energies

Article

A Preliminary Study on Dependence of Mercury Distribution on the Degree of Coalification in Ningwu Coalfield, Shanxi, China

Yinjiao Su [1,*], Xuan Liu [1], Yang Teng [1] and Kai Zhang [1,2,*]

[1] Beijing Key Laboratory of Emission Surveillance and Control for Thermal Power Generation, North China Electric Power University, Beijing 102206, China; lllliuxuan@ncepu.edu.cn (X.L.); tengyang@ncepu.edu.cn (Y.T.)
[2] Key Laboratory of Power Station Energy Transfer Conversion and System (North China Electric Power University), Ministry of Education, Beijing 102206, China
* Correspondence: sssyj@ncepu.edu.cn (Y.S.); kzhang@ncepu.edu.cn (K.Z.); Tel.: +86-010-6177-2413 (K.Z.)

Abstract: Mercury (Hg) is a toxic trace element emitted from coal conversion and utilization. Samples with different coal ranks and gangue from Ningwu Coalfield are selected and investigated in this study. For understanding dependence of mercury distribution characteristics on coalification degree, Pearson regression analysis coupled with Spearman rank correlation is employed to explore the relationship between mercury and sulfur, mercury and ash in coal, and sequential chemical extraction method is adopted to recognize the Hg speciation in the samples of coal and gangue. The measured results show that Hg is positively related to total sulfur content in coal and the affinity of Hg to different sulfur forms varies with the coalification degree. Organic sulfur has the biggest impact on Hg in peat, which becomes weak with increasing the coalification degree from lignite to bituminous coal. Sulfate sulfur is only related to Hg in peat or lignite as little content in coal. However, the Pearson linear correlation coefficients of Hg and pyritic sulfur are relatively high with 0.479 for lignite, 0.709 for sub-bituminous coal and 0.887 for bituminous coal. Hg is also related to ash content in coal, whose Pearson linear correlation coefficients are 0.504, 0.774 and 0.827 respectively, in lignite, sub-bituminous coal and bituminous coal. Furthermore, Hg distribution is directly depended on own speciation in coal. The total proportion of F2 + F3 + F4 is increased from 41.5% in peat to 87.4% in bituminous coal, but the average proportion of F5 is decreased from 56.8% in peat to 12.4% in bituminous coal. The above findings imply that both Hg and sulfur enrich in coal largely due to the migration from organic state to inorganic state with the increase of coalification degree in Ningwu Coalfield.

Keywords: coal; Hg; coalification; sulfur; ash; correlation; speciation

Citation: Su, Y.; Liu, X.; Teng, Y.; Zhang, K. A Preliminary Study on Dependence of Mercury Distribution on the Degree of Coalification in Ningwu Coalfield, Shanxi, China. *Energies* **2021**, *14*, 3119. https://doi.org/10.3390/en14113119

Academic Editor: Nikolaos Koukouzas

Received: 15 March 2021
Accepted: 25 May 2021
Published: 27 May 2021

1. Introduction

Mercury (Hg) is considered to be one of the most toxic metal elements which exist in coal. With a huge amount of coal consumed, coal utilization remains one of the largest anthropogenic sources of Hg in the environment. Due to the increasing environmental pollution and the enhancement of analytical technique, the geochemical study on Hg in coal has caused a rise in public concern [1–3]. The Hg content in coal varies considerably, from 0.025 mg/kg to 1000 mg/kg, with a worldwide average of 0.10 ± 0.01 mg/kg regardless of location and coal rank [4–6]. Coal is mainly composed of organic matter and some minerals, and the Hg bound to organic matters may be redistributed in the process of coal mineralization. Therefore, the source of Hg in coal is accompanied by the migration and transformation of minerals in the process of coal formation [7,8].

In order to reduce Hg and the other trace harmful elements in coal mining, processing and utilization of potential hazards, various studies have been conducted on the abundance and speciation of Hg in coal, such as by Chelgani et al. [9], Zhang et al. [10], Nikolay et al. [11] and Zhao et al. [12]. The affinity of Hg to sulfur in coal usually depends on pyrite and other sulfides. Finkelman [7,13,14] performed a series of works on Hg speciation in coal through sink-float separation experiments and further evaluated the correlation coefficient between Hg and pyrite. Liu et al. [8] reported that the Hg content was closely related to sulfur, and the correlation between Hg and pyrite was stronger than that between organic sulfur. Feng et al. [15] showed that Hg combined in organic state was the highest in coal. The Hg content in coal is related to the coal-forming environment and also is affected by geological revolution process, which results from the distribution of inorganic and organic matters in coal.

Coal is heterogeneous in the bulk phase which leads to its complex components. The Hg content mainly refers to the combination state with both organic matter and inorganic minerals in coal. It should be pointed out that the Hg content in coal varies remarkably depending on the coal-forming conditions. As a result, the Hg species behave with significant differences for different coals. The enrichment of Hg in coal and its geochemical behavior can be explored by studying the Hg speciation of in coal. Moreover, the Hg speciation in coal can determine the migration and transformation of Hg during the process of coal conversion or utilization [12,16].

Various methods have been attempted to identify the Hg speciation in coal and the relationship between Hg and sulfur in coal [14,17–22]. Diehl et al. [17] found that there was a positive correlation between Hg and sulfur in two kinds of coals from the United States, and they concluded that the existence of organic Hg led to the low correlation. Jae et al. [18] thought an uncorrelation between Hg and sulfur in low-sulfur coal from South Korea. Zheng et al. [20] showed Hg had a significant correlation with total sulfur or pyritic sulfur but not related to ash. However, Kolker et al. [19] reported that Hg in Canadian subbituminous coal was positively correlated with ash content but weakened with sulfur content. Because the sulfur in coal is mainly composed of pyritic sulfur, sulfate sulfur and organic sulfur [14,21,22], the correlation between Hg and sulfur in coal is not only limited to total sulfur but also related to various sulfur forms. For example, Zheng et al. [21] showed Hg speciation depending on sulfur content for either high-sulfur coal or low-sulfur coal. However, only a few studies [8,20] attempted the relationship between Hg and different forms of sulfur in coal. The content and distribution of Hg and sulfur in coal are affected by either region difference or coalification degree. Ningwu Coalfield is located in Shanxi, one of the major coal-produced regions in China, which covers an area of about 3087 km^2 and produces over 37 million tons of coal per year [23]. In this article, 71 samples are selected from three coal mines and two coal washing plants in Ningwu Coalfield. Pearson regression analysis coupled with Spearman rank correlation is implemented to investigate the relationship between Hg and total sulfur content, Hg and virous sulfur forms, as well as Hg and ash content for better understanding the dependence of mercury content on the degree of coalification. Moreover, the speciation and distribution of Hg in coal samples are explored by using the sequential chemical extraction technique.

2. Materials and Methods

2.1. Coal Samples Collection

As shown in Figure 1, the analyzed coal samples in this study are conducted from Ningwu Coalfield (upper Carboniferous Taiyuan Formation, Lower Permian Shanxi Formation) in Shanxi Province, China. The geological structure of Ningwu Coalfield is relatively simple. A total of 71 samples are chosen, including 59 samples with various rank coals from three coal mines and 12 gangue samples from two washing coal plants.

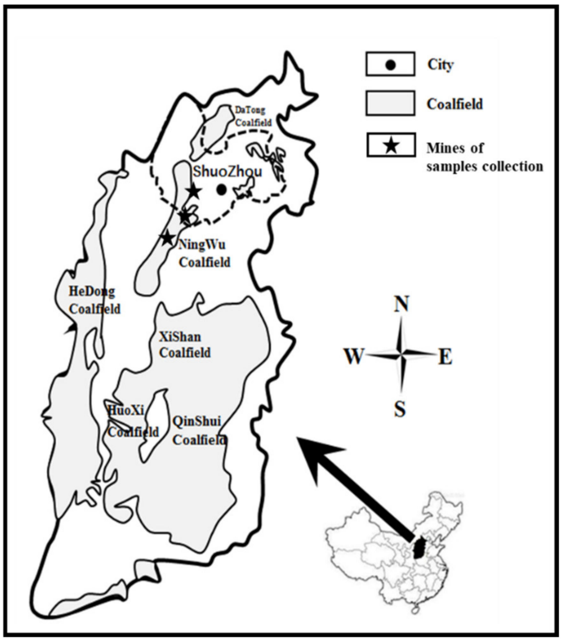


Figure 1. Locations of samples from Ningwu Coalfield, Shanxi, China.

