1.00
	Winter	0.18	0.00,0.35	1.20
	Spring	-0.12	-0.28,0.05	0.89
	Summer	-0.55	-0.9,-0.2	0.58
Number of hours burning fuel standardized by number of used stoves§		0.00	-0.02,0.01	1.00
Variation explained, %				
	Between individual subjects		36	
	Between villages		63	
Reference value†, ln-μg/m^3			4.60	

‡Geometric mean ratio = GM(estimate)/GM(reference) = exp(β).
§Median period 4.3 hrs; IQR 2.2 to 9.6 hrs per stove.
†Reference value represents base value of ln-transformed $PM_{2.5}$ in model for reference group (smokeless coal burnt in a vented stove, during autumn in a room with no windows).

Chapter 4

Polycyclic Aromatic Hydrocarbon exposure in household air pollution from solid fuel combustion among the female population of Xuanwei and Fuyuan counties, China

George S. Downward
Wei Hu
Nat Rothman
Boris Reiss
Guoping Wu
Fusheng Wei
Robert S. Chapman
Lutzen Portengen
Lan Qing
Roel Vermeulen

(Environmental Science and Technology, 2014, 48(24), 14635-41)

Abstract

Exposure to polycyclic aromatic hydrocarbons (PAHs) from burning “smoky” (bituminous) coal has been implicated as a cause of the high lung cancer incidence in the counties of Xuanwei and Fuyuan, China. Little is known about variations in PAH exposure from throughout the region nor how fuel source and stove design affects exposure. Indoor and personal PAH exposure resulting from solid fuel combustion in Xuanwei and Fuyuan was investigated using repeated 24-hr particle bound and gas-phase PAH measurements, which were collected from 163 female residents of Xuanwei and Fuyuan. 549 particle bound (283 indoor and 266 personal) and 193 gas phase (all personal) PAH measurements were collected. Mixed effect models indicated that PAH exposure was up to 6 times higher when burning smoky coal than smokeless coal and varied by up to a factor of 3 between different smoky coal geographic sources. PAH measurements from unventilated firepits were up to 5 times that of ventilated stoves. Exposure also varied between different room sizes and season of measurement. These findings indicate that PAH exposure is modulated by a variety of factors, including fuel type, coal source, and stove design. These findings may provide valuable insight into potential causes of lung cancer in the area.

Introduction

Xuanwei and its neighbouring county of Fuyuan, located in Yunnan province, China, have among the nation's highest lung cancer rates in both men and women, irrespective of smoking status. [1-3] Previous research has associated the domestic combustion of locally sourced "smoky" (bituminous) coal with this excess cancer rate. [4,5] Solid fuels are used for heating and cooking throughout Xuanwei and Fuyuan, of which coal is the most common (alternative fuels include wood, corn cobs and tobacco stems). There are multiple active coal mines throughout both counties with mines typically producing either smoky or "smokeless" (anthracite) coal (the terms smoky and smokeless refer to the amount of visible smoke released on combustion). Historically, residents have typically purchased coal from their nearest mine.

Two major features have been observed to drive lung cancer rates among those burning smoky coal. The first feature relates to stove design. Historically people burnt fuel in unvented firepits. In recent decades, these have been replaced with a variety of differing stove designs which have the purpose of more efficient burning characteristics and reducing household air pollution (HAP). These improved stoves have resulted in reduced cancer rates[6,7] (as well as reduced non-malignant lung disease),[8] indicating that exposure to carcinogenic material(s) is reduced through these designs. The second feature is the observation that lung cancer rates among smoky coal users vary (by up to 20 times) between geographic locations.[4,9] Given that lifestyle factors are largely similar throughout Xuanwei and Fuyuan, this suggests that there may be constitutional differences between coals sourced from different locations, whether in the geological formation, or in varying practises of coal preparation (e.g. briquetting). Evidence to support geological differences in coal from different areas comes from the State Standard of China Coal Classification which recognises at least four "sub-types" of smoky coal in the region.[10] These sub-types are based upon a variety of criteria including the degree of coalification (measured as the dry ash free volatile matter) and the caking property of the coal (which is a combination of the caking index, the maximum thickness of the plastic layer and the Audibert-Arnu dilation).[10,11]

Research investigating the properties of uncombusted coal, collected from coal mines and from homes of Xuanwei and Fuyuan residents has shown that smoky coal contains high amounts of volatile organic compounds (i.e. hydrocarbon content) and quartz but generally low levels of trace elements when compared to smokeless coal.[11] Research investigating the emissions of coal combustion has found that smoky coal (compared to smokeless coal) emits high amounts of nanoparticles,[12] particulate matter,[13] and Polycyclic Aromatic Hydrocarbons (PAHs), specifically Benzo[a]Pyrene (BaP).[1] BaP is considered a known carcinogen by the International Agency for Research on Cancer (IARC).[14] Stove improvements have resulted in reduced indoor BaP levels, which parallels observations of reduced lung cancer rates following stove improvement. However, reduced BaP exposure has not been explicitly linked to reduced cancer rates and ventilation has also been shown to reduce other components than BaP.[7,15,16] Additionally, variation in indoor BaP levels has been observed between different geographic locations in Xuanwei,[2] reflecting to some extent the geographic variability in lung cancer rates. However, the geographic variations in BaP exposure observed were related to a variety of fuel sources and stove designs and have not explicitly been linked to a single fuel type. Furthermore, the bulk of the published research thus far has been limited by small sample sizes, limited geographical scope,

limited number of PAHs assessed and a reliance upon the use of HAP measurements as a proxy for personal exposure.

The goal of this paper is to investigate indoor and personal exposure to PAHs resulting from domestic solid fuel combustion in Xuanwei and Fuyuan homes. Particular attention will be paid to the relationship between different fuel types, fuel sources, and different stove designs.

Methods

Study design

This paper is part of a cross-sectional epidemiology study aimed at comprehensively cataloguing the constituents of smoky coal and other solid fuels used in Xuanwei and Fuyuan and associating those constituents with lung cancer risk and early biological effect markers in a case-control study of lung cancer among never-smoking females. The full details are provided elsewhere[11] but briefly: 15 villages were selected from each county. Up to five houses were selected from each village and a non-smoking female between the ages of 20 and 80 from each house was enrolled for personal monitoring of airborne pollutants and activity monitoring. All study participants provided written informed consent prior to their enrolment in the study. At all stages, selection was targeted to represent the population present in the case-control study with regard to age and typical living arrangements and therefore would also reflect historical stove and fuel usage in the area, thus houses were preferentially selected for enrolment if they were at least ten years old and had not altered their stoves for at least the past five years. Each house was measured and sketched. Stoves and other pertinent features (e.g. doors, windows and stairways) were recorded. Study enrolees reported current and historical fuel and stove usage in addition to medical histories and social demographic information.

Data was collected over two time periods, August 2008 to February 2009 and March to June 2009. In the first collection period, all 30 villages were visited, with 148 participants recruited. In the second, 16 villages were revisited (villages selected reflected the overall population) with 53 of the initial subjects re-sampled and 15 new subjects recruited. During each period, samples were taken during two consecutive 24-hour periods.

Stove and fuel information

During each sampling period, subjects activities were documented. When a subject used a particular coal type (smoky or smokeless), geochemical analysis on the solid coal[11] was used to confirm the coal classification. Subjects using coal reported their supplying coal mine. Smoky coal subtypes were identified by linking the Chinese State Standard coal classification to the reported mine.

Following a review of the activity logs, descriptive categories for fuel and stove design were established. For fuel usage, the categories were: smoky, smokeless, “other” coal (referring to combinations of coal types and usage of processed coal products such as briquettes), wood, plant products (referring to combinations bamboo shoots, tobacco stems and corn cobs, sometimes in combination with wood) and “other” fuel (referring to combinations of coal and plants). Only homes which exclusively used smoky or smokeless coal were classified as such.

Stove categories used for final analysis are: ventilated stoves, unventilated stoves, firepits, portable stoves (stoves designed to be lit outside and then carried indoors for use), "mixed"

(usage of multiple types of stoves with differing ventilation) and "unknown" (where stove type was not recorded).

Sample collection and analysis

The PAHs assessed were a combination of particle bound (high molecular weight) and gas phase (low molecular weight) PAHs. The particle bound PAHs analysed were: fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]flouranthene (BkF), benzo[a]pyrene (BaP), dibenz(ah)anthracene (DBA), benzo[ghi]perylene (BPE), and indeno(1,2,3-cd)pyrene (IPY). The gas phase PAHs assessed were: fluorine (FLU), naphthalene (NAP), acenaphthylene (ANY), phenanthrene (PHE), acenaphthene (ANA), and anthracene (ANT).

Particle bound PAHs were measured through the use of personal and indoor measurements. Particulate matter was collected on a 37mm Teflon filter using a cyclone with an aerodynamic cut-off of 2.5 µm, powered by a BGI AFC400S pump. Pumps were calibrated prior to each measurement. Flow rates were measured pre and post-measurement and samples were not accepted if the flow rates varied by more than 10%.The median flow rate was 3.3L/min (inter-quartile range: 3.24 - 3.47L/min). For personal measurements, the pumps were carried by participants with the cyclone attached in proximity to their breathing zone. Overnight, personal devices were placed adjacent to subjects beds. For indoor measurements, pumps were placed approximately 0.25m from the wall and between 1 and 2 metres from the main stove (as allowed by the size of the room).

Personal gas phase PAHs were measured through the use of XAD-2 sorbent tubes at a median air flow rate of 63mL/min (inter-quartile range: 47 - 80 mL/min).

Filters and XAD-2 resin were inserted in separate extraction tubes after which 5mL of dichloromethane (DCM) was added and the tube was capped. Tubes were ultrasonically extracted for 60 minutes at 60°C. After cooling to room temperature, the extract was filtered into a sampling vial using a 0.45µm polytetrafluoroethylene (PTFE) membrane filter. Extraction recoveries were determined by spiking the pre-extracted sample with 500nl (100µl of 5ng/ µl) of 6 deuterated internal standards containing Acenaphthene-d10, Chrysene-d12 (CHR-D12), 1,4-Dichlorobenzene-d4 (1,4-DCB-D4), Naphthalene-d8, Perylene-d12, and Phenanthrene-d10.

A gas chromatograph connected to a mass spectrometer (Shimadzu QP2010 plus) was used to determine the 16 PAH species. Separation of the compounds was carried out on a DB-5MS columns (Agilent 30m×0.32mm×0.25µm). Target PAHs were identified based on the retention time and qualitative ions of the standards in a selected ion monitoring mode that were quantified by the internal standards. The quantity of each PAH was calculated in nanograms. The limit of detection was set to 12.5ng (0.00025 ug/ml). Only values for gas-phase PAHs collected from XAD-2 resin and particle bound PAHs collected from teflon filters were retained for statistical analysis (the median non-detect rate for particle bound PAHs on XAD-2 resin and gas phase PAHs on teflon filters was 97%).

For quality control purposes, field blank samples were analysed in conjunction with the exposed filters. Field blanks reported nondetect measurements for greater than 97% of measurements, thus no blank correction was required. The average recovery rate of internal standards was 96%. Median recovery rates ranged from 87%(1,4-DCB-D4) to 101%(CHR-D12). In view of the high recovery we did not correct results for recovery efficiency. We analysed 13 field duplicate samples for particle and gas bound PAH's. The coefficient of variation for duplicate PAH measurements ranged from 7% (CHR) to 47%(PHE) with a

median value of 25%.Values for total PAH content (sum of PAHs) and BaP equivalent (calculated using previously reported toxic equivalency factors for PAHs[17]) were calculated and are available in the supplement.

Statistical analysis

Levels of ANT and ANA were below the limit of detection for 78% of the samples collected and were excluded from statistical analysis. Of the remaining PAHs, between 78% (FLT) and 98% (BbF) of the particle bound PAHs and between 68% (FLU) and 95% (NAP) of the gas phase PAHs were above the limit of detection (median detection rates of 93% and 80% for particle-bound and gas phase measurements respectively). Measurements below the limit of detection were imputed from a log-normal probability distribution via a multiple imputation procedure. [18] PAH concentrations were calculated by dividing the measured PAH value (in ng) by the total volume of air (in m^3) drawn through either filters or the XAD2 tubes.

Normal probability plots indicated that PAH values followed a log-normal distribution. Descriptive statistics included arithmetic means (AM) geometric means (GM) and geometric standard deviations (GSD). ANOVA and Tukey HSD testing on log-transformed PAH values was performed to assess for variation between fuel types and stove types.

The presence of possible latent exposure variables was explored with factor analysis on log-transformed values using varimax rotation to provide non-correlated factors.[19] Factors with an eigen value greater than one were retained and individual variables within each identified factor with loading values of greater than 0.5 were considered to significantly contribute to that factor. Subsequently, a single PAH from each factor was selected to act as a proxy for its respective factor in the construction of predictive linear mixed effect models. Model construction was targeted towards a single, parsimonious model which could be applied to each proxy PAH. Villages and individual subjects were assigned as random effects. Variables considered for inclusion as fixed effects included: fuel type, fuel source, weight of fuel used, stove design, room size, number of windows/doors, the presence of stairways, meteorological conditions and the season when measurements were taken. A list of all considered variables is available in the supplement (table S1). The following formula can be used to summarise the model:

$$y_{ijf} = \mu + \beta_1 x_1 + \beta_2 x_2 \ldots \beta_n x_n + bI_i + bJ_{ij} + \varepsilon_{ijf}$$

Where y_{ijf} represents the natural log transformed value of the PAH exposure levels for village i, person j on day f. μ represents the intercept (i.e. the "background" level). β_1 through β_n represent fixed effect variable coefficients for variables x_1 through x_n. b_{Ii} represents the random effect coefficient for village i. b_{Jij} represents the random effect coefficient for subject j, living in village i. ε_{ijf} represents the error for village i, person j on day f.

All statistical testing was carried out in R version 3.03[20] using the lme4 package.[21] p values less than 0.05 were considered to indicate statistical significance.

Results

Overview

In total, 163 subjects were recruited. 549 measurements of particle phase PAHs (283 indoor and 266 personal measurements) were collected. 268 of these (137 indoor and 131 personal) reflected exclusive use of smoky coal. Of that 268, 258 (132 indoor and 126

personal) could be associated with an individual coal mine. 193 personal measurements of gas phase PAHs were taken, of which 96 reflected smoky coal use, 93 of which could be associated with an individual coal mine. A map of Xuanwei and Fuyuan, containing the locations of enrolled villages, reported coal mines and coal subtypes is shown in Figure 1. In Xuanwei, all smoky coal used was the subtype "coking coal". Smoky coal from Fuyuan consisted of the "coking coal", "1/3 coking coal", "meagre lean coal", and the "gas fat coal" subtypes.[10,11]

Indoor and personal particle phase PAH measurements showed a moderate to good correlation, with Spearman correlation coefficients ranging from 0.56 (DBA) to 0.80 (BaA) with a median correlation value of 0.76 (Pearson correlation of log-transformed values : 0.56 [DBA] to 0.82 [FLT], median 0.76). Results of personal measurements were generally slightly lower than indoor measurements (2%). However, we observed the difference between personal and indoor measurements was influenced by the season of measurement. During winter, the median difference between personal and indoor measurements ranged from personal being 19% higher (BaA) to 8% lower (DBA) with an overall median difference of personal measurements being 7% higher than indoor. In contrast, during the spring and summer months , personal measurements were on median 8% lower than indoor measurements.

Factor analysis

The results of factor analysis are shown in Table 1. Particle bound and gas phase personal PAH measurements were analysed separately. Three factors were identified among the particle bound PAHs while all four of the gas phase PAHs contributed to a single factor. Among the factors identified from the particle phase PAHs, the first factor consisted primarily of PAHs with 5 and 6 rings - BPE, BbF, DBA, BaP, BkF, IPY, CHR and BaA. The second factor consisted primarily out of PAHs with 4 and 5 rings - BaP, BkF, PYR, FLT, CHR and BaA while the third factor consisted of CHR and BbF (4 and 5 rings respectively)

Table 1 – Exploratory factor analysis of log transformed personal PAH values

	Particle Phase			*Gas Phase*	
	Factor1	**Factor2**	**Factor3**		**Factor1**
EV(% variance explained)	4.5(45%)	3.7(37%)	1.3(13%)	EV(% variance explained)	3.7(91%)
Benzo[ghi]perylene (6)	**0.81**	0.44	0.29	Naphthalene(2)	**0.94**
Benzo[b]fluoranthene (5)	**0.70**	0.47	**0.51**	Phenanthrene (3)	**0.98**
Dibenz[ah]anthracene(5)	**0.80**	0.29	0.30	Acenaphthylene (3)	**0.90**
Benzo[a]pyrene (5)	**0.73**	**0.60**	0.30	Fluorine (4)	**0.99**
Benzo[k]fluoranthene (5)	**0.72**	**0.56**	0.33		
Indeno[1,2,3-cd]pyrene (5)	**0.83**	0.48	0.18		
Pyrene(4)	0.43	**0.87**	0.25		
Fluoranthene(4)	0.39	**0.88**	0.25		
Chrysene(4)	**0.56**	**0.57**	**0.60**		
Benzo[a]anthracene (4)	**0.62**	**0.65**	0.41		

Values in bold (Eigen value > 0.5) are considered to be contributory to that factor
Numbers in parentheses represent number of carbon rings for respective PAH
Factor analysis was performed with varimax rotation

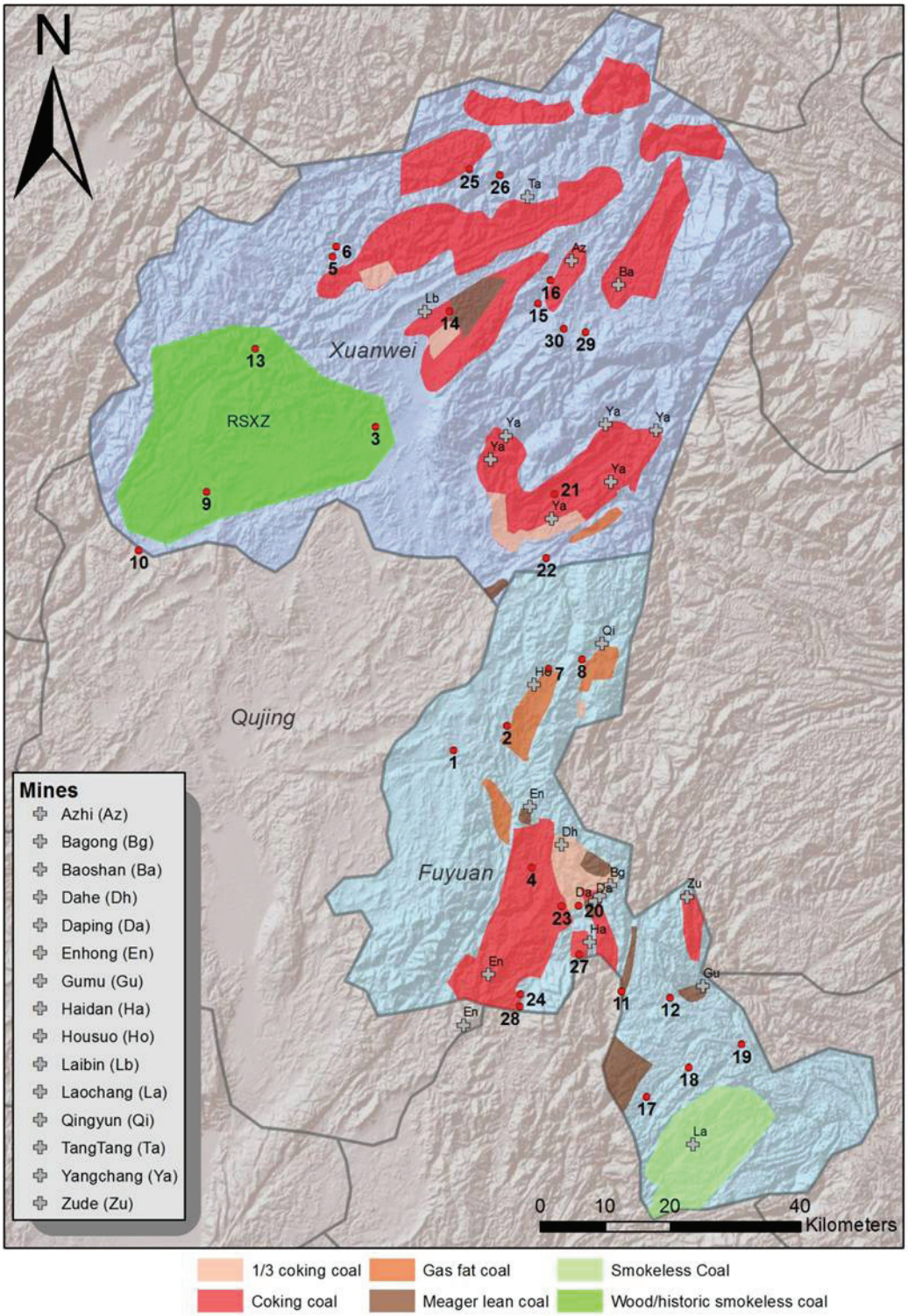

Figure 1:Map of Xuanwei and Fuyuan counties showing approximate locations of study villages, reported coal mines and coal sub-types

Villages enrolled in the study are marked numerically 1 to 30

Mine locations indicate functioning mine entrances, therefore, some mines may be indicated more than once. Only mines reported by study participants are indicated.

Descriptive statistics

One PAH from each factor described above was selected as a proxy for that factor and for the displaying of descriptive statistics. Descriptive statistics for the complete dataset is available in the supplement. BaP was selected to represent the first factor. This selection was based upon the relative high loading of BaP (0.73), previous research on BaP in smoky coal and the classification of BaP as carcinogenic to humans by IARC.[14] The second factor was represented by FLT. This selection was based upon the relative high loading that FLT provides towards the second factor (0.88). CHR was selected to represent the third factor as it was the highest loading variable from that factor (0.58). NAP was selected to represent the gas-phase PAHs as it loaded well towards the single identified factor (0.93) and has been classified as possibly carcinogenic to humans by IARC.[22]

An overview of personal exposure to the selected PAHs is given in Table 2. Particle-bound PAHs (BaP, FLT, and CHR) were between 3 and 8 times higher in homes burning smoky coal compared to smokeless coal burning homes ($p<0.05$). Particle-bound PAH measurements were also observed to be between 4 and 10 times lower among homes burning smoky coal in ventilated stoves when compared to homes burning smoky coal in unvented firepits ($p<0.05$). Among homes using unventilated stoves, up to a100 fold difference between smoky and smokeless coal emissions was observed (FLT values of 108.2 and 1.7 ng/m^3 respectively, $p<0.05$). Gas phase PAHs (NAP) were present in significantly higher concentrations in plant product burning homes (20,000ng/m^3) than smoky coal burning homes (2,900ng/m^3, $p<0.05$). NAP concentrations in smoky coal burning homes using firepits (14,000ng/m^3) were significantly higher than homes using ventilated stoves (2,500ng/m^3). Descriptive statistics for all PAHs, in addition to calculated BaP equivalent and total PAH values, are available in the supplementary material.

Mixed effect modelling

Model construction was aimed at constructing a single, parsimonious model for all four proxy PAHs. Of the approximately 25 variables and combinations of variables considered (table S1), three variables consistently showed a significant effect on all of the measured PAHs with a fourth variable significantly effecting three of the four proxy PAHs. The first variable reflected fuel usage and was entered as a combination of designated fuel types with smoky coal subtypes and their broad geographic source. The second variable reflected stove design, the third variable reflected room volume (divided into quartiles) and the fourth variable represented the season in which measurements were taken (with Spring and Summer merged due to few observations in summer). Descriptive statistics and preliminary analyses indicated that the combustion products of wood and plant products did not significantly vary between different stove designs, therefore, all plant and wood burning homes were considered to be using firepits for the purpose of model construction. An estimate of the strength of effect of each variable (beta (β) effect estimates), 95% confidence intervals and GMR's (GMR= geometric mean ratio = GM(estimate)/GM(reference)=exp(β)) for each selected PAH are available in Table 3.

The model explains 37% of the variance between subjects for BaP, 36% for FLT, 35% for CHR and 100% for NAP. It also explains 54% of the variance between villages for BaP, 51% for FLT, 66% for CHR and 72% for NAP. The use of smoky coal, plant products and wood all result in higher modelled PAH levels than smokeless coal. The use of smoky coal from an unknown source results in the highest GMR for BaP, FLT and CHR (3.42, 5.38 and 6.16 respectively) while the use of meagre lean coal resulted in the highest GMR for NAP

Table 2- Personal exposure to selected PAHs (in ng/m3) by fuel type and stove design

		BaP			FLT			CHR				NAP		
	N(k)	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	N(k)	AM	GM	GSD
Smoky Coal	**131(82)**	**74.4**	**44.7**	**2.8**	**65.3**	**19.3**	**4.7**	**94.3**	**44**	**3.6**	**96(60)**	**4200**	**2900**	**2.4**
Ventilated Stove	72	50.2	38.1	2.1	28.7	15.6	3.3	54.3	34.5	2.8	53	2900	2500	1.9
Unventilated Stove	6	224.5	160.3	2.4	273.6	108.2	5.1	374.8	217.3	3.2	4	11000	6300	3
Portable Stove	13	41.5	31.5	2.2	17.2	9.2	3.2	68.7	45	2.7	12	4900	3900	2.1
Firepit	11	186.4	151.5†	2	228.7	147.6†	2.7	245.2	186.4†	2.1	4	17000	14000	2.1
Mixed Ventilation	25	85.7	48.1	3.2	84.1	21.9	5.4	103	45.5	4.1	19	3900	2600	3.2
Unknown	4	13.2	7.7	3	1.6	1.4	1.8	7.9	4.4	3.2	4	1300	1100	2
Smokeless Coal	**27(16)**	**15.1**	**10.6***	**2.5**	**5.6**	**2.8***	**3.2**	**29.3**	**12.6***	**3.5**	**17(11)**	**3100**	**2800**	**1.6**
Ventilated Stove	2	5.6	5.5	1.3	3.9	2.7	3.7	7	4.8	3.8	0	-	-	-
Unventilated Stove	14	13.8	9.4*	2.7	2.4	1.7*	2.2	12.6	8.3*	2.6	9	2800	2600	1.6
Portable Stove	10	19.3	14.2	2.4	10.7	5.4	3.9	58.7	27.3	4	7	3600	3400	1.5
Firepit	0	-	-	-	-	-	-	-	-	-	0	-	-	-
Mixed Ventilation	1	10.6	10.6	-	4.2	4.2	-	13.7	13.7	-	1	2000	2000	-
Unknown	0	-	-	-	-	-	-	-	-	-	0	-	-	-
"Other" Coal	**24(16)**	**61.5**	**39.7**	**2.8**	**44**	**15.6**	**5.5**	**89.1**	**43.2**	**3.9**	**14(10)**	**8300**	**5400**	**2.8**
Ventilated Stove	10	38.8	26.9	2.6	23.7	8.4	4.8	39.1	21.9	3.4	6	3200	2500	2.3
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	0	-	-	-
Portable Stove	9	95.6	68	2.8	65.1	31.1	5.2	159.4	91.1	3.8	7	13000	11000	2.1
Firepit	1	21.8	21.8	-	3.3	3.3	-	7.6	7.6	-	0	-	-	-
Mixed Ventilation	4	51.7	36.4	3.2	57.4	23.7	7.6	76.2	67.4	1.8	1	5900	5900	-
Unknown	0	-	-	-	-	-	-	-	-	-	0	-	-	-
Wood	**14(8)**	**66.6**	**58.2**	**1.7**	**73.7**	**34.7**	**4**	**66.2**	**54.3**	**2**	**7(4)**	**14000**	**5900**	**6.4**
Ventilated Stove	5	73.4	61.2	1.9	73.5	19.1	6.2	73.3	51.6	2.9	2	13000	13000	1.3
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	0	-	-	-
Portable Stove	4	78.4	70.1	1.7	41.2	33.5	2.4	72.2	60	2	3	21000	14000	3.1
Firepit	5	50.2	47.7	1.4	99.8	64.8	3.2	54.4	52.7	1.3	2	2000	730	10.9
Mixed Ventilation	0	-	-	-	-	-	-	-	-	-	0	-	-	-
Unknown	0	-	-	-	-	-	-	-	-	-	0	-	-	-
Plant	**4(4)**	**95.6**	**83.8**	**1.9**	**144.8**	**118.5**	**2.2**	**128.7**	**121.5**	**1.5**	**3(3)**	**26000**	**20000***	**2.4**
Ventilated Stove	0	-	-	-	-	-	-	-	-	-	0	-	-	-
Unventilated Stove	1	116.1	116.1	-	170	170	-	171.2	171.2	-	1	54000	54000	-
Portable Stove	1	39.5	39.5	-	104.7	104.7	-	91.9	91.9	-	0	-	-	-
Firepit	1	67.3	67.3	-	42.2	42.2	-	81	81	-	1	10000	10000	-
Mixed Ventilation	1	159.5	159.5	-	262.1	262.1	-	170.9	170.9	-	1	15000	15000	-
Unknown	0	-	-	-	-	-	-	-	-	-	0	-	-	-
"Other" Fuel	**66(35)**	**73.8**	**36.9**	**3.3**	**82.6**	**17.4**	**6.6**	**96.3**	**37.3**	**4.3**	**56(28)**	**7600**	**4300**	**3.1**
Ventilated Stove	12	37.5	26.5	2.6	32.4	8.6	5.5	33.6	17.8	3.5	9	4500	3100	2.4
Unventilated Stove	13	158.8	73	4.7	197.2	42.9	10.7	242.5	102.3	5.5	11	20000	13000	3.4
Portable Stove	6	62	40.9	2.9	37.8	17.6	4.9	81.6	49.1	3.2	5	4400	4000	1.6
Firepit	0	-	-	-	-	-	-	-	-	-	0	-	-	-
Mixed Ventilation	32	60	33.5	3	70	17.4	5.6	70.8	35.5	3.5	28	4500	3300	2.7
Unknown	3	21.3	16.5	2.5	12	5.4	5.4	15.7	8.7	4.2	3	4400	2500	3.7

*- significant difference with smoky coal for same PAH and strata (Tukey HSD test)
† - significant difference with ventilated stove for same PAH within fuel strata (Tukey HSD test)
Mixed ventilation – use of multiple stoves with differing ventilation designs
N – number of samples
k – number of individual subjects
BaP - benzo[a]pyrene, FLT – fluoranthene, CHR – chrysene, NAP - naphthalene

Table 3 – Determinants of personal BaP, FLT, CHR and NAP exposure

	BaP			FLT			CHR			NAP		
Reference/ Background Value (Intercept)	2.55			1.45			2.4			7.45		
Fuel Type	Estimate	95%CI	GMR	Estimate	95%CI	GMR	Estimate	95%CI	GMR	Estimate	95%CI	GMR
Smokeless Coal (FY & XW)	Ref		1	Ref		1	Ref		1	Ref		1
Coking Coal from North XW	1.1	0.46,1.73	3.01	1.02	0.08,1.95	2.77	1.34	0.59,2.08	3.83	0.12	-0.53,0.76	1.12
Coking Coal from South XW	0.57	-0.53,1.66	1.77	0.47	-1.19,2.1	1.6	0.59	-0.65,1.84	1.8	-	-	-
Coking Coal from FY	0.9	0.13,1.67	2.47	0.71	-0.42,1.84	2.04	1.21	0.29,2.12	3.35	-0.16	-0.53,0.76	0.85
1/3 Coking coal FY	0.23	-0.72,1.14	1.26	0.48	-0.94,1.85	1.61	0.76	-0.34,1.81	2.14	-0.03	-1.16,0.86	0.97
Gas Fat coal FY	0.26	-0.51,1.01	1.3	0.19	-0.94,1.3	1.21	0.12	-0.76,0.98	1.13	-0.06	-1.34,1.28	0.94
Meagre Lean coal FY	0.82	-0.57,2.2	2.26	0.16	-1.88,2.19	1.18	1.15	-0.5,2.79	3.15	0.66	-0.86,0.71	1.93
Multiple Coal Types	0.86	0.27,1.44	2.35	0.86	-0.01,1.73	2.37	1.07	0.38,1.75	2.9	0.59	-0.64,1.95	1.8
Multiple Fuel Types	0.81	0.25,1.36	2.24	0.95	0.12,1.77	2.57	1.07	0.42,1.72	2.92	0.58	-0.11,1.28	1.78
Smoky Coal of uncertain source†	1.23	0.32,2.15	3.42	1.68	0.34,3.03	5.38	1.82	0.72,2.92	6.16	0.53	-0.05,1.19	1.7
Plant Products	0.03	-1.13,1.19	1.03	-0.22	-1.94,1.52	0.8	0.5	-0.89,1.9	1.65	0.45	-0.32,1.39	1.57
Wood	0.44	-0.51,1.39	1.55	0.3	-1.08,1.7	1.35	0.9	-0.23,2.05	2.47	-0.55	-0.95,1.86	0.58
Stove Design												
Ventilated Stove	Ref		1	Ref		1	Ref		1	Ref		1
Unventilated Stove	0.43	-0.04,0.9	1.54	0.34	-0.36,1.04	1.41	0.62	0.05,1.19	1.86	0.72	-1.76,0.66	2.06
Fire Pit	1.08	0.4,1.76	2.94	0.16	0.73,2.71	5.62	1.06	0.24,1.87	2.9	1.37	0.1,1.02	3.95
Portable Stove	0.18	-0.24,0.6	1.2	1.73	-0.46,0.78	1.18	0.66	0.15,1.16	1.93	0.56	0.16,1.28	1.76
Mixed Ventilation	0.02	-0.3,0.35	1.02	0.11	-0.37,0.59	1.12	0.17	-0.23,0.56	1.18	-0.08	0.49,2.25	0.93
Unknown ventilation	-1.01	-1.75,-0.25	0.37	-1.33	-2.43,-0.23	0.26	-1.27	-2.17,-0.37	0.28	-0.58	-0.44,0.29	0.56
Room Size (in m^3)												
<40m^3	Ref		1	Ref		1	Ref		1	Ref		1
40m^3 to 49m^3	-0.19	-0.61,0.24	0.83	0.62	-0.47,0.75	1.15	-0.46	-0.97,0.05	0.63	-0.2	-0.19,0.42	0.82
50m^3 to 67m^3	0.56	0.1,1.01	1.74	-0.63	0.21,1.54	2.39	0.49	-0.06,1.04	1.63	0.49	-0.68,0.27	1.64
>67m^3	0.18	-0.28,0.64	1.2	0.14	-0.2,1.13	1.59	-0.04	-0.6,0.51	0.96	0.13	-0.02,0.97	1.14
Unknown	0.12	-0.31,0.56	1.13	0.87	-0.28,0.99	1.42	-0.09	-0.61,0.44	0.92	0.05	-0.36,0.61	1.06
Season												
Autumn	Ref		1	Ref		1	Ref		1	Ref		1
Winter	0.17	-0.14,0.48	1.19	0.46	0.15,1.09	1.86	0.41	0.04,0.77	1.51	0.53	-1.27,0.12	1.7
Spring/Summer	-0.06	-0.33,0.21	0.94	0.35	-1.04,-0.23	0.53	-0.28	-0.6,0.03	0.75	0.11	0.14,0.9	1.12
Variance Explained												
Between Subjects		37			36			35			100	
Between Villages		54			51			66			72	

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
BaP - benzo[a]pyrene, FLT – fluoranthene, CHR – chrysene, NAP – naphthalene
†: Refers to smoky coal samples collected from a village in a smokeless coal producing area of Fuyuan.
Example calculation: BaP value for "intercept" home = exp(2.55) = 12.8
BaP value for home using smoky coal from North Xuanwei = exp(2.55+1.1)=38.5, which corresponds to a GMR of 3.01

(1.93). Among coals with an identified source (i.e. coals which can be directly linked to a producing mine), coking coal from north Xuanwei results in the highest GMR for BaP, FLT, and CHR (3.01, 2.77, and 3.83 respectively). Variation in GMR was observed between the various coal sources. Using BaP as an example of this variation, GMR's ranged between 3.01 (coking coal, north Xuanwei) and 1.26 (1/3 coking coal from Fuyuan).

On investigation for the effect of stove design, ventilated stoves resulted in lower PAH exposures than unventilated stoves, portable stoves and firepits. Firepits were associated with the highest GMR's (as compared to ventilated stoves) for BaP, FLT, CHR and NAP (2.94, 5.62, 2.94 and 3.95 respectively).

Room size was found to impact exposure. Larger rooms (those in the third and fourth quartiles) resulted in higher predicted exposure levels for BaP (GMR 1.74 and 1.2 respectively) and FLT (GMR 2.39 and 1.59 respectively) as compared to the first quartile. The second quartile of room size resulted in reduced predicted levels of PAH exposure for BaP, CHR and NAP (GMR 0.83, 0.63 and 0.82 respectively).

Predicted exposure also varied between different seasons. Measurements taken during winter were found to result in the highest predicted levels as compared to measurements taken in autumn (GMR 1.19, 1.86, 1.10 and 1.70 respectively)

Discussion

Xuanwei and Fuyuan counties, located in Yunnan province, China have among the highest lung cancer rates in the nation, which is directly associated with the domestic combustion of locally sourced smoky(bituminous) coal.[1-3] Geographic variation in cancer rates[4,9] suggests spatial variation in exposure while a reduction in cancer rates following stove improvement programs [6,7] suggests reduced exposure following improved stove ventilation. Previous research has shown that smoky coal from the region emits high levels of BaP[1,23] when compared to the smokeless (anthracite) variety of coal. Relatively little is known regarding PAH exposure, in particular personal exposure levels in the two counties.

Descriptive statistics show up to an 8 fold difference in particle bound PAH exposure between smoky and smokeless coal. PAH exposure is also up to 10 times lower in smoky coal burning homes using ventilated stoves compared to homes using firepits. These findings parallel previous findings of increased organic material in smoky coal samples,[11] higher levels of overall particulate matter[15] and BaP[23] in smoky coal emissions and reduced BaP exposure with the use of ventilated stoves.[16] No significant difference in gas phase PAHs was observed between smoky coal and smokeless coal. However, up to a 6 fold reduction in gas-phase PAHs was observed among smoky coal burning homes using ventilated stoves compared to firepits.

We note that particle bound PAH measurements among wood and plant burning homes appear to be roughly equivalent to smoky coal burning homes. This finding appears to largely be a feature of stove design. The use of unventilated firepits, is associated with higher particle bound PAH exposure when using smoky coal (GM for BaP– 151.5ng/m^3) than when using wood (GM – 47.7ng/m^3), however, in homes using ventilated stoves we observe similar PAH values between wood and smoky coal (GM for BaP 61.2 and 38.1ng/m^3 respectively). We postulate that this is due to the stoves' designs, which were specifically intended to hold and burn coal. Wood therefore, does not fit properly in these stoves which leads to an underperformance of ventilation and thus little or no reduction in PAH emission. A similar phenomena has also been noted by an IARC working group on

HAP.[14] Efficient wood burning stoves are used in some countries. For example, a Tanzanian study observed a reduction of PAH emissions (by approximately 75%) among stoves designed to more efficiently burn wood compared to conventional stoves.[24]

Mixed effect models, created for the purpose of predicting personal PAH exposure levels, provide an expanded view upon the multiple variables which play a role in PAH exposure. The model identifies variations in PAH exposure between differing smoky coal producing areas and differing smoky coal subtypes. Focusing upon smoky coal burning homes which could identify their supplying mine, we observed that coking coal from North Xuanwei (which includes Laibin - the area with the highest lung cancer mortality rate) has the highest GMR (i.e. predicts the highest PAH exposure) when compared to the other smoky coals. The model also predicts reduced PAH exposure of between approximately 3 (BaP, CHR) and 5 (FLT) times between ventilated stoves and firepits. We note that the model indicates that homes with "unknown" stove designs (n=7) have lower levels of predicted PAH exposure than the other stove design categories. These homes represent geographically distinct locations, using a variety of fuel sources from a variety of locations and there is no immediate explanation for this observation. The relationship between relative room size and PAH exposure has not previously been reported. Larger rooms appear to relate to higher PAH exposure, which is unintuitive. A possible explanation, based on field observations, is that smaller rooms indicate financially poorer households, which would have worse construction, allowing for increased general ventilation and reduction in HAP through imperfections in the room's structure. This hypothesis is supported by some of the information collected from the study participants which included a survey of socio-economic indicators. The majority of study participants who reported that they did not regularly have enough to eat (68%) lived in homes in the first and second size quartiles. Conversely, the majority of participants who reported having surplus food (70%) lived in homes in the third and fourth size quartiles. Alternatively, it could be that the larger homes used relatively more fuel. Fuel consumption was accurately recorded during the field survey by weighing the fuel stock pile before and after the measurements. We did not observe a difference in fuel consumption by room size arguing in favour of the fact that in some regards room size reflects social economic status and consequently home design. The role of season in predicted PAH levels, with PAHs being higher during winter, is consistent with expected practices during colder temperatures such as closing windows and spending more time indoors and matches findings of other research which shows increased PAH exposure during colder months[25]. Meteorological indicators (temperature, rainfall, humidity etc.) were also observed to have a role in predicted levels, however the season category was found to more accurately predict PAH exposure than separate meteorological indicators.

We would not expect tobacco smoking to influence the findings of this study. All of the study enrolees reported that they were not either current or past smokers and over 90% of them reported that at least one of their direct (male) family members regularly smoked. Previous research[26,27] has indicated that HAP attributable to tobacco smoke is less than 1ng/m^3 thus it is unlikely that the current findings were influenced in any meaningful manner by tobacco smoking.

BaP levels reported here are generally consistent with other research performed in the Xuanwei and Fuyuan counties suggesting that our results are consistent with exposures experienced in the past (these studies typically report the arithmetic mean [AM] of measurements). Lv et.al[28] reported BaP levels of between 7.7 and 380 ng/m^3 (stove design not reported), Tian et.al[16] reported BaP concentrations among unventilated homes burning

smoky coal of 901ng/m^3 and among ventilated homes of 143ng/m^3, He et.al[2] reported BaP levels of between 286ng/m^3 and 2485ng/m^3 for homes burning a variety of solid fuels in unventilated firepits and Lan et al[7] reported BaP levels of 1660ng/m^3 among homes burning smoky coal in unvented stoves, compared to 250ng/m^3 for ventilated stoves. These findings are all substantially lower than those previously reported by Mumford et.al,[23] who reported indoor BaP concentrations of AM 14.7 μg/m^3 (14,700ng/m^3) in Xuanwei homes burning smoky coal in unvented firepits. The reason for this disparity lays in the fact that Mumford only measured during active cooking periods, which is when exposure is highest. Work by Hosgood et. Al, in the Xuanwei region, has indicated that emission levels can vary by a factor of up to 60 between cooking and non-cooking periods.[12] Therefore, measurements taken only during these times are likely to be much higher than those taken over 24hr periods. Of note, if we adjust the AM for BaP resulting from smoky coal being burnt in a fire pit (186.4ng/m^3) and adjust it for the noted 60-fold difference between cooking and non-cooking periods, we would expect exposure levels for BaP of approximately 10μg/m^3 during peak cooking periods, which is consistent with the reported levels by Mumford et. al.

The Chinese national criteria of BaP exposure levels is 1ng/m^3 for indoor environments,[28] a level which was exceeded by every measurement taken, regardless of fuel type or stove design. The overall AM for BaP concentration among smoky coal homes is 74.4ng/m^3. In a broader context, this is higher than that observed many other studies throughout China. including coal burning homes from a rural area in north eastern China with a notably high rate of oesophageal cancer[29] (39.6ng/m^3), traffic policemen working in high density Chinese urban environments[30] (26.2ng/m^3), urban and rural residents of northern China using a variety of fuels[25] (18.9ng/mg^3) and villagers from northern China using a variety of biomass[31] (24ng/m^3) . In the international context, we see that BaP levels reported here are relatively high when compared to homes in Poland using coal[32] (28ng/m^3) in urban India[33] (13.6ng/m^3) and in coal burning rural Indian homes[34] (56ng/m^3).

This is the most comprehensive assessment of PAH exposure in Xuanwei and Fuyuan counties to date. These findings parallel observed lung cancer epidemiology in the region. However, risk estimates indicate that the measured PAH concentrations may only account for a three-fold increase in lung cancer risk[35-38], which is insufficient to fully explain the lung cancer epidemic in the region. Therefore it is possible that the risk estimates, which were primarily constructed based on observations of adult men working in coking plants (who would therefore only be exposed during working hours) are inapplicable to women who have been exposed since birth onwards. Alternatively, other compounds, either separate to or in combination with PAHs may play an important role in lung cancer aetiology.

Acknowledgements

This project was supported by the National Institutes of Health (HHSN261201400122P) intramural research program. The content of this publication does not necessarily reflect the views or policies of the Department of Health and Human Services, nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government. The authors would like to acknowledge Johan Beekhuizen and Meng Wang from the Institute for Risk Assessment Sciences, Utrecht University for their support in the production of figure 1.

Competing financial interests declaration

The authors declare that there is no competing financial interest in the planning, analysis or publication of this research.

