A health hazard assessment model of fine particles generated from coal-fired boilers and its case analysis

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Abstract. A novel health hazard assessment model of fine particles generated from five groups of coal-fired boilers is built based on AHP. In our assessment model, some important factors are taken into account, including the number from uncontrolled emission, and mass from uncontrolled emission, the particle size distribution of Rosin-Rammler function of fine particles, and the total content of toxic chemical compositions (including Cr, V, Mn, Ni, Pb, Cd, As, Se, Hg, OC and EC). By calculation, PM\textsubscript{2.5} from the industrial grate-fired boilers are much more harmful to human health than those from the other types of coal-fired boilers, which is not recommended to choose grate-fired burners as a burner of a new boiler or a modification boiler. PM\textsubscript{2.5} from industrial fluidized-bed boilers are more harmful to human health than that of utility CFB boilers; PM\textsubscript{2.5} from the large-capacity utility pulverized coal boilers (\(\geq 450\,\text{MW}\)) are more harmful to human health than those from the small-capacity utility pulverized coal boilers (<450MW). It is necessary to install a high performance dust removal device.

1. Introduction
Fine particles (PM\textsubscript{2.5}) are the particles with the aerodynamic diameters of less than 2.5\textmu m. PM\textsubscript{2.5} can easily enter the alveolus region of a lung through the respiratory tract without a fine particle filtration capacity. The toxic chemical substances carried by PM\textsubscript{2.5} can be absorbed into the body’s blood circulation [1], which can lead to many diseases, such as pneumonia, thrombus, Intrauterine Growth Retardation(IUGR), and cancers [2, 3]. PM\textsubscript{2.5} are not only pretty harmful to human health, but also can lead to harsh natural environment, such as atmospheric quality and atmospheric visibility [4-6]. In China, coal combustion is a main source of PM\textsubscript{2.5} in the ambient air\textsuperscript{1}, and is mainly applied for utility and industrial boilers. PM\textsubscript{2.5} generated and emitted from utility and industrial boilers tend to be enriched with toxic chemical compositions [7], such as heavy metals. Thus, PM\textsubscript{2.5} from coal-fired emission may be more harmful to human health.

Many researches of PM\textsubscript{2.5} emissions of coal-fired boilers have been launched. Nielson et al. [8] found that the particle mass with the particle size range of 10-100 \textmu m accounted for the largest proportion, but the PM\textsubscript{2.5} mass made up 50%-80% of the particles mass in flue gas. In transmission electron micrographs, coarse particles were spherical, and PM\textsubscript{2.5} were dendritic clusters which was
individually composed of several particles of 20-30 nm. Elemental analyses show that the mass percentages of Si and Al in PM$_{2.5}$ increased with the increasing particle sizes, the percentages of Ca and S decreased with the increasing particle sizes, but the percentages of K and Fe were independent of particle sizes. Lind et al. [9] researched the vaporization process of particles in an 80MW circulating fluidized bed (CFB) boiler. The result shows that the number size distribution of particles of 0.01-1μm in flue gas was bimodal at 0.02 μm formed by vaporization-condensation and 0.3 μm formed by partial melting of fine mineral particles, and the number concentration of 0.02 μm mode was two orders of magnitude lower than that from a BFB boiler, and was up to three orders of magnitude lower than that from the pulverized coal combustion. The mass size distribution of particles of 0.01-70μm in flue gas was unimodal at 20μm, the mass of the submicron particles accounted for less than 1% of the total mass, and the mass (larger than 0.3 μm) accounted for 70% of the total submicrometer particle mass. Scanning electron micrograph (SEM) results show that there were few ultrafine particles from the CFB, and the particles shapes at 0.3μm were irregular. The 90% of Mg mass was organically bound, and reacted with quartz and aluminosilicate minerals in coal, so there was no gas-phase Mg in flue gas, and the mass size distribution of Mg was independent of particle size distributions. And a part of Cl, Br and I could get into the gas phase during coal combustion, which became one of the components of PM$_{2.5}$.

Grate-fired boilers are extensively used as coal-fired industrial boilers, and PM$_{2.5}$ emission characteristics of grate-fired have been paid more attention in China. Li et al. [10] researched the concentration characteristics and chemical composition of PM$_{10}$ and PM$_{2.5}$ generated from seven industrial grate-fired boilers, they found that the number and mass size distributions of PM$_{2.5}$ before and after the dust-collectors displayed unimodal distributions with peaks near 0.12-0.2μm. The content of SO$_4^{2-}$ in PM$_{2.5}$ was in the range of 1.5-55.2%, and the total content of SO$_4^{2-}$, NH$_4^+$, Cl$^-$ and NO$_3^-$ was in the range of 13.2-62.3%. The contents of organic carbon (OC) and elemental carbon (EC) in PM$_{2.5}$ were in the ranges of 3.7-21.4% and 4.2-24.6%, respectively. And, the dust removal processes would make the mass emission ratios of the PM$_{2.5}$ and PM$_{10}$ relatively high. Wang et al. [11] collected and separated PM$_{2.5}$ samples generated from five grate-fired boilers with a two-stage dilution sampling system. Results show that the mass size distributions of PM$_{2.5}$ displayed unimodal or bimodal distribution, the fine modes were located at 0.14 μm, and the coarse modes were located at >1 μm.