2.2. Sample Grouping and Property Analysis

The details of 59 coal samples from 3 main coal mines in Ningwu Coalfield are divided into 4 groups in the following way: (1) 9 peat samples including 5 from Shentou coal mine and 4 from Xuangang coal mine, (2) 18 lignite samples including 9 from Shentou coal mine and 5 from Antaibao coal mine and 4 from Xuangang coal mine, (3) 22 sub-bituminous coal samples including 4 from Shentou coal mine and 8 from Xuangang coal mine, and (4) 10 bituminous coal samples including 3 are from Shentou coal mine and 7 are from Antaibao coal mine. To understand the effect of ash content on Hg in coal, 12 gangue samples are also collected from two coal washing plants in Shentou and Xuangang coal mines.

Hg content in coal is determined by the RA-915M Zeeman cold vapor atomic absorption spectrum (CVAAS) Hg analyzer coupled with Pyro-915 + pyrolysis attachment (Lumex Co., Ltd., Russia). RA-915M Hg Analyzer with pyrolizer Pyro-915 + can eliminate the influence of impurity on the test procedure through Zeeman background correction. To make sure analytical accuracy for Hg in coal, the blank pre-experiment is conducted and of Hg standard sample is checked before each measurement. Each coal sample is tested three times, and the average value is regarded as the experimental result.

The sulfur content in coal is tested for exploring the relationship between Hg and sulfur. Usually, Sulfur in coal is classified as organic sulfur and inorganic sulfur, of which the inorganic sulfur mainly includes sulfate sulfur and pyritic sulfur. The forms of sulfur in samples are measured according to the China National Standard GB/T 215-2003 as shown in Table 1.

Table 1. Test method for total sulfur and forms of sulfur in coal.

Parameter	Method	Principle
Total sulfur ($S_{t,ad}$)	GB/T214-2007	Coulometric titration method
Sulfate sulfur ($S_{s,ad}$)	GB/T 215-2003	According to the quality of barium sulfate to calculate the content of sulfate in coal
Pyritic sulfur ($S_{p,ad}$)	GB/T 215-2003	According to the quality of the mass of iron to calculate the content of sulfur in iron sulfide
Organic sulfur ($S_{o,ad}$)	GB/T 215-2003	$S_{o,ad} = S_{t,ad} - S_{s,ad} - S_{p,ad}$

ad—air drying basis.

The ranges of proximate analysis of 59 coal samples and 12 gangue samples are respectively listed in Tables 2 and 3, and their maximum and minimum of Hg contents, sulfur contents and various forms of sulfur contents are listed in Tables 4 and 5. It can be found from Table 4 that the Hg average content of coal samples selected in this study is 0.1691 mg/kg, which is close to the average value of 0.154 mg/kg by the United States Geological Survey and the range between 0.170 mg/kg and 0.190 mg/kg in Chinese coal [24,25].

Table 2. Proximate analysis of the coal samples.

Group	Number of Samples	Value	Proximate Analysis, wt %					$Q_{b,v,ad}$, MJ/kg
			M_{ad}, %	A_{ad}, %	V_{ad}, %	FC_{ad}, %	V_{daf}, %	
peat	9	Min	0.74	28.96	30.51	20.65	57.12	15.11
		Max	8.83	44.72	39.07	27.19	62.80	21.00
		Average	2.58	37.58	35.12	24.72	58.69	18.02
lignite	18	Min	1.18	24.57	24.16	37.89	38.94	20.50
		Max	3.43	36.86	34.44	44.08	47.56	24.56
		Average	2.35	30.58	28.09	38.98	41.84	22.84
sub-bituminous coal	22	Min	1.54	18.76	18.18	41.87	30.27	20.74
		Max	3.29	37.50	28.16	53.65	36.74	28.31
		Average	2.37	24.72	25.01	47.90	34.31	25.65
bituminous coal	10	Min	0.96	17.49	19.06	45.68	27.46	20.16
		Max	2.94	33.08	22.95	57.82	29.60	30.14
		Average	1.55	26.02	20.52	51.92	28.34	25.91
total	59	Min	0.74	17.49	18.18	20.65	27.46	15.11
		Max	8.83	56.04	39.07	57.82	62.80	30.14
		Average	2.26	28.69	26.73	42.32	39.32	23.67

M—moisture content, A—ash content, V—volatile matter content, FC—fixed carbon content, $Q_{b,v}$—heating value, ad—air drying basis, daf—dry ash-free basis.

Table 3. Proximate analysis of the gangue samples.

Group	Number of Samples	Value	Proximate Analysis, wt %					$Q_{b,v,ad}$, MJ/kg
			M_{ad}, %	A_{ad}, %	V_{ad}, %	FC_{ad}, %	V_{daf}, %	
gangue	12	Min	0.54	51.84	13.36	12.52	45.76	8.15
		Max	1.72	71.56	25.58	23.70	60.12	15.00
		Average	1.03	62.03	19.37	17.56	52.42	10.78

M—moisture content, A—ash content, V—volatile matter content, FC—fixed carbon content, $Q_{b,v}$—heating value, ad—air drying basis, daf—dry ash-free basis.

Table 4. Contents of Hg, sulfur, organic sulfur and inorganic sulfur in coal samples.

Group	Number of Samples	Value	$Hg_{t,ad}$, ppb	$S_{t,ad}$, %	Organic Sulfur	Inorganic Sulfur	
					$S_{o,ad}$, %	$S_{s,ad}$, %	$S_{p,ad}$, %
peat	9	Min	69.3	0.40	0.22	0.08	0.05
		Max	286.9	1.55	0.95	0.35	0.46
		Average	188.7	1.07	0.64	0.20	0.23
lignite	18	Min	139.5	0.53	0.07	0.10	0.10
		Max	292.6	3.12	2.12	0.36	0.65
		Average	190.1	1.03	0.47	0.23	0.33
sub-bituminous coal	22	Min	92.8	0.91	0.01	0.00	0.19
		Max	248.6	1.94	0.83	0.28	1.21
		Average	143.0	0.94	0.30	0.09	0.55

Table 4. *Cont.*

Group	Number of Samples	Value	$Hg_{t,ad}$, ppb	$S_{t,ad}$, %	Organic Sulfur	Inorganic Sulfur	
					$S_{o,ad}$, %	$S_{s,ad}$, %	$S_{p,ad}$, %
bituminous coal	10	Min	163.2	2.11	0.31	0.12	0.50
		Max	216.7	2.76	0.87	0.46	1.54
		Average	170.9	2.15	0.55	0.39	1.20
total	59	Min	69.3	0.40	0.01	0.00	0.05
		Max	292.6	3.12	2.12	0.46	1.54
		Average	169.1	1.19	0.44	0.20	0.54

Hg_t—total Hg content, S_t—total sulfur content, S_o—organic sulfur, S_s—sulfate sulfur, S_p—pyritic sulfur.

Table 5. Contents of Hg, sulfur, organic sulfur and inorganic sulfur in gangue samples.

Group	Number of Samples	Value	$Hg_{t,ad}$, ppb	$S_{t,ad}$, %	Organic Sulfur	Inorganic Sulfur	
					$S_{o,ad}$, %	$S_{s,ad}$, %	$S_{p,ad}$, %
gangue	12	Min	521.7	1.29	0.32	0.39	0.56
		Max	1544.0	3.14	0.56	0.72	2.03
		Average	1049.2	2.17	0.44	0.47	1.26

Hg_t—total Hg content, S_t—total sulfur content, S_o—organic sulfur, S_s—sulfate sulfur, S_p—pyritic sulfur.

2.3. Statistical Analysis of Mercury and Sulfur in Coal

Spearman rank correlation coefficient is a non-parametric index to measure the dependence of two variables, which is used to evaluate the significance of the connection between these two variables. In this study, Spearman rank correlation coefficient is employed to obtain the correlation between mercury and total sulfur, organic sulfur or inorganic sulfur in coal. Then, Pearson regression analysis is used to determine the dependence between the above two variables for the samples meeting with the significance of Spearman rank correlation coefficient [26]. The significance level (α) is determined as 0.05 for Spearman correlation coefficient, and the Pearson regression analysis based on least square method is used to determine the interdependence between two variables for better describing the relationship between Hg and other component in coal as accurately as possible.

2.4. Determination of Hg Speciation in Coal

For determining Hg speciation in coal or gangue, all samples are treated with the sequential chemical extraction technique. A modified chemical extraction method is suggested as shown in Figure 2. Hg speciation in coal can be divided into Hg as exchangeable Hg (F1), carbonate + sulfate + oxide bound Hg (F2), silicate + aluminosilicate bound Hg (F3), sulfide bound Hg (F4) and residual Hg (F5). Among of them, Hg that is bound with weak polar bonds to coal components is called exchangeable Hg (F1), which can be extracted by $MgCl_2$ solution. Carbonate + sulfate + oxide bound Hg (F2) are extracted by HCl solution. Clay minerals in coal mainly include silicate and silicate. HF can dissolve such materials to obtain silicate + aluminosilicate bound Hg (F3). HNO_3 can dissolve sulfides such as pyrite, marcasite, sphalerite and galena, to obtain sulfide bound Hg (F4). Residual Hg (F5) is insoluble in any of the above reagents, mainly including organic bound Hg.