References

1. Mumford, J. L.; He, X. Z.; Chapman, R. S.; Cao, S. R.; Harris, D. B.; Li, X. M.; Xian, Y. L.; Jiang, W. Z.; Xu, C. W.; Chuang, J. C. Lung cancer and indoor air pollution in Xuan Wei, China. Science 1987, 235, 217-220.
2. He, X. Z.; Chen, W.; Liu, Z. Y.; Chapman, 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 Perspect. 1991, 94, 9-13.
3. Barone-Adesi, F.; Chapman, R. S.; Silverman, D. T.; He, X.; Hu, W.; Vermeulen, R.; Ning, B.; Fraumeni, J. F.,Jr; Rothman, N.; Lan, Q. Risk of lung cancer associated with domestic use of coal in Xuanwei, China: retrospective cohort study. BMJ 2012, 345, e5414.
4. Lan, Q.; He, X.; Shen, M.; Tian, L.; Liu, L. Z.; Lai, H.; Chen, W.; Berndt, S. I.; Hosgood, H. D.; Lee, K. M.; Zheng, T.; Blair, A.; Chapman, R. S. Variation in lung cancer risk by smoky coal subtype in Xuanwei, China. Int. J. Cancer 2008, 123, 2164-2169.
5. Chapman, R. S.; Mumford, J. L.; Harris, D. B.; He, Z. Z.; Jiang, W. Z.; Yang, R. D. The epidemiology of lung cancer in Xuan Wei, China: current progress, issues, and research strategies. Arch. Environ. Health 1988, 43, 180-185.
6. Hosgood, H. D.,3rd; Chapman, R.; Shen, M.; Blair, A.; Chen, E.; Zheng, T.; Lee, K. M.; He, X.; Lan, Q. Portable stove use is associated with lower lung cancer mortality risk in lifetime smoky coal users. Br. J. Cancer 2008, 99, 1934-1939.
7. 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.
8. Shen, M.; Chapman, R. S.; Vermeulen, R.; Tian, L.; Zheng, T.; Chen, B. E.; Engels, E. A.; He, X.; Blair, A.; Lan, Q. Coal use, stove improvement, and adult pneumonia mortality in Xuanwei, China: a retrospective cohort study. Environ. Health Perspect. 2009, 117, 261-266.
9. Lin, H.; Ning, B.; Li, J.; Ho, S. C.; Huss, A.; Vermeulen, R.; Tian, L. Lung Cancer Mortality Among Women in Xuan Wei, China: A Comparison of Spatial Clustering Detection Methods. Asia. Pac. J. Public. Health. 2012.
10. Chen, P. Study on integrated classification system for Chinese coal. Fuel Process Technol 2000, 62, 77-87.
11. Downward, G. S.; Hu, W.; Large, D.; Veld, H.; Xu, J.; Reiss, B.; Wu, G.; Wei, F.; Chapman, R. S.; Rothman, N.; Qing, L.; Vermeulen, R. Heterogeneity in coal composition and implications for lung cancer risk in Xuanwei and Fuyuan counties, China. Environ. Int. 2014, 68, 94-104.
12. Hosgood, H. D.; Lan, Q.; Vermeulen, R.; Wei, H.; Reiss, B.; Coble, J.; Wei, F.; Jun, X.; Wu, G.; Rothman, N. Combustion-derived nanoparticle exposure and household solid fuel use in Xuanwei and Fuyuan, China. Int. J. Environ. Health Res. 2012, 22, 571-581.
13. Tian, L.; 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.
14. IARC monographs on the evaluation of carcinogenic risks to humans. Volume 95, Household Use of Solid Fuels and High-temperature Frying. 2010.
15. Hu, W.; Downward, G.; Reiss, B.; Rothman, N.; Xu, J.; Bassig, B.; Hosgood, D.; Zhang, L.; Wu, G.; Chapman, R.; Wei, F.; Lan, Q.; Vermeulen, R. Personal and indoor fine particulate matter exposure from vented and unvented stoves in Xuanwei and Fuyuan county, China. Environ Sci Technol 2014, 48, 8456-64.
16. Tian, L.; Lan, Q.; Yang, D.; He, X.; Yu, I. T. S.; Hammond, S. K. Effect of chimneys on indoor air concentrations of PM10 and benzo[a]pyrene in Xuan Wei, China. Atmos. Environ. 2009, 43, 3352-3355.
17. Nisbet, I. C.; LaGoy, P. K. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 1992, 16, 290-300.
18. Lubin, J. H.; Colt, J. S.; Camann, D.; Davis, S.; Cerhan, J. R.; Severson, R. K.; Bernstein, L.; Hartge, P. Epidemiologic Evaluation of Measurement Data in the Presence of Detection Limits. Environ. Health Perspect. 2004, 112, 1691-1696.

19. Gorsuch, R. L. Exploratory Factor Analysis: Its Role in Item Analysis. J. Pers. Assess. 1997, 68, 532-560.
20. R Development Core Team R: A Language and Environment for Statistical Computing. 2014.
21. Bates, D.; Maechler, M.; Bolker, B.; Walker, S. lme4: Linear mixed-effects models using Eigen and S4. 2014.
22. IARC Some traditional herbal medicines, some mycotoxins, naphthalene and styrene. IARC Monogr. Eval. Carcinog. Risks Hum. 2002, 82, 1-556.
23. Mumford, J. L.; Chapman, R. S.; Harris, D. B.; He, X. Z.; Cao, S. R.; Xian, Y. L.; Li, X. M. Indoor air exposure to coal and wood combustion emissions associated with a high lung cancer rate in Xuan Wei, China. Environ. Int. 1989, 15, 315-320.
24. Titcombe, M. E.; Simcik, M. Personal and indoor exposure to $PM_{2.5}$ and polycyclic aromatic hydrocarbons in the southern highlands of Tanzania: a pilot-scale study. Environ. Monit. Assess. 2011, 180, 461-476.
25. Duan, X.; Wang, B.; Zhao, X.; Shen, G.; Xia, Z.; Huang, N.; Jiang, Q.; Lu, B.; Xu, D.; Fang, J.; Tao, S. Personal inhalation exposure to polycyclic aromatic hydrocarbons in urban and rural residents in a typical northern city in China. Indoor Air 2014.
26. Fromme, H.; Lahrz, T.; Piloty, M.; Gebhardt, H.; Oddoy, A.; Ruden, H. Polycyclic aromatic hydrocarbons inside and outside of apartments in an urban area. Sci. Total Environ. 2004, 326, 143-149.
27. Fromme, H.; Dietrich, S.; Heitmann, D.; Dressel, H.; Diemer, J.; Schulz, T.; Jorres, R. A.; Berlin, K.; Volkel, W. Indoor air contamination during a waterpipe (narghile) smoking session. Food Chem. Toxicol. 2009, 47, 1636-1641.
28. Lv, J.; Xu, R.; Wu, G.; Zhang, Q.; Li, Y.; Wang, P.; Liao, C.; Liu, J.; Jiang, G.; Wei, F. Indoor and outdoor air pollution of polycyclic aromatic hydrocarbons (PAHs) in Xuanwei and Fuyuan, China. J. Environ. Monit. 2009, 11, 1368-1374.
29. Deziel, N. C.; Wei, W. Q.; Abnet, C. C.; Qiao, Y. L.; Sunderland, D.; Ren, J. S.; Schantz, M. M.; Zhang, Y.; Strickland, P. T.; Abubaker, S.; Dawsey, S. M.; Friesen, M. C.; Roth, M. J. A multi-day environmental study of polycyclic aromatic hydrocarbon exposure in a high-risk region for esophageal cancer in China. J. Expo. Sci. Environ. Epidemiol. 2013, 23, 52-59.
30. Hu, Y.; Bai, Z.; Zhang, L.; Wang, X.; Zhang, L.; Yu, Q.; Zhu, T. Health risk assessment for traffic policemen exposed to polycyclic aromatic hydrocarbons (PAHs) in Tianjin, China. Sci. Total Environ. 2007, 382, 240-250.
31. Ding, J.; Zhong, J.; Yang, Y.; Li, B.; Shen, G.; Su, Y.; Wang, C.; Li, W.; Shen, H.; Wang, B.; Wang, R.; Huang, Y.; Zhang, Y.; Cao, H.; Zhu, Y.; Simonich, S. L.; Tao, S. Occurrence and exposure to polycyclic aromatic hydrocarbons and their derivatives in a rural Chinese home through biomass fuelled cooking. Environ. Pollut. 2012, 169, 160-166.
32. Junninen, H.; Mønster, J.; Rey, M.; Cancelinha, J.; Douglas, K.; Duane, M.; Forcina, V.; Mu¨ller, A.; Lagler, F.; Marelli, L.; Borowiak, A.; Niedzialek, J.; Paradiz, B.; Mira-Salama, D.; Jimenez, J.; Hansen, U.; Astorga, C.; Stanczyk, K.; Viana, M.; Querol, X.; Duvall, R. M.; Norris, G. A.; Tsakovski, S.; Wåhlin, P.; Hora´k, J.; Larsen, B. R. Quantifying the Impact of Residential Heating on the Urban Air Quality in a Typical European Coal Combustion Region. Environ. Sci. Technol. 2009, 43, 7964-7970.
33. Masih, J.; Masih, A.; Kulshrestha, A.; Singhvi, R.; Taneja, A. Characteristics of polycyclic aromatic hydrocarbons in indoor and outdoor atmosphere in the North central part of India. J. Hazard. Mater. 2010, 177, 190-198.
34. Raiyani, C. V.; Jani, J. P.; Desai, N. M.; Shah, S. H.; Shah, P. G.; Kashyap, S. K. Assessment of indoor exposure to polycyclic aromatic hydrocarbons for urban poor using various types of cooking fuels. Bull. Environ. Contam. Toxicol. 1993, 50.
35. Vermeulen, R.; Rothman, N.; Lan, Q. Coal combustion and lung cancer risk in XuanWei: a possible role of silica? Med. Lav. 2011, 102, 362-367.
36. Strunk, P.; Ortlepp, K.; Heinz, H.; Rossbach, B.; Angerer, J. Ambient and biological monitoring of coke plant workers -- determination of exposure to polycyclic aromatic hydrocarbons. Int. Arch. Occup. Environ. Health 2002, 75, 354-358.

37. Armstrong, B.; Hutchinson, E.; Unwin, J.; Fletcher, T. Lung Cancer Risk after Exposure to Polycyclic Aromatic Hydrocarbons: A Review and Meta-Analysis. Environ. Health Perspect. 2004, 112, 970-978.
38. Armstrong, B. G.; Gibbs, G. Exposure-response relationship between lung cancer and polycyclic aromatic hydrocarbons (PAHs). Occup. Environ. Med. 2009, 66, 740-746.

Chapter 4

Appendix - Supplementary information: Polycyclic Aromatic Hydrocarbon exposure in household air pollution from solid fuel combustion among the female population of Xuanwei and Fuyuan counties, China

(Online: http://pubs.acs.org/doi/suppl/10.1021/es504102z)

Table S1 - Variables considered for inclusion in mixed model creation

Broad Category	Details
Stove Design	**Stove ventilated, unventilated mixed portable stove or firepit**
	Stove ventilated, unventilated or mixed ventilation*
	Stove ventilated, unventilated mixed or firepit
	Stove either firepit or other design (or mixed)
	Stove design as reported by study participant£
Fuel Type/Source	**Major fuel type including smoky coal subtypes and county from which coal sourced (Xuanwei divided into north/south)**
	County from which fuel purchased
	Major fuel type
	Fuel type including smoky coal subtypes
	Fuel type including individual smoky coal mines
	Fuel type including smoky coal subtypes
	Weight of fuel used†
Meteorological conditions	**Season of visit**
	Average daily temperature
	Average daily high temperature
	Average daily low temperature
	Average daily humidity
	Average daily wind speed
	Average daily maximum wind speed
	Average daily dew point
	Average daily rainfall
Other Variables	**Room size**†
	Age of participant
	Month of visit
	Phase of study during visit
	Administrative borders‡
	Number of stoves operated
	Number of hours spent using stove(s)

* - refers to the use of multiple stoves with different ventilation designs
£ - Categories are high stove, low stove (with or without ventilation), portable stove, firepit and multiple stoves
† - divided into quartiles
‡ - townships/areas as defined by local administrative bodies

Table S2a - Personal exposure to particle bound PAHs (in ng/m^3) by ventilation

		BaP			PYR			BbF			DBA			BaA		
	N	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Smoky Coal	**131**	**74.4**	**44.7**	**2.8**	**71.8**	**22.6**	**4.6**	**119.6**	**69.8**	**2.8**	**27.8**	**13.8**	**3.4**	**102.4**	**49.0**	**3.5**
Ventilated Stove	72	50.2	38.1	2.1	33.1	18.2	3.2	75.5	56.9	2.2	16.8	10.6	2.7	61.1	40.9	2.6
Unventilated Stove	6	224.5	160.3	2.4	290.3	131.5	4.4	406.7	269.4	2.7	92.1	54.2	3.1	357.5	205.9	3.3
Portable Stove	13	41.5	31.5	2.2	22.4	10.4	3.9	88.5	66.6	2.2	17.5	11.4	2.6	56.2	35.4	2.8
Firepit	11	186.4	151.5†	2.0	247.7	164.5†	2.6	302.6	243.6†	2.0	76.5	61.4†	1.9	282.6	216.3†	2.1
Mixed Ventilation	25	85.7	48.1	3.2	90.4	26.7	5.0	129.2	71.6	3.2	31.7	15.6	3.9	119.7	52.7	4.2
Unknown	4	13.2	7.7	3.0	2.0	1.5	2.2	19.7	11.4	3.0	5.0	2.7	3.2	9.3	4.5	3.6
Smokeless Coal	**27**	**15.1**	**10.6***	**2.5**	**6.8**	**3.1***	**3.5**	**50.4**	**28.6***	**2.9**	**8.8**	**5.1***	**2.9**	**13.3**	**7.5***	**3.2**
Ventilated Stove	2	5.6	5.5	1.3	3.8	2.5	4.2	12.4	12.4	1.1	8.2	4.8	4.9	5.4	3.7	3.8
Unventilated Stove	14	13.8	9.4*	2.7	2.7	1.7*	2.5	33.1	22.9*	2.7	7.2	4.6*	2.7	9.4	5.4*	3.0
Portable Stove	10	19.3	14.2	2.4	13.4	6.9	3.8	85.1	47.8	3.3	11.9	6.7	3.3	20.6	13.4	3.1
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	1	10.6	10.6	-	4.2	4.2	-	20.1	20.1	-	1.5	1.5	-	10.6	10.6	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
"Other" Coal	**24**	**61.5**	**39.7**	**2.8**	**54.7**	**20.1**	**5.4**	**103.9**	**63.1**	**3.0**	**26.0**	**13.2**	**3.4**	**82.7**	**43.4**	**3.7**
Ventilated Stove	10	38.8	26.9	2.6	29.2	10.1	5.2	53.3	36.9	2.6	10.3	7.4	2.6	41.8	24.2	3.3
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	9	95.6	68.0	2.8	83.8	41.0	4.8	175.2	118.1	3.1	50.5	34.4	2.7	142.6	91.2	3.4
Firepit	1	21.8	21.8	-	4.4	4.4	-	34.8	34.8	-	5.4	5.4	-	8.7	8.7	-
Mixed Ventilation	4	51.7	36.4	3.2	65.5	33.7	5.2	87.4	68.3	2.6	15.4	8.0	3.8	68.6	52.5	2.7
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Wood	**14**	**66.6**	**58.2**	**1.7**	**85.1**	**44.8**	**3.6**	**91.2**	**80.4**	**1.7**	**14.2**	**10.3**	**2.6**	**74.2**	**62.5**	**1.9**
Ventilated Stove	5	73.4	61.2	1.9	83.2	24.7	5.8	106.3	91.8	1.9	20.9	18.3	1.8	75.5	57.4	2.4
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	4	78.4	70.1	1.7	57.1	47.5	2.3	103.8	93.5	1.7	14.1	11.3	2.1	89.8	77.8	1.8
Firepit	5	50.2	47.7	1.4	109.5	77.4	2.8	65.9	62.4	1.5	7.8	5.3*	2.9	60.5	57.0	1.5
Mixed Ventilation	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Plant	**4**	**95.6**	**83.8**	**1.9**	**157.2**	**130.0**	**2.1**	**146.6**	**131.5**	**1.8**	**20.5**	**13.9**	**3.7**	**129.6**	**114.4**	**1.8**
Ventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unventilated Stove	1	116.1	116.1	-	191.1	191.1	-	177.0	177.0	-	23.5	23.5	-	170.0	170.0	-
Portable Stove	1	39.5	39.5	-	109.0	109.0	-	59.8	59.8	-	2.0	2.0	-	56.6	56.6	-
Firepit	1	67.3	67.3	-	49.1	49.1	-	126.6	126.6	-	29.7	29.7	-	86.7	86.7	-
Mixed Ventilation	1	159.5	159.5	-	279.7	279.7	-	222.7	222.7	-	26.9	26.9	-	205.1	205.1	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
"Other" Fuel	**66**	**73.8**	**36.9**	**3.3**	**92.7**	**21.0**	**6.3**	**119.1**	**62.2**	**3.3**	**25.7**	**10.2**	**3.9**	**101.0**	**37.6**	**4.4**
Ventilated Stove	12	37.5	26.5	2.6	35.4	10.1	5.2	51.8	35.3	2.7	10.5	7.2	2.9	42.1	21.4	3.9
Unventilated Stove	13	158.8	73.0	4.7	224.5	52.3	10.2	272.7	145.5	4.1	71.1	30.6	4.4	230.7	89.3	6.0
Portable Stove	6	62.0	40.9	2.9	49.6	21.4	5.2	104.8	78.4	2.5	19.8	10.7	3.7	80.8	41.9	3.9
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	32	60.0	33.5	3.0	75.9	21.2	5.3	93.0	56.5	2.9	15.8	7.9	3.4	81.8	35.4	3.8
Unknown	3	21.3	16.5	2.5	15.4	7.0	5.5	30.8	26.1	2.0	6.8	4.7	2.9	19.2	13.2	3.2

*- significant difference with smoky coal for same PAH and strata via Tukey HSD test
† - significant difference with ventilated stove for same PAH within fuel strata via Tukey HSD test
N – number of samples
BaP - benzo[a]pyrene, PYR - pyrene, BbF - benzo[b]fluoranthene DBA - dibenz(ah)anthracene, BaA - benzo[a]anthracene

Table S2b - Personal Exposure to particle bound PAHs (in ng/m^3) by ventilation

		BkF			BPE			CHR			FLT			IPY		
	N	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Smoky Coal	**131**	**26.5**	**15.7**	**2.8**	**81.5**	**47.1**	**3.0**	**94.3**	**44.0**	**3.6**	**65.3**	**19.3**	**4.7**	**45.7**	**28.3**	**2.8**
Ventilated Stove	72	18.9	13.9	2.2	53.7	39.1	2.2	54.3	34.5	2.8	28.7	15.6	3.3	33.6	25.4	2.1
Unventilated Stove	6	78.1	45.8	3.2	230.2	165.1	2.5	374.8	217.3	3.2	273.6	108.2	5.1	112.4	71.8	2.8
Portable Stove	13	13.9	9.7	2.4	48.0	33.1	2.8	68.7	45.0	2.7	17.2	9.2	3.2	23.6	17.0	2.3
Firepit	11	62.5	50.4†	1.9	220.7	185.3†	1.9	245.2	186.4†	2.1	228.7	147.6†	2.7	109.5	92.9†	1.8
Mixed Ventilation	25	30.3	17.5	3.0	92.4	51.8	3.5	103.0	45.5	4.1	84.1	21.9	5.4	52.9	31.0	3.3
Unknown	4	5.4	2.9	3.2	17.6	8.4	3.6	7.9	4.4	3.2	1.6	1.4	1.8	12.8	5.6	4.0
Smokeless Coal	**27**	**11.9**	**4.4***	**3.0**	**17.6**	**11.1***	**2.9**	**29.3**	**12.6***	**3.5**	**5.6**	**2.8***	**3.2**	**13.7**	**9.7***	**2.5**
Ventilated Stove	2	1.8	1.8	1.2	7.2	4.9	3.8	7.0	4.8	3.8	3.9	2.7	3.7	8.8	7.4	2.4
Unventilated Stove	14	4.9	3.6*	2.3	15.8	9.9*	2.9	12.6	8.3*	2.6	2.4	1.7*	2.2	12.5	8.7*	2.6
Portable Stove	10	24.4	7.0	4.2	23.1	15.1	3.0	58.7	27.3	4.0	10.7	5.4	3.9	17.1	12.4	2.5
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	1	4.2	4.2	-	10.6	10.6	-	13.7	13.7	-	4.2	4.2	-	6.3	6.3	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
"Other" Coal	**24**	**21.4**	**13.8**	**2.9**	**69.3**	**41.9**	**2.9**	**89.1**	**43.2**	**3.9**	**44.0**	**15.6**	**5.5**	**40.3**	**26.4**	**2.7**
Ventilated Stove	10	12.8	8.8	2.7	36.5	27.4	2.3	39.1	21.9	3.4	23.7	8.4	4.8	22.7	17.8	2.2
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	9	33.2	23.1	2.9	118.4	80.7	2.8	159.4	91.1	3.8	65.1	31.1	5.2	64.2	47.4	2.4
Firepit	1	9.8	9.8	-	23.9	23.9	-	7.6	7.6	-	3.3	3.3	-	17.4	17.4	-
Mixed Ventilation	4	19.1	14.5	2.7	52.4	31.7	3.4	76.2	67.4	1.8	57.4	23.7	7.6	36.2	20.9	3.9
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Wood	**14**	**24.5**	**20.6**	**1.8**	**55.2**	**44.2**	**2.0**	**66.2**	**54.3**	**2.0**	**73.7**	**34.7**	**4.0**	**59.7**	**47.2**	**2.0**
Ventilated Stove	5	29.3	24.7	1.9	70.9	60.6	1.9	73.3	51.6	2.9	73.5	19.1	6.2	66.9	50.8	2.2
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	4	27.8	23.6	1.9	60.2	48.4	2.1	72.2	60.0	2.0	41.2	33.5	2.4	71.0	57.5	2.0
Firepit	5	17.0	15.3	1.7	35.5	30.1	1.9	54.4	52.7	1.3	99.8	64.8	3.2	43.4	37.4	1.9
Mixed Ventilation	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Plant	**4**	**37.1**	**29.2**	**2.3**	**73.7**	**62.1**	**2.2**	**128.7**	**121.5**	**1.5**	**144.8**	**118.5**	**2.2**	**58.8**	**49.3**	**2.0**
Ventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unventilated Stove	1	39.9	39.9	-	93.8	93.8	-	171.2	171.2	-	170.0	170.0	-	69.2	69.2	-
Portable Stove	1	9.6	9.6	-	19.2	19.2	-	91.9	91.9	-	104.7	104.7	-	20.3	20.3	-
Firepit	1	26.2	26.2	-	94.7	94.7	-	81.0	81.0	-	42.2	42.2	-	39.9	39.9	-
Mixed Ventilation	1	72.5	72.5	-	87.0	87.0	-	170.9	170.9	-	262.1	262.1	-	105.7	105.7	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
"Other" Fuel	**66**	**25.8**	**13.5**	**3.2**	**80.1**	**34.7**	**3.6**	**96.3**	**37.3**	**4.3**	**82.6**	**17.4**	**6.6**	**43.5**	**26.2**	**2.7**
Ventilated Stove	12	11.8	8.5	2.7	45.4	27.6	3.1	33.6	17.8	3.5	32.4	8.6	5.5	25.3	20.1	2.2
Unventilated Stove	13	55.4	28.3	4.2	200.5	77.2	5.3	242.5	102.3	5.5	197.2	42.9	10.7	90.8	50.4	3.6
Portable Stove	6	19.0	13.0	2.7	88.9	45.7	3.8	81.6	49.1	3.2	37.8	17.6	4.9	34.6	24.2	2.5
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	32	22.0	13.1	2.8	48.3	27.6	3.1	70.8	35.5	3.5	70.0	17.4	5.6	34.9	23.0	2.6
Unknown	3	7.4	5.4	2.7	18.3	18.0	1.3	15.7	8.7	4.2	12.0	5.4	5.4	20.8	20.4	1.3

*- significant difference with smoky coal for same PAH and strata via Tukey HSD test
† - significant difference with ventilated stove for same PAH within fuel strata via Tukey HSD test
N – number of samples
BkF - benzo[k]flouranthene BPE - benzo[ghi]perylene, CHR – chrysene, FLT - fluoranthene, IPY - indeno(1,2,3-cd)pyrene.

Table S3 - Personal Exposure to Gas phase PAHs (in ng/m^3) by fuel type and stove design

		NAP			ANY			FLU			PHE		
	N	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Smoky Coal	96	4200	2900	2.4	700	450	2.7	430	260	2.7	620	360	2.8
Ventilated Stove	53	2900	2500	1.9	510	400	2.1	260	200	2.1	350	260	2.1
Unventilated Stove	4	11000	6300	3.0	960	710	2.4	920	660	2.7	1300	820	3.3
Portable Stove	12	4900	3900	2.1	750	510	2.5	530	430	1.9	970	770	2.0
Firepit	4	17000	14000	2.1	3000	2600	1.8	2200	1800†	2.1	3200	2300†	2.3
Mixed Ventilation	19	3900	2600	3.2	750	460	3.5	420	250	3.3	560	340	3.4
Unknown	4	1300	1100	2.0	200	150	2.2	110	82	2.2	190	140	2.3
Smokeless Coal	17	3100	2800	1.6	470	370	2.1	210	200	1.5	420	370	1.7
Ventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-
Unventilated Stove	9	2800	2600	1.6	480	380	2.2	180	160	1.6	340	310	1.6
Portable Stove	7	3600	3400	1.5	490	370	2.3	260	260	1.2	530	480	1.7
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	1	2000	2000	-	310	310	-	190	190	-	260	260	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-
"Other" Coal	14	8300	5400	2.8	950	590	3.0	610	360	3.4	1000	570	3.5
Ventilated Stove	6	3200	2500	2.3	450	310	2.8	190	130	2.7	320	220	2.8
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	7	13000	11000	2.1	1400	1000	2.7	1000	800	2.2	1600	1300	2.5
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	1	5900	5900	-	630	630	-	450	450	-	670	670	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-
Wood	7	14000	5900	6.4	3300	1600*	6.0	730	380	5.0	1100	600	4.9
Ventilated Stove	2	13000	13000	1.3	3200	3200	1.1	730	730	1.2	1100	1100	1.3
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	3	21000	14000	3.1	5200	3800	2.7	1100	850	2.5	1700	1300	2.5
Firepit	2	2000	730	10.9	570	200	11.1	150	62	8.5	240	100	8.3
Mixed Ventilation	0	-	-	-	-	-	-	-	-	-	-	-	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-
Plant	3	26000	20000*	2.4	6400	5700*	1.8	1400	1300*	1.6	2500	2500*	1.3
Ventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-
Unventilated Stove	1	54000	54000	-	11000	11000	-	2200	2200	-	3300	3300	-
Portable Stove	0	-	-	-	-	-	-	-	-	-	-	-	-
Firepit	1	10000	10000	-	3600	3600	-	1100	1100	-	2300	2300	-
Mixed Ventilation	1	15000	15000	-	4500	4500	-	960	960	-	2000	2000	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-
"Other" Fuel	56	7600	4300	3.1	1300	730*	3.4	600	300	3.4	1000	500	3.6
Ventilated Stove	9	4500	3100	2.4	860	600	2.5	310	220	2.4	460	330	2.4
Unventilated Stove	11	20000	13000	3.4	3100	2100	3.4	1700	1100	3.5	2900	1800†	3.6
Portable Stove	5	4400	4000	1.6	820	700	1.9	410	340	1.9	780	630	2.1
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	28	4500	3300	2.7	910	550	3.4	320	220	2.8	570	360	3.1
Unknown	3	4400	2500	3.7	1100	450	5.8	280	140	4.3	510	240	4.6

*- significant difference with smoky coal for same PAH and strata via Tukey HSD test
† - significant difference with ventilated stove for same PAH within fuel strata via Tukey HSD test
N – number of samples
NAP - naphthalene, ANY – acenaphthylene, FLU – fluorine, PHE - phenanthrene

Table S4 -Personal exposure to particle phase PAHs (in ng/m^3) by smoky coal source

				BaP			FLT			PYR			BbF			DBA		
County	Smoky coal subtype	Mine Name	N	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Xuanwei	**Coking Coal**		**77**	72.4	47.5	2.6	56.7	19.9	4.4	63.5	24.7	4.1	106.4	69.7	2.6	27.1	15.5	3.1
		Azhi	21	86.6	58.4	2.7	66.7	24.5	4.2	72.4	30.1	3.7	132.2	92.3	2.5	31.7	20.3	2.9
		Baoshan	8	103.9	63.6	3.6	96.2	31.1	8.4	110.3	39.4	7.0	160.8	101.1	3.5	47.2	24.2	4.2
		Laibin	23	57.0	44.6	2.1	29.7	16.7	3.5	39.0	21.9	3.2	79.3	60.9	2.3	23.5	14.9	2.8
		Tangtang	16	81.2	47.0	3.1	82.0	21.3	6.3	86.2	26.0	6.0	114.5	66.3	3.0	24.1	12.6	3.3
		Yangchang	9	30.0	26.5	1.7	13.1	10.9	2.0	15.0	12.4	2.0	43.8	38.2	1.8	11.9	8.9	2.5
Fuyuan	**Overall**		**60**	76.7	39.2*	3.0	80.9	18.3*	5.4	86.2	19.5*	5.7	136.5	65.8*	3.2	28.6	10.9*	3.9
	Coking Coal		21	152.8	81.4†	3.3	199.3	45.8†	8.4	212.4	55.4†	7.6	280.4	155†	3.1	65.1	34.8†	3.2
		Daping	7	29.5	24.9	1.9	10.1	4.6	3.5	13.9	6.5	3.7	59.5	51.9	1.8	11.9	11.0	1.6
		Enhong	9	118.9	99.6	1.9	134.3	89.7	2.6	150.4	102.2	2.6	210.3	179.8	1.8	45.8	39.3	1.9
		Haidan	5	397.1	338.8	2.1	596.7	436.8	3.1	618.8	475.3	2.7	734.4	617.4	2.2	178.6	157.7	1.9
	1/3 Coking Coal		8	42.0	27.7†	2.9	36.5	17.1†	4.8	37.1	15.3†	5.5	98.6	60.7†	3.5	18.6	10.2†	3.7
		Bagong	6	53.3	43.3	2.2	47.9	35.2	2.4	49.1	34.5	2.6	127.1	107.7	1.9	24.0	17.2	2.8
		Dahe	2	7.9	7.2	1.8	2.2	1.9	2.2	1.4	1.4	1.3	12.9	10.8	2.4	2.4	2.2	1.8
	Gas Fat Coal		24	37.5	27.1	2.2	19.8	10.9	2.9	21.0	11.0	3.2	51.1	37.0	2.2	7.4	4.9	2.4
		Housuo	23	37.4	26.7	2.2	20.0	10.7	2.9	21.1	10.8	3.3	50.8	36.3	2.2	7.4	4.8	2.4
		Qingyun	1	39.9	39.9	-	15.7	15.7	-	18.1	18.1	-	56.9	56.9	-	8.5	8.5	-
	Meager Lean Coal (Gumu)		2	59.0	32.0	5.6	16.1	6.9	8.3	25.5	8.5	12.1	132.3	83.3	4.3	24.0	14.3	4.8
			N		BaA			BkF			BPE			CHR		IPY		
				AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Xuanwei	**Coking Coal**		**77**	95.5	53.5	3.3	26.0	16.9	2.6	79.2	50.1	2.8	82.3	46.5	3.2	46.9	30.0	2.8
		Azhi	21	116.9	73.0	3.0	32.9	22.6	2.5	94.6	66.6	2.6	102.4	65.2	3.0	54.6	37.7	2.6
		Baoshan	8	142.0	71.2	5.3	33.0	21.6	3.2	126.3	71.0	4.0	122.6	67.6	4.1	69.8	39.6	4.0
		Laibin	23	69.5	46.1	3.0	18.4	14.2	2.2	67.5	46.7	2.8	61.0	41.1	2.9	36.6	26.3	2.5
		Tangtang	16	113.4	55.3	3.8	30.5	17.0	3.2	77.2	43.6	3.1	95.4	45.9	4.0	50.7	28.5	3.0
		Yangchang	9	30.3	26.1	1.8	12.4	10.2	2.0	30.8	28.5	1.6	23.8	20.6	1.8	24.5	19.9	2.2
Fuyuan	**Overall**		**60**	114.3	42.1*	4.1	28.0	14.0*	3.1	83.2	40.9*	3.3	111.5	38.0*	4.4	44.6	25.6*	2.8
	Coking Coal		21	252.3	115.4†	3.9	55.0	27.8†	3.5	163.2	83.9†	3.8	248.5	114.6†	3.9	83.1	50.2†	3.0
		Daping	7	35.2	29.0	2.0	10.0	8.4	1.9	33.8	30.6	1.6	40.4	31.3	2.4	18.7	16.5	1.8
		Enhong	9	184.9	149.6	2.0	39.6	32.3	2.1	135.3	87.3	3.9	176.9	139.2	2.1	69.9	62.4	1.7
		Haidan	5	695.7	581.8	2.2	149.7	127.7	2.1	406.3	354.6	2.0	686.0	572.2	2.2	203.1	183.0	1.8
	1/3 Coking Coal		8	66.5	34.7†	4.5	16.7	10.7†	3.2	48.6	31.4†	3.0	87.2	45.5†	4.9	25.3	16.5†	2.9
		Bagong	6	87.1	70.9	2.1	21.4	18.0	2.0	61.4	48.5	2.2	114.3	98.3	1.9	32.2	25.7	2.3
		Dahe	2	5.0	4.1	2.5	2.4	2.2	1.8	10.1	8.5	2.3	6.0	4.5	3.1	4.5	4.4	1.4
	Gas Fat Coal		24	37.4	23.0	2.7	13.9	10.0	2.2	41.5	29.3	2.3	25.3	16.6	2.6	26.1	19.3	2.2
		Housuo	23	37.5	22.6	2.7	14.1	10.0	2.3	40.8	28.5	2.3	25.1	16.3	2.6	25.7	18.8	2.2
		Qingyun	1	35.1	35.1	-	9.7	9.7	-	58.1	58.1	-	29.0	29.0	-	35.1	35.1	-
	Meager Lean Coal (Gumu)		2	95.2	33.0	11.4	18.5	8.8	7.0	63.4	17.4	16.2	123.3	47.3	9.8	25.6	16.4	4.2

*- significant difference between smoky coal subtypes from Fuyuan

† - significant variation within designated smoky coal subtype

N – number of samples

BaP - benzo[a]pyrene, PYR - pyrene, BbF - benzo[b]fluoranthene DBA - dibenz(ah)anthracene, BaA - benzo[a]anthracene, BkF - benzo[k]flouranthene

BPE - benzo[ghi]perylene, CHR – chrysene, FLT - fluoranthene, IPY - indeno(1,2,3-cd)pyrene

Table S5 - Personal Exposure to Gas Phase PAHs (in ng/m^3) by Smoky Coal Source

				NAP			ANY			FLU			PHE		
County	Smoky coal subtype	Mine Name	N	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Xuanwei	**Coking Coal**		**61**	3600	2700	2.4	590	400	2.6	340	230	2.6	460	310	2.7
		Azhi	19	3300	2700	2.0	560	420	2.3	330	250	2.3	440	320	2.5
		Baoshan	7	6100	4200	2.5	900	580	2.9	520	290	3.3	730	420	3.4
		Laibin	19	2700	2100	2.7	380	290	2.7	250	190	2.7	340	260	2.7
		Tangtang	16	4100	3000	2.3	740	490	2.6	390	240	2.7	520	320	2.7
Fuyuan	**Overall**		**30**	5100	2900	2.7	930	530	3.0	560	290*	2.9	850	420*	3.1
	Coking Coal		5	15000	7100†	5.0	2300	960†	6.0	1700	820†	4.3	2600	1400†	3.8
		Daping	2	1300	1300	1.2	140	140	1.1	190	190	1.1	370	370	1.1
		Haidan	3	25000	22000	1.9	3800	3400	1.7	2700	2200	2.2	4200	3400	2.2
	1/3 Coking Coal (Dahe)		2	2300	1800	2.6	370	320	2.2	310	230	3.3	480	390	2.7
	Gas Fat Coal (Housuo)		21	2900	2400	2.1	680	500	2.5	310	230	2.4	390	290	2.3
	Meager Lean Coal(Gumu)		2	5500	4400	2.6	580	440	3.1	640	460	3.3	1600	1200	2.9

*- significant difference between smoky coal subtypes from Fuyuan
† - significant variation within designated smoky coal subtype
N – number of samples
NAP - naphthalene, ANY – acenaphthylene, FLU – fluorine, PHE - phenanthrene

Table S6a - Indoor measurements of particle phase PAHs (in ng/m^3) by fuel type and stove design

		BaP			PYR			BbF			DBA			BaA		
	N	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Smoky Coal	**137**	**73.5**	**47.6**	**2.5**	**76.0**	**26.6**	**4.4**	**115.2**	**72.0**	**2.7**	**31.2**	**16.9**	**3.1**	**97.0**	**53.0**	**3.2**
Ventilated Stove	75	52.6	39.3	2.1	40.6	19.5	3.2	78.5	57.0	2.3	19.9	12.8	2.7	65.6	42.1	2.7
Unventilated Stove	6	110.0	75.4	2.5	147.2	62.6	4.4	194.0	131.4	2.5	60.7	40.7	2.9	164.6	101.1	2.8
Portable Stove	13	66.7	45.0	2.6	58.2	23.7	4.7	145.6	86.2	2.9	29.6	16.7	3.1	92.2	49.5	3.6
Firepit	12	164.1	150.4†	1.6	242.8	203.0†	1.9	272.9	247.4†	1.6	80.3	60.8†	2.5	243.4	219.6†	1.6
Mixed Ventilation	27	95.4	56.6	2.6	103.8	34.1	4.5	129.7	82.7	2.5	37.3	19.6	2.8	119.5	66.4	2.9
Unknown	4	12.2	9.8	2.2	1.7	1.6	1.6	15.6	12.4	2.1	13.3	7.0	4.1	7.9	5.6	2.6
Smokeless Coal	**25**	**15.3**	**10.4***	**2.7**	**4.3**	**2.1***	**3.1**	**49.8**	**34.9***	**2.6**	**12.2**	**6.9***	**3.1**	**12.4**	**7.3***	**3.0**
Ventilated Stove	2	2.0	2.0*	1.2	0.7	0.6	1.4	26.5	19.6	3.2	17.6	5.7	12.7	1.2	1.2*	1.3
Unventilated Stove	13	18.6	12.8	2.7	5.1	2.3*	3.2	53.9	37.9	2.6	11.0	7.3	2.8	14.9	9.4*	2.8
Portable Stove	9	12.6	10.2	2.2	3.4	2.0	3.0	50.7	35.2	2.8	13.4	6.5	3.2	10.1	6.7	2.7
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	1	23.5	23.5	-	9.1	9.1	-	34.4	34.4	-	7.2	7.2	-	23.5	23.5	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
“Other” Coal	**26**	**46.2**	**35.0**	**2.2**	**45.5**	**19.9**	**3.8**	**73.2**	**54.1**	**2.3**	**19.6**	**12.6**	**2.8**	**56.1**	**38.1**	**2.5**
Ventilated Stove	10	41.5	33.6	2.1	21.5	14.3	3.1	52.8	42.6	2.1	24.2	14.2	3.2	42.8	30.7	2.4
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	9	53.6	35.7	2.7	79.8	30.1	5.0	86.9	60.0	2.6	17.3	10.5	3.1	72.2	42.8	3.2
Firepit	1	44.0	44.0	-	14.7	14.7	-	127.2	127.2	-	24.5	24.5	-	59.7	59.7	-
Mixed Ventilation	6	43.2	34.8	2.1	39.3	19.3	3.8	77.5	59.8	2.3	14.6	12.0	2.1	53.6	42.4	2.2
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Wood	**14**	**55.2**	**47.9**	**1.7**	**98.3**	**63.0**	**3.2**	**73.2**	**64.2**	**1.7**	**6.6**	**5.7***	**1.8**	**61.9**	**51.0**	**2.0**
Ventilated Stove	5	67.6	54.3	2.1	109.4	48.8	6.0	87.5	71.8	2.1	7.1	6.8	1.4	67.8	47.4	2.8
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	3	45.9	42.4	1.6	45.1	38.4	2.0	60.4	56.5	1.6	7.8	5.8	2.5	55.0	47.9	1.9
Firepit	5	48.0	43.8	1.7	119.7	100.4	1.9	65.6	59.6	1.7	5.6	4.8*	2.0	59.1	54.0	1.6
Mixed Ventilation	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unknown	1	57.6	57.6	-	96.1	96.1	-	77.9	77.9	-	5.1	5.1	-	66.7	66.7	-
Plant	**5**	**69.2**	**65.1**	**1.5**	**164.6**	**145.2**	**1.7**	**100.8**	**94.7**	**1.5**	**12.4**	**8.6**	**2.9**	**90.8**	**85.1**	**1.5**
Ventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unventilated Stove	1	47.6	47.6	-	90.7	90.7	-	71.9	71.9	-	24.4	24.4	-	68.6	68.6	-
Portable Stove	1	59.3	59.3	-	191.4	191.4	-	88.4	88.4	-	2.0	2.0	-	83.9	83.9	-
Firepit	2	61.0	59.6	1.4	112.8	108.6	1.5	92.2	86.7	1.7	13.3	10.4	2.9	70.2	69.4	1.3
Mixed Ventilation	1	116.9	116.9	-	315.4	315.4	-	159.2	159.2	-	8.8	8.8	-	161.2	161.2	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
“Other” Fuel	**75**	**100.1**	**37.4**	**3.8**	**161.0**	**21.1**	**8.0**	**163.8**	**64.2**	**3.6**	**40.0**	**13.4**	**3.9**	**142.0**	**36.1**	**5.0**
Ventilated Stove	14	44.3	27.8	2.9	85.8	17.0	6.6	58.2	34.3	3.2	14.1	11.5	2.1	51.6	23.4	4.3
Unventilated Stove	21	174.9	62.5	5.3	322.4	47.8	12.0	314.6	126.1	4.6	77.1	22.3	5.8	258.2	72.0	6.9
Portable Stove	6	50.4	41.6	2.1	38.2	18.8	4.9	95.9	82.2	1.9	31.5	23.5	2.4	58.1	38.9	3.0
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	31	91.3	32.0	3.5	122.2	15.5	6.4	135.0	57.5	2.9	31.8	10.8	3.4	131.9	30.5	4.3
Unknown	3	25.5	17.0	3.1	28.9	5.7	10.2	33.8	20.3	3.5	2.6	2.3	1.9	21.6	10.6	4.2

*- significant difference with smoky coal for same PAH and strata via Tukey HSD test
† - significant difference with ventilated stove for same PAH within fuel strata via Tukey HSD test
N – number of samples
BaP - benzo[a]pyrene, PYR - pyrene, BbF - benzo[b]fluoranthene DBA - dibenz(ah)anthracene, BaA - benzo[a]anthracene,

Table S6b - Indoor measurements of particle phase PAHs (in ng/m^3) by fuel type and stove design

		BkF			BPE			CHR			FLT			IPY		
	N	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Smoky Coal	**137**	**26.6**	**17.0**	**2.6**	**92.6**	**53.5**	**2.7**	**91.2**	**47.3**	**3.3**	**65.2**	**22.0**	**4.6**	**47.7**	**31.8**	**2.5**
Ventilated Stove	75	20.4	14.2	2.3	58.3	42.6	2.3	55.2	35.4	2.7	36.2	16.8	3.3	36.9	27.2	2.2
Unventilated Stove	6	37.4	23.5	2.8	148.5	108.0	2.4	176.2	108.6	2.7	128.9	50.0	4.6	73.1	51.5	2.6
Portable Stove	13	23.4	15.2	2.6	82.1	51.6	2.8	111.8	59.3	3.6	48.8	19.0	4.9	31.3	23.1	2.3
Firepit	12	59.5	53.2†	1.7	211.4	177.7†	1.9	251.7	207.8†	1.9	217.8	178.3†	2.0	108.7	94.4†	1.8
Mixed Ventilation	27	31.5	21.3	2.5	138.8	62.6	2.8	103.4	55.5	2.9	81.3	26.0	4.9	57.5	37.1	2.4
Unknown	4	4.4	3.1	2.5	19.5	13.8	2.9	8.6	5.9	2.9	1.0	1.0	1.2	16.2	10.6	3.5
Smokeless Coal	**25**	**6.2**	**4.7***	**2.2**	**21.7**	**13.9***	**2.8**	**25.6**	**15.1***	**3.2**	**3.5**	**1.9***	**2.8**	**15.5**	**11.4***	**2.4**
Ventilated Stove	2	1.7	1.7	1.2	14.7	6.7	7.5	19.1	7.2	10.0	0.9	0.8	1.4	15.5	7.2	7.2
Unventilated Stove	13	7.0	5.4	2.3	23.4	14.9	2.7	24.2	15.3	2.9	4.0	1.9*	3.0	15.8	12.5	2.1
Portable Stove	9	5.6	4.5	2.1	20.8	14.1	2.7	29.9	16.8	3.4	2.9	1.9	2.7	15.3	10.7	2.4
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	1	10.0	10.0	-	21.7	21.7	-	19.0	19.0	-	7.2	7.2	-	14.5	14.5	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
"Other" Coal	**26**	**16.6**	**11.8**	**2.5**	**51.9**	**37.1**	**2.4**	**55.8**	**36.7**	**2.6**	**38.5**	**16.0**	**3.9**	**32.6**	**24.2**	**2.3**
Ventilated Stove	10	15.1	10.8	2.6	48.2	37.3	2.3	36.6	26.1	2.4	16.3	11.1	3.0	36.1	28.7	2.2
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	9	18.8	11.9	2.9	61.9	37.7	3.0	70.9	45.1	2.9	68.5	25.2	5.0	32.6	20.3	2.9
Firepit	1	16.6	16.6	-	64.6	64.6	-	152.7	152.7	-	12.7	12.7	-	26.4	26.4	-
Mixed Ventilation	6	15.8	12.5	2.2	41.1	32.8	2.2	49.1	37.5	2.4	34.8	15.4	4.5	27.9	23.7	2.0
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Wood	**14**	**21.8**	**18.6**	**1.8**	**33.2**	**29.4**	**1.7**	**52.6**	**42.4**	**2.1**	**86.7**	**48.6**	**4.0**	**37.4**	**32.6**	**1.7**
Ventilated Stove	5	27.5	22.2	2.1	42.4	36.1	1.9	52.0	35.7	2.8	96.9	33.2	8.2	45.9	38.1	2.1
Unventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Portable Stove	3	19.1	17.4	1.7	27.1	25.5	1.5	45.0	38.6	2.0	33.6	28.0	2.2	33.8	30.6	1.7
Firepit	5	17.9	15.9	1.8	28.0	25.7	1.6	56.8	50.1	1.8	109.0	88.5	2.0	31.7	28.6	1.7
Mixed Ventilation	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unknown	1	21.2	21.2	-	31.4	31.4	-	57.6	57.6	-	83.9	83.9	-	34.4	34.4	-
Plant	**5**	**34.0**	**28.6**	**1.9**	**44.3**	**41.1**	**1.5**	**88.3**	**85.0**	**1.4**	**159.5**	**137.6**	**1.8**	**39.9**	**38.0**	**1.4**
Ventilated Stove	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unventilated Stove	1	64.2	64.2	-	43.2	43.2	-	68.6	68.6	-	85.2	85.2	-	35.4	35.4	-
Portable Stove	1	15.7	15.7	-	24.6	24.6	-	92.9	92.9	-	185.8	185.8	-	26.9	26.9	-
Firepit	2	20.6	19.7	1.5	51.4	46.6	1.9	75.7	73.5	1.4	104.6	99.0	1.6	37.1	36.4	1.3
Mixed Ventilation	1	49.1	49.1	-	51.1	51.1	-	128.7	128.7	-	317.4	317.4	-	62.9	62.9	-
Unknown	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
"Other" Fuel	**75**	**36.4**	**14.6**	**3.6**	**106.7**	**39.2**	**3.7**	**149.0**	**38.6**	**4.8**	**143.8**	**17.7**	**8.1**	**63.5**	**29.0**	**3.2**
Ventilated Stove	14	17.4	10.7	3.3	41.2	30.3	2.4	42.0	18.2	4.3	87.9	14.1	7.6	34.0	26.6	2.0
Unventilated Stove	21	65.4	26.6	4.8	208.8	63.7	5.7	262.8	82.7	5.9	280.3	40.0	12.2	109.7	47.1	4.4
Portable Stove	6	15.7	13.4	1.9	95.4	67.7	2.7	54.3	40.2	2.6	31.0	17.0	4.3	40.4	33.6	2.0
Firepit	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mixed Ventilation	31	31.9	12.7	3.1	78.1	32.1	3.1	151.1	38.3	3.7	110.1	13.0	6.4	54.5	22.7	3.1
Unknown	3	8.8	5.0	3.7	16.5	11.5	2.8	19.0	6.3	6.6	24.1	4.9	10.0	17.6	13.3	2.4

*- significant difference with smoky coal for same PAH and strata via Tukey HSD test
† - significant difference with ventilated stove for same PAH within fuel strata via Tukey HSD test
N – number of samples
BkF - benzo[k]flouranthene , BPE - benzo[ghi]perylene, CHR – chrysene, FLT - fluoranthene, IPY - indeno(1,2,3-cd)pyrene.

