Mercury is a poisonous element with high chemical and biochemical activity. It is a natural component of coal that is released during its combustion. This is one of the major sources of Hg emission into the atmosphere [1–3]. The main problem is the ability of its compounds for phase transformation, persistence in the atmosphere for long periods and mobility over long distances [4].

Most researchers focus on average mercury concentration in the delivered coal. The detailed information on the source of coal is either not provided or very general. This can lead to erroneous conclusions regarding the sources of atmospheric pollution and hinder the reduction of emissions. An example are the data on mercury content in bituminous coal imported to the Netherlands, including that from Poland, presented by R. Meij and B.H. te Winkel [5]. These data suggest incorrectly that Polish bituminous coal is characterized by a very high Hg content (0.33 mg/kg), two to six times higher than that delivered from other countries.

The previous research is mostly focused on mercury content in mined coal [4,6–18]. As a rule, the data on average concentrations in coal from the whole coal basin or from individual mines are given. Overly general information on the source of coal may lead to misconceptions about its real quality.

The detailed study on the mode of Hg occurrence in coal, factors influencing its distribution and origin was presented by Yudovich and Ketris [3,19], however the results of the detailed study of mercury content in particular coal seams are seldom reported. Mastalerz and Drobnia [20] have studied the coal seams in Indiana and demonstrated varied mercury content in the different sampling
sites and in the seam vertical section. The aim of the present paper is to point out, using an example of coal deposits in Poland, the importance of a more detailed such study of mercury content in coal, which varies not only among and within coal basins, but also within particular coal seams.

2. Mercury Content in the Polish Coals

The bituminous coal deposits in Poland occur in the three coal basins (Figure 1): Upper Silesian (USCB), Lublin (LCB), and Lower Silesian (LSCB). They differ greatly in mercury content (Figure 2).

![Coal basins in Poland](image)

**Figure 1.** Coal basins in Poland.

![Average mercury content in the hard coal from Poland deposit](image)

**Figure 2.** Average mercury content in the hard coal from Poland deposit (USCB—Upper Silesian Coal Basin, LCB—Lublin Coal Basin, LSCB—Lower Silesian Coal Basin). Source: USCB [4,6–9]; USCB* [21]; LCB [7]; LSCB [6].

The highest concentrations of this element can be found in the Lower Silesian Coal Basin (where the average Hg content in bituminous coal for the Nowa Ruda mine was 0.339 ppm [6]. A much lower average Hg content was recorded for both the LCB and USCB coal basin but in the LCB, it is higher than in the USCB (Figures 2 and 3).

The data on the mercury content in bituminous coal imported from Poland to the Netherlands presented by R. Meij and B.H. te Winkel [5] probably refer to high quality coal from the Lower Silesian Coal Basin.
rules of such variation, and the dependence of their stratigraphic position was not noticed, maybe due to the insufficient number of samples analyzed.

Wierzchowski et al. [22] have studied the mercury content in the coal seams grouped according to their stratigraphic position. They found that mercury content in ash-free coal is low. It shows a tendency to decrease with the seams age. The increased mercury content can only be found locally.

The insufficient data on the mercury content in individual coal seams make it difficult to predict the mercury content in the mined bulk coal. Without such knowledge, the management of Hg content in the exploited coal and the attempts to keep it within the acceptable limits, as well as the prediction of its emission to the atmosphere, as a result of coal combustion is impossible.

The problems of mercury content assessment in bituminous coal are presented by the pilot studies carried out, with the aim of determination of its content variation in relation to the location within the coal seam and barren partings.

3. Materials and Methods

The mercury content was studied in the three coal seams named: A, B, C, located within the Upper Baschkirian coal bearing series in one of coal mines (Figure 4). The mine owner did not allow the mine location to be disclosed, but this is irrelevant for the aim of the present study.

