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Concentration, distribution and occurrence of mercury in Chinese coals

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Abstract. Mercury in coals is one of the important sources of atmospheric mercury, which is potentially harmful to the ecological environment. Based on the data of 970 coal samples, the concentration, spatial distribution and occurrence of mercury in Chinese coals were analyzed. The main conclusions are as follows: The distribution of mercury concentration in Chinese coalfields is uneven; medium and high mercury coals are mainly distributed in southwest China and eastern Inner Mongolia. The mercury concentrations in various coal-forming periods are as follows: K (0.320 mg/kg) > P_2 (0.220 mg/kg) > C_3 (0.179 mg/kg) > J (0.177 mg/kg) > D (0.165 mg/kg) > P_1 (0.136 mg/kg) > C_1 (0.090 mg/kg) > E (0.086 mg/kg) > T_3 (0.066 mg/kg). The mercury concentrations in different coal ranks are as follows: Lignite (0.164 mg/kg), long flame coal (0.078 mg/kg), non-caking coal (0.256 mg/kg), weakly caking coal (0.086 mg/kg), gas coal (0.151 mg/kg), fat coal (0.122 mg/kg), coking coal (0.171 mg/kg), lean coal (0.393 mg/kg), meagre coal (0.161 mg/kg), anthracite (0.160 mg/kg). Sulfide bound state is the main form of mercury in coals, and pyrite is the main occurrence medium.

1 Introduction

Mercury is a highly toxic and volatile heavy metal, which is widely present in terrestrial, atmospheric, freshwater and marine ecosystems [1-2]. Anthropogenic mercury emissions account for 60-80% of the total global emissions, of which more than 90% of mercury comes from fuel combustion [3-4]. China is the largest mercury emitter, accounted for more than 20% of global anthropogenic mercury emissions [5]. Coal combustion is one of the important anthropogenic mercury sources. In China, approximately 400 tons of mercury were emitted annually due to coal burning, accounting for nearly half of anthropogenic atmospheric mercury emissions [6-9].

Due to the massive consumption of coal and the high toxicity of mercury, it has become one of the most concerned harmful trace elements in coals. Mercury can stay in the atmosphere for 0.5 to 2 years, and participates in the global cycle [10-11]. The concentration, distribution and occurrence of mercury in coals have attracted the attention of many scholars. Zheng [12], Dai [13], Wu [14], Huang [15], Song [16], Gao [17], and Wang [18] et al. have studied mercury content in coals from different regions successively. However, there are relatively few studies on the distribution of mercury in coals based on the national scale. In this paper, the concentration and spatial distribution of mercury in Chinese coals were analyzed, and the occurrence mode was discussed.

2 Method

The data of 970 coal samples were used in this paper, which obtained from the Trace Elements in Coal of China (TECC) database [19]. ArcGIS software was used to carry out inverse distance weight interpolation analysis on the data, and create a spatial distribution map of mercury in Chinese coalfields. The specific calculation formula is shown in Formula 1:

$$z=[\sum_{i=1}^{n}\frac{z_i}{d_i^j}]/[\sum_{i=1}^{n}\frac{1}{d_i^j}] \qquad (1)$$

Where Z is the estimated value of the predicted point; Z_i is the i-th (i=1, 2, 3,..., n) measured value; d_i is the distance between the interpolation point and the sample point; j is the power value of the distance, which is generally 1 or 2. This study used the default value of 2; n is the number of sample points involved in interpolation, n=970.

3 Distribution of mercury in Chinese coals

3.1 Spatial distribution of mercury in Chinese coals

Based on 970 coal samples, the mercury concentration of most Chinese coals ranges from 0.002 to 56.20 mg/kg. The arithmetic average value is 0.14 mg/kg, which is

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lower than the content value calculated by Yang et al. [20] (0.20 mg/kg, n=1793) and Ren et al. [21] (0.195 mg/kg, n=1413). It is close to the result calculated by Zhao et al. [22] (0.20 mg/kg, n=1466). And it is between the world coal (0.1 mg/kg) [23] and the USA coal (0.17 mg/kg) [24], which is 2.3 times of the Australia coal (0.06 mg/kg) [22].

Table 1. The classification of mercury content in coal in Chinese standards [25].

