Atmospheric Research 169 (2016) 17–23

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

Mineralogical characterization of ambient fine/ultrafine particles emitted from Xuanwei C1 coal combustion

Senlin Lu [a,*], Xiaojie Hao [a], Dingyu Liu [a], Qiangxiang Wang [a], Wenchao Zhang [a], Pinwei Liu [a], Rongci Zhang [a], Shang Yu [b], Ruiqi Pan [a], Minghong Wu [a], Shinich Yonemochi [c], Qingyue Wang [d]

[a] School of environmental and chemical engineering, Shanghai University, Shanghai 200444, China
[b] Institute for Environmental pollution and health, Shanghai University, Shanghai 200444, China
[c] Center for Environmental Science in Saitama, Saitama 374-0115, Japan
[d] School of Science and Engineering, Saitama University, Saitama 338-8570, Japan]

ARTICLE INFO

Article history:
Received 12 April 2015
Received in revised form 21 September 2015
Accepted 24 September 2015
Available online 3 October 2015

Keywords:
Xuanwei C1 coal
Ambient ultrafine/nano-mineral particles
Lung cancer

ABSTRACT

Nano-quartz in Xuanwei coal, the uppermost Permian (C1) coal deposited in the northwest of Yuanan, China, has been regarded as one of factors which caused high lung cancer incidence in the local residents. However, mineralogical characterization of the fine/ultrafine particles emitted from Xuanwei coal combustion has not previously been studied. In this study, PM_1 and ultrafine particles emitted from Xuanwei coal combustion were sampled. Chemical elements in the ambient particles were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), and mineralogical characterization of these ambient particles was investigated using scanning electronic microscopy (SEM/EDX) and transmission electronic microscopy, coupled with energy-dispersive spectroscopy (TEM/EDX). Our results showed that the size distribution of mineral particles from the coal combustion emissions ranged from 20 to 200 nm. Si-containing particles and Fe-containing particles accounted for 50.7% of the 150 individual particles measured, suggesting that these two types of particles were major minerals in the ambient particles generally. The nano-mineral particles were identified as quartz (SiO_2) and gypsum ($CaSO_4$) based on their crystal parameters and chemical elements. Additionally, there also existed unidentified nano-minerals. Armed with these data, toxicity assessments of the nano-minerals will be carried out in a future study.

1. Introduction

Coal consumption is highly correlated with emissions of nitrogen oxide (NOx), sulfur dioxide (SO_2), and dust (Zhang and Smith, 2007). The combustion products from smoky (i.e., bituminous) coal have been found to be more carcinogenic and mutagenic than those products from smokeless (i.e., anthracite) coal in Xuanwei, with a high lung cancer incidence in Yunnan, China (Mumford et al., 1987, 1989; He et al., 1991; Lan et al., 2001, 2004, 2008; Lu et al., 2014; Shao et al., 2015). A number of previous studies have reported that the higher lung cancer incidence was associated with PAHs in airborne particles and smoke due to indoor local coal combustion (Lv et al., 2009). However, Tian (2005), Tian et al. (2008) hypothesized that nano- or fine particles of quartz, released into the air during coal combustion, was a possible cause of the lung cancer epidemic in the Xuanwei area. On the other hand, Large et al. (2009) used a "potential of silica-volatile interaction" (PSVI) method to assess the combined influence of silica and volatile organic matter, in a re-evaluation of the existing ecological data. They found a stronger correlation between lung cancer mortality and PSVI values than between mortality and volatiles, or mortality and silica, alone, with Xuanwei coal. More recently, Downward et al. (2014) reported that the raw coal composition itself might provide leads concerning the cancer risk observed in the Xuanwei area. In a previous study (Lu et al., 2014), we found that ambient particles (mainly from local coal combustion) in the Xuanwei atmosphere had the ability to produce free radicals, which had potential toxicity to human health. These limited data demonstrated that mineral particles from Xuanwei coal combustion might have a role in explaining the mechanism producing the high lung cancer rates in the area. Although the mineral particles distributed were mainly in the coarse ($PM_{10-2.5}$), a large number of nano-sized mineral particles could still be found in the fine ($PM_{2.5}$) and ultrafine particle fractions (Lu et al., 2006; Murra and Garza, 2009). Until now, few papers on mineral nano-particles from coal combustion have been reported (Martinello et al., 2014). In order to determine the physicochemical characterization of the nano-sized mineral particles emitted from Xuanwei coal combustion, in this study scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDX); selected-area electron diffraction (SAED); and high-resolution transmission electron microscopy (HRTEM), were employed to investigate the morphology, crystalline phase and electronic structure of individual particles from Xuanwei coal combustion emissions.

* Corresponding author. Tel.: +86 21 6613 7511; fax: +86 21 6613 7787.
E-mail address: senlinlv@staff.shu.edu.cn (S. Lu).