Zhao et al. have ever researched the PM$_{2.5}$ generation and emission characteristics in an industrial CFB boiler [1]. Results show that the number size distributions of PM$_{2.5}$ before and after the FF displayed bimodal distributions, the mass size distributions of PM$_{2.5}$ before and after the FF showed no peak, because the pulse back blowing of the FF led to the PM$_{2.5}$ removal efficiency reducing from 99.449% to 99.029%, and its minimum removal efficiency occurred in the particle size range of 0.1-1 μm. Na, K and Zn contents decreased with the increasing particle size, while Ca and Ti contents enriched with the increasing particle size. But, Si, Al, Mg, Fe and Mn showed no enrichment with particle size variation. However, the PM$_{2.5}$ harmfulness evaluation of coal-fired boilers cannot consider particle fineness up to now [12-15]. Up to now, there have been some researches on PM$_{2.5}$ generation and emission of the coal-fired boiler. However, the researches on health hazard assessment of PM$_{2.5}$ generated from the coal-fired boiler are very few to date. Shi et al. [16] developed a hazard evaluation model of the particulates generated and emitted from six utility boilers and a CFB boiler to launch the comparative researches of the hazards of PM$_{2.5}$, PM$_{0.38}$ and PM$_{0.38-2.5}$. The model is expressed as follows:

$$AI = \sum_{i=1}^{n} \sqrt{M_i \times N_i \times REF_i \times Hg_i}$$

(1)

where $AI$ is the index value of the hazard assessment of PM$_i$ (PM$_{2.5}$, PM$_{0.38}$ or PM$_{0.38-2.5}$) one coal-fired boiler, $M_i$ and $N_i$ are the mass and number concentrations of PM$_i$ in flue gas, respectively, $REF_i$ is the relative enrichment factor of Hg in PM$_i$, and Hg$_i$ is the content of Hg in PM$_i$. 


\[
REF = \frac{C_{fi}}{C_{oi}} A_f
\]

where \(C_f\) is the content of Hg in PM, \(C_{oi}\) is the content of Hg in the corresponding fuel coal, \(A_f\) is the ash content in the corresponding fuel coal. In this model, the mass and number, and the Hg content in PM were only taken into account, but it was not appropriate sufficiently. PM\(_{2.5}\) from the coal-fired boiler contained many types of toxic elements, such as As, Se, Cd, Pb, Cr [17]. Therefore, the Hg was used to represent the toxic chemical composition in PM\(_{2.5}\), which is not appropriate. Besides, the health hazards of the PM\(_{2.5}\) are not only concerned with the number, mass and the content of fine particles, but also with the particle size level of fine particles. The finer the particle size level is, the more easily the fine particles enter into the alveolus region of the lungs. Meanwhile, PM\(_{2.5}\) tend to enrich more toxic chemical compositions than that of coarse ones, and it will easily absorb more pernicious bacterium on its surface in the environmental atmosphere, because PM\(_{2.5}\) have larger specific surface areas. Furthermore, PM\(_{2.5}\) can float in ambient air for a longer time than the coarse ones, and are more likely inhaled into human body. Some research results have showed that the ultrafine particle (diameter of less than 0.1μm) could enter into human body through the skin pore participating into blood circulation. Therefore, the particle size level is a very important factor determining the health hazards of the fine particles, but it was not involved in this model. Besides, a model introduced in U. S. EPA’s Exposure Factors Handbook [18] can be used to assess the health hazards of fine particles from the coal-fired boiler, but the model is excessively complicated, and the calculation parameters are based on many empirical values, which may greatly reduce the credibility of the calculative results. Therefore, it needs a relatively simple health hazard assessment model with as few empirical parameters as possible. Ohlströ et al. [19] indicated that the health hazards of PM\(_{2.5}\) mainly depended on their chemical compositions, deposition in lungs and behavior in respiratory organs. The PM\(_{2.5}\) from coal-fired boilers tend to be easier to enter into human bodies, and be enriched with more condensed heavy metals. The toxic chemical compositions in PM\(_{2.5}\) were not only the heavy metals, but also the organic composition. The research of Zhang et al. [20] shows that all of organics in PM\(_{2.5}\) are harmful to human health. Therefore, the health hazard factors of PM\(_{2.5}\) from coal combustion usually includes: toxic chemical composition, particle size, number and mass.

In this work, a novel health hazard assessment modal of PM\(_{2.5}\) from the coal-fired boilers was built to launch a comparative research on the health hazards of PM\(_{2.5}\) generated from different types of the coal-fired boilers, based on the PM\(_{2.5}\) generation characteristics of forty-nine utilities and industrial coal-fired boilers. The number and mass form uncontrolled emission factors, the content of toxic chemical composition and the particle size level of PM\(_{2.5}\) were taken into account as four factors of the health hazards of PM\(_{2.5}\) in our model. It can be hoped to provide a more reasonable evaluation system.