During each experimental procedure, 5.0 g (±0.001 g) of the sample is weighed, and the above four solutions are added successively. After stirring, shock and centrifugation, five speciation of Hg can be obtained. The Hg content of extract solution is measured by Leeman Hydra II AA automatic Hg analyzer. In order to reduce the experimental error, all reagents are at analytical grade, and deionized water is used. All vessels used are soaked in 10% nitric acid solution overnight and then rinse with deionized water. To ensure the effectiveness and reliability of Hg as a trace element in coal by the modified chemical extraction, Hg mass balance is conducted in the whole extraction process. The result shows that Hg recovery rate is between 87% and 109%, which is better than the range from 70% to 130% suggested by the U.S. Environmental Protection Agency (EPA) [27].

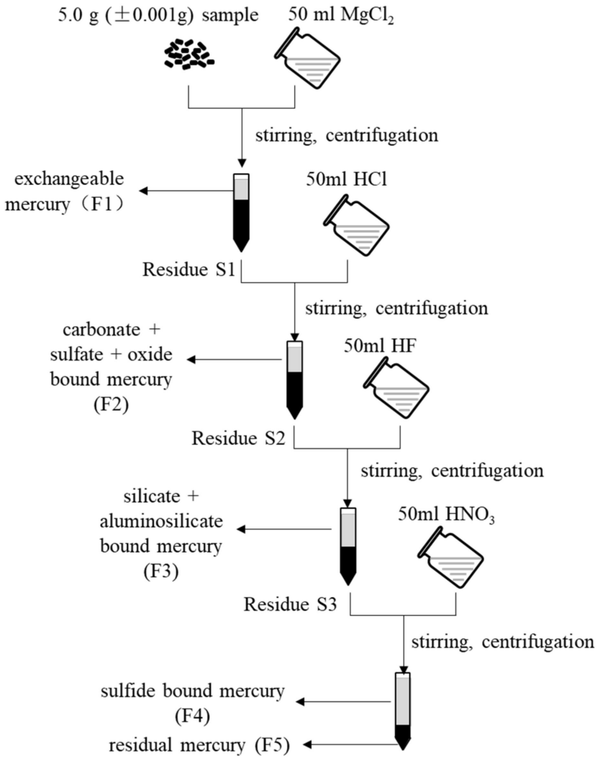


Figure 2. Schematic diagram of sequential-chemical-extraction procedure.

3. Results and Discussion

3.1. Statistical Analysis Using Spearman Rank Correlation

Tables 6 and 7 summarize the Spearman rank correlation analysis for 71 samples of coal and gangue from Ningwu Coalfield. Generally, when Spearman rank correlation coefficient (r_s) is higher than the critical value at a significance level α_s of 0.05, it can be believed that there is a significant correlation between the Hg and other component in a group of samples. Based on the above hypothesis, the significant correlation results are indicated in bold font.

As shown in Table 6 for 59 coal samples with different ranks, the Spearman rank correlation coefficient between $Hg_{t,ad}$ and $S_{t,ad}$ (r_s) is 0.571, which is greater than the corresponding critical value (0.251) at the significance level α_s of 0.05. Therefore, there is a significant correlation between Hg and total sulfur in coal, which is consistent with experiments by Liu et al. [8]. Furthermore, the difference can be found among different rank coals based on r_s as 0.750 for peat, 0.611 for lignite, 0.427 for sub-bituminous coal and 0.891 for bituminous coal. On one hand, only peat shows a significant correlation with Spearman rank correlation coefficient(r_s) of 0.817 for Hg and organic sulfur in coal. On the other hand, lignite, sub-bituminous coal or bituminous coal indicates a significant correlation with Spearman rank correlation coefficient(r_s) of 0.618, 0.719 or 0.745 for Hg and ash in coal, which is in a good agreement with 12 gangue samples in Table 7.

3.2. Statistical Analysis Using Pearson Linear Regression

To quantitatively describe the correlation between Hg and other component in coal, Pearson linear regression method is used to analysis the data with significant Spearman rank correlation coefficients in Tables 6 and 7. Then, Pearson correlation coefficient R is obtained to further investigate the dependence of Hg on other component in coal.

Table 6. Correlation coefficients (r_s) of Spearman rank correlation between Hg and other component in coal samples.

Group of Research	**Number of Samples**	**Critical Values (α_s = 0.05)**	**Spearman Rank Correlation Coefficients (r_s)**				
			$Hg_{t,ad}$-$S_{t,ad}$	**$Hg_{t,ad}$-$S_{o,ad}$**	**$Hg_{t,ad}$-$S_{s,ad}$**	**$Hg_{t,ad}$-$S_{p,ad}$**	**$Hg_{t,ad}$-A_{ad}**
peat	9	±0.700	**0.750**	**0.817**	**0.783**	**0.817**	−0.383
lignite	18	±0.472	**0.611**	0.298	**0.792**	**0.577**	**0.618**
sub-bituminous coal	22	±0.425	**0.427**	−0.071	0.310	**0.616**	**0.719**
bituminous coal	10	±0.648	**0.891**	0.394	0.103	**0.721**	**0.745**
Total	59	±0.251	**0.571**	**0.342**	**0.546**	0.241	**0.487**

Bold is the significant correlation at significance level α_s of 0.05.

Table 7. Correlation coefficients (r_s) of Spearman rank correlation between Hg and other component in gangue samples.

Group of Research	**Number of Samples**	**Critical Values (α_s = 0.05)**	**Spearman Rank Correlation Coefficients (r_s)**				
			$Hg_{t,ad}$-$S_{t,ad}$	**$Hg_{t,ad}$-$S_{o,ad}$**	**$H_{t,ad}g$-$S_{s,ad}$**	**$Hg_{t,ad}$-$S_{p,ad}$**	**$Hg_{t,ad}$-A_{ad}**
gangue	12	±0.587	**0.648**	0.084	**0.720**	**0.657**	**0.839**

Bold is the significant correlation at significance level α_s of 0.05.

3.2.1. Correlation Analysis of Hg with Total Sulfur

As shown in Figure 3, the correlation coefficient R of $Hg_{t,ad}$ and $S_{t,ad}$ in 59 coal samples is 0.503 by using Pearson linear regression method, which means the relationship between Hg and total sulfur in coal heavily depends on the degree of coalification. Figure 4 displays the Pearson correlation between $Hg_{t,ad}$ and $S_{t,ad}$ in coal samples with different ranks. It can be found the correlation coefficients are, respectively, 0.966, 0.674, 0.588 and 0.973 for the samples of peat, lignite, sub-bituminous coal and bituminous coal from Figure 4a–d. For the coal samples from Ningwu Coalfield, Hg mainly depends on total sulfur in peat and bituminous coal, but Hg has a relatively weak relationship with total sulfur in lignite, sub-bituminous coal by considering the Spearman rank correlation coefficients in Table 6. To comprehend the relationship between the Hg and ash content in coal, 12 samples of gangue are selected from 2 coal washing plants in Ningwu Coalfield. the Pearson linear correlation coefficient R between $Hg_{t,ad}$ and $S_{t,ad}$ is 0.625 in Figure 5, which means non-sulfur minerals also have the effect on mercury content in the samples of gangue and coal.