Table S7 - Indoor measurements of particle phase PAHs (in ng/m^3) by smoky coal source

County	Smoky coal subtype	Mine Name	N	BaP AM	BaP GM	BaP GSD	FLT AM	FLT GM	FLT GSD	PYR AM	PYR GM	PYR GSD	BbF AM	BbF GM	BbF GSD	DBA AM	DBA GM	DBA GSD
Xuanwei	**Coking Coal**		**77**	79.1	50.0	2.5	66.3	20.9	4.8	79.3	26.7	4.4	111.0	70.8	2.7	32.0	17.6	3.0
		Azhi	21	79.6	63.2	2.0	70.9	30.6	4.2	76.2	38.1	3.4	122.7	98.1	2.0	24.7	18.8	2.2
		Baoshan	8	103.7	62.0	3.1	115.2	26.0	9.6	132.5	34.8	8.0	153.4	87.8	3.4	55.8	34.5	3.1
		Laibin	23	87.0	45.6	3.0	49.2	15.8	4.7	76.7	21.4	4.7	109.3	60.6	3.1	35.4	14.1	3.6
		Tangtang	16	79.2	47.5	2.8	88.5	20.6	6.4	94.8	26.0	5.6	110.7	66.2	2.9	36.2	21.0	3.6
		Yangchang	9	35.8	33.2	1.5	15.9	14.9	1.5	18.3	17.0	1.6	51.4	45.7	1.6	11.5	10.6	1.6
Fuyuan	**Overall**		**60**	63.9	42.9*	2.5	61.9	21.9*	4.4	68.4	24.5*	4.4	110.8	68.9*	2.7	28.2	15.2*	3.2
	Coking Coal		21	97.4	67.7†	2.5	119.5	52.1†	4.6	132.2	61.7†	4.3	177.4	120.3†	2.6	48.3	29.3†	3.0
		Daping	7	29.4	26.6	1.6	13.2	9.4	2.5	17.6	12.1	2.6	54.7	45.3	2.0	11.8	9.7	2.2
		Enhong	9	99.8	85.6	1.8	110.1	88.4	2.1	124.0	101.1	2.0	176.1	153.0	1.8	42.5	36.8	1.8
		Haidan	5	188.1	163.7	1.9	285.1	221.8	2.3	307.2	248.0	2.2	351.4	306.0	1.8	109.7	91.4	2.0
	1/3 Coking Coal		8	66.9	44.7	3.2	61.9	25.9	5.3	67.6	27.9	5.0	126.4	85.4	3.2	27.5	16.6	3.7
		Bagong	6	63.1	55.4	1.7	61.6	33.7	3.1	66.7	34.6	3.2	122.0	106.4	1.8	29.1	22.0	2.3
		Dahe	2	78.4	23.4	14.3	62.7	11.8	28.1	70.4	14.6	24.3	139.6	44.1	13.1	22.6	7.2	12.9
	Gas Fat Coal		24	34.2	28.8	1.8	15.4	10.7	2.5	16.8	11.4	2.6	46.5	38.4	1.9	11.1	8.0	2.3
		Housuo	23	33.4	28.0	1.8	14.3	10.1	2.5	15.6	10.7	2.5	45.3	37.3	1.9	10.8	7.7	2.3
		Qingyun	1	53.7	53.7	-	39.4	39.4	-	44.9	44.9	-	74.5	74.5	-	17.5	17.5	-
	Meager Lean Coal (Gumu)		2	55.3	36.4	4.0	16.6	7.2	8.2	22.8	9.2	9.1	119.3	94.0	2.8	26.4	22.4	2.3

County	Smoky coal subtype	Mine Name	N	BaA AM	BaA GM	BaA GSD	BkF AM	BkF GM	BkF GSD	BPE AM	BPE GM	BPE GSD	CHR AM	CHR GM	CHR GSD	IPY AM	IPY GM	IPY GSD
Xuanwei	**Coking Coal**		**77**	101.6	57.1	3.0	27.4	17.6	2.6	100.4	53.9	2.8	85.4	48.7	3.0	51.3	33.2	2.5
		Azhi	21	109.3	79.2	2.3	29.9	23.7	2.0	80.0	64.1	2.0	94.2	69.5	2.2	46.6	36.7	2.1
		Baoshan	8	140.0	70.6	4.0	41.2	23.3	3.9	133.8	80.6	2.9	122.0	66.8	3.4	75.8	53.0	2.4
		Laibin	23	100.1	48.0	3.6	24.3	14.8	2.8	137.1	47.1	3.7	89.2	40.8	3.6	47.8	25.5	3.0
		Tangtang	16	109.4	57.2	3.5	28.7	16.0	3.0	94.4	55.5	3.1	81.6	48.8	3.1	62.9	37.6	3.1
		Yangchang	9	39.2	34.4	1.7	14.6	12.9	1.6	34.9	33.5	1.4	29.9	25.1	1.8	28.5	27.1	1.4
Fuyuan	**Overall**		**60**	87.3	45.4*	3.4	24.9	15.8*	2.6	76.8	50.0*	2.5	92.9	42.0*	3.7	43.3	29.8*	2.4
	Coking Coal		21	149.7	92.0†	3.1	39.6	25.1†	2.9	121.3	80.5†	2.6	169.0	93.4†	3.5	63.2	43.4†	2.5
		Daping	7	35.5	27.8	2.2	9.0	8.3	1.6	35.2	30.5	1.8	44.0	28.0	3.1	17.1	16.6	1.3
		Enhong	9	147.0	128.4	1.8	47.0	35.9	2.3	112.8	98.8	1.7	140.1	121.8	1.8	65.0	55.2	1.8
		Haidan	5	314.4	269.9	1.9	69.0	61.9	1.7	257.0	216.3	2.0	395.8	312.8	2.2	124.4	107.6	1.9
	1/3 Coking Coal		8	90.9	54.5	4.3	24.3	17.6	2.8	73.5	47.5	3.3	103.5	62.8	4.4	42.9	30.2	3.3
		Bagong	6	87.3	75.2	1.8	24.7	21.6	1.8	63.0	57.3	1.6	101.9	89.3	1.8	45.1	41.7	1.5
		Dahe	2	101.8	20.7	25.0	23.0	9.5	8.7	105.2	27.2	17.7	108.2	21.8	25.4	36.3	11.4	13.2
	Gas Fat Coal		24	32.4	23.8	2.3	13.0	10.4	1.9	40.3	33.9	1.9	23.0	17.9	2.1	27.6	22.2	2.0
		Housuo	23	31.3	22.9	2.3	12.6	10.1	1.9	39.5	33.0	1.9	22.2	17.2	2.1	26.6	21.4	1.9
		Qingyun	1	59.2	59.2	-	21.9	21.9	-	60.3	60.3	-	41.6	41.6	-	50.4	50.4	-
	Meager Lean Coal (Gumu)		2	75.0	29.9	9.2	16.6	11.9	3.4	60.5	43.6	3.3	89.8	53.1	4.9	25.6	19.2	3.1

*- significant difference between smoky coal subtypes from Fuyuan
† - significant variation within designated smoky coal subtype
N – number of samples
BaP - benzo[a]pyrene, PYR - pyrene, BbF - benzo[b]fluoranthene DBA - dibenz(ah)anthracene, BaA - benzo[a]anthracene, BkF - benzo[k]flouranthene
BPE - benzo[ghi]perylene, CHR – chrysene, FLT - fluoranthene, IPY - indeno(1,2,3-cd)pyrene

Table S8- Exploratory factor analysis of log transformed indoor PAH values

	Factor 1	Factor 2	Factor 3
EV(% variance explained)	3.9(39%)	3.7(37%)	1.8(18%)
Benzo[ghi]perylene (6)	0.49	**0.77**	0.38
Benzo[b]fluoranthene (5)	0.47	**0.56**	**0.66**
Dibenz[ah]anthracene(5)	0.28	**0.81**	0.31
Benzo[a]pyrene (5)	**0.63**	**0.61**	0.41
Benzo[k]fluoranthene (5)	**0.61**	**0.58**	0.42
Indeno[1,2,3-cd]pyrene (5)	**0.53**	**0.77**	0.27
Pyrene(4)	**0.87**	0.39	0.29
Fluoranthene(4)	**0.88**	0.35	0.31
Chrysene(4)	**0.55**	**0.52**	**0.62**
Benzo[a]anthracene (4)	**0.69**	**0.56**	0.42

Values in bold (Eigen value > 0.5) are considered to be contributory to that factor
Numbers in parentheses represent number of carbon rings for respective PAH
Factor analysis was performed with varimax rotation

Table S9 - Mixed effect model for indoor PAH measurements (using PAHs and variables selected for personal measurements)

		BaP			FLT			CHR	
Reference/Background Value (Intercept)*		3.04			1.65			3.0	
Fuel Type	Estimate	95% CI	GMR	Estimate	95% CI	GMR	Estimate	95% CI	GMR
Smokeless Coal (FY & XW)	Ref		1	Ref		1	Ref		1
Coking Coal from North XW	0.82	0.19,1.44	2.27	1.1	0.16,2.03	3	1.01	0.29,1.72	2.75
Coking Coal from South XW	0.93	-0.22,2.07	2.54	1.51	-0.2,3.22	4.53	0.83	-0.42,2.11	2.3
Coking Coal from FY	0.47	-0.24,1.19	1.61	0.84	-0.23,1.93	2.33	0.75	-0.11,1.6	2.11
1/3 Coking coal FY	0.8	-0.17,1.75	2.23	1.76	0.33,3.17	5.79	1.21	0.15,2.25	3.35
Gas Fat coal FY	0.26	-0.5,1.02	1.3	0.48	-0.64,1.6	1.62	0.01	-0.85,0.86	1.01
Meagre Lean coal FY	0.67	-0.66,2	1.95	0.45	-1.54,2.44	1.56	1.07	-0.51,2.66	2.92
Multiple Coal Types	0.53	-0.04,1.1	1.7	1.11	0.27,1.96	3.04	0.76	0.09,1.42	2.13
Multiple Fuel Types	0.64	0.11,1.16	1.89	1.23	0.46,2.02	3.43	0.69	0.07,1.3	1.98
Smoky Coal of uncertain type	1.42	0.53,2.3	4.12	3.31	1.98,4.65	27.39	1.91	0.84,2.98	6.77
Plant Products	0.02	-1.05,1.1	1.02	0.83	-0.78,2.48	2.3	0.22	-1.07,1.51	1.24
Wood	0.05	-0.84,0.97	1.06	0.95	-0.4,2.34	2.59	0.13	-0.95,1.23	1.14
Stove Design									
Ventilated Stove	Ref		1	Ref		1	Ref		1
Unventilated Stove	0.51	0.07,0.95	1.67	0.67	0,1.34	1.95	0.73	0.2,1.25	2.07
Fire Pit	0.92	0.24,1.58	2.51	1.54	0.52,2.52	4.66	1.02	0.21,1.81	2.77
Portable Stove	0.14	-0.26,0.54	1.15	0.17	-0.43,0.76	1.18	0.37	-0.11,0.84	1.44
Mixed Ventilation	0.29	-0.01,0.59	1.33	0.22	-0.23,0.67	1.25	0.44	0.08,0.81	1.56
Unknown ventilation	-0.79	-1.49,-0.09	0.45	-1.53	-2.58,-0.47	0.22	-1.2	-2.03,-0.36	0.3
Room size (in m^3)									
<40m^3	Ref		1	Ref		1	Ref		1
40m^3 to 49m^3	-0.42	-0.81,-0.03	0.66	-0.51	-1.1,0.06	0.6	-0.69	-1.17,-0.22	0.5
50m^3 to 67m^3	0.07	-0.35,0.49	1.08	0.41	-0.23,1.04	1.5	0	-0.5,0.51	1
>67m^3	0.11	-0.31,0.53	1.12	0.5	-0.14,1.12	1.64	-0.03	-0.53,0.48	0.97
Room Size Unknown	-0.35	-0.76,0.06	0.7	-0.21	-0.82,0.39	0.81	-0.47	-0.96,0.02	0.63
Season									
Autumn	Ref		1	Ref		1	Ref		1
Winter	-0.15	-0.47,0.17	0.86	0.17	-0.32,0.65	1.18	0.06	-0.31,0.42	1.06
Spring/Summer	-0.09	-0.37,0.18	0.91	-0.62	-1.03,-0.21	0.54	-0.32	-0.63,0	0.73
Variance explained (%)									
Between Subjects		46			57			39	
Between Villages		24			36			50	

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
BaP - benzo[a]pyrene, FLT – fluoranthene, CHR – chrysene

Table S10a- Mixed effect models for personal exposure to particle bound PAHs

	BPE			BbF			DBA		
Reference/Background Value (Intercept)*	2.4			3.08			1.05		
Fuel Type	Estimate	95% CI	GMR	Estimate	95% CI	GMR	Estimate	95% CI	GMR
Smokeless Coal (FY & XW)	Ref		1	Ref		1	Ref		1
Coking Coal from North XW	1.27	1.96,0	3.58	1.12	0.5,1.73	3.07	1.42	0.71,2.12	4.15
Coking Coal from South XW	0.72	1.86,0	2.05	0.43	-0.53,1.39	1.53	0.77	-0.37,1.92	2.16
Coking Coal from FY	0.9	1.74,0	2.46	1.14	0.36,1.9	3.11	1.36	0.5,2.21	3.89
1/3 Coking coal FY	0.39	1.37,0	1.48	0.44	-0.46,1.28	1.55	0.51	-0.54,1.51	1.67
Gas Fat coal FY	0.35	1.18,0	1.42	0.27	-0.46,0.98	1.31	0.07	-0.77,0.89	1.07
Meagre Lean coal FY	0.22	1.74,0	1.25	1.24	-0.15,2.61	3.45	1.45	-0.12,3.01	4.27
Multiple Coal Types	0.93	1.57,0	2.53	0.78	0.2,1.35	2.18	1.04	0.37,1.71	2.83
Multiple Fuel Types	0.9	1.49,0	2.45	0.87	0.32,1.42	2.39	0.79	0.17,1.4	2.2
Smoky Coal of uncertain type	1.38	2.39,0	3.97	1.49	0.55,2.42	4.42	1.16	0.08,2.23	3.18
Plant Products	-0.01	1.25,0	0.99	0.24	-0.95,1.43	1.27	-0.09	-1.44,1.26	0.91
Wood	0.2	1.24,0	1.23	0.45	-0.51,1.41	1.57	0.04	-1.02,1.11	1.04
Stove Design									
Ventilated Stove	Ref		1	Ref		1	Ref		1
Unventilated Stove	0.51	1.02,0	1.66	0.67	0.18,1.15	1.95	0.73	0.17,1.29	2.07
Fire Pit	1.24	1.98,0	3.44	1.08	0.38,1.76	2.93	1.18	0.41,1.94	3.24
Portable Stove	0.35	0.82,0	1.43	0.52	0.09,0.95	1.69	0.48	-0.01,0.97	1.62
Mixed Ventilation	0	0.36,0	1	0.09	-0.25,0.42	1.09	-0.02	-0.41,0.36	0.98
Unknown ventilation	-0.97	-0.14,0	0.38	-0.91	-1.67,-0.14	0.4	-0.94	-1.8,-0.08	0.39
Room size (in m^3)									
<40m^3	Ref		1	Ref		1	Ref		1
40m^3 to 49m^3	-0.34	0.13,0	0.71	-0.46	-0.9,-0.03	0.63	-0.37	-0.86,0.11	0.69
50m^3 to 67m^3	0.63	1.13,0	1.87	0.4	-0.07,0.86	1.49	0.48	-0.05,0.99	1.61
>67m^3	0.21	0.71,0	1.24	-0.14	-0.61,0.33	0.87	0.1	-0.42,0.63	1.11
Room Size Unknown	0.07	0.55,0	1.08	-0.08	-0.53,0.37	0.92	0.04	-0.47,0.53	1.04
Season									
Autumn	Ref		1	Ref		1	Ref		1
Winter	0.12	0.47,0	1.13	0.28	-0.02,0.58	1.33	0.28	-0.09,0.64	1.33
Spring/Summer	0.12	0.41,0	1.13	-0.04	-0.3,0.23	0.97	0.52	0.19,0.84	1.68
Variance explained									
Between Subjects		40			32			32	
Between Villages		53			80			72	

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
BPE – Benzo[ghi]perylene, BbF – Benzo[b]fluoranthene, DBA – Dibenz[ah]anthracene,

Table S10b- Mixed effect models for personal exposure to particle bound PAHs

	IPY			PYR			BaA		
Reference/Background Value (Intercept)*	2.2			1.55			2.21		
Fuel Type	Estimate	95% CI	GMR	Estimate	95% CI	GMR	Estimate	95% CI	GMR
Smokeless Coal (FY & XW)	Ref		1	Ref		1	Ref		1
Coking Coal from North XW	1.01	0.39,1.61	2.73	1.12	0.19,2.04	3.06	1.55	0.78,2.31	4.72
Coking Coal from South XW	0.53	-0.46,1.5	1.7	0.52	-1.13,2.13	1.68	0.95	-0.37,2.26	2.59
Coking Coal from FY	0.92	0.18,1.65	2.51	0.73	-0.4,1.85	2.07	1.37	0.44,2.3	3.94
1/3 Coking coal FY	0.03	-0.9,0.9	1.03	0.09	-1.33,1.45	1.09	0.57	-0.59,1.67	1.76
Gas Fat coal FY	0.33	-0.41,1.04	1.39	0.06	-1.07,1.16	1.06	0.48	-0.43,1.37	1.62
Meagre Lean coal FY	0.73	-0.61,2.06	2.08	0.27	-1.75,2.28	1.31	1.06	-0.6,2.73	2.9
Multiple Coal Types	0.79	0.21,1.37	2.21	0.95	0.08,1.81	2.58	1.23	0.53,1.93	3.43
Multiple Fuel Types	0.82	0.28,1.37	2.28	0.98	0.16,1.8	2.66	1.24	0.58,1.9	3.45
Smoky Coal of uncertain type	0.83	-0.09,1.76	2.3	1.51	0.17,2.86	4.54	1.66	0.56,2.75	5.25
Plant Products	0.14	-1.02,1.3	1.15	-0.23	-1.94,1.49	0.8	0.38	-1.02,1.78	1.46
Wood	0.52	-0.4,1.44	1.68	0.45	-0.92,1.83	1.56	0.95	-0.19,2.09	2.57
Stove Design									
Ventilated Stove	Ref		1	Ref		1	Ref		1
Unventilated Stove	0.34	-0.13,0.81	1.41	0.33	-0.36,1.02	1.39	0.45	-0.12,1.02	1.57
Fire Pit	1.05	0.39,1.7	2.85	1.73	0.74,2.7	5.62	1.16	0.34,1.98	3.2
Portable Stove	0.11	-0.31,0.52	1.11	0.2	-0.41,0.82	1.23	0.36	-0.15,0.87	1.43
Mixed Ventilation	-0.01	-0.34,0.31	0.99	0.12	-0.36,0.6	1.13	0.06	-0.33,0.45	1.06
Unknown ventilation	-0.8	-1.53,-0.06	0.45	-1.31	-2.4,-0.22	0.27	-1.29	-2.19,-0.39	0.27
Room size (in m^3)									
$<40m^3$	Ref		1	Ref		1	Ref		1
$40m^3$ to $49m^3$	-0.22	-0.64,0.19	0.8	0.1	-0.5,0.71	1.11	-0.27	-0.78,0.24	0.77
$50m^3$ to $67m^3$	0.47	0.03,0.92	1.61	0.84	0.18,1.5	2.31	0.59	0.03,1.14	1.8
$>67m^3$	0.12	-0.33,0.56	1.12	0.44	-0.23,1.1	1.55	0.13	-0.42,0.68	1.14
Room Size Unknown	0.03	-0.4,0.46	1.03	0.38	-0.25,1.01	1.46	0.08	-0.45,0.6	1.08
Season									
Autumn	Ref		1	Ref		1	Ref		1
Winter	0.17	-0.15,0.47	1.18	0.68	0.22,1.14	1.98	0.36	-0.01,0.74	1.44
Spring/Summer	0.23	-0.04,0.5	1.26	-0.56	-0.96,-0.16	0.57	-0.26	-0.58,0.06	0.77
Variance explained									
Between Subjects		32			36			35	
Between Villages		65			54			62	

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
IPY – Indeno[1,2,3-cd]pyrene, PYR – Pyrene, BaA – Benzo[a]anthracene

Table S10c- Mixed effect models for personal exposure to particle bound PAHs

		BkF	
Reference/Background Value (Intercept)*		1.53	
Fuel Type	Estimate	95% CI	GMR
Smokeless Coal (FY & XW)	Ref		1
Coking Coal from North XW	1.12	0.47,1.76	3.08
Coking Coal from South XW	0.56	-0.5,1.6	1.75
Coking Coal from FY	0.93	0.14,1.7	2.52
1/3 Coking coal FY	0.26	-0.7,1.17	1.3
Gas Fat coal FY	0.38	-0.4,1.14	1.46
Meagre Lean coal FY	0.7	-0.71,2.1	2.02
Multiple Coal Types	0.82	0.21,1.43	2.27
Multiple Fuel Types	0.84	0.26,1.41	2.31
Smoky Coal of uncertain type	0.99	0.04,1.94	2.69
Plant Products	0.13	-1.08,1.34	1.14
Wood	0.45	-0.52,1.42	1.57
Stove Design			
Ventilated Stove	Ref		1
Unventilated Stove	0.45	-0.04,0.94	1.57
Fire Pit	1.07	0.38,1.76	2.92
Portable Stove	0.2	-0.23,0.63	1.22
Mixed Ventilation	0.1	-0.23,0.44	1.11
Unknown ventilation	-0.96	-1.72,-0.19	0.38
Room size (in m^3)			
<40m^3	Ref		1
40m^3 to 49m^3	-0.28	-0.71,0.15	0.76
50m^3 to 67m^3	0.47	0,0.94	1.61
>67m^3	-0.01	-0.47,0.46	0.99
Room Size Unknown	-0.02	-0.47,0.43	0.98
Season			
Autumn	Ref		1
Winter	0.29	-0.03,0.6	1.33
Spring/Summer	0.02	-0.26,0.29	1.02
Variance explained			
Between Subjects		31	
Between Villages		65	

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
BkF – Benzo[k]fluoranthene

Table S11 - Mixed effect models for personal exposure to gas-phase PAHs

		PHE			ANY			FLU	
Reference/Background Value (Intercept)*		4.84			5.49			4.39	
Fuel Type	Estimate	95% CI	GMR	Estimate	95% CI	GMR	Estimate	95% CI	GMR
Smokeless Coal (FY & XW)	Ref		1	Ref		1	Ref		1
Coking Coal from North XW	0.43	4.16,5.55	1.54	0	4.73,6.27	1	0.51	3.69,5.09	1.67
Coking Coal from South XW	-	-	-	-	-	-	-	-	-
Coking Coal from FY	0.66	-0.26,1.08	1.94	-0.36	-0.75,0.73	0.7	0.39	-0.17,1.18	1.48
1/3 Coking coal FY	0.78	-0.47,1.66	2.17	0.06	-1.5,0.81	1.06	0.76	-0.69,1.47	2.14
Gas Fat coal FY	0.32	-0.62,2.18	1.37	0.06	-1.43,1.55	1.06	0.43	-0.62,2.16	1.53
Meagre Lean coal FY	1.54	-0.49,1.08	4.67	0.27	-0.85,0.95	1.3	0.98	-0.39,1.22	2.65
Multiple Coal Types	0.65	0.16,2.9	1.92	0.19	-1.21,1.73	1.21	0.63	-0.38,2.31	1.88
Multiple Fuel Types	0.81	-0.09,1.38	2.24	0.58	-0.61,0.99	1.78	0.76	-0.1,1.36	2.13
Smoky Coal of uncertain type	0.67	0.16,1.43	1.96	0.27	-0.15,1.29	1.31	0.86	0.11,1.39	2.37
Plant Products	0.85	-0.28,1.63	2.34	0.78	-0.7,1.23	2.18	0.44	-0.05,1.76	1.55
Wood	-0.53	-0.67,2.34	0.59	-0.36	-0.82,2.38	0.69	-0.73	-1.03,1.91	0.48
Stove Design									
Ventilated Stove	Ref		1	Ref		1	Ref		1
Unventilated Stove	1.2	-1.83,0.76	3.33	0.69	-1.74,1.01	1.99	1.02	-1.99,0.53	2.78
Fire Pit	1.75	0.51,1.5	5.73	1.52	-0.13,0.91	4.56	1.79	0.39,1.34	6.01
Portable Stove	1.01	0.59,1.76	2.73	0.4	0.07,1.31	1.49	0.87	0.44,1.61	2.38
Mixed Ventilation	0.11	0.75,2.72	1.12	-0.03	0.52,2.52	0.97	0.05	0.85,2.72	1.05
Unknown ventilation	-0.47	-0.28,0.51	0.62	-0.69	-0.44,0.38	0.5	-0.73	-0.33,0.43	0.48
Room size (in m^3)									
<40m^3	Ref		1	Ref		1	Ref		1
40m^3 to 49m^3	-0.25	0.13,0.76	0.78	0.01	-0.15,0.53	1.01	-0.11	-0.01,0.61	0.9
50m^3 to 67m^3	0.51	-0.8,0.29	1.67	0.79	-0.53,0.55	2.2	0.7	-0.63,0.4	2.02
>67m^3	0.13	-0.05,1.06	1.13	0.36	0.22,1.33	1.44	0.25	0.15,1.22	1.28
Room Size Unknown	-0.11	-0.42,0.67	0.89	0.22	-0.18,0.91	1.25	0.08	-0.27,0.75	1.09
Season									
Autumn	Ref		1	Ref		1	Ref		1
Winter	0.52	-1.24,0.29	1.67	0.42	-1.48,0.11	1.52	0.46	-1.46,0.01	1.58
Spring/Summer	0.45	0.14,0.88	1.56	0.19	-0.01,0.83	1.21	0.31	0.07,0.83	1.36
Variance explained									
Between Subjects		67			100			87	
Between Villages		100			71			84	

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
PHE - Phenanthrene, ANY - Acenaphthylene, FLU - Fluorine

Table S12a - Mixed effect models for indoor measurements of particle bound PAHs

	BPE			BbF			DBA		
Reference/Background Value (Intercept)*	3.12			3.63			1.79		
Fuel Type	Estimate	95% CI	GMR	Estimate	95% CI	GMR	Estimate	95% CI	GMR
Smokeless Coal (FY & XW)	Ref		1	Ref		1	Ref		1
Coking Coal from North XW	0.89	0.23,1.54	2.44	0.78	0.16,1.39	2.18	1.02	0.32,1.71	2.78
Coking Coal from South XW	0.76	-0.39,1.9	2.13	0.62	-0.4,1.67	1.86	0.38	-0.7,1.46	1.46
Coking Coal from FY	0.53	-0.24,1.3	1.7	0.61	-0.13,1.34	1.84	0.81	-0.02,1.64	2.26
1/3 Coking coal FY	0.82	-0.16,1.79	2.28	0.89	0.01,1.75	2.43	0.7	-0.28,1.66	2.01
Gas Fat coal FY	0.22	-0.6,1.01	1.24	0.07	-0.66,0.8	1.08	0.19	-0.64,1.01	1.21
Meagre Lean coal FY	0.69	-0.74,2.12	1.99	1.08	-0.29,2.44	2.93	1.6	0,3.19	4.93
Multiple Coal Types	0.49	-0.13,1.11	1.63	0.48	-0.1,1.05	1.61	0.55	-0.13,1.23	1.74
Multiple Fuel Types	0.63	0.07,1.19	1.88	0.62	0.09,1.15	1.86	0.57	-0.06,1.2	1.77
Smoky Coal of uncertain type	1.69	0.73,2.64	5.4	1.48	0.54,2.42	4.39	1.53	0.42,2.65	4.64
Plant Products	-0.51	-1.66,0.66	0.6	0.08	-1.04,1.21	1.08	-0.64	-1.95,0.68	0.53
Wood	-0.48	-1.44,0.49	0.62	-0.04	-0.98,0.92	0.96	-0.78	-1.86,0.33	0.46
Stove Design									
Ventilated Stove	Ref		1	Ref		1	Ref		1
Unventilated Stove	0.41	-0.06,0.88	1.51	0.67	0.22,1.12	1.96	0.43	-0.1,0.96	1.54
Fire Pit	0.92	0.19,1.62	2.51	0.88	0.17,1.57	2.42	0.71	-0.11,1.5	2.04
Portable Stove	0.16	-0.27,0.58	1.17	0.31	-0.1,0.72	1.36	0.09	-0.4,0.58	1.1
Mixed Ventilation	0.23	-0.1,0.55	1.26	0.39	0.07,0.7	1.47	0.11	-0.27,0.49	1.12
Unknown ventilation	-0.87	-1.61,-0.12	0.42	-0.82	-1.54,-0.09	0.44	-0.96	-1.83,-0.1	0.38
Room size (in m^3)									
$<40m^3$	Ref		1	Ref		1	Ref		1
$40m^3$ to $49m^3$	-0.47	-0.89,-0.06	0.62	-0.58	-1,-0.17	0.56	-0.43	-0.92,0.05	0.65
$50m^3$ to $67m^3$	0.08	-0.37,0.52	1.08	-0.01	-0.45,0.44	0.99	0.08	-0.44,0.6	1.08
$>67m^3$	0.11	-0.34,0.55	1.11	-0.09	-0.53,0.35	0.91	0.12	-0.38,0.63	1.13
Room Size Unknown	-0.36	-0.79,0.08	0.7	-0.56	-0.98,-0.13	0.57	-0.18	-0.68,0.33	0.84
Season									
Autumn	Ref		1	Ref		1	Ref		1
Winter	-0.03	-0.37,0.31	0.97	-0.05	-0.37,0.25	0.95	0.39	0.03,0.73	1.47
Spring/Summer	-0.09	-0.38,0.21	0.92	-0.1	-0.37,0.17	0.91	0.14	-0.19,0.46	1.14
Variance explained									
Between Subjects		52			35			39	
Between Villages		28			47			74	

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)

GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)

BPE – Benzo[ghi]perylene, BbF – Benzo[b]fluoranthene, DBA – Dibenz[ah]anthracene, BkF – Benzo[k]fluoranthene

Table 12b- Mixed effect models for indoor measurements of particle bound PAHs

	IPY			PYR			BaA		
Reference/Background Value (Intercept)*	2.83			1.8			2.72		
Fuel Type	Estimate	95% CI	GMR	Estimate	95% CI	GMR	Estimate	95% CI	GMR
Smokeless Coal (FY & XW)	Ref		1	Ref		1	Ref		1
Coking Coal from North XW	0.72	0.12,1.31	2.05	1.15	0.24,2.06	3.15	1.24	0.5,1.97	3.45
Coking Coal from South XW	0.71	-0.31,1.73	2.04	1.46	-0.21,3.13	4.31	1.35	0.01,2.69	3.86
Coking Coal from FY	0.41	-0.29,1.11	1.51	0.78	-0.26,1.84	2.19	0.85	0.01,1.7	2.33
1/3 Coking coal FY	0.38	-0.53,1.26	1.46	1.64	0.23,3.04	5.16	1.24	0.11,2.35	3.45
Gas Fat coal FY	0.24	-0.49,0.96	1.28	0.38	-0.72,1.48	1.47	0.45	-0.44,1.34	1.57
Meagre Lean coal FY	0.65	-0.66,1.96	1.91	0.41	-1.52,2.36	1.51	0.72	-0.84,2.29	2.05
Multiple Coal Types	0.42	-0.15,0.99	1.52	1.11	0.29,1.95	3.05	0.95	0.28,1.62	2.57
Multiple Fuel Types	0.57	0.05,1.09	1.77	1.16	0.4,1.92	3.18	0.94	0.34,1.55	2.57
Smoky Coal of uncertain type	0.92	0.02,1.82	2.5	3.36	2.08,4.66	28.93	2.14	1.1,3.19	8.53
Plant Products	-0.14	-1.22,0.94	0.87	0.75	-0.82,2.34	2.11	0.32	-0.94,1.6	1.38
Wood	0.02	-0.87,0.93	1.02	0.95	-0.35,2.29	2.58	0.36	-0.69,1.44	1.43
Stove Design									
Ventilated Stove	Ref		1	Ref		1	Ref		1
Unventilated Stove	0.33	-0.11,0.76	1.39	0.75	0.11,1.4	2.13	0.7	0.18,1.22	2.02
Fire Pit	0.73	0.07,1.38	2.08	1.5	0.53,2.44	4.5	1.04	0.24,1.81	2.84
Portable Stove	-0.09	-0.49,0.3	0.91	0.14	-0.43,0.72	1.15	0.16	-0.31,0.63	1.18
Mixed Ventilation	0.12	-0.19,0.42	1.13	0.26	-0.18,0.7	1.29	0.36	0.01,0.71	1.43
Unknown ventilation	-0.65	-1.35,0.05	0.52	-1.43	-2.44,-0.4	0.24	-1.17	-1.99,-0.35	0.31
Room size (in m3)									
$<40m^3$	Ref		1	Ref		1	Ref		1
$40m^3$ to $49m^3$	-0.43	-0.82,-0.05	0.65	-0.53	-1.09,0.03	0.59	-0.5	-0.96,-0.05	0.6
$50m^3$ to $67m^3$	0.01	-0.41,0.44	1.01	0.34	-0.26,0.95	1.41	0.11	-0.38,0.61	1.12
$>67m^3$	0.06	-0.36,0.47	1.06	0.5	-0.11,1.1	1.65	0.14	-0.36,0.63	1.15
Room Size Unknown	-0.33	-0.73,0.08	0.72	-0.2	-0.79,0.38	0.82	-0.4	-0.88,0.07	0.67
Season									
Autumn	Ref		1	Ref		1	Ref		1
Winter	0.09	-0.22,0.4	1.1	0.22	-0.25,0.7	1.25	0	-0.38,0.37	1
Spring/Summer	0.02	-0.25,0.29	1.02	-0.48	-0.89,-0.08	0.62	-0.27	-0.59,0.05	0.76
Variance explained									
Between Subjects	39			62			48		
Between Villages	40			36			39		

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
BPE – Benzo[ghi]perylene, BbF – Benzo[b]fluoranthene, DBA – Dibenz[ah]anthracene, BkF – Benzo[k]fluoranthene

Table 12c- Mixed effect models for indoor measurements of particle bound PAHs

		BkF	
Reference/Background Value (Intercept)*		1.98	
Fuel Type	Estimate	95% CI	GMR
Smokeless Coal (FY & XW)	Ref		1
Coking Coal from North XW	0.85	0.22,1.48	2.34
Coking Coal from South XW	0.64	-0.46,1.72	1.91
Coking Coal from FY	0.62	-0.11,1.35	1.85
1/3 Coking coal FY	0.96	0.03,1.88	2.62
Gas Fat coal FY	0.37	-0.38,1.12	1.45
Meagre Lean coal FY	0.86	-0.49,2.21	2.37
Multiple Coal Types	0.51	-0.08,1.11	1.67
Multiple Fuel Types	0.74	0.2,1.28	2.1
Smoky Coal of uncertain type	1.42	0.5,2.34	4.13
Plant Products	0.39	-0.72,1.52	1.48
Wood	0.19	-0.73,1.13	1.21
Stove Design			
Ventilated Stove	Ref		1
Unventilated Stove	0.45	0,0.89	1.56
Fire Pit	0.85	0.16,1.51	2.33
Portable Stove	0.02	-0.39,0.43	1.02
Mixed Ventilation	0.31	0,0.62	1.37
Unknown ventilation	-0.93	-1.64,-0.21	0.4
Room size (in m^3)			
<40m^3	Ref		1
40m^3 to 49m^3	-0.4	-0.8,-0.01	0.67
50m^3 to 67m^3	0.05	-0.38,0.48	1.05
>67m^3	-0.02	-0.45,0.4	0.98
Room Size Unknown	-0.48	-0.9,-0.07	0.62
Season			
Autumn	Ref		1
Winter	0.03	-0.29,0.35	1.03
Spring/Summer	0.09	-0.19,0.37	1.09

Variance explained	
Between Subjects	45
Between Villages	39

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
BkF – Benzo[k]fluoranthene

Table S13 - Total PAH values and BaP_{eq} values by fuel type and stove design

		Total PAH			BaP_{eq}		
	N	AM	GM	GSD	AM	GM	GSD
Smoky Coal	**96**	**6600**	**4500**	**2.5**	**243.07**	**134.63**	**2.98**
Ventilated Stove	53	4500	3800	1.9	172.88	121.21	2.37
Unventilated Stove	4	16000	9900	2.9	701.53	455.93	2.78
Portable Stove	12	7500	6100	2	159.22	112.34	2.38
Firepit	4	28000	24000†	2	1065.05	907.3†	1.93
Mixed Ventilation	19	6300	4200	3.2	263.98	148.72	3.3
Unknown	4	1800	1500	2.1	44.91	25.42	3.06
Smokeless Coal	**17**	**4400**	**4100**	**1.5**	**91.33**	**66.01**	**2.38**
Ventilated Stove	0	-	-	-	-	-	-
Unventilated Stove	9	4000	3700	1.6	73.73	57.04	2.25
Portable Stove	7	5300	5000	1.4	123.39	91.36	2.46
Firepit	0	-	-	-	-	-	-
Mixed Ventilation	1	2800	2800	-	25.28	25.28	-
Unknown	0	-	-	-	-	-	-
"Other" Coal	**14**	**12000**	**7500**	**2.9**	**287.98**	**167.19**	**3.4**
Ventilated Stove	6	4400	3300	2.4	110.18	70.15	3.06
Unventilated Stove	0	-	-	-	-	-	-
Portable Stove	7	18000	15000	2.1	429.69	315.1	2.56
Firepit	0	-	-	-	-	-	-
Mixed Ventilation	1	8500	8500	-	362.89	362.89	-
Unknown	0	-	-	-	-	-	-
Wood	**7**	**20000**	**11000**	**3.7**	**222.36**	**182.72**	**2.05**
Ventilated Stove	2	20000	19000	1.2	324.87	321.76	1.22
Unventilated Stove	0	-	-	-	-	-	-
Portable Stove	3	30000	21000	2.9	228.44	193.13	1.98
Firepit	2	3500	2500	3.5	110.72	95.48	2.2
Mixed Ventilation	0	-	-	-	-	-	-
Unknown	0	-	-	-	-	-	-
Plant	**3**	**38000**	**31000***	**2.1**	**331.58**	**327.52**	**1.22**
Ventilated Stove	0	-	-	-	-	-	-
Unventilated Stove	1	72000	72000	-	352.24	352.24	-
Portable Stove	0	-	-	-	-	-	-
Firepit	1	18000	18000	-	262.47	262.47	-
Mixed Ventilation	1	24000	24000	-	380.01	380.01	-
Unknown	0	-	-	-	-	-	-
"Other" Fuel	**56**	**11000**	**6400**	**3**	**239.83**	**115.28**	**3.23**
Ventilated Stove	9	6500	4600	2.4	123.68	94.92	2.49
Unventilated Stove	11	30000	19000	3.4	706.9	378.71	3.96
Portable Stove	5	6900	6100	1.7	151.96	95.69	2.87
Firepit	0	-	-	-	-	-	-
Mixed Ventilation	28	6700	4900	2.6	127.55	85.01	2.62
Unknown	3	6500	3500	4	69.97	61.75	1.92

*- significant difference with smoky coal for same strata via Tukey HSD test

† - significant difference with ventilated stove for same PAH within fuel strata via Tukey HSD test

N – number of samples

Total PAH: Sum concentration of all 14 reported PAH measurements, restricted to samples where measurements for all 14 PAHs were available (n=193, personal only)

BaP toxic equivalent values (BaPeq) are calculated using toxic equivalencies as stated by Nisbet and Lagoy, 1992 (Nisbet, I.C.; Lagoy, P.K. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regulatory Toxicology and Pharmacology, 1992, 16(3), 290-300). Bapeq was calculated as follows:

BaPeq= 5xDBA + 1xBaP + 0.1xBaA + 0.1xBbF + 0.1xIPY + 0.01xBPE + 0.01xCHR + 0.001xANY + 0.001xFLU + 0.001xNAP+0.001xPHE+0.001xPYR

Table S14 - Total PAH values and BaPeq values by smoky coal source

			Total PAH			BaP_{eq}		
		N	AM	GM	GSD	AM	GM	GSD
Xuanwei	**Coking Coal**	**61**	**5700**	**4200**	**2.4**	**246.3**	**156.7**	**2.8**
	Azhi	19	5200	4300	2	245.1	175.5	2.5
	Baoshan	7	9300	6200	2.7	375	194.8	4.1
	Laibin	19	4200	3300	2.6	205	145.9	2.5
	Tangtang	16	6500	4600	2.4	240.4	135.4	3.1
Fuyuan	**Overall**	**30**	**8200**	**4600**	**2.7**	**232.9**	**90.0***	**3.4**
	Coking	5	25000	12000†	4.8	896.4	411.2†	5.1
	Daping	2	2300	2300	1.2	96.5	82.3	2.3
	Haidan	3	40000	35000	1.9	1429.6	1201.6	2.2
	1/3 Coking (Dahe)	2	3500	2800	2.6	25.9	23.2	1.9
	Gas Fat (Haidan)	21	4600	3700	2.1	96.2	68.8	2.2
	Meager Lean (Gumu)	2	8900	6900	2.9	216.2	126.3	5

*- significant difference between smoky coal subtypes from Fuyuan
† - significant variation within designated smoky coal subtype
N – number of samples
Total PAH: Sum concentration of all 14 reported PAH measurements, restricted to samples where measurements for all 14 PAHs were available (n=193, personal only)
BaP toxic equivalent values (BaPeq) are calculated using toxic equivalencies as stated by Nisbet and Lagoy, 1992 (Nisbet, I.C.; Lagoy, P.K. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regulatory Toxicology and Pharmacology, 1992, 16(3), 290-300). Bapeq was calculated as follows:
BaPeq= 5xDBA + 1xBaP + 0.1xBaA + 0.1xBbF + 0.1xIPY + 0.01xBPE + 0.01xCHR + 0.001xANY + 0.001xFLU + 0.001xNAP+0.001xPHE+0.001xPYR

Table S15 - Mixed effect models for total PAH values and BAP_{eq} values

		Total PAH			BaP_{eq}	
Reference/Background Value (Intercept)*		7.82			3.83	
Fuel Type	Estimate	95%CI	GMR	Estimate	95%CI	GMR
Smokeless Coal (FY & XW)	Ref		1	Ref		1
Coking Coal from North XW	0.17	-0.44,0.78	1.19	1.16	0.46,1.86	3.2
Coking Coal from South XW	-	-	-	-	-	-
Coking Coal from FY	-0.08	-1.04,0.89	0.92	1.01	-0.18,2.17	2.75
1/3 Coking coal FY	0.1	-1.13,1.34	1.11	-0.26	-1.57,1.05	0.77
Gas Fat coal FY	-0.03	-0.79,0.7	0.97	0.2	-0.68,1.03	1.22
Meagre Lean coal FY	0.72	-0.51,1.95	2.06	1.24	-0.16,2.61	3.44
Multiple Coal Types	0.53	-0.12,1.19	1.7	1.04	0.31,1.76	2.82
Multiple Fuel Types	0.58	-0.01,1.17	1.79	0.76	0.1,1.41	2.14
Smoky Coal of uncertain type	0.6	-0.21,1.4	1.81	1.13	0.17,2.09	3.08
Plant Products	0.4	-0.92,1.74	1.5	-0.04	-1.54,1.47	0.96
Wood	-0.39	-1.53,0.75	0.67	-0.13	-1.45,1.21	0.88
Stove Design						
Ventilated Stove	Ref		1	Ref		1
Unventilated Stove	0.72	0.19,1.25	2.05	0.77	0.16,1.37	2.16
Fire Pit	1.48	0.64,2.3	4.38	1.54	0.52,2.55	4.69
Portable Stove	0.57	0.14,1	1.77	0.32	-0.2,0.84	1.38
Mixed Ventilation	-0.07	-0.41,0.28	0.93	-0.16	-0.56,0.23	0.85
Unknown ventilation	-0.64	-1.3,0.02	0.53	-0.85	-1.63,-0.07	0.43
Room size (in m^3)						
$<40m^3$	Ref		1	Ref		1
$40m^3$ to $49m^3$	-0.22	-0.67,0.23	0.8	-0.56	-1.13,0.01	0.57
$50m^3$ to $67m^3$	0.55	0.07,1.01	1.74	0.3	-0.27,0.87	1.35
$>67m^3$	0.11	-0.35,0.56	1.12	-0.27	-0.84,0.31	0.77
Room Size Unknown	0.05	-0.42,0.5	1.05	-0.06	-0.63,0.5	0.94
Season						
Autumn	Ref		1	Ref		1
Winter	0.51	0.15,0.86	1.66	0.38	-0.02,0.75	1.46
Spring/Summer	0.17	-0.12,0.45	1.18	0.25	-0.05,0.56	1.29
Variance explained						
Between Subjects		100			37	
Between Villages		73			90	

*Reference value represents log transformed PAH value (in ng/m^3) for the reference model entry (smokeless coals from Fuyuan, burnt in a ventilated stove in a "small" room)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
BPE – Benzo[ghi]perylene, BbF – Benzo[b]fluoranthene, DBA – Dibenz[ah]anthracene, BkF – Benzo[k]fluoranthene
Total PAH: Sum concentration of all 14 reported PAH measurements, restricted to samples where measurements for all 14 PAHs were available (n=193, personal only)
BaP toxic equivalent values (BaPeq) are calculated using toxic equivalencies as stated by Nisbet and Lagoy, 1992 (Nisbet, I.C.; Lagoy, P.K. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regulatory Toxicology and Pharmacology, 1992, 16(3), 290-300). Bapeq was calculated as follows:
BaPeq= 5xDBA + 1xBaP + 0.1xBaA + 0.1xBbF + 0.1xIPY + 0.01xBPE + 0.01xCHR + 0.001xANY + 0.001xFLU + 0.001xNAP+0.001xPHE+0.001xPYR

Chapter 5

Quartz in coal, ash, and air in a high lung cancer incidence area in China.

George Downward
Wei Hu
Nat Rothman
Boris Reiss
Guoping Wu
Fusheng Wei
Jun Xu
Wei Jie Seow
Robert S. Chapman
Lan Qing
Roel Vermeulen

(Submitted paper)

Abstract

Background:

Exposure to quartz from the domestic combustion of locally sourced “smoky” (bituminous) coal has been suggested as a potential cause of the lung cancer epidemic in Xuanwei, and its neighbouring county of Fuyuan, China. However, relatively little is known regarding the extent of quartz exposure in the area and how it compares to alternative fuels including locally sourced “smokeless” (anthracite) coal.