2. Materials and methods

The bituminous coal is extensively utilized in utility and industrial coal-fired boilers in China. Pulverized coal boilers are extensively used in coal-fired units of power plants, and the grated-fired boiler are generally used as the industrial boiler, and fluidized-bed boilers are largely used as utility and industrial boilers for low NOx and SOx emissions. The dust collector is a significant pollution controlling device to remove particulate matters from coal-fired boilers. Based on these situations, we selected four types (five groups) of coal-fired boilers with regular capacities as our research objects. The boilers involved eighteen utility pulverized-coal boilers, five utility-CFB boilers, fourteen industrial-grate-fired boilers and twelve industrial-FB boilers, respectively. The capacities of the boilers and their flue gas purification devices are shown in Table 1-4. During the test periods, the boilers were operating normally and the boiler loads were relatively steady.
Table 1. Capacities of utility CFB boilers and their purification devices.

| No. | capacity (MW) | flue gas purification devices |
|-----|---------------|------------------------------|
|     |               | denitrator | dust-collector | desulfurizer |
| 1   | 1060          | LNBs\(^a\) + SCR\(^b\) | ESP\(^c\) | WFGD\(^d\) |
| 2   | 1000          | LNBs + SCR | ESP   | WFGD   |
| 3   | 1000          | LNBs + SCR | ESP   | WFGD   |
| 4   | 600           | LNBs + SCR | ESP   | WFGD   |
| 5   | 660           | LNBs + SCR | ESP   | WFGD   |
| 6   | 600           | LNBs + SCR | ESP   | WFGD   |
| 7   | 600           | LNBs + SCR | COHPAC\(^e\) | WFGD |
| 8   | 600           | LNBs + SCR | COHPAC | WFGD   |
| 9   | 600           | LNBs + SCR | ESP   | WFGD   |
| 10  | 300           | LNBs + SCR | ESP   | WFGD   |
| 11  | 300           | LNBs + SCR | ESP   | WFGD   |
| 12  | 300           | LNBs + SCR | ESP   | WFGD   |
| 13  | 300           | LNBs + SCR | ESP   | WFGD   |
| 14  | 300           | LNBs + SCR | FF    | WFGD   |
| 15  | 220           | LNBs + SCR | COHPAC | WFGD   |
| 16  | 220           | LNBs + SCR | COHPAC | WFGD   |
| 17  | 220           | LNBs + SCR | COHPAC | WFGD   |
| 18  | 220           | LNBs + SCR | COHPAC | WFGD   |

\(^a\) LNBs stand for low NO\(_x\) burners;  
\(^b\) SCR stands for selective catalytic reduction;  
\(^c\) ESP stands for electrostatic precipitator;  
\(^d\) WFGD stands for wet flue gas desulfurization;  
\(^e\) COHPAC stands for compact hybrid dust collector;  
\(^f\) FF stand for fabric filter.

Table 2. Capacities of industrial grate-fired boilers and their purification devices.

| No. | capacity (t/h) | flue gas purification devices |
|-----|---------------|------------------------------|
|     |               | dust-collector | desulfurizer |
| 1   | 20            | W-CDC\(^a\) | —— |
| 2   | 20            | W-CDC        | WFGD |
| 3   | 30            | WDC\(^b\)    | —— |
| 4   | 30            | WDC          | WFGD |
| 5   | 35            | WDC          | —— |
| 6   | 35            | WDC          | WFGD |
| 7   | 35            | CDC\(^c\)    | —— |
| 8   | 35            | WDC          | —— |
| 9   | 35            | CDC          | —— |
| 10  | 40            | CDC          | —— |
| 11  | 45            | CDC          | WFGD |
| 12  | 45            | CDC          | —— |
| 13  | 83            | FF           | WFGD |
| 14  | 63            | FF           | WFGD |

\(^a\) W-CDC stands for wet-cyclone dust collector;  
\(^b\) WDC stand for wet dust collector;  
\(^c\) CDC stand for cyclone dust collector.
Table 3. Capacities of utility CFB boilers and their purification devices.

| No. | capacity (MW) | flue gas purification devices | dust-collector | desulfurizer |
|-----|---------------|-------------------------------|----------------|-------------|
| 1   | 300           | COHPAC                        |                | DFGD+WFGD   |
| 2   | 300           | COHPAC                        |                | DFGD+WFGD   |
| 3   | 300           | FF                            |                | DFGD        |
| 4   | 300           | FF                            |                | DFGD        |
| 5   | 300           | ESP                           |                | DFGD        |

*DFGD stands for dry flue gas desulfurization.

Table 4. Capacities of industrial fluidized-bed boilers and their purification devices.

| No. | capacity (t/h) | flue gas purification devices | dust-collector | desulfurizer |
|-----|---------------|-------------------------------|----------------|-------------|
| 1   | 20            | ESP                           |                | DFGD        |
| 2   | 20            | ESP                           |                | DFGD        |
| 3   | 20            | FF                            |                | DFGD        |
| 4   | 30            | FF                            |                | DFGD        |
| 5   | 35            | ESP                           |                | DFGD        |
| 6   | 40            | ESP                           |                | DFGD        |
| 7   | 40            | FF                            |                | DFGD        |
| 8   | 40            | FF                            |                | DFGD        |
| 9   | 60            | ESP                           |                | DFGD        |
| 10  | 75            | ESP                           |                | DFGD        |
| 11  | 56            | FF                            |                | DFGD        |
| 12  | 75            | FF                            |                | DFGD        |

In this work, fuel coals are almost all bituminous coal from China. Proximate and ultimate analyses of the fuel coals are in Table 5-8.

