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

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ABSTRACT

Exposure to crystalline silica (quartz) has been implicated as a potential cause of the high lung cancer rates in the neighbouring counties of Xuanwei and Fuyuan, China, where the domestic combustion of locally sourced “smoky” coal (a bituminous coal) is responsible for some of the highest lung cancer rates in the nation, irrespective of gender or smoking status. Previous studies have shown that smoky coal contains approximately twice as much quartz when compared to alternative fuels in the area, although it is unclear how the quartz in coal relates to household air pollution.

Samples of ash and fine particulate matter ($PM_{2.5}$) were collected from 163 households and analysed for quartz content by Fourier transformed infrared spectroscopy (FT-IR). Additionally, air samples from 12 further households, were analysed by scanning electron microscopy (SEM) to evaluate particle structure and silica content.

The majority (89%) of household air samples had undetectable quartz levels ($<0.2\ \mu g/m^3$) with no clear differences by fuel-type. SEM analyses indicated that there were higher amounts of silica in the smoke of smoky coal than smokeless coal ($0.27\ \mu g/m^3$ vs. $0.03\ \mu g/m^3$). We also identified fibre-like particles in a higher concentration within the smoke of smoky coal than smokeless coal (5800 fibres/m^3 vs. 550 fibres/m^3). Ash analysis suggested that the bulk of the quartz in smoky coal went on to form part of the ash.

These findings indicate that the quartz within smoky coal does not become adequately airborne during the combustion process to cause significant lung cancer risk, instead going on to form part of the ash. The identification of fibre-like particles in air samples is an interesting finding, although the clinical relevance of this finding remains unclear.

1. Introduction

The lung cancer epidemic in Xuanwei and its neighbouring county of Fuyuan, located in Yunnan province, China, is causally linked to the domestic combustion of locally sourced “smoky” coal (a bituminous coal) (Mumford et al., 1987; He et al., 1991; Chapman et al., 1988). Users of smoky coal have, regardless of smoking status or gender, been found to experience lung cancer rates of up to one hundred times that of those using alternative fuels (Barone-Adesi et al., 2012). Smoky coal is the primary fuel in use throughout the region, being used by approximately 75% of the population for their day-to-day cooking and heating. The alternative fuels available include “smokeless” coal (an anthracite coal), wood, and various plant materials (including corn cobs and tobacco stems). (Barone-Adesi et al., 2012).

Previous epidemiological studies have provided some insight regarding which constituents of smoky coal (and its associated smoke) contribute to lung cancer risk in the area. Most notable has been the finding that smoky coal users are exposed to high levels of

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polycyclic aromatic hydrocarbons (PAHs), including the known carcinogen benzo[*a*]pyrene (BaP) (Downward et al., 2014a; Lv et al., 2009; Lan et al., 2002; Mumford et al., 1993, 1995). However, more recently, exposure to crystalline silica (quartz) has gained increasing attention as a potential contributor (Large et al., 2009; Li et al., 2013; Tian, 2005; Tian et al., 2008; Vermeulen et al., 2011; He et al., 2012). This attention is largely derived from several small studies which have identified higher amounts of quartz in samples of smoky than smokeless coal and a positive correlation between quartz content of smoky coal and lung cancer rates in the area. To date, these studies have largely been based upon small sample sizes, sourced solely from Xuanwei. A larger study, incorporating samples from Fuyuan in addition to Xuanwei did not identify any relationship between quartz and lung cancer rates (He et al., 2012). Further, no evidence of quartz related lung disease has been reported within the area.

We recently confirmed based on a large survey of coal samples ($n = 146$) collected from both Xuanwei and Fuyuan, that higher amounts of quartz within smoky coal exist than in smokeless coal (4.6% vs. 2.2%) (Downward et al., 2014b). However, the contribution of this quartz to household air pollution (and thus personal exposure) needs to be established. In the current paper we present the findings of quartz in household air and fuel ash from households in Xuanwei and Fuyuan. We also present the findings of field emission gun scanning electron microscopy in combination with X-ray analysis (FEG-SEM/EDX) on additional air samples collected to study the physico-chemical characteristics of the air particulate matter.