Methods:

Samples of fuel, ash and indoor air were collected from 163 households from throughout Xuanwei and Fuyuan. Quartz content in coal samples was established via scanning electron microscopy and X-ray fluorescence while quartz in air and ash samples was established by Fourier transformed infrared spectroscopy.

Results:

Analysis found that uncombusted smoky coal contained approximately 3 times as much quartz than smokeless coal ($p<0.05$). The majority of quartz air measurements (89%) were below the limit of detection ($< 0.2\ \mu g/m^3$) with no significant difference between smoky and smokeless coal. Respirable quartz in ash was present in slightly higher amounts in smoky than smokeless coal ash (0.11 and 0.08% respectively).

Conclusion:

These findings suggest that, despite being present in higher quantities in coal, actual exposure to quartz from smoky coal use is relatively low. This suggests that exposure to quartz may be insufficient to explain the lung cancer epidemic in Xuanwei and Fuyuan.

Introduction

Coal, wood and other solid fuels are used by approximately 3 billion people worldwide for domestic tasks such as heating and cooking.[1] Household air pollution produced by solid fuel burning has been associated with multiple health complications, including both malignant and non-malignant disease.[2,3] These health risks are well illustrated in Xuanwei, and its neighbouring county of Fuyuan, located in Yunnan province, China, where the domestic combustion of "smoky" coal (a bituminous coal) has been associated with up to a hundred fold increase in risk of lung cancer, irrespective of smoking status.[4-6] Smoky coal is the primary fuel source for residents of Xuanwei and Fuyuan and is available from many active coal mines throughout the region. Approximately 25% of residents use alternative solid fuels[6] such as “smokeless” coal (an anthracite coal), wood and various plant materials (including corn cobs and tobacco stems). The terms "smoky" and “smokeless” coal are made in reference to the amount of visible smoke released upon combustion.

While the carcinogenic constituents of smoky coal are currently unknown, the lung cancer rates among smoky coal users appear to be modulated by two main factors. The first factor relates to stove design. Traditionally, people burnt fuels in unvented fire pits, which have over recent years been replaced with stoves that provide improved ventilation and burning efficiencies. This improvement in stove design resulted in a reduction in malignant and non-malignant lung disease,[7-9] suggesting that exposure to (carcinogenic) emissions from smoky coal reduces following stove improvements. The second feature is the observation of variation in lung cancer rates between different geographic locations,[10,11] suggesting that there are either constitutional differences in coals sourced from different locations or that there are regional differences in coal preparation (it is a common local practise to mix coal with soil/clay in an effort to extend the burning time of the coal). The assertion of constitutional differences in coal makeup is supported in part by the State Standard of China Coal Classification[12] which has divided smoky coal in the region into the following categories: coking coal, 1/3 coking coal, gas fat coal and meagre lean coal. This sub-categorization is based upon several categories, including the proportion of free volatile matter, layer of plastic dilatation and Audi-Audibert dilatation.[12,13]

At present there are two primary hypotheses regarding the underlying carcinogenic properties of smoky coal. The first is referred to as the “polycyclic aromatic hydrocarbon (PAH) hypothesis” and reflects the multiple lines of research which have indicated that smoky coal emits high levels of PAHs when burnt.[4,8,14] Additionally, genetic studies have shown that mutations in genes responsible for metabolizing PAHs are associated with higher lung cancer rates.[15] The second hypothesis is referred to as the “quartz hypothesis” and refers to analyses of uncombusted coal samples, collected from coal mines and homes from throughout Xuanwei and Fuyuan which have found that smoky coal, when compared to smokeless coal, contains relatively high levels of quartz (i.e. free crystalline silica).[13,16-18] Controlled burning experiments[19] have indicated that smoky coal emits similar levels of quartz to smokeless coal, but that there was a positive correlation between quartz emitted by smoky coal and the lung cancer rates in the geographic area that the smoky coal was sourced from. This finding is consistent with the variation in lung cancer rates between different geographic locations but fails to address the stark difference in cancer rates between smoky and smokeless coal. However, research on airborne quartz measurements so far has been limited to estimating quartz levels on the basis of an assumed ratio between silicon and aluminium air concentrations. Furthermore, this research has been limited by small sample sizes (n=15)[19] and it is not known how quartz measured in coal correlates to

quartz emitted during burning. Additionally, it is inconsistent for there to be elevated quartz in smoky coal, yet similar levels in the emissions of both smoky and smokeless coal. This raises the possibility of the presence of elevated quartz in the ash of smoky coal, which has not previously been explored and, as this is regularly handled by residents, may provide another exposure route.

This paper presents a comprehensive analysis of quartz exposure resulting from solid fuel use in Xuanwei and Fuyuan. It will present quartz levels in coal samples, household air pollution samples and ash samples in order to provide a complete overview of quartz exposure. Special attention will be placed upon variations between smoky coal and other fuel types in addition to variation within the smoky coal type itself.

Methods

Study design

This paper is part of a larger case-control and cross-sectional molecular epidemiology study aimed at comprehensively cataloguing the constituents of domestically used solid fuel and its emissions in Xuanwei and Fuyuan and ultimately associating those constituents with lung cancer risk. 15 villages were selected from each county to reflect the general population and the variety of fuel types available. Approximately five households with a non-smoking female head between the ages of 20 and 80 were selected from each village. Subject and household selection was aimed at representing the population present in the case-control study with regard to age, gender (all case control participants are non-smoking females), stove and fuel use. This meant that households which were at least 10 years old and had not had any stove alterations undertaken in the prior 5 years were preferentially selected.

Each home was measured and sketched. Stoves and other features (windows, stairs, doors etc.) were recorded. Indoor measurements of airborne pollutants were collected over two consecutive 24 hour periods. The adult female head of each was enrolled and had their daily activities documented during each measurement period. All enrolees provided written informed consent prior to enrolment.

Data was collected over two time periods, the first was from August 2008 to February 2009 and the second was from March to June 2009. In the first collection period, all 30 villages were visited and 148 participants were recruited. In the second data collection period, 16 of the initial 30 villages were revisited with 53 of the initial subjects re-sampled and 15 new subjects recruited (for a total of 163 study enrolees).

Stove and fuel information

When enrolees used a stove during the measurement period, the stove type, fuel type, purpose of use and length of use was recorded. When the use of smoky or smokeless coal was reported, geochemical analysis on coal samples, collected from each home, was performed to confirm the reported coal type.[13] Enrolees would also report which coal mine they purchased their coal from. Using the Chinese State Standard of Classification[12] the smoky coal subtype was then established by matching the mine name to its documented subtype produced.

Descriptive categories were established for fuel types and stove design. For fuel usage, the categories were smoky coal, smokeless coal, “other” coal (which refers to combinations of coal types and/or usage of processed coal products such as “beehive” briquettes), wood, plant products (includes bamboo shoots, tobacco stems and corn cobs in addition to wood

being burnt in combination with other plant products) and "other" fuel (which refers to combinations of coal and plants/wood). In total, 77 enrolees were categorised as using smoky coal, 9 smokeless, 8 wood, 3 plant products, 18 other coal and 48 other fuel.

Descriptive categories for stove design were developed around whether or not stove ventilation was present. The categories designated were: ventilated stoves, unventilated stoves, firepits, portable stoves (a type of stove that is designed to be lit outdoors and then carried indoors for usage), mixed ventilation (usage of multiple types of stoves with differing ventilation) and "unknown" (where the stove type was not reported or recorded). Overall, 60 enrolees used ventilated stoves, 11 unventilated, 19 portable stoves, 10 firepits. 59 enrolees had mixed ventilation, and the stove type was unknown for 4 enrolees.

Coal Sample collection and analysis

The quartz analysis methods and results reported in the current study are based upon previously reported coal analysis.[13] Briefly, coal samples were collected from the homes of study participants and defined as described above. Quartz composition was established in two ways. Firstly, quartz levels were estimated for 145 coal specimens based upon an assumed ratio of silicon to aluminium which had previously been used to estimate quartz levels in coal sourced from Xuanwei.[19] Silicon and aluminium levels were established via X-ray fluorescence (XRF) on glass beads prepared from dry coal ash. Coal ash was obtained via thermogravimetric analysis, which used a controlled temperature program from 105 to 1000 degrees Celsius. Results of XRF were adjusted for moisture loss during the temperature program to give levels of SiO_2 and Al_2O_3 as a percentage of the coal analysed. Quartz content (as a percentage of coal) was subsequently estimated by use of the following formula (previously used to estimate quartz content in Xuanwei coal specimens):

$$\text{Estimated Quartz} = (SiO_2)_{total} - 1.5 \times Al_2O_3$$

This formula is based upon the assumption that all silicon present exists either as quartz or as aluminosilicates and that the expected ratio between quartz and aluminosilicates is 1:1.5, with the excess representing quartz. Estimated quartz levels of 0 or below (n=5) were replaced with the lowest positive estimated value (0.13%) divided by the square root of two.

The second method for establishing quartz content involved scanning electron microscopy (SEM) of 25 coal specimens. This provided measurements for both total quartz and quartz of grain size less than 9.6 micrometers, which represents "respirable" quartz (i.e. of a size small enough to reach the end alveoli).[20] Measurements were given as a percentage of the coal specimen.

Air sample collection and analysis

Indoor measurements of quartz were collected on a 37mm Teflon filter using a cyclone with an aerodynamic cut-off of 2.5 µm ($PM_{2.5}$), powered by a BGI AFC400S pump (the median flow rate was 3.3L/min with an inter-quartile range of 3.2 to 3.4L/min). Pumps were calibrated prior to each use and flow was measured pre and post measurement. Cyclones were placed approximately 0.25m from the wall and between 1 and 2 metres from the main stove (as allowed by the physical size of the room). For analysis, the filters were ashed at 600 degrees Celsius before being pressed into a 13mm potassium bromide (KBr) pellet.[21] Pellets were then analysed by Fourier transform infrared spectroscopy (FT-IR), giving quartz levels in µg. The limit of detection (LOD) for this methodology was 1µg (approximately 0.2 $\mu g/m^3$ based on a 24-hour measurement).

Ash collection and analysis

A total of 147 ash samples were collected from the homes of study participants. The contributing fuel types were defined as outlined above. Ash and fuel samples were collected on the same day. Approximately 5g of each ash sample was deagglomerated in 50mL of a standard solution containing water and sodium hexametaphosphate before being transferred to a 250mL measuring cylinder (the remaining 200mL volume was filled with standard solution). This mixture was homogenised and, after a pre-determined standing period (to allow for sedimentation of the non-respirable fraction), the fluid was extracted and evaporated – with the remaining material being weighed. A known portion of the remaining material was, after weighing, pressed into a KBr pellet and analysed by FT-IR for quartz content as a percentage of the ash.[22]

Statistical analysis

Normal probability plots indicated that the analytical values tended towards log-normal distribution. Thus descriptive statistics included arithmetic means (AM), geometric means (GM) and standard deviation (GSD). Statistical testing was carried out on log transformed values. T-tests, ANOVA and Tukey HSD testing was used to assess for differences between fuel types, smoky coal subtypes (including variation between coal mines within the designated smoky coal subtypes), and stove designs. When assessing smoky coal subtypes, only samples gathered from homes which exclusively used coal consistent with that produced from the reported region were retained for analysis (this represents 95% of smoky coal samples).

All statistical testing was carried out in R version 3.0.2. [23] A p value of less than 0.05 was considered to indicate statistical significance.

Results

Overview of fuel types and sources

A total of 145 coal specimens (of which 137 came from separate homes, the additional 8 samples were from homes which used multiple coal types) were collected. Of the 145, 116 were smoky coal, of which 110 could be linked to a coal mine. 159 indoor air measurements (from 157 separate homes) were taken for direct quartz analysis, 80 of which represented the use of smoky coal (79 of which were linked to a coal mine). For ash analysis, 146 ash samples were collected (all from separate homes), of which 75 represented smoky coal (74 of which could be linked to a coal mine). In Xuanwei, all identified coal mines were of the coking coal type (the mine names were: Azhi, Baoshan, Laibin, Tangtang and Yangchang [Figure 1]). In Fuyuan there were a variety of smoky coal subtypes represented. Coking coal was mined in the Daping, Enhong, Haidan, and Zude mines. The 1/3 coking coal subtype was mined in the Bagong and Dahe mines. Gas fat coal was mined in the Housuo and Qingyun mines. Meagre lean coal was mined in the Gumu mine. Smokeless coal was supplied by 2 coal mines. In Fuyuan, smokeless coal was mined by the Laochang mine, while in Xuanwei, smokeless coal was historically mined in the RSXZ region (although many residents currently use wood as their primary solid fuel), which is the combination of the Reshui and Xize areas.

Quartz in coal

As previously reported,[13] estimated quartz content, based on aluminium and silica content, revealed that smoky coal had a significantly higher proportion of estimated quartz than smokeless coal (GM 9.4% versus 3.2% (Table 1)). On assessment for variation within and

between smoky coal subtypes, no statistically significant variation within the coking coal subtype from Xuanwei was observed. Significant variation was observed within the Fuyuan coking coals, with the GM ranging from 0.8% for coals from the Zude mine to 9% for coals from the Enhong mine. However, if the low value from Zude was excluded from analysis, no statistically significant variation among Fuyuan coking coal was observed. A significant difference in estimated quartz between the two smokeless coal producing mines was also observed with coal from LaoChang containing 5.9% estimated quartz and coal from the RSXZ region containing 0.1% estimated quartz.

Quartz content was further established on a subset of coal samples via the use of SEM (n=25). Smoky coal was found to have significantly higher amounts of total quartz (GM 5.0%) than smokeless coal (1.9%). This extended to quartz within the respirable fraction (2.3% versus 0.6%). Total and respirable quartz levels were found to be highly correlated with each other with a Spearman correlation coefficient of 0.87 ($p<0.01$). No variation within designated smoky coal subtypes was observed.

Estimated and measured quartz levels correlated moderately well for the 25 measurements where both estimated and measured values were available. The Spearman correlation coefficient between the two measurement methods was 0.58 ($p<0.01$).

Quartz in air

159 indoor measurements were analysed for quartz content. The vast majority of measurements (n=141) did not contain detectable levels of quartz (LOD: approximately 0.2 $\mu g/m^3$ [Table 2]). Only 18 measurements (11%) contained detectable quartz, (all of which represented individual households). Of the 80 smoky coal samples, 11 (14%) had detectable quartz. 1 of the 9 wood burning measurements (11%) had detectable quartz. Of the 5 plant samples, 1 (20%) had detectable quartz. There were 30 samples from homes burning "other" fuel, of which 3 (10%) had detectable quartz. 2 of the 17 (12%) measurements from subjects burning multiple coal types had detectable quartz. None of the 17 smokeless coal measurements had detectable quartz. Fisher's exact testing indicated that the observed differences in detection rates between the fuel types was not statistically significant. Among the detected quartz measurements, the highest concentration of quartz was from a home burning multiple different fuels (in this case, a combination of wood and smokeless coal – concentration: $0.9\mu g/m^3$). The geometric mean of quartz concentrations among smoky coal homes ($0.4\mu g/m^3$) was similar to that of other fuel types (Table 2). ANOVA testing indicated that there was no significant variation in quartz concentrations between fuel sources.

Quartz in ash

147 ash samples were analysed by FT-IR for respirable quartz content (Table 3). The geometric mean for respirable quartz content in ash from smoky coal (0.11%) was slightly higher than that for ash from smokeless coal (0.08%), however this difference was not statistically significant. Levels of respirable quartz in smoky coal ash were significantly higher than that of wood (0.01%) and plant (0.01%) ash.

No significant effect of stove design or smoky coal source was observed (tables S1 and S2 in the supplementary materials).

Relationships among quartz samples from coal, ash, and air

By matching ash, coal and air samples from homes that had the samples taken on the same day we assessed the Spearman rank correlation of quartz measurements between these

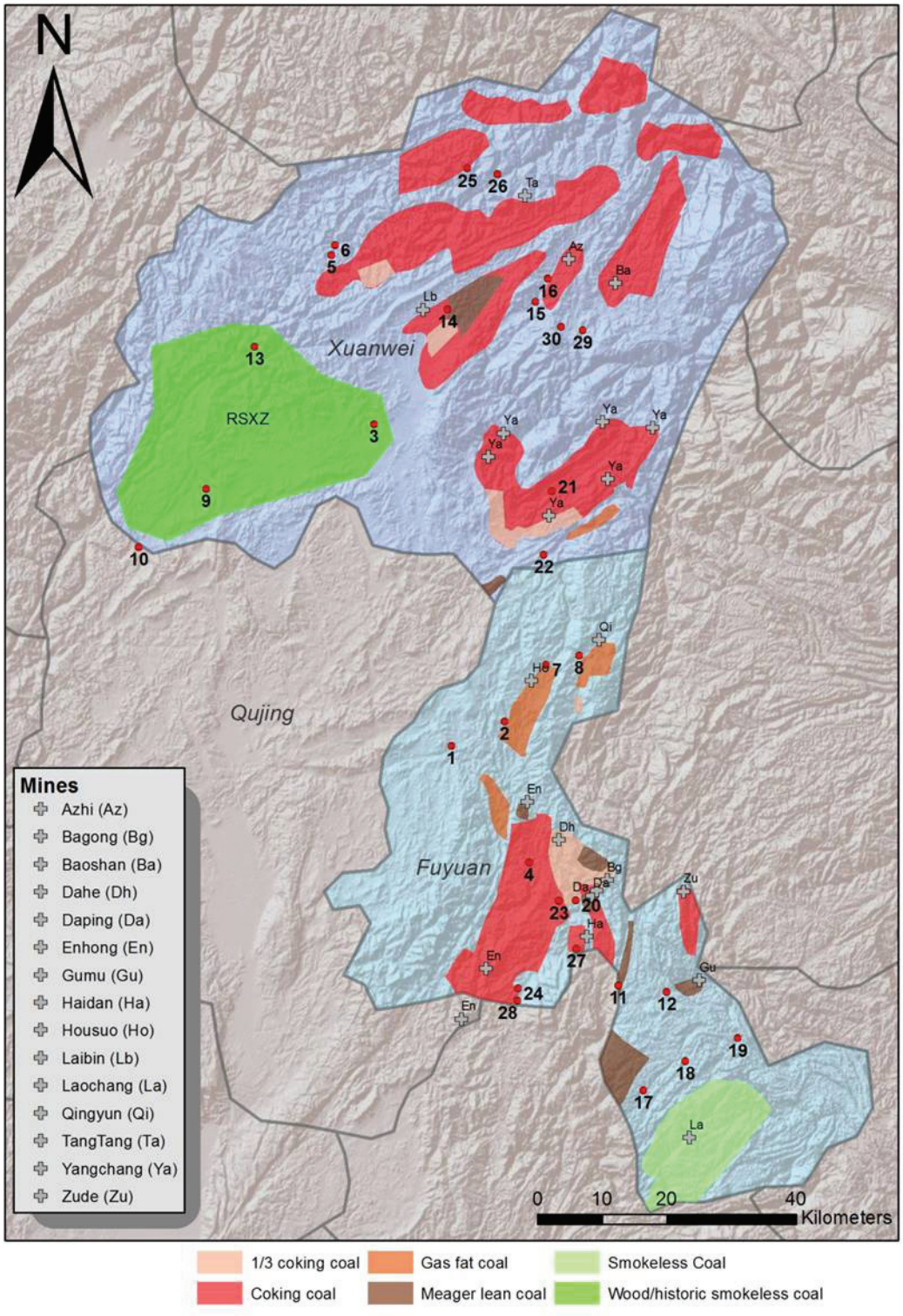

Figure 1:Map of Xuanwei and Fuyuan counties showing approximate locations of study villages, reported coal mines and coal sub-types

Villages enrolled in the study are marked numerically 1 to 30

Mine locations indicate functioning mine entrances, therefore, some mines may be indicated more than once. Only mines reported by study participants are indicated.

Table 1 - Estimated and measured quartz in coal samples by coal source

					Estimated Quartz (% of coal)			Measured Quartz (% of coal)						
								Total Quartz				Respirable Quartz		
Major Coal Type	County	Coal Sub-type	Coal Mine	N	AM	GM	GSD	N	AM	GM	GSD	AM	GM	GSD
Smoky				116	12.3	9.4*	2.5	19	7.7	5.0*	2.6	3.9	2.3*	2.7
	Xuanwei			65	14.7	13.0	1.7	11	8.3	6.6	2.0	4.2	3.2	2.0
		Coking Coal		63	14.7	13.0	1.7	10	9.0	7.4	1.9	4.4	3.5	2.0
			Azhi	15	12.4	11.2	1.7	2	4.1	4.1	1.0	2.3	2.3	1.3
			Baoshan	5	11.3	10.2	1.7	1	6.4	6.4	-	3.8	3.8	-
			Laibin	14	15.2	13.5	1.8	2	10.5	10.3	1.3	5.7	5.6	1.3
			Tangtang	22	18.3	16.4	1.7	4	10.5	7.8	2.5	5.8	4.2	2.4
			Yangchang	7	10.0	9.5	1.4	1	12.0	12.0	-	1.3	1.3	-
	Fuyuan			51	9.1	6.2	3.0	8	6.8	3.5	3.2	3.5	1.5	3.3
		Coking Coal		15	8.2	6.9‡	2.1	3	5.3	5.1	1.4	1.8	1.6	1.7
			Daping	4	7.5	6.6	1.9	1	3.8	3.8	-	0.9	0.9	-
			Enhong	4	9.4	9.0	1.4	1	7.4	7.4	-	2.5	2.5	-
			Haidan	6	9.1	8.6	1.5	1	4.6	4.6	-	1.9	1.9	-
			Zude	1	0.8	0.8	-	0	-	-	-	-	-	-
		1/3 Coking		8	5.5	3.5	3.6	2	1.9	1.7	1.9	1.0	0.9	1.7
			Bagong	5	3.8	2.1	4.2	1	1.1	1.1	-	0.6	0.6	-
			Dahe	3	8.3	8.1	1.3	1	2.7	2.7	-	1.3	1.3	-
		Gas Fat		23	12.0	7.9	3.4	2	16.5	5.2	13.3	9.8	2.7	15.9
			Housuo	20	11.4	7.6	3.6	2	16.5	5.2	13.3	9.8	2.7	15.9
			Qingyun	3	16.0	10.9	2.8	0	-	-	-	-	-	-
		Meagre Lean	Gumu	1	4.2	4.2	-	1	2.0	2.0	-	1.0	1.0	-
Smokeless				29	7.0	3.2‡	5.6	6	2.3	1.9	2.0	1.0	0.6	2.8
	Fuyuan		Laochang	19	7.1	5.9	1.9	4	2.6	2.1	2.1	1.4	1.0	2.6
	Xuanwei		RSXZ	5	0.1	0.1	1.2	2	1.8	1.6	2.0	0.3	0.3	1.8

*: significant difference ($p<0.05$) when compared to smokeless coal via Tukey HSD test
‡: significant variation ($p<0.05$) within coal (sub)type via ANOVA test
Respirable Quartz: Quartz of grain size less than 9.6µm
Spearman correlation between estimated and total quartz: 0.58
Spearman correlation between total and respirable quartz: 0.85
Table adapted from Downward et al, 2014 [13]

modalities (Table 4). Measurements of total and respirable quartz in coal correlated moderately to respirable quartz measured in ash (coefficients 0.30 and 0.38 respectively, $p>0.05$, n=23) and with quartz measurements in air (coefficient 0.31 for both total and respirable quartz, $p>0.05$, n=12). Airborne $PM_{2.5}$ quartz samples correlated poorly with measurements of respirable quartz in ash (coefficient: -0.02, $p>0.05$, n=55).

Discussion

Xuanwei and its neighbouring county of Fuyuan, in Yunnan province, China are subject to some of the highest lung cancer rates in the country. This has been previously associated with the domestic combustion of locally sourced smoky coal. [4-6] Significant geographic variation in lung cancer rates has been observed[10,11] suggesting constitutional variation in coal composition between geographical locations while reductions in lung cancer rates following the installation of chimneys, [7-9] suggests that exposure to carcinogenic compounds is reduced following improved home ventilation.

Previous research has indicated that smoky coal contains high levels of quartz, leading some to hypothesise that exposure to quartz may be the primary driving factor for the lung cancer aetiology in the region.[16,19,24,25] Much of this previous research has been based purely upon measurements of coal samples, and estimated values from controlled burning experiments which may not accurately reflect actual personal exposure.

This paper has investigated the role of quartz and solid fuel use from many perspectives, including direct measurements of quartz and estimations. Measurements of coal samples revealed that smoky coal contained approximately 2.5 times as much of quartz as smokeless coal, a finding consistent with previous research.[16,19,26] However, it appears that this elevated quartz fails to translate to household air pollution. Direct measurements of quartz in the air indicated that very little quartz was present (only 11% of samples showed detectable quartz levels). Smokeless coal users had zero detectable quartz filters, however, with only 17 samples from smokeless coal homes, it is difficult to reach a definitive conclusion. A potential criticism of this finding may be that our limit of detection was insufficient to accurately identify very low concentrations of quartz. The limit of detection was 1μg per filter, which over a 24 hour measurement period equates to approximately 0.2μg/m^3. To put this in context, the occupational exposure limits for quartz within Europe[27] ranges from 25μg/m^3 to 300μg/m^3, which is 2 or three orders of a magnitude higher than the detection limit in this study. In a pooled exposure analysis of multiple cohorts of quartz exposed workers, Steenland et.al. concluded that the excess lung cancer risk for a worker exposed to 100μg/m^3 (again, a level which would have been easily detectable by our methodology) of quartz for 45 years would have a risk of lung cancer death approximately 1.5 times that of if they had not been exposed[28]. Given that these reports have measured quartz in concentrations which would have been detectable by our methodology and provide risk estimates far beneath that are associated with the risk of lung cancer and smoky coal use in Xuanwei and Fuyuan (up to 100 times, dependent upon fuel source[10]), it seems unlikely that lower levels of quartz (<0.2 ug/m^3), not detected by our methodology, would be of relevance to the lung cancer risk in the region. Furthermore, for the small number of measurements where quartz was detectable, all measurements were far beneath those detailed above (maximum measured value 0.85μg/m^3). However, we also note that occupational exposure limits and occupational exposure surveys may not be fully applicable to the community situation in Xuanwei and Fuyuan, as exposure there is lifelong and continues throughout large parts of the day, while occupational exposure only occurs

Table 2–Detects versus non-detects of airborne quartz and concentrations of detected quartz (in $\mu g/m^3$) by fuel type

	Detected Quartz			Quartz concentrations in measurements > LOD (11 % of all measurements)			
	Detects (%)	Non-detects (%)	Total n	N	AM	GM	GSD
Smoky Coal	11(14)	69(86)	80	11	0.4	0.4	1.3
Smokeless Coal	0(0)	17(100)	17	0	-	-	-
Other Coal†	2(12)	15(88)	17	2	0.4	0.4	1.2
Wood	1(11)	8(89)	9	1	0.3	0.3	-
Plant‡	1(20)	4(80)	5	1	0.6	0.6	-
Other Fuel$	3(10)	27(90)	30	3	0.5	0.5	1.8

Limit of detection – approximately $0.2 \mu g/m^3$
†: Other coal refers to either using both smoky and smokeless coal simultaneously or the use of pre-prepared briquettes
‡: Refers to the use of corn cobs and/or tobacco stems (sometimes in combination with wood)
$: Refers to the use of both coal and plant materials

Table 3 - Respirable quartz as percentage of ash content

	N	AM	GM	GSD
Smoky Coal	75	0.29	0.11	5.0
Smokeless Coal	13	0.14	0.08	4.0
Other Coal†	12	0.30	0.14	3.6
Wood	7	0.01	0.01*	1.6
Plant‡	4	0.01	0.01*	1.8
Other Fuel$	35	0.21	0.06	7.2

*: Significant difference ($p<0.05$) when compared to smoky coal (via Tukey HSD)
†: Other coal refers to either using both smoky and smokeless coal simultaneously or the use of pre-prepared briquettes
‡: Refers to the use of corn cobs and/or tobacco stems (sometimes in combination with wood)
$: Refers to the use of both coal and plant materials

Table 4 – Spearman correlation coefficients between quartz in coal, air, and ash

	Respirable Quartz in Ash	Quartz in air
Quartz in Coal		
Total	0.30	0.31
Respirable	0.38	0.31
N†	23	12
Quartz in Air	-0.02	-
N	55	-

†:Number of samples taken on same day contributing to correlation calculation

during working hours and during adult life. We also note that differences in quartz concentration between smoky and smokeless coal below that of our detection limit, cannot be assessed or commented upon and that we have not investigated the underlying crystalline structure of any quartz present in the emission products of smoky and smokeless coal. A potential criticism of our measurement methodology may be that our use of indoor measurements limits our ability to relate to personal exposure. The relationship between indoor and personal measurements has previously been explored in this population with regards to both $PM_{2.5}$ exposure.[29] This study found that indoor measurements had a high correlation and degree of agreement with personal measurements. Therefore, we believe that our results are reliable approximations of personal exposure.

Previous research on airborne quartz measurements has used estimated measurements of quartz, based upon assumed ratios of aluminium and silicon[19]. We attempted to replicate this estimation using airborne measurements of aluminium and silicon taken in tandem with the reported results and analysed via XRF (data not shown). As with previously reported measurements, we observed similar estimated quartz levels between smoky and smokeless coal, with smoky coal having the highest overall estimated levels (3.49μg/m^3 vs.1.99μg/m^3, difference non-significant). However, we observed a poor correlation (r=-0.04) between measured quartz and estimated quartz levels taken from measurements on the same day (n=147), which became strongly negative (-0.66) if we restricted to only measurements where detectable quartz was present (n=15). This would suggest that, at least in the context of Xuanwei and Fuyuan, estimated airborne quartz values may not accurately reflect true values and should be interpreted with caution. On the basis of these findings, previous assertions of a high correlation between estimated quartz values in smoky coal and lung cancer rates in Xuanwei may not accurately reflect the true exposure relationship in the area.

Measurements of ash samples provide, for the first time, the opportunity to explore an alternative path for quartz during the coal combustion process. The current study has observed that ash from smoky coal contains more respirable quartz (GM 0.11%) than smokeless coal (0.08%, $p>0.05$) and that there is a moderate correlation between respirable quartz in coal and ash (Spearman coefficient: 0.38, $p>0.05$). While these findings do not reach statistical significance, they suggest that the increased quartz observed in smoky coal goes on to form part of the ash during the combustion process. It is conceivable that ash handling provides an additional route of quartz exposure, however, as already reported, the very low levels of quartz detected in indoor air, coupled with the poor correlation between respirable quartz in ash and airborne quartz (-0.02) makes this unlikely. Further support for the assertion that the quartz in coal largely goes into ash comes from a limited FT-IR analysis of a subset of ash samples (17 smoky coal ash, 2 smokeless coal ash, and 12 ash samples resulting from the use of multiple fuels) which evaluated total quartz content. This analysis found that smoky coal ash had approximately 9 times as much total quartz as smokeless coal ash (GM: 28.3% vs 3.3%, $p<0.05$ via paired t-test).

The overall findings presented in this study indicate that the elevated quartz identified in smoky coal fails to become airborne during the combustion process. There is a possibility that it instead goes on to form part of the ash but there remains uncertainty regarding the size distribution of any quartz particles present. The available findings suggest that the quartz in ash is largely in the non-respirable fraction but due to limitations of the available data, we are unable to make a definitive conclusion regarding this possibility. However, as these findings do not show a viable route of exposure for quartz, it appears unlikely that

quartz exposure can be an important contributor to the lung cancer epidemic in Xuanwei and Fuyuan.

Acknowledgements

This project was supported by the National Institutes of Health intramural research program (HHSN261201400122P). The content of this publication does not necessarily reflect the views or policies of the Department of Health and Human Services, nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government. The authors would like to acknowledge Johan Beekhuizen and Meng Wang from the Institute for Risk Assessment Sciences, Utrecht University for their support in the production of figure 1; David Large from the Department of Chemical and Environmental Engineering, Nottingham University and Harry Veld from the Department of Applied Microbiology and Geochemistry, Deltares, The Netherlands for their work in analysing coal samples; and RPS Analyse bv, The Netherlands for their work in analysing ash and air samples.

Conflict of interest statement

The authors declare that there is no competing financial interest in the planning, analysis or publication of this research.

References

1. World Health Organization Fuel for Life: Household Energy And Health; World Health Organization: Geneva, 2006.
2. Lim, W. Y.; Seow, A. Biomass fuels and lung cancer. Respirology 2012, 17, 20-31.
3. Torres-Duque, C.; Maldonado, D.; Perez-Padilla, R.; Ezzati, M.; Viegi, G. Biomass Fuels and Respiratory Diseases: A Review of the Evidence. Proceedings of the American Thoracic Society 2008, 5, 577 -590.
4. Mumford, J. L.; He, X. Z.; Chapman, R. S.; Cao, S. R.; Harris, D. B.; Li, X. M.; Xian, Y. L.; Jiang, W. Z.; Xu, C. W.; Chuang, J. C. Lung cancer and indoor air pollution in Xuan Wei, China. Science 1987, 235, 217-220.
5. He, X. Z.; Chen, W.; Liu, Z. Y.; Chapman, 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 Perspect. 1991, 94, 9-13.
6. Barone-Adesi, F.; Chapman, R. S.; Silverman, D. T.; He, X.; Hu, W.; Vermeulen, R.; Ning, B.; Fraumeni, J. F.,Jr; Rothman, N.; Lan, Q. Risk of lung cancer associated with domestic use of coal in Xuanwei, China: retrospective cohort study. BMJ 2012, 345, e5414.
7. Hosgood, H. D.,3rd; Chapman, R.; Shen, M.; Blair, A.; Chen, E.; Zheng, T.; Lee, K. M.; He, X.; Lan, Q. Portable stove use is associated with lower lung cancer mortality risk in lifetime smoky coal users. Br. J. Cancer 2008, 99, 1934-1939.
8. 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.
9. Shen, M.; Chapman, R. S.; Vermeulen, R.; Tian, L.; Zheng, T.; Chen, B. E.; Engels, E. A.; He, X.; Blair, A.; Lan, Q. Coal use, stove improvement, and adult pneumonia mortality in Xuanwei, China: a retrospective cohort study. Environ. Health Perspect. 2009, 117, 261-266.
10. Lan, Q.; He, X.; Shen, M.; Tian, L.; Liu, L. Z.; Lai, H.; Chen, W.; Berndt, S. I.; Hosgood, H. D.; Lee, K. M.; Zheng, T.; Blair, A.; Chapman, R. S. Variation in lung cancer risk by smoky coal subtype in Xuanwei, China. Int. J. Cancer 2008, 123, 2164-2169.
11. Lin, H.; Ning, B.; Li, J.; Ho, S. C.; Huss, A.; Vermeulen, R.; Tian, L. Lung Cancer Mortality Among Women in Xuan Wei, China: A Comparison of Spatial Clustering Detection Methods. Asia. Pac. J. Public. Health. 2012.
12. Chen, P. Study on integrated classification system for Chinese coal. Fuel Process Technol 2000, 62, 77-87.
13. Downward, G. S.; Hu, W.; Large, D.; Veld, H.; Xu, J.; Reiss, B.; Wu, G.; Wei, F.; Chapman, R. S.; Rothman, N.; Qing, L.; Vermeulen, R. Heterogeneity in coal composition and implications for lung cancer risk in Xuanwei and Fuyuan counties, China. Environ. Int. 2014, 68, 94-104.
14. Tian, L.; Lan, Q.; Yang, D.; He, X.; Yu, I. T. S.; Hammond, S. K. Effect of chimneys on indoor air concentrations of PM10 and benzo[a]pyrene in Xuan Wei, China. Atmos. Environ. 2009, 43, 3352-3355.
15. Lan, Q.; He, X.; Costa, D. J.; Tian, L.; Rothman, N.; Hu, G.; Mumford, J. L. Indoor coal combustion emissions, GSTM1 and GSTT1 genotypes, and lung cancer risk: a case-control study in Xuan Wei, China. Cancer Epidemiol. Biomarkers Prev. 2000, 9, 605-608.
16. Large, D. J.; Kelly, S.; Spiro, B.; Tian, L.; Shao, L.; Finkelman, R.; Zhang, M.; Somerfield, C.; Plint, S.; Ali, Y.; Zhou, Y. Silica-volatile interaction and the geological cause of the Xuan Wei lung cancer epidemic. Environ. Sci. Technol. 2009, 43, 9016-9021.
17. Li, G. J.; Huang, Y. C.; Tian, L. W.; Liu, Y. J.; Guo, L.; Xiao, Y. Z.; Hou, W. J.; Yang, K.; Chen, Y.; Zhao, G. Q.; Lei, Y. J. Relationship between high incidence of lung cancer among non-smoking women and silica in C1 bituminous coal in Xuanwei, Yunnan Province, China [article in Chinese]. Zhonghua Lao Dong Wei Sheng Zhi Ye Bing Za Zhi 2013, 31, 30 - 6.
18. He, J.; Cai, Y.; Lv, J.; Zhang, L. Primary investigation of quartz as a possible carcinogen in coals of Xuanwei and Fuyuan, high lung cancer incidence area in China. Environmental Earth Sciences 2012;, 67, 1679 - 1684.

19. Tian, L. W. Coal Combustion Emissions and Lung Cancer in Xuan Wei, China (PhD dissertation), University of California, Berkeley, California, 2005.
20. World Health Organization Hazard prevention and control in the work environment: Airborne dust. 1999.
21. NIOSH In Method 7602, Silica, Crystalline by IR. In NIOSH. (DHHS Pub. No. 94-113); Manual of Analytical Methods, 4th ed; NIOSH: Cincinnati, Ohio, 1994.
22. Pensis, I.; Luetzenkirchen, F.; Friede, B. SWeRF--A method for estimating the relevant fine particle fraction in bulk materials for classification and labelling purposes. Ann. Occup. Hyg. 2014, 58, 501-511.
23. R Development Core Team R: A Language and Environment for Statistical Computing. 2014.
24. Tian, L.; Dai, S.; Wang, J.; Huang, Y.; Ho, S. C.; Zhou, Y.; Lucas, D.; Koshland, C. P. Nanoquartz in Late Permian C1 coal and the high incidence of female lung cancer in the Pearl River Origin area: a retrospective cohort study. BMC Public Health 2008, 8, 398.
25. Vermeulen, R.; Rothman, N.; Lan, Q. Coal combustion and lung cancer risk in XuanWei: a possible role of silica? Med. Lav. 2011, 102, 362-367.
26. Dai, S.; Tian, L.; Chou, C.; Zhou, Y.; Zhang, M.; Zhao, L.; Wang, J.; Yang, Z.; Cao, H.; Ren, D. Mineralogical and compositional characteristics of Late Permian coals from an area of high lung cancer rate in Xuan Wei, Yunnan, China: Occurrence and origin of quartz and chamosite. International Journal of Coal Geology 2008, 76, 318-327.
27. IMA Europe Respirable Dust OELs, May 2010, IMA Europe. http://www.ima-europe.eu/content/respirable-dust-oels-may-2010 (accessed February 27, 2014).
28. Steenland, K.; Mannetje, A.; Boffetta, P.; Stayner, L.; Attfield, M.; Chen, J.; Dosemeci, M.; DeKlerk, N.; Hnizdo, E.; Koskela, R.; Checkoway, H.; International Agency for Research on Cancer Pooled exposure-response analyses and risk assessment for lung cancer in 10 cohorts of silica-exposed workers: an IARC multicentre study. Cancer Causes Control 2001, 12, 773-784.
29. Hu, W.; Downward, G.; Reiss, B.; Rothman, N.; Xu, J.; Bassig, B.; Hosgood, D.; Zhang, L.; Wu, G.; Chapman, R.; Wei, F.; Lan, Q.; Vermeulen, R. Personal and indoor fine particulate matter exposure from vented and unvented stoves in Xuanwei and Fuyuan county, China. Environ Sci Technol 2014, 48, 8456-64.

Chapter 5

Appendix 1 – Supporting information: Quartz in coal, ash, and air in a high lung cancer incidence area in China.

(Submitted paper)

Table S1 - Respirable Quartz in fuel ash (%) by fuel type and ventilation

Fuel Type	Stove Design	N	AM	GM	GSD
Smoky Coal		**75**	**0.29**	**0.11**	**5.0**
	Ventilated Stove	41	0.44	0.17	5.2
	Unvented Stove	2	0.25	0.15	4.9
	Firepit	6	0.18	0.15	2.0
	Portable Stove	7	0.08	0.05	4.3
	Multiple Stove Types	17	0.08	0.04	3.9
	Unknown/Missing£	2	0.24	0.14	5.0
Smokeless Coal		**13**	**0.14**	**0.08**	**4.0**
	Ventilated Stove	2	0.05	0.03	4.7
	Unvented Stove	5	0.13	0.12	1.3
	Firepit	0	-	-	-
	Portable Stove	5	0.20	0.10	6.4
	Multiple Stove Types	1	0.01	0.01	-
	Unknown/Missing	0	-	-	-
"Other" Coal†		**12**	**0.30**	**0.14**	**3.6**
	Ventilated Stove	4	0.61	0.34	3.2
	Unvented Stove	0	-	-	-
	Firepit	0	-	-	-
	Portable Stove	6	0.12	0.07	3.4
	Multiple Stove Types	2	0.22	0.22	1.1
	Unknown/Missing	0	-	-	-
Wood		**7**	**0.01**	**0.01***	**1.6**
	Ventilated Stove	2	0.01	0.01	1.1
	Unvented Stove	0	-	-	-
	Firepit	4	0.01	0.01	1.6
	Portable Stove	1	0.02	0.01	-
	Multiple Stove Types	0	-	-	-
	Unknown/Missing	0	-	-	-
Plant‡		**4**	**0.01**	**0.01***	**1.8**
	Ventilated Stove	0	-	-	-
	Unvented Stove	1	0.01	0.01	-
	Firepit	1	0.01	0.01	-
	Portable Stove	1	0.02	0.02	-
	Multiple Stove Types	1	0.01	0.01	-
	Unknown/Missing	0	-	-	-
"Other" Fuel$		**35**	**0.21**	**0.06**	**7.2**
	Ventilated Stove	4	0.24	0.20	2.2
	Unvented Stove	6	0.20	0.03	16.9
	Firepit	0	-	-	-
	Portable Stove	3	0.22	0.12	4.7
	Multiple Stove Types	22	0.21	0.05	6.6
	Unknown/Missing	0	-	-	-

*: Significant difference ($p<0.05$) when compared to smoky coal (via Tukey HSD)
£: Stove type either unknown or not reported
†: Other coal refers to either using both smoky and smokeless coal simultaneously or the use of pre-prepared briquettes
‡: Refers to the use of corn cobs and/or tobacco stems (sometimes in combination with wood)
$: Refers to the use of both coal and plant materials

Table S2 - Respirable quartz in ash (%) from smoky coal by coal source

County	Smoky Coal Subtype	Mine	N	AM	GM	GSD
Xuanwei	*Coking Coal*		*44*	*0.17*	*0.08*	*4.3*
		Azhi	13	0.10	0.05	3.3
		Baoshan	4	0.25	0.08	7.9
		Laibin	8	0.14	0.06	5.4
		Tangtang	13	0.22	0.10	4.6
		Yangchang	6	0.22	0.14	3.6
Fuyuan			*30*	*0.48*	*0.18*	*5.5*
	Coking Coal		9	0.09	0.06	3.5
		Daping	3	0.05	0.02	6.9
		Enhong	4	0.11	0.09	1.7
		Haidan	2	0.12	0.11	1.8
	1/3 Coking Coal		7	0.33	0.29	1.8
		Bagong	5	0.36	0.33	1.6
		Dahe	2	0.28	0.23	2.5
	Gas Fat Coal		12	0.91	0.33	8.2
		Housuo	11	0.98	0.40	8.4
		Qingyun	1	0.05	0.05	-
	Meagre Lean Coal (Gumu)		2	0.14	0.09	4.6

Italicised values represent overall values for smoky coal for that county

Chapter 5

Appendix 2: Short communication; fibrous quartz exposure due to the combustion of solid fuels in Xuanwei and Fuyuan, China

George S Downward
Peter Tromp
Kees Meliefste
Wei Hu
Wei Jie Seow
Nat Rothman
Lan Qing
Roel Vermeulen

(To be submitted)

Exposure to crystalline silica/quartz from the emissions of “smoky” (bituminous) coal has been implicated as a potential causative agent in the lung cancer epidemic in Xuanwei and Fuyuan.[1-4] Recently we presented findings of a large-scale exposure assessment survey in which we reported quartz concentrations in coal, ash and indoor air samples collected from throughout Xuanwei and Fuyuan.[5] In this publication we reported that quartz, including quartz in the respirable fraction is present in higher amounts in samples of "smoky" coal (5%) when compared to "smokeless" coal (2.1%, $p<0.05$). Smokeless coal is an anthracite coal available to a smaller proportion of the region and associated with lower lung cancer rates than smoky coal.[6] However, these findings of elevated quartz in coal samples failed to translate to elevated air concentrations. Indoor measurements of quartz were below the limit of detection ($0.2\mu g/m^3$) for the majority (89%) of measurements. Among the indoor air samples with detectable quartz (n=18), none came from homes exclusively burning smokeless coal while 11 (61%) came from homes burning smoky coal. However, the number of samples collected from smokeless and smoky coal burning homes was not equal (17 and 80 respectively) making it was unclear whether this represented a true difference between the two fuel types (difference not statistically significant by Fishers exact testing). Furthermore, ash analysis revealed that quartz, especially quartz in the non-respirable fraction was present in smoky coal ash to a significantly greater extent than smokeless coal ash (28.3% vs 3.3%, $p<0.05$).

These findings led to the conclusion that the increased quartz observed in coal samples most likely went on to join the ash. However, previous research had not only postulated that increased levels of quartz in smoky coal samples could contribute to the increased lung cancer incidence but that differing morphologies of airborne quartz between fuels could play a role.

To investigate the morphological differences we carried out a small scale study in select Xuanwei villages in October 2013 covering air samples from households burning smoky and smokeless coal for cooking and heating. We selected two villages with primarily smokeless coal using residents and three villages with smoky coal using residents for sample collection. We purposefully selected smoky coal villages which, in our previous analysis, provided air samples with detectable quartz. Indoor air samples were collected on nickel coated track-etched polycarbonate filters (0.4µm 25mm, Nuclepore) using SKC airchek XR 5000 pumps set at flow rates of 2L/min for 60 minutes. In total, 12 samples were collected for analysis (8 from smoky and 4 from smokeless coal using households).

FEG-SEM-EDX

Field emission gun scanning electron microscopy in combination with X-ray analysis (FEG-SEM/EDX) was used for physico-chemical characterization, semi-quantitative estimation of the concentration and determination of the particle size distribution for silica (SiO_2) and fibre-like particles. The microscope used was a Tescan MIRA-LMH FEG-SEM with a Bruker AXS spectrometer and a XFlash 4010 detector. The filters were screened at magnifications between 200x - 5000x. Qualitative data was obtained about the type, size and shape of sampled particles, and the degree of agglomeration or aggregation.

