Characteristics and risks of composite pollutants formed by C1 bituminous coal combustion particulates and polycyclic aromatic hydrocarbons (PAHs) in Xuanwei area

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Abstract. The Xuanwei area of Yunnan Province in China has been the high incidence area of lung cancer and mortality worldwide since 1980s. The high incidence factors of lung cancer in Xuanwei area were studied in epidemiology, atmospheric science and molecular biology. We believed that the high incidence of lung cancer was not a single factor but the result of the interaction of many high risk factors, such as the use of coal and indoor air pollution may be a cause of high incidence of lung cancer in Xuanwei. However, the risk factors of stove type, life habits and so on need to be further studied. This paper mainly analyzed the causes of high incidence of lung cancer from two aspects: fine particles produced by coal combustion and polycyclic aromatic hydrocarbons (PAHs) in Xuanwei area. We concluded that the form of Fe+ in the bituminous coal was helpful for the emission of PAHs, and the PAHs on the surface of fine particles bring lung health risks.

1. Introduction

Xuanwei, located in the northeast of Yunnan Province, which is a county-level city under the jurisdiction of Qujing, Yunnan Province. In the area, heavy industry is underdeveloped, but there is riched in coal resources, large and small coal kilns are everywhere. Most of the local people live on agriculture, directly acquiring untreated lignite from nearby coal kilns as fuel for production and daily use. Most of them use open stove and have poor ventilation, besides, there is no smoke removal equipment. Therefore, the smoke from lignite combustion is discharged directly into the home, resulting in serious indoor air pollution. The main components of the particles include silica, PAHs, transition metal elements and some heavy metals and so on. It is reported that PAHs loaded on the surface of Nan scale silica particles can directly affect the lungs after inhalation, which brought health risks. Most of the men go out to work, and women live at home about 17 hours. Therefore, it is found that the incidence and mortality of female patients were higher than that of men. This paper mainly reviewed the indoor air pollution and the related research progress and the research status. More importantly, it was aimed at put forward the mechanism of high incidence of lung cancer in Xuanwei area.
2. Indoor air pollution

2.1. Characteristics of indoor air pollution
The existence state of indoor pollutants in air is indoor air pollutants (HAPs). Indoor air pollutants mainly exist in two forms of gas and solid. The study of Y Guo et al showed that indoor air pollution were positively related to the incidence of lung cancer. Zhou Lin and Shao Longyi found that the daily average of PM2.5 is 166 μg/m³, which was far higher than the air quality standard (75 μg/m³) set by the state. The toxicity of PM10 in high incidence area of lung cancer was much higher than that of PM10 in the low incidence area of lung cancer. This difference was statistically significant (P<0.05), which was consistent with the results of KH Lui [1]. Q Liu et al [2] evaluated the risk of indoor air pollution and lung cancer. It showed that the ratio of exposure to men is 2.1 (95%CI 1.2-3.8), and that of women is 3.6 (95%CI 1.4-9.3). Behera D et al showed that the use of mixed fuels was associated with lower risk of lung cancer (OR = 3.04, 95%CI 1.1-8.38) [3]. However, the type of fuel used in rural areas in Xuanwei area is relatively simple. Some foreign scholars believed that the emission of high pollutants was the essential factor [4] for accumulating cancer risk. Zhang Rongchi et al found that there was significant difference in the toxicity equivalent of the same size particles. The toxic equivalent of fine particles accounted for 87.4% of the total toxicity equivalent of PAHs in inhalable particles, which was much higher than that of coarse particles (12%) and ultrafine particles (0.4%) of the toxic equivalent. According to SH Cho et al [5] in the presence of carbon, the coal data indicated that ultrafine particles containing carbon black were more toxic than fine particles or coarse particles containing carbon in the presence of carbon. D Wu et al [6] identified and quantified 18 PAHs in PM 2.5 and PM 10 by GC-MS in 5 places of E’erduosizai, and they found that the concentration of PAHs produced by coal combustion accounted for 42% -84% and 75% -82% of PAHs in PM 2.5 and PM 10, respectively. Compared with the emissions of wood and anthracite, the coal with black smoke has high concentration of sub-micron particles with high concentration of mutagenic organisms. Especially aromatic and polar parts are more likely to cause serious indoor air pollution.