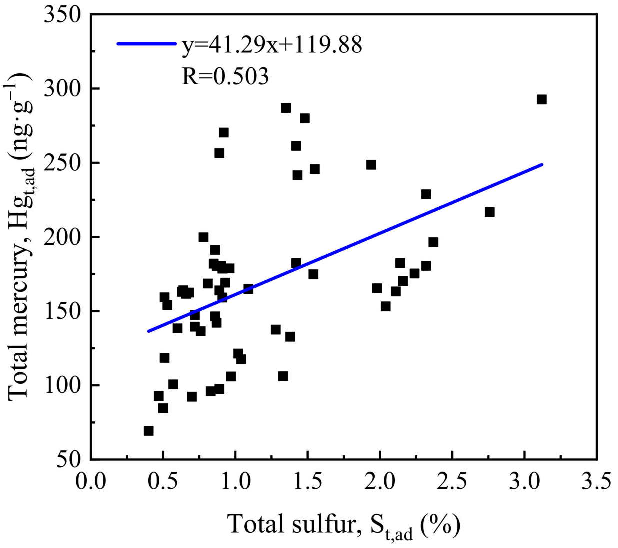
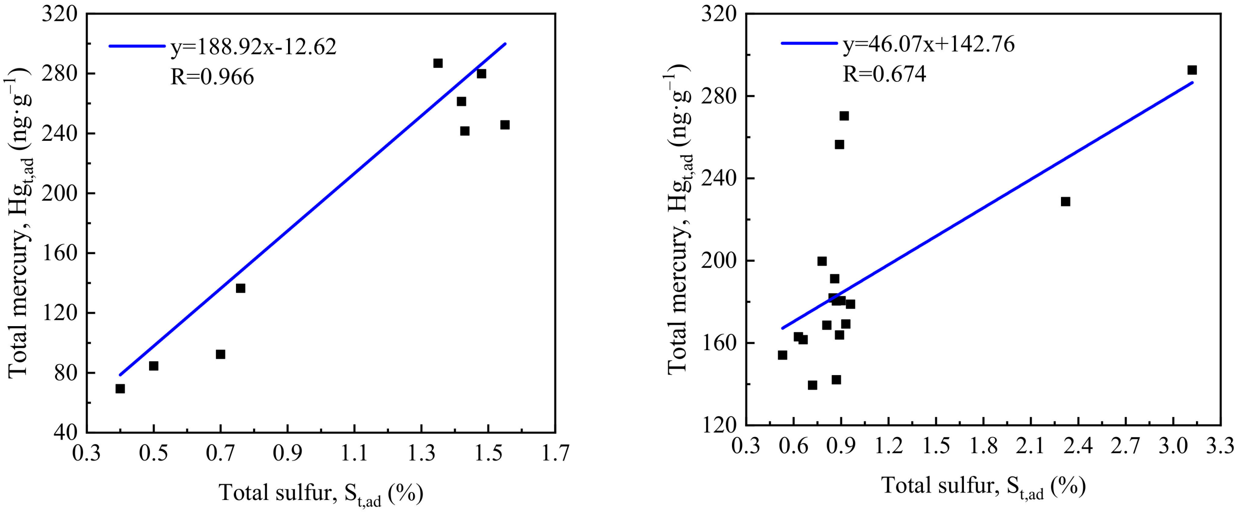
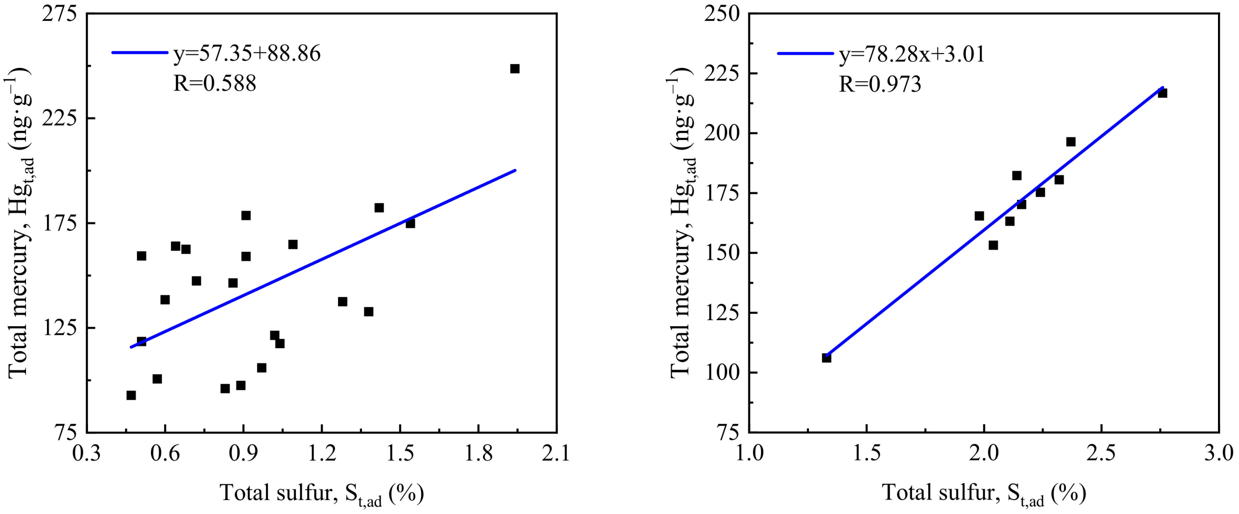


Figure 3. Correlation between Hg and total sulfur in 59 coal samples.



(**a**) peat (**b**) lignite



(**c**) sub-bituminous coal (**d**) bituminous coal

Figure 4. Correlation between Hg and total sulfur for coal samples with different ranks.

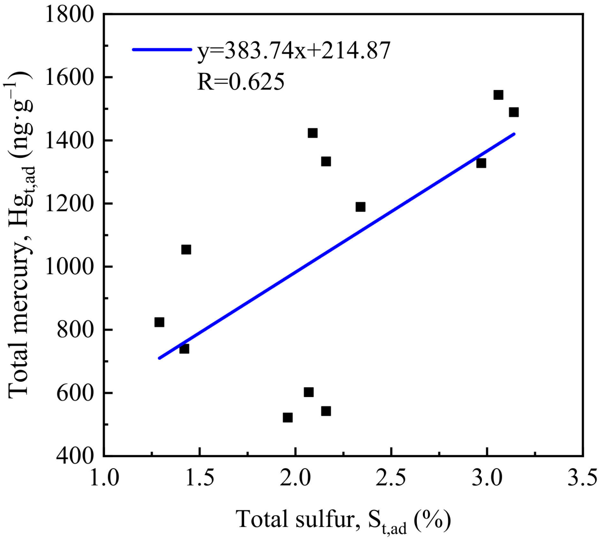


Figure 5. Correlation between Hg and total sulfur in gangue samples.

3.2.2. Correlation Analysis of Hg with Organic Sulfur

Sulfur in coal can be classified as organic sulfur and inorganic sulfur. Based on Spearman rank correlation coefficients in Table 6, the influence of organic sulfur on Hg in all coal samples with different ranks is conducted, and more attention is paid for peat samples. It can be found that there is an obviously scattered distribution with the Pearson linear correlation coefficient of 0.525 for 59 samples (Figure 6), but a strong correlation between Hg and total sulfur with the correlation coefficient of 0.954 for peat samples (Figure 7). Compared to lignite, sub-bituminous coal or bituminous coal, peat has the highest volatile matter with an average value of 58.69% in Table 2 and the highest organic sulfur with an average value of 0.64% in Table 4, which may consider that the dependency of Hg on organic sulfur becomes weak with the increase of coalification degree.

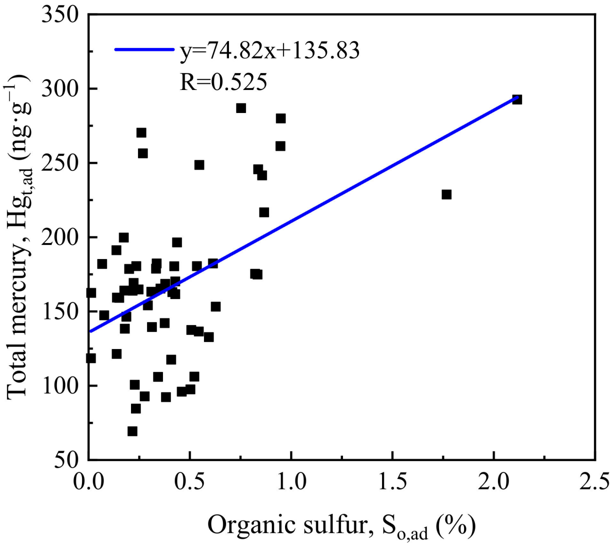


Figure 6. Correlation between Hg and organic sulfur in 59 coal samples.

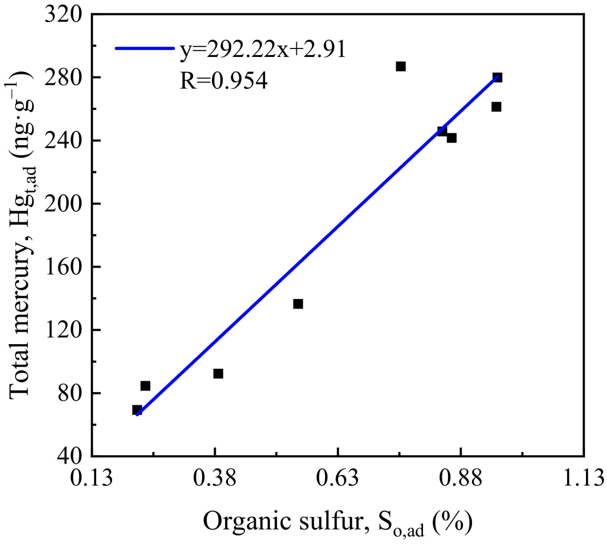


Figure 7. Correlation between Hg and organic sulfur in peat.