Content classification	Range (mg/kg)
Ultra-low mercury coal	≤ 0.150
Low mercury coal	> 0.150~0.250
Middle mercury coal	> 0.250~0.600
High mercury coal	> 0.600

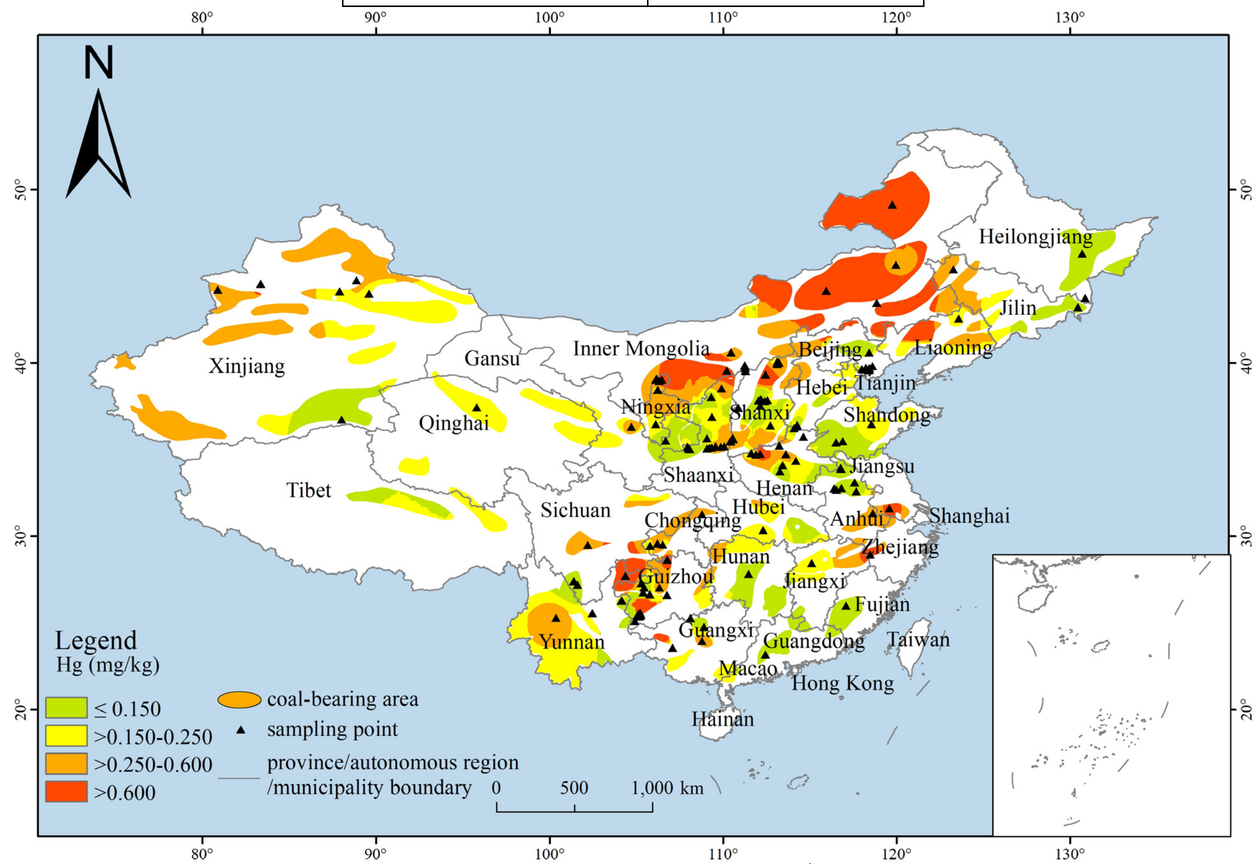

Fig.1. The distribution of mercury content in Chinese coalfields.

To facilitate the discussion of the mercury content distribution in Chinese coals, mercury was divided into four categories according to China national standard *"Classification for content of harmful elements in coal-Part 4: Mercury"* (GB/T 20475.4-2012) [25] (Tab. 1). The distribution of mercury content in Chinese coals is uneven (Fig. 1). Medium and high mercury coals are mainly concentrated in the southwest and northeast regions, including Guizhou, Yunnan and eastern Inner Mongolia. In addition, some medium-high mercury coals also exist in northern Ningxia, southern Anhui, northern Shanxi and western Henan. Low mercury and ultra-low mercury coals are widely distributed, mainly in Hubei, Hunan, Guangxi and Jiangxi in southern China, as well as northern China, including Shaanxi Province, Henan province, central Shanxi, northern Anhui, and western Shandong.

The mercury enrichment in coals in most areas is caused by magma intrusion. In the process of hydrothermal intrusion, the mercury activated will enter the coal seam along with the volatile matter, resulting in the increase of mercury content in coals. Dai et al. [13] analyzed the coal sample content of Xingren county, Guizhou province, which reached 12.1 mg/kg, and believed that the reason for high concentration of mercury in coals was the effect of low-temperature hydrothermal fluids. Huang et al. [15] studied the distribution of mercury in Wolong Lake coal mine and found that the closer to the magma intrusion, the greater the mercury content in coals. Moreover, hydrothermal activity may also be an important factor causing mercury enrichment in coals [26].