For quartz, automated particle analysis was performed using Scandium imaging software (Olympus Soft Imaging Solutions GmbH, Germany). From each particle/cluster of particles the projected area equivalent diameter (dpa) was measured and an EDX spectrum recorded. To measure dpa between 0.4 – 40 µm, three magnifications of 200X, 1000X, and 5000X were selected. These magnifications cover 8 size groupings: 0.65-1.0, 1.0-1.6, 1.6-2.5, 2.5-

4.0, 4.0-6.5, 6.5-10, 10-16 and, 16-25 µm. Approximately 50 inorganic particles were measured per size grouping, totalling 400 particles per sample. From the EDX-spectrum, silica particles were defined as having greater than 95% silicon and oxygen in the total particle, conglomerate or aggregate.

For silica and fibre-like particles the numerical concentration per particle type and size bin is calculated in accordance with ISO 14966.[7] The standard deviation (95% confidence interval) is calculated on the basis of Poisson distribution. Fibre-like particles are defined as particles with a length greater than 5µm, a diameter less than 3µm, and a length:diameter ratio greater than 3. For silica, the numerical concentration was converted into a mass concentration, using the particle size (dpa), a particle density (ρp) of 2.65 g/cm^3 and a volumetric shape factor (Sv) of 1.3. The mass of a particle is estimated as $(\pi/6) \bullet \rho p \bullet (dpa / Sv)^3$. The contribution of a single particle to mass concentration was calculated by multiplying the numerical concentration with the mass of the particle.

Observed silica particles could either be crystalline (including quartz, cristobalite, trydimite, etc) or amorphous.

Results

Eight samples from smoky coal homes and 4 from smokeless coal homes were analysed. Results of analysis showed quartz concentrations (in the $PM_{2.5}$ fraction) of between 0 and 1.1µg/m^3, median 0.27µg/m^3 for smoky coal homes, compared to 0 to 0.19µg/m^3, median 0.03µg/m^3 for smokeless coal homes. Semi-quantitative SEM/EDX results on a limited number of samples are consistent with these quartz analyses: mean silica concentration 0.3±0.1 µg/m^3 (n=2) for smoky coal homes and <0.1 µg/m^3 (n=2) for smokeless coal homes. This indicates that the majority of the observed silica particles with SEM/EDX are crystalline.

In general the observed silica material consisted of dense particles with smooth surfaces, with both round shapes as well as sharp edges (Figure.1A). They were either present as single particles or part of larger conglomerates/aggregates together with silicate and carbonaceous particles (Figure.1C,D). No differences in morphology of the silica particles between the smoky coal and smokeless coal burning homes was observed. However, there were clear differences in the relative percentage of silica particles relative to the total amount of particles in the air samples. For $PM_{2.5}$, PM_{10} and PM_{25}, the percentage of silica particles was 3-4 times higher in indoor air samples from smoky coal homes than smokeless coal homes (Table 1). For PM_{10} and PM_{25} this difference was statistically significant ($p<0.05$ via paired t-test). In addition, the percentages of silica particles in the air samples correspond to the amounts of quartz in “smoky” coal and “smokeless” coal. A difference was also observed in the amount of silicon present in particulate matter. The mean silicon percentage in particulate matter was 33.1 ± 2.1 for smokeless coal homes, compared to 41.4 ± 4.2 for smoky coal homes. These findings were in agreement with SEM observations of the examined conglomerates/aggregates and suggest a higher amount of silica structures within the particle clusters from smoky coal homes compared to smokeless coal homes. Especially within silicate particle clusters, a clear difference in the amount of silicon was observed (Figure 2).

Fibre-like particles were also observed in the air samples with SEM/EDX. The mean concentration of the observed fibre-like materials in smoky coal homes was 5,800 (95% confidence interval (CI) = 4,200 – 7,800) fibres/m^3 compared to 550 (95% CI = 67 – 2,000)

Table 1. Relative percentage (mean ± SD) of single silica particles relative to total particles ($PM_{2.5}$, PM_{10} and PM_{25}) in indoor air samples of smokeless (n=4) and smoky coal homes (n=8), analysed with SEM/EDX.

Particulate matter (PM)	Smoky coal	Smokeless coal
$PM_{2.5}$	6.3 ± 5.9	1.7 ± 1.9
PM_{10}	16.7* ± 11.0	4.5 ± 5.2
PM_{25}	8.8* ± 5.6	2.5 ± 1.2

***: significant difference between smoky and smokeless coal via paired t-test**

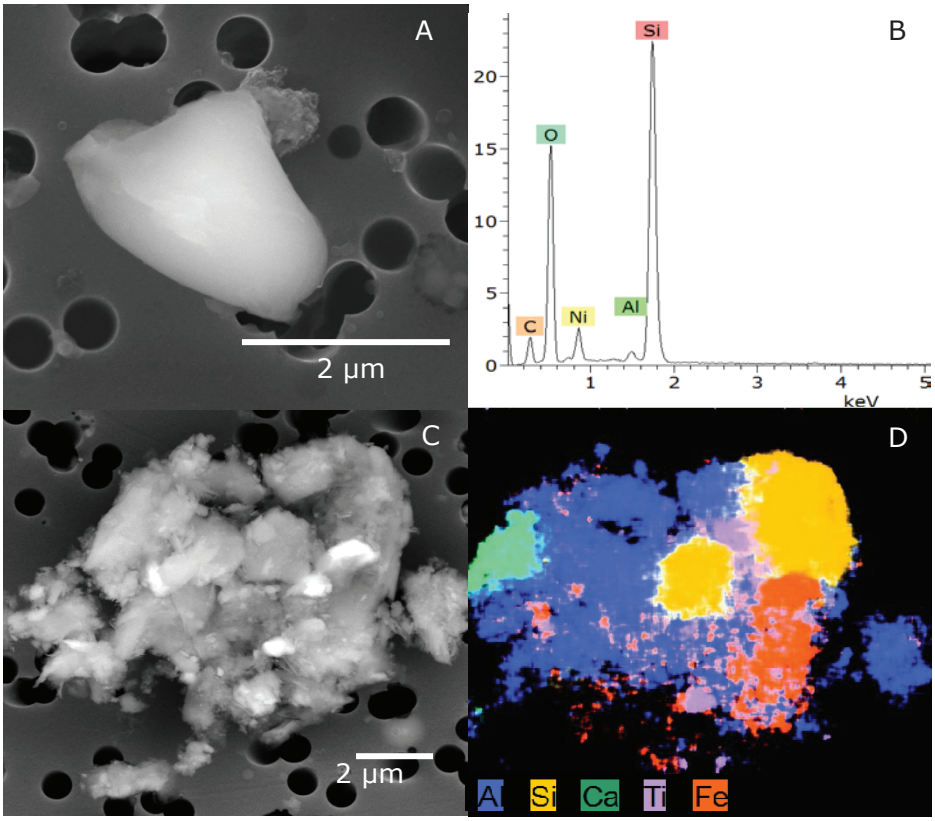

Figure 1. SEM images and EDX analysis of two quartz structures (source: smoky coal)
SEM image of a solid quartz particle (A) and corresponding EDX spectrum (B)
SEM image of a conglomerate of alumino-silicate and quartz/SiO_2 (C) including EDX mapping (D).
The elements nickel (Ni) and carbon (C) originate from the filter.

fibres/m^3 for smokeless coal homes. This difference in concentration, based on the 95% confidence interval (Poisson distribution), was statistically significant. The fibre-like particles did not appear as clear crystalline fibres (e.g. asbestos, ceramic fibres, etc.), but did meet the criteria for fibres in accordance with ISO 14966. Between and within the air samples the fibre-like particles had different shapes, sizes and morphology (Figure 3) and a non-uniform elemental composition. In general, the elemental composition was similar to the non-fibre-like inorganic particulate matter in the air samples. Most of the fibre-like particles consisted of silicon-, aluminium-, iron-, magnesium- and potassium-oxides and carbon, but in different ratios. The source of these fibre-like materials is unclear. Variations in the Si:Al ratio between smoky and smokeless (3.3±1.0 and 1.8±0.4 respectively, $p<0.05$ from paired t-test) coal particles may suggest differing mineral properties, however the heterogeneity in particle shape and morphology (which may be an artefact of high temperature combustion) undermine our ability to attribute single mineralogical attributes to these particles.

In summary, we observed that there were differences in fibrous quartz concentrations between smoky and smokeless coal, however at concentrations beneath those considered to be harmful (for example, the occupational exposure limits range from 25µg/m^3 [Portugal] to 300µg/m^3 [Poland]).[8,9] The finding of fibre-like materials in the emission products of smoky coal has not been reported in the past and is of potential interest, however further research is required before the clinical significance of this finding can be established.

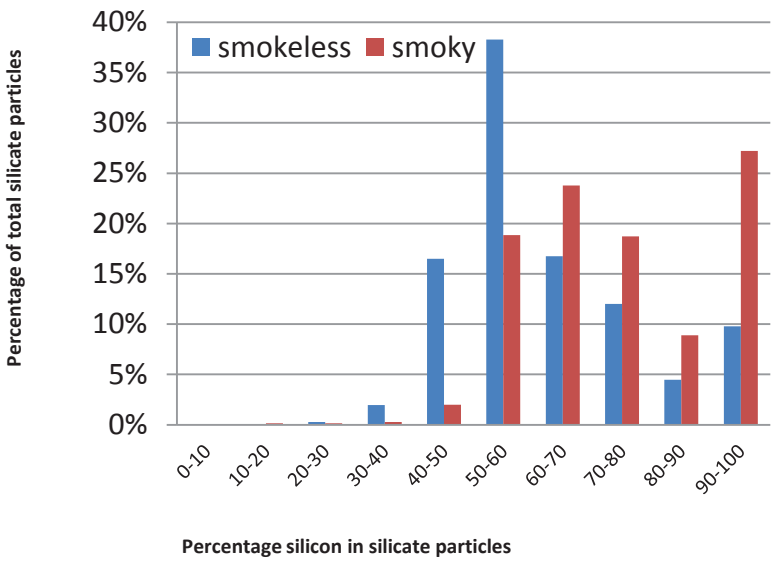

Figure 2. Particle distribution of silicate particles based on the relative percentage of silicon in indoor air samples of smokeless coal homes (n=4) and smoky coal homes (n=8), analysed with SEM/EDX

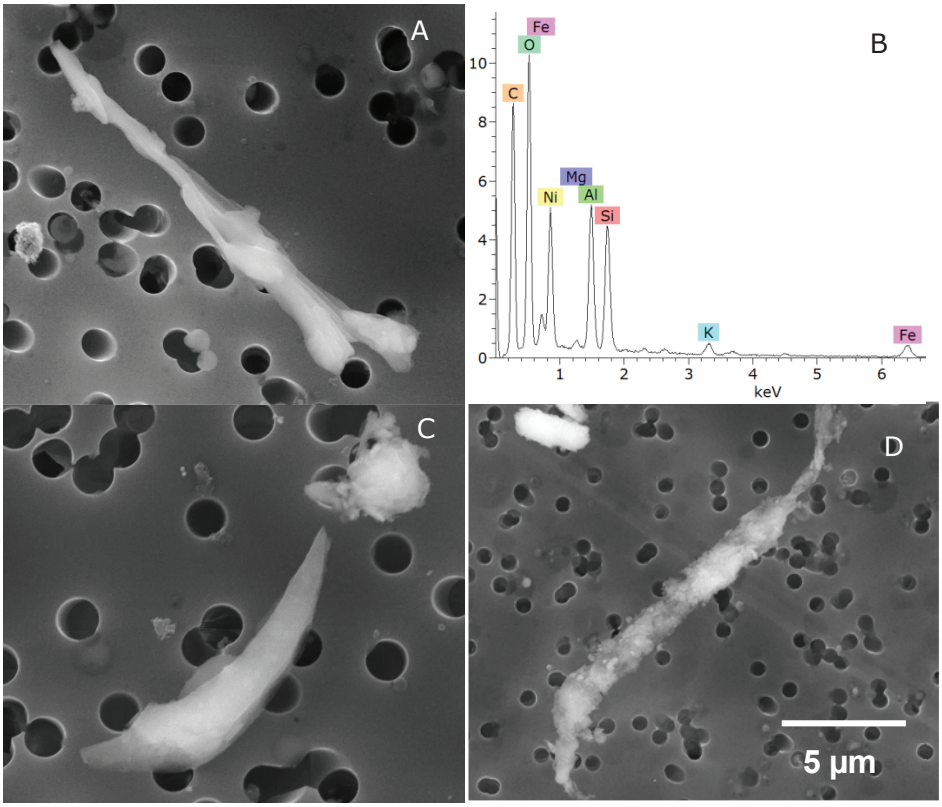

Figure 3. SEM images (A,C,D) and EDX spectrum (B) of typical fibre-like particles (source A, B, C: smoky coal, D: smokeless coal).
The element nickel (Ni) originates from the filter.

References

1. Large, D. J.; Kelly, S.; Spiro, B.; Tian, L.; Shao, L.; Finkelman, R.; Zhang, M.; Somerfield, C.; Plint, S.; Ali, Y.; Zhou, Y. Silica-volatile interaction and the geological cause of the Xuan Wei lung cancer epidemic. Environ. Sci. Technol. 2009, 43, 9016-9021.
2. Tian, L. Coal Combustion Emissions and Lung Cancer in Xuan Wei, China (PhD dissertation), University of California, Berkeley, California, 2005.
3. Tian, L.; Dai, S.; Wang, J.; Huang, Y.; Ho, S. C.; Zhou, Y.; Lucas, D.; Koshland, C. P. Nanoquartz in Late Permian C1 coal and the high incidence of female lung cancer in the Pearl River Origin area: a retrospective cohort study. BMC Public Health 2008, 8, 398.
4. He, J.; Cai, Y.; Lv, J.; Zhang, L. Primary investigation of quartz as a possible carcinogen in coals of Xuanwei and Fuyuan, high lung cancer incidence area in China. Environmental Earth Sciences 2012;, 67, 1679 - 1684.
5. Downward, G. S.; Hu, W.; Rothman, N.; Reiss, B.; Wu, G.; Wei, F.; Xu, J.; Seow, W. J.; Chapman, R. S.; Qing, L.; Vermeulen, R. Quartz in coal, ash, and air in a high lung cancer incidence area in China (submitted paper).
6. Barone-Adesi, F.; Chapman, R. S.; Silverman, D. T.; He, X.; Hu, W.; Vermeulen, R.; Ning, B.; Fraumeni, J. F.,Jr; Rothman, N.; Lan, Q. Risk of lung cancer associated with domestic use of coal in Xuanwei, China: retrospective cohort study. BMJ 2012, 345, e5414.
7. ISO ISO 14966: Ambient air - Determination of numerical concentration of inorganic fibrous particles -- Scanning electron microscopy method, International Organization for Standardization. 2002.
8. IMA Europe Respirable Dust OELs, May 2010, IMA Europe. http://www.ima-europe.eu/content/respirable-dust-oels-may-2010 (accessed February 27, 2014).
9. Vermeulen, R.; Rothman, N.; Lan, Q. Coal combustion and lung cancer risk in XuanWei: a possible role of silica? Med. Lav. 2011, 102, 362-367.

Chapter 6

Outdoor, indoor, and personal black carbon exposure from cookstoves burning solid fuels

George Downward
Wei Hu
Nat Rothman
Boris Reiss
Guoping Wu
Fusheng Wei
Jun Xu
Wei Jie Seow
Robert S. Chapman
Lan Qing
Roel Vermeulen

(Submitted paper)

Abstract

Background:

Black Carbon (BC) emissions from fossil and solid fuel combustion are associated with increased morbidity and mortality and are an important driver of climate change. We studied indoor, personal, and outdoor BC exposure levels, approximated by particulate matter ($PM_{2.5}$) absorbance, in villages and households in Yunnan province, China using a variety of solid fuels for cooking and heating including: bituminous and anthracite coal, and wood.

Methods

Indoor, personal, and outdoor (village background) $PM_{2.5}$ measurements were taken over 2 consecutive 24hr periods from 163 households in 30 villages. Absorbance of the filters was measured using an EEL 043 Smoke Stain Reflectometer. Mixed effect models were used to identify determinants of BC exposure levels.

Results

Absorbance measurements were higher in wood burning households ($16.3 \times 10^{-5} m^{-1}$) than bituminous and anthracite coal households than anthracite (12 and $5.5 \times 10^{-5} m^{-1}$ respectively). Among bituminous coal users exposure varied by a factor two depending on the coal source. Using portable stoves (which are lit outdoors and brought indoors for use) was associated with reduced BC levels. Outdoor measurements were 50% lower than indoor and personal measurements, positively correlated to indoor and personal measurements (0.43 and 0.49 respectively ($p<0.01$)), and higher among villages which primarily burned bituminous coal (compared to anthracite coal).

Conclusion

These findings indicate that indoor, personal, and outdoor exposure to BC is primarily modulated by fuel type and source. These findings provide valuable insight into potential morbidity, mortality and climate change contributions of burning solid fuels for cooking and domestic heating.

Introduction

Xuanwei, and its neighbouring county of Fuyuan, located in Yunnan province, China have among the highest lung cancer rates in the nation, regardless of gender or smoking status [1,2]. The residents of Xuanwei and Fuyuan, like approximately 3 billion people world-wide, are largely dependent upon the use of solid fuels (coal, wood etc.) for their daily heating and cooking needs [3]. Locally sourced "smoky" coal (a bituminous coal) is the primary fuel source mined and used throughout the Xuanwei and Fuyuan counties (Figure 1) and has, through multiple lines of research, been identified as the cause of the excess lung cancer mortality in the region.[1,2,4,5] Approximately 25% of residents use alternative fuels, including "smokeless" coal (an anthracite coal available in a few locations), wood, corn cobs, and tobacco stems.

Previous research has identified that smoky coal emissions (when compared to smokeless coal) contain relatively high amounts of particulate matter ($PM_{2.5}$) and polycyclic aromatic hydrocarbons (PAH).[6,7] However, nothing is known regarding black carbon (BC) emissions. Black carbon is released via the incomplete combustion of solid and fossil fuels and is an important predictor of mortality and other adverse health effects in studies of ambient air pollution.[8,9] In a meta-analysis of time series studies, Janssen et. al. found that each increase in 1 x $10^{-5}m^{-1}$ in BC exposure is associated with a 0.68% increase in all-cause mortality.[10] Black carbon exposure has also been associated with increased blood pressure, type 2 diabetes and respiratory infections among children under 36 months of age.[11-13] Road-side studies conducted in Europe[14] have reported mean BC measurements of up to 5 x $10^{-5}m^{-1}$, indicating that even in high income nations, BC presents a public health concern.

An additional feature of BC is that by absorbing heat and reducing albedo (reflected sunlight) it is an important climate change driver.[15-17] Unlike carbon dioxide, BC only remains in the atmosphere for a short time (days to several weeks)[18], meaning that reductions in BC emissions will have an immediate impact upon climate forcing. Up to 80% of BC emissions in Africa and Asia have been attributed to residential solid fuel use[19] and there is evidence to suggest that improved stove designs can significantly reduce BC emission. A study in Indian households found up to a 90% reduction in indoor BC emissions if stoves with forced (i.e. fan driven) ventilation were utilized.[20] In Xuanwei and Fuyuan, solid fuels were historically burnt in unvented firepits while recent decades have seen the implementation of stove improvements, aimed at increasing burning efficiency and venting fuel emissions outdoors. These ventilated stoves have been associated with reduced $PM_{2.5}$ and PAH emissions[6,7,21] in addition to reductions in both malignant and non-malignant lung disease.[22-26] However, as the stove improvements carried out in Xuanwei and Fuyuan were focussed upon the installation of fixed cook-stoves with attached chimneys and did not include fan-forced ventilation, it is unclear whether a reduction in indoor BC emissions would be achieved. Furthermore, the consequences for the general outdoor air quality are unknown.

Given the importance of BC, from both a public health and climate change perspective, there is value in understanding BC emissions from solid fuel use in Xuanwei and Fuyuan. This paper will present personal, indoor, and outdoor BC measurements and explore the various roles that fuel type, fuel source and stove design play on measured concentrations.

Methods

Data for this paper was collected as part of a large cross-sectional molecular epidemiology study aimed at cataloguing the emission products of solid fuels from throughout Xuanwei

and Fuyuan and associating those emission products with biological effect markers and lung cancer risk in a case control study of lung cancer among never-smoking females. The full details are provided elsewhere [27] but briefly, 15 villages were selected from each county (30 in total). Approximately 5 households with a healthy non-smoking adult female resident were selected from each village. Household selection was directed towards reflecting the population in the case control study, which represents fuel and stove usage for the previous several decades. Therefore houses which were at least 10 years old and had not had any stove alterations undertaken in the past 5 years were preferentially selected. One non-smoking female, between the ages of 20 and 80 who resided in the household and was primarily responsible for cooking, was enrolled for personal monitoring of pollutants. Written informed consent was gained prior to enrolment.

Homes were measured and sketched. Pertinent features (e.g. stoves, doors, windows and stairways) were recorded. Data was collected during 2 collection periods. The first was between August 2008 and February 2009. During this period 148 participants were recruited from all 30 villages. During the second collection period, between March and June 2009, 16 of the original 30 villages were re-visited (villages were selected based upon how well they represented the overall population), 53 of the original households and enrolees were re-visited and 15 new subjects were enrolled. During each collection period, measurements were taken during 2 consecutive 24 hour periods.

Following a review of reported fuel types, the following categories for fuel type were identified: smoky coal, smokeless coal, "other" coal (combinations of smoky coal, smokeless coal and processed coal products such as briquettes), wood, plant products (combinations of corn cobs, tobacco stems and bamboo shoots, sometimes in combination with wood) and "other" fuels (combinations of coal and plants). When a subject reported using coal, geochemical analysis was used to confirm coal type.[27] Subsequently, smoky coal sub-types were classified according to the Chinese State Standard for coal classification (the subtypes are: coking coal, 1/3 coking coal, gas fat coal and meagre lean coal [Figure 1]).[28]

Stoves were categorized based upon their design with the following categories used for analysis: ventilated stoves, unventilated stoves, firepit, portable stove (which is designed to be lit outside and carried indoors for use), "mixed" (which refers to the use of multiple stoves with differing ventilations) and unknown (where stove type was not recorded).

Sample collection

Black carbon was measured through the commonly used proxy measurement of light absorbance of the fine particulate matter ($PM_{2.5}$).[29] Personal and indoor $PM_{2.5}$ measurements were collected on 37 mm Teflon filters attached to a cyclone with an aerodynamic cut-off of 2.5μm (model BGI, GK 2.05SH) at a flow rate of 3.5 L/min (±20%). Pumps underwent calibration prior to all measurements and flow rates were recorded pre and post sampling. If the post-sampling flow deviated by more than 10%, data was not accepted for further analysis. Filters were changed after 24 hours of operation. For personal measurements, the pump was packed in a hip bag and the cyclone was attached near the breathing zone. Overnight, the equipment was put next to the subject's bed. Indoor measurements were collected using the same methods as described above with samplers being placed in the main living area. Samplers were placed at least 0.25m from each wall and 1-2m from stoves (as allowed by indoor space). If there was a separate room which contained a stove for cooking or heating, then an additional indoor measurement was taken

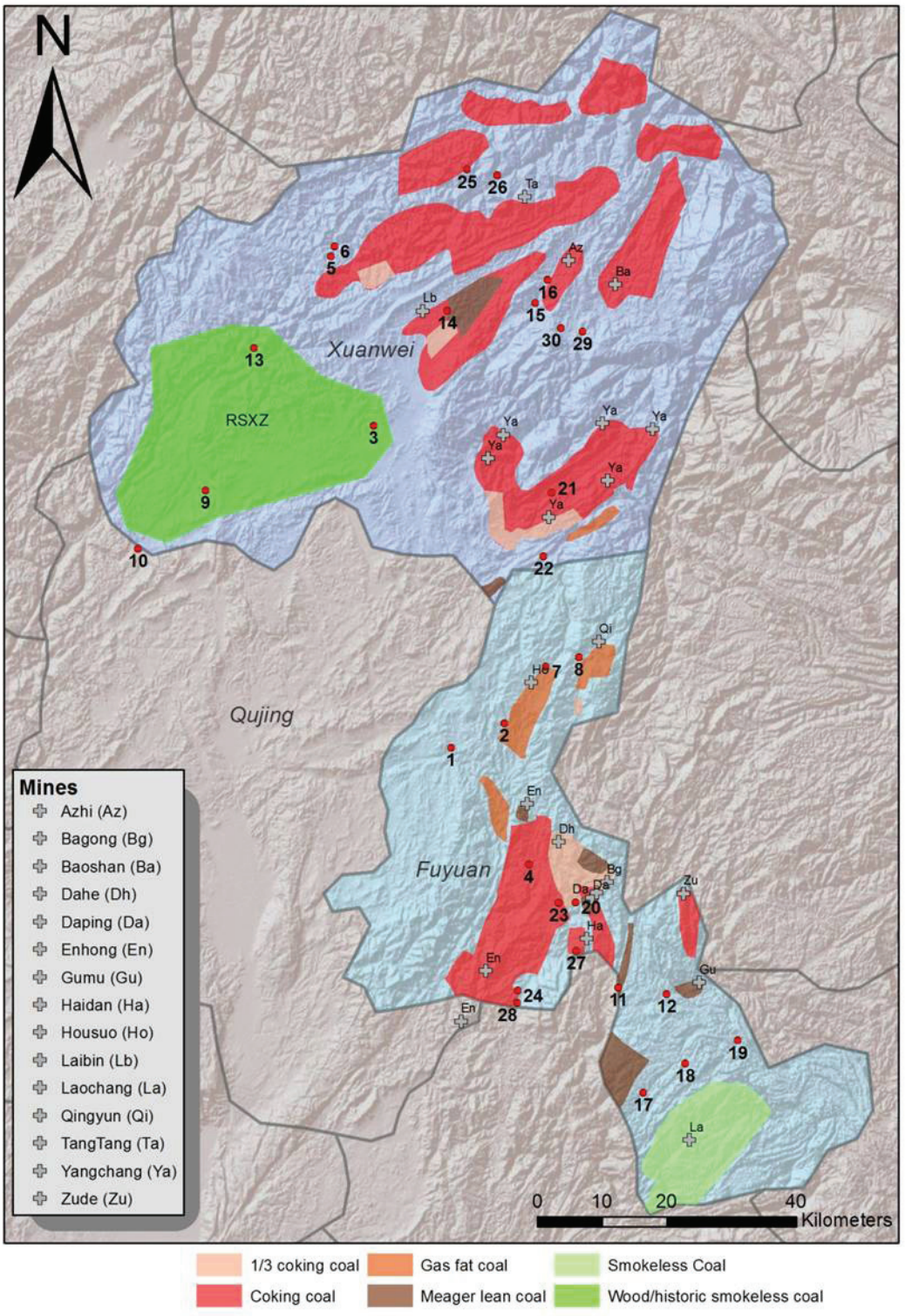

Figure 1:Map of Xuanwei and Fuyuan counties showing approximate locations of study villages, reported coal mines and coal sub-types

Villages enrolled in the study are marked numerically 1 to 30

Mine locations indicate functioning mine entrances, therefore, some mines may be indicated more than once.

Only mines reported by study participants are indicated.

in that room (this represents 6% of indoor measurements). Outdoor measurements were taken at a central location in each village away from any direct local emission sources (such as chimneys). External sources of pollution (factories, power plants etc.) within 5km of each village were documented.

After sample collection, all exposed filters were individually packed into petri slides and stored in zipped amber plastic bags while in transit for analysis.

Sample analysis

Light reflectance was measured across 5 different spots on the filter (to compensate for variation across the filter) using an EEL 043 Smoke Stain Reflectometer. The average reflectance across the 5 points was transformed into an absorption value using the following formula.[30]

$$a = \frac{A}{2V} \ln\left(\frac{R_0}{R_f}\right) \times 100{,}000$$

Where a represents the absorption coefficient (in $10^{-5}m^{-1}$), A the area of the loaded filters ($0.00078m^2$), V the volume of sampled air (in m^3), R_0 the average reflectance of field blanks (102%) and R_f the reflectance of the sampled filter (%).

Quality Control

As stated above, all samples were blank corrected. Reflectance of filters was completed over several measurement "batches". During each "batch", approximately 10% of filters in that batch had their measurements repeated. If the average reflectance of the repeat measurement deviated by more than 3%, all filters being measured were re-measured. Additionally, field duplicates were taken for approximately 25% of all samples (n=211 [203 indoor and 8 personal measurements]). The median relative percentage difference of these repeat measurements was 7% (Interquartile range [IQR] 3.4 to 13.5%).

Statistical Analysis

Normal probability plots indicated that measured absorbance values tended towards log-normality. Descriptive statistics include arithmetic means (AM), geometric means (GM) and geometric standard deviations (GSD). Analysis of variance (ANOVA) and Tukey Honestly Significant Difference (HSD) testing, carried out on log-transformed values, was used to assess for differences between fuel types, stove designs and smoky coal sources. When assessing between smoky coal sources, only smoky coal which could be linked to a specific coal mine was included for analysis. In general, subjects in a certain village would use coals from a similar mine, therefore, for analysis of village based measurements, we assumed that if a fuel type and/or stove design were used by greater than 50% of our study enrolees, then those would likely represent the primary fuel and stove types used in the village.

In order to further explore the factors influencing absorbance measurements, linear mixed effect models (on the log transformed values) were constructed. In the construction of models, individual subjects, and the villages that they resided in were assigned as random effects. Approximately 25 variables, including fuel source, stove design, season and meteorology were considered for inclusion as fixed effects. Inclusion of variables in the final model was based on the combination of how they influenced the Akaike information criterion (AIC) score and how they best described the observed data. The model can be represented with the following formula:

$$y_{ijf} = \mu + \beta_1 x_1 + \beta_2 x_2 \ldots \beta_n x_n + bI_i + bJ_{if} + \varepsilon_{ijf}$$

Where y_{ijf} represents the natural log transformed value of absorbance measurements for village i, person j on day f. μ represents the intercept (i.e. the "background" level). β_1 through β_n represent fixed effect variable coefficients for variables x_1 through x_n. bI_i represents the random effect coefficient for village i. bJ_{if} represents the random effect coefficient for subject j, living in village i. ε_{ijf} represents the error for village i, person j on day f.

All statistical testing was carried out using R version 3.0.2[31] using the lme4 package.[32] A p value of less than 0.05 was considered to indicate statistical significance.

Results

In total, 924 absorbance measurements were collected (415 personal, 443 indoor, and 66 village based measurements). 411 measurements (202 personal and 209 indoor) represented the exclusive use of smoky coal, 398 of which (195 personal and 203 indoor) could be assigned to individual mines. In Xuanwei, all smoky coal producing mines reported were of the coking coal subtype while in Fuyuan smoky coal mines were a variety of subtypes: coking coal, 1/3 coking coal, gas fat coal and meagre lean coal. Among village based samples, 40 samples were collected from villages where smoky coal was the dominant fuel used, 14 smokeless, and 12 villages where there was no clear dominant fuel type used.

Personal and Indoor measurements

Indoor and personal measurements correlated well with each other, with a Spearman correlation coefficient of 0.70 ($p<0.01$). In general, personal measurements were similar to indoor (median percentage difference: +6.6% IQR:-21.7% to +26.9%). A mixed effect model was constructed to explore variables which may contribute to the observed difference between indoor and personal measurements (table S2 in the supplement) which indicated that personal measurements would be higher (relative to indoor measurements) during colder temperatures, during periods when more fuel (in kg) was used and during periods of extended stove usage.

An overview of $PM_{2.5}$ absorbance is shown in Table 1. Households burning wood had the highest absorbance measurements for both personal ($16.3 \times 10^{-5} m^{-1}$) and indoor ($15.0 \times 10^{-5} m^{-1}$) measurements and for personal measurements they were significantly higher than households burning smoky coal ($12 \times 10^{-5} m^{-1}$, $p<0.05$). Households exclusively burning smoky coal had significantly higher absorbance measurements than households burning smokeless coal for both personal ($12 \times 10^{-5} m^{-1}$ vs $5.5 \times 10^{-5} m^{-1}$, $p<0.05$) and indoor ($11.8 \times 10^{-5} m^{-1}$vs $4.7 \times 10^{-5} m^{-1}$, $p<0.05$) measurements. On investigation for the role of stove design, households burning smoky coal in portable stoves had significantly lower indoor measurements than those using unventilated stoves ($7.7 \times 10^{-5} m^{-1}$ vs $12.2 \times 10^{-5} m^{-1}$, $p<0.05$). No other significant difference between stove designs (e.g. ventilation) was observed.

On assessing for variation between different smoky coal sources (Table 2), gas fat coal from the Fuyuan mine of "Qingyun" had the highest personal and indoor absorbance measurements ($23.7 \times 10^{-5} m^{-1}$ and $21.3 \times 10^{-5} m^{-1}$ respectively) while the coking coal mine "Daping" also located in Fuyuan had the lowest ($6.8 \times 10^{-5} m^{-1}$ and $6.0 \times 10^{-5} m^{-1}$). ANOVA testing revealed significant variation within coking coals sourced from within Xuanwei (range for personal measurements $10.7 \times 10^{-5} m^{-1}$ to $16.4 \times 10^{-5} m^{-1}$, $p<0.05$), within the smoky coal subtypes produced in Fuyuan (range $5.2 \times 10^{-5} m^{-1}$ for meagre lean coal to 13.2

Table 1 - Personal and indoor absorbance measurements (in 10−5m−1) by fuel type and stove design

		Personal				Indoor			
Fuel Type	Stove Design	N(k)	AM	GM	GSD	N(k)	AM	GM	GSD
Smoky Coal	**Overall**	**202(89)**	**13.8**	**12.0**	**1.7**	**209(87)**	**13.3**	**11.8**	**1.7**
	Ventilated	108(48)	14.7	13.0	1.6	114(51)	13.6	12.2	1.7
	Unventilated	8(3)	10.5	10.0	1.4	8(3)	9.3	8.7	1.5
	Portable Stove	22(9)	8.9	7.3	2.0	21(8)	10.1	7.7†	2.1
	Firepit	13(7)	14.4	13.7	1.4	13(6)	14.9	14.4	1.3
	Mixed	44(19)	15.3	13.5	1.8	45(15)	14.8	13.7	1.5
	Unknown	7(3)	7.8	7.2	1.6	8(4)	10.7	9.4	1.8
Smokeless Coal	**Overall**	**47(20)**	**9.7**	**5.5***	**2.1**	**45(18)**	**5.5**	**4.7***	**1.8**
	Ventilated	5(2)	7.6	6.1	2.0	5(2)	8.0	5.1*	2.6
	Unventilated	18(6)	15.0	5.9	2.6	17(5)	5.6	5.1	1.6
	Portable Stove	19(8)	6.1	5.1	1.9	18(7)	4.6	4.1	1.7
	Firepit	3(3)	3.8	3.7	1.3	3(3)	3.4	3.4	1.3
	Mixed	2(1)	10.0	9.9	1.2	2(1)	9.5	9.5	1.1
	Unknown	0	-	-	-	0	-	-	-
”Other” Coal	**Overall**	**37(20)**	**11.1**	**9.5**	**1.8**	**41(20)**	**9.6**	**8.1**	**1.9**
	Ventilated	13(6)	10.0	9.1	1.6	14(6)	10.2	9.0	1.7
	Unventilated	0	-	-	-	0	-	-	-
	Portable Stove	14(8)	11.5	9.2	2.2	14(8)	9.0	6.9	2.3
	Firepit	1(1)	9.8	9.8	-	1(1)	8.1	8.1	-
	Mixed	9(5)	12.4	10.8	1.7	12(5)	9.7	8.6	1.7
	Unknown	0	-	-	-	0	-	-	-
Wood	**Overall**	**23(11)**	**17.4**	**16.3***	**1.4**	**23(11)**	**15.5**	**15.0**	**1.3**
	Ventilated	8(4)	14.6	13.5	1.5	8(4)	15.4	14.7	1.4
	Unventilated	0	-	-	-	0	-		
	Portable Stove	6(2)	17.5	17.2	1.2	5(1)	14.8	14.5	1.3
	Firepit	9(5)	19.8	18.6	1.4	9(5)	15.9	15.3	1.3
	Mixed	0	-	-	-	0	-	-	-
	Unknown	0	-	-	-	1(1)	16.3	16.3	-
Plant	**Overall**	**13(9)**	**13.4**	**12.5**	**1.5**	**13(9)**	**13.0**	**12.6**	**1.3**
	Ventilated	3(2)	11.0	10.9	1.2	3(2)	8.5	8.5	1.1
	Unventilated	3(1)	18.6	18.6	1.1	3(2)	15.0	15.0	1.0
	Portable Stove	2(1)	14.6	14.6	1.0	2(1)	14.2	13.9	1.3
	Firepit	4(4)	9.3	8.5	1.6	4(4)	13.6	13.2	1.3
	Mixed	1(1)	19.4	19.4	NA	1(1)	15.9	15.9	-
	Unknown	0	-	-	-	0	-	-	-
“Other” Fuel	**Overall**	**93(48)**	**12.0**	**10.3**	**1.8**	**112(49)**	**12.3**	**10.1**	**2.0**
	Ventilated	17(8)	10.2	9.3	1.6	22(9)	10.6	9.1	1.8
	Unventilated	17(10)	13.5	11.4	2.0	26(11)	14.4	11.8	2.0
	Portable Stove	7(4)	9.5	8.5	1.7	7(4)	8.7	7.9	1.6
	Firepit	0	-	-	-	0	-	-	-
	Mixed	48(24)	12.9	11.1	1.8	53(23)	12.8	10.4	2.0
	Unknown	4(2)	7.2	6.4	1.8	4(2)	7.6	6.6	1.8

*: Significant difference with smoky coal for same ventilation strata (Tukey HSD test)
†: Significant difference with ventilated stove for that fuel type (Tukey HSD test)
N:Number of samples
k:Number of individuals subjects
Mixed: use of multiple stoves with differing ventilation designs

x $10^{-5}m^{-1}$ for gas fat coal) and within the Fuyuan coking coals (6.8 x $10^{-5}m^{-1}$ to 14.7 x $10^{-5}m^{-1}$), 1/3 coking coals (7.1 x $10^{-5}m^{-1}$ to 11.6 x $10^{-5}m^{-1}$, personal measurements only) and the gas fat coal subtypes (11.7 x $10^{-5}m^{-1}$ to 21.3 x $10^{-5}m^{-1}$, indoor measurements only).

Mixed effect modelling

Construction of a linear mixed effect model indicated that fuel type and source, stove design, the season of measurements and the presence or absence of a stairway all contributed to absorbance levels. An estimate of the strength of effect of each variable (beta (β) effect estimates), 95% confidence intervals and GMR's (GMR= geometric mean ratio = GM(estimate)/GM(reference)=exp(β)) are available in Table 3.

The model explains 17% of the variance between subjects and 66% of the variance between villages for personal measurements (28% and 47% respectively for indoor measurements). It indicates that the use of wood as a fuel source results (when compared to smokeless coal) in the highest absorbance measurements (GMR 2.22 for personal and 1.67 for indoor measurements). Variation in absorbance measurements was observed between the differing smoky coal types and sources (e.g. among personal measurements the GMR ranges from 0.92 for meagre lean coal to 1.79 for gas fat coal). The exclusive use of a portable stove resulted in the lowest predicted absorbance levels (GMR 0.84 for both indoor and personal measurements). The presence or absence of stairways also impacted absorbance measurements. Homes without stairways had lower absorbance measurements than those with them (GMR 0.88 for both indoor and personal measurements). Measurements taken during winter resulted in the highest absorbance measurements (GMR 1.32 for personal measurements and 1.19 for indoor measurements) while those taken in Summer resulted in the lowest (GMR 0.85 for personal measurements and 0.77 for indoor measurements)

Table 2 - Personal and indoor absorbance measurements (in 10−5m−1) by smoky coal source

			Personal				Indoor			
County	Smoky Coal Subtype	Mine Name	N(k)	AM	GM	GSD	N(k)	AM	GM	GSD
Xuanwei	*Coking Coal*		*117(47)*	*14.7*	*13.2**	*1.7*	*123(47)*	*14.7*	*13.2**	*1.7*
		Azhi	32(13)	17.9	16.4	1.6	33(13)	18.3	17.1	1.5
		Baoshan	12(4)	13.8	12.9	1.5	12(4)	14.9	14.6	1.2
		Laibin	28(10)	11.6	10.7	1.6	31(10)	11.8	10.7	1.7
		Tangtang	31(14)	15.2	12.8	1.9	33(14)	14.2	11.9	1.9
		Yangchang	14(6)	13.3	12.9	1.3	14(6)	13.8	13.3	1.3
Fuyuan			*85(39)*	*13.0*	*10.9†*	*1.8*	*86(38)*	*11.5*	*10.3†*	*1.7*
	Coking Coal		21(10)	10.5	9.4*	1.7	25(10)	9.8	8.8*	1.6
		Daping	9(4)	7.6	6.8	1.7	10(4)	6.6	6.0	1.5
		Enhong	7(4)	11.1	10.5	1.4	9(4)	10.8	10.4	1.4
		Haidan	5(2)	14.9	14.7	1.2	6(2)	13.5	13.1	1.4
	1/3 Coking coal		13(7)	11.1	10.4	1.4	12(7)	13.5	12.5	1.5
		Bagong	10(5)	12.2	11.6*	1.4	9(5)	14.0	13.3	1.4
		Dahe	3(2)	7.3	7.1	1.3	3(2)	11.7	10.1	2.0
	Gas fat coal		40(20)	15.6	13.2	1.7	39(19)	12.9	12.1*	1.5
		Housuo	38(19)	15.2	12.8	1.7	37(18)	12.4	11.7	1.4
		Qingyun	2(1)	23.8	23.7	1.2	2(1)	21.5	21.3	1.2
	Meagre lean	Gumu	4(2)	5.2	4.0	2.4	4(2)	3.4	3.0	1.8

*:Significant variation within designated coal subtype (ANOVA test)
†: Significant variation between smoky coal subtypes within Fuyuan (ANOVA test)
N:Number of samples
k:Number of individual subjects

Table 3 - Determinants of absorbance measurements

		Personal			Indoor		
	Reference/Background Value (Intercept)*	2.02			2.00		
Fuel Type		Estimate	95% CI	GMR	Estimate	95% CI	GMR
	Smokeless Coal (FY & XW)	Ref		1	Ref		1
	Coking Coal from North XW	0.45	0.15,0.74	1.56	0.3	0.03,0.58	1.35
	Coking Coal from South XW	0.4	-0.11,0.89	1.49	0.23	-0.31,0.77	1.26
	Coking Coal from FY	0.15	-0.16,0.47	1.17	-0.05	-0.34,0.24	0.95
	1/3 Coking coal FY	0.33	-0.11,0.76	1.39	0.4	-0.06,0.84	1.49
	Gas Fat coal FY	0.58	0.25,0.9	1.79	0.2	-0.14,0.54	1.23
	Meagre Lean coal FY	-0.09	-0.67,0.5	0.92	-0.32	-0.9,0.26	0.73
	Smoky Coal of uncertain type	0.35	-0.07,0.77	1.42	0.47	0.03,0.91	1.6
	Multiple Coal Types	0.31	0.05,0.56	1.36	0.07	-0.17,0.31	1.07
	Wood	0.8	0.48,1.11	2.22	0.51	0.21,0.81	1.67
	Plant Products	0.5	0.15,0.84	1.64	0.3	-0.03,0.62	1.35
	Multiple Fuel Types	0.39	0.16,0.62	1.48	0.21	0,0.42	1.23
Stove Design							
	Ventilated	Ref		1	Ref		1
	Unventilated	-0.11	-0.28,0.07	0.9	0.01	-0.16,0.18	1.01
	Portable Stove	-0.17	-0.35,-0.002	0.84	-0.18	-0.35,-0.01	0.84
	Mixed	-0.04	-0.17,0.1	0.96	-0.01	-0.14,0.12	0.99
	Unknown	-0.49	-0.85,-0.12	0.61	-0.2	-0.5,0.1	0.82
Presence of Stair hole							
	Present	Ref		1	Ref		1
	Absent	-0.13	-0.26,-0.01	0.88	-0.13	-0.26,-0.01	0.88
	Unknown	-0.04	-0.84, 0.75	0.96	-0.24	-1,0.52	0.79
Season							
	Autumn	Ref		1	Ref		1
	Winter	0.28	0.13,0.43	1.32	0.17	0.02,0.32	1.19
	Spring	-0.01	-0.14,0.12	0.99	-0.07	-0.2,0.05	0.93
	Summer	-0.16	-0.47,0.15	0.85	-0.26	-0.55,0.04	0.77
Variance explained (%)							
	Between Subjects/households		17			28	
	Between Villages		66			47	

*Reference value represents log transformed absorbance value for the reference model entry (smokeless coal, burnt in a stove with a chimney in a room with a stair hole attached, during Autumn)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)

Village based outdoor measurements

Village based outdoor measurements correlated moderately well with both the average indoor and personal measurements of study enrolees per village (Spearman correlation coefficients 0.43 and 0.49 respectively, $p<0.05$ for both measurement types [Figure S1 in supplemental material]). In general, village based measurements were lower than both indoor and personal measurements (median percent difference -54% [IQR: -66% to -45%] and -57% [IQR: -67% to -49%] respectively.

Village based absorbance measurements were highest among villages where smoky coal was the dominant fuel used (GM: 6.1 x $10^{-5}m^{-1}$) and lowest among smokeless coal using villages

(GM: 3.3 x $10^{-5}m^{-1}$, p value for difference <0.05, Table 4). There was no significant variation observed in outdoor absorbance measurements between the dominant stove types used by our subjects. Investigation for variation among smoky coal sources showed no significant variation in absorbance measurements. On assessment for the role of external pollutant sources, there was a weak but statistically significant correlation between the total number of pollution sources (e.g. factories, power plants) and absorbance measurements (Spearman correlation coefficient: 0.28, $p<0.05$).

Construction of a linear mixed effect model indicated that log-transformed indoor absorbance measurements, the average outdoor relative humidity and the season of measurement contributed to outdoor absorbance levels. Effect estimates (β), 95% confidence intervals and GMR's are available in Table 5.

The model explains 52% of the variance between villages and indicates that outdoor absorbance measurements are highest during winter (GMR 1.41). Increasing indoor absorbance measurements result in an increase in outdoor measurements and increasing outdoor humidity results in a decrease in outdoor absorbance measurements. The number of external pollution sources did not contribute to the final model.