2. Methods

2.1. Study design

This paper forms part of a larger case-control and cross-sectional epidemiology study aimed at cataloguing the constituents of solid fuels and its associated household air pollution in Xuanwei and Fuyuan, before ultimately associating those constituents with lung cancer risks and biological effect markers among non-smoking women. The details of the study design have been discussed elsewhere (Hu et al., 2014) but briefly, households with a non-smoking female head between the ages of 20 and 80 were selected from villages throughout Xuanwei and Fuyuan (Fig. 1). Village and participant selection was aimed at representing the population present in the case-control study with regard to age, gender, and stove and fuel use. Therefore, households which were at least 10 years old and had not had any stove alterations undertaken in the prior five years were preferentially selected.

Households were measured and sketched with stoves and other pertinent features (windows, doors, etc.) documented. The female household head had her daily activities documented during each measurement period and provided biographical information including residential history, medical history, and socio-economic indicators.

The data for the current paper was collected during two study periods: a large-scale exposure assessment study undertaken in 2008 and 2009; and a follow-up study undertaken in 2013.

2.1.1. Primary study – large exposure assessment study

A total of 163 healthy (disease-free) female heads of household were recruited from 30 villages across Xuanwei and neighbouring Fuyuan. Visit 1 was conducted from August 2008 to February 2009 and 148 women were enrolled. Visit 2 was conducted between March and June of 2009 and an additional 15 participants were enrolled. Fifty-three participants were assessed at both visits. Up to five households were selected in each village based on: 1) having a stove that used solid fuel; 2) the residence was more than 10 years old; 3) use of the same cooking or heating equipment for the past 5 years; and 4) presence of a non-smoking healthy woman aged 20–80 years, who was primarily responsible for cooking.

Indoor air measurements were collected on 37 mm Teflon filters using a cyclone with an aerodynamic cut-off of 2.5 μm ($PM_{2.5}$), powered by a BGI AFC400S pump with a median flow rate of 3.3 L/min. Pumps were calibrated prior to each use and flow rates were measured pre and post-measurement. Cyclones were placed approximately 0.25 m from the wall and between one and two metres from the main stove (as allowed by the size of the room).

For analysis, filters were ashed at 600 degrees Celsius before being pressed into 13 mm potassium bromide (KBr) pellets which were analysed by Fourier transformed infrared spectroscopy (FT-IR), giving quartz levels in μg which were transformed into a mass concentration as a function of the volume of air (in m^3 (Chapman et al., 1988)) drawn through the filter. The limit of detection (LOD) of this methodology was 1 μg (approximately 0.2 μg/m^3 based on a 24 h measurement).

Approximately 5 g of each ash sample was deagglomerated in 50 mL of a standard solution containing water and sodium hexametaphosphate before being transferred to a 250 mL measuring cylinder and being topped up with standard solution. This mixture was homogenised and after a period of standing to allow for the sedimentation of the non-respirable fraction, the fluid was extracted and evaporated – with the remaining material being weighed. After weighing, a known portion of the remaining material was pressed into a KBr pellet and analysed by FT-IR for quartz content as a percentage of the ash.

2.1.2. Secondary study – follow-up exposure study

A secondary study was undertaken in 2013 to collect household air samples from a smaller sub-selection of villages within Xuanwei. Indoor air samples were collected on nickel coated track-etched polycarbonate filters (0.4 μm 25 mm, Nuclepore) using SKC airchek XR 5000 pumps set at flow rates of 2 L/min for 60 min. In total, 12 samples were collected for analysis (8 from smoky and 4 from smokeless coal using households).

The silica content of these filters was established using field emission gun scanning electron microscopy in combination with X-ray analysis (FEG-SEM/EDX) which was used for physico-chemical characterization, semi-quantitative estimation of the concentration, and determination of the particle size distribution for silica and fibre-like particles. Analysis was performed on a Tescan MIRA-LMH FEG-SEM with a Bruker AXS spectrometer and a XFlash 4010 detector. The filters were screened at magnifications between 200× - 5000×. Qualitative data was obtained about the type, size and shape of sampled particles, and the degree of agglomeration or aggregation. For identification of silica, automated particle analysis was performed using Scandium imaging software. From each particle/cluster of particles, the projected area equivalent diameter (dpa) was measured and an EDX spectrum recorded. 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 is calculated in accordance with ISO 14966 (ISO ISO 14966, 2002). Fibre-like particles are defined as particles with a length greater than 5 μm, a diameter less than 3 μm, 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 $(\pi/6) \bullet \rho p \bullet (dpa/Sv)$ (Chapman et al., 1988). The contribution of a single particle to mass concentration was calculated by multiplying the numerical concentration with the mass of the