



Review article

Mercury in coal: a review Part 1. Geochemistry

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Received 19 March 2004; received in revised form 26 September 2004; accepted 30 November 2004
Available online 27 January 2005

Abstract

This is the first of two papers that review approximately 200 publications on mercury (Hg) in coal; topics reviewed in this paper include: (a) analytical and historical introduction; (b) some peculiarities of Hg environmental geochemistry; (c) estimation of the Hg coal Clarke value; (d) occurrence of high-Hg coals; (e) mode of Hg occurrence in coal; (f) factors influencing the distribution of Hg in coal; and (g) origins of Hg in coal. Aspects of the environmental impact of Hg due to coal combustion and coking are noted throughout the review, and are more fully examined in second and final paper of this review.

The Clarke value for Hg in coal (world-wide average Hg content) is 0.10 (± 0.01) ppm Hg, regardless of coal rank. However, if the Hg content is expressed on an ash basis, bituminous rank coals average 0.87 (± 0.08) ppm Hg, and lower rank coals average 0.62 (± 0.06) ppm. In general, Hg is a very “coalophile” element; that is, it has a strong affinity for organic and inorganic coal matter, but is obligatory authigenic.

There are some coals that are enriched in Hg by 1 to 2 orders of magnitude above the Clarke value. Such coals are located in the Donbas (Ukraine), Appalachian basin and Texas (USA), Russian Far East, and Southern China. Mercury in these coals is usually accompanied by other chalcophile trace elements.

In low-sulfur coals, which are generally poor in Hg, only two Hg sites dominate: Hg_{org} and Hg_{sulfide} (commonly pyritic mercury, Hg_{pyr}). High-sulfur coals usually contain higher amounts of Hg, which is typically in the Hg_{pyr} form. In the unique Hg-enriched Donbas coals, both HgS and metallic mercury (Hg⁰) also occur.

Because of the extremely strong affinity of Hg²⁺ for humic matter, it is theoretically possible for syngenetic (or early epigenetic) Hg to accumulate in peats and lignites. Indeed, the amount of Hg in some tropic and moderate zone peats is greater than or equal to the Hg content of typical coal. Until the recent discovery of syngenetic volcanic Hg accumulations in Canadian coals, such Hg accumulations in coal were unknown.

The most important type of Hg enrichment in coals is an epigenetic, low-temperature hydrothermal process; the Nikitovka (Ukraine), Warrior (USA), and Guizhou (China) basins are good examples. In the two latter coal basins, the paragenetic association Hg–As–Au–Tl is similar to Carlin-type Au deposits.

The most notably Hg-rich basin is the Donbas–Donetsk coal basin situated in the Ukraine and Russia. Numerous coalfields in the Donbas are enriched in Hg by one order of magnitude above the coal Clarke level. The Hg in the Donbas was due to

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hydrothermal mineralization passing through sheared zones. The extraction and use of Hg-bearing Donbas coals have created very difficult environmental problems for the Ukrainian people.

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Keywords: Mercury; Coal; Geochemistry; Coal combustion; Environmental impacts

Contents

| | | |
|--------|---|-----|
| 1. | Introduction | 109 |
| 1.1. | Some analytical comments | 109 |
| 2. | Peculiarities of Hg geochemistry in hypergene zone | 110 |
| 2.1. | Mercury in air | 110 |
| 2.2. | Mercury in natural waters | 110 |
| 2.2.1. | Methylation of mercury | 110 |
| 2.3. | Mercury in sedimentary rocks | 111 |
| 2.4. | Mercury in humic organics | 111 |
| 2.5. | Mercury in vegetation and peats | 112 |
| 2.5.1. | Peat bogs as a natural record of atmospheric mercury emission | 113 |
| 3. | An estimation of coal Clarke value of Hg | 113 |
| 3.1. | New Hg coal Clarke estimations | 114 |
| 3.2. | Some average estimations | 115 |
| 3.3. | Expressing Hg content on an energy basis | 115 |
| 4. | “Coal affinity index” (coalphile coefficient) of Hg | 115 |
| 5. | Some Hg-bearing coals | 116 |
| 5.1. | Russia: bituminous and brown coals | 116 |
| 5.2. | Ukraine: bituminous coals and lignites. | 116 |
| 5.2.1. | The Donbas mercury phenomenon | 116 |
| 5.2.2. | Novo-Dmitrov deposit | 117 |
| 5.3. | Former East Germany brown coals | 117 |
| 5.4. | Greece: Miocene lignites | 117 |
| 5.5. | China: the Guizhou phenomenon | 117 |
| 5.6. | USA: various coals. | 118 |
| 6. | Modes of occurrence | 118 |
| 6.1. | Sulfide form | 118 |
| 6.1.1. | Mercury in pyrite | 119 |
| 6.1.2. | Other sulfides and selenides | 121 |
| 6.2. | Organic form | 121 |
| 6.3. | Elemental form | 122 |
| 6.4. | Distribution of Hg forms (based on complex procedures) | 122 |
| 7. | Factors controlling Hg distribution | 123 |
| 7.1. | Influence of ash yield | 124 |
| 7.1.1. | Russia: Pennsylvanian age bituminous coals and anthracites, East Donbas | 124 |
| 7.1.2. | Kazakhstan: Jurassic brown coals | 124 |
| 7.1.3. | Belgium: Pennsylvanian bituminous coals and anthracites | 124 |
| 7.1.4. | Greece: Miocene lignites | 124 |
| 7.1.5. | USA: Eocene lignites | 125 |
| 7.1.6. | Canada: Cretaceous subbituminous coals | 125 |
| 7.2. | Influence of sulfur content. | 125 |
| 7.3. | Position of sample in the coal bed column | 126 |
| 8. | General topics | 126 |
| 8.1. | Syngenetic processes | 126 |
| 8.1.1. | Volcanic enrichment | 127 |

| | |
|--|-----|
| 8.1.2. Hg-enrichment of high-sulfur coal benches | 127 |
| 8.2. Thermal epigenetic processes | 127 |
| 9. Conclusions | 128 |
| Acknowledgements | 129 |
| References. | 129 |

1. Introduction

Mercury is, as a general rule, among the least abundant elements in coal. Nevertheless, it has been, in recent years, one of the most studied elements in coal due to its extremely toxic effects and its tendency to bioaccumulate through the food chain (USEPA, 2000, 2003). Coal combustion, because of the huge amount of coal consumed, accounts for a significant portion of the anthropogenic releases of Hg into the environment. Over 40 tons of mercury from coal combustion is emitted to the atmosphere per year in the United States and even greater amounts are emitted in China. As a consequence, the U.S. Environmental Protection Agency (USEPA) has proposed rules to reduce Hg emissions from coal-fired power plants. The rules are based on existing U.S. law (USEPA, 1990), reports on mercury in the environment (USEPA, 1996, 1997, 1995), and data collected from U.S. power plants during 1999 (USEPA, 2003). Although the proposed rules are not as strict as anticipated when the intent to regulate mercury emissions was first announced, the final rules will still require significant reductions of Hg emissions. Understanding the nature of Hg in coals used for power generation, and the partitioning of Hg in combustion systems, is a fundamental part of an emission-control strategy. In this paper, we outline some of the basic studies of Hg in coal, with a view towards new developments in Hg studies.