Discussion

Black carbon (BC) emissions from the domestic combustion of solid fuels has important ramifications for both human health and global climate change.[15-17] This is the first study to investigate BC emissions from the combustion of solid fuels in the Chinese counties of Xuanwei and Fuyuan, where the combustion of coal is associated with multiple health complications, including the highest lung cancer rates in the nation.[1,2] Enrolees burning wood were found to have the highest personal BC exposure (16.3 x $10^{-5}m^{-1}$) followed by plant and smoky coal (12.5 and 12.0 x $10^{-5}m^{-1}$ respectively). This indicates

Table 4 - Outdoor absorbance measurements (in 10−5 m−1) by dominant fuel type† used

Fuel Type†	N(k)	AM	GM	GSD
Smoky Coal	40(15)	6.6	6.1	1.5
Smokeless Coal	14(5)	3.5	3.3*	1.4
Other‡	12(4)	4.3	4.2*	1.3

*:Significant difference when compared to Smoky coal (Tukey HSD test)
N:Number of samples
k:Number of individual villages
†: Refers to fuel used by > 50% of study enrollees per village
‡: Refers to any other combination of fuels

that BC exposure alone is likely insufficient to explain the lung cancer epidemic in the area (as smoky coal emissions, which carry the highest lung cancer risk would be expected to have the highest BC measurements). However, BC exposure in the area is still of significant public health concern as the measurements reported in the current study are high when compared to other studies. Our personal/indoor BC levels are up to 15 times higher than those measured in Western dwellings. For example, in a study investigating personal exposure to air pollution among coronary patients in Amsterdam and Helsinki, geometric means of 1.33 and 1.26 x 10^{-5} m^{-1} are reported.[33] Another study, investigating indoor exposure to black carbon in homes in the Bronx and northern Manhattan, New York during cold months reported indoor measurements of 0.97 x $10^{-5}m^{-1}$(arithmetic mean).[34]

High levels of BC are not only observed indoors. Xuanwei and Fuyuan are primarily rural areas, with less than half of enrolled villages having an identified external pollution source (e.g. a factory), but the average outdoor absorbance measurements reported in the current study (6 x 10^{-5} m^{-1}) are frequently in excess of those by a European urban roadside. For example, several large multi-centre studies exploring air pollution throughout Europe, have reported average absorbance concentrations of less than 2 x $10^{-5}m^{-1}$.[14,35]

A global strategy to mitigate the health and climate change impacts of solid fuel use has been cook-stove improvement, allowing for a more efficient use of fuel, resulting in a reduction in BC emissions[18]. In Xuanwei and Fuyuan, the installation of improved stoves has resulted in reductions in both malignant and non-malignant lung disease, which has been reflected by reductions in personal exposure to (and indoor measurement of) pollutants.[6,7,22-24,26] The finding that ventilated stoves in Xuanwei and Fuyuan do not result in significantly reduced BC emissions when compared to unventilated stoves and firepits is contrary to these previous findings. However, they mirror those reported in an Indian study.[20] who found that stoves operating without some form of forced ventilation (e.g. a fan) showed no difference in indoor BC emissions between unventilated cookstoves and those with un-forced ventilation. This indicates that, in order to properly mitigate contributions to climate change and minimize local morbidity and mortality, further stove improvements, or preferably, replacing solid fuel stoves with alternative cooking and heating sources (e.g. biogas or electric stoves) are warranted.

The reduction in BC measurements among households using portable stoves is likely a reflection of how these stoves are operated. Portable stoves are designed to be lit outdoors and only brought indoors after the initial ignition period, which is the period during which

Table 5 - Determinants of outdoor absorbance measurements

Reference/Background Value (Intercept)*		0.67	
	Estimate	95% CI	GMR
Log-transformed indoor absorbance measurement	0.44	0.23,0.64	1.55
Average outdoor humidity (%)	-0.01	-0.01,-0.001	0.99
Season			
Autumn	Ref		1
Winter	0.34	0.10,0.58	1.41
Spring/summer†	0.25	-0.010.50	1.28
Variance explained%			
Between Villages		52	

*Reference value represents log transformed absorbance value for the reference model entry (Indoor measurement(log transformed) and humidity measurements of zero, during Autumn)
GMR: = geometric mean ratio = GM(estimate)/GM(reference)=exp(Estimate)
†: Merged due to few outdoor measurements in summer

particulate emissions are maximal.[36] As the stove is moved away from the indoor measurement devices, and residents leave the stoves unattended while outdoors, it therefore follows, that BC concentrations will be lower.

We note also that one of the outputs of the mixed effect model for personal and indoor BC exposure was that homes without a stairway had lower BC measurements than homes with one. This appears counter-intuitive as it would otherwise be expected that the presence of a stairway could reduce BC measurements as a result of increasing the overall circulating volume. A possible explanation is that having a stairway is an indicator of economic status and home construction. Based upon field observations, poorer households are less likely to possess homes with stairways and are less structurally sound, resulting in increased ventilation of the rooms through structural imperfections. Socio-economic information gathered from study participants appears to support this hypothesis. Approximately 86% of people living in homes without stairways reported either having "not enough" or "just enough" food to eat, compared to 65% of people living in homes with stairways.

We note that the situation in Xuanwei and Fuyuan is unique and that the coals used in the region may not be constitutionally similar to other coals of the same rank (i.e. bituminous, anthracite) sourced in other areas. Therefore, the results of the current study may be of limited generalizability to other coal-using regions. Additionally, the attribution of specific fuel types to outdoor BC measurements needs to be interpreted with caution. While the assumption that the fuel use used by the majority of study participants is representative of fuel used as well as the stove types by the whole village is consistent with field observations, this assumption was not formally checked.

Summary and Conclusion

The emissions from the use of solid fuels in Xuanwei and Fuyuan (especially smoky coal) is related to high amounts of both malignant and non-malignant lung disease. Exposure to black carbon in the area is in excess of that seen at urban road sides in high income nations, which is of concern from both a climate change and public health perspective. The ventilated stove designs currently used in Xuanwei and Fuyuan, which have previously been associated with reduced malignant and non-malignant respiratory disease in addition to reductions in $PM_{2.5}$ and PAH emissions do not appear to be associated with reduced BC emissions, indicating that further stove improvements would be required before health and climate effects of BC production would be mitigated. As BC emissions from wood burning is greater than that of smoky coal, it is likely that even though exposure to BC is likely to be of significant public health concern, it alone is not sufficient to explain the lung cancer epidemic in the region.

Acknowledgements

This project was supported by the National Institutes of Health (HHSN261201400122P) intramural research program. The content of this publication does not necessarily reflect the views or policies of the Department of Health and Human Services, nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government. The authors would like to acknowledge Johan Beekhuizen and Meng Wang from the Institute for Risk Assessment Sciences, Utrecht University for their support in the production of figure 1.

Competing financial interests declaration

The authors declare that there is no competing financial interest in the planning, analysis or publication of this research.

References

1. Barone-Adesi, F.; Chapman, R. S.; Silverman, D. T.; He, X.; Hu, W.; Vermeulen, R.; Ning, B.; Fraumeni, J. F.,Jr; Rothman, N.; Lan, Q. Risk of lung cancer associated with domestic use of coal in Xuanwei, China: retrospective cohort study. *BMJ* 2012, 345, e5414.
2. Mumford, J. L.; He, X. Z.; Chapman, R. S.; Cao, S. R.; Harris, D. B.; Li, X. M.; Xian, Y. L.; Jiang, W. Z.; Xu, C. W.; Chuang, J. C. Lung cancer and indoor air pollution in Xuan Wei, China. *Science* 1987, 235, 217-220.
3. World Health Organization Fuel for Life: Household Energy And Health; World Health Organization: Geneva, 2006.
4. Chapman, R. S.; Mumford, J. L.; Harris, D. B.; He, Z. Z.; Jiang, W. Z.; Yang, R. D. The epidemiology of lung cancer in Xuan Wei, China: current progress, issues, and research strategies. Arch. Environ. Health 1988, 43, 180-185.
5. He, X. Z.; Chen, W.; Liu, Z. Y.; Chapman, 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 Perspect. 1991, 94, 9-13.
6. Hu, W.; Downward, G.; Reiss, B.; Rothman, N.; Xu, J.; Bassig, B.; Hosgood, D.; Zhang, L.; Wu, G.; Chapman, R.; Wei, F.; Lan, Q.; Vermeulen, R. Personal and indoor fine particulate matter exposure from vented and unvented stoves in Xuanwei and Fuyuan county, China. Environ Sci Technol 2014, 48, 8456-64.
7. Downward, G. S.; Hu, W.; Reiss, B.; Rothman, N.; Wu, G.; Wei, F.; Chapman, R. S.; Portengen, L.; Lan, Q.; Vermeulen, R. Polycyclic Aromatic Hydrocarbon exposure in household air pollution from solid fuel combustion among the female population of Xuanwei and Fuyuan counties, China. Environ. Sci. Technol. 2014.
8. Bond, T. C.; Streets, D. G.; Yarber, K. F.; Nelson, S. M.; Woo, J.; Klimont, Z. A technology-based global inventory of black and organic carbon emissions from combustion. Journal of Geophysical Research: Atmospheres 2004, 109, - D14203.
9. Grahame, T. J.; Klemm, R.; Schlesinger, R. B. Public health and components of particulate matter: The changing assessment of black carbon. J. Air Waste Manage. Assoc. 2014, 64, 620 - 660.
10. Janssen, N. A.; Hoek, G.; Simic-Lawson, M.; Fischer, P.; van Bree, L.; ten Brink, H.; Keuken, M.; Atkinson, R. W.; Anderson, H. R.; Brunekreef, B.; Cassee, F. R. Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM_{10} and $PM_{2.5}$. Environ. Health Perspect. 2011, 119, 1691-1699.
11. Baumgartner, J.; Zhang, Y.; Schauer, J. J.; Huang, W.; Wang, Y.; Ezzati, M. Highway proximity and black carbon from cookstoves as a risk factor for higher blood pressure in rural China. Proceedings of the National Academy of Sciences 2014, 111, 13229-13234.
12. Krämer, U.; Herder, C.; Sugiri, D.; Strassburger, K.; Schikowski, T.; Ranft, U.; Rathmann, W. Traffic-Related Air Pollution and Incident Type 2 Diabetes: Results from the SALIA Cohort Study. Environ. Health Perspect. 2010, 118, 1273-1279.
13. Macintyre, E. A.; Gehring, U.; Molter, A.; Fuertes, E.; Klumper, C.; Kramer, U.; Quass, U.; Hoffmann, B.; Gascon, M.; Brunekreef, B.; Koppelman, G. H.; Beelen, R.; Hoek, G.; Birk, M.; de Jongste, J. C.; Smit, H.; Cyrys, J.; Gruzieva, O.; Korek, M.; Bergstrom, A.; Agius, R. M.; de Vocht, F.; Simpson, A.; Porta, D.; Forastiere, F.; Badaloni, C.; Cesaroni, G.; Esplugues, A.; Fernandez-Somoano, A.; Lerxundi, A.; Sunyer, J.; Cirach, M.; Nieuwenhuijsen, M. J.; Pershagen, G.; Heinrich, J. Air Pollution and Respiratory Infections during Early Childhood: An Analysis of 10 European Birth Cohorts within the ESCAPE Project. Environ. Health Perspect. 2013.
14. Eeftens, M.; Tsai, M.; Ampe, C.; Anwander, B.; Beelen, R.; Bellander, T.; Cesaroni, G.; Cirach, M.; Cyrys, J.; de Hoogh, K.; De Nazelle, A.; de Vocht, F.; Declercq, C.; Dedele, A.; Eriksen, K.; Galassi, C.; Gražuleviciene, R.; Grivas, G.; Heinrich, J.; Hoffmann, B.; Iakovides, M.; Ineichen, A.; Katsouyanni, K.; Korek, M.; Krämer, U.; Kuhlbusch, T.; Lanki, T.; Madsen, C.; Meliefste, K.; Mölter, A.; Mosler, G.; Nieuwenhuijsen, M.; Oldenwening, M.; Pennanen, A.; Probst-Hensch, N.; Quass, U.; Raaschou-Nielsen, O.; Ranzi, A.; Stephanou, E.; Sugiri, D.; Udvardy, O.; Vaskövi, É; Weinmayr, G.; Brunekreef, B.; Hoek, G. Spatial variation of $PM_{2.5}$, PM_{10}, $PM_{2.5}$ absorbance and

PMcoarse concentrations between and within 20 European study areas and the relationship with NO2 – Results of the ESCAPE project. Atmos. Environ. 2012, 62, 303-317.
15. Schmidt, C. W. Black carbon: the dark horse of climate change drivers. Environ. Health Perspect. 2011, 119, A172-5.
16. Martin, W. J.,II; Hollingsworth, J. W.; Ramanathan, V. In Chapter 13, Household Air Pollution from Cookstoves: Impacts on Health and Climate; Pinkerton, K. E., Rom, W. N., Eds.; Global Climate Change and Public Health, Springer Science+Business Media: New York, 2014; .
17. Anenberg, S. Technology: Clean stoves benefit climate and health. Nature 2012, 490, 343.
18. United Nations Environment Programme and World Meteorological Organization Integrated Assessment of Black Carbon and Tropospheric Ozone. 2011.
19. Bond, T. C.; Doherty, S. J.; Fahey, D. W.; Forster, P. M.; Berntsen, T.; DeAngelo, B. J.; Flanner, M. G.; Ghan, S.; Kärcher, B.; Koch, D.; Kinne, S.; Kondo, Y.; Quinn, P. K.; Sarofim, M. C.; Schultz, M. G.; Schulz, M.; Venkataraman, C.; Zhang, H.; Zhang, S.; Bellouin, N.; Guttikunda, S. K.; Hopke, P. K.; Jacobson, M. Z.; Kaiser, J. W.; Klimont, Z.; Lohmann, U.; Schwarz, J. P.; Shindell, D.; Storelvmo, T.; Warren, S. G.; Zender, C. S. Bounding the role of black carbon in the climate system: A scientific assessment. Journal of Geophysical Research: Atmospheres 2013, 118, 5380-5552.
20. Kar, A.; Rehman, I. H.; Burney, J.; Puppala, S. P.; Suresh, R.; Singh, L.; Singh, V. K.; Ahmed, T.; Ramanathan, N.; Ramanathan, V. Real-time assessment of black carbon pollution in Indian households due to traditional and improved biomass cookstoves. Environ. Sci. Technol. 2012, 46, 2993-3000.
21. Tian, L.; Lan, Q.; Yang, D.; He, X.; Yu, I. T. S.; Hammond, S. K. Effect of chimneys on indoor air concentrations of PM_{10} and benzo[a]pyrene in Xuan Wei, China. Atmos. Environ. 2009, 43, 3352-3355.
22. Chapman, R. S.; He, X.; Blair, A. E.; Lan, Q. Improvement in household stoves and risk of chronic obstructive pulmonary disease in Xuanwei, China: retrospective cohort study. BMJ 2005, 331, 1050.
23. Hosgood, H. D.,3rd; Chapman, R.; Shen, M.; Blair, A.; Chen, E.; Zheng, T.; Lee, K. M.; He, X.; Lan, Q. Portable stove use is associated with lower lung cancer mortality risk in lifetime smoky coal users. Br. J. Cancer 2008, 99, 1934-1939.
24. Shen, M.; Chapman, R. S.; Vermeulen, R.; Tian, L.; Zheng, T.; Chen, B. E.; Engels, E. A.; He, X.; Blair, A.; Lan, Q. Coal use, stove improvement, and adult pneumonia mortality in Xuanwei, China: a retrospective cohort study. Environ. Health Perspect. 2009, 117, 261-266.
25. Lee, K. M.; Chapman, R. S.; Shen, M.; Lubin, J. H.; Silverman, D. T.; He, X.; Hosgood, H. D.,3rd; Chen, B. E.; Rajaraman, P.; Caporaso, N. E.; Fraumeni, J. F.,Jr; Blair, A.; Lan, Q. Differential effects of smoking on lung cancer mortality before and after household stove improvement in Xuanwei, China. Br. J. Cancer 2010, 103, 727-729.
26. 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.
27. Downward, G. S.; Hu, W.; Large, D.; Veld, H.; Xu, J.; Reiss, B.; Wu, G.; Wei, F.; Chapman, R. S.; Rothman, N.; Qing, L.; Vermeulen, R. Heterogeneity in coal composition and implications for lung cancer risk in Xuanwei and Fuyuan counties, China. Environ. Int. 2014, 68, 94-104.
28. Chen, P. Study on integrated classification system for Chinese coal. Fuel Process Technol 2000, 62, 77-87.
29. Cyrys, J.; Heinrich, J.; Hoek, G.; Meliefste, K.; Lewné, M.; Gehring, U.; Bellander, T.; Fischer, P.; Vliet, P. v.; Brauer, M.; Wichmann, H.; Brunekreef, B. Comparison between different traffic-related particle indicators: Elemental carbon (EC), $PM_{2.5}$ mass, and absorbance. J. Expo. Anal. Environ. Epidemiol. 2003, 13, 134 -143.
30. ISO ISO 9835: Ambient air — determination of a black smoke index. 1993.
31. R Development Core Team R: A Language and Environment for Statistical Computing. 2014.
32. Bates, D.; Maechler, M.; Bolker, B.; Walker, S. lme4: Linear mixed-effects models using Eigen and S4. 2014.

33. Lanki, T.; Ahokas, A.; Alm, S.; Janssen, N. A. H.; Hoek, G.; De Hartog, J. J.; Brunekreef, B.; Pekkanen, J. Determinants of personal and indoor $PM_{2.5}$ and absorbance among elderly subjects with coronary heart disease. Journal of Exposure Science and Environmental Epidemiology 2007, 17, 124-133.
34. Jung, K. H.; Patel, M. M.; Moors, K.; Kinney, P. L.; Chillrud, S. N.; Whyatt, R.; Hoepner, L.; Garfinkel, R.; Yan, B.; Ross, J.; Camann, D.; Perera, F. P.; Miller, R. L. Effects of Heating Season on Residential Indoor and Outdoor Polycyclic Aromatic Hydrocarbons, Black Carbon, and Particulate Matter in an Urban Birth Cohort. Atmos. Environ. (1994) 2010, 44, 4545-4552.
35. Durant, J. L.; Beelen, R.; Eeftens, M.; Meliefste, K.; Cyrys, J.; Heinrich, J.; Bellander, T.; Lewné, M.; Brunekreef, B.; Hoek, G. Comparison of ambient airborne $PM_{2.5}$, $PM_{2.5}$ absorbance and nitrogen dioxide ratios measured in 1999 and 2009 in three areas in Europe. Sci. Total Environ. 2014, 487, 290-298.
36. Hosgood, H. D.; Lan, Q.; Vermeulen, R.; Wei, H.; Reiss, B.; Coble, J.; Wei, F.; Jun, X.; Wu, G.; Rothman, N. Combustion-derived nanoparticle exposure and household solid fuel use in Xuanwei and Fuyuan, China. Int. J. Environ. Health Res. 2012, 22, 571-581.

Chapter 6

Appendix – Supporting information : Outdoor, indoor, and personal black carbon exposure from cookstoves burning solid fuels

(Submitted paper)

Table S1 - Variables considered for inclusion in mixed effect model creation

Broad Category	Detailed variables
Stove design	**Stove ventilation (ventilated, unventilated, mixed, portable stove or firepit)**
	Stove ventilated, unventilated or mixed ventilation*
	Stove ventilated, unventilated mixed or firepit
	Stove either firepit or other design (or mixed)
	Stove design as reported by study participant£
Fuel type/source	**Major fuel type including smoky coal subtypes and county from which coal sourced (Fuyuan was divided into north/south)**
	County from which fuel purchased
	Broad fuel types (smoky coal, smokeless coal, "mixed" coal, wood, plant materials, "mixed" fuels)
	Fuel type including smoky coal subtypes
	Fuel type including individual smoky coal mines
	Fuel type including smoky coal subtypes
	Weight of fuel used†
Meteorological conditions	**Season of measurement**
	Average daily temperature
	Average daily high temperature
	Average daily low temperature
	Average daily humidity
	Average daily wind speed
	Average daily maximum wind speed
	Average daily dew point
	Average daily rainfall
Other variables	Room size†
	Phase of study during visit
	Number of owned stoves
	Number of doors in main cooking room
	Number of windows in main cooking room
	Presence or absence of a stairway in the main cooking room
	Hours of stove use standardized by number of used stoves
	Hours of stove use per measurement period
	Age of participant
	Month of visit
	Number of hours of stove operation
	Number of hours of stove operation per stove

*refers to the use of multiple stoves with different ventilation designs.
£categories are high stove, low stove (with or without ventilation), portable stove, firepit and multiple stoves.
†divided into quartiles.
Variables in bold were selected for model construction.

Table S2 - Determinants of the differences between personal and indoor measurements

		Estimate (β)	95%CI	GMR[‡]
Ln(indoor absorbance measurement)		0.54	0.47,0.61	1.72
Average daily temperature		-0.01	-0.02,-0.001	0.99
Burning time per stove[¥]		0.01	0.001,0.02	1.01
Weight of fuel (in quartiles)				
	1st quartile	Ref.		1.00
	2nd quartile	0.05	-0.09,0.2	1.06
	3rd quartile	0.17	0.02,0.32	1.18
	4th quartile	0.17	0.01,0.32	1.18
	Unknown	0.22	0.04,0.39	1.24
Variance explained*				
	Between subjects		0%	
	Between villages		100%	
Reference value[†] (ln personal measurement), ln-μg/m^3			2.28	

[‡]Geometric mean ratio = GM(estimate)/GM(reference) = exp(β).
[¥]Total hours spent using a stove, standardized by the number of stoves owned
[†]Reference value represents base value of ln-transformed absorbance in model for reference group [low weight fuel used coinciding with lowest ln-transformed indoor absorbance (-0.44), temperature (-0.4°C) and stove usage (0.5hrs) recorded.
*As a result of the high correlation between indoor and personal measurements, no additional variance between subjects was explained, however, all remaining residual variance between villages was explained

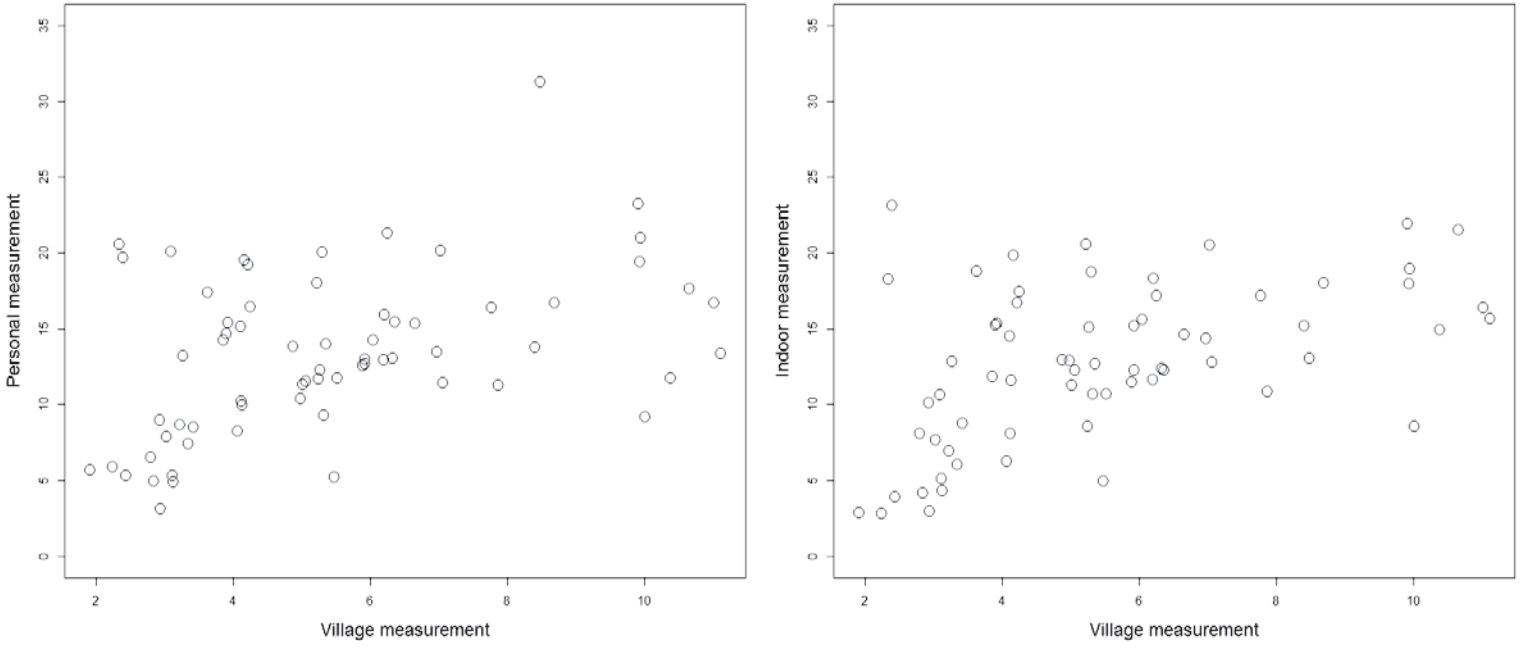

Figure S1 - Scatter plot showing relationship between average personal (left) and average indoor (right) measurements with village based measurements (all measurements in $10^{-5}m^{-1}$)

Chapter 7

General Discussion

The lung cancer epidemic in Xuanwei and Fuyuan, China is primarily caused by the domestic combustion of smoky coal.[1-5] Previous research has implicated two potential carcinogens identified within the constituents of household air pollution (HAP) caused by smoky coal: polycyclic aromatic hydrocarbons (PAHs) and quartz.[2,6-9] However, owing to small sample sizes and limited scope, the ability to clearly link these findings to cancer risk are limited. The purpose of this thesis has been to catalogue the constituents of solid fuels and their associated HAP in Xuanwei and Fuyuan. This is the largest exposure assessment carried out in the area to date and has been performed using a multi-modal analysis of fuel, air and ash samples. The findings presented in this thesis have direct implications to the hypotheses regarding lung cancer risk and the use of solid fuels, both locally and internationally. These findings will ultimately be applied to future epidemiological studies including a large case-control study of biological effect markers and lung cancer in the area.

Implications for the current carcinogenic hypotheses

As stated above, two potential carcinogenic compounds in smoky coal and its emissions have been implicated as potential causative factors in the lung cancer epidemic in Xuanwei and Fuyuan: PAHs and quartz. While the analyses presented in this thesis are purely exploratory and have not directly related their findings to specific cancer risks, there are several inferences, based upon what is already known regarding lung cancer epidemiology in the region, which will allow for a limited assessment of these carcinogenic hypotheses. First, it is reasonable to expect that measured values of any component which may be related to lung cancer risk in the area will be higher among samples collected from households using smoky coal (as this is the fuel type directly associated to the lung cancer risk). Second, in order to parallel the reduction in lung cancer rates following stove improvements,[10-13] we would expect measurements taken in the setting of ventilated stoves to be lower than those taken in the setting of unventilated stoves and firepits. Finally, to parallel the observed geographic variation in lung cancer rates among smoky coal users,[14] we would expect geographic variation in the characteristics of potential carcinogenic agents within smoky coal subtypes.

The PAH hypothesis

The PAH hypothesis considers exposure to polycyclic aromatic hydrocarbons (PAHs) from smoky coal combustion as the primary cause of the lung cancer epidemic in Xuanwei and Fuyuan. Previous research has reported that the emissions of smoky coal contain relatively high amounts of PAHs, including Benzo[a]pyrene (BaP), when compared to smokeless coal.[6] Research has also identified some degree of regional variation in PAH emission[15] and that the use of ventilated stoves resulted in reduced BaP emissions.[16] However, this research was limited in that it typically had a very small number of households and samples (max n=48) and would generally focus upon either fuel type, stove design, or geographic location, without investigating the inter-relationship between these factors.

Some of the findings of this thesis appear to support the PAH hypothesis. From a geochemical perspective, smoky and smokeless coal represent coals of different ranks (bituminous and anthracite respectively). One of the consequences of this rank difference is that bituminous coal generally contains higher amounts of volatile organic matter (including PAHs) than anthracite coals.[17,18] In Chapter 2, we investigate the constituents of smoky and smokeless coal and observe a clear demarcation in geochemical parameters (S1 - hydrocarbon generation during controlled pyrolysis at 300 degrees Celsius, S2 - hydrocarbon generation during programmed pyrolysis from 300 to 600 degrees Celsius

[heating at a rate of 25 degrees per minute], and Tmax, the temperature at which maximal hydrocarbon generation occurs) between smoky and smokeless coal. We also observe that the volatile organic components (approximated with the S1 and S2 values) within smoky coal are up to eight times higher than those of smokeless coal. While this measurement does not exclusively represent PAH content, it strongly suggests that smoky coal contains a higher amount of volatile organic components, including PAHs than smokeless coal. This assertion is supported by the findings presented in Chapter 4, a presentation of PAH measurements from the combustion of a variety of fuel types. In this chapter we find that particle phase PAH emissions (i.e. those of higher molecular weight) are up to 6 times higher in smoky coal burning homes when compared to those burning smokeless coal. As discussed in Chapter 4, wood burning homes also appear to be associated with high PAH emissions but this is largely a feature of inefficient burning in particular stove designs. This particular finding was used in the construction of mixed effect models wherein households burning wood were treated as if they were using firepits. This allowed us to more accurately represent the role that stove design has in exposure related to coal combustion (i.e. reduced PAH measurements in homes burning coal in ventilated stoves when compared to unventilated stoves and firepits). The finding of geographic variation in PAH measurements between differing smoky coal sources is also of interest as this parallels the geographic variation in lung cancer rates. However, this relationship is only indirect thus far, and no etiological analysis comparing our PAH measurements to cancer epidemiology has yet been performed

It is possible to assess the relationship between the hydrocarbon content reported in Chapter 2 and the PAH content reported in Chapter 4. Using BaP as an example, we observe that there is a positive correlation between the S1 and S2 values in coal samples and indoor BaP measurements among homes using either unventilated stoves or firepits (Spearman correlation coefficient = 0.6 for S1 and 0.57 for S2, n=9), which supports the previous assertion that S1 and S2 could be used to indicate differing amounts of PAH content. The correlation is no longer apparent in the setting of ventilated stoves (0.25 for S1 and -0.21 for S2, n=36), which may be an indication of variation in the effectiveness of differing stoves resulting in varying amounts of emission products being vented outdoors.

Although much of the information presented thus far appears to support the PAH hypothesis, the degree of lung cancer risk attributable to smoky coal is higher than what is usually attributable to even extreme amounts of PAH exposure. Research investigating lung cancer among people employed in industries with high levels of PAH exposure (e.g. coke oven and factory workers - many of whom are often exposed to PAH levels similar to, or in excess of those reported in this thesis) found a maximum relative risk estimate of approximately 3.[8,19-21] Armstrong and Gibbs[19] calculated an exposure response relationship between BaP exposure and lung cancer risk and found a relative risk of 2.68 for lung cancer per 100 $\mu g/m^3$BaP years (i.e. cumulative lifetime occupational exposure to BaP) when compared to those with negligible BaP exposure. In Xuanwei and Fuyuan, lung cancer risk is typically calculated relative to smokeless coal use. The exposure difference between those burning smoky coal in firepits (i.e. those we would expect to be at high risk – geometric mean 0.15 $\mu g/m^3$) and those burning smokeless coal in ventilated stoves (i.e. low risk – geometric mean 0.0055$\mu g/m^3$) is 0.1445$\mu g/m^3$. Over a period of 56 years (the mean age of lung cancer diagnose in our sample population) this equates to a cumulative exposure of approximately 8 $\mu g/m^3$BaP years. The exposure response interaction reported by Armstrong and Gibbs was however based upon occupational exposure, which only

occurs during working hours while the values reported in this thesis represent constant exposure, requiring us to convert exposure occurring 24 hours a day, 365 days a year, to the equivalent dose that one would get when exposure only occurs 8 hours a day (multiply by 3), for 220 days a year (multiply by 1.7):

0.1445 x 56 x 3 x 1.7 = 41μg/m^3 BaP years.

This estimate corresponds to a relative risk of 2.3 which is lower than the odds ratio of 7.4 (95% CI: 4.1 - 13.1) reported by Lan et. al. in their comparison of lung cancer risk between smoky and smokeless coal users.[14] This suggests that PAH exposure alone may explain some, but not all, of the lung cancer risk in the area. It should be noted that there are some limitations to the estimated relative risk derived here.

It is unclear how reliable such an approach is and therefore, the relative risk may not be a full representation of the true underlying risk. Further, this calculation is for BaP exposure alone and the mixture of PAHs experienced in occupational settings is likely to differ from that experienced in HAP, possibly leading to differing cancer risks. An additional consideration is that the age at which exposure first occurs is different between those who are occupationally exposed and those exposed in their residences. There is evidence to suggest that exposure to PAHs and other air pollutants (e.g. car exhaust) at earlier stages in life results in increased risks of malignancy at later stages in life.[22,23] Additionally, prenatal exposure to PAHs has been associated with post-natal lung dysfunction, growth retardation, and chromosomal aberrations which may predispose for future malignancies.[24-27]

The quartz hypothesis

The quartz hypothesis asserts that exposure to quartz from smoky coal combustion is responsible for the lung cancer epidemic in the area. The evidence to support this hypothesis stems largely from findings of increased quartz in uncombusted smoky coal.[28,29] Further evidence comes from a finding of a positive correlation between estimated quartz content in smoky coal emissions and lung cancer rates in Xuanwei and autopsy findings which report silica crystals in the tumour tissues of smoky coal users.[7] However, this research faces similar limitations to those discussed for the PAH hypothesis. The report of lung tissues from autopsy cases lacks controls (i.e. people not exposed to smoky coal) while in the studies of quartz in coal, comparisons to smokeless coal are often lacking. In the cases where comparisons to smokeless coal are available, sample sizes of coal specimens are limited (max n = 15). Finally, the finding of a positive correlation between lung cancer rates and quartz in air pollution depends upon estimating quartz concentrations, has a very small sample size (n= 15), and relies upon not including smokeless coal samples in the correlation equation. In this thesis, Chapter 2 reports that the total and respirable quartz content of smoky coal (4.58% and 1.93% respectively) was higher than that observed for smokeless coal (2.24% and 0.60%). This finding is consistent with previous reports and adds to the evidence base that quartz is present in higher amounts in smoky coal than in smokeless coal. Additionally, variation in quartz content is observed between the various smoky coal subtypes, although this variation did not reach statistical significance, which may be due to insufficient numbers. It is also possible to use the ratio of aluminium and silicon identified within the coal samples to provide an estimate of quartz content. This estimate correlates moderately well with the measured quartz values (Spearman correlation: 0.6) and shows a similar relative difference in quartz content between smoky (11%) and smokeless (5.8%) coals to what was observed in direct mineralogical analysis. Evaluating

the estimated quartz for regional variation found that significant variation was observed between smoky coal subtypes and sources.

Although elevated quartz is observed in smoky coal, this does not correspond to elevated levels of airborne quartz. In Chapter 5, we explore the fate of quartz from coal to air and ash. In this chapter airborne quartz is largely undetectable in HAP samples (non-detect rate 89%, LOD: 0.2μg/m^3). The most likely fate of quartz in coal if it is not becoming airborne during combustion, is that it is going on to form part of the ash. Analysis of ash samples shows similar levels of respirable quartz in ash formed by smoky and smokeless coal. When the total quartz in ash is evaluated however, we find that the amount in smoky coal ash (28.3%) is 8 times higher than that in smokeless coal ash (3.3%). This supports the assertion that the quartz in coal contributes directly to ash. This assertion is further supported by the finding of a positive correlation between quartz in coal and ash (Spearman coefficient 0.79 between total quartz in coal and total quartz in ash). This raises the possibility of an alternative exposure route as ash is handled during both stove cleaning and planting of crops. However, because we observed no difference in the ash levels of respirable quartz between smoky and smokeless coal, there is unlikely to be meaningful exposure during cleaning or crop fertilizing. Additionally, the pattern of lung cancer (disproportionately affecting women) does not match the pattern of crop work (performed by both men and women).

Unpublished findings which may influence quartz hypothesis

Unpublished results, investigating the elemental composition of both personal and indoor air pollution measurements provides an additional avenue to explore quartz exposure. These findings will be discussed in greater detail later in this chapter, but of relevance to quartz exposure, we estimated quartz concentrations through the use of an assumed ratio between silicon and aluminium in air measurements. Silicon (Si), aluminium (Al), and other elements had their composition determined using energy dispersive x-ray spectrometer (EDXRF) on 37mm Teflon filters collected from residents and households (120 personal measurements and 54 indoor measurements). The following formula was used to estimate quartz content, in a manner intended to be comparable to previous estimations of quartz in air.[7]

Quartz(est)= 2.1392xSi-(0.39x(1.8895xAl))

An overview for the values of estimated quartz are available in Tables 1 and 2. The geometric mean of the estimated quartz value for smoky coal (1.99μg/m^3) is less than that observed for both smokeless coal and wood burning homes (GM 3.49μg/m^3 and 4.13μg/m^3 respectively), although these differences did not reach statistical significance. Subjects burning smoky and smokeless coal in unventilated stoves had higher levels of estimated quartz (GM 6.44μg/m^3 and 9.53μg/m^3 respectively) than subjects using ventilated stoves (GM 2.01μg/m^3 and 2.54μg/m^3 respectively), however there are relatively few measurements from unventilated stoves and these differences failed to reach statistical significance. On investigation for variation between smoky coal sources, significant variation in estimated quartz values was observed within the coking coal subtype sourced from within Xuanwei (range 0.66 g/m^3 for coal from Yangchang mine to 5.84μg/m^3 for coal from Laibin mine).

The finding of higher amounts of estimated quartz in the emissions of smokeless coal than smoky coal is consistent with previous use of this estimation. However, when comparing estimated quartz values to measured values, we find that there is a very poor correlation

between estimated and measured quartz measurements (Spearman correlation coefficient of -0.04, n=147) which worsens if we restrict to only samples with detectable quartz (-0.66, n=15). This poor relationship between estimated and measured quartz calls into question the reliability of using this method of estimation of airborne quartz to implicate lung cancer risk in Xuanwei.

Further possibilities for quartz

It has been proposed that a synergistic relationship between quartz and volatile components (specifically PAHs) may be responsible for the excess lung cancer.[28] This proposition is based upon the finding of a positive correlation between the "Potential for silica-volatile interaction" (PSVI) and lung cancer mortality. The PSVI is defined as a function of the amount of volatiles (per mJ) times the amount of free silica (per mJ) in coal samples. This positive correlation (0.661) was higher than that which the researchers observed for silica (0.533) and volatile components alone (-0.055). In the context of the previously discussed

Table 1 - Estimated personal exposure to quartz by fuel type ($\mu g/m^3$)

		Estimated Quartz		
	N	AM	GM	GSD
Smoky Coal	60	2.98	1.99	2.89
Smokeless Coal	15	5.54	3.49	3.08
Other Coal	13	2.33	1.38	5.21
Wood	6	5.01	4.13	2.01
Plant	5	2.63	1.98	2.74
Other Fuel	20	3.5	2.7	2.18

Table 2 - Estimated personal exposure to quartz by smoky coal source ($\mu g/m^3$)

		Estimated Quartz			
		N	AM	GM	GSD
Xuanwei (coking)		**35**	**3.35**	**2.04***	**3.47**
	Azhi	10	3.25	1.89	2.77
	Baoshan	3	1.65	1.54	1.55
	Laibin	6	7.19	5.84	2.21
	Tangtang	11	2.53	2.22	1.76
	Yangchang	5	1.75	0.66	11.03
Fuyuan		**24**	**2.31**	**1.83**	**2.07**
Coking		*5*	*3.37*	*2.19*	*3.18*
	Daping	2	1.19	0.89	3.05
	Enhong	2	3.66	2.97	2.57
	Haidan	1	7.16	7.16	-
1/3 coking		*4*	*1.69*	*1.27*	*2.27*
	Bagong	3	0.89	0.86	1.37
	Dahe	1	4.09	4.09	-
Gas Fat		*13*	*2.29*	*2.19*	*1.38*
	Housuo	12	2.27	2.16	1.4
	Qingyun	1	2.56	2.56	-
Meager Lean (Gumu)		*2*	*0.96*	*0.77*	*2.66*

* - Significant variation between coal mines within smoky coal subtype (ANOVA)

relationship between estimated quartz in smoky coal emissions and lung cancer rates, this synergistic relationship would provide some explanation for the positive relationship between estimated quartz in smoky coal emissions and lung cancer rates despite similar estimated levels in smokeless coal emissions and a lack of relationship between smokeless coal emissions and lung cancer rates. However, as already stated, very little airborne quartz is detectable in our population, meaning that the potential for any meaningful interaction is very low. Further, other research, investigating the potential interaction between silica exposure, smoking and lung cancer[30] found no synergistic (or antagonistic) effect of the two, suggesting that an interaction between PAHs and silica may be unlikely.

A further possibility is that differences in the levels of quartz below the limit of detection used in Chapter 5 (0.2μg/m^3) may provide further insight regarding lung cancer risk in the area. This possibility is briefly explored in Appendix 2 for Chapter 5 where, using scanning electron microscopy we compare quartz measurements in indoor air from households using smoky and smokeless coal. This analysis finds that there are differences in quartz concentrations between smoky and smokeless coal (median values 0.27 and 0.03μg/m^3 respectively) but that the measured levels are frequently below the limit of detection for the analysis presented in Chapter 5 (all samples from smokeless coal burning homes and 50% from smoky coal homes are below 0.2 μg/m^3). This finding of increased quartz in smoky coal burning households compared to smokeless coal households is the opposite to what would be expected using the previously outlined method for estimating quartz emissions,[7] further calling into question the reliability of such a technique in Xuanwei and Fuyuan. In terms of the potential lung cancer risk attributable to the observed exposures, Steenland et. al, in a pooled exposure analysis of 10 cohorts of silica exposed workers reported a linear exposure-response relationship between silica exposure and lung cancer risk.[31] In this analysis they reported an odds ratio of 1.6 (95% confidence interval: 1.3 - 2.1) for their highest exposed groups of workers, who had a lifetime exposure to silica of greater than 12.8mg/m^3 years. In contrast, using the highest quartz value measured in this thesis (1.1μg/m^3 - gathered from a smoky coal burning home) and treating that as though it were the "typical" quartz exposure for Xuanwei and Fuyuan, then over a course of 56 years, this would equate to 314μg/m^3 years (0.314mg/m^3 years), which falls into the reference category for lung cancer risk assignment (i.e. odds ratio of 1). This calculation faces similar limitations to those already outlined for the calculation of lifetime exposure to BaP, in that exposures experienced 24 hours a day, 365 days a year, had to be converted into equivalent values for 8 hours a day, 220 days a year. The possibility of differences in the physical structure of quartz was also explored, but no difference in the structure of quartz between smoky and smokeless coal burning homes was observed. An additional finding of interest is the observation of fibre-like materials which are present in higher amounts in smoky coal burning homes than smokeless coal burning homes (mean values: 5800 fibres/m^3 and 550 fibres/m^3 respectively). While these materials did meet the definition of fibre (particles with a length greater than 5μm, a diameter less than 3μm, and a length:diameter ratio greater than 3) they did not have a uniform shape or elemental composition. Thus it is unclear as to what (if any) significance this finding has beyond re-affirming our previous finding of higher indoor concentrations of particulate matter among smoky coal burning homes than smokeless.

Additional possibilities

The findings presented thus far appear to refute the quartz hypothesis while moderately supporting the PAH hypothesis, however it is important to note that this does not make the

PAH hypothesis automatically correct. The bulk of the research in Xuanwei and Fuyuan has focused upon identifying smoky coal use and its association with lung cancer rate. Prior to this thesis, exposure assessments were relatively small and had focussed upon only a few pollutants. There are multiple additional pollutants and sources of exposure which have not yet been assessed that may yet yield additional insights. For example: nitrated PAH species (nitro-PAHs), which have not been tested for in this thesis, have been implicated in general lung cancer risk[32] and have been identified in other rural households in China.[33] Methylated PAHs, which were also not assessed in this thesis have been observed in Xuanwei at a level of 4.8 times that of their parent species.[34] There has been some (albeit limited) evidence that free radicals (a molecular species capable of independent existence containing an unpaired electron in an atomic orbital) are present in the emissions of smoky coal to a greater extent than they are in smokeless coal,[7] which by various mechanisms (e.g. oxidative stress, pro-inflammatory states) may result in carcinogenicity.[35] An additional source of exposure which has not been given any previous consideration is soil. It is a common practise for Xuanwei and Fuyuan residents to mix their coal with dirt and clay in an effort to extend the life of the coal. Nothing is known regarding the constitution of soil in the area, nor if those constituents play any active role in carcinogenesis.

A further possibility, not directly related to fuel use is that differences in the microbiome may contribute to lung cancer risk. In a small case control study (n=16) of lung cancer among never smokers in Xuanwei, Hosgood et. al.[36] reported that the diversity of bacterial species in sputum collected from lung cancer cases was significantly different to that of the never smoking controls. While it is possible that this difference in bacterial diversity may be due by the same HAP exposure which contributes to lung cancer risk, it was also postulated that differences in the microbiome may contribute to different abilities to metabolize pollutants in the host, leading to differing lung cancer risks. Further to this is the possibility of zoonotic infection. It is a frequent practise in Xuanwei and Fuyuan to keep livestock (typically pigs and chickens) indoors, typically in the main living area. A meta-analysis of 60 studies investigating lung cancer risk among workers in the meat and poultry industry found a 30% excess risk of lung cancer among meat and poultry workers after adjusting for smoking status.[37] The studies reviewed included both the care of live animals and the handling of animal carcasses indicating that exposure to the animals themselves play some role in carcinogenesis, suggesting the presence of some zoonotic infection (the meta-analysis also identified an increased lung cancer risk associated with the wrapping of meat prior to shipping or sales, which was considered due to fumes from wrapping material and separate from the zoonotic based carcinogenesis). There are several candidate oncogenic infectious agents, including human and animal papilloma viruses. The close proximity of Xuanwei and Fuyuan residents to their livestock make zoonotic infections a likely occurrence. These infections may in turn play some role in lung cancer risk.

While we are not presently actively advocating either of these possibilities as factors of importance in Xuanwei and Fuyuan, they have been raised to highlight that there are still aspects of exposure in the area that are largely unknown.

Additional Findings

This thesis has also presented findings which do not directly relate to either of the main carcinogenesis hypotheses. In Chapter 3 we investigate indoor concentrations of particulate matter ($PM_{2.5}$) from solid fuels in the area. $PM_{2.5}$ is a heterogeneous mixture of various materials containing both organic and non-organic components. Globally, exposure to

$PM_{2.5}$ is associated with a variety of illnesses including cardiovascular diseases and lung cancer.[38,39] This chapter reported that concentrations of $PM_{2.5}$ among smoky coal burning households were approximately 1.3 times higher than those from smokeless coal households but indicate that it is unlikely that the lung cancer epidemic can be solely explained by exposure to $PM_{2.5}$. The major reason for this assertion is that $PM_{2.5}$ measurements from wood burning homes were approximately twice that of smoky coal and three times that of smokeless coal burning homes, which is inconsistent with the observed lung cancer epidemiology in the region. An additional finding of importance in this chapter is the role of stove design in $PM_{2.5}$ exposure. In the mixed effect model, we observed that stoves without ventilation were associated with $PM_{2.5}$ concentrations that were approximately 1.5 times higher than ventilated stoves. Despite our conclusion that $PM_{2.5}$ is unlikely to be the sole driver of lung cancer in the region, $PM_{2.5}$ exposure is still associated with increased risks of both malignant and non-malignant disease in general. Therefore, any findings which indicate reductions in $PM_{2.5}$ exposure represent important public health findings.

