Concentration, distribution, and mode of occurrence of mercury in Bulgarian high-sulphur coals

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Abstract. The goal of this study is to determine the mercury content, distribution, and modes of occurrence in high-sulphur coals from the Maritza-West, Maritza-East, and Stanyantsi basins in Bulgaria. The investigation is based on 51 samples representing the whole coal beds. The average concentration of Hg for all studied samples is 0.34 ppm and the values vary from 0.07 to 1.20 ppm; the average is 6.8-times higher than the Hg value in the upper continental crust and 3.4-times higher than the average values for world coals. The highest average Hg concentration (0.57 ppm) was found in the Maritza-West samples, followed by the Maritza-East (0.30 ppm), and the Stanyantsi (0.15 ppm) lignite. These data correspond with the sulphur content, i.e, the highest-Hg lignite has the highest S content. A weak positive correlation between Hg and the total and sulphide S and a negative correlation between Hg and the organic S content for the Maritza-West lignite were observed. It is suggested that the Hg is predominantly incorporated in pyrite, which is present in high amount in these coals. The tendency in the distribution of Hg and S forms for the Maritza-East and Stanyantsi basins shows that Hg may be closely connected with S-bearing organic compounds, especially for the Maritza-East lignite. Consequently, the main part of Hg in the high-S coals from the Maritza-East and Stanyantsi basins is closely connected with organic sulphur complexes and may be with inorganic matter other than sulphide minerals. The data determined from this study partially confirms the results for other high-S world coals reported earlier. For the typical high-S Maritza-West lignite it may be suggested that there is a strong connection between Hg and pyrite and especially with epigenetic pyrite infilling the coal veins and cleats, while for high-S Maritza-East and Stanyantsi lignite the Hg is predominantly incorporated in organic matter and especially in sulphur-bearing organic compounds.

1. Introduction
Mercury is considered to be a global pollutant due to its potential toxicity and global movement, as well as due to its highly volatile nature and tendency to be emitted during coal combustion [1,2]. Industrial coal combustion is a significant source of Hg to the environment and, according to data from the U.S. Environmental Protection Agency, it accounts for about 34 % of Hg released to the atmosphere. Yudovich and Ketris [1] suggested that the average values for world-wide coals, ashes derived from low-rank coals, and ashes derived from high-rank coals are 0.1, 0.62, and 0.87 ppm, respectively.
Numerous publications have discussed the modes of occurrence of Hg in coals. For example, Feng and Hong [3] used sequential extraction to show that Hg in Chinese coals was primarily present in pyrite and a significant variation in Hg between different pyrite grains was also observed. Zhang and coauthors [4] found that low-temperature hydrothermal calcite and pyrite contained more Hg than other minerals in some Late Permian coals in southwestern China. A subsequent study of coal in fault zones showed that the concentrations of Hg and other toxic elements like As, Se, and Sb are directly related to the distance from noble metal ores [4]. In a similar geological environment, [5] found an association between Hg and hydrothermal sulphides in coal from Alabama. However, some studies indicated that Hg in coal does not exclusively occur in pyrite. The Hg-bearing calcite and chlorite in Chinese coals [6], Hg-rich gold in coals from Russian Far East region [7], and Hg-bearing clausthalite and marcasite in coal from Kentucky [8-10] were also found, although the Hg-pyrite association is the dominate form. Coal from the Central Asturian coal basin contains hydrothermal cinnabar, metacinnabar, and native mercury, along with other Hg-bearing minerals [11]. Some other studies attributed high Hg levels to both Hg-organic complexes and Hg-rich minerals (e.g., Hg-bearing pyrite, cinnabar, kleinite, and native Hg) [12]. Despite its various modes of occurrence, Fe-sulphides appear to be the primary host of Hg in many coals. However, it should also be noted that the sulphides can vary considerably in their Hg content within the same coal [9].