3.2.3. Correlation Analysis of Hg with Ash

The correlation of ash with trace element content has important implication for descripting of the original element in coal, which can offer the relationship of the affinity between the Hg and inorganic compounds in coal. Similar to the relationship of Hg and total sulfur (Figure 3) and that of Hg and organic sulfur in all 59 coal samples (Figure 6), Figure 8 demonstrates a relatively small correlation coefficient R of Hg and ash content is 0.406 by using Pearson linear regression method, which indicates that Hg in coal is affected by both organic matter and non-sulfur minerals.

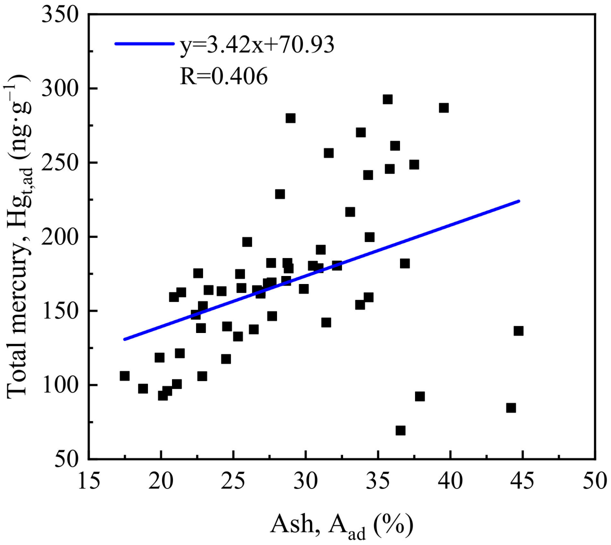
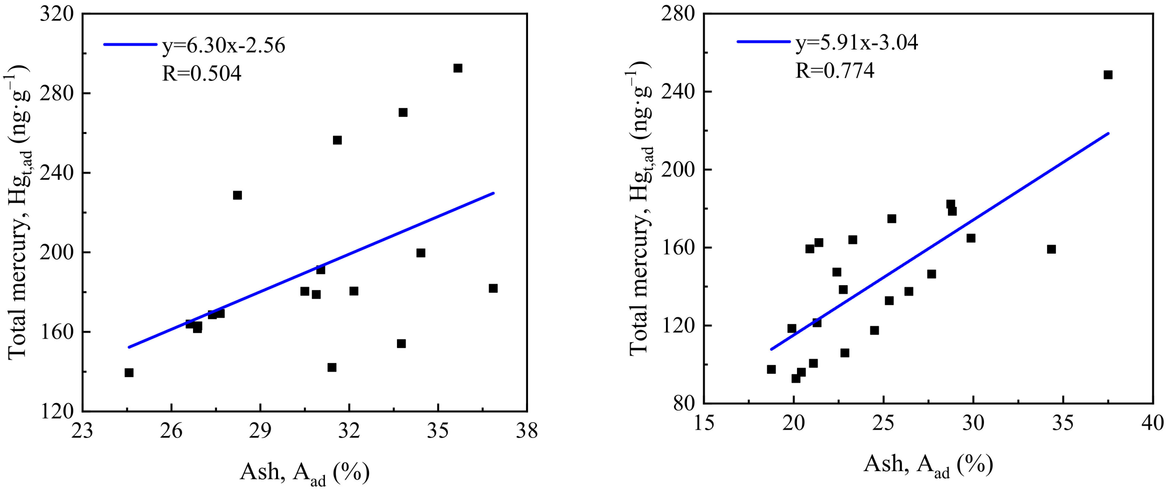


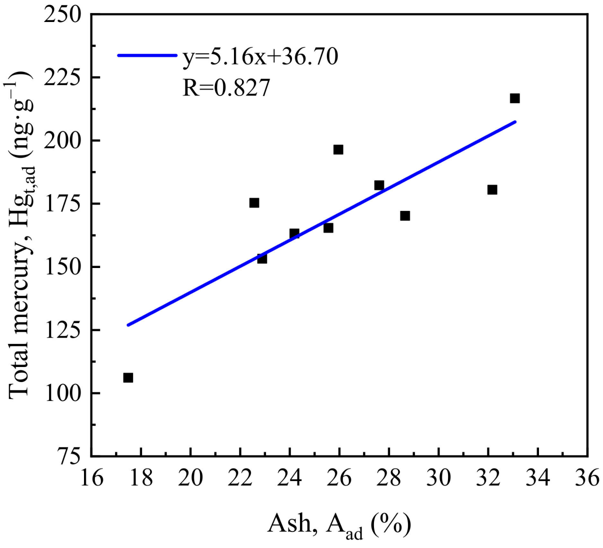
Figure 8. Correlation between Hg and ash in 59 coal samples.

The relationship between Hg and ash content is investigated for understanding the dependency on the degree of coalification in Ningwu Coalfield. A very week correlation between Hg and ash in peat is identified by Spearman rank correlation coefficient in Table 6. Furthermore, Figure 9 shows the relationship between Hg and ash content in the other three kinds of coal samples. The Pearson linear correlation coefficients are 0.504, 0.774 and 0.827 for lignite, sub-bituminous coal and bituminous coal, respectively, which means that the influence of inorganic minerals on Hg in coal is gradually increased with the increase of coalification degree. Moreover, the relationship between Hg and ash content in coal can be indirectly confirmed by 12 gangue samples with a correlation coefficient R of 0.869 in Figure 10. The above results indicate that Hg in coal is largely enriched in inorganic minerals. Therefore, coal washing process should play an important role in Hg removal before combustion and other conversion processes.



(**a**) lignite (**b**) sub-bituminous coal

Figure 9. *Cont.*



(**c**) bituminous coal

Figure 9. Correlation between Hg and ash for coal samples with different ranks.

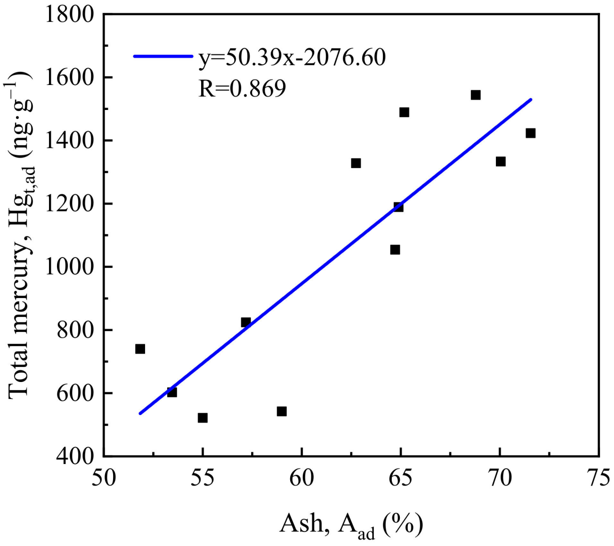


Figure 10. Correlation between Hg and ash in gangue samples.

3.2.4. Correlation Analysis of Hg with Inorganic Sulfur

Inorganic sulfur in coal can be generally regarded as sulfate sulfur and pyritic sulfur. Sulfate sulfur includes calcium sulfate mainly as gypsum and a few ferrous sulfates such as copperas. Comparing the total of 59 coal samples with Pearson linear correlation coefficient of 0.450 in Figure 11, peat and lignite with the coefficients of 0.784 in Figure 12a and 0.723 in Figure 12b, respectively, implies that the significant correlation between Hg and sulfate sulfur appears only in peat or lignite.