The intersection between solid fuel use, health effects and climate change is explored in Chapter 6. Black Carbon (BC) is an important driver of both human morbidity and mortality in addition to climate change.[40-44] In this chapter we identify that BC emissions from smoky coal are greater than those from smokeless coal, but, similarly to what is observed in Chapter 3, the burning of wood contributes to emissions higher than smoky coal. To some degree, this finding is to be expected as we observe a positive correlation between $PM_{2.5}$ emissions and BC measurements (Spearman coefficient: 0.68). Interestingly, unlike the $PM_{2.5}$ measurements, BC emissions do not appear to be mitigated by the use of ventilated stoves. This suggests that even if the currently installed stove improvements do reduce lung cancer rates (as the evidence indicates that they do), then BC emissions continue unabated. The consequence of this is that the negative health effects of BC exposure can still be expected in addition to its climate change effects. We also identified that indoor BC is likely the major contributor to outdoor BC. This is evidenced by a positive correlation (Spearman coefficient 0.43) between indoor and outdoor measurements and the construction of mixed models which indicated that indoor BC measurements were major predictors of outdoor measurements. The overall number of outdoor pollution sources (e.g. factories) only weakly correlated with outdoor BC measurements (Spearman coefficient 0.28) and the construction of mixed effect models indicated that the number of outdoor pollution sources failed to be a significant predictor of outdoor BC. A possible explanation for this may be that larger townships may have more factories and power plants within accessible distance of them as that provides a larger worker pool. In turn, these larger townships will, by virtue of their larger population, produce higher total amounts of indoor air pollution, contributing directly to outdoor pollution. In support of this, there is a positive correlation between the population of a village (information supplied by local health officials) and the total number of other pollutant sources (Spearman coefficient 0.43).

Unpublished findings on elemental composition

Additional findings, which are as yet unpublished, explore the elemental composition of personal and indoor air measurements. The elements available for analysis were as follows: magnesium (Mg), Aluminium (Al), Silicon(Si), Phosphorus(P), Sulfur(S), Chlorine(Cl), Potassium(K), Calcium(Ca), Titanium(Ti), Vanadium(V), Chromium(Cr), Manganese(Mn), Iron(Fe), Nickel(Ni), Copper(Cu), Zinc(Zn), Arsenic(As), Selenium(Se), Bromine(Br),

Yttrium(Y), Molybdenum(Mo), Cadmium (Cd), and lead(Pb). As mentioned previously, elemental composition was determined on 37mm Teflon filters from both personal and indoor measurements (120 and 54 measurements respectively) analysed via EDXRF. The EDXRF analysis provided measurements in µg, which was converted into concentrations as a function of the volume of air drawn through the filters. The limit of detection for the EDXRF analysis varied between elements but ranged from 0.1µg (Cr, K, Mn, P and V) to 0.5µg (Cu and Fe).

Levels of Cd, Cu and V were below the limit of detection for all measurements. Cr was under the limit of detection for 98% of measurements, Ni for 97%, Mg for 90%, Y for 76% and Mo for 70%. Thus these elements were excluded from further analysis. Between 0%(S, Cl, K, Ca and Fe) and 24%(Pb) of the remaining elements were below the limit of detection (median value 3%). Measurements below the limit of detection were replaced with values imputed from a log-normal probability function via a multiple imputation method.[45]

Normal probability plots indicated that the elemental results tended towards log-normal distribution. Therefore statistical analysis was performed on (naturally) log transformed values.

An overview of the elemental composition results between the different fuel types is available in Table 3. Personal and indoor measurements correlated well with each other (range 0.57 to 0.98), thus only personal measurements are presented. In general, measurements from subjects burning smoky coal had lower elemental composition than subjects burning other solid fuels. With the exception of Phosphorus, (which has equivalent geometric means between smoky and smokeless coal), the geometric means of the measurements from smoky coal were between 12%(Fe) and 56%(Mn) lower than measurements from smokeless coal burning homes. Significant differences between smoky and smokeless coal were observed for Sulfur (3.79µg/m^3 vs. 7.18µg/m^3 respectively, $p<0.05$). Measurements of Potassium among wood and plant burning homes (3.22µg/m^3 and 4.63µg/m^3 respectively) were significantly higher than smoky coal burning homes(1.1µg/m^3, $p<0.05$). On investigation for the role of stove design, no statistically significant difference between the various stove designs was observed when stratifying within individual fuel types.

These findings are similar to those presented in Chapter 2, where it is observed that smoky coal is relatively elementally deplete when compared to smokeless coal. The finding of elevated Sulfur in HAP from smokeless coal burning homes is consistent with the finding of elevated Sulfur in smokeless coal samples. Chronic exposure to Sulfur (typically as SO_2) is associated with increased lung cancer mortality and there is evidence to suggest that short term Sulfur exposure is associated with an increased risk of all-cause mortality.[46-48] This indicates that even though smokeless coal is considered "safe" when compared to smoky coal there are still components of exposure related to smokeless coal use which are potentially detrimental to human health. Typically, exposure to SO_2 is used in the discussion of safety limits and health effects of sulfur exposure. Therefore, how the measurements presented here directly relate to health effects are unclear. SO_2 measurements were collected as a broader part of the exposure assessment campaign performed for this thesis and will be presented at a later date.

The relationship between personal and indoor measurements

A common finding, which has been reported throughout this thesis, is the positive correlations between indoor and personal measurements. Previous research in Xuanwei and

Fuyuan has primarily been restricted to indoor measurements with no knowledge of how this would relate to personal exposure. Studies investigating HAP from solid fuel use have reported that indoor measurements may not necessarily reflect personal exposure.[49] For example, a study investigating exposures to $PM_{2.5}$ and BC among biomass using households in Ghana reported that personal $PM_{2.5}$ concentrations were not predicted by indoor measurements and that personal BC measurements were higher than indoor measurements, suggesting the possibility of additional exposure sources.[50] Additionally, the relationship between indoor and personal exposure may vary between differing stove designs. A study investigating the effect of stove improvements in rural Mexico found that personal $PM_{2.5}$ measurements were approximately 61% as high as indoor measurements if open fires were used, compared to 77% if ventilated stoves were used.[51] In this thesis, we have observed that indoor and personal measurements in Xuanwei and Fuyuan generally were well correlated with each other and of similar levels (Table 4). We found no role of stove design in the differences between personal and indoor measurements, instead identifying that personal measurements would increase (relative to indoor measurements) during colder temperatures and seasons. One of the previously mentioned limitations of previous studies in the area was that they had frequently relied upon indoor measurements,

Table 3 - personal exposure to trace elements by fuel type ($\mu g/m^3$)

		Silicon (Si)			Aluminium (Al)			Arsenic (As)			Bromine (Br)			Calcium (Ca)		
Coal Type	N	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Smoky Coal	60	1.75	1.27	2.4	1.05	0.84	1.9	0.06	0.05	1.6	0.12	0.04	5.0	0.99	0.67	2.2
Smokeless Coal	15	3.28	2.15	2.9	2.01	1.38	2.5	0.1	0.08	2.3	0.11	0.06	3.7	1.07	0.88	1.9
Other Coal	13	1.47	1.19	2.1	1.13	0.95	1.7	0.09	0.07	1.9	0.4	0.11	5.5	1.12	0.72	2.3
Wood	6	3	2.5	2.0	1.92	1.63	1.9	0.06	0.06	1.6	0.03	0.02	2.1	1.7	1.5	1.7
Plant	5	1.57	1.29	2.2	1	0.9	1.7	0.06	0.06	1.8	0.1	0.02	7.3	1.15	1.07	1.5
Other Fuel	20	2.14	1.67	2.1	1.45	1.15	2.0	0.07	0.06	1.7	0.07	0.04	3.6	0.93	0.81	1.7
		Manganese (Mn)			Phosphorus (P)†			Lead (Pb)			Sulfur (S)†			Selenium (Se)†		
		AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Smoky	60	0.08	0.04	2.9	0.13	0.07	2.8	0.13	0.09	2.1	4.5	3.79	1.8	0.06	0.02	5.5
Smokeless Coal	15	0.19	0.08	4.9	0.08	0.07	1.9	0.2	0.14	2.7	9.32	7.18*	2.4	0.06	0.04	2.8
OtherCoal	13	0.09	0.05	3.3	0.09	0.07	2.4	0.28	0.14	3.5	5.9	4.85	1.9	0.11	0.06	3.9
Wood	6	0.13	0.11	1.8	0.22	0.21	1.4	0.12	0.1	1.9	6.23	6.12	1.2	0.01	0	2.6
Plant	5	0.15	0.11	2.3	0.19	0.19	1.2	0.15	0.12	2.1	5.54	5.5	1.1	0.03	0.01	7.5
OtherFuel	20	0.1	0.07	2.6	0.12	0.1	1.9	0.13	0.11	2.0	5.21	4.28	2.0	0.04	0.02	4.6
		Chlorine (Cl)			Iron (Fe)			Potassium (K) †			Titatium (Ti)			Zinc (Zn)		
		AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD	AM	GM	GSD
Smoky Coal	60	6.4	3.57	3.1	1.04	0.81	2.0	1.82	1.1	2.2	0.16	0.13	1.9	0.23	0.15	2.3
Smokeless Coal	15	6.67	4.62	3.0	1.21	0.91	2.3	1.84	1.37	2.2	0.23	0.17	2.4	0.22	0.17	2.2
Other Coal	13	9.22	5.78	3.2	0.93	0.81	1.8	3.15	1.82	3.0	0.16	0.14	1.7	0.19	0.15	2.0
Wood	6	4.52	3.65	2.2	1.68	1.55	1.6	3.43	3.22*	1.5	0.27	0.25	1.5	0.19	0.17	1.6
Plant	5	6.95	6.56	1.5	1.07	1.01	1.5	4.98	4.63*	1.6	0.19	0.18	1.6	0.2	0.16	2.0
Other Fuel	20	6.14	4.36	2.5	1.22	0.97	2.0	2.63	2.04	2.1	0.22	0.18	2.0	0.18	0.15	2.0

† - Significant variation between fuel types via ANOVA testing

* - Significant difference in comparison to smoky coal via Tukey HSD test)

Not displayed owing to insufficient detectable samples: Cadmium, Copper , Vanadium, Chromium, Nickel, Magnesium, Yttrium, and Molybdenum

using them to approximate personal exposure. Our finding of a good relationship between indoor and personal measurements supports the use of this approach in previous research and provides additional flexibility in future study designs.

Representation of prior exposure

The findings presented in this thesis are intended to be used to approximate historical exposure in a large case control study recently conducted in Xuanwei and Fuyuan. In this study, historical fuel and stove usage is reported by enrolees with the findings of this thesis being used to assign exposures for those usages. This relies heavily upon the assumption that the measurements reported in this thesis can reliably be applied to the past. There are 2 important aspects to this assumption that need to be addressed. First, the practises of stove usage for which exposures are being assigned need to be largely unchanged. On the basis of field experience, the only notable change over recent decades in stove usage has been the change from unvented firepits to standing stoves. Also, the enrolment practises of the studies presented in this thesis were aimed to represent stoves and households which had been in use for many years previously. Further, any individuals still using firepits were preferentially approached for enrolment. The purpose of these selection methodologies was to represent home and stove designs which have been used historically.

The second aspect relates to the contents of the solid fuels used. A core assumption in the application of these findings to prior exposure is that the coal currently being used is geologically similar enough to the coal that has historically been used to allow the assignment of retrospective exposures. It is conceivable that over decades of mining, sufficient movement through coal deposits has occurred to result in geochemically different coal being used. In order to assess this possibility coal samples collected in 1987 directly from coal mines were analysed by Rock-Eval analysis. These findings were compared to

Table 4 - Spearman correlation coefficient between indoor and personal measurements for trace elements, particle bound polycyclic aromatic hydrocarbons, $PM_{2.5}$, and Black Carbon

Trace Elements	Correlation Coefficient	Percentage difference between personal and indoor measurements (IQR)†	Polycyclic Aromatic Hydrocarbons	Correlation Coefficient	Percentage difference between personal and indoor measurements (IQR)
Phosphorus (P)	0.98	-0.5(-20.7:29)	Fluoranthene (FLT)	0.81	-9 (-83:30.9)
Zinc (Zn)	0.94	5.8(-11.7:23.4)	Benzo[a]anthracene (BaA)	0.81	0.2 (-50.5:35.5)
Silicon (Si)	0.91	15.4(-6.3:46.7)	Pyrene (PYR)	0.80	-5.9 (-87.3:30.7)
Arsenic (As)	0.89	3(-7.5:18.6)	Chrysene (CHR)	0.79	1.9 (-47.7:32.5)
Potassium (K)	0.88	-4.9(-14.8:8.6)	Benzo[a]pyrene (BaP)	0.78	-2.4 (-47:35.1)
Sulfur (S)	0.83	-5.2(-18.1:7.9)	Benzo[b]fluoranthene (BbF)	0.76	-0.1 (-43.2:34.6)
Iron (Fe)	0.82	12.1(-2.1:38.5)	Benzo[ghi]perylene (BPE)	0.73	1.4 (-54.4:32)
Lead (Pb)	0.80	-0.5(-64.7:28.3)	Benzo[k]fluoranthene (BkF)	0.71	-1.8 (-65.3:32.2)
Manganese (Mn)	0.76	10.1(-10.3:31.6)	Indeno[1,2,3-cd]pyrene (IPY)	0.65	-0.7 (-68.6:34.8)
Aluminium (Al)	0.73	16.9(-7.5:42.4)	Dibenz[ah]anthracene (DBA)	0.56	-2.2 (-102.9:39.4)
Titatium (Ti)	0.64	27.2(-2.4:58.6)	All Others		
Chlorine (Cl)	0.63	0.9(-13.2:26.1)	$PM_{2.5}$	0.70	6.5 (-21.9:26.5)
Selenium (Se)	0.59	12.4(-31.6:57.9)	Black Carbon	0.70	6.7 (-21.7:26.9)
Bromine (Br)	0.58	11(-13.6:52.5)			
Calcium (Ca)	0.57	22.6(1.7:38.6)			

†: Percentage difference relative to personal measurement. Positive value indicates personal measurement higher than indoor and negative value indicates personal lower than indoor

the Rock-eval findings of geographically similar coals collected for the current study. The comparisons between the historical and the recent coal samples are presented in Table 5. In the case where more than one sample was available, the median value for all coals from that area was used. This analysis found a positive correlation between historical samples and recently collected samples (Pearson coefficient for S1:0.52, S2:0.79, and Tmax:0.99 [Spearman coefficients: 0.3, 0.3, and 0.7 respectively]). Additionally, in absolute terms, values were similar to each other. The relative percentage differences between the historical and recently collected samples were: 22% for S1, 20% for S2 and 1.3% for Tmax.

These findings are supported by a report by Large et. al who in 2009 performed an analysis of coal samples collected from Xuanwei in 1987 and compared their mineralogical, elemental and volatile matter content to samples collected in 2007. While it is not clear whether historical and current coals were matched by geographic location, Large et. al. reported that the coal collected in 1987 was similar in composition to the coal collected in 2007. This led them to conclude that no significant change had occurred in coal from Xuanwei between the two periods.[28]

These mutually supportive findings indicate that the coal and HAP measurements reported in this thesis appear to be comparable to the historical usage and exposure profile in the area.

Solid fuels and international development

Solid fuels are used by approximately 50% of the world's population, primarily in low and middle income nations, for domestic tasks including cooking and heating.[52] The ramifications of solid fuel use extend beyond health effects and have profound impacts upon social and economic development within communities. The United Nations' Millennium Development Goals (MDGs) is an internationally agreed upon blueprint for international development which contains a list of 8 development goals intended to have been achieved by 2015 (Table 6).[53] These goals are purposefully broad and impact upon many aspects of daily life. The health and social ramifications of solid fuel use both directly and indirectly impacts the ease with which these goals can be achieved. Using the MDGs as a framework, we will briefly discuss how solid fuel use impacts these goals in Xuanwei, Fuyuan, and the international setting.

Table 5 - Comparison between geochemical evaluation of historical coal samples and geographically matched coal samples from the current thesis

Sample Area (n)	S1 Original	S1 Current	S2 Original	S2 Current	Tmax Original	Tmax Current
Baoshan (1)	2.52	2.24	101.76	61.59	459	463
Laibin (3)	2.57	2.15	64.24	76.01	454	460
Tangtang (1)	6.87	1.62	75.7	61.99	450	464
Yangchang (1)	5.01	4.03	100.23	138.69	449	443
RSXZ (2)	0.13	0.29	6.04	6.49	574	572

S1: mg of hydrocarbons (per gram of coal) released under controlled burning at 300^{o}C.
S2 : mg of hydrocarbons (per gram of coal) released during maximal release of hydrocarbons under controlled burning.
Tmax: temperature at which S2 occurs
Historical: represents coal collected and stored for several decades
Current: represents coal collected during the current study
n: The number of historical specimens from that area

Goal 1: Eradicate extreme poverty and hunger.

There is a direct link between poverty and the use of solid fuels.[54] Many fuels, typically wood and animal dung, do not need to be purchased, instead merely needing to be collected. In some areas of Xuanwei and Fuyuan, residents are able to gather coal by themselves from easily accessible sources. Fuel gathering is a time consuming task and the time spent collecting fuels represents an economic drain as the time spent collecting these fuels could have been utilised in employment, education, or economic advancement. Alternatively, some solid fuels are available for purchase, which is the common situation currently at play in Xuanwei and Fuyuan, where coal is typically delivered to residents (Figure 1). Whether paid for or collected, solid fuel use continues to represent an ongoing financial burden in Xuanwei, Fuyuan, and internationally, which limits financial independence and social mobility, leaving many trapped in a cycle of poverty.

Goal 2: To achieve universal primary education

This goal does not directly relate to solid fuel use. It could be argued however that the time and physical labour spent in the collection and usage of solid fuels (as outlined in Goal 1 above), may indirectly produce barriers to the completion of this goal (e.g. parents unable to take children to school, children needing to collect fuel before being able to attend schooling etc.).

Goal 3: Promote gender equality and empower women

The collection and usage of solid fuels is a task primarily carried out by women.[55] It therefore follows that the negative impacts of solid fuel collection and use disproportionately affect women. In Xuanwei and Fuyuan, the primary role of women in domestic cooking and heating is largely responsible for them having one of the highest lung cancer rates world-wide. Additionally, since women are the primary group responsible for the collection and use of solid fuels, they are also disproportionately restricted in their ability to pursue education, employment, or economic gain due to the time cost of fuel collection and food preparation. Therefore, any efforts to improve access to improved stove designs, or safer or more efficiently burning fuels, will have a direct impact upon both the health and independence of women.

Goal 4: Reduce child mortality

The domestic use of solid fuels has direct implications for child morbidity and mortality (using the WHO definition of a child being an individual under 5 years of age[56]). The WHO estimates that up to 50% of the premature deaths in children are attributable to pneumonia caused as a result of particle inhalation from solid fuel use and that solid fuel use is

Table 6 - Millennium Development Goals (Source: WHO[53])

Goal No.	
1	To eradicate extreme poverty and hunger
2	To achieve universal primary education
3	To promote gender equality and empower women
4	To reduce child mortality
5	To improve maternal health
6	To combat HIV/AIDS, malaria, and other diseases
7	To ensure environmental sustainability
8	To develop a global partnership for development

responsible for at least half a million deaths annually among children.[57] Further, although not directly related to mortality, children exposed to the emissions of solid fuels from unvented stoves have been found to have worsened lung function than those either not using solid fuels, or using ventilated stoves.[58]

Child mortality rates are not known for Xuanwei and Fuyuan, however, the child mortality rates in rural China in 2012 was 16.2 per 1,000 live births, which is more than twice that of children living in urban China (5.9 per 1,000 live births).[59] It is reasonable to expect that a notable portion of these deaths in rural areas is attributable to solid fuel use and that improved stove designs or fuel sources would play a significant role in reducing child mortality. Additionally cohort studies have shown that in Xuanwei, the installation of ventilated stoves results in reductions in the lifelong risk of chronic obstructive pulmonary disease (COPD), pneumonia, and lung cancer, indicating that modifications in early life exposure may have important effects later in life.[10,12,60]

Goal 5: Improve maternal health

Nothing is known regarding pregnancy outcomes in Xuanwei or Fuyuan. However, exposure to household fuel emissions has implications for both the health of pregnant women and their pregnancy outcomes. For example, a recent study in India found that pregnant women using biomass for their cooking and heating were more likely to report symptoms of pre-eclampsia/eclampsia than women using a non-biomass fuel.[61] Additionally, exposure to solid fuel emissions has been associated with preterm birth, a reduction in birth weight, and an increased risk of stillbirth.[62-64] Further, as mentioned during the discussion of the PAH hypothesis, ante-natal exposure to PAHs is associated with developmental, respiratory and chromosomal abnormalities which may develop into significant health effects later in life.[24-27]

Figure 1 - Truck bearing coal for delivery to a Xuanwei village

Goal 6: Combat HIV/AIDS, malaria and other diseases

The 4 million deaths per year attributed to solid fuel usage is higher than the annual deaths attributable to HIV/AIDS and malaria combined (approximately 1.6 million deaths and 627,000 deaths in 2012 respectively[65,66]). Exposure to HAP has been identified as a risk factor in the development of tuberculosis[67] and research focussed particularly in Xuanwei and Fuyuan has identified that chronic infection with tuberculosis is associated with an increased risk of the development of lung cancer[68,69]

In addition to infectious diseases and their consequences, the role of HAP exposure in non-communicable diseases is well established. The role of solid fuels in the development of lung malignancy has been covered extensively thus far. Additional illnesses associated with solid fuel combustion include both respiratory based disorders (e.g. asthma, chronic obstructive lung disease) and systemic diseases such as cardiovascular disease.[54,70]

Goal 7: Ensure environmental sustainability

Black carbon (BC) and volatile organic emissions are important contributors to global climate change.[40-44,71] Among low and middle income countries, domestic solid fuel use contributes up to 80% of their BC emissions.[72] Improving stove designs is an important part of the global strategy to reduce BC emissions. However, in Xuanwei and Fuyuan, we observed little change in BC emissions between differing stove designs, a finding which has been seen elsewhere,[73] indicating that only specific stove designs (e.g. fan forcing) result in meaningful reductions in BC emissions.

In addition to the climate change impacts directly from the use of solid fuels, increased solid fuel reliance results in increased amounts of deforestation, either for the use of the wood itself as a fuel or ingredient in coking, or the construction of additional coal mines. At the local level this can result in increased soil erosion, pollution of water supplies, changing patterns of disease transmission, and loss of biodiversity. At the global level, increased deforestation contributes to increased amounts carbon dioxide in the atmosphere, furthering the contribution of solid fuels to global climate change.[74,75]

Goal 8: Develop a global partnership for development

This goal largely refers to integrative efforts to improve trade, development and assistance at a global scale between international partners. As an example of how this impacts solid fuel use - The Global Alliance for Clean Cookstoves (website: http://www.cleancookstoves.org/)[76] represents an international partnership designed with the intent of improving access to more efficient fuels, stoves, and the dissemination of ongoing research. The WHO also serves as part of this global partnership and provides both advocacy for improving fuel and stove use in addition to air quality guidelines to assist policy makers in the decision making process.[77]

A Common Solution

A common theme throughout the discussion of the MDGs is that improving access to stoves or solid fuels which provide more efficient combustion represents an incomplete solution. This is easily reflected in the research presented from Xuanwei and Fuyuan. In general, research from Xuanwei and Fuyuan has used smokeless coal as a de facto "control" group. This has been the case for both exposure assessments and epidemiological studies. The reasons for doing so are largely self-evident - little variation in personal habits and local customs has been observed across the counties, making those who use smokeless coal similar to those using smoky coal in most aspects, except for fuel usage. While this is an

appropriate method for investigating risks and exposures directly associated with using smoky coal, it also reveals that the emissions measured from the use of smokeless coal is generally in excess of acceptable limits. For example, the geometric mean for BaP exposure among smokeless coal users is 10.6ng/m^3, which is much lower than that for smoky coal users (44.7ng/m^3). However, even this "low" level is in excess of the Chinese national criteria of 1ng/m^3 for indoor environments and higher than the levels of BaP that would be expected in the residence of a smoker.[15,78,79] Further, this thesis has presented findings where measured pollutants (e.g. Sulfur) are present in higher amounts in smokeless coal than smoky coal. This theme is continued in the exploration of stove design, where because reductions in lung cancer rates have been observed following stove improvements, ventilated stoves are generally used as "control" stove designs when assessing the impact of stove design. This has the same drawback as using smokeless coal as the reference fuel group. For example, the geometric mean for BaP among users of ventilated stoves (34.8 ng/m^3) is lower than among users of unventilated firepits (94.3 ng/m^3) but is still in excess of acceptable levels. An additional complication is that over the course of many years of use, stoves may fall into disrepair, potentially undermining the benefit of their installation. Further, this thesis has identified that certain pollutants (e.g. Black Carbon) are not sufficiently mitigated by the ventilated stoves in Xuanwei and Fuyuan, meaning that the health and environmental benefits of these stoves is limited.

These findings, combined with the common theme shown through the discussion of the MDGs leads to the conclusion that there is no combination of solid fuel and/or stove design which can be considered wholly safe. Changing to solid fuels with reduced emission profiles and to stoves which more efficiently burn solid fuels will have an immediate impact upon morbidity and mortality, and as such, are interventions which must be pursued in the short term. However, as we have seen in this thesis, even fuels and stove designs considered to be "safe" still result in personal exposures which are likely to be detrimental to human health. Additionally, even with different solid fuels and stoves, many of the previously discussed disparities (e.g. the need for collecting fuels and the disproportionate impact upon women) will still persist. Therefore, long term interventions must focus upon providing alternatives to solid fuels (e.g. electricity or gas), thereby removing solid fuels from use entirely. In many locations, improvements in infrastructure (roads, power lines etc.) will likely be required before this can be realized.

Limitations of thesis

Generalizability to external populations

Our ability to generalise our findings to populations outside of Xuanwei and Fuyuan is somewhat limited. Among the 3 billion people using solid fuels, the proportion of those using coal varies between locations (e.g. in India, an estimated 3% of households use coal while in China 31% are estimated to use coal[80]). These coals represent a variety of ranks and types and in terms of the geological period of their formation, relatively little coal was formed during the same period as the coal used in Xuanwei and Fuyuan (colloquially referred to as the “coal gap”[81]). Further, lung cancer rates among coal users is highly variable between different areas with, as yet, nowhere else having lung cancer rates comparable to Xuanwei and Fuyuan. Therefore the constituents of the coals from Xuanwei and Fuyuan may differ from those of coals even of the same rank. For these reasons, it is inadvisable to consider that the results presented in this thesis can be generalized to the contents and emission products of bituminous and anthracite coals in other settings. It must

be noted though, that the WHO guidelines for indoor air quality in relation to household fuel combustion considers all unprocessed coal products (meaning coal that has not been chemically, thermally, or physically treated to reduce contaminants) to be sufficiently carcinogenic for them to advise that these products not be used in any situation.[77]

With this limitation in mind, our findings of a relative reduction in exposure to emission products among households using ventilated stoves (when compared to firepits and unventilated stoves) may be applicable to external settings. This is because while the absolute values may not be externally generalizable, the finding of a reduction in emission products with improved stove designs is consistent with multiple other acts of research internationally which has identified similar findings.[82]

Sample size

While this is the largest exposure assessment in Xuanwei and Fuyuan to date, we still face several sample size limitations. The original study protocol conceived of 7 parameters which would be of interest in the exposure assessment (fuel type, fuel source, stove type [e.g. firepit vs. standing], personal activities, amount of fuel used, chimney usage, and season) and planned to enrol 20 subjects per parameter (total 140). We enrolled 163 subjects which was in excess of this planned sample size, however our sampling was still insufficient to explore every possibility. For example, in the Laibin coal area (which had historically the highest lung cancer rates[14]), we were unable to assess exposure to smoky coal emissions from coal burnt in firepits. The reason for this is that because of the high lung cancer rates in the Laibin area, almost all people converted to using either fixed or portable stoves. Additionally, since we were collecting measurements while people were carrying out their regular tasks and using their usual fuels, we were unable to gather equal amounts of data for every permutation of fuel and stove design (e.g. limited encounters of people using smokeless coal in firepits are available). Further, if individuals were to use multiple different fuel types (the "other coal" and "other fuel" groups) we were unable to assign their measured exposures to individual fuel types, further limiting our dataset. However, through the use of mixed effect models we are able to minimise these limitations by estimating these missing permutations of fuel and stove design. For example, we would estimate personal BaP exposure among firepit users of smoky coal in Laibin to be approximately 113ng/m^3 (assuming reference groups for room size and season). This approach does have some inherent uncertainty but will allow for an estimation of exposure for a variety of situations.

Handling of tobacco exposure

Tobacco is a source of $PM_{2.5}$, PAHs and other air pollutants; however this thesis has almost completely disregarded exposure to tobacco as an exposure of importance. Smoking rates among men in Xuanwei and Fuyuan are very high (over 90%) but almost non-existent among women (none of the subjects in the current study reported themselves to be smokers). There is the possibility that environmental tobacco smoke (ETS) may have had an influence on our findings, although since 90% of enrolees reported having at least one family member who smoked, we would expect a fairly uniform contribution of tobacco smoke across our population. Additionally, studies investigating BaP concentrations in indoor air as a result of tobacco smoke in controlled simulations and the residences of smokers (BaP concentrations of 0.61ng/m^3 and 0.65ng/m^3 respectively)[78,79] have shown that tobacco smoke likely contributes relatively little when compared to the solid fuels in Xuanwei and Fuyuan (arithmetic mean for all personal BaP measurements: 67ng/m^3). A

further consideration is that the role of smoky coal in lung cancer genesis appears to be much stronger than that of smoking. A study by Kim et. al. found that smoky coal use almost completely attenuated any lung cancer risk associated with smoking.[4] A study by Lee et. al. found that no excess lung cancer risk was visible among smokers who used smoky coal until they carried out stove improvements (at which point the lung cancer risk from coal smoke had reduced enough for the effect of smoking to be visible).[13] Since these studies were carried out among active smokers, it is highly likely that environmental tobacco smoke will play a negligible role in lung cancer genesis in the area.

Measurement of time allocation and stove proximity

In the bulk of our constructed models, stove design and fuel type were the primary factors contributing to exposure. While this is likely in large part due to the important role that these play in exposure, research in other settings[83] has suggested that in addition to stove usage, the proximity of individuals to stoves also plays a major role in overall exposure. In this thesis, activities of study participants were reported to field workers who primarily focussed upon stove usage with a lesser focus upon time spent within proximities to stoves, meaning that we had insufficient information to fully explore this possibility. Future research in Xuanwei and Fuyuan may benefit from the use of devices such as real-time stove use monitors and personal tracking devices, (e.g. ultrasound personal locators), which have recently been used in other settings to better understand stove usage and proximity and their role in personal exposure.[84-86]

Future applications

As has been previously mentioned, the findings presented in this thesis will be used to epidemiological studies, most notable of which is an ongoing case-control study of lung cancer in Xuanwei and Fuyuan. In Chapter 2 we observed that, on the basis of geochemical evaluation, approximately 10% of study enrolees misreported their fuel type (6% of the smoky coal users and 15% of the smokeless coal users miss-reported their coal type). In addition to being able to more accurately assign exposure to fuel types for this thesis, this information will be of value in future studies. Using this rate of misreporting will allow for the use of sensitivity analyses where the impacts of misreporting fuel type upon calculated lung cancer risks can be evaluated.

The mixed effect models presented in this work will form the basis of the estimation of exposure for people using solid fuels in Xuanwei and Fuyuan. For example, someone who reports using smoky coal sourced from the south of Xuanwei (which is of the subtype coking coal), in a ventilated stove would have an annual personal BaP exposure estimate of approximately 23ng/m^3 (95% CI: 6.2ng/m^3 to 85ng/m^3), which may vary further dependent upon the size of their home and unlike occupational exposures, will be considered to be present for the entire day, for every day of the year. These exposure estimates will vary over an individual's life course as they move homes and change fuel types (e.g. for the first 20 years, an individual lived in a home burning smoky coal in a firepit, after getting married, the individual moved to a location where smokeless coal in a ventilated stove was used - both time periods will have exposure estimates performed) and will provide an overview to personal exposures from a life-course approach. This approach will allow us to associate overall exposures with specific cancer risk in addition to time-specific exposures (e.g. associating levels of exposure under the age of 5 with eventual cancer risk).

Conclusion

The domestic use of locally sourced smoky coal is primarily responsible for the lung cancer epidemic in the Chinese counties of Xuanwei and Fuyuan. This thesis has sought to understand the constituents and emission products of the solid fuels used in this area, with a specific focus upon what differentiates smoky coal from the alternative fuels available. The most significant finding is that smoky coal emits high amounts of PAHs, many of which are known carcinogens. This knowledge, in addition to the other measurements gathered will allow us to assess lung cancer risk in the population of Xuanwei and Fuyuan in addition to providing an insight into lung cancer risks elsewhere. Finally, while this information will provide valuable insights into how coal use relates to lung cancer risk, it is vital that from a public health perspective, sufficient evidence of harm already exists in order to advocate the wide-spread access to cleaner fuels and energies (i.e. non-solid fuels) for this population.

References

1. Barone-Adesi, F.; Chapman, R. S.; Silverman, D. T.; He, X.; Hu, W.; Vermeulen, R.; Ning, B.; Fraumeni, J. F.,Jr; Rothman, N.; Lan, Q. Risk of lung cancer associated with domestic use of coal in Xuanwei, China: retrospective cohort study. BMJ 2012, 345, e5414.
2. Chapman, R. S.; Mumford, J. L.; Harris, D. B.; He, Z. Z.; Jiang, W. Z.; Yang, R. D. The epidemiology of lung cancer in Xuan Wei, China: current progress, issues, and research strategies. Arch. Environ. Health 1988, 43, 180-185.
3. He, X. Z.; Chen, W.; Liu, Z. Y.; Chapman, 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 Perspect. 1991, 94, 9-13.
4. Kim, C.; Chapman, R. S.; Hu, W.; He, X.; Hosgood, H. D.; Liu, L. Z.; Lai, H.; Chen, W.; Silverman, D. T.; Vermeulen, R.; Tian, L.; Bassig, B.; Shen, M.; Zhang, Y.; Ma, S.; Rothman, N.; Lan, Q. Smoky coal, tobacco smoking, and lung cancer risk in Xuanwei, China. Lung Cancer 2014, 84, 31-35.
5. Mumford, J. L.; He, X. Z.; Chapman, R. S.; Cao, S. R.; Harris, D. B.; Li, X. M.; Xian, Y. L.; Jiang, W. Z.; Xu, C. W.; Chuang, J. C. Lung cancer and indoor air pollution in Xuan Wei, China. Science 1987, 235, 217-220.
6. Mumford, J. L.; Chapman, R. S.; Harris, D. B.; He, X. Z.; Cao, S. R.; Xian, Y. L.; Li, X. M. Indoor air exposure to coal and wood combustion emissions associated with a high lung cancer rate in Xuan Wei, China. Environ. Int. 1989, 15, 315-320.
7. Tian, L. Coal Combustion Emissions and Lung Cancer in Xuan Wei, China (PhD dissertation), University of California, Berkeley, California, 2005.
8. Vermeulen, R.; Rothman, N.; Lan, Q. Coal combustion and lung cancer risk in XuanWei: a possible role of silica? Med. Lav. 2011, 102, 362-367.
9. He, J.; Cai, Y.; Lv, J.; Zhang, L. Primary investigation of quartz as a possible carcinogen in coals of Xuanwei and Fuyuan, high lung cancer incidence area in China. Environmental Earth Sciences 2012;, 67, 1679 - 1684.
10. Chapman, R. S.; He, X.; Blair, A. E.; Lan, Q. Improvement in household stoves and risk of chronic obstructive pulmonary disease in Xuanwei, China: retrospective cohort study. BMJ 2005, 331, 1050.
11. Hosgood, H. D.,3rd; Chapman, R.; Shen, M.; Blair, A.; Chen, E.; Zheng, T.; Lee, K. M.; He, X.; Lan, Q. Portable stove use is associated with lower lung cancer mortality risk in lifetime smoky coal users. Br. J. Cancer 2008, 99, 1934-1939.
12. 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.
13. Lee, K. M.; Chapman, R. S.; Shen, M.; Lubin, J. H.; Silverman, D. T.; He, X.; Hosgood, H. D.,3rd; Chen, B. E.; Rajaraman, P.; Caporaso, N. E.; Fraumeni, J. F.,Jr; Blair, A.; Lan, Q. Differential effects of smoking on lung cancer mortality before and after household stove improvement in Xuanwei, China. Br. J. Cancer 2010, 103, 727-729.
14. Lan, Q.; He, X.; Shen, M.; Tian, L.; Liu, L. Z.; Lai, H.; Chen, W.; Berndt, S. I.; Hosgood, H. D.; Lee, K. M.; Zheng, T.; Blair, A.; Chapman, R. S. Variation in lung cancer risk by smoky coal subtype in Xuanwei, China. Int. J. Cancer 2008, 123, 2164-2169.
15. Lv, J.; Xu, R.; Wu, G.; Zhang, Q.; Li, Y.; Wang, P.; Liao, C.; Liu, J.; Jiang, G.; Wei, F. Indoor and outdoor air pollution of polycyclic aromatic hydrocarbons (PAHs) in Xuanwei and Fuyuan, China. J. Environ. Monit. 2009, 11, 1368-1374.
16. Tian, L.; Lan, Q.; Yang, D.; He, X.; Yu, I. T. S.; Hammond, S. K. Effect of chimneys on indoor air concentrations of PM_{10} and benzo[a]pyrene in Xuan Wei, China. Atmos. Environ. 2009, 43, 3352-3355.
17. Achten, C.; Hofmann, T. Native polycyclic aromatic hydrocarbons (PAH) in coals - a hardly recognized source of environmental contamination. Sci. Total Environ. 2009, 407, 2461-2473.
18. Laumann, S.; Micic, V.; Kruge, M. A.; Achten, C.; Sachsenhofer, R. F.; Schwarzbauer, J.; Hofmann, T. Variations in concentrations and compositions of polycyclic aromatic hydrocarbons (PAHs) in coals related to the coal rank and origin. Environ. Pollut. 2011, 159, 2690-2697.

19. Armstrong, B. G.; Gibbs, G. Exposure-response relationship between lung cancer and polycyclic aromatic hydrocarbons (PAHs). Occup. Environ. Med. 2009, 66, 740-746.
20. Armstrong, B.; Hutchinson, E.; Unwin, J.; Fletcher, T. Lung Cancer Risk after Exposure to Polycyclic Aromatic Hydrocarbons: A Review and Meta-Analysis. Environ. Health Perspect. 2004, 112, 970-978.
21. Rota, M.; Bosetti, C.; Boccia, S.; Boffetta, P.; La Vecchia, C. Occupational exposures to polycyclic aromatic hydrocarbons and respiratory and urinary tract cancers: an updated systematic review and a meta-analysis to 2014. Arch. Toxicol. 2014, 88, 1479-1490.
22. Bonner, M. R.; Han, D.; Nie, J.; Rogerson, P.; Vena, J. E.; Muti, P.; Trevisan, M.; Edge, S. B.; Freudenheim, J. L. Breast cancer risk and exposure in early life to polycyclic aromatic hydrocarbons using total suspended particulates as a proxy measure. Cancer Epidemiol. Biomarkers Prev. 2005, 14, 53-60.
23. Nie, J.; Beyea, J.; Bonner, M. R.; Han, D.; Vena, J. E.; Rogerson, P.; Vito, D.; Muti, P.; Trevisan, M.; Edge, S. B.; Freudenheim, J. L. Exposure to traffic emissions throughout life and risk of breast cancer: the Western New York Exposures and Breast Cancer (WEB) study. Cancer Causes Control 2007, 18, 947-955.
24. Jedrychowski, W. A.; Perera, F. P.; Majewska, R.; Mrozek-Budzyn, D.; Mroz, E.; Roen, E. L.; Sowa, A.; Jacek, R. Depressed height gain of children associated with intrauterine exposure to polycyclic aromatic hydrocarbons (PAH) and heavy metals: The cohort prospective study. Environ. Res. 2015, 136, 141-147.
25. Jedrychowski, W. A.; Perera, F. P.; Maugeri, U.; Majewska, R.; Mroz, E.; Flak, E.; Camann, D.; Sowa, A.; Jacek, R. Long term effects of prenatal and postnatal airborne PAH exposures on ventilatory lung function of non-asthmatic preadolescent children. Prospective birth cohort study in Krakow. Sci. Total Environ. 2015, 502, 502-509.
26. Jedrychowski, W. A.; Perera, F. P.; Camann, D.; Spengler, J.; Butscher, M.; Mroz, E.; Majewska, R.; Flak, E.; Jacek, R.; Sowa, A. Prenatal exposure to polycyclic aromatic hydrocarbons and cognitive dysfunction in children. Environmental Science and Pollution Research 2014.
27. Orjuela, M. A.; Liu, X.; Warburton, D.; Siebert, A. L.; Cujar, C.; Tang, D.; Jobanputra, V.; Perera, F. P. Prenatal PAH exposure is associated with chromosome-specific aberrations in cord blood. Mutat. Res. 2010, 703, 108-114.
28. Large, D. J.; Kelly, S.; Spiro, B.; Tian, L.; Shao, L.; Finkelman, R.; Zhang, M.; Somerfield, C.; Plint, S.; Ali, Y.; Zhou, Y. Silica-volatile interaction and the geological cause of the Xuan Wei lung cancer epidemic. Environ. Sci. Technol. 2009, 43, 9016-9021.
29. Tian, L.; Dai, S.; Wang, J.; Huang, Y.; Ho, S. C.; Zhou, Y.; Lucas, D.; Koshland, C. P. Nanoquartz in Late Permian C1 coal and the high incidence of female lung cancer in the Pearl River Origin area: a retrospective cohort study. BMC Public Health 2008, 8, 398.
30. Yu, I. T.; Tse, L. A. Exploring the joint effects of silicosis and smoking on lung cancer risks. International Journal of Cancer 2007, 120, 133-139.
31. Steenland, K.; Mannetje, A.; Boffetta, P.; Stayner, L.; Attfield, M.; Chen, J.; Dosemeci, M.; DeKlerk, N.; Hnizdo, E.; Koskela, R.; Checkoway, H.; International Agency for Research on Cancer Pooled exposure-response analyses and risk assessment for lung cancer in 10 cohorts of silica-exposed workers: an IARC multicentre study. Cancer Causes Control 2001, 12, 773-784.
32. Talaska, G.; Underwood, P.; Maier, A.; Lewtas, J.; Rothman, N.; Jaeger, M. Polycyclic aromatic hydrocarbons (PAHs), nitro-PAHs and related environmental compounds: biological markers of exposure and effects. Environ. Health Perspect. 1996, 104, 901-906.
33. Ding, J.; Zhong, J.; Yang, Y.; Li, B.; Shen, G.; Su, Y.; Wang, C.; Li, W.; Shen, H.; Wang, B.; Wang, R.; Huang, Y.; Zhang, Y.; Cao, H.; Zhu, Y.; Simonich, S. L.; Tao, S. Occurrence and exposure to polycyclic aromatic hydrocarbons and their derivatives in a rural Chinese home through biomass fuelled cooking. Environ. Pollut. 2012, 169, 160-166.
34. Mumford, J. L.; Li, X.; Hu, F.; Lu, X. B.; Chuang, J. C. Human exposure and dosimetry of polycyclic aromatic hydrocarbons in urine from Xuan Wei, China with high lung cancer mortality associated with exposure to unvented coal smoke. Carcinogenesis 1995, 16, 3031-3036.

35. Pryor, W. A. Cigarette smoke radicals and the role of free radicals in chemical carcinogenicity. Environ. Health Perspect. 1997, 105, 875-882.
36. Hosgood, H. D.; Sapkota, A. R.; Rothman, N.; Rohan, T.; Hu, W.; Xu, J.; Vermeulen, R.; He, X.; White, J. R.; Wu, G.; Wei, F.; Mongodin, E. F.; Lan, Q. The potential role of lung microbiota in lung cancer attributed to household coal burning exposures. Environ. Mol. Mutagen. 2014, 55, 643-651.
37. Johnson, E. S.; Choi, K. -. Lung Cancer Risk in Workers in the Meat and Poultry Industries - A Review. Zoonoses and Public Health 2012;, 59, 303-313.
38. Englert, N. Fine particles and human health--a review of epidemiological studies. Toxicol. Lett. 2004, 149, 235-242.
39. Kappos, A. D.; Bruckmann, P.; Eikmann, T.; Englert, N.; Heinrich, U.; Höppe, P.; Koch, E.; Krause, G. H. M.; Kreyling, W. G.; Rauchfuss, K.; Rombout, P.; Schulz-Klemp, V.; Thiel, W. R.; Wichmann, H. -. Health effects of particles in ambient air. Int. J. Hyg. Environ. Health 2004, 207, 399-407.
40. Bond, T. C.; Streets, D. G.; Yarber, K. F.; Nelson, S. M.; Woo, J.; Klimont, Z. A technology-based global inventory of black and organic carbon emissions from combustion. Journal of Geophysical Research: Atmospheres 2004, 109, - D14203.
41. Grahame, T. J.; Klemm, R.; Schlesinger, R. B. Public health and components of particulate matter: The changing assessment of black carbon. J. Air Waste Manage. Assoc. 2014, 64, 620 - 660.
42. Anenberg, S. C.; Schwartz, J.; Shindell, D.; Amann, M.; Faluvegi, G.; Klimont, Z.; Janssens-Maenhout, G.; Pozzoli, L.; Van Dingenen, R.; Vignati, E.; Emberson, L.; Muller, N. Z.; West, J. J.; Williams, M.; Demkine, V.; Hicks, W. K.; Kuylenstierna, J.; Raes, F.; Ramanathan, V. Global air quality and health co-benefits of mitigating near-term climate change through methane and black carbon emission controls. Environ. Health Perspect. 2012, 120, 831-839.
43. Martin, W. J.,II; Hollingsworth, J. W.; Ramanathan, V. In Chapter 13, Household Air Pollution from Cookstoves: Impacts on Health and Climate; Pinkerton, K. E., Rom, W. N., Eds.; Global Climate Change and Public Health, Springer Science+Business Media: New York, 2014; .
44. Schmidt, C. W. Black carbon: the dark horse of climate change drivers. Environ. Health Perspect. 2011, 119, A172-5.
45. Lubin, J. H.; Colt, J. S.; Camann, D.; Davis, S.; Cerhan, J. R.; Severson, R. K.; Bernstein, L.; Hartge, P. Epidemiologic Evaluation of Measurement Data in the Presence of Detection Limits. Environ. Health Perspect. 2004, 112, 1691-1696.
46. Tseng, C. Y.; Huang, Y. C.; Su, S. Y.; Huang, J. Y.; Lai, C. H.; Lung, C. C.; Ho, C. C.; Liaw, Y. P. Cell type specificity of female lung cancer associated with sulfur dioxide from air pollutants in Taiwan: an ecological study. BMC Public Health 2012, 12, 4-2458-12-4.
47. Lee, W. J.; Teschke, K.; Kauppinen, T.; Andersen, A.; JÃ¤ppinen, P.; Szadkowska-Stanczyk, I.; Pearce, N.; Persson, B.; Bergeret, A.; Facchini, L. A.; Kishi, R.; Kielkowski, D.; Rix, B. A.; Henneberger, P.; Sunyer, J.; Colin, D.; Kogevinas, M.; Boffetta, P. Mortality from lung cancer in workers exposed to sulfur dioxide in the pulp and paper industry. Environ. Health Perspect. 2002, 110, 991-995.
48. Chen, R.; Huang, W.; Wong, C. M.; Wang, Z.; Thach, T. Q.; Chen, B.; Kan, H.; CAPES Collaborative Group Short-term exposure to sulfur dioxide and daily mortality in 17 Chinese cities: the China air pollution and health effects study (CAPES). Environ. Res. 2012, 118, 101-106.
49. Clark, M. L.; Peel, J. L.; Balakrishnan, K.; Breysse, P. N.; Chillrud, S. N.; Naeher, L. P.; Rodes, C. E.; Vette, A. F.; Balbus, J. M. Health and household air pollution from solid fuel use: the need for improved exposure assessment. Environ. Health Perspect. 2013, 121, 1120-1128.
50. Van Vliet, E. D.; Asante, K.; Jack, D. W.; Kinney, P. L.; Whyatt, R. M.; Chillrud, S. N.; Abokyi, L.; Zandoh, C.; Owusu-Agyei, S. Personal exposures to fine particulate matter and black carbon in households cooking with biomass fuels in rural Ghana. Environ. Res. 2013, 127, 40-48.