A number of publications have addressed the different aspects of Hg in bulk coal and fly ashes from Bulgarian thermolectric power plants [13-17], but there is insufficient information about the Hg concentration and distribution in Bulgarian coal basins. The aim of the present study is to perform a detailed investigation of Hg in some high-sulphur Bulgarian coals, with a focus on (1) providing new data about Hg concentrations in high-sulphur Bulgarian coals, and comparing these data with previously reported for the upper continental crust, for USA, Australian, Chinese, and world coals; (2) determining the correlation between Hg and sulphur forms values; and (3) making some assumptions about the mode of occurrence of Hg in high-sulphur Bulgarian coals.

2. Sampling and methods
The Neogene Maritza-East, Maritza-West, and Stanyantsi basins were selected for sampling because of high-sulphur contents in the coals. The Maritza-East and Maritza-West basins are located in the Tracian province and the Stanyantsi basin is in the Sofia coal province. This study is based on 51 samples including 17 coal samples taken from the Maritza-East open-pit mine (representative for second and third coal seams), 24 samples taken from the active face in the Maritza-West underground mine (representative for Kipra coal seam), and 10 samples taken from the Stanyantsi open-pit coal mine. All samples were obtained by the channel method from the top to the bottom of coal seams and represented the entire coal beds. More information about sampling was published earlier (Kostova and Zdravkov, 2007; Kostova and Isaeva, 2016). The proximate and ultimate analyses of studied samples were performed by following the ISO standards. The total sulphur and sulphur forms are determined using Eschka and ASTM D2492 methods, respectively. The classification of Chou [18] concerning the concentration of sulphur in coal was applied; the coals are divided as follows: < 1 % - low-S, from 1 to 3 % - medium-S, and ≥ 3 % - high-S coals. The observation of the size and morphology of pyrite and other minerals was performed with a Leica DM 2500 P optical microscope and JEOL JSM-5510 scanning electron microscope equipped with an EDAX analyzer. The bulk Hg content was determined by using a LECO AMA-254 automatic mercury analyzer, which is a unique atomic absorption spectrometer, without sample pre-treatment or sample pre-concentration and complying with EPA Method 7343. The Hg analyzer has a 0.01 ng-Hg detection limit (a working range from 0.05 to 600 ng Hg), reproducibility smaller than 1.5%, and five minutes analysis time.

3. Geological settings
The Maritza depression is interpreted as an intra-orogenic extensional basin [19], which formed during the Late Eocene–Oligocene as a final stage of continental collision in southern Bulgaria (Figure 1a).
Some young faults subdivide the Maritza coal basin into two sub-basins: Maritza West and Maritza East (Figure 1b).

Sedimentation in the Maritza depression commenced in a marine environment with the deposition of thick, coarse-grained fan sediments grading upwards into an alternation of sandstones, marls, limestones, latitite tuffs, and tuff-breccias of Eocene–Oligocene age [20]. These sediments overlie Precambrian, Palaeozoic, and Mesozoic crystalline rocks, marbles, dolomitized limestones, dolomites, conglomerates, and sandstones and are overlain by carbonaceous shales and marls [21]. During the Late Oligocene–Early Miocene, the marine environment was replaced by limnic conditions due to a gradual eastward regression of the Black Sea [22] and the sediments of the (late Oligocene–) Miocene Maritza Formation (Figure 1b) started to accumulate. The lower part of Maritza Formation is represented by clays, marls, and clayey limestones with rare sandstone layers [20]. In the western part of the Maritza Depression, up to six lignite seams were deposited (Brod Member). Their equivalents in the eastern part are the three lignite seams of the Troyanovo Member [23]. Subsequently, the interfingering of sediments from different fluvial sources resulted in the deposition of horizontally and vertically alternating layers of yellowish and greenish silty to sandy clays and layers of fine- to coarse-grained sands (Figure 1b); [20].