Given the comparatively low abundance of mercury in coal, there are few early quantitative measurements of mercury in coal and coal products. Although Stutzer (1914) reports information about a cinnabar discovery in German coals, more than a decade passed until Kirkby (1927) reported about 0.15 ppm Hg in coal-derived tar. Later, Stock and Cucuel (1934) found that coal soot collected from flues contained a remarkable 28 ppm Hg; they also determined the Hg content of coals from Great Britain (0.012 ppm), as well as the Saar (0.008 ppm) and Ruhr (0.010 ppm) basins in Germany. They found up to 0.022 ppm Hg in some coal

samples. Saukov (1946) found 41 ppm Hg in soot from the flue of boiler-house consuming Donets basin (Donbas) coals. This high figure was not noted and the exceptionally high Hg content of Donbas coal did not attract attention for another 20 years.

Our knowledge about Hg in coal is still rather poor, and the most accurate assay values have been obtained in recent decades. Besides the relatively low abundance of mercury in coal, the volatility of mercury has also contributed to the difficulty obtaining accurate mercury assays. Analysis of coal ash for mercury is not informative because up to 90% of Hg in coal is not retained in the ash. Moreover, Saukov (1946), the founder of Russian Hg geochemistry, also noted that atomic-emission spectrographic analysis of coal specimens prepared without ashing can also result in a large depletion in Hg.

1.1. Some analytical comments

The conventional methods of Hg analyses of solids (atomic absorption analysis of bomb combustion residue by ASTM D-3684), and flue gas (Ontario-Hydro, mercury speciation method by EPA 28, EPA 101 A), are imprecise (ASTM D-3684), time-consuming, or expensive. For example, a single Hg assay of flue gas costs as much as \$ 30,000 (US), is difficult to repeat, and can also be dangerous where samples are collected at height.

Better methods to determine mercury in flue gas are needed. **The best available method for Hg analysis of solids (coal, ash and sulfate wastes) is EPA-7473 using an instrument such as the DMA-80 (a direct mercury analyser, Milestone).** In this instrument, a 0.75 g specimen is dried in a ceramic boat at 120 °C and decomposed in a tube furnace. Vapor Hg is carried by a continuous gas flow into a thermostated central part of the furnace, where it is completely converted to the Hg⁰ form. The Hg is quantitatively amalgamated on gold wire and determined by atomic absorption. The method is cost-effective, sensitive,

and accurate; a single determination can be accomplished in about 5 min (Boylan et al., 2003).

2. Peculiarities of Hg geochemistry in hypergene zone

Hypergene Hg geochemistry, which was rarely studied earlier, attracted a great deal of attention in the mid 20th century because of ecological problems, especially those related to highly soluble monomethylmercury $[\text{Hg}(\text{CH}_3)]^+$ compounds.

2.1. Mercury in air

The Hg content of air above Europe and North America is approximately 3 ng/m^3 , and nearly 2 ng/m^3 above the Atlantic Ocean. In the Southern hemisphere, the atmospheric Hg content is distinctly lower (1.3 ng/m^3), due to less anthropogenic Hg. About 90% of the Hg vapor in air is present as Hg° (elemental Hg) and the rest is likely Hg^{2+} (probably as HgCl_2 and methylmercury). The methylmercury background in the atmosphere varies widely from 0.005 to 1.3 ng/m^3 (Carpi, 1997).

The amount of particulate Hg (Hg_p) in the atmosphere is several orders of magnitude less than vaporized Hg; whereas the total Hg content of air is expressed as ng/m^3 , particulate Hg in air is expressed as pg/m^3 ($1 \text{ pg}=1000 \text{ ng}$). Keeler et al. (1995) showed that particulate Hg contents in rural areas of Vermont and the Michigan (United States) were 11.2 and 18.6 pg/m^3 , respectively, whereas particulate mercury in an urban area (downtown Detroit, Michigan) averaged 94 pg/m^3 (range of 22 to 225 pg/m^3). The fine dust fraction, with particle diameters less $2 \mu\text{m}$, contains 60% to 100% of the total particulate mercury (Keeler et al., 1995). The relative contribution of particulate Hg to the total atmospheric Hg loading varies from place to place. Xiao et al. (1991, cited after Carpi, 1997) observed that particulate Hg accounted for 15% ($\pm 3.3\%$) of total atmospheric mercury in an industrial area, but only 5% ($\pm 1\%$) of total atmospheric mercury in nearby rural and residential areas.

In the aerosols collected in Geneva, no positive correlation was found between $^{206}\text{Pb}/^{204}\text{Pb}$ ratio and Hg content although such a correlation was expected (by analogy with Zn, Pb, and Cu), because Pb and Hg

have a common local sources (petrol, wastes incineration and coal combustion; the latter only in winter). The unexpected conclusion was made: gaseous Hg° may transform to particulates via its oxidation by the “traffic-related” atmospheric gases, such as O_3 , NO_3 and, probably, also RO_2 , OH, H_2O_2 , HO_2 (Chiardia and Cupelin, 2000).

2.2. Mercury in natural waters

In most natural waters, Hg contents are very low; for example, in bog waters (moderate humic zone, average mineralization 89.5 mg/l and pH 5.7), the Hg Clarke¹ value is 58 ng/l (Shvatrsev, 1998). The mercury content of rainwater typically varies from 2 to 20 ng/l but values up to 90 ng/l have been observed. The methylmercury content of rainwater is several orders of magnitude less, and varies from 0.05 to 0.6 ng/l (Carpi, 1997).

Extremely high Hg concentrations (up to $110,000 \text{ ng/kg}$) were observed in a fumarole condensate from the Kamchatka Peninsula of Russia with corresponding high Hg contents (up to $18,000 \text{ ng/m}^3$) in the free carbonaceous gases. In Guatemala and Japan, the Hg contents of condensates are even greater, up to $400,000 \text{ ng/kg}$. In the platform brines, Hg varies from $15,000$ to $27,000 \text{ ng/kg}$. It is assumed that Hg is transported in acid thermal systems as $\text{Hg}(\text{HS})_2$, and as $\text{Hg}(\text{HS})_3^-$ in alkali thermal systems (Baskov and Surikov, 1989).

2.2.1. Methylation of mercury

Hg^{2+} may be methylated to $\text{Hg}(\text{CH}_3)^+$ by bacteria and to a lesser extent by abiotic chemical reactions (Stolzenburg et al., 1986, p. 47; Kuzubova et al., 2000, p. 17).

Upon entering surface water, a fraction of the Hg can firmly bind with organic matter to form soluble organic complexes. In weakly mineralized waters, the primary organic Hg compound seems to be the highly-mobile methylmercury ion HgCH_3^+ (USGS, 1970), and also hydroxymethylmercury, HgCH_3OH . For methylmercury formation, it is sufficient for dissolved Hg^{2+} and $(\text{CH}_3)^-$ to be present. The latter can be of various origins, but a bacterial origin is especially likely:

¹ A Clarke value — a widely used term in Russian literature refers to the “worldwide chemical element average content” — in the earth crust, in sedimentary rocks etc.

“... a methyl mercury yield is positively correlated with general microbiological activity of an environment. A sterilization of samples lowers the methylization speed on the orders of magnitude... Besides ... the dimethyl mercury formation speed some thousand times less than one for methyl mercury” (Kuzubova et al., 2000, p. 17).

In natural waters, the main methyl group donors are fulvic acid (FA) and humic acid (HA), with optimization of methylation in the 6–8 pH range, where the ionization of FA is greatly increased. In an anaerobic hydrosulfide environment, insoluble HgS formation strongly competes with methylation. Mercury methyl-derivatives are very different. Being a main toxic agent, $\text{Hg}(\text{CH}_3)^+$ penetrates cell membranes and blocks enzymes (Kuzubova et al., 2000, p. 18). P. Greeson noted that “Dimethyl mercury, although stable in alkaline solutions, dissociates to ionic methyl mercury at low pH values” (Greeson, 1970, p. 32–34).