2.2. Characteristics and risk of emission fine particles
Silicon dioxide, which is quartz, widely exists in nature. However, it rarely appears in the form of single substance. Silicon dioxide is not usually considered a carcinogen. But occupations characterized by high exposure to crystalline silica has high lung cancer mortality. Tian et al [7] found that there were a lot of kaolin (the main component is Al₂O₃•2SiO₂•2H₂O) in the C1 coal seam, which was rich in Nan scale silica crystals less than 100nm. But in the form of complex silicate or silica, widely found in rocks, gravel and dust. Previous studies [8] showed that the silicon dioxide in Xuanwei area was mostly of micron grade, (the size of the particle is mostly between 1-2 μm). G JLı et al [9] measured the content of silica in C1 bituminous coal and its combustion products in the high incidence area of lung cancerin

Figure 1. The use of local open stove
Xuanwei City, Yunnan Province. The results showed that the diameter of the silica particles in bottom ash was 120～500nm, which with different shapes. Besides, it contained iron, aluminum, calcium, potassium, etc. What’s more, the silica particles in soot were mainly Nan scale in diameter between 37～80nm. W Lin et al [10] used crystalline silica as a positive control in cultured cells derived from human Broncho alveolar carcinoma. The cytotoxicity of 15nm and 46nm silica nanoparticles was studied, which found that ROS was significantly increased while glutathione content decreased in alveolar cells exposed to SiO₂ nanoparticles, while the increased release of malondialdehyde and lactate dehydrogenase in cells suggests that the lipid peroxidation and cell membrane damage. The study of Fan JS and Zhou L suggested that composition of indoor pollutant in Xuanwei high incidence area of lung cancer ranged from high to low: spherical > particles > mineral particles > soot aggregates > unknown particles, while the low incidence area, it ranged from high to low: unknown particles > soot aggregates > mineral particles > spherical particles. However, more than 70% of indoor respirable particles contain elements of O and Si, silicon dioxide occupied a large volume in particulate matter in high incidence areas. S Lu indicated that fine particles were the main component of Xuanwei atmospheric particles, and the PIXE results showed that crustal elements (Ca, Ti, Si, Fe) are mainly distributed in the coarse particles, while trace metals in the fine fraction (Cr, Mn, Ni, Cu, Zn, Pb) are dominant. The correlation coefficient (R2) between the fluorescence intensity of free radical strength and size produced by decomposition of particles were 0.535 and 0.507 respectively, which indicated that the ambient air particles in Xuanwei atmosphere have the ability to produce free radicals. Fine and ultrafine particles may cause harm to the local residents. Some metal ions can react with the silanol group on the surface of silica to change the ability to produce free radicals on the surface, which further affects the toxicity of silica.

The lung is the target organ of silicon dioxide. Experiments have shown that Nan scale silica has a greater health risk than micron-sized silicon dioxide. Nanoscale silica may be caused by pyrolysis of lignite during the combustion process. Mice experiments showed that the smaller particles, the greater the damage to their lungs, which may be due to the fact that small particles were inhaled and stay in the deep part of the lungs. It is not easy to be removed from the body and the free radicals carried on the surface of the silica particles can cause irreversible damage to the lung cells.