Later, block displacements split the depression into two parts, i.e., the Maritza-West and the Maritza-East basins, both characterized by distinct evolution. While the eastern part was subjected to general uplift and erosion, in the Maritza-West basin sedimentation continued for some time. During the transition from lacustrine to fluvio-deltaic environment, the clayey and sandy sediments of the Kipra Member (Figure 2a, b) were deposited.
The thickness of the Kipra Member ranges from 20 to 40 m, including four lignite seams with a total thickness of up to 5 m. However, only two of them have economic significance. The Kipra lignite seam (1.75–2.9-m thick; Figure 1b) comprises the largest lignite reserves within the Maritza-West basin. The coal seam is split by three clay layers, which indicates that subsidence was relatively low during peat accumulation, allowing for the frequent change between lacustrine/fluvial and swampy environments.

The Maritza Coal Member includes three seams (Figure 1b). The uppermost (first) seam is considered uneconomic and is restricted to the center of the sub-basin [24]. The main coal reserves are located in the second seam, with an average thickness of 15 m [20]. It lies approximately 4–5-m below the first seam. The third seam, 3–9-m thick, is separated from the second by a 1–28-m-thick parting. The coal of the third seam grades into coaly shales near the basin margins.

The Maritza Formation is overlain by up to 100-m-thick Mio-/Pliocene alluvial, prolluvial, and talus deposits which cover most of the Maritza depression [20].

The sedimentary filling of the Maritza depression is characterized by extended faulting. In addition, during the Pliocene and Quaternary, folding processes due to movements along the major fault systems took place within the Maritza-West basin and produced two shallow synclines and one anticline [25]. As a result, the sediments and lignite layers were extensively deformed by multiple low-amplitude faults and cleavage cracks favouring the infiltration and circulation of meteoric precipitations.

The Stanyantsi basin was formed in an extensive E-W orientated graben with a size of about 22 km in length and 3–4 km in width on the territory of Serbia and Bulgaria (Figure 1a). The main part of the basin is located in Eastern Serbia, but the main lignite resources are found in Bulgaria [24].

The sediments of the Stanyantsi basin are of the Late Miocene age. They were deposited in the small graben structure which is bound to the southern margin of Vidlich Mountain from the West Balkan tectonic unit [26]. According to Zagorchev [27], the graben formed as a result of the general crustal extension and initial rifting of the region during the Tertiary. The geological settings of Stanyantsi basin along with two cross-sections across the coal bearing strata are shown in Figure 1c.

The Neogene sediments within the Stanyantsi basin, as described by Vatsev [26], include four lithostratigraphic units (Figure 1c). Deposition within the graben commenced in the Late Miocene with the sedimentation of the rocks of Dvechke Formation, which is represented by coarse gray sandy mudstones and clayey sandstones of fluvial origin. These rocks overlie highly denuded basement rocks composed mainly of Triassic and Jurassic limestone and dolomite [26]. The overlying sediments are represented by lacustrine silty, sandy, and limy clays and marls of the Belozem Formation. At the base of this formation, the main lignite seam, with thickness up to 20 m, is composed mainly of high-ash coal with rare xylite fragments [28]. Thin layers and lenses of mudstones are interbedded in the lignite seam close to its base and top, as well as near the basin margins. The lacustrine/palustrine sediments of Belozem Formation are up to 30-m thick and are represented by vertically alternating mudstones and limestones [26]. This phase of basin development ended during the Late Pontian–Early Pliocene with changing of lacustrine to fluvial sedimentation environment. Upwards in the cross-section, the sandy and gravelly mudstones up to 60-m thick and the clayey sandstones of Zainitsa Formation were deposited. During the Late Pliocene–Pleistocene the overlying sediments, represented by the alternation of proluvial reddish gravels, breccias, sandstones, and sandy mudstones of the Strania Formation, were deposited [26].
4. Results and discussion

4.1. Coal characteristics and sulphur distribution

The proximate and ultimate analyses, sulphur forms, and mercury content of the coal samples are presented in Table 1.