Table 5. Proximate and ultimate analyses of fuel coals consumed by utility pulverized coal boilers.

| No. | Proximate analysis results (%) | Ultimate analysis results (%) |
|-----|--------------------------------|-------------------------------|
|     | \( M_{ad} \) | \( V_{ad} \) | \( A_{ad} \) | \( FC_{ad} \) | \( C_{ad} \) | \( H_{ad} \) | \( O_{ad} \) | \( S_{ad} \) |
| 1   | 5.48  | 26.34  | 12.58  | 55.60  | 65.31  | 3.46  | 12.05  | 0.38  |
| 2   | 4.18  | 28.38  | 15.76  | 51.68  | 60.63  | 3.77  | 13.65  | 0.85  |
| 3   | 3.78  | 28.21  | 15.59  | 52.42  | 61.36  | 3.73  | 13.65  | 0.86  |
| 4   | 2.64  | 21.55  | 36.57  | 39.24  | 44.11  | 5.89  | 9.10   | 0.90  |
| 5   | 3.38  | 29.50  | 18.10  | 49.02  | 56.53  | 3.06  | 16.58  | 1.65  |
| 6   | 5.12  | 31.50  | 18.36  | 45.02  | 55.53  | 2.95  | 15.59  | 1.53  |
| 7   | 6.46  | 27.98  | 20.81  | 44.75  | 54.72  | 3.52  | 12.54  | 0.82  |
| 8   | 8.46  | 28.58  | 19.89  | 43.07  | 53.63  | 4.01  | 11.97  | 0.76  |
| 9   | 8.86  | 21.15  | 19.70  | 50.29  | 54.46  | 3.63  | 11.76  | 0.58  |
| 10  | 2.21  | 25.43  | 32.69  | 39.67  | 50.12  | 3.71  | 9.28   | 1.20  |
| 11  | 1.70  | 16.30  | 28.74  | 53.26  | 60.09  | 2.60  | 6.1    | 0.20  |
| 12  | 4.20  | 33.91  | 18.19  | 43.70  | 62.09  | 4.02  | 10.34  | 0.20  |
| 13  | 9.90  | 20.66  | 28.48  | 40.96  | 48.32  | 3.57  | 8.56   | 0.27  |
| 14  | 7.28  | 23.56  | 24.62  | 55.46  | 66.05  | 3.29  | 12.84  | 0.36  |
| 15  | 7.41  | 28.11  | 20.23  | 44.25  | 56.27  | 3.33  | 10.17  | 1.77  |
| 16  | 1.40  | 26.62  | 33.84  | 38.14  | 50.27  | 3.30  | 9.65   | 0.72  |
| 17  | 2.38  | 27.00  | 34.78  | 35.84  | 49.81  | 3.30  | 8.17   | 0.65  |
| 18  | 1.26  | 26.07  | 36.66  | 36.01  | 48.23  | 3.30  | 9.12   | 0.70  |
Table 6. Proximate and ultimate analyses of fuel coals consumed by utility CFB boilers.

| No. | Proximate analysis results (%) | Ultimate analysis results (%) |
|-----|-------------------------------|-------------------------------|
|     | $M_{ad}$ | $V_{ad}$ | $A_{ad}$ | $FC_{ad}$ | $C_{ad}$ | $H_{ad}$ | $O_{ad}$ | $S_{ad}$ |
| 1   | 1.91    | 21.76   | 44.76   | 31.57   | 38.76   | 3.53    | 8.53    | 1.99    |
| 2   | 1.83    | 22.57   | 42.44   | 33.16   | 40.98   | 3.58    | 9.11    | 1.52    |
| 3   | 5.16    | 26.79   | 33.01   | 35.04   | 45.75   | 3.28    | 11.15   | 0.86    |
| 4   | 2.16    | 26.79   | 31.01   | 40.04   | 50.75   | 3.28    | 11.15   | 0.86    |
| 5   | 5.36    | 20.53   | 33.63   | 40.48   | 46.53   | 3.53    | 8.18    | 1.56    |

Table 7. Proximate and ultimate analyses of fuel coals consumed by industrial grate-fired boilers.