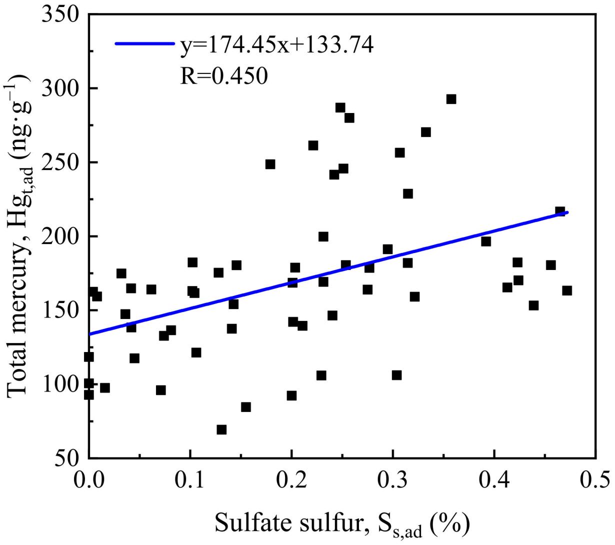
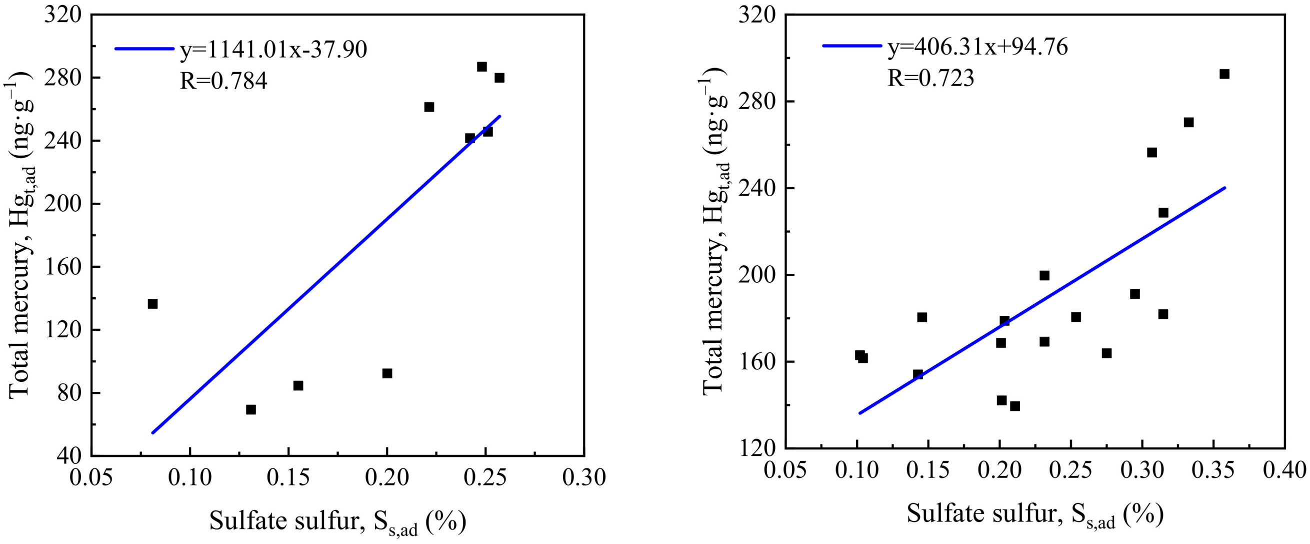


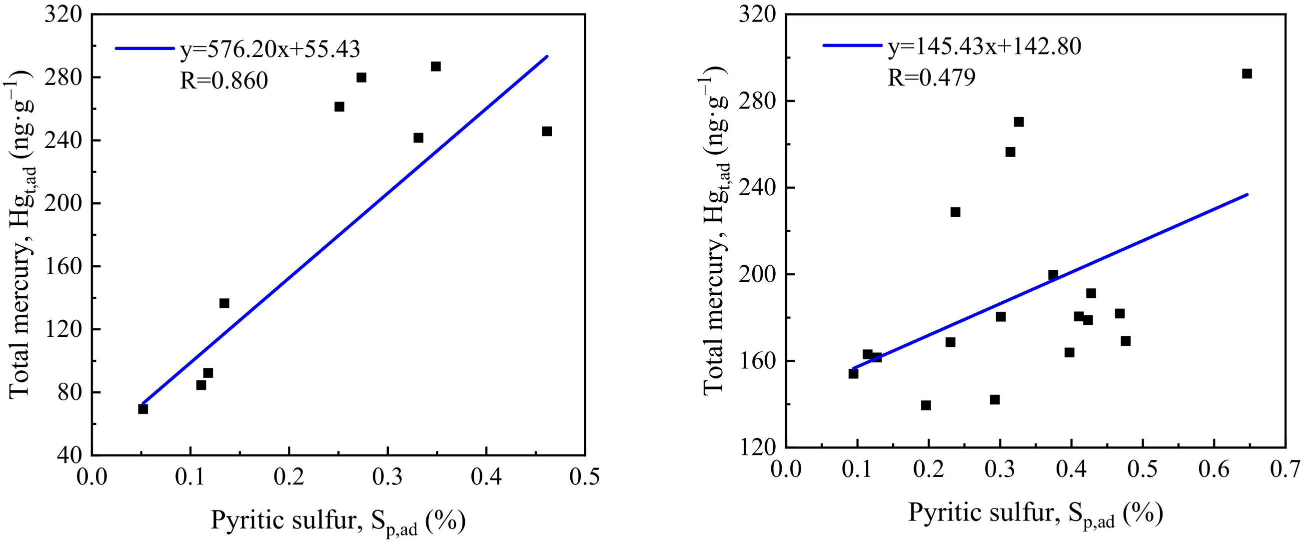
Figure 11. Correlation between Hg and sulfate sulfur in 59 coal samples.



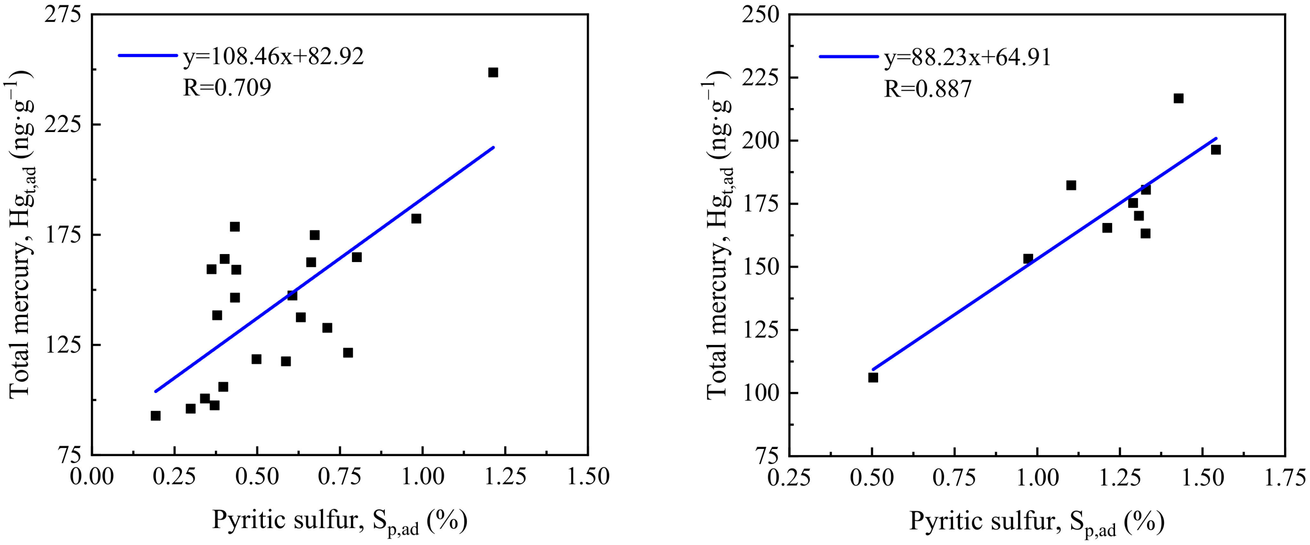
(**a**) peat (**b**) lignite

Figure 12. Correlation between Hg and sulfate sulfur for coal samples with different ranks.

The correlation between the Hg and pyritic sulfur in different rank coals is shown in Figure 13. It can be found that Pearson linear correlation coefficient is 0.860 in Figure 13a, demonstrating Hg is also significantly correlated with pyritic sulfur in peat. Combining with Figures 6 and 12a, Hg depends on organic sulfur, sulfate sulfur and pyritic sulfur. From Figure 13b–d, the correlation coefficients of Hg and pyritic sulfur in lignite, sub-bituminous coal and bituminous coal are 0.479, 0.709 and 0.887, respectively, which means the dependence of Hg on pyritic sulfur is enhanced with the increase of coalification degree.



(**a**) peat (**b**) lignite



(**c**) sub-bituminous coal (**d**) bituminous coal

Figure 13. Correlation between Hg and pyritic sulfur for coal samples with different ranks.

3.3. Distribution of Hg Speciation in Coals

The trace elements mainly combine with minerals [28], and Hg also has an affinity for organic matter in coal [29,30]. As shown in Figure 2, a modified sequential chemical extraction procedure [31] is performed on 71 samples from Ningwu Coalfield. The ranges and arithmetic means of Hg in five fractions are summarized in Table 8 for 59 coal samples and in Table 9 for 12 gangue samples. There are little Hg extracted by both $MgCl_2$ and HF solutions, in which the percentages of exchangeable Hg (F1) are 1.7% in bituminous coal, 0.1% in sub-bituminous coal, 0.1% in lignite, 0.2% in peat and 0.1% in gangue, and those of silicate + aluminosilicate bound Hg (F3) are 1.5%, 1.0%, 4.1%, 5.1% and 4.0% in bituminous coal, sub-bituminous coal, lignite, peat and gangue, respectively. A large fraction is in the carbonate + sulfate + oxide bound association (F2) with an average value of 24.3%. It should be noticed that sulfide bound Hg (F4) accounts for 37.6% to 69.7% of total Hg and is the main speciation in all samples except for peat samples, which is in a fair agreement with the low-sulfur coal in Huaibei Coalfield by Zheng et al. [21]. The residual Hg (F5) mainly includes organic Hg with an average value of 25.8% in all coal samples.