**Table 1.** Proximate analysis (ash yield %, moisture %, volatile matter %), ultimate analysis (C, H, N, S, and O %), sulphur forms (wt. %), and mercury content (ppm), all presented on a dry whole-coal basis, in lignite samples from the Maritza-East, Maritza-West, and Stanyantsi basins, Bulgaria

| Samples       | Proximate analysis | Ultimate analysis | Total sulphur and forms of sulphur | Mercury ppm |
|---------------|--------------------|-------------------|------------------------------------|-------------|
|               | A      | W   | VM  | C  | H   | N   | O   | %  | %   | %   | %   | %   | S   | S   | S   | S   | ppm |
| Maritza-East  |        |      |     |    |     |     |     |    |     |     |     |     |     |     |     |     |     |
| ME 1          | 15.2   | 10.4 | 47.2 | 50.50 | 5.36 | 0.54 | 23.86 | 4.1 | 1.1 | 0.1 | 2.9 | 0.39 |
| ME 2          | 15.9   | 10.8 | 56.8 | 49.91 | 5.30 | 0.63 | 23.67 | 4.5 | 1.0 | 0.3 | 3.2 | 0.36 |
| ME 3          | 16.1   | 11.2 | 58.7 | 49.61 | 5.23 | 0.74 | 23.83 | 3.9 | 1.5 | 0.1 | 2.3 | 0.38 |
| ME 4          | 17.1   | 10.8 | 56.5 | 48.52 | 5.19 | 0.64 | 23.97 | 4.1 | 1.4 | 0.2 | 2.5 | 0.31 |
| ME 5          | 17.6   | 11.2 | 57.5 | 48.13 | 5.01 | 0.70 | 24.05 | 4.1 | 1.5 | 0.2 | 2.4 | 0.32 |
| ME 6          | 16.4   | 10.8 | 56.1 | 49.20 | 5.19 | 0.60 | 23.87 | 4.2 | 1.6 | 0.4 | 2.2 | 0.39 |
| ME 7          | 16.3   | 10.9 | 57.1 | 49.45 | 5.34 | 0.60 | 23.63 | 4.1 | 1.1 | 0.2 | 2.8 | 0.40 |
| ME 8          | 12.8   | 10.2 | 59.5 | 52.29 | 5.56 | 0.54 | 23.74 | 4.6 | 1.8 | 0.2 | 2.6 | 0.37 |
| ME 9          | 17.1   | 9.7  | 56.8 | 48.69 | 5.36 | 0.49 | 22.22 | 5.0 | 2.3 | 0.2 | 2.5 | 0.38 |
| ME 10         | 18.6   | 9.7  | 61.7 | 48.46 | 5.39 | 0.46 | 21.88 | 4.5 | 1.7 | 0.3 | 2.5 | 0.31 |
| ME 11         | 26.6   | 10.4 | 58.0 | 36.94 | 4.23 | 0.47 | 24.77 | 6.7 | 4.7 | 0.6 | 1.4 | 0.17 |
| ME 12         | 29.1   | 8.8  | 65.3 | 40.74 | 4.73 | 0.36 | 20.33 | 3.9 | 1.7 | 0.3 | 1.9 | 0.20 |
| ME 13         | 18.6   | 8.1  | 67.2 | 48.88 | 5.54 | 0.32 | 21.11 | 4.8 | 2.8 | 0.4 | 1.6 | 0.18 |
| ME 14         | 63.7   | 7.8  | -    | 13.72 | 2.75 | 0.28 | 16.11 | 3.2 | 1.9 | 0.8 | 0.5 | 0.27 |
| ME 15         | 76.5   | 4.6  | -    | 7.92  | 1.91 | 0.23 | 10.96 | 3.1 | 2.6 | 0.4 | 0.1 | 0.12 |
| ME 16         | 21.4   | 9.7  | 54.0 | 40.50 | 4.55 | 0.37 | 25.18 | 9.4 | 5.4 | 1.6 | 2.4 | 0.23 |
| ME 17         | 23.5   | 9.5  | 61.8 | 39.65 | 4.51 | 0.36 | 24.64 | 8.7 | 4.6 | 1.6 | 2.5 | 0.24 |
| Average       | 24.9   | 7.1  | -    | -    | -    | -    | 4.6   | 2.3 | 0.5 | 2.1 | 0.30 |