| No. | Proximate analysis results (%) | Ultimate analysis results (%) |
|-----|-------------------------------|-------------------------------|
|     | $M_{ad}$ | $V_{ad}$ | $A_{ad}$ | $FC_{ad}$ | $C_{ad}$ | $H_{ad}$ | $O_{ad}$ | $S_{ad}$ |
| 1   | 3.78    | 30.37   | 12.59   | 53.26   | 64.23   | 3.53    | 13.96   | 0.89    |
| 2   | 2.86    | 33.47   | 12.54   | 51.13   | 64.30   | 3.16    | 14.64   | 1.23    |
| 3   | 3.77    | 29.72   | 9.53    | 56.98   | 66.24   | 3.41    | 14.13   | 1.40    |
| 4   | 4.77    | 31.39   | 12.28   | 51.56   | 63.79   | 3.75    | 13.72   | 0.56    |
| 5   | 3.40    | 29.72   | 12.96   | 53.92   | 66.89   | 4.01    | 11.17   | 0.27    |
| 6   | 4.77    | 31.39   | 12.38   | 51.46   | 64.08   | 3.96    | 12.72   | 0.76    |
| 7   | 5.59    | 29.12   | 13.40   | 51.89   | 62.76   | 3.95    | 12.17   | 0.84    |
| 8   | 5.92    | 31.35   | 8.13    | 54.60   | 68.00   | 4.85    | 11.01   | 0.35    |
| 9   | 8.87    | 27.81   | 9.98    | 53.34   | 66.29   | 3.79    | 9.59    | 0.29    |
| 10  | 3.23    | 32.97   | 12.79   | 51.01   | 62.61   | 3.25    | 15.52   | 1.28    |
| 11  | 5.77    | 30.39   | 11.28   | 52.56   | 63.79   | 3.75    | 13.72   | 0.56    |
| 12  | 5.34    | 32.13   | 12.54   | 50.79   | 61.87   | 3.98    | 14.53   | 0.66    |
| 13  | 4.94    | 29.57   | 12.61   | 52.88   | 62.86   | 3.71    | 13.87   | 0.92    |
| 14  | 7.05    | 30.64   | 11.33   | 50.98   | 63.32   | 3.87    | 12.9    | 0.37    |

Table 8. Proximate and ultimate analyses of fuel coals consumed by industrial fluidized bed boilers.

| No. | Proximate analysis results (%) | Ultimate analysis results (%) |
|-----|-------------------------------|-------------------------------|
|     | $M_{ad}$ | $V_{ad}$ | $A_{ad}$ | $FC_{ad}$ | $C_{ad}$ | $H_{ad}$ | $O_{ad}$ | $S_{ad}$ |
| 1   | 6.90    | 23.48   | 49.36   | 20.26   | 35.51   | 3.43    | 3.49    | 0.24    |
| 2   | 3.64    | 22.12   | 49.31   | 24.93   | 31.95   | 2.91    | 10.86   | 0.27    |
| 3   | 6.90    | 23.48   | 49.36   | 20.26   | 35.51   | 3.43    | 3.49    | 0.24    |
| 4   | 1.51    | 21.20   | 47.04   | 30.25   | 40.87   | 3.51    | 5.55    | 0.34    |
| 5   | 3.39    | 24.85   | 41.52   | 30.24   | 40.73   | 2.84    | 10.32   | 0.41    |
| 6   | 4.03    | 25.12   | 41.07   | 29.78   | 39.84   | 2.76    | 11.05   | 0.39    |
| 7   | 5.10    | 21.06   | 45.01   | 28.83   | 36.12   | 2.76    | 9.74    | 0.41    |
| 8   | 5.52    | 23.85   | 45.93   | 24.70   | 34.85   | 2.76    | 9.57    | 0.42    |
| 9   | 5.33    | 22.00   | 46.98   | 25.69   | 34.63   | 2.17    | 10.00   | 0.18    |
| 10  | 6.09    | 29.54   | 38.99   | 25.38   | 38.32   | 2.11    | 13.00   | 0.26    |
| 11  | 5.42    | 27.82   | 40.13   | 26.63   | 36.43   | 2.51    | 14.06   | 0.21    |
| 12  | 4.72    | 22.56   | 47.12   | 25.60   | 37.06   | 2.11    | 8.10    | 0.16    |

The locations of sampling points are shown in Figure 1. The sampling points tended to be located at the inlets of precipitators. Sampling methods for PM$_{2.5}$ can be found in the experimental section of Zhao et al. The number, mass, particle size and the content of toxic chemical compositions in PM$_{2.5}$ can be represented by $EF_{WB}(N)$, $EF_{WB}(M)$, $b$ and $MDHX$, respectively. $EF_{WB}(N)$ and $EF_{WB}(M)$ are number and mass from uncontrolled emission factors in PM$_{2.5}$. $b$ is the particle size distribution coefficient of Rosin-Rammler function of PM$_{2.5}$. $MDHX$ is the total content of toxic chemical
compositions in PM$_{2.5}$, which includes Cr, V, Mn, Ni, Pb, Cd, As, Se, Hg, organic matters. The total content of organic matter can be summed by the content of OC and EC in PM$_{2.5}$.

AN ELPI was applied to measure the number and mass size distributions in PM$_{2.5}$. The contents of Cr, V, Mn, Ni, Pb, Cd, As, Se, Hg in PM$_{2.5}$ were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). The contents of OC and EC are analyzed by the interagency monitoring of protected visual environment, thermos-optical reflection (IMPROVE TOR). The emission factor of PM$_{2.5}$ from the coal-fired boiler based on 1 kg coal consumption is calculated as follows:

$$EF_{WB} = EC \times V_0$$

(3)

where $EF_{WB}$ is the emission factor that represents the PM$_{2.5}$ number or mass emission when a kilogram of fuel coal is consumed (10$^{10}$/kg or g/kg), $EC$ is the number or mass concentration of PM$_{2.5}$ in flue gas (10$^{10}$/Nm$^3$ or g/Nm$^3$), $V_0$ represents the volume of flue gas when a kilogram of fuel coal is consumed (Nm$^3$/kg), and $V_0$ is calculated as follows:

$$V_0 = \frac{(1 - A_{ad} + \frac{\rho_{kg} \alpha V^0}{\rho_{yg}})}{100}$$

(4)

where $A_{ad}$ is the ash content in fuel coal (%), $\alpha$ is the excess air coefficient of flue gas, $\rho_{kg}$ is the air density, 1.29kg/m$^3$, $\rho_{yg}$ is the density of flue gas, 1.3kg/m$^3$, $V^0$ is the air mass consumed when a kilogram of fuel coal burns out (Nm$^3$/kg), and is calculated as follows:

$$V^0 = 0.0889 \times (C_{ad} + 0.375 S_{ad}) + 0.265 H_{ad} - 0.0333 O_{ad}$$

(5)

where $C_{ad}$, $S_{ad}$, $H_{ad}$, $O_{ad}$ are the mass percentage contents of C, S, H and O in fuel coal, respectively (%). Rosin-Rammler function is extensively used to fit the cumulative mass size distribution of the dust particles, and its formula is as follows:

$$R = 100 \exp \left(-bD_p^a\right)$$

(6)

where $D_p$ is aerodynamic diameter of dust particle (μm), $R$ is the mass percentage content of particles of more than $D_p$ (%) in total particle mass, $b$ is particle size distribution coefficient; $n$ is particle size distribution index.

$$D = 100 - R = 100 \left(1 - \exp \left(-bD_p^a\right)\right)$$

(7)

where $D$ is the mass percentage content of particles of less than $D_p$ (%) in total particle mass. Zhang et al. [21] point out that the larger the particle size distribution coefficient $b$ is, the finer the particle sizes of the dust particles are. Therefore, the particle size levels of PM$_{2.5}$ can be represented by $b$.  

**Figure 1.** Locations of sampling points.
In this study, health hazard assessment model of fine particles is built through the Analytic Hierarchy Process (AHP), which is a multi-criterion decision-making method by Saaty et al. [22]. The importance of a factor (criteria) is determined by pair-contrast data between two factors, and its importance compares to another factor could be provided by a series of continuous cardinal numbers or even ones in the range from 1/9 to 9, as show in Table 9.

### Table 9. Ratios of relative importance between one factor and another.

| Importance degrees of A:B | The most important | Very important | Important | A little important | Equally important |
|---------------------------|--------------------|---------------|-----------|-------------------|-------------------|
| Value                     | 9                  | 7             | 5         | 3                 | 1                 |
| Importance degrees of A:B | A little unimportant | Unimportant | Very unimportant | The least important |
| Value                     | 1/3                | 1/5           | 1/7       | 1/9               |

Then, the numbers are listed in a matrix $A(n \times n)$ as follows, and the $a_{ij}$ represents the relative importance of $A_i$ compared to $A_j$. It is noteworthy that $a_{ij} > 1$ means that $A_i$ is more important than $A_j$, meanwhile, $a_{ij} > 0$, $a_{ii}=1$, $a_{ij}=1/a_{ji}$. Besides, according to the AHP model, $A(n \times n)$ must meet a consistency requirement, where $a_{ij}$ must be more than $a_{mn}$, when $a_{ij}$ is more than $a_{kl}$ and $a_{kl}$ is more than $a_{mn}$ in the matrix $A(n \times n)$. It can be verified by Formula 8 as follows,

$$CR = \frac{CI}{RI}$$ (8)

where $CR$ is the relative consistency index of $A(n \times n)$, and $CR$ must be less than or equal to 0.1, which indicates that the matrix $A(n \times n)$ can meet the consistency requirement of AHP; $CI$ is the absolute consistency index of $A(n \times n)$; $RI$ is the average consistency index of $A(n \times n)$. The values of $RI$ are listed in Table 10, and $CI$ is calculated by Formula 9 as follows,

$$CI = \frac{\lambda_{max}}{n-1}$$ (9)

Where $\lambda_{max}$ is the maximal proper value of the matrix $A(n \times n)$, $n$ is the order of the matrix $A(n \times n)$.

### Table 10. Values of average coincidence indicator $RI$.

| $n^a$ | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|-------|----|----|----|----|----|----|----|----|----|----|
| $RI$  | 0  | 0  | 0.58 | 0.90 | 1.12 | 1.24 | 1.32 | 1.41 | 1.45 | 1.49 |

*a is the order of the matrix A(n \times n).

The weight value of each influent factor is calculated by Formula 10-12 as follows:

$$\bar{\omega}_i = \frac{\omega_i}{\sum_{j=1}^{n} \omega_j}$$ (10)

$$\omega_j = \frac{\omega}{\sqrt{m_i}}$$ (11)

$$m_i = \prod_{j=1}^{n} a_{ij} \quad (i=1, 2, \ldots, n)$$ (12)

where $m_i$ is the product of the elements in line $i$ of the matrix $A(n \times n)$, $\bar{\omega}_i$ is the weighted value of the influent factor $A_i$, and $\sum_{i=1}^{n} \bar{\omega}_i = 1$.

