Speciation of major heavy metals in ambient fine particles collected in the atmospheres of Xuanwei, Yunan, a higher lung incidence area in China

Senlin Lu¹, Fei Yi¹, Jun Lin², Jingjing Ren¹ and Xiaojie Hao¹

¹Shanghai Applied Radiation Institute, Shanghai University, Shanghai, 200444, Shanghai
²Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

Email: senlinlv@shu.edu.cn; jlin1978@gmail.com

Abstract. Xuan Wei area, Yunnan province of China, has one of the highest lung cancer mortality rates in China. Heavy metals in the aerosol are potential facts that might attribute to the cause of lung cancer, and speciation of heavy metals could play a key role in toxicity of heavy metals. Therefore, we try to reveal speciation of major heavy metals by using of synchrotron radiation techniques in this study. Mass concentration of chemical elements in ambient particles were analyzed by PIXE (Proton induced X-ray emission), and speciation of Cu was investigated by XAFS (X-ray absorption near-edge structure). Our results demonstrated that mass levels of heavy metals ranked as Fe (791.62 ng/m³) >Zn (479.49 ng/m³) >Pb(154.76 ng/m³) >Cu(28.51 ng/m³) >Co (11.79 ng/m³) >Ni (8.20 ng/m³). The Cu speciation in the different size fraction was different. Speciation of Cu in fine particles (PM₀.₅₆⁻₀.₃₂) is present as Cu (I), and significant amount of Cu is present as Cu (II) in the ultrafine particles (PM₀.₁).

1. Introduction

Numerous epidemiological and toxicological studies have shown that a statistical association between health effects and ambient particle concentrations, especially the submicron fraction that can be easily penetrated into the alveolar region of the lungs [1-5]. Airborne particulate matter is a very complex mixture that includes particles in a wide range of sizes and with varied composition. These biological effects varied with number, size, and chemical composition of particulate matter [6-8]. Being a rural county with a population of more than 1.4 million in north-east of Yunnan province, China, Xuanwei is famous for its unusually high incidence of lung cancer, which is eight and four times higher than that of the Chinese national average incidence for women and men, respectively[9]. A number of studies of Xuanwei lung cancer has been conducted since 1970s [10,11,12]. However, a recent report by Vermeulen R. [13] et al found that crystalline silica was another contributing factor to the high lung incidence. Most of previous studies focused on PM10 emitted from coal combustion rather than fine or ultrafine particles. This study will focus on physicochemical characterization of fine and ultrafine particles in the atmosphere of the high lung incidence area and our results could provide new essential data for evaluation of the high lung incidence.
2. Experiments

2.1 Sample collections

The study area located in Laibin town (26° 13.883′ N, 106° 13.883′ E), a suburb of Xuanwei, Yunnan Province, China. Size-separated aerosol particles were collected by using a 13-stage MOUDI125B (Micro-Orifice Uniform Deposit Impactor, MSP, Co., Minneapolis, USA) with the flow rate of 10 L/min. The sampling campaigns were performed from April 21 to 25, 2011. A total of three groups (39 samples) of size-segregated ambient particle samples were collected. The sampling period for each group was set at 48 hr. The sampled filters were kept in desiccators for analysis.

2.2 Chemical analysis by PIXE

The concentration of 22 elements (Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Mo, Pb) in size-resolved particles were determined by PIXE analysis using a 1.7MeV proton beam from a Tandem accelerator in the Department of Science and Technology of Nuclear sciences, Beijing Normal University. The X-rays were detected by means of a Si(Li) detector. The proton beam size is 10 mm × 4 mm.

2.3 X-ray Absorption Fine Structure analysis

Speciation of toxic chemical copper in the size-resolved particles was investigated by XANES. Cu L-edge XANES spectra were measured at Beamline 4B7B of the Beijing Synchrotron Radiation Facility (BSRF), Beijing, China. The electron energy in the storage ring is ~2.2 GeV with a current of about 100mA. The L-edge absorption of copper was measured with a Monk-Gillieson monochromator. The energy region of X-ray selected is about from 900 to 980 eV. CuO, Cu2O, CuSO4, the possible components of copper in the PM samples, were selected as reference materials. Background removal, normalization and deconvolution of XANES spectra were carried out using IFEFFIT package.