| Samples       | Proximate analysis | Ultimate analysis | Total sulphur and forms of sulphur | Mercury ppm |
|---------------|--------------------|-------------------|------------------------------------|-------------|
| Maritza-West  |        |      |     |    |     |     |     | %  | %   | %   | %   | %   | S   | S   | S   | S   | ppm |
| MW 1          | 53.3   | 9.3  | -    | 21.54 | 1.87 | 0.41 | 19.18 | 3.4 | 1.7 | 1.1 | 0.8 | 0.67 |
| MW 2          | 96.4   | 4.0  | -    | 1.79  | 1.47 | 0.59 | 5.94  | 1.4 | 0.7 | 0.6 | 0.1 | 0.98 |
| MW 3          | 26.8   | 9.9  | 58.4 | 37.62 | 3.88 | 1.32 | 23.13 | 12.6 | 8.7 | 3.6 | 0.3 | 1.13 |
| MW 4          | 28.6   | 9.9  | 58.0 | 34.23 | 3.80 | 1.13 | 23.76 | 11.1 | 7.6 | 3.4 | 0.1 | 0.99 |
| MW 5          | 24.9   | 9.7  | 60.1 | 33.50 | 3.55 | 0.89 | 24.23 | 8.1 | 5.1 | 2.2 | 0.8 | 1.10 |
| MW 6          | 14.4   | 12.0 | 60.6 | 49.75 | 4.80 | 0.99 | 25.67 | 5.7 | 1.5 | 0.4 | 3.8 | 0.46 |
| MW 7          | 21.5   | 11.1 | 60.5 | 39.24 | 3.98 | 1.16 | 25.76 | 5.5 | 2.7 | 0.7 | 2.1 | 0.38 |
| MW 8          | 49.2   | 9.2  | 61.6 | 19.54 | 1.69 | 0.41 | 19.18 | 4.4 | 2.6 | 0.8 | 1.0 | 0.79 |
| MW 9          | 14.9   | 12.6 | 53.6 | 50.80 | 4.84 | 1.10 | 25.52 | 4.1 | 1.9 | 0.2 | 2.0 | 0.40 |
| MW 10         | 57.6   | 4.8  | -    | 19.55 | 1.87 | 0.41 | 19.18 | 3.2 | 2.6 | 0.5 | 0.1 | 0.51 |
| MW 11         | 29.8   | 11.5 | 72.7 | 39.30 | 4.01 | 1.12 | 20.44 | 2.7 | 2.1 | 0.3 | 0.3 | 0.39 |
| MW 12         | 34.7   | 11.3 | 76.3 | 35.60 | 3.26 | 0.64 | 24.51 | 4.5 | 1.9 | 0.4 | 2.2 | 0.51 |
| MW 13         | 31.8   | 11.9 | 61.4 | 38.99 | 3.94 | 0.96 | 20.77 | 7.5 | 3.1 | 0.7 | 3.7 | 0.43 |
| MW 14         | 36.0   | 9.0  | 59.2 | 34.60 | 3.27 | 0.59 | 25.07 | 5.2 | 2.3 | 0.7 | 2.2 | 0.20 |
| MW 15         | 80.8   | 4.8  | -    | 10.03 | 2.55 | 0.66 | 2.30  | 7.8 | 5.4 | 1.9 | 0.5 | 0.28 |
range of pyrite texture, including individual grains, crystals, and aggregates, as well as infilling plant
content. The total S varies from 1.0 to 6.6 % with a mean value of 3.1 %. Sulphide S predominates.