Li Guangjian et al characterized and separated the Nan scale silicon dioxide produced after the burning of Xuanwei lignite. It is found that the silicon dioxide in coal is mostly micron scale and the silica produced after burning lignite is mostly nanometer level (150nm-200nm). Besides, it is significantly higher than that of other areas (P<0.05). The particle size of fine particles determines where they are deposited in the respiratory tract of the human body after they are inhaled by human body. IARC has defined crystalline silicon dioxide as the first human carcinogen in humans. Nan scale silica has more unique physical and chemical properties than crystalline silicon dioxide. Because of its small size, large specific surface area and the existence of unsaturated bonds, the distribution in cells and the formation of free radicals may be affected. Therefore, Nan scale silica has greater health risk than micron sized silicon dioxide.

Mice experiments showed that exposure to nano-silica for a short time with large dose did not induce lung cancer. Therefore, one of the inducements for cancer patients in Xuanwei area may be caused by prolonged but low dose exposure to a large amount of silica. In the case of silica exposed at low concentration for a long time, the inflammation is a major manifestation of nano silica caused lung injury, but in most cases does not cause tumor response. If inflammation persists, some inflammatory compounds will destroy surrounding normal tissues, causing gene mutations or cell death or even other lesions. According to the study of Zhao Guangqiang et al, nano silica was mainly enriched in bronchial epithelial cells and exists in the cytoplasm, which damaged some organelles such as endoplasmic reticulum and mitochondria. On the particle surface free radicals may interfere with DNA replication and transcription. Li Guangjian et al studied the accumulation of silica in lung of local lung cancer patients, and they found that the concentration of silica in the lung of the patients was (225.78nm + 120.29nm * 237.24 + 163.2nm), which mainly existed in nuclear membrane and cytoplasmic borders, and directly induced DNA damage. Y Zhou et al [11] also examined the size distribution of quartz in
coal combustion in Xuanwei area by means of electron microscopy and centrifugation. They found that
the use of C1 coal and cumulative exposure to nano quartz were associated with increased risk of lung
cancer. As a kind of special fine particles produced by burning coal, nanometer silica has attracted more
and more attention of researchers because of its health risks.

2.3. Risk characteristics of PAHs produced by coal-burning coal

PAHs are volatile toxic and harmful compounds linked together by two or more benzene rings in the
form of straight chains, horns, or beads, mostly colorless or yellowish crystals, with fluorescence
properties and decomposition and metamorphism under the action of light and oxygen under the action
of light and oxygen. PAHs have strong chemical stability because of this reason, PAHs can migrate long
distances, and are persistent organic pollutants (POPs). Previous studies have shown that the combustion
of lignite in Xuanwei area can produce a large number of PAHs. The international cancer agency has
classified PAHs and PAHs mixture as possible or identified carcinogenic. Although the content of PHAs
is very low in the environment, it has strong carcinogenic teratogenicity, mutagenic effect, besides, it
has the effect of bioaccumulation. Some foreign scholars pointed out that benzo a pyrene is considered
to be the strongest of carcinogenic PHAs. It is usually used as a marker for carcinogenicity of PHAs.
The concept of toxic equivalent factor (TEF) is proposed, and the toxicity equivalent factor of benzo a
pyrene is set to 1, which is used to measure the environmental impact of other PAHs. For the human
body, benzo a pyrene is a clear human carcinogen. Exposure to PAHs carries a risk of lung cancer, and
lung injury is strongly related to the direct exposure to PAHs. The related literature showed that the
pollution level of benzo a pyrene in the high incidence area of lung cancer in Xuanwei was 132-fold,
which was 0.133 μg/m3. Cai Y et al found that PHAs present in the local diet of Xuanwei, but far below
its indoor PAHs. The study of Lan Qing et al [12, 13] showed that the dominant ratio (OR) of lung
cancer risk for residents exposed to burning bituminous coal for a long time (OR) was 7.7, which far
higher than the rest of the world. Z Xia et al [14] found that women inhaled higher levels of PAHs per
year than men in the same season and area.