In each of the studied coal seams, the samples of 20–25 cm vertical length and about 2 kg weight were cut separately in coal and in barren partings. Their location was varied (Figure 5):

- Seam “A” in two locations separated by a 10-m distance, in the bottom part where clarain coal occurs and in barren partings of claystone, coal laminated;
- Seam “B” in two locations separated by a 22-m distance, in the bottom, middle and upper part formed by vitrain and clarain coal, respectively;
- Seam “C” in the central part built of vitrain coal and in the bottom part of vitrain coal with iron sulfide in the cleats.

The samples were crushed to a 2-mm grain size and afterwards 250 g was pulverized to analytical size. The chemical analyses were carried out at the Acme Analytical Laboratories, Canada by ICP Mass Spectroscopy according to the AQ251-EXT standard procedure with a 0.005 ppm Hg
detection limit. Ten samples of coal and two samples of gangue partings from the examined seams (A, B, and C) were analyzed. The results were presented with the use of classical statistical methods: evaluation of basic distribution measures and graphically by the box-and-whiskers plot. The varied models of distribution were tested and the best fitting empirical data were verified through the Kolmogorov–Smirnov and Shapiro–Wilk tests.

**Figure 4.** Localization of studied coal seams within coal B series (only the main coal seams are presented). The maximum thickness of the coal bearing series is 400 m.

**Figure 5.** A sampling scheme in seams A, B and C.

The enrichment factors of mercury content in relation to Clarke values were calculated according to this formula [23]:

$$EF^* = \frac{p_i}{o_i} [-]$$

$$EF^{**} = \frac{s_i}{o_i} [-]$$
where: $p_i$—the average content of a given element in bituminous coal samples from studied coal seams, $s_i$—the average content of mercury in bituminous coal worldwide, according to Ketris, Yudovich [24], $o_i$—the Clarke value for sedimentary rocks.

Explanations: The mercury enrichment factor in the studied area (EF*) and worldwide bituminous coals (EF**).

4. Results

The Hg content in the analyzed coal samples varies considerably (Figure 6, Table 1). The average in the studied area is 0.140 ppm and is slightly higher than average reported by Bojakowska and Sokołowska [7].

![Figure 6](image-url) The content of Hg in coal seams A, B, and C (red dashed line—average content of Hg in the studied area).

| Coal Seam and Sample Location | Hg (ppm) | S (ppm) | As (ppm) |
|-------------------------------|----------|---------|----------|
| A Bottom Part | 0.074 | 3000 | 0.7 |
| A Bottom Part | 0.02 | 3400 | 0.9 |
| B Upper Part | 0.043 | 5900 | 4.2 |
| B Upper Part | 0.143 | 8300 | 2.6 |
| B Bottom Part | 0.259 | 18,400 | 46.1 |
| B Upper Part | 0.051 | 5100 | 4.7 |
| B Central Part | 0.075 | 5900 | 1.2 |
| B Bottom Part | 0.272 | 15,000 | 19.4 |
| C Central Part | 0.445 | 20,100 | 37.7 |
| C Bottom Part | 0.022 | 3500 | 0.7 |

| Element | Number | Average | Median | Standard Deviation | Variation Coefficient | Min. | Max. |
|---------|--------|---------|--------|-------------------|-----------------------|------|------|
| Hg (ppm) | 10 | 0.140 | 0.075 | 0.141 | 100.4% | 0.020 | 0.445 |
| S (ppm) | 10 | 0.886 | 0.590 | 0.650 | 73.3% | 0.300 | 2.010 |
| As (ppm) | 10 | 11.82 | 3.40 | 16.912 | 142.1% | 0.70 | 46.10 |

The calculated basic statistical parameters of mercury content are presented in Table 1. The probability distribution of Hg content is characterized by a moderate asymmetry. On the box and whiskers plot, no outliers and anomalous high values for the Hg have been registered (Figure 7). The Birnbaum–Saunders distribution is the best in describing the observed mercury content empirical data (Figure 8).
The calculated basic statistical parameters of mercury content are presented in Table 1. The probability distribution of Hg content is characterized by a moderate asymmetry. On the box and whiskers plot, no outliers and anomalous high values for the Hg have been registered (Figure 7). The Birnbaum–Saunders distribution is the best in describing the observed mercury content empirical data (Figure 8).