Various modes of pyrite occurrence were observed, suggesting several generations of mineral formation during the syngenetic and epigenetic stages and substages. The syngenetic pyrite is represented by frambooidal and euhedral crystals, which are situated along with stratified bands or infilling cell openings of plant debris. Some pyrite precipitated epigenetically due to the infiltration and circulation of hydrothermal solutions through the cleats and fractures [29, 30]. The high-S content in the Maritza-East and especially in the Maritza-West lignite is remarkable considering the absence of an obvious marine or brackish influence (see part 3 “Geological settings”). The high-S contents are most likely related to 1) a neutral to alkaline depositional environment; 2) the presence of sulphide ore deposits and mineralized zones contained in the basement rocks, which are probably the main source of sulphates; and 3) the presence of S-bearing hydrothermal fluids, which contributed to the epigenetic mineralization [29]. Extensive data concerning pyrite occurrence and distribution in both basins were published previously [29].

The lignite from the Stanyantsi basin has a low- to medium-ash yield and a medium- to high-S content. The total S varies from 1.0 to 6.6 % with a mean value of 3.1 %. Sulphide S predominates. Detailed information about mineralogy, including sulphur-bearing minerals, their forms, and the origin of the samples was published by [31]. Frambooidal pyrite is present in all studied samples, but a wide range of pyrite texture, including individual grains, crystals, and aggregates, as well as infilling plant

| Stanyantsi Basin | St 1 | 15.0 | 13.3 | 59.8 | 48.15 | 4.92 | 1.03 | 30.84 | 2.3 | 1.0 | 0.2 | 1.1 | 0.16 |
|------------------|-----|-----|-----|-----|------|-----|-----|------|-----|-----|-----|-----|-----|
| St 2             | 10.8| 14.7| 59.7| 48.11| 5.25 | 1.21| 28.95| 1.0  | 0.2 | 0.3 | 0.5 | 0.14|
| St 3             | 12.3| 14.7| 60.2| 47.86| 5.13 | 1.33| 35.36| 1.1  | 0.3 | 0.2 | 0.6 | 0.07|
| St 4             | 24.4| 13.6| 63.5| 38.42| 4.51 | 1.08| 26.95| 4.7  | 1.2 | 0.3 | 3.2 | 0.20|
| St 5             | 15.1| 14.5| 63.7| 43.39| 4.80 | 1.25| 28.58| 2.1  | 1.3 | 0.1 | 0.8 | 0.13|
| St 6             | 23.0| 12.8| 62.5| 46.93| 5.14 | 1.33| 29.41| 6.2  | 4.5 | 0.9 | 0.8 | 0.13|
| St 7             | 19.7| 13.3| 60.3| 40.13| 4.53 | 1.35| 26.48| 1.7  | 1.1 | 0.1 | 0.5 | 0.22|
| St 8             | 12.6| 14.7| 57.9| 47.16| 5.02 | 1.54| 33.93| 1.5  | 0.7 | 0.2 | 0.6 | 0.16|
| St 9             | 28.3| 12.6| 66.2| 43.05| 4.81 | 1.38| 27.76| 3.4  | 2.2 | 0.8 | 0.4 | 0.13|
| St 10            | 25.7| 12.8| 62.2| 40.76| 4.53 | 1.34| 24.43| 6.6  | 5.2 | 0.6 | 0.8 | 0.16|
| Average          | 16.4| 13.7| -   | -    | -    | -   | 3.1  | 1.8  | 0.2 | 0.9 | 0.15|

A, ash yield; W, moisture; VM, volatile matter.
cell structure also can be observed. Despite the fresh-water environment during the coal deposition, the high-S content may have been caused by the presence of a sulphate-rich depositional environment in the peat bog [31].