PHAs can be produced per combustion of 1kg coal up to 6×105 μg-14×105μg [15]. M Srivastava et
al [16] found that PHAs have toxic effects on humans and ecosystems. Benzo (a) pyrene (BaP) is one of
the most carcinogenic PHAs, which is effectively combined with atmospheric particles and transported.
Some domestic scholars have detected the production of PHAs by fine particles produced by coal
burning in Xuanwei area. They found that the mass concentration of PAHs was between 5-77359.21ng
and M-3, and the highest content was benzo pyrene. The other major PAHs were as follows: Qu and
benzo (b) fluoranthene, benzo (a) anthracene, fluoranthene, two benzene and (a, H) anthracene,
phenanthrene and benzo (k) fluoranthene, Indeno (1, 2, 3-cd) pyrene. The strong carcinogenic
compounds benzopyrene (BaP) concentration was high, which was 10060.13ng m-3. While some
foreign scholars also found that the concentration of PHAs in indoor air of Xuanwei area was higher
than that in outdoor air. The content of Bap in all indoor air samples was higher than that in China's
national standard (10ng/m³). M Shen et al found that the installation of chimneys reduced the risk of
lung cancer by local residents to a certain extent. The result is consistent with the result of the research
of Lan Q.

PHAs into the body through a series of reactions such as the cytochrome P450 and epoxide hydrolase
to form BPDE (anti benzo (a) pyrenediol epoxide, BPDE), which can be combined to form DNA
adducts with DNA (DNA adduct). Research by M Rojas et al [17] on patients with lung cancer pointed
out that BPDE-N 2-dG adducts were almost exclusively concentrated in bronchial epithelial cells. The
higher the content of adducts, the greater the risk of lung cancer in humans. Research showed that
mutations induced by BPDE in these cells were similar to those found in p-53 genes isolated from human
lung tumors. When the key gene mutation causes cells to lose control, it can be lead to cancer. PHAs,
like other poisons, are metabolically activated to produce biological activity, and are metabolically inactivated and expelled from the body. Therefore, the activity of metabolic enzymes has a
great influence on the biological effects of PAHs. The PAHs can affect the level of [18, 19] metabolic
enzymes in a certain extent. JL Mumford et al [20] found that the level of PAH metabolites in urine of
Xuanwei residents was higher than that of Kunming and Chinese American control group, while the concentration of 9-hydroxyl BaP in Xuanwei female urine was significantly higher than that in Kunming control group (P < 0.05). Alkylated PAHs is the main mutagens in Xuanwei’s indoor air. The level of adducts shows the enrichment of PAHs in the human body, and at the same time, it can react to the actual carcinogenic content in human body after metabolism. We generally regard DNA-PAHs as an indicator of carcinogenicity 

Kai Yun Yang et al found in lung tissues of Xuanwei female lung cancer by expression of PAHS-DNA adducts is significantly higher than that of non Xuanwei female membership, long-term exposure to indoor pollution of female is higher than that of anthracite coal contacts. HDH Iii et al pointed out that PHAs on mitochondria affinity was stronger, the content of mitochondrial DNA was positively related to the risk of lung cancer. PAHs causes frequent mutations in tumor suppressor gene p-53. This increases the risk of lung cancer the relationship between PHAs and lung cancer has been studied a lot at home and abroad, but the Xuanwei area of Yunnan Province has its particularity. We concluded that a large number of PAHs emitted into the relatively closed indoor environment may bring huge risk of lung health.

3. Interaction of PAHs with Radicals

3.1. Association of C1 bituminous coal with the increase of PHAs emissions

Coal burning is a more complex compound that is linked to by some aromatic compounds through aliphatic or special structural oxygen bridges. There are three main ways of producing PHAs from coal and one is the volatilization of raw coal. Lawrence et al found that the volatilization of coal comes from some PHAs with small molecular weight by hydrogen bonding. Because the hydrogen bonds were easy to be destroyed, this way was carried out at room temperature [24]. The second way is to decompose the aromatic compounds with high molecular weight at high temperature to produce free radicals during the combustion of coal, and then form a closed benzene ring by combining the free radicals with each other [25, 26, 27]. This model is consistent with the model proposed by Bitter et al [28, 29]. The third approach is the cracking of some PAHs connected by chemical bonds during the heating process. Li Xiaodong et al showed that the content of PAHs from bituminous coal (6.2311 g g$^{-1}$) was much higher than that of anthracite (2.9057 g g$^{-1}$) and lean coal produced (0.2923 g g$^{-1}$). The results are in accordance with the results of the Yan Wang et al.