51. ArmendÃ¡riz-Arnez, C.; Edwards, R. D.; Johnson, M.; Rosas, I. A.; Espinosa, F.; Masera, O. R. Indoor particle size distributions in homes with open fires and improved Patsari cook stoves. Atmos. Environ. 2010, 44, 2881-2886.
52. World Health Organization Fuel for Life: Household Energy And Health; World Health Organization: Geneva, 2006; .
53. AnonymousUnited Nations Millennium Development Goals. http://www.un.org/millenniumgoals/ (accessed 12/19/2014, 2014).
54. Gordon, S. B.; Bruce, N. G.; Grigg, J.; Hibberd, P. L.; Kurmi, O. P.; Lam, K. H.; Mortimer, K.; Asante, K. P.; Balakrishnan, K.; Balmes, J.; Bar-Zeev, N.; Bates, M. N.; Breysse, P. N.; Buist, S.; Chen, Z.; Havens, D.; Jack, D.; Jindal, S.; Kan, H.; Mehta, S.; Moschovis, P.; Naeher, L.; Patel, A.; Perez-Padilla, R.; Pope, D.; Rylance, J.; Semple, S.; Martin, W. J. Respiratory risks from household air pollution in low and middle income countries. The Lancet Respiratory Medicine 2014.
55. Rehfuess, E.; Mehta, S.; Prüss-Üstün, A. Assessing Household Solid Fuel Use: Multiple Implications for the Millennium Development Goals. Environ. Health Perspect. 2006, 114, 373-378.
56. AnonymousWHO | Child mortality. http://www.who.int/maternal_child_adolescent/topics/child/mortality/en/ (accessed 12/19/2014, 2014).
57. World Health Organization Burden of disease from Household Air Pollution for 2012. http://www.who.int/phe/health_topics/outdoorair/databases/HAP_BoD_results_March2014.pdf (accessed 11/25/2014, 2014).
58. Roy, A.; Chapman, R. S.; Hu, W.; Wei, F.; Liu, X.; Zhang, J. Indoor air pollution and lung function growth among children in four Chinese cities. Indoor Air 2012, 22, 3-11.
59. Xi, B.; Zhou, C.; Zhang, M.; Wang, Y.; Xu, L. Maternal and child mortality in China. The Lancet 2014, 383, 953-954.
60. Robert S Chapman; Xingzhou He; Aaron E Blair; Qing Lan Improvement in household stoves and risk of chronic obstructive pulmonary disease in Xuanwei, China: retrospective cohort study. BMJ 2005, 331, 1050.
61. Agrawal, S.; Yamamoto, S. Effect of Indoor air pollution from biomass and solid fuel combustion on symptoms of preeclampsia/eclampsia in Indian women. Indoor Air 2014.
62. Wylie, B. J.; Coull, B. A.; Hamer, D. H.; Singh, M. P.; Jack, D.; Yeboah-Antwi, K.; Sabin, L.; Singh, N.; MacLeod, W. B. Impact of biomass fuels on pregnancy outcomes in central East India. Environ. Health 2014, 13, 1.
63. Amegah, A. K.; Quansah, R.; Jaakkola, J. J. Household air pollution from solid fuel use and risk of adverse pregnancy outcomes: a systematic review and meta-analysis of the empirical evidence. PLoS One 2014, 9, e113920.
64. Sehgal, M.; Rizwan, S. A.; Krishnan, A. Disease burden due to biomass cooking-fuel-related household air pollution among women in India. Glob. Health. Action 2014, 7, 25326.
65. UNAIDS UNAIDS report on the global AIDS epidemic. 2013.
66. WHO World Malaria Report. 2013.
67. Kurmi, O. P.; Sadhra, C. S.; Ayres, J. G.; Sadhra, S. S. Tuberculosis risk from exposure to solid fuel smoke: a systematic review and meta-analysis. J. Epidemiol. Community Health 2014, 68, 1112-1118.
68. Engels, E. A.; Shen, M.; Chapman, R. S.; Pfeiffer, R. M.; Yu, Y. Y.; He, X.; Lan, Q. Tuberculosis and subsequent risk of lung cancer in Xuanwei, China. Int. J. Cancer 2009, 124, 1183-1187.
69. HosgoodIII, H. D.; Chapman, R. S.; He, X.; Hu, W.; Tian, L.; Liu, L. Z.; Lai, H.; Chen, W.; Rothman, N.; Lan, Q. History of lung disease and risk of lung cancer in a population with high household fuel combustion exposures in rural China. Lung Cancer 2013, 81, 343-346.
70. Rajagopalan, S.; Brook, R. D. The Indoor-Outdoor Air-Pollution Continuum and the Burden of Cardiovascular Disease: an Opportunity for Improving Global Health. Glob. Heart 2012, 7, 207-213.

71. Collins, W. J.; Derwent, R. G.; Johnson, C. E.; Stevenson, D. S. The Oxidation of Organic Compounds in the Troposphere and their Global Warming Potentials. Clim. Change 2002, 52, 453-479.
72. Bond, T. C.; Doherty, S. J.; Fahey, D. W.; Forster, P. M.; Berntsen, T.; DeAngelo, B. J.; Flanner, M. G.; Ghan, S.; Kärcher, B.; Koch, D.; Kinne, S.; Kondo, Y.; Quinn, P. K.; Sarofim, M. C.; Schultz, M. G.; Schulz, M.; Venkataraman, C.; Zhang, H.; Zhang, S.; Bellouin, N.; Guttikunda, S. K.; Hopke, P. K.; Jacobson, M. Z.; Kaiser, J. W.; Klimont, Z.; Lohmann, U.; Schwarz, J. P.; Shindell, D.; Storelvmo, T.; Warren, S. G.; Zender, C. S. Bounding the role of black carbon in the climate system: A scientific assessment. Journal of Geophysical Research: Atmospheres 2013, 118, 5380-5552.
73. Kar, A.; Rehman, I. H.; Burney, J.; Puppala, S. P.; Suresh, R.; Singh, L.; Singh, V. K.; Ahmed, T.; Ramanathan, N.; Ramanathan, V. Real-time assessment of black carbon pollution in Indian households due to traditional and improved biomass cookstoves. Environ. Sci. Technol. 2012, 46, 2993-3000.
74. AnonymousWHO | Indoor air pollution and household energy. http://www.who.int/heli/risks/indoorair/indoorair/en/ (accessed 12/21/2014, 2014).
75. IARC IARC monographs on the evaluation of carcinogenic risks to humans. Volume 95, Household Use of Solid Fuels and High-temperature Frying. 2010.
76. AnonymousGlobal Alliance for Clean Cookstoves. http://www.cleancookstoves.org/ (accessed 12/26/2014, 2014).
77. WHO Indoor air quality guidelines: household fuel combustion. 2014.
78. Fromme, H.; Dietrich, S.; Heitmann, D.; Dressel, H.; Diemer, J.; Schulz, T.; Jorres, R. A.; Berlin, K.; Volkel, W. Indoor air contamination during a waterpipe (narghile) smoking session. Food Chem. Toxicol. 2009, 47, 1636-1641.
79. Fromme, H.; Lahrz, T.; Piloty, M.; Gebhardt, H.; Oddoy, A.; Ruden, H. Polycyclic aromatic hydrocarbons inside and outside of apartments in an urban area. Sci. Total Environ. 2004, 326, 143-149.
80. Desai, M. A.; Mehta, S.; Smith, K. R. Indoor smoke from solid fuels: Assessing the environmental burden of disease at national and local levels (WHO Environmental Burden of Disease Series, No. 4). . 2004.
81. Retallack, G.,J; Veevers, J.,J; Morante, R. Global coal gap between Permian-Triassic extinction and Middle Triassic recovery of pear-forming plants. Geol. Soc. Am. Bull. 1996, 108.
82. WHO Household air pollution and health. http://www.who.int/mediacentre/factsheets/fs292/en/ (accessed 12/3/2014, 2014).
83. Ezzati, M.; Saleh, H.; Kammen, D. M. The contributions of emissions and spatial microenvironments to exposure to indoor air pollution from biomass combustion in Kenya. Environ. Health Perspect. 2000, 108, 833-839.
84. Barron, M.; Lam, N.; Pillarisetti, A. TAMS: Time Activity Monitoring System v2 (Presentation). http://cega.berkeley.edu/assets/cega_programs/10/Time-Activity_Monitoring_System_v2.pdf.
85. Allen-Piccolo, G.; Rogers, J. V.; Edwards, R.; Clark, M. C.; Allen, T. T.; Ruiz-Mercado, I.; Shields, K. N.; Canuz, E.; Smith, K. R. An ultrasound personal locator for time-activity assessment. Int. J. Occup. Environ. Health 2009, 15, 122-132.
86. Burwen, J.; Levine, D. I. A rapid assessment randomized-controlled trial of improved cookstoves in rural Ghana. Energy for Sustainable Development 2012, 16, 328-338.

Summary

Solid fuels (coal, wood, animal dung, etc.) are used by approximately half of the world's population for domestic cooking and heating. Household air pollution (HAP) produced as a result of solid fuel use is responsible for approximately 4 million premature deaths annually. The health risks associated with solid fuel use are well illustrated in the neighbouring counties of Xuanwei and Fuyuan, in Yunnan province, China. These predominantly rural counties have a population of approximately 2 million, who almost exclusively use solid fuels for their daily cooking and heating, and have among the highest lung cancer rates in China regardless of gender or smoking status. The high lung cancer rates in these counties have been causally linked to the domestic combustion of locally sourced "smoky" coal, a bituminous coal mined throughout the region and called "smoky" because of the large amount of visible smoke emitted when it is burnt. Lung cancer rates are approximately 7 times higher among users of smoky coal than users of "smokeless" coal (an anthracite coal available in limited parts of Xuanwei and Fuyuan). Variations in lung cancer risks have been observed between differing geographic areas (in some areas the lung cancer risk is 100 times higher among smoky coal users than smokeless coal users), likely indicating variation in the underlying constituents of coal. Additionally, lung cancer rates have reduced by approximately 50% in areas where cookstoves have been upgraded from unvented firepits to standing stoves with attached chimneys, indicating that carcinogenic constituent(s) of fuel emissions are likely reduced with improved stove ventilation.

Limited research has thus far implicated exposure to polycyclic aromatic hydrocarbons (PAHs) and quartz (crystalline silica) in HAP as potential causative agents. However, due to limitations in sample size and geographic scope, further research is required to better understand the relationship between HAP components and lung cancer risk. This thesis details the findings of the largest exposure assessment survey in Xuanwei and Fuyuan to date. Personal and indoor air pollution measurements were collected from 163 non-smoking adult women and their homes from throughout Xuanwei and Fuyuan in addition to fuel and ash samples. The purpose of this thesis is to catalogue the constituents of solid fuels and their associated household air pollution throughout Xuanwei and Fuyuan and to identify determinants of these exposures such as fuel source and stove design. The results of this thesis are intended to be used to estimate exposure in a large case-control study of lung cancer in Xuanwei and Fuyuan.

Results of coal analysis are presented in Chapter 2, where the geochemical, mineralogical, and elemental composition of smoky and smokeless coal specimens are compared. This chapter reports that smoky and smokeless coal have multiple constitutional differences. The measurements S1 and S2, which are indicators of volatile organic content (S1 represents hydrocarbon generation at 300 degrees Celsius and S2 represents the peak amount of hydrocarbon generation between temperatures of 300 and 650 degrees Celsius), are approximately 8 times higher in smoky coal than smokeless coal (S2: 71.5 and 8.4 mgHC/g coal respectively). Additionally, variation in the volatile components of smoky coal was observed between differing smoky coal sources. Mineralogical analysis revealed that smoky coal contained more quartz (4.6% of coal), including quartz in the respirable fraction (1.9%) than smokeless coal (2.2 and 0.6% respectively). Finally, in terms of elemental composition, smoky coal was generally elementally deplete when compared to smokeless coal, although smoky coal did contain more silicon (92,100 ppm) than smokeless coal (84,000 ppm).

Analyses of personal and indoor HAP are first presented in Chapter 3 with a presentation of $PM_{2.5}$ (particulate matter with and aerodynamic diameter smaller than 2.5μm) measurements. The main findings of this chapter are that the use of smoky coal is associated with higher $PM_{2.5}$ measurements than smokeless coal (personal measurements: 148 and 115 $\mu g/m^3$ respectively) but less than the use of wood (personal measurement: 289 $\mu g/m^3$). The use of ventilated stoves resulted in reduced $PM_{2.5}$ measurements when compared to unventilated stoves and firepits (e.g. personal measurement for smoky coal in a firepit - 277 $\mu g/m^3$ versus 134 $\mu g/m^3$ in a ventilated stove). As the highest $PM_{2.5}$ concentrations are associated with wood burning it is likely that exposure to $PM_{2.5}$ alone would be insufficient to explain lung cancer risk in the area as wood burning has not been associated with similar lung cancer risks to those seen with smoky coal.

The analysis of air pollution measurements is continued in Chapter 4 with a presentation of particle bound (high molecular weight) and gas phase (low molecular weight) polycyclic aromatic hydrocarbons (PAHs). The main finding of this chapter is that the use of smoky coal resulted in measurements of particle phase PAHs that were between 2 and 9 times higher than the use of smokeless coal. This includes Benzo[a]pyrene (BaP) a known carcinogen (personal BaP measurements among smoky coal users was $44.7ng/m^3$, compared to $10.6ng/m^3$ among smokeless coal users). Similarly to what was observed in Chapter 3, PAH measurements were reduced when fuel was burnt in a ventilated stove when compared to unventilated stoves and firepits (e.g. personal BaP measurements among smoky coal users was $151.5ng/m^3$ when burnt in a firepit, and $38.1ng/m^3$ when burnt in a ventilated stove). In addition to these findings, variation in PAH measurements was observed between differing geographic sources, differing room sizes and differing seasons. Collectively, these findings indicate that PAH exposure parallels some of the known lung cancer epidemiology, specifically, reductions in exposure with ventilated stoves and geographic variations in PAH exposure. While these have not yet been explicitly linked to lung cancer epidemiology, they provide valuable insight into potential carcinogenic factors.

In Chapter 5 we explore the fate of quartz as it progresses from coal to air and/or ash. The presence of quartz in coal had already been established in Chapter 2 and this chapter expands upon those findings. In this chapter we observe that the elevated quartz in smoky coal (4.6% and 2.2% for smoky and smokeless coal respectively) largely fails to become airborne during the combustion process. A total of 159 indoor air samples were analysed for quartz content, however only 18 (11%) contained detectable levels of quartz (level of detection[LOD]: $0.2\mu g/m^3$). This finding, in combination with the finding of high amounts of total quartz in smoky coal ash (28.3% vs. 3.3% in smokeless coal ash) led us to conclude that the quartz in smoky coal largely goes on to form part of the ash with very little (if any) of it becoming airborne. The possibility that differences in airborne quartz measurements exist below our LOD or that there are morphological differences in quartz is explored in Appendix 2 of this chapter. In this appendix we describe a small ancillary study where scanning electron microscopy is used to identify quartz in samples of indoor air collected from 12 homes from 5 Xuanwei villages. This study identified that there were differences in quartz concentrations between smoky and smokeless coal burning homes (median values 0.27 and 0.03 $\mu g/m^3$ respectively) but that there was no morphological difference in the structure of quartz between the different fuel types Detected quartz levels are well beneath those considered dangerous in the occupational setting (e.g. the occupational exposure limit for quartz in The Netherlands is 75 $\mu g/m^3$). An additional finding of potential interest from this ancillary study was the detection of fibre-like particles in samples of both smoky and

smokeless coal users.Smoky coal users experienced higher concentrations than smokeless coal users (5,800 fibres/m^3 and 550 fibres/m^3 respectively). The source and relevance of these fibre-like particles is as yet unclear . Further research is required before the clinical significance of these fibre-like particles can be established.

The role of solid fuel use in both environmental and personal health is explored in Chapter 6, where indoor, personal, and outdoor black carbon (BC) measurements are presented. Black carbon is an important driver of both global climate change and adverse health outcomes. The findings of this chapter reveal that the use of smoky coal results in BC measurements that are approximately twice as high as those collected during the use of smokeless coal (personal measurements: 12 vs. 5.5 x $10^{-5}m^{-1}$) but 25% less than when wood is used (personal measurement: 16.3 x $10^{-5}m^{-1}$). Similarly to Chapter 3, this suggests that exposure to BC alone would be insufficient to explain lung cancer risk in the region. Unlike previous chapters, we did not observe a reduction in measurements with the use of ventilated stoves. Outdoor BC measurements were found to be largely driven by indoor fuel use and that villages in which its residents primarily burnt smoky coal had higher outdoor BC measurements than villages which burnt smokeless coal (6.1 vs. 3.3 x $10^{-5}m^{-1}$ respectively). These collective findings indicate that while BC may not be solely responsible for the lung cancer risk in the area, the other adverse health and climate impacts of BC mean that further efforts to reduce BC emissions in the area require investigation.

The overall findings of this thesis are discussed in Chapter 7. Overall we have observed several differences between smoky and smokeless coal. Most importantly, we found that PAH measurements were strongly influenced by fuel type, and specifically were highest when smoky coal was burnt in traditional firepits. This finding supports previous research which has reported high PAHs in association with the use of smoky coal. An additional finding of importance was that while we did observe some difference in airborne quartz measurements between smoky and smokeless coal use, this difference occurred at levels well below what would be considered harmful. Other findings of note include differences in the constitution of smoky and smokeless coals, and differences in airborne $PM_{2.5}$ and BC between the various solid fuels used with smoky coal users experiencing higher concentrations than smokeless, but less than wood users. These findings provide valuable insight into potential carcinogenicity risks and will ultimately be applied to a case control study investigating fuel use and lung cancer risk where these measurements will be used to approximate life-long HAP exposure to specific constituents. It must be pointed out however, that many of the measurements reported here, regardless of fuel type, are at levels considered detrimental to human health and thus, we consider there to be sufficient evidence to strongly advocate for improved access to non-solid (e.g. gas or electric) fuels for this population.

Samenvatting

Vaste brandstoffen (steenkool, hout, en dierlijke mest) worden door ongeveer de helft van de wereldbevolking gebruikt als primaire brandstof voor koken en verwarmen van het huis. Het gebruik van vaste brandstoffen binnenshuis leidt tot hoge concentraties luchtvervuiling. De World Health Organisation (WHO) schat dat ten gevolge van het gebruik van deze vaste brandstoffen jaarlijks ongeveer 4 miljoen mensen prematuur sterven aan ziektes zoals longinfecties, longaandoeningen waaronder longkanker en hart en vaatziekten.

De gezondheidsrisico's die in verband worden gebracht met het gebruik van vaste brandstoffen zijn duidelijk zichtbaar in de naburige regio's Xuanwei en Fuyuan in de provincie Yunnan, China. Deze twee regio's hebben een bevolking van ongeveer 2 miljoen inwoners, die voornamelijk in rurale gebieden wonen en hoofdzakelijk vaste brandstoffen gebruiken voor het koken en verwarmen van het huis. Kenmerkend voor de regio is dat het een van de hoogste longkankerincidenties van China heeft ongeacht het geslacht en rookgewoontes van de mensen. De voornaamste reden voor deze hoge longkanker aantallen is het gebruik van 'smoky' steenkool, een bitumineuze steenkool uit lokale mijnen die 'rokerig' genoemd wordt vanwege de grote hoeveelheid zichtbare rook die vrijkomt als het wordt verbrand. De longkankerincidenties onder huishoudens die 'smoky' steenkool gebruiken is ongeveer 7 maal hoger dan huishoudens die zogenaamde 'smokeless' steenkool gebruiken. Deze 'smokeless' steenkool is een antracietachtige steenkool welke alleen beschikbaar is in bepaalde delen van Xuanwei en Fuyuan. Opvallend is dat er binnen de 'smoky' steenkoolgebruikers een grote variatie in longkankerrisico's wordt waargenomen. Deze variatie lijkt bepaald te worden door het precieze gebied waarvan men de 'smoky' steenkool krijgt. Dit wijst er mogelijk op dat binnen de classificatie van 'smoky' steenkool er variaties voorkomen in chemische en fysische samenstelling. Interventiestudies in de regio hebben laten zien dat het aantal longkankergevallen ongeveer gehalveerd wordt in 'smoky' steenkool huishoudens indien men is overgestapt van open vuur naar kachels met een schoorsteen. Dit duidt er ten eerste op dat inderdaad het gebruik van 'smoky' steenkool leidt tot een verhoging van het kankerrisico en tevens dat het ventileren van de kankerverwekkende rook naar buiten leidt tot een reductie van het risico.

Onderzoek tot nu toe duidt er op dat polycyclische aromatische koolwaterstoffen (PAK's) en mogelijk kwarts (kristallijne silica) bijdragen aan de geobserveerde longkankerrisico's. Echter deze observatie is gebaseerd op studies die voornamelijk gedaan zijn in zeer specifieke hoog risicogebieden en waren in het algemeen beperkt in omvang. Om specifieker te bepalen welke stoffen in de emissies van 'smoky' steenkool bijdragen aan de longkankerrisico's in dit gebied was nieuw grootschalig blootstellingsonderzoek nodig.

Dit proefschrift beschrijft de resultaten van dit grootschalig blootstellingsonderzoek waarbij in 163 huishoudens in XuanWei en Fuyuan uitgebreide omgevings- en persoonlijke metingen zijn verricht. Het doel van dit proefschrift is het karakteriseren van de samenstelling van de vaste brandstoffen en de daarmee samenhangende luchtvervuiling binnenshuis. Op basis van deze gegevens is geprobeerd om de determinanten van de blootstelling te identificeren zoals bijvoorbeeld de brandstofbron, stoofontwerp en huiskarakteristieken. Naast het beschrijven van de luchtverontreiniging binnenshuis en de determinanten van deze vervuiling zullen de resultaten van het onderzoek ook gebruikt worden in een patiënt-controle onderzoek naar longkanker dat tegelijkertijd in de regio is uitgevoerd.

De resultaten van de geochemische, mineralogische en elementaire samenstelling van 'smoky' en 'smokeless' steenkool afkomstig van verschillende gebieden in XuanWei en Fuyuan worden beschreven in hoofdstuk 2. De hoeveelheid vluchtige koolwaterstoffen (KW) in 'smoky' steenkool is ongeveer 8 keer hoger dan in 'smokeless' steenkool (71,5 en 8,4 mg KW productie per gram steenkool tussen 300 en 650 °C, respectievelijk). De hogere KW productie per gram steenkool varieerde sterk tussen de verschillende gebieden waar de 'smoky' steenkool vandaan kwam. De mineralogische analyse toonde ook aan dat 'smoky' steenkool meer kwarts bevat (4,6% van de steenkool, waarvan 1.9% in de respirabele fractie) dan in 'smokeless' steenkool (2,2% en 0,6% resp.). Tenslotte was 'smoky' steenkool in elementaire samenstelling over het algemeen minder gevarieerd in vergelijking met 'smokeless' steenkool, met uitzondering van silicium waarvan meer aanwezig was in 'smoky' steenkool (92.100 ppm) dan 'smokeless' steenkool (84.000 ppm). De resultaten van verhoogde concentraties koolwaterstoffen en kwarts in 'smoky' steenkool komen overeen met de primaire hypothese dat aromatische verbindingen en kwarts mogelijk een rol spelen in de longkankeretiologie in deze regio.

In hoofdstuk 3 worden de resultaten beschreven van de persoonlijke- en binnenshuis metingen van fijnstof ($PM_{2,5}$; deeltjes met een diameter kleiner dan 2,5 micrometer (µm)). De resultaten laten zien dat het gebruik van 'smoky' steenkool geassocieerd is met licht verhoogde $PM_{2,5}$ concentraties vergeleken met 'smokeless' steenkool (155 en 148 µg/m^3 resp.) maar met lagere concentraties vergeleken met het gebruik van hout als primaire brandstof (289 µg/m^3). Het gebruik van geventileerde stoven resulteerde in een vermindering van $PM_{2.5}$ concentraties in vergelijking met niet geventileerde stoven en open vuur (bijv. 'smokeless' steenkool in een open vuur leidt tot een $PM_{2.5}$ concentratie van 277 µg/m^3 en een geventileerde stoof tot 134 µg/m^3). Aangezien de hoogste $PM_{2.5}$ concentraties worden gevonden bij houtverbranding, terwijl het risico voor longkanker voor houtverbranding in de regio veel lager is dan voor 'smoky' steenkool, is het niet aannemelijk dat de blootstelling aan $PM_{2,5}$ het longkankerrisicoverschil tussen 'smoky' en 'smokeless' steenkool verklaart.

In hoofdstuk 4 beschrijven we de resultaten van de PAKs analyses. De belangrijkste conclusie in dit hoofdstuk is dat het gebruik van 'smoky' steenkool leidt tot negen keer hoger concentraties aan deeltjesgebonden PAKs dan wanneer 'smokeless' steenkool gebruikt wordt. Ter illustratie de Benzo[a]pyreen (BaP) concentratie bij 'smoky' steenkoolgebruikers was 44,7 ng/m^3 en bij 'smokeless' steenkoolgebruikers 10,6 ng/m^3. Overeenkomstig met de waarnemingen beschreven in hoofdstuk 3, nam de luchtconcentratie aan PAKs af als de brandstof werd verbrand in een geventileerde stoof in vergelijking met niet geventileerde stoven en open vuren (bijv. BaP luchtconcentraties bij 'smoky' steenkoolgebruikers was 151,9 ng/m^3 bij het gebruik van een open vuurplaats en 38,1 ng/m^3 bij het gebruik van een geventileerde stoof). Daarnaast werd een variatie waargenomen in de PAKs luchtconcentraties voor 'smoky' steenkool afkomstig van verschillende geografische gebieden, verschillende kamerafmetingen en de verschillende seizoenen. Samenvattend wijzen deze bevindingen er op dat de blootstelling aan PAKs parallellen vertoont met een aantal bekende karakteristieken van de longkankeretiologie in het gebied, in het bijzonder een vermindering in blootstelling bij het toepassen van geventileerde stoven, het grote verschil in luchtconcentraties tussen 'smoky' en 'smokeless' steenkool en de geografische variaties in de PAK-blootstelling. Hoewel deze nog niet expliciet te koppelen zijn aan de longkankerepidemiologie geven ze wel inzicht in de waarschijnlijkheid dat PAKs een rol spelen in de longkankeretiologie in dit gebied.

De aanwezigheid van verhoogd kwarts in 'smoky' steenkool was al beschreven in hoofdstuk 2. In dit hoofdstuk bestuderen we de levenscyclus van kwarts en het potentieel van het kwarts om in de lucht terecht te komen en/of in het verbrandingsas. De voornaamste observatie van deze studie is dat het kwarts in steenkool nauwelijks tot verhoogde luchtconcentraties aan kwarts leidt. Van de 159 luchtmonsters werd er slechts in 18 (11%) een detecteerbare hoeveelheid kwarts gevonden (detectiegrens 0,2 $\mu g/m^3$). Deze observatie, in combinatie met de observatie van hoge kwartspercentages in het as van 'smoky' steenkool (28,3% versus 3,3% in as van 'smokeless' steenkool), geeft aanleiding om te veronderstellen dat het kwarts in 'smoky' steenkool voornamelijk in het as terechtkomt en dat er maar weinig (of geen) als aerosolen in de lucht terechtkomt. In de appendix van dit hoofdstuk beschrijven we een additioneel klein onderzoek waarbij gebruik is gemaakt van elektronenmicroscopie om het kwarts in binnenluchtmonsters van 12 huizen in Xuanwei te kwantificeren en morfologisch te beschrijven. Deze beperkte studie gaf aanwijzingen dat er misschien toch verschillen zijn in kwartsluchtconcentraties tussen huizen waarin 'smoky' en 'smokeless' steenkool is gebruikt (mediaan 0,27 en 0,03 $\mu g/m^3$ resp.) maar dat er geen verschil is in de morfologie van de kwartsstructuur van de deeltjes afkomstig van de verschillende type brandstof. Echter deze gemeten kwartsniveaus zijn beduidend lager dan de waarden die gevaarlijk worden geacht. Ter vergelijking de limiet voor kwartsblootstelling in de werkomgeving 75 $\mu g/m^3$). Een andere, mogelijk interessante, uitkomst van dit onderzoek is het detecteren van vezelachtige deeltjes in monsters van zowel 'smoky' als 'smokeless' steenkoolgebruikers. De bron en de relevantie van deze vezelachtige deeltjes is nog niet duidelijk, maar 'smoky' steenkoolgebruikers worden aan hogere luchtconcentraties blootgesteld dan gebruikers van 'smokeless' steenkool (5800 vezels/m^3 en 550 vezels/m^3 resp.). Additioneel onderzoek is echter nodig om de gezondheidsrelevantie van deze vezelachtige deeltjes nader te duiden.

De invloed van het gebruik van vaste brandstoffen op het milieu en de humane gezondheid wordt verder onderzocht in hoofdstuk 6 door analyses van black carbon (roet) in de binnen- en buitenlucht, en in de persoonlijke ademslucht. Black carbon is een belangrijke oorzaak van zowel wereldwijde klimaatveranderingen als van ernstige gezondheidsproblemen. De resultaten van het hier beschreven onderzoek tonen aan dat het gebruik van 'smoky' steenkool leidt tot roetmetingen die bijna twee keer zo hoog zijn als wanneer er gemeten wordt bij het gebruik van 'smokeless' steenkool (12 versus 5.5 x $10^{-5}m^{-1}$) maar 25% minder dan wanneer hout werd gebruikt (16.3 x $10^{-5}m^{-1}$). Overeenkomstig hetgeen in hoofdstuk 3 is beschreven voor $PM_{2,5}$, suggereert dit dat de blootstelling aan roet alleen onvoldoende is om het risico op longkanker in de regio te verklaren. In tegenstelling tot het eerder beschreven onderzoek namen we geen roetconcentratievermindering waar bij het gebruik van geventileerde stoven. Dit wijst erop dat niet alle stoffen met dezelfde efficiëntie worden geventileerd. Een deel van de studie focuste op de roetconcentraties in de buitenlucht die, hoewel XuanWei een rurale omgeving is, relatief hoog zijn 6,1 x $10^{-5}m^{-1}$. Het feit dat de buitenluchtroetconcentraties correleerde aan de binnenluchtmetingen terwijl er geen duidelijke bronnen buitenshuis zijn wijst erop dat het verbranden van vaste brandstoffen significant bijdraagt aan de roetconcentratie in de buitenlucht. Deze gezamenlijke uitkomsten wijzen erop dat het reduceren van het gebruik van vaste brandstoffen niet alleen van belang is vanuit een gezondheids- maar ook vanuit een klimaatperspectief.

De algemene bevindingen van dit proefschrift worden bediscussieerd in hoofdstuk 7. De diverse hoofdstukken hebben inzicht gegeven in de vele verschillen die er zijn in

luchtconcentraties tussen huishoudens die ‘smoky’ steenkool gebruikten versus ‘smokeless’ steenkool. De belangrijkste uitkomst is dat PAKs concentraties sterk worden beïnvloed door het type vaste brandstof, en dat die het hoogste zijn als ‘smoky’ steenkool werd gebruikt in traditionele open vuren. Dit resultaat sluit aan op de uitkomsten van eerder onderzoek waarin ook hogere PAKs luchtconcentraties werden gemeten in huishoudens die ‘smoky’ steenkool gebruikte. Een andere belangrijke uitkomst is dat er mogelijk meer kwarts in de verbrandingslucht van ‘smoky’ steenkool zit dan van ‘smokeless’ steenkool, maar dat deze niveaus ver onder de niveaus liggen die we in zijn algemeenheid als schadelijk achten. Andere vermeldingswaardige resultaten zijn de verschillen in $PM_{2,5}$ en roetconcentraties in relatie tot de verschillende gebruikte brandstoffen waarbij ‘smoky’ steenkoolgebruikers hogere concentraties ervaren dan ‘smokeless’ steenkoolgebruikers, maar minder dan zij die hout als brandstof gebruiken. Deze uitkomsten geven waardevolle inzichten in de mogelijke stoffen die gerelateerd zouden kunnen zijn met de geobserveerde kankerrisico’s. Dit kan echter pas beter gekwantificeerd worden als deze blootstellingsinzichten worden toegepast in een recent uitgevoerde patiënt-controle onderzoek naar longkanker in XuanWei en Fuyuan.

Wel moet er op gewezen worden dat het gebruik van vast brandstoffen, onafhankelijk van het brandstoftype, resulteren in luchtconcentraties van vele stoffen die schadelijk zijn voor de volksgezondheid. Dit pleit dus sterk voor een betere toegang tot niet-vaste brandstoffen (bijv. gas of elektrisch) voor deze populatie.

总结

目前，全球大约有一半人口依靠燃烧固体燃料（煤、木柴、动物粪便等）作为家庭烹饪和取暖用途。燃烧固体燃料所产生的家庭室内空气污染（household air pollution/HAP），每年造成全球大约400万人过早死亡。

位于中国云南省东北部的宣威市和富源县，当地约有200万居民（主要以偏远农村居民为主）日常烹饪和取暖几乎全部使用固体燃料。 宣威、富源地区是全国肺癌发病率最高地区之一。前期调查研究显示该地区肺癌高发现象，与居民性别及是否吸烟状况并无关联，并确定“烟煤”的大量使用是造成民众肺癌频发的主要原因。 烟煤是当地出产的一种煤，燃烧时会产生大量浓烟。 有研究显示，用烟煤烹饪取暖的人群，肺癌发病率平均是使用无烟煤（无烟煤仅在宣威和富源有限的几个地方开采和燃用）人群的7倍；在某些特定的烟煤使用区，肺癌发病率更是无烟煤地区的100倍，显示肺癌高发原因可能与煤里不同的成分有关联。此外，另有研究显示，把无烟囱的火塘改换为有烟囱的炉灶，能使肺癌发病率降低约50%，证明改善通风能减少燃料燃烧时空气中致癌物的浓度。

目前部分研究显示，肺癌可能与HAP中的多环芳烃（PAHs）和石英（晶体硅）含量有关。但是，由于现有研究受样本量小、地域范围狭隘所局限，需要更多的详细研究，才能进一步加强对肺癌与HAP 之间关系的了解。

本论文描述的研究是在宣威、富源地区迄今为止最大规模的暴露评估调查。论文同时详细讨论了项目的研究结果。个体取样和室内空气取样涉及163位非吸烟成年女性及其居室。研究范围还包括燃料取样、煤灰取样等。主要目的是调查宣威、富源地区固体燃料的成分、室内空气污染水平，并鉴定不同污染物暴露的决定因素（如燃料种类和炉灶设计等）。同时，本研究结果将应用于宣威、富源地区另一大型肺癌病例对照项目的暴露评估。

本文第二章主要描述对燃料样本地球化学、矿物学、基本元素成分的分析结果，指出烟煤和无烟煤成分的多种差异。热解分析显示，烟煤中挥发性有机成份含量S1和S2大约是无烟煤的8倍（烟煤S2：71.5 mgHC/g、 无烟煤 S2：8.4 mgHC/g)。其中，S1和S2分别是热解分析中，300摄氏度和300至650摄氏度释放的有机碳。此外，不同产地的烟煤，当中挥发性成分亦有不同。矿物分析显示，烟煤中总石英量、呼吸性石英粉尘含量为4.6%、1.9%，都比无烟煤高（总石英2.2%、呼吸性适应粉尘0.6%）。元素成分分析显示，无烟煤整体元素成分比烟煤多，只有硅含量少于烟煤（烟煤92100 ppm、无烟煤84000 ppm）。

第三章描述个人和室内PM 2.5（空气动力学直径小于2.5微米的颗粒物）暴露的测量结果。主要结果包括，燃烧烟煤产生的$PM_{2.5}$平均浓度比燃烧无烟煤的高（分别为148 $\mu g/m^3$和115 $\mu g/m^3$），但比燃木柴产生的$PM_{2.5}$低（289 $\mu g/m^3$）。使用有烟囱炉灶的$PM_{2.5}$平均浓度比使用传统火塘的低（例如，火塘中燃用烟煤的$PM_{2.5}$为277 $\mu g/m^3$，而有烟囱炉灶的$PM_{2.5}$为134 $\mu g/m^3$）。尽管燃烧木柴的家庭拥有最高的$PM_{2.5}$浓度，但许多数据显示，此类家庭成员的肺癌发病率远低于宣威、富源地区人群的发病率。由此可见，宣威、富源地区肺癌高发现象，并不能单纯以$PM_{2.5}$的暴露来解释。

第四章描述空气污染检测分析中，颗粒相（高分子量）和气相（低分别量）多环芳烃（PAHs）的分布。主要研究结果是，使用烟煤时，颗粒相PAHs浓度比使用无烟煤

时高，个别颗粒相PAHs浓度更是无烟煤的9倍。其中，致癌物苯并[a]芘（BaP）的浓度，烟煤使用者平均为44.7 ng/m^3；无烟煤使用者平均为10.6 ng/m^3。与使用火塘比较，用有烟囱炉灶能减少室内PAHs浓度。以BaP浓度为例，使用火塘燃烧烟煤时，BaP平均浓度为151.5 ng/m^3，而用排烟炉灶燃烧时则下降至38.1 ng/m^3。调查结果同时显示，室内PAHs浓度亦会因地理环境、室内面积、不同季节而产生变化。总之，虽然研究结果未能将PAHs暴露与宣威、富源地区肺癌发病率明确关联，但依然为深入研究潜在的致癌因子提供了有价值的数据。

第五章主要描述煤燃烧后，石英于空气及煤灰的分布。之前已于第二章讨论过烟煤和无烟煤中的石英含量，本章再以此为基础，进一步分析煤中的石英成分能否在燃烧过程中释放，被人体吸入。尽管烟煤的石英含量比无烟煤高，空气样本分析显示，石英成分很大程度上并没有在燃烧时进入空气。在159次空气取样中，只有18（11%）个样本检测出石英含量（石英检测限：0.2 μg/m^3）。同时，煤灰化验结果显示，烟煤灰石英含量为28.3%，远高于无烟煤的3.3%。由此可见，烟煤中的石英成分绝大部分都在燃烧过程中成为煤灰，只有极少部分可能进入空气。本章附录二进一步探讨了空气中石英浓度比检测限小（小于0.2 μg/m^3），或石英有不同形态差异的可能。附录中描述的是一个使用扫描电子显微镜来鉴定空气样本石英含量的小型调查。调查分别于宣威地区12个不同家庭进行空气取样，发现在以烟煤为燃料的家庭空气样本中，平均石英浓度为0.27 μg/m^3， 高于以无烟煤为燃料的家庭（0.03 μg/m^3）。值得一提的是，我们在室内空气检测出的石英浓度，远低于可能危害健康的荷兰职业接触限值（75 μg/m^3）。另外，观察显示石英形态在燃烧不同燃料时，没有任何变化。调查另一可能具有意义的结果是，在烟煤和无烟煤空气样本中发现了纤维形状的颗粒物。燃烧烟煤时，纤维颗粒物的浓度为5,800 fibres/m^3, 远高于燃烧无烟煤时的浓度（550 fibres/m^3）。 这些纤维颗粒物的来源以及它们对人体健康的影响暂时不明确，有待日后进一步研究。

第六章主要描述使用固体燃料时黑碳（black carbon/BC）的排放。黑碳对全球气候变暖及人类健康都具有较强影响。室内、室外、个人空气采样显示，燃烧烟煤平均产生的BC浓度为12 x $10^{-5}m^{-1}$， 大约是燃烧无烟煤时的两倍（5.5 x $10^{-5}m^{-1}$），但却比燃烧木柴所产生的BC浓度少25%(16.3 x $10^{-5}m^{-1}$)。与第三章类似，单纯暴露于BC并不足以解释该地区肺癌的高发。与前章节的$PM_{2.5}$及PAHs结果不同，本研究并未观察到通风会减少室内BC浓度。研究发现室外BC主要与室内燃用固体燃料有关。使用烟煤作为燃料的村庄室外BC浓度（6.1 x $10^{-5}m^{-1}$）大约是使用无烟煤村庄的两倍（3.3 x $10^{-5}m^{-1}$）。从这些发现来看，虽然BC暴露并不能单纯对该地区肺癌高发作出解释，但BC对环境和健康的影响预示着应加强在该地区控制使用固体燃料所引起的BC排放的研究。

第七章对研究的结果作出总结、讨论。研究总体发现，烟煤和无烟煤对HAP有不同的影响。最重要的是，我们发现室内PAHs浓度与燃用不同种类的燃料有关，特别是在传统火塘中燃用烟煤时为最高。此发现支持了先前研究报道的使用烟煤与高浓度PAHs与使用烟煤有关。此外的一个重要发现是燃烧烟煤比无烟煤在空气中产生较高的石英浓度，但平均浓度远低于危害健康的标准数值。其他研究结果包括烟煤和无烟煤的成分差异，及燃烧烟煤与无烟煤相比产生的$PM_{2.5}$、BC浓度更高，但比燃用木柴的浓度低。这些发现都对深入探究固体燃料所产生的可能致癌物提供有价值的数

据，并将应用于一个肺癌的病例对照研究中，对研究对象的终身HAP暴露量提供评估。最后必须提出的是，本研究所报道的污染物浓度已达到或超过危害人体健康的水平，我们认为已有足够证据支持在宣威、富源地区，提倡并加强向非固体燃料（如煤气和电）转化。

Affiliation of contributors

Bert Brunekreef
Institute for Risk Assessment Sciences (IRAS), Division of Environmental Epidemiology, Utrecht University, Utrecht, The Netherlands
Julius Center for Health Sciences and Primary Care, University Medical Center Utrecht, Utrecht, The Netherlands

Roel Vermeulen
Institute for Risk Assessment Sciences (IRAS), Division of Environmental Epidemiology, Utrecht University, Utrecht, The Netherlands
Julius Center for Health Sciences and Primary Care, University Medical Center Utrecht, Utrecht, The Netherlands
School of Public Health, Imperial College London, London, United Kingdom
School of Public Health, Environmental Health Sciences, University of California, Berkeley, United States of America

Nat Rothman, Lan Qing, Wei Hu, Wei Jie Seow, H. Dean Hosgood, Bryan A. Bassig
Division of Cancer Epidemiology and Genetics, National Cancer Institute, NIH, DHHS, Bethesda, Maryland, Unitd States of America

Lutzen Portengen, Kees Meliefste, Boris Reiss
Institute for Risk Assessment Sciences (IRAS), Division of Environmental Epidemiology, Utrecht University, Utrecht, The Netherlands

Guoping Wu, Fusheng Wei, Linlin Zhang
China National Environmental Monitoring Centre, Beijing, China

David Large
Department of Chemical and Environmental Engineering, University of Nottingham, United Kingdom

Harry Veld
Deltares, Department of Applied Microbiology and Geochemistry, Utrecht, The Netherlands

Jun Xu
Department of Community Medicine, School of Public Health, The University of Hong Kong, Hong Kong

Robert S. Chapman
College of Public Health Sciences, Chulalongkorn University, Bangkok, Thailand

Linwei Tian
Chinese University of Hong Kong, Hong Kong, China

Peter Tromp
Netherlands Organization for Applied Research, TNO, Utrecht, The Netherlands

Acknowledgements

These past 4 years have been an amazing journey, not only in terms of my personal education and growth, but also in terms of having the opportunity to travel around the world and meet some truly amazing people. I would like to take the time to thank the people who through their kindness and support have made the completion of my studies not only possible, but also enjoyable.

I would first like to thank my copromotor and daily supervisor, Roel Vermeulen for all of the guidance, teaching, and support that he has given me over the years. Thanks to Roel I have had experiences that I never would have imagined, in parts of the world that I would never have thought that I would see. I would also like to thank my promotor Bert Brunekreef for his guidance over these past four years and Lutzen Portengen for his invaluable statistical support. The maps that you see throughout this thesis are there largely thanks to the efforts of Johan Beekhuizen and Meng Wang, who during their time at IRAS were kind enough to offer their assistance in producing these maps. I would also like to thank Ingrid Dahmen and Calvin Ge for their assistance in translating my thesis title and summaries into Dutch and Chinese respectively.

The work carried out in this thesis is a truly international effort and would not have been possible without the support of people from all over the world. I would like to thank my colleagues at the NCI in the USA, especially Qing Lan, Nat Rothman, Hu Wei, and Wei Jie Seow for their valuable support and experience throughout the carrying out. I would also like to thank everyone who spent time in the field collecting samples, especially Boris Reiss who played a vital role in the planning and implementing of much of the field work. I would also like to thank the previous and current heads of the Quijing CDC, Gouqing Yin and Jun He, for their enthusiasm in our project and helping us obtain amazing access to Xuanwei and Fuyuan. I am also grateful the many people who provided invaluable in the field including Kees Meliefste (from IRAS), Jun Xu, Qinfen Xu, Xiaowei Long, Jiazheng Yin, Jihua Li, Zhen Li, and Zhangyan Zhou.

I would also like to thank all of the lovely people at IRAS of whom there are far too many to mention one by one. Over these past four years they have been the source of much friendship and support. I'd like to thank everyone there for their company, cakes, and friendship.

My family has of course been a great source of love and support over the past 4 years. My parents, George and Marilyn Downward have always supported me throughout my life and my endeavors, even when they result in drastic changes to career and country of residence. I would also like to thank my brother and sister, Alan and Joan, who have supported me with much kindness and love throughout my years.

I must also thank my lovely partner Alice, without whom I can confidently say that I would not be here, thank you for your love, support, and for just being you.

Finally, to Flotsam, good dog.

About the author

George Downward was born in Christchurch, New Zealand on February 25, 1982. After graduating high school in the end of 1999, he moved to the student town of Dunedin to enter medical school. After graduating in 2005, George worked as a doctor at Dunedin hospital until 2009, where a new opportunity would see him travel to Umeå, Sweden. While in Sweden, he completed a Masters in Public Health programme under the supervision of Anna-Karin Hurtig at the Department of Epidemiology and Global Health at Umeå University. After completing these studies and a Masters thesis investigating diabetes and diabetic complications among the Sami population of Sweden, George relocated to The Netherlands to work as a PhD student for Bert Brunekreef and Roel Vermeulen, studying the characteristics of household air pollution in Xuanwei and Fuyuan China. The results of this PhD study are presented in this thesis.