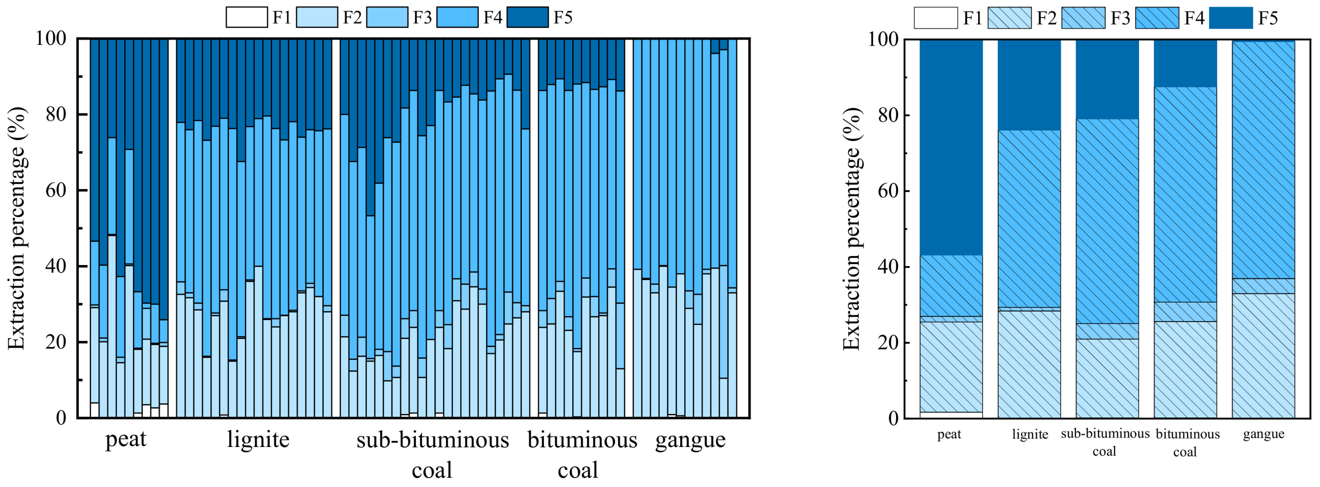
Table 8. Hg speciation in 59 coal samples with different ranks.

Kinds of Samples		Hg Speciation in Coal, %				
		Exchangeable Hg (F1)	Carbonate + Sulfate + Oxide Bound Hg (F2)	Silicate + Aluminosilicate Bound Hg (F3)	Sulfide Bound Hg (F4)	Residual Hg (F5)
peat	Min	0.0	14.6	0.3	1.4	26.1
	Max	4.0	48.1	8.1	30.2	74.1
	Average	1.7	23.8	1.5	16.2	56.8
lignite	Min	0.0	15.0	0.0	41.0	21.0
	Max	0.8	40.0	3.3	61.0	32.4
	Average	0.1	28.3	1.0	46.8	23.9
sub-bituminous coal	Min	0.0	9.8	0.0	37.6	9.6
	Max	1.3	35.0	8.4	67.4	46.7
	Average	0.1	20.8	4.1	54.0	20.9
bituminous coal	Min	0.0	13.0	0.7	49.9	10.8
	Max	1.3	34.5	17.3	69.7	13.8
	Average	0.2	25.4	5.1	56.9	12.4
Total	Min	0.0	9.8	0.0	1.4	9.6
	Max	1.3	48.1	17.3	69.7	74.1
	Average	0.3	24.3	2.9	46.5	25.8

Table 9. Hg speciation in 12 gangue samples.

Kinds of Samples		Speciation of Hg in Coal, %				
		Exchangeable Hg (F1)	Carbonate + Sulfate + Oxide Bound Hg (F2)	Silicate + Aluminosilicate Bound Hg (F3)	Sulfide Bound Hg (F4)	Residual Hg (F5)
gangue	Min	0.0	10.5	0.0	56.6	0.0
	Max	0.9	40.0	29.7	67.4	3.9
	Average	0.1	32.9	4.0	62.5	0.6

The distribution characteristics of Hg speciation in the samples of different rank coal and gangue are summarized in Figure 14. Clearly, as shown in Figure 14a, F1 is not major speciation of Hg in each of the samples, and most of which is lower than the limit of detection. Figure 14b displays the average proportion of F2 in different rank coals are 23.8% for peat, 28.3% for lignite, 20.8% for sub-bituminous coal and 25.4% for bituminous coal, which is similar to 26% for sub-bituminous coal and 22% for bituminous coal obtained by Bool et al. [32]. The proportions of F3 host in sub-bituminous coal, bituminous coal and gangue account for 4.1%, 5.4% and 4.0% of total Hg, respectively, but they are less significant in the other samples contributing 1.5% and 1.0% of total Hg in peat and lignite samples. The relatively low proportion of F3 in the measured all samples may be related to the weak affinity of Hg with clay minerals in coal. F4 is the maximum Hg speciation in all samples except for peat, which is consistent with the general opinion that Hg is primarily combined with pyrite in coal [6,33–35]. The percentage of 56.8% F5 is found in peat samples, whilst F5 is near to zero in gangue samples. However, the summation of F2 + F3 + F4 is the proportion of Hg combined with inorganic minerals. The total proportion of F2 + F3 + F4 shown in Figure 14b is gradually increased from 41.5% in peat to 87.4% in bituminous coal with the increase of coalification degree, which is consistent with the above-mentioned correlation between Hg and ash in coal samples and matches with the results in gangue samples. As the dominant speciation of Hg in peat, F5 decreased from 56.8% in peat to 12.4% in bituminous coal, which is also consistent with the strong correlation between Hg and organic sulfur in Figure 7.



(**a**) Hg speciation in all samples

(**b**) Average proportion of the five Hg speciation in samples.

Figure 14. Distribution characteristics of five Hg speciation in samples.

4. Conclusions

The dependence of Hg distribution in coal on the coalification degree is explored by using the statistical method of Pearson regression analysis coupled with Spearman rank correlation based on the experimental data using sequential chemical extraction technique. The main conclusions for the relationship of Hg with total sulfur, various forms of sulfur and ash in coal can be drawn as below:

(1) Hg is positively correlated with total sulfur in coal. The affinity of Hg to different sulfur forms varies with the coalification degree. Hg in peat depends on organic sulfur, sulfate sulfur and pyritic sulfur. The strong correlation between Hg and organic sulfur is found in peat samples with the highest volatile matter. The correlation coefficients of Hg and pyritic sulfur are 0.479, 0.709 and 0.887, respectively, in lignite, sub-bituminous coal and bituminous coal, which means the dependence of Hg on pyritic sulfur is enhanced with the increase of coalification degree.

(2) Hg is also related to ash content in coal. The Pearson linear correlation coefficients of Hg and ash are 0.504, 0.774 and 0.827, respectively, in lignite, sub-bituminous coal and bituminous coal, which implies that both mercury and sulfur enrich in coal largely due to the migration from organic state to inorganic state with the increase of coalification degree. This phenomenon can be indirectly confirmed by gangue samples and indicates that Hg in coal is largely enriched in inorganic minerals.

(3) Hg distribution is affected by the combined action of organic matter and sulfate sulfur in low rank coal such as peat or lignite, whilst Hg distribution is mainly influenced by pyritic sulfur in high rank coal such as bituminous coal.

(4) Hg distribution directly depends on its own speciation in coal. The total proportion of F2 + F3 + F4 is increased from 41.5% in peat to 87.4% in bituminous coal, but the average proportion of F5 is decreased from 56.8% in peat to 12.4% in bituminous coal. Both Hg and sulfur enrich in coal largely due to the migration from organic state to inorganic state with the increase of coalification degree.