4.2. Distribution of mercury in high-sulphur coals
There is a wide Hg variation in individual samples, ranging from 0.07 to 1.20 ppm across all deposits. The average concentration of Hg in all studied samples is 0.34 ppm. These data are compared with others concerning Hg content in coals from other areas and with the average value for world coals reported by Ketris and Yudovich [32] (Table 2).

|                      | Hg range (ppm) | Hg average value (ppm) | Number of samples |
|----------------------|----------------|------------------------|-------------------|
| Bulgarian high-sulphur coal (present study) | 0.07 – 1.20 | 0.34 | 51 |
| Bulgarian low-sulphur coals | 0.03 – 0.57 | 0.23 | 29 |
| Chinese coal | - | 0.16 | 1666 |
| Upper continental crust | - | 0.05 | - |
| American coal | 0 – 10.0 | 0.17 | 7649 |
| Australian coal | 0.01 – 0.14 | 0.06 | - |
| The global Clarke value | - | 0.10 ± 0.01 | - |

The mean value for Bulgarian high-sulphur coals are 6.8-times higher than the Hg value in the upper continental crust [35], 5.7-times higher than Australian coals [37], 2.1-times higher than Chinese coals based on 1666 analyzed samples [34], and 2-times higher than USA coals based on 7649 analyzes [36]. The data for Bulgarian high-S coals are 3.4-times higher than average world coal value [32]. When compared the results obtained for low- and high-sulphur Bulgarian coals, it is obvious that the concentration of Hg in high-S samples is much higher than in low-S coals.

4.3. Correlation between mercury concentration and sulphur forms
Correlation between Hg, ash yield, and the total, pyritic, and organic sulphur in Maritza-West lignite is presented in Figure 2. The data show a positive correlation between mercury and total and pyrite content (with $R^2=0.0779$ and $R^2=0.1009$ respectively) and a negative correlation between Hg and organic sulphur.
sulphur (with $R^2=0.0634$). However, it is emphasized that none of the correlations are significant. Nevertheless, it is hypothesized that the mercury in these lignites probably has a mixed affinity of pyrite and organic matter and is predominantly incorporated in pyrite crystals, which are abundant in these coals, and S-bearing organic compounds.

![Figure 2](image_url)

**Figure 2.** Correlation between Hg content (ppm), ash yield, and different sulphur forms (%) in the lignite from Maritza-West basin

The lignites from the Maritza-East and Stanyantsi basins have high-S contents although they are lower than those in the Maritza-West basin. The correlation between mercury and pyrite and organic sulphur concentrations in both basins are given in Figure 3. The tendency in the distribution of Hg and S forms suggests that mercury in Maritza-East basin is closely connected with sulphur-bearing organic compounds (with $R^2=0.5134$). It should be emphasized that almost half of the total S in Maritza-East lignite is present in organic form (2.3 % pyritic S versus 2.1 % organic S) and may be a factor in the observed association. The negative correlation between Hg and pyrite S content for the Maritza-East lignite has been determined (with $R^2=0.3823$). The correlation dependencies between Hg and pyrite and organic sulphur for the Stanyantsi basin are rather ambiguous regarding Hg affinity. It can be concluded that may be mercury is connected to both S-bearing substances - pyrite and organic matter. There is also a possibility for an association between Hg and other inorganic matter different from pyrite.
4.4. Modes of occurrence of mercury in high-sulphur coals.