Because Xuanwei area is located in the special coal seam of Late Permian C1, the content of Fe element in the bituminous coal is higher. The average value is 3.5%, and the coal quality is different so there is a big gap between the PAHs produced. The bituminous coal is directly used without any treatment, which increases the emissions of PAHs. In the process of coal combustion, due to the presence of active center or site on the surface of a metal or metal content, they can reduce the number of radicals in the flame, because the metal ions with positively or negatively they gain or lose electrons, thereby generating reaction of PAHs occurs between different kinds of free radicals. The burning of local bituminous coal is significantly associated with the high incidence of lung cancer. The use of open stoves greatly increased indoor air pollution and made a large number of fine particles directly discharged into the home. Fine particles as carriers of PAHs increased the average daily exposure of PAHs in local women.

3.2. Association between PAHs and free radical emissions

We simulated the burning of bituminous coal in the local people's rooms in the laboratory, added Fe (Simple, purity 99%) to the coal at 1:70, and set up a control group. When coal was placed in a muffle furnace at 350°C / 500°C / 700°C, the nitrogen was pyrolyzed to room temperature under anaerobic conditions, and the free radicals and PAHs remaining on the coal solid phase were detected by electron paramagnetism. The following data were obtained:
Figure 2. The generation of free radicals after adding Fe at 350°C

Figure 3. The generation of free radicals after adding Fe at 500°C

Figure 4. The generation of free radicals after adding Fe at 700°C
Figure 5. Comparison of three temperatures

It can be seen from the diagram that the intensity of free radicals produced by coal burning at 350°C was greatly increased by adding iron powder. We inferred that the strength of free radicals increased when iron powder acted as a catalyst at 350°C. However, the catalytic activity of iron powder decreased obviously at 500°C, and the strength of free radical began to decrease.

We also tested the PAHs on the solid phase and obtained the following data:

Figure 6. The production of polycyclic aromatic hydrocarbons at three temperatures

From the data we found when the content of PAHs produced at 350°C was higher than that at 500°C, and the free radical content was the highest when iron element was added at the secondary temperature. The polycyclic PAHs with high content were found to be high cyclic aromatic hydrocarbons (PAHs), such as PHE (3 ring), BKF (5), Bap (5 ring), Icdp (6), DaA (5, ring), which were all high cyclic aromatic hydrocarbons. However, the toxicity of high cyclic aromatic hydrocarbons was much higher than that of low cyclic aromatic hydrocarbons. The main ways to produce PAHs from coal combustion were as follows:

A In the process of pyrolysis, some of the rings in the coal would broke, and some of the low ring substances were combined together to form PAHs. The reaction process was as follows:
Dehydrogenation to form a single benzene ring

Another form of formation of benzene ring

Formation of several benzene rings

In the process of coal pyrolysis, the bridge bonds connected in the coal would break up and produce free radicals, and the polymerization between free radicals produces PAHs. This was in accordance with the results of the front, and the strength of the free radical rised first at 500 and reached the highest, and continued to heat and then decreased. The free radicals could produce the benzene ring through the polymerization.

Therefore, we inferred that the increase of free radicals also helps to increase the emission of PAHs. Especially at the 350 degrees, the content of PAHs was highest. We inferred that the metal elements existing in bituminous coal at 350℃ may have the maximum catalytic activity. PAHs could be produced by catalytic polymerization between free radicals to a certain extent, and the special geological structure in Xuanwei area determined the high content of transition metal elements in local bituminous coal, thus increasing the emissions of PAHs.