Author Contributions: All authors contributed to the study conception and design. K.Z. and Y.S. designed the experiments, performed the experiments and the statistical analysis, wrote the paper; K.Z., Y.T. and X.L. participated in the correction. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Natural Science Foundation of China (U1910215) and the Fundamental Research Funds for the Central Universities (2019QN020, 2019QN019).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Li, X.; Teng, Y.; Zhang, K.; Peng, H.; Cheng, F.; Yoshikawa, K. Mercury migration behavior from flue gas to fly ashes in a commercial coal-fired CFB power plant. *Energies* **2020**, *13*, 1040. [CrossRef]
2. Zhao, L.; Wu, Y.-W.; Han, J.; Wang, H.-X.; Liu, D.-J.; Lu, Q.; Yang, Y.-P. Density functional theory study on mechanism of mercury removal by CeO_2 modified activated carbon. *Energies* **2018**, *11*, 2872. [CrossRef]
3. Li, H.; Wang, S. FeCl3-modified Co–Ce oxides catalysts for mercury removal from coal-fired flue gas. *Chem. Pap.* **2017**, *71*, 2545–2555. [CrossRef]
4. Duan, P.P.; Wang, W.F.; Liu, X.H.; Qian, F.; Sang, S.; Xu, S. Distribution of As, Hg and other trace elements in different size and density fractions of the Reshuihe high-sulfur coal, Yunnan Province, China. *Int. J. Coal Geol.* **2017**, *173*, 129–141. [CrossRef]
5. Marczak, M.; Faustyna, W.; Burmistrz, P.; Strugaa, A.; Lech, S. Investigation of subbituminous coal and lignite combustion processes in terms of mercury and arsenic removal. *Fuel* **2019**, *251*, 572–579. [CrossRef]
6. Yudovich, Y.E.; Ketris, M.P. Mercury in coal: A review: Part 1. geochemistry. *Int. J. Coal Geol.* **2005**, *62*, 107–134. [CrossRef]
7. Riley, K.W.; French, D.H.; Farrell, O.P.; Wood, R.A.; Huggins, F.E. Modes of occurrence of trace and minor elements in some australian coals. *Int. J. Coal Geol.* **2012**, *94*, 214–224. [CrossRef]
8. Liu, G.; Zheng, L.; Zhang, Y.; Qi, C.; Chen, Y.; Peng, Z. Distribution and mode of occurrence of As, Hg and Se and sulfur in coal Seam 3 of the Shanxi Formation, Yanzhou Coalfield, China. *Int. J. Coal Geol.* **2007**, *71*, 371–385. [CrossRef]
9. Chelgani, S.C. Investigating the occurrences of valuable trace elements in african coals as potential byproducts of coal and coal combustion products. *J. Afr. Earth Sci.* **2019**, *150*, 131–135. [CrossRef]
10. Zhang, G.; Song, S.; Yang, W.; Zhang, B.; Wang, J. Occurrence characteristics of Hg in high-Hg coal and distribution rule of Hg in products of an air dense medium fluidized bed. *Int. J. Min. Sci. Technol.* **2018**, *28*, 1015–1020. [CrossRef]
11. Nikolay, R.; Mashyanov, S.E.P.; Elena, G.; Nikolay, P.; Vladimir, R. Determination of Hg thermospecies in coal. *Fuel* **2017**, *203*, 973–980.
12. Zhao, S.; Pudasainee, D.; Duan, Y.; Gupta, R.; Liu, M.; Lu, J. A review on mercury in coal combustion process: Content and occurrence forms in coal, transformation, sampling methods, emission and control technologies. *Prog. Energy Combust. Sci.* **2019**, *73*, 26–64. [CrossRef]
13. Finkelman, R.B. Modes of occurrence of potentially hazardous elements in coal: Levels of confidence. *Fuel Process. Technol.* **1994**, *39*, 21–34. [CrossRef]
14. Ribeiro, J.; Flores, D. Occurrence, leaching, and mobility of major and trace elements in a coal mining waste dump: The case of douro coalfield, portugal-sciencedirect. *Energy Geosci.* **2020**. [CrossRef]
15. Feng, X.; Hong, Y. Modes of occurrence of Hg in coals from Guizhou, People's Republic of China. *Fuel* **1999**, *78*, 1181–1188. [CrossRef]
16. Ohki, A.; Taira, M.; Hirakawa, S.; Haraguchi, K.; Kanechika, F.; Nakajima, T. Determination of mercury in various coals from different countries by heat-vaporization atomic absorption spectrometry: Influence of particle size distribution of coal. *Microchem. J.* **2014**, *114*, 119–124. [CrossRef]
17. Diehl, S.F.; Goldhaber, M.B.; Hatch, J.R. Modes of occurrence of Hg and other trace elements in coals from the warrior field, Black Warrior Basin, Northwestern Alabama. *Int. J. Coal Geol.* **2004**, *59*, 193–208. [CrossRef]
18. Jae, J.H.W.; Tai, G.L. Hg analysis of various types of coal using acid extraction and pyrolysis methods. *Energy Fuel* **2006**, *20*, 2413–2416.
19. Kolker, A.; Senior, C.; Alphen, C.V.; Koenig, A.; Geboy, N. Mercury and trace element distribution in density separates of a south african highveld (#4) coal: Implications for mercury reduction and preparation of export coal. *Int. J. Coal Geol.* **2017**, *170*, 7–13.
20. Zheng, L.; Liu, G.; Qi, C.; Zhang, Y.; Wong, M. The use of sequential extraction to determine the distribution and modes of occurrence of Hg in Permian Huaibei coal, Anhui Province, China. *Int. J. Coal Geol.* **2008**, *73*, 139–155. [CrossRef]
21. Zheng, L.; Liu, G.; Chou, C.L. Abundance and modes of occurrence of Hg in some low-sulfur coals from China. *Int. J. Coal Geol.* **2008**, *73*, 19–26. [CrossRef]
22. Hu, J.; Zheng, B.; Finkelman, R.; Wang, B.; Wang, M.; Li, S. Content and distribution of sixty-one elements in coals from DPR Korea. *Fuel* **2006**, *85*, 679–688. [CrossRef]
23. Zhao, Y.; Hu, H.; Jin, L.; He, X.; Wu, B. Pyrolysis behavior of vitrinite and inertinite from Chinese Pingshuo coal by TG–MS and in a fixed bed reactor. *Fuel Process. Technol.* **2011**, *92*, 780–786. [CrossRef]
24. Gao, W.D.; Jiang, W.; Zhou, M. The spatial and temporal characteristics of Hg emission from coal combustion in China during the year 2015. *Atmos. Pollut. Res.* **2019**, *10*, 776–783. [CrossRef]
25. Zheng, L.; Liu, G.; Chou, C.L. The distribution, occurrence and environmental effect of Hg in Chinese coals. *Sci. Total Environ.* **2007**, *384*, 374–383. [CrossRef]

26. Dziok, T.; Strugała, A.; Rozwadowski, A.; Macherzyński, M. Studies of the correlation between Hg content and the content of various forms of sulfur in Polish hard coals. *Fuel* **2015**, *159*, 206–213. [CrossRef]
27. Henderson, E.L. 'PAL' lends a helping hand: NSR reform aids efforts by major stationary sources to meet EPA air emissions levels. *Met. Finish.* **2006**, *104*, 50–53. [CrossRef]
28. Luo, G.Q.; Ma, J.; Han, J.; Yao, H.; Xu, M.H.; Zhang, C. Hg occurrence in coal and its removal before coal utilization. *Fuel* **2013**, *104*, 70–76. [CrossRef]
29. Jongwana, L.T.; Crouch, A.M. Hg speciation in South African coal. *Fuel* **2012**, *94*, 234–239. [CrossRef]
30. Huggins, F.E.; Seidu, L.B.A.; Shah, N.; Huffman, G.P.; Honaker, R.Q.; Kyger, J.R. Elemental modes of occurrence in an Illinois #6 coal and fractions prepared by physical separation techniques at a coal preparation plant. *Int. J. Coal Geol.* **2009**, *78*, 65–76.
31. Su, Y.; Liu, X.; Teng, Y.; Zhang, K. Mercury speciation in various coals based on sequential chemical extraction and thermal analysis methods. *Energies* **2021**, *14*, 2361. [CrossRef]
32. Bool, L.E.; Helble, J.J. A laboratory study of the partitioning of trace elements during pulverized coal combustion. *Energy Fuel* **1995**, *9*, 880–887. [CrossRef]
33. Kolker, A.; Senior, C.L.; Quick, J.C. Mercury in coal and the impact of coal quality on mercury emissions from combustion systems. *Appl. Geochem.* **2006**, *21*, 1821–1836. [CrossRef]
34. Goodarzi, F. Mineralogy, elemental composition and modes of occurrence of elements in Canadian feed-coals. *Fuel* **2002**, *81*, 1199–1213. [CrossRef]
35. Luttrell, G.H.; Kohmuench, J.N.; Yoon, R.-H. An evaluation of coal preparation technologies for controlling trace element emissions. *Fuel Process. Technol.* **2000**, *65*, 407–422. [CrossRef]