The analytical data on Hg content in samples of barren partings in the bituminous coal seam have shown their great difference, while the sampling sites are located at a 10-m distance only (Table 2). In sample 2, this is comparable with that observed in the coal, while in sample 1 it is very high (fourteen times higher). Such data show that the elevated concentrations of mercury occur in small zones of limited extent.

Table 2. The mercury content in the barren parting in seam A.

| Sample     | Sample 1 | Sample 2 |
|------------|----------|----------|
| Hg (ppm)   | 0.649    | 0.045    |
| S (%)      | 2.20     | 0.12     |
| As (ppm)   | 10.50    | 1.20     |

In the studied coal there is clear relationship between mercury and sulfur, as well as arsenic content (Figure 9). It suggests that mercury bearing might be iron sulfides. However, the presence of visible iron sulfide is not followed by outstanding Hg content.
5. Discussion

The existing up-to-date data on mercury content in coal in Poland demonstrate that it varies depending on the coal basin. The average Hg content in the USCB is lower than in the LCB and LSCB. The increased mercury content in the LSCB may be related to the hydrothermal mineralization accompanying younger volcanic activity and intrusions of igneous rocks [25,26]. Elevated mercury concentration in the LCB is probably related to the location in the zone of deep disturbances, commonly referred to as the Karpinsky lineament. The Donets Coal Basin in Ukraine with Nikitowka mercury ore deposit [27] is located in this zone. Elevated Hg content is reported in the same zone within the territory of Poland in the lignite Belchatów deposit [28] and in natural gases in the north-west Polish lowlands [29] (Figure 10) [30].

The average Hg content in bituminous coals from the studied area is higher than other coals worldwide and other sedimentary rocks [24]. This is also well presented by the appropriate enrichment factors (Figure 11).

The present study demonstrates great variation of mercury content within individual seams. They also suggest the association of mercury with iron sulfides (arsenic-bearing).
Figure 10. Karpinsky lineament (hatched line) according to Ozerova 29 traced by the location of the mercury-bearing gas and oil–gas deposits (A), approximate trend of the elevated mercury (Hg) concentrations zone in Poland (B).

Figure 11. The comparison of the average concentration of mercury in bituminous coal from the studied area* and the Clarke values [24] (A), the mercury enrichment factor in the studied area (EF*) and worldwide bituminous coals (EF**) (B).

The association of mercury content in coal with the presence of iron sulfides, is common [21,31–33]. Such a relationship was also suggested by Dziok et al. [34,35] based on analytical data of coking coal and coal ash. The elevated mercury content associated with pyrite, often arsenic-bearing, allows the supposition of their epigenetic formation by migrating fluids, and the distance to their source [21,36]. The barren partings look favorable for mercury concentration.

Very high variability coefficient of mercury content in the studied coal, close to 100% advocates for its local enrichment sites. The nature of elevated mercury content is enigmatic. Some relation to tectonic phenomena may be supposed. The fault zones may be the site of its concentration, especially
if some hydrothermal processes were possible [3,20]. The elevated Hg content close to fault zones, as well as the other metallic elements were suggested in the LCB [37]; there, the deep sited sources of mercury and migration of hydrothermal metamorphic fluids may be admitted, as the basin is located in the zone of supposed Karpinski lineament.

6. Conclusions

Numerous studies were devoted to studying the mercury content and the mode of occurrence in coal. Much effort is spent for reducing its emission into the atmosphere as a result of coal combustion. Varied modes of its removal are proposed [38]. In the present study, we try to demonstrate the variation of mercury content among and within the particular coal seams. The detailed “in situ” coal sampling might allow the detection of mercury-enriched zones. It is supposed that such zones may be tectonically controlled.

The knowledge of mercury content distribution within coal seams would allow for better prediction and management of mined coal quality. The possibility of avoiding mercury-enriched coal extraction should be considered in the discussion on the mode of reduction the environmental impact of mercury emission.

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