3.2 Mercury content in coals of various coal-forming periods

The 970 coal samples analyzed cover all coal-forming periods in China, including Devonian (D), Early Carboniferous (C_1), Late Carboniferous (C_3), Early Permian (P_1), Late Permian (P_2), Late Triassic (T_3), Jurassic (J), Cretaceous (K), Paleogene (E). The distribution of mercury in C_3, P_1, and P_2 periods is relatively concentrated. The mercury concentration in coals varies greatly in different coal-forming periods (Fig. 2). The decreasing order of mercury concentration in coals: K (0.320 mg/kg) > P_2 (0.220 mg/kg) > C_3 (0.179 mg/kg) > J (0.177 mg/kg) > D (0.165 mg/kg) > P_1 (0.136 mg/kg) > C_1 (0.090 mg/kg) > E (0.086 mg/kg) > T_3 (0.066 mg/kg).

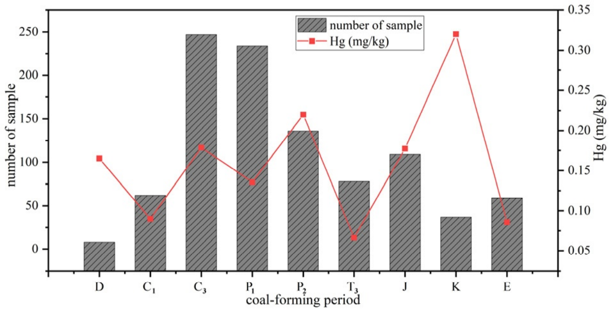

Fig. 2. Concentration of mercury in coals of different coal-forming periods.

3.3 Mercury content in coals of different ranks

Fig. 3 shows the mercury concentration in different coal ranks. Mercury is more widely distributed in gas coal, coking coal, anthracite, long-flame coal and lignite. The concentration of lean coal is the highest, while in long flame coal is the lowest. High rank meagre coal and anthracite have similar mercury concentrations. The mercury concentrations of different coal ranks are as follows: Lignite (0.164 mg/kg), long flame coal (0.078 mg/kg), non-caking coal (0.256 mg/kg), weakly caking coal (0.086 mg/kg), gas coal (0.151 mg/kg), fat coal (0.122 mg/kg), coking coal (0.171 mg/kg), lean coal (0.393 mg/kg), meagre coal (0.161 mg/kg), anthracite (0.160 mg/kg).

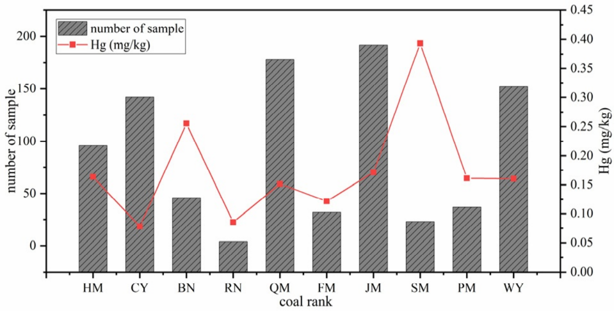

Fig. 3. Mercury content in coals of different ranks. (HM, CY, BN, RN, QM, FM, JM, SM, PM, WY represent lignite, long flame coal, non-caking coal, weakly caking coal, gas coal, fat coal, coking coal, lean coal, meagre coal, anthracite, respectively.)

4 Occurrence of mercury in coals

4.1 Correlation analysis of mercury and ash content in coals

Based on the data of 385 coal samples, the relationship between mercury and ash content in coals was analyzed (Fig. 4). There is no obvious correlation between mercury and ash in coals (R=0.193, $p<0.01$, n=385). Similar to the results of this analysis, Ge et al. [27] pointed out that the correlation between mercury and ash in Huainan coal mines is poor, and it does not exist in natural minerals, but exists in the form of organic matter. However, Cheng [4], Zhao [28], Pan [29], and Dai [30] et al. showed a positive correlation between mercury and ash content. Overview, the occurrence of mercury in coals has not yet produced a unified conclusion.

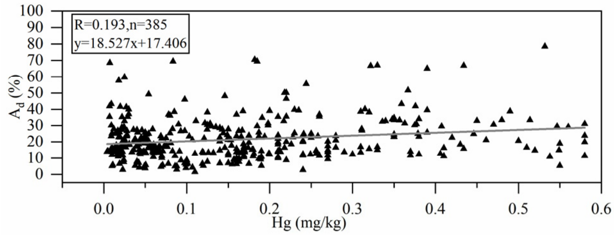

Fig. 4. Correlation between mercury and ash content in coals.