http://dx.doi.org/10.1016/j.atmosres.2015.09.020
0169-8095/

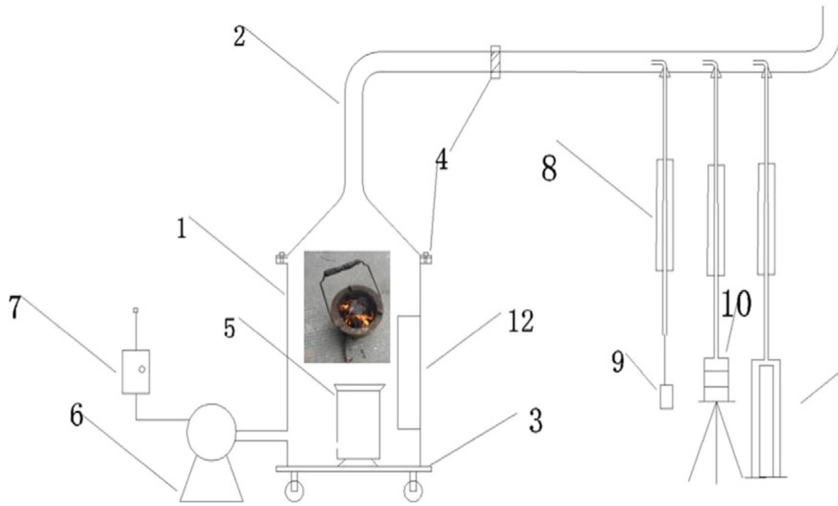

Fig. 1. Schematic map of ambient particles sampling system. 1—chamber; 2—stainless steel pipe; 3—plate support; 4—flange; 5—coal stove; 6—pump; 7—frequency converter; 8—condusing tube; 9—temperature sensor; 10—MCI sampler; 11—nano-MOUDI sampler; 12—chamber's window.

2. Materials and methods

2.1. Particle sampling

Raw coals were sampled from coal mines located in Laibin town (one of the high lung cancer incidence areas in Xuanwei). A description of the C1 coal, which lies in the uppermost portion of the Xuan Wei Formation (Upper Permian), has been made elsewhere (Dai et al., 2008; Hao et al., 2013; Shao et al.;, 2015). In this study, C1 coal from the Guangming coal mine was selected to study the mineralogical characterization of nano-particles from coal combustion. Coal combustion particle sampling was carried out using the sampling system shown in Fig. 1.

The combustion system was designed in accordance with the coal combustion pattern used by local residents as fuel for cooking and heating. The coal stove used here was purchased from the local market. Atmospheric dusts were removed from the hood via a filter (Wuxi Hengchang Section Steel Technology Co., LTD.) attached to the air-inlet of the pump.

After the coal in the stove was ignited using alcohol, the stove was transferred into the chamber. Because: (1) the mass concentration of particles from combustion in the chamber is extremely high, and (2) the temperature of the smoke is high, clean air was fed into the chamber at a rate of 80 L/min, using an air pump with a 50 Hz frequency converter. The clean air was used to dilute the high mass concentrations of smoke during particle sampling. The smoke from the coal stove, conducted through a stainless hood pipe and conducting tube, was collected directly by the particle samplers. Combustion conditions, including relative humidity, smoke temperature, and exact duration, were recorded during the experiment.

Sampling time was set at10 min after the stove was moved into the chamber. Particles were sampled on polycarbonate filters (Millipore, 47 mm diameter, 0.6 μm pore size) using a multi-nozzle cascade impact, MCI) sampler at a flow rate of 20 L/min. The MCI effectively separated the particulate matter into 3 ranges (at 50% efficiency) with the following equivalent cutoff diameters (μm), <1, 1–10, and >10 μm. A nano-MOUDI sampler was used (which could effectively separate the particulate matter into 12 ranges, at 50% efficiency), with the following equivalent cutoff diameters (μm): 10–5.6, 5.6–3.2, 3.2–1.8, 1.8–1.0, 1.0–0.56, 0.56–0.32, 0.32–0.18, 0.18–0.1, 0.1–0.056, 0.056–0.032, 0.032–0.018, and 0.018–0.010 μm). The sampler was also used to collect ultrafine/fine particles at a flow rate of 10 L/min. A total of 5 groups of PM_1 and PM_{1-10} samples, and 2 groups of size-resolved particles using the MOUDI sampler, were examined in this study.

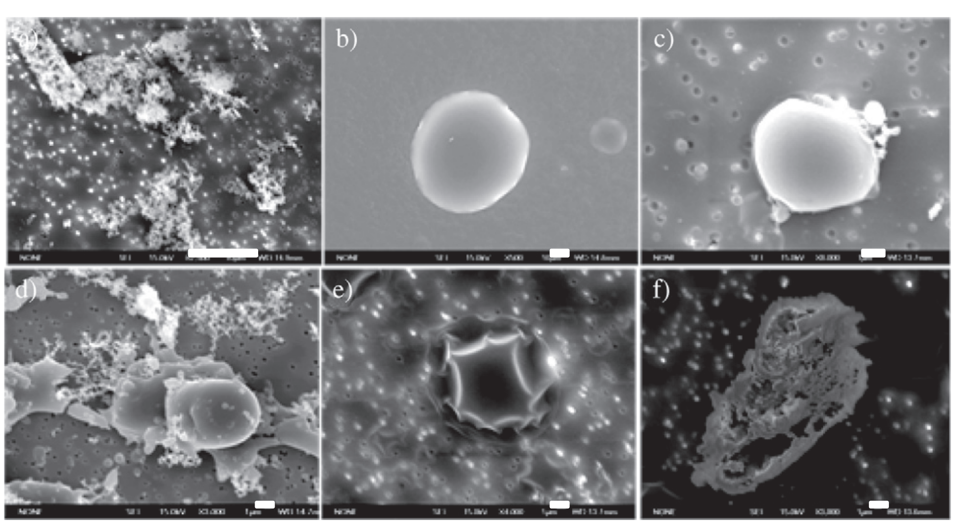

Fig. 2. Microscopic image of individual particles from Xuanwei coal combustion. a—soot aggregates; b—fly ash; c—fly ash (flatted); d—minerals; e, f—char particles. Scale bar was marked in the image, a,b—10 μm; c,d,e,f—1 μm.