There is much evidence that Hg in coal associates dominantly with sulphide minerals. The association of Hg with pyrite and especially with epigenetic pyrite has been reported for many coals worldwide [6]; [37]; [38]; [39]; [40]; [41]; [33]. Diehl et al. [5] study of Alabama coals documented that high-Hg is closely associated with late-stage pyrite occurring as overgrowths and in veins and a significantly lower Hg amount is incorporated in other geochemical entities such as silicates, carbonates, or the organic fractions. For Pennsylvanian Indiana coals, Mastalertz and coauthors [40] reported that Hg was associated, to a large extent, with mineral matter, and particularly with pyrite and the connection with pyrite is especially distinct when the coals have high pyritic sulphur amount. When the coals have low pyritic-S content, however, Hg associations with pyrite are less distinct. In low-S coals, Hg has no relationship to pyritic S or to total S and a slightly negative correlation to ash yield. Based on the facts mentioned above it is suggested that Hg in low-S coals associated, to a significant extent, with the coal’s organic fraction. In a study of Chinese Triassic coals, Fu et al. [42] grouped Hg with TOC and total S in the cluster analyses and demonstrated that Hg occurs mainly as an organic-bound form and partly as a sulphide minerals. Briefly, the most common mode of occurrence of Hg in coals is as a solid solution in pyrite, rarely in other sulphide minerals like marcasite and sphalerite [3;5]. The mercury also has a strong organic and clay-bound affinity [1;12].

The data obtained during the present investigation only partially confirm the latter statements. For the typical high-sulphur Maritza-West lignite, two modes of Hg occurrence as a part of pyrite and sulphur-bearing organic compounds may be suggested. We assume that the main part of Hg connected with pyrite is a close connected especially with epigenetic pyrite infilling the coal veins and cleats. Kostova and Zdravkov [29] described various modes of pyrite occurrence which suggesting several generations of mineral formation during the syngenetic and epigenetic stages and some substages in Maritza-West basin. Along with syngenetic pyrite represented by framboids and euhedral crystals some
amount of pyrite precipitated epigenetically due to the infiltration and circulation of meteoric precipitations in coal cleats and fractures. The numerous sulphide ore deposits and mineralized zones contained within the Mesozoic carbonaceous basement rocks were probably the main sulphate source. In addition, sulphate-bearing waters from Merichleri gypsum-anhydrite deposit (Pliocene), located in the western part of the basin, contributed to the formation of epigenetic pyrite mineralization. Polycrystalline fine-grained masses of pyrite, clay and carbonate minerals or clusters of well-shaped pyrite crystals were described. Taking into consideration all mentioned above, it may be suggested that the part of Hg in Maritza-West lignite is present as a solid solution in epigenetic pyrite but some parts may incorporate in clays or carbonate minerals and sulphur organic compounds as well.

Regarding the high-S Maritza-East lignite, the Hg is predominantly incorporated in organic matter and especially in sulphur-bearing organic compounds (Figure 2). Kostova et al. [16] made humic extraction of lignite from Maritza-East basin in order to determine some Hg organic compounds in organic matter and concluded that the main proportion of mercury in low-rank coal is closely connected with organic compounds of humic acids. The lignite from Stanyantsi basin has two main modes of mercury occurrence. Simultaneously, with the organic form of presence, some parts of Hg may be incorporated in an inorganic matter as well.

5. Conclusions
The mercury in Bulgarian high-S coals are 3.4-times higher than average world coal value. In comparison with Bulgarian low-S coals and many other worldwide coals, it can be concluded that Bulgarian high-S coals are characterized by high-Hg concentration for all studied basins. It can be assumed that high-S content may be the main reason for the increased Hg concentrations in all investigated coal samples.

The typical high-sulphur Maritza-West lignite has the following modes of Hg occurrence. The first is as a part of pyrite and the second is as a sulphur-bearing organic compound. We suppose that the main part of Hg related to pyrite is a close connected especially with epigenetic pyrite infilling the coal veins and cleats and presents as a solid solution. It is possible some small Hg amount to be incorporate in clays or carbonate minerals. In the high-S Maritza-East lignite, the Hg is predominantly connected with organic matter and especially with sulphur-bearing organic compounds. The lignite from Stanyantsi basin has two main modes of mercury occurrence and simultaneously, with the organic form of presence some part of Hg may be incorporated in an inorganic matter.

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