### 3. Results and discussion

$EF_{WB}(N)$, $EF_{Wb}(M)$, and $M_{DLS}$ can be calculated by Formulas 3 and 6, and $b$ can be calculated by Formula 6. The average values of $EF_{Wb}(N)$, $EF_{Wd}(M)$, $b$ and $M_{DLS}$ of different types of coal-fired boilers are listed in Table 11.
Table 11. Average values of health hazardous factor of PM2.5 from all the furnace types.

| Boiler types | UPC1   | UPC2   | UCFB   | IGF    | IFB    |
|--------------|--------|--------|--------|--------|--------|
| $E_{Wd}(N)$  | 10365.41 | 7944.48 | 2535.22 | 200023.57 | 7363.26 |
| $E_{Wd}(M)$  | 3.66   | 3.23   | 11.34  | 1.11   | 15.89  |
| $b$          | 0.1332 | 0.1035 | 0.0819 | 1.1439 | 0.1176 |
| $M_{DHX}$    | 1.3024 | 1.4461 | 2.6823 | 16.1765 | 4.6515 |

$a$ UPC1 represents the utility pulverized coal boilers with the capacities of more than 450MW; $b$ UPC2 represents the utility pulverized coal boilers with the capacities of less than 450MW; $c$ UCFB represents the utility circulating fluidized bed boilers; $d$ IGF represents the industrial grate-fired boilers; $e$ IFB represents the industrial fluidized bed boilers.

Yue et al. [23] point out that the number of dust particles has a larger effect on the health hazard than that of the mass. While the mass concentrations of two groups of dust particles are the same, the number concentration of one group may be three orders of magnitude higher than that of the other group. When the mass of dust particles is sufficiently little, the content of toxic chemical compositions would also be relatively little, and the dust particles should be almost not harmful to people’s health; however, when the content of toxic chemical compositions is sufficiently little, the dust particles are still harmful to people’s health by destroying the respiratory system. Hence, the mass has a larger effect on the health hazard than that of toxic compositions in the PM$_{2.5}$. The finer the particles are, the larger the toxic-element contents are, such as As, Se and Cd [24, 25]. However, if the fine particles cannot absorb more toxic compositions, they are little harmful to human health. Hence, the content of toxic chemical compositions has a larger effect on the health hazard than the particle size level. As a result, the importance order of the four factors on health hazards of the PM$_{2.5}$ is listed in Figure 2.

![Figure 2. The importance order of the influent factors on the health hazards.](image)

The hierarchical structure of the AHP is shown in Figure 3, which is health hazard assessment of PM$_{2.5}$. The alternatives are alternative types of coal-fired boilers. In the AHP model, the influent-factor values need to normalize. Therefore, the influent-factor values in Table 11 have been transformed into the sum of normalized values in Table 12.
Figure 3. Hierarchical structure for AHP in this study.

Table 12. Average values of each hazardous factor of PM2.5 generated from all the furnace types.

| Boiler types | UPC1 | UPC2 | UCFB | IGF | IFB |
|--------------|------|------|------|-----|-----|
| $EF_{\text{WD}}(N)^{\text{a}}$ | 0.0454 | 0.0348 | 0.0111 | 0.8764 | 0.0323 |
| $EF_{\text{WD}}(M)^{\text{a}}$ | 0.1039 | 0.0917 | 0.3219 | 0.0315 | 0.4510 |
| $b^{\text{a}}$ | 0.0843 | 0.0655 | 0.0518 | 0.7239 | 0.0744 |
| $M_{\text{DLS}}^{\text{a}}$ | 0.0496 | 0.0551 | 0.1021 | 0.6160 | 0.1771 |

$^a$ represents the values via the normalization treatment.

According to the importance order of the four factors on the health hazards of PM2.5 in Figure 2, the matrix $A(4 \times 4)$ is shown as follows. The number, mass, particle size level and the total content of toxic chemical compositions) are represented by $A_1$, $A_2$, $A_3$ and $A_4$ in hierarchical analysis, respectively.

$$
A = \begin{bmatrix}
1 & 3 & 7 & 5 \\
1/3 & 1 & 5 & 3 \\
1/7 & 1/5 & 1 & 1/3 \\
1/5 & 1/3 & 3 & 1
\end{bmatrix}
$$

(13)

The weight value of each factor was calculated by Formula 10, and these weight values are listed into a weight vector of all the influent factors is $\Gamma = (0.5638, 0.2634, 0.0550, 0.1178)^T$. And the maximal proper value $\lambda_{\text{max}}$ of the matrix $A(4 \times 4)$ is 4.1170. And then the value of $CR$ is 0.043 by Formula 8, which is of less than 0.1. Therefore, the matrix $A(4 \times 4)$ can meet the consistency requirement of AHP. According to the AHP model, the health hazard assessment model of PM2.5 generated from a type of coal-fired boilers is shown as Formula 14as follows:

$$
\kappa = \sum_{i=1}^n (\alpha_i Q_i)
$$

(14)

where $\kappa$ is the health hazard assessment coefficient, which represents the health hazards of PM2.5 generated from the certain type of coal-fired boilers when a kilogram of coal is consumed, and the larger the value of $\kappa$ is, the more harmful the PM2.5 generated from a certain type of coal-fired boilers is to human health; $\alpha_i$ is the element in the weight vector $\Gamma = (\alpha_1, \alpha_2, \alpha_3, \alpha_4) = (0.5638, 0.2634, 0.0550, 0.1178)^T$; $Q_i$ represents the values of the influent factors in Table 12. The health hazard assessment coefficients of PM2.5 generated from the five groups of coal-fired boilers was calculated, and the results were shown in Figure 4.