4. PAHs and particulate characteristics

4.1. Interaction characteristics of PAHs and fine particles
In the early years, the research of domestic scholars showed that the smaller the particle size of the sediment, the larger the specific surface area, which led to a significant difference in the adsorption capacity of particulate matter to PAHs. The study of Weber et al. Showed that the different particle size resulted in the different adsorption ability, which was caused by the difference of the physical and chemical properties of the particles, but not related to the particle size. Zhao Chengmei et al studies also
showed that the adsorption capacity of carbon to PAHs in soot increased with the increase of carbon content. KUN YANG and others found that nanomaterials also had adsorption on PAHs. R Vermeulend and other studies used indoors benzo [a] pyrene (BaP), silica level and lung cancer mortality data to explore Xuanwei’s etiology hypothesis of lung cancer. Their study proposed the hypothesis of the risk of interaction between silica and PAHs exposure [30]. A variety of pollutants, including particulate matter, black carbon, PAHs, and crystalline silicon dioxide, were analyzed by GS and Downward [31], and compared between different fuels (such as bituminous coal, anthracite, wood) and furnace types (e.g. furnace ventilation, ventilation furnaces). Their results showed that bituminous coal produced more fine particles and PAHs than anthracite, suggesting that lung cancer is not a single factor.

The results of P Cocco study showed that in the SiO2 exposed population, many risk factors interacted in complex ways to change the risk of lung cancer [32]. A Valavanidis and others believed that the redox transition metal contained in PM is synergistic with PAHs to produce ROS [33]. These ROS are considered to be the main mechanisms of the cytotoxic and carcinogenic potential of PM, leading to oxidative stress, lung tissue and DNA damage. Similarly, D Cavallo [34] found that organic compounds adsorption of fine particles in the air can occur in various interactions with other PM components or the physical factors (additive or synergistic effect), which enhanced the adverse health effects of air pollution. Fine particles have strong adsorption properties due to their small particle size and large specific surface area. However, some metal or metal ions discharged into the air after coal combustion can easily adsorb on the surface and form compound pollutants, which brings greater risk. Compared with the single system of pollution, compound pollution formation mechanism is more complex, its toxic effects may also be completely different, because the main mechanism of ultrafine particles is oxidant injury in the environment causes adverse health effects of nano particle pollutant has cytotropic properties[35], to bind to a cell oxidative damage. However, the mechanism of the interaction of PAHs and fine particles is rarely studied, and the specific mechanism remains to be further studied by scholars.

5. Conclusion
A large number of documents confirmed that the lung cancer was not a single factor, but because of the special geological structure in Xuanwei area, so we considered the analysis of high incidence of lung cancer from the coal species. The emission of PAHs in Xuanwei area was far higher than the national standard. There were mainly silicon elements in bituminous coal produced in Xuanwei area, mainly in the form of oolitic chlorite in Xuanwei area that was, the complex of Si Fe, and the active sites on the surface of metal or metal oxide in coal combustion have catalytic effect on the emission of PAHs. The experiment part of this study was to pyrolysis PAHs at different temperatures after adding metal Fe to coal. It was found that coal combustion with iron powder at 350 °C can produce more PAHs. Most of these PAHs were above 4 rings, and at this temperature, the intensity of free radicals was the strongest. In addition, PAHs produced by the polymerization between free radicals increase the concentration of PAHs during the pyrolysis of coal. According to the experimental results, we inferred that the metal or metal elements in bituminous coal have the strongest catalytic activity for PAHs at 350°C. The air pollution caused by bituminous coal combustion, especially the emission of large amounts of PAHs, and the use of open stove in Xuanwei area may be related to the high incidence and high mortality rate of lung cancer in Xuanwei area.

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