3. Results and discussion

3.1 Mass concentration of the size-resolved particles

Our result showed that mass level of different size particles was different. The highest mass concentration was found in the 1.0-0.56 μm size range (71.78±2.8 μg/m3), while the lowest mass level was in the 10-5.6 μm size range (9.55±1.2 μg/m3). The total mass concentration of the ambient variously size-resolved particles was 316.9 μg/m3.

![Figure 1](image.png)

**Figure 1**: Mass concentrations of size-segregated particles collected in Xuanwei spring atmosphere.
3.2 Mass concentration of chemical elements in size-resolved ambient particles

Chemical elemental analysis results showed that the total mass concentration of the 22 chemical elements was 8747.37 ng/m³ (Figure 2). Sulfur was the most abundance element in Laibin ambient particles with mass level 2624.04 ng/m³, and mainly distributed in the fine particles. Being a typical anthropogenic element, sulfur in ambient particles mainly contributed by coal combustion. Crustal elements, including Ca, Si, Al, Fe (four dominant elements) mainly distributed in the coarse particles. Mass concentrations of Ca in coarse, fine and ultrafine particles was 876.99, 120.6, and 9.81 ng/m³ respectively. Correspondingly, Si was 963.04, 638.44, and 6.33 ng/m³, Al was 386.61, 254.72, 5.05 ng/m³, Fe was 521.53, 186.82, 10.07 ng/m³. Anthropogenic elements, such as Zn, Ni, Pb, Cr Co, Cu, were richer in fine particles. The mass levels of Zn and Pb in fine particles was 310.57 and 43.64 ng/m³ respectively. Other metal elements in fine particles ranked in the following order: Zn (28.51 ng/m³) > Mn (28.31 ng/m³) > Ni (8.2 ng/m³) > Cr (7.77 ng/m³), while that for winter was Mn (106.41 ng/m³) > Ni (23.19 ng/m³) > Cr (15.89 ng/m³) > Cu (12.86 ng/m³).

3.3 Speciation of Cu in different ambient size particles

XANES results showed that the spectra of reference materials Cu2O [Cu(I)] and CuO [Cu(II)] is different (Figure 3). The spectrum of Cu+ has a conspicuous preedge peak at approximately 930 eV,

![Figure 2: The mass concentration of 22 elements in Xuanwei ambient particles](image)

![Figure 3: Cu–L edge XANES spectra of the size-fractionated aerosol sample in Xuanwei, reference spectra of Cu(II) sulfate, Cu(II) oxide are plotted for comparison. Particles with diameter 0.56–0.32, 0.32–0.18 and 0.1–0.056 μm could be collected through the stage 7, stage 8 and stage 10 respectively.](image)
while Cu$^{2+}$ exhibits a very weak pre-edge structure. The speciation of Cu in the fine fraction (<2.5 μm) was found the same as the Cu in fine particles (at the two stage, stage7 and stage 8). Cu L-edge absorption spectrum in the ultrafine particles (<0.1 μm) showed differently compared with that in the fine particles. Significant amount of Cu is present as Cu (I) in the ultrafine particles.

4. Conclusions

1. Mass level of the size-resolved ambient particles collected in the atmosphere of Xuanwei high lung cancer area showed differently. The highest mass concentration was found in the 1.0-0.56 μm size range (71.78±2.8μg/m3), while the lowest mass level was in the 10-5.6μm size range (9.55±1.2μg/m3), suggest that fine particles be the main fraction in airborne particles.

2. Mass concentration of chemical elements in the size-resolved particles (aerodynamic diameter, 10 nm –10µm) in spring varied from 0.24 to 9.92 g/m3, mass levels of heavy metals ranked as Fe (791.62 ng/m3)>Zn (479.49 ng/m3)>Pb (154.76 ng/m3)>Cu (28.51 ng/m3)>Co (11.79 ng/m3)>Ni (8.20 ng/m3).

3. The Cu speciation in the different size fraction was different. Speciation of Cu in fine particles (PM0.56–0.32 ) is present as Cu (I), and significant amount of Cu is present as Cu (II) in the ultrafine particles (PM 0.1).

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