2.3. Mercury in sedimentary rocks

According to recent estimations, the Hg Clarke value for sedimentary rocks is 0.03–0.06 ppm; substantially more than in igneous rocks². Highly dispersive materials, mainly clays, are chiefly responsible for strong Hg sorption in sediments and sedimentary rocks (Saukov, 1946). Other strong Hg scavengers include Fe-hydroxides and humic organic matter. Sorption of Hg by Fe-hydroxides is efficient in the 7–8 pH range, where most Hg exists as $\text{Hg}(\text{OH})_2$ (Andersson, 1970). The Hg Clarke value for black shales is as much as 0.23 ± 0.03 ppm (Yudovich and Ketris, 1988, p. 245; 1997, p. 46).

2.4. Mercury in humic organics

In the “soil humus–water Hg-solution” system, the Hg distribution coefficient (K_d) approaches 1618, corresponding to a Hg concentration of 1000 ppm at pH 3. At a Hg^{2+} /humus ratio of 1:200, the optimum

Hg sorption was observed at pH 5 (Andersson, 1970). An investigation of humic matter isolated from English surface waters using a gel-filtration technique showed that more than 90% of the Hg was firmly bound to humic matter. The stability constant ($\log K_0$) for Hg with a variety of isolated humic compounds at pH 8, was many orders of magnitude more than for other two-valence ions, following the general order: $\log K_0$ for $\text{Hg} > \text{Cu} > \text{Ni} \sim \text{Zn} > \text{Co} > \text{Mn} \sim \text{Cd} > \text{Ca} > \text{Mg}$ (Mantoura et al., 1978).

In experiments with the Beipazary lignite from Turkey, 30 ppm mercury was efficiently sorbed from a nitric acid solution (pH 4) with a solid/liquid ratio of 1:100. The sorption equilibrium was reached after 30 min and was well approximated with a Langmuire equation. After sorption, the Hg concentration in lignite was as much as 1550 ppm (1.55 mg Hg/g lignite). Although captured Hg could be re-extracted with 25 mmol/l EDTA, the lignite retained its sorption capacity during 10 sorption/desorption cycles (Karabulut et al., 2001).

Overall, the Hg^{2+} ion stands out among other two-valence ions, having the strongest bonding with humic organics. Even at Hg^{2+} concentrations of 0.5×10^{-5} M in a very acid medium, humic acid gels extracted 85% of the mercury from solution, whereas less than 10% extraction was observed from solutions containing Cu^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , and Mn^{2+} . Complete (100%) extraction of Hg^{2+} by humic gels is observed in slightly more alkaline solutions (pH 4.7), even where the Hg concentration is an order of magnitude higher (0.5×10^{-4} M). Further evidence of the exceptional affinity of Hg for humic organics is demonstrated by its preferential sorption on a humic gel from a mixed solution containing nine other metal ions; the preferential sorption of Hg^{2+} by the gel is demonstrated by increasing gel Hg content and decreasing gel contents of the other nine metals (Kerndorff and Schnitzer, 1980).

As Moscow geochemists have shown, with respect to Hg, the *geochemical functions* of fulvic acid (FA) and humic acid (HA) are opposite: FA has a *transporting* function, whereas HA has a *barrier* (trapping) function (for details see Yudovich and Ketris, 1994). With the interaction of 15–30 ml of dark Moscow river water containing FA (19–310 mg/ml) with Hg° (40.6 mg) and HgS (20 mg), high-molecular weights complexes were formed, with a ratio of $\text{Hg}/\text{FA}=1:1$

² Mason and Moore (1982) list figures for shales, sandstones, and carbonates, respectively listed as 0.4, 0.3, and 0.2 ppm. However, these figures are undoubtedly greatly overestimated. All the averages for sedimentary rocks provided in Russian literature show that mean Hg content for the *non-ore-bearing* (!) areas are within a range 0.03–0.06 ppm.

and a stability constant of 3.6×10^7 . “A firm fulvate complexes formation results in a sharp increase in mercury solubility... and, thus, to an increase of the mercury migration ability in the environment” (Varshal et al., 1999, p. 274). At the same time, the interaction of 40 ml $\text{Hg}(\text{NO}_3)_2$ (4.456 mg/ml) with peat HA (100 mg) at a pH 3 and a duration of 3 h to 20 days, demonstrated a remarkably high Hg sorption on HA (350 to 370 mg Hg/g HA, corresponding to 35% to 37% Hg sorption). Although such low pH values are not very realistic in natural peat bogs, these data strikingly illustrate the exceptional efficiency of HA as a geochemical scavenger (barrier) for Hg^{2+} .

Unfortunately, Hg immobilization by means of Hg^{2+} complexing with HA cannot fully save the biosphere from Hg poisoning. This is because HA can reduce sorbed Hg^{2+} to elemental Hg^0 , which is subsequently desorbed from the humic matter by volatilization. For example, it was shown experimentally that soil HA slowly reduces Hg^{2+} captured from solutions containing HgCl_2 ; nearly 33% of the captured Hg was released as elemental Hg^0 over 290 h at a pH 6.5. An electron-spin resonance study of the interaction of Hg^{2+} with HA showed that free radicals from the HA served as electron donors (Alberts et al., 1974). Soil FA with standard electric potential 0.5 V is an even more active mercury reductant. At a pH 2, in a solution containing FA, 100% of the Hg^{2+} was converted to Hg^0 , and at a pH of 5.5 to 8, nearly 30% of the Hg^{2+} was converted to Hg^0 (Skogerboe and Wilson, 1981).

2.5. Mercury in vegetation and peats

The mercury content of plants, expressed as a fraction of plant ash, usually varies between 0.10 and 1.0 ppm with anomalies up to 1200 ppm. This usual

range is slightly greater than the mercury content of most sedimentary rocks. Plants do not concentrate mercury relative to surrounding soils, except in areas with Hg-rich soils, where ordinary birch and some other plants can be enriched in mercury (Kowalewski, 1974, p. 67, Horvat et al., 2003).

The average Hg content of dry oceanic plankton is 0.14 ppm, which indicates a high biological accumulation coefficient of 4.5×10^3 (Yudovich and Ketris, 1994, p. 11). The Hg Clarke value for black shales is 0.23–0.32 ppm (Yudovich and Ketris, 1994, p. 52), which is more than one order of magnitude greater than for ordinary sedimentary rocks. Soils have a Clarke value of 0.10 ppm Hg (Swaine, 1990, p. 185), although a correct estimate is difficult due to industrial soil contamination.

Table 1 shows the mean Hg content of plant and peat samples collected from The Great Vassyugan Bog in western Siberia (the largest peat accumulation on earth). The mean values were calculated for 53 plant samples and 306 peat samples (excluding peats from drained bogs), which were assayed by instrumental neutron activation analysis for Hg content. The variation of plant Hg content does not show any strong relation with plant taxonomy or peat bog type. Notably, the peat contains an order of magnitude more Hg than the plants. It is evident that a large part of the Hg in the peat originated from surface waters rather than from Hg accumulated by the peat-forming plants.