As shown in Figure 4, the $\kappa$ values of PM2.5 generated from the industrial grate-fired and fluidized-bed boilers are larger than those from utility pulverized coal and CFB boilers. The $\kappa$ value of PM2.5 generated from the industrial grate-fired boiler is obviously larger than those from the other types of coal-fired boilers, which is approximately 4 times than the industrial fluidized-bed boiler, 5 times than the utility CFB boiler, and 10 times than the utility pulverized coal boiler. The $EF_{\text{WD}}(M)$ value of the industrial grate-fired boilers is less than those of the other boilers in Table 11, but its $EF_{\text{WD}}(N)$, $b$ and
$M_{D_{50}}$ values are much higher than others. One potential explanation is that PM$_{2.5}$ from the industrial grate-fired boilers with the higher number, and the content of toxic chemical compositions is much more than those from the other boilers. And the fine particles with the higher number and toxic-chemical content can enter into human body more easily, consistent with literature [26,27]. As a result, PM$_{2.5}$ generated from the industrial grate-fired boiler is more harmful to human health.

![Figure 4](image_url)

**Figure 4.** Health hazard assessment coefficients of PM2.5 generated from coal-fired boilers.

As shown in Figure 4, the $\kappa$ value of PM$_{2.5}$ from the industrial fluidized-bed boiler is larger than those from the utility CFB boiler. This result is caused by the local high temperature in the industrial fluidized-bed boilers. In our experimental data, many industrial fluidized-bed boilers were retrofitted from industrial grate-fired boilers, which could transform their original dense-phase zones into high-temperature reducing zones with the unreasonable designs of the boiler hearths. More submicron particles would be formed by vaporization-condensation, and more super-micrometer particles would be generated during coal/char fragmentation. The high-temperature reducing atmosphere can make a larger amount of volatile heavy metals to vaporize from fuel coal, and then the gas-phase heavy metals will transform to be particle-phase during condensation or surface reaction [28]. The number, mass and the content of toxic chemical compositions of PM$_{2.5}$ from the industrial fluidized-bed boiler much higher than those from the utility CFB boiler with the unreasonable designs of the boiler hearths.

The $\kappa$ value of PM$_{2.5}$ from the large-capacity utility pulverized coal boilers is larger than those from the small-capacity utility pulverized coal boilers. This result is caused by longer residence time of pulverized coal particles in the boiler hearths. According to the result of Lv et al. [29], the larger the capacities of pulverized coal boilers are, the longer the residence times of pulverized coal particles are. The long residence times of pulverized coal particles can lead to the long residence times in the high-temperature flame zones, which will promote mineral-element evaporation and particle fragmentation. Hence, the long residence times are beneficial to more submicron particles and super-micrometer particles formed by vaporization, condensation and char fragmentation. A larger amount of heavy-metal elements can be incorporated into the PM$_{2.5}$ with the vaporization and condensation, while drastic fragmentation can make the char particles smaller. When the coal of per unit mass burns out, the fine particles with the higher number, mass and the total content of toxic chemical compositions are more harmful to human health. Therefore, the $\kappa$ value of PM$_{2.5}$ generated from the large-capacity utility pulverized coal boilers is larger than those from the small-capacity utility pulverized coal boilers.
4. Conclusions
A novel health hazard assessment model of PM$_{2.5}$ generated from different types of coal-fired boilers is built based on AHP. In our assessment model, the number, the mass, the particle size and the total content of toxic chemical compositions are taken into account as important factors on health hazards of PM$_{2.5}$. The number and mass of PM$_{2.5}$ generated from coal-fired boilers are represented by number and mass from uncontrolled emission factor, respectively, the particle size of PM$_{2.5}$ is represented by the particle size distribution coefficient of Rosin-Rammler function of fine particles, and the content of toxic chemical compositions of PM$_{2.5}$ is represented by the total content of Cr, V, Mn, Ni, Pb, Cd, As, Se, Hg, OC and EC. Results are shown as follows:

(1) The of PM$_{2.5}$ from industrial coal-fired boilers are more harmful to human health than utility coal-fired boilers, and PM$_{2.5}$ from the industrial grate-fired boilers are much more harmful to human health than those from the other types of boilers because of its higher number, mass and total content of toxic chemical compositions of fine particles; It is not recommended to choose grate-fired burners as a burner of a new boiler or a modification boiler.

(2) The of PM$_{2.5}$ from industrial fluidized-bed boilers are more harmful to human health than that of utility CFB boilers, because many industrial fluidized-bed boilers, which could transform their original dense-phase zones into high-temperature reducing zones with the unreasonable designs of the boiler hearths, are retrofitted from industrial grate-fired boilers;

(3) The of PM$_{2.5}$ from the large-capacity utility pulverized coal boilers (≥450MW) are more harmful to human health than those from the small-capacity utility pulverized coal boilers (<450MW) because the residence times of pulverized coal particles in large-capacity pulverized coal boilers is longer than those in small-capacity pulverized coal boilers. It is necessary to install a high performance dust removal device.

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