4.2 Correlation analysis of mercury and sulfur content in coals

Fig. 5 shows the relationship between different forms of sulfur and mercury content in coals. Mercury concentration is closely related to total sulfur content, with the correlation coefficient (R) of 0.328 ($p<0.01$, n=425) (Fig. 5a). Specifically, the correlation coefficient between mercury and pyrite sulfur is significant (R=0.451, $p<0.01$, n=198), showing a strong positive correlation (Fig. 5b). However, there is no significant correlation between mercury content in coals and organic sulfur and sulfate sulfur (Fig. 5c, Fig. 5d). These indicate that pyrite may be the most important occurrence carrier of mercury. Dai [30], Kolker [31], Dziok [32], and Bai [33] et al. have also reached the same conclusion.

In fact, scholars have a variety of views on the occurrence of mercury. Most scholars recognize the close relationship between mercury and pyrite. Liu et al. [34] found that compared with organic sulfur, mercury in Yanzhou coalfield was more correlated with pyrite sulfur. It was reported that mercury was mainly combined with pyrite sulfur, and the presence of organic mercury in the form of secondary. Song et al. [16] analyzed the relationship between mercury and inorganic elements in Xinmi coal, and inferred that mercury was mainly related to pyrite or kaolinite. Kostova I et al. [35] found a strong relationship between mercury and pyrite in high-sulfur Maritsa-West lignite, especially epigenetic pyrite. In addition, some scholars believe that mercury can be bound by organic matter or dispersed and tightly mixed in the form of submicron particle size inside organic matter, but it is not organic mercury in the true sense [18, 27, 28].

In summary, the sulfide bound state is considered to be the main form of mercury, especially pyrite as the main occurrence medium.

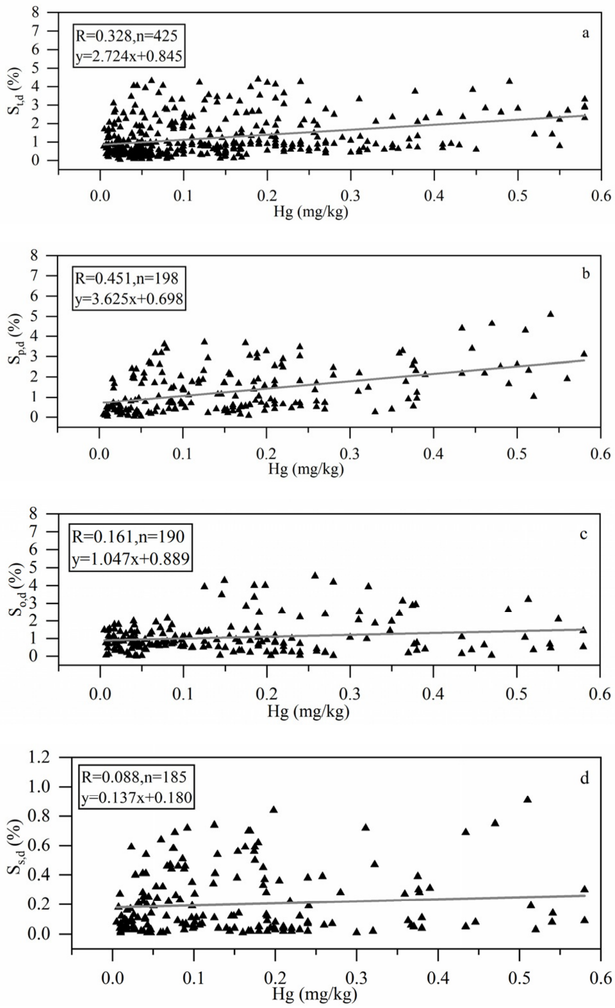

Fig. 5. Correlation between mercury and different forms of sulfur content in coals.

5 Conclusion

Based on 970 coal samples, the average content of mercury in Chinese coals is 0.14 mg/kg. The distribution of mercury content is unevenly distributed. The middle and high mercury coals are mainly distributed in southwest and northeast China. Low mercury coals and ultra-low mercury coals are mainly concentrated in north China. The mercury concentration decreases in the following order in different coal-forming periods: K (0.320 mg/kg) > P_2 (0.220 mg/kg) > C_3 (0.179 mg/kg) > J (0.177 mg/kg) > D (0.165 mg/kg) > P_1 (0.136 mg/kg) > C_1 (0.090 mg/kg) > E (0.086 mg/kg) > T_3 (0.066 mg/kg). The mercury concentrations of various coal ranks are as follows: Lignite (0.164 mg/kg), long flame coal (0.078 mg/kg), non-caking coal (0.256 mg/kg), weakly caking coal (0.086 mg/kg), gas coal (0.151 mg/kg), fat coal (0.122 mg/kg), coking coal (0.171 mg/kg), lean coal (0.393 mg/kg), meagre coal (0.161 mg/kg), anthracite (0.160 mg/kg). Mercury in coals has no obvious correlation with ash, organic sulfur and sulfate sulfur content, but has a strong affinity with total sulfur and pyrite sulfur. Pyrite is the main carrier of mercury in coals.

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