The ability of peat (as well as soil humus) to strongly bond with Hg is well known. For example, in the warm temperate Okefenokee peat bog (southeast Georgia, USA) there are high Hg contents: 0.19 ppm in “marsh peat” and 0.60 ppm in “bog peat” (Casagrande and Erchull, 1976). Similar enrichment of Hg is shown for peat from The Great Vassyugan

Table 1
Mean Hg content in plants and peats of The Great Vassyugan Bog (compiled from data by Bernatonis et al., 2002, p. 209–212)

| Material | Peat bog type | | | | | | Average content ^a | |
|----------|-----------------|----------------|---------------------|----------------|-----------------|----------------|------------------------------|----------------|
| | Raised peat bog | | Transition peat bog | | Valley peat bog | | Ash (%), dry) | Hg (ppm), dry) |
| | Ash (%), dry) | Hg (ppm), dry) | Ash (%), dry) | Hg (ppm), dry) | Ash (%), dry) | Hg (ppm), dry) | | |
| Trees | 2.03 | 0.19 | 2.02 | 0.43 | 2.51 | 0.11 | 2.19 | 0.24 |
| Bushes | 2.51 | 0.12 | 2.15 | 0.45 | 6.17 | 0.11 | 3.61 | 0.23 |
| Herbage | 7.40 | 0.61 | 6.18 | 0.09 | 12.27 | 0.15 | 8.62 | 0.28 |
| Mosses | 3.17 | 0.11 | 3.45 | 0.16 | 9.78 | 0.33 | 5.44 | 0.20 |
| Peats | 2.95 | 2.15 | 6.20 | 2.79 | 8.30 | 2.58 | 5.82 | 2.51 |

^a Our calculation.

Bog (Table 1; Bernatonis et al., 2002). Such peat Hg contents are equivalent to, or slightly greater than, those typically observed in coal.

2.5.1. Peat bogs as a natural record of atmospheric mercury emission

At the beginning of 1980, the Hg content in Dutch raised bogs was in the range 0.067 to 0.523 mg/kg, but averaged between 0.200 and 0.300 mg/kg. ^{210}Pb dating of the peats showed that, during last 100 to 200 years, the rate of Hg deposition into the peat increased from 10 to 20 mg/m² per year, to between 50 and 100 mg/m² per year (Madsen, 1981). While the explanations of such an increase are ambivalent, Hg originating from human activity (such as agriculture, fuel combustion, ceramic industry) as well as from volcanism and climatic change (including those related to atmospheric precipitates and pressure changes) are certainly possible. However, peak Hg accumulation rates are correlated with historic eruptions of Icelandic volcanoes (during 1783 to 1784, 1875, and 1947).

A study of a 6.5-m-thick column from the highland domed peat bog in the Swiss Jura (Roos-Barraclough et al., 2002) allowed dating the rate of Hg deposition during the last 14,500 years (after the last glaciation). The Hg deposition rate varied from 0.3 to 8 µg/m² during Holocene, with peak values correlated to intervals of dry, cold climate, and to volcanic events. Starting with the industrial historical period (about 1860), Hg deposition increased to 15 times pre-industrial levels; this increase has been attributed to coal combustion. Although the mercury content of the peat positively correlated with bromine content, some samples had higher mercury contents than indicated by the Hg/Br correlation. These exceptions correspond to periods of volcanic activity in prehistoric times suggesting that excess Hg identified using a regression equation between Br and the log of Hg in coal is an indicator of volcanic events. The remarkable correlation observed between Hg and Br in prehistoric peat, where excess Hg indicates contributions from volcanic emissions, is also significant to historic (modern) peat accumulations. Roos-Barraclough et al. (2002) show that the peak anthropogenic Hg deposition rates (107.6 µg/m² during 1911, 78.8 µg/m² during 1973, and 63.12 µg/m² during 1988) are one to two orders of magnitude higher than prehistoric

atmospheric Hg deposition rates. They also suggest that anthropogenic emissions of bromine-containing compounds (and possibly other halogens) may promote the oxidation of atmospheric Hg⁰, and subsequently increase the deposition of Hg²⁺.

Column samples collected from ombrotrophic (rain-water-fed) peatbogs are generally thought to be accurate records of atmospheric mercury deposition whereas samples from minerotrophic (groundwater-fed) peatbogs are not. This is because minerotrophic bogs may also contain mercury from fluvial detrital minerals whereas ombrotrophic bogs only contain mercury from atmospheric sources. However, this distinction is not necessarily true. For example, the vertical Hg distribution for accurately-dated, minerotrophic peatbogs in South Greenland, is surprisingly similar to the Hg distribution in an ombrotrophic Danish peatbog. Peak mercury deposition rates during 1953 to 1954 are observed in both locations (164 µg/m² Hg in Greenland and 184 µg/m² Hg in Denmark) and are accompanied by Pb and As peaks, which indicates that coal combustion was the main source of all three toxic elements (Shotyk et al., 2003). Moreover, Biester et al. (2003) showed that historic Hg deposition rates determined from ombrotrophic bogs may vary according to the rate of organic matter decomposition at different sites. Their work further suggests that modern mercury deposition rates are potentially overestimated where peat accumulation rates are not corrected for peat mass loss due to decomposition.

The data presented show that when Hg-bearing waters exist (for example as hydrothermal waters), or in the vicinity of volcanoes, the coal-forming peat bogs might be syngenetically enriched in Hg. In such instances, the Hg can be present as elemental Hg, in addition to the more ubiquitous Hg–humate complexes. If the elemental Hg does not fully evaporate during coal metamorphism, it may be retained in bituminous coals.

3. An estimation of coal Clarke value of Hg

In 1985, coal Clarke values for Hg were calculated by Yudovich et al. (1985, p. 211) as 0.1 to 0.2 ppm for lignite and subbituminous coal, and 0.30 ± 0.16 ppm for bituminous coals. These values correspond to 1 to 3 ppm Hg expressed on an ash basis. However, con-

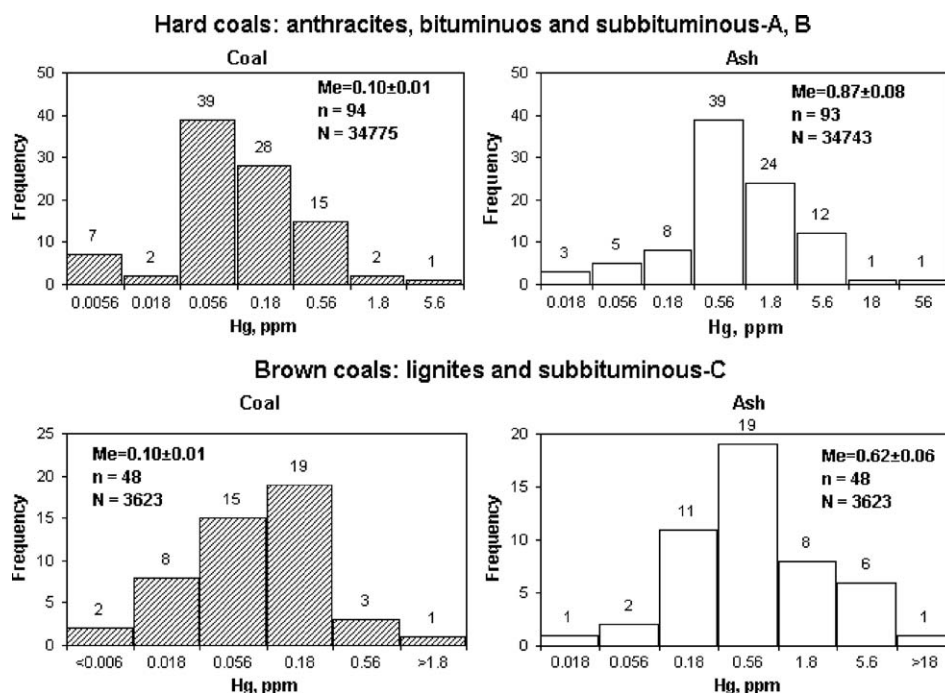


Fig. 1. The frequency distribution of Hg in world coals, where N is the number of analyses, n is the number of random samples, Me is the median Hg content, for hard coals (including subbituminous A and B coal, bituminous coal and anthracite) and brown coals (including lignite and subbituminous C coal). Data are presented on both a dry, whole-coal basis (Coal) and on an ash basis (Ash).

confidence in these values is low because of the very small number of samples used for the statistical calculation.³

3.1. New Hg coal Clarke estimations

Recently, Marina Ketris calculated a new Clarke value for Hg in coal. The detailed calculation procedure was published elsewhere (Ketris and Yudovich, 2002), but the main idea is emphasized here. The concept involves *stepped averaging*, from minor to large: one coal bed \Rightarrow several coal beds \Rightarrow coalfield (deposit) \Rightarrow coal area (several coal fields) \Rightarrow coal basin or province \Rightarrow totality of the coal basins. In other words, the Clarke value totality consisted of several dozen random samples representing many thousands of analyses. As a rule, the

median is used for the Clarke estimation because it is a very stable statistical parameter that is little influenced by large sample dispersions. This recent estimate of the Hg Clarke values for coals is based on approximately 190 samples that were randomly selected to represent nearly 70,000 analyses (Fig. 1).

The new Hg Clarke value for hard coal (0.10 ± 0.01 ppm) is sharply lower than the 1985 Clarke value (0.30 ± 0.16 ppm) calculated by Yudovich et al. (1985). The new value for brown coal (0.10 ± 0.01 ppm) is slightly lower than the 1985 Clarke value (0.1 to 0.2 ppm). These changes resulted from a much greater number of new analyses. Therefore, within the precision of estimate, the Clarke values of the hard and brown coals are equal, but if expressed on an ash basis, hard coal contains more Hg than brown coal (0.87 ± 0.08 ppm vs. 0.62 ± 0.06 ppm).

As Shpirt supposed, as the number of Hg content studies increases, the average Hg content also increases(!). In particular, he noted that an earlier background Hg content of USSR coals (0.05 ppm) was seemingly underestimated (Shpirt, 2002, p. 73).

³ Unfortunately, in the book by Yudovich et al. (1985) some disappointing discrepancies exist. On page 166, the Hg coal Clarke values were reported to be 0.04 ± 0.01 ppm and 0.20 ± 0.04 ppm for lignite and bituminous coals. However, in the conclusion (page 211), the figures were increased, and are as mentioned above.

3.2. Some average estimations

Most average Hg contents for large regions are generally near the Clarke level. For example, Swaine, (1990, p. 128) examined many data sets and observed that most average Hg values are between 0.02 and 1.0 ppm. Australian coals varied between 0.01 and 0.25 ppm with an average near 0.10 ppm. For the former USSR coals, the background Hg content was 0.05 ppm, with locally enriched coals between 5 and 100 ppm and a maximum value of 1000 ppm (Kler, 1988, p. 68). According to a modern estimate for world lignite (based on 2066 analyses) the average Hg content is 0.08 ppm (Bouška and Pešek, 1999).

The average Hg content of 109 bituminous feed coals imported from 13 countries and burned at Dutch Electric Power Plants (EPPs), varied from 0.04 ppm (Indonesian coals) up to 0.35 ppm (Polish coals), with a weighted average of 0.11 ± 0.2 ppm and variation coefficient of 174% (Meij et al., 2002). Sabbioni et al. (1983) examined 29 hard coals originating from Belgium, Britain, Czechoslovakia, France, Germany, and South Africa that were burned at EPPs in the European community countries. The Hg content of the coals varied between 0.025 ppm and 1.0 ppm Hg, with the highest values observed for German coals (average of six German coals = 0.42 ppm Hg). Feed coals originating from 13 British coalfields varied between 0.02 and 1.0 ppm Hg and averaged 0.28 ppm Hg, and Goetz et al. (1981) observed that four German feed coals contain an average 0.4 ppm Hg, within a range of 0.1 to 1 ppm.

For the nine Turkish coal regions (mostly lignites), some coals from the Southern Marmor Sea and Aegean Sea regions are enriched in Hg. The average Hg contents of the coals are (18 and 62 analyses) 0.12 (0.03–0.67) and 0.15 (0.03–0.66) ppm, or, calculated on an ash basis, 0.44 and 0.58 ppm accordingly (Tuncali et al., 2001, p. 651, 653).

3.3. Expressing Hg content on an energy basis

The United States coal data base (USGS COALQUAL database version 2.0) contains more than 7000 analyses of raw coals (Bragg et al., 1998). Toole-O'Neil et al. (1999) note that the average Hg content for the entire database is about 0.2 ppm, and varies between an average 0.08 ppm for the San

Juan and Uinta basins up to an average 0.22 ppm for Gulf Coast lignites. For the Pennsylvanian-age bituminous coals, average Hg contents is about 0.18 ppm (Interior Province) and 0.20 (Eastern Province; Kennedy et al., 1971). Western U.S. coals (Tertiary- and Late Cretaceous-age coals in the Rocky Mountain and Northern Great Plains Provinces) contain substantially less Hg (about 0.10 ppm Hg; Gluskoter et al., 1977).

However, if we normalize Hg content by the calorific value of the coals, the distribution is somewhat different. In such normalizing, the highest Hg coals are the Gulf Cost lignites (average 36.4 lb Hg/10¹² Btu) whereas the lowest Hg coals are from the Hams Fork basin in the Rocky Mountain Province (average 4.8 lb Hg/10¹² Btu)⁴. By this, routine coal cleaning of the high-sulfur (but also high heating value) bituminous coals of the Appalachian and Interior provinces “give them equal rights” with low-sulfur (but often low heating value) western USA coals, which are used without cleaning. On average, coal cleaning decreases the Hg content expressed on an energy basis by 37% (Toole-O'Neil et al., 1999).

4. “Coal affinity index” (coalphile coefficient) of Hg

“The Clarke of concentration” (called the CC by V.I. Vernadski) is calculated by dividing the Hg content of coal (expressed as fraction of the coal ash) by the Clarke value for sedimentary rocks. This value has also been called the “coalphile coefficient” as well as the “coal affinity index” which is the term used in this report. It worth noting that “coal affinity” is *not* the same thing as “organic affinity.” Coal affinity refers to an element’s affinity for all *authigenic* coal matter, which includes organics and inorganics such as sulphides, carbonates, and some silicates (etc.), but excludes extraneous terrigenous or volcanogenic mineral clastics. The coal affinity index calculated from the 1985 coal Clarke value is ≥ 10 . Therefore, Hg was a *high-coalphile* element. This is not surprising considering the strong affinity of Hg for humus matter (as was seen above). Based on the new Hg coal Clarke calculation, coal affinity index (coalphile coefficient) is:
$$\frac{\text{average } 0.75 \text{ ppm Hg in coal (ash)}}{\text{average } 0.05 \text{ ppm Hg in sedimentary rocks}} = 15.$$

⁴ The conversion from Btu/lb to MJ/kg: 1 MJ/kg = 429.92 Btu/lb.

5. Some Hg-bearing coals

This section discusses the ranges of Hg concentrations in some coals in the major basins of Russia, the Ukraine, eastern Germany, China and the United States. Frequency histograms of Hg content in coals have a right asymmetry (Fig. 1) due to some anomalies that are one to two orders of magnitude more than background (near-Clarke) Hg values.

5.1. Russia: bituminous and brown coals

Some Hg anomalies are noted in East Donets anthracites: “On the INAA data, Hg contents in coal beds are, on average, in the range from 0.15 (seam 3) up to 1.23 ppm (seam m_8^1)” (Sokolov et al., 2000, p. 83), with an overall average content of 0.75 ppm Hg (Kizilstein and Kholodkov, 1999). In the Pechora basin Permian bituminous coals, Hg content reaches up to 0.8 ppm (Yudovich and Zolotova, 1994, p. 21). In the “Ulug” seam riders at the Mezhedey and Elegest deposits (Tuva Republic), the Hg content reaches up to 0.77 ppm, with an average of 0.07 ppm (Bykadorov et al., 2002). In Paleogene lignites of the Taldy-Dyurgun deposit (Mountain Altai), the maximum Hg content is 0.98 ppm, with averages (two beds) of 0.25 and 0.60 ppm (Arbuzov et al., 2000). In Jurassic lignites of the Kansk-Achinsk basin, Hg contents are near-Clarke level, in the range of 0.1 to 0.4 ppm for five deposits. The Barandat deposit stands out against this background, with values of 0.9 ppm and even 1.0 ppm in its southern part. The genesis of these anomalies is unknown (Russian... 2002, p. 87). In the Miocene Ge-bearing lignites of the Pacific coast (Seredin and Shpirt, 1995; Seredin et al., 1999), the Hg content is as high as 10 to 15 ppm. For example, in the Shkotov deposit (Uglovsk basin) the Hg content of individual samples is as high as 6 to 8 ppm (Sedykh, 1997, p. 173). In coals with gold–platinum–group mineralization (Seredin, 1998; Seredin and Povarennykh, 1995; Seredin et al., 1994), a Hg–Sb–As–Tl assemblage is observed (Seredin and Danilcheva, 2000); this assemblage is also observed in Carlin-type gold deposits.

5.2. Ukraine: bituminous coals and lignites

Ukrainian coals, especially those of bituminous rank, have anomalously high Hg contents, which has

caused difficult environmental problems for many years.

5.2.1. The Donbas mercury phenomenon

Voluminous Russian and Ukrainian literature discuss the anomalously high Hg contents of the coals of the Donetsk basin (Donbas) (Karasik and Dvornikov, 1963, 1968). Although an outline made in the book by Dvornikov and Kirikilitza (1987) is insufficient in scope, the book does contain a lot of useful analytical information. As one can understand from Dvornikov and Kirikilitza (1987), there are four Hg-bearing zones in the Donetsk basin. Unfortunately, the characteristics of these zones are only partly known. The zones are (1) Central, (2) Schetov-Gukovsk, (3) Northern, and (4) Makeev-Amvrosievsk. Within the first zone, several Hg deposits are situated, including the well-known Nikitov ore field, and also the base metal ore fields of the Nagol’ny Ridge. Within the second zone, six Hg-bearing areas are noted, but only one is characterized. Within the third zone, seven Hg-bearing areas are noted, but none are named or characterized. Data about the fourth zone are absent.

In general, the mercury content of Donbas coals shows a polymodal distribution and include a background (low-Hg) population, an enhanced (“dissiminated mineralization”) population and sharply enhanced (“concentrated mineralization”) population with very high Hg contents. Consequently, two or three modes are typically seen on frequency histograms showing the distribution of Hg content in Donbas coals. A general tectonic control of mercury enrichment appears highly likely. Indeed, all of the anomalously high Hg concentrations are in anticline structures, or in the areas of fault intersections.

Coals containing the highest Hg content are from the Central zone, where there are wide Hg aureoles surrounding the ore fields. A large deep thrust zone, called the Central-Donetsk Deep Break, is located in the Central zone, in the axial part of the Main Donbas Anticline. This lineament, and related structures, served as conducting pathways for the Hg-bearing thermal solutions discharged to the coal-bearing strata (mainly Pennsylvanian age; that is, Middle Carboniferous and partly Upper Carboniferous strata). Consequently, even the background Hg contents of anthracites in this area are enhanced, with values of 0.06 to 0.07 ppm Hg, compared to background Hg

contents of 0.025 ppm in the East Donbas, 0.008 ppm in the West Donbas, and only 0.004 ppm in the South Donbas.

A second location with high Hg concentrations is the North Zone. This zone also has a large anticline, the North Anticline. In the southern part of the anticline, background Hg concentrations are as high as 0.09 ppm. Areas of “concentrated mineralization” in the East Donbas average 2.6 ppm Hg and the Central Donbas may have more.

The Donbas parts are different by the contribution of the Hg anomalies in coal; they are 50% in the Central Donbas, near 25% in the East Donbas, only minor percent in the South Donbas (though little analyses are available) and none % in the West Donbas.

Prof. B.S. Panov kindly provided his collected data on some average Hg contents for eight of the nine coal-industrial Donbas regions (Table 2).

As seen in Table 2, the coals of the Krasnoarmeesky (Red Army) region have an average Hg content of 2.37 ppm with an extremely high maximum value of 60 ppm.

5.2.2. Novo-Dmitrov deposit

Sharply enhanced Hg contents, up to 200 ppm, are also known in the unique (as regards to its genesis) Novo-Dmitrov Paleogene brown coal deposit (Kler and Nenakhova, 1981, p. 54). This coal deposit was formed in the depression above dissolving salt dome.

Table 2
Average Hg contents of coals from nine coal-industrial Donbas regions

| Coal-industrial region | Number of samples | Hg content in coal (ppm) | |
|------------------------------|-------------------|--------------------------|-----------|
| | | Average | Range |
| Donetsk-Makeevsky | 165 | 0.99 | 0.17–3.09 |
| Krasnoarmeesky (Red Army) | 43 | 2.37 | <0.01–60 |
| Bokov-Khrustalsky | 299 | 0.478 | <0.01–3.8 |
| Dolzhan-Roven'kovsky | 148 | 0.299 | <0.01–3.2 |
| Almaz-Marievsky | 216 | 0.12 | <0.01–8.4 |
| Central (Gorlovsky) | 1198 | 1.21 | 0.01–30 |
| Chistyakov-Snezhnyansky | 8 | 0.26 | 0.1–0.4 |
| Seleznevsky (Kommunarsky) | 599 | 0.52 | 0.02–3.0 |

The data presented by prof. B.S. Panov, 2004.

5.3. Former East Germany brown coals

In these Eocene–Miocene coals (15 samples), Hg contents ranged from 0.16 up to 1.5 ppm, with an average of 0.33 ppm. The highest values were found in the Geiseltam deposit, Weisel basin, and for the I–III and IV seams in the Lausitz and Bitterfeld deposits, respectively (Rösler et al., 1977).

5.4. Greece: Miocene lignites

Upper Miocene Domeniko lignites (Elassona basin in central Greece), in 38 samples from two drillholes, contain, on average, 0.34 ppm Hg in 850 °C ash⁵. Highest content (1.21 ppm) is found in lignite with 10.7% ash (Pentari et al., 2004, p. 264–266), at average ash yield 18.5% (our calculation).

5.5. China: the Guizhou phenomenon

The mean geometric Hg content for 36 Chinese coals is 0.578 ppm (range of 0.046–4.8; Ren et al., 1999).

Over 234 analyses representing 14 coal-producing Chinese provinces provide a weighted average Hg content of 0.22 ppm with a range of 0.03 ppm (Xinjiang, marginal NW China) up to 0.34 ppm (Beijing province). Individual Hg analyses are often much higher with a maximum of 1.95 ppm from Shanxi province (Wang et al., 2000; Zhang et al., 2002). However, these data may not represent the highest Hg figures for Chinese coals because data from the Hg-rich Guizhou province, which has an annual coal production of about 20 million tons, were not available.

Previously, some isolated Hg data on Chinese coals have been published. Anthracites from southwest Guizhou province (which are known for being very enriched in arsenic and fluorine) contain up to 45 ppm Hg (!). The sample with the highest Hg content is also rich in gold (0.57 ppm; Ding et al., 2001, p. 1357). As Finkelman noted, TI-bearing Guizhou coals used for home drying of the vegetables may contain up to 55 ppm Hg! This may, probably, result in blindness of the farmers (Finkelman, 2004, p. 23).

⁵ Editor's note: +post-publication analyses were not able to confirm the published levels.

A special study of 48 column samples from the 19 coal fields in four Guizhou “basins” provides an average Hg content of 0.53 ppm (0.54 ppm in the Triassic bituminous coals and 0.42 ppm in the Permian anthracites). For the individual analyses, the Hg content reaches up to 2.67 ppm (Feng et al., 2002).

In the Qianxi Fault Depression Area, southwest Guizhou province, coals were sampled from small pits (Zhang et al., 2003, 2004); 13 Triassic-age coals (bituminous) averaged 1.421 ppm Hg whereas 47 Permian age coals (bituminous and anthracite) averaged 0.821 ppm. In this area, the maximum Hg content in the Permian anthracites was 10.5 ppm.

At last, in Quanxi Fault Depression Area, three areas were noted with coal containing more than 0.5 ppm Hg. Two areas are with Upper Permian coals and one with Upper Triassic (Zhang et al., 2004, p. 58). Upper Permian coals (on average over 32 analyses) contain 1.1 ppm Hg (ranged from 0.04 to 5.1 ppm), and Upper Triassic (14 analyses) contain 1.6 (0.06–10.5) ppm (Zhang et al., 2004, p. 55–56). That is, on an ash calculated, 3.8 and 11.1 ppm.⁶

5.6. USA: various coals

Joensuu (1971) reported high Hg-contents for a number of USA coals. For example, high anomalies are reported in Franklin County, Pennsylvania (10.5 ppm); Clay County, West Virginia (22.8 ppm); and also in Richland County, Montana (33 ppm). The latter two results are questionable for two reasons: first, similar high values have not been reported for other coals in these regions and, second, the locations of the coals cannot be verified based on the information supplied in the paper. While it appears, based on an acknowledgment, that the coals were obtained from the Penn State coal collection, there is no way to determine the exact origins of the coals. Further, even the county locations must be questioned. For example, there is no coal-bearing formation present in Franklin County, Pennsylvania.

High Hg-contents were noted in coals with epigenetic mineralization, but apart from common sulfide forms, some other Hg forms seem to be

present, including Hg_{org} (Brownfield et al., 1994, cit. after: Kolker and Finkelman, 1998). In the Gulf Coast lignites (248 analyses), the average Hg content is 0.19 ppm, and the anomalies reach up to 1.0 ppm, in Arkansas coals (Warwick et al., 1995).

6. Modes of occurrence

As seen above from supergene mercury geochemistry, no less than three Hg forms may be present in coals: as clays (Hg_{clay}), organic matter (Hg_{org}), and sulfides (Hg_{sulf}). Within coals, mercury resides in several components, including: biogenic (from coal-forming plants; Hg_{bio}), sorption (Hg_{sorb}), terrigenous (or volcanogenic) clastics (Hg_{clast}) and, diagenetic or epigenetic (infiltration) mineral fractions (Hg_{inf}).

In coal cleaning, as much as 50% to 60% of the Hg remains in the cleaned coal product and the rest is disseminated in tails, sludges, and middlings. It is obvious that Hg in the cleaned coal product is dominantly authigenic (primarily Hg_{org} and “shielded” micro-mineral forms such as Hg_{sulf}). Given that these two forms of Hg are dominant, their occurrence controls the Hg distribution in coal.

6.1. Sulfide form

Finkelman (1980) concluded that there is strong evidence that a significant proportion of the Hg in coal is associated with pyrite, probably of secondary origin. The occurrence of Hg in sulfide forms is indicated either indirectly (by correlation between S and Hg contents), or directly (by means of sulfide analyses). In coals extremely enriched in Hg, an Hg-sulfide (cinnabar: HgS) can occur, as well as Hg-bearing Zn and Pb sulfides (Dvornikov and Kirikilitsa, 1987). For example, in the high-Hg coals of the Guizhou, the sulfide form of Hg dominates. This is indirectly proved by three observations (Feng and Hong, 1999). First, an earlier study by Feng and co-workers demonstrated a positive correlation ($R=0.4$) between mercury and the total sulfur content of 27 coals from Guizhou province. Second, highly significant correlations ($R=0.97$ and 0.99) were observed between Hg content and mineral sulfide abundance for two sets of 10 density fractions (<1.40 up to >2.8 g/cm³) from two coal samples. Third, sequential

⁶ Our recalculation on an ash basis; average calculated ash yield of Permian and Triassic coals (25 and 10 samples) is 29.0% and 14.5%.

leaching of the 32 coal samples, showed the highest Hg extraction was observed using hot HNO₃; the contribution of exchangeable Hg (ammonium acetate, pH 7) and Hg in carbonates or sulfates (ammonium acetate, pH 5) was negligible. About 83% of the total mercury in these coals was soluble in hot HNO₃, which preferentially dissolves sulfide minerals.

6.1.1. Mercury in pyrite

In most early studies, the pyrite-enriched heavy coal fractions, or sometimes, handpicked pyrite grains were examined. During the last decade, direct microprobe analyses of the pyrite grains observed in polished sections of coal polished sections have been used.

The occurrence of Hg in coal pyrite may result from several processes (Dvornikov, 1967a,b,c, 1981; Finkelman et al., 1979; Porritt and Swaine, 1976; Ruch et al., 1971). First, pyrites may contain microinclusions of cinnabar (e.g., Lower Cretaceous Irgen brown coals of the Transbaikal (Meytov, 2001, p. 297). Second, Hg can be isomorphically introduced into pyrite during its formation in hydrothermal solutions (Dvornikov, 1981). Third, due to its special electrochemical and sorption properties, pyrite can scavenge Hg from its surroundings at 200 °C and higher temperatures (Khairtadinov, 1971). This implies that hydrothermal pyrites in coal may serve as Hg collectors, capturing Hg from gases or hydrothermal solutions.

There are many examples of coal pyrites or heavy fractions that are enriched in Hg. A few examples from different world basins are discussed below.

6.1.1.1. *Russia: different coals.* Anomalously high Hg contents (0.1 to 7.5 ppm Hg) have been noted in waste tailings from the Progress, Nikulinskaya and Kimovskaya coal cleaning plants of the Near Moscow coal basin (Pavlova and Timofeev, 2000, p. 121). These high values are clearly due to Hg in sulfide minerals. In the East Donbas, i₃ anthracite seam, Hg concentrations are partitioned as follows: Hg_{org}=0.3 ppm, Hg_{clay}=0.6 ppm, and Hg_{pyr}=5.9 ppm (Kizilstein et al., 1989, p. 134). Hg contents in organic and clay matter are near the Clarke value, whereas Hg is enhanced in pyrite. This may indicate a diagenetic transformation process, where Hg_{org} changes to Hg_{pyr}.

6.1.1.2. *Ukraine: Pennsylvanian-age Donbas coals.* In the northern part of the Small-Folded Zone, in

subbituminous-B coals, six to seven times more Hg is present in heavy fractions of coals than in light fractions (Dvornikov, 1967b). However, because the heavy fractions only account for 1.48% to 6.08% of the coal mass, most of the total mercury in these coals is in the light fraction. Thus, in these coals, the sulfide fraction is a *concentrator* of Hg but organic matter is a *carrier* of Hg.⁷ An average Hg content of 0.15 ppm (252 analyses) was observed for the seam l₆, Almaz-Marievsky region, whereas a pyrite from this coal contains 3.6 ppm (40 analyses; Karasik and Dvornikov, 1968). Although the mercury content of the 1.50 to 1.55 g/cm³ density fraction of the k₅ anthracite seam in the Bokov-Khrustal region, is relatively high (1 ppm), the pyrite-rich >1.8 g/cm³ fraction from this seam is about 7 ppm (Dvornikov, 1967a). A plot of “S_{pyr} vs. Hg” for 24 coal samples from ten working Donbas mines shows a distinct linear correlation, suggesting that pyrite is the primary carrier of mercury in the Donbas samples (Kolker et al., 2002).

The highest measured Hg content of pyrite found in the Donbas coals is for the h₈ seam, in the Tomashevskaya Yuzhnaya coal mine of the Small-Folded Zone. Although the average Hg content in the coal from this seam (10 samples) is very high (8.1 ppm), the average Hg content of pyrite from this seam (70 samples) is an even more remarkable 116.8 ppm (Dvornikov and Kirikilitza, 1987, p. 79).

6.1.1.3. *Great Britain: Pennsylvanian-age bituminous coals.* Bushell and Williamson (1995, p. 168) report the Hg content and mineral composition of five coals used for gas production. If one arranges the coals by pyrite content, multiple the fractional percent pyrite in

⁷ Such terms have been introduced in Russian geochemistry as early as the start of the 1960s. So, a *concentrator* is a phase (mineral phase), which has the highest concentration of a trace element, and a *carrier* is a phase (mineral phase or phases), which contributes most of the gross (total) element concentration in the coal. This comment is very important for the correct definition of the “organic affinity” in coal geochemistry! “Organic affinity” is the highest concentration of an element in coal organic matter rather than the main part of the total element content in coal contributed by organic matter (that is wrong because it is evidently influenced by an ash content in coal!). Thus, “organic affinities” calculated by the “Illinois Research Team” (Fiene et al., 1979) by means of coal cleaning curves are the *contributions of organic matter* and not the element properties (as the term “organic affinity” is assumed in chemistry!).

the low temperature ash by the wt.% high temperature ash, the following sets emerge: 0.0, 0.6, 1.2, 1.2, 3.2 (percent pyrite in coal), and the corresponding, <0.01, 0.07, 0.04, 0.07, 0.10 (ppm Hg in coal). A simple correlation is absent, although coals with the highest and the lowest pyrite content follow the same trend for Hg content.

6.1.1.4. Spain: Pennsylvanian anthracites. Fig. 2 shows density fraction data on three Spanish Pennsylvanian anthracites (Martínez-Tarazona et al., 1997). In the samples 2 and 3, pyrite seems to be only a carrier of Hg; in sample 1, the pyrite and Hg curves are not fully concave.

A large Spanish power plant combusts a 95% subbituminous/5% bituminous coal blend; the coal has a relatively high ash and mercury content (27% ash, 0.19 ppm Hg). Using statistical data processing (mineralogical and chemical analyses of density fractions), it was calculated that Hg is fully (100%) in a sulfide form (Querol et al., 1995, p. 336).

6.1.1.5. India: Gondwana bituminous coals. Fractionation of four Indian coals with Hg contents ranging from 0.15 to 0.87 ppm showed Hg enrichment in heavy fractions (typically $>1.7 \text{ g/cm}^3$) and high ash contents (typically, between 50% and 73% ash). A maximum of 3.21 ppm Hg was observed for the $+1.7 \text{ g/cm}^3$ fraction from the Kalakot coal; this specimen also contained 73.5% ash (Ghosh et al., 1994). It is evident that, in this instance, the Hg is concentrated in pyrite, because clastogenic minerals do not contain so much mercury.

6.1.1.6. China: Upper Permian anthracites. Microprobe analyses on the rims of two pyrite grains from two extremely As-enriched coals from the Guizhou province showed Hg contents in the range from 200 up to 4700 ppm (Ding et al., 2001, p. 1357). The remarkably high values for the sulfide minerals are magnitudes greater than the 8.5 ppm Hg content of the parent coal that they were obtained from.

6.1.1.7. USA: bituminous coals, Warrior basin. The Hg content of sulfide grains was directly measured by laser ablation inductively coupled mass spectroscopy in samples of As- and Hg-bearing mineralized coals from three mines in the Warrior basin, Alabama; altogether tens of measurements were

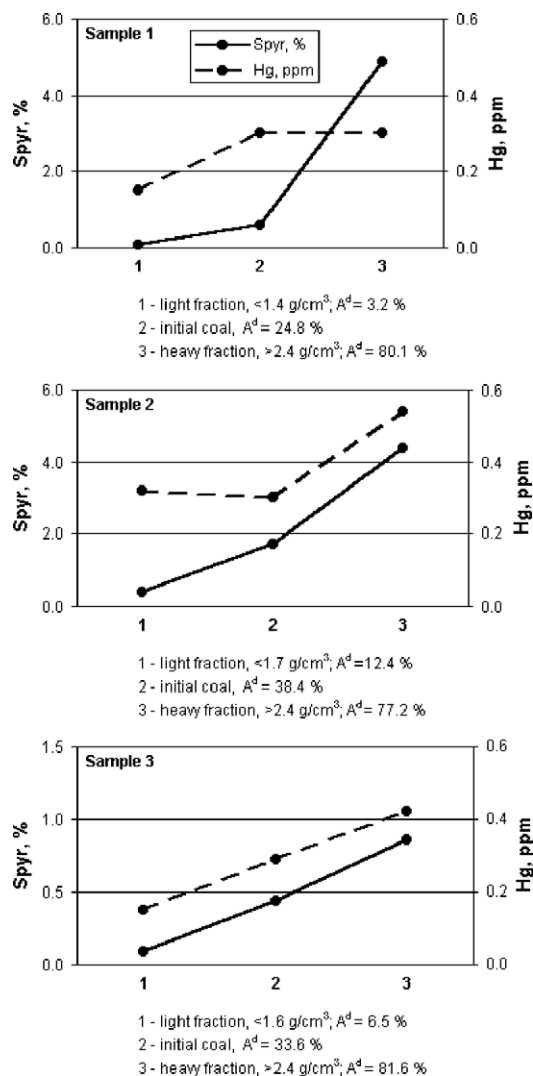


Fig. 2. Some data about density fractions of three Spanish anthracites. Compiled from: (Martínez-Tarazona et al., 1997, p. 399).

made on 13 populations of sulfide minerals exposed in polished coal samples. The highest average Hg content (Kellerman mine, 30 ppm!) was detected in cross-cutting pyritic veins superposed on an earlier pyrite; the highest individual concentration was 140 ppm. Notably, the highest average Hg content of the coal samples hosting the pyrite grains is no more than 0.30 ppm, with a maximum Hg content for the host coals of only 5 ppm. Thus, pyrite is a concentrator and carrier of Hg in these coals (Diehl et al., 2002, 2004).

6.1.2. Other sulfides and selenides

In Dvornikov and Kirikilitza's (1987) book, some analyses of different hydrothermal minerals in Donbas coals are presented. All of the hydrothermal minerals are Hg-bearing, including silicates and carbonates. *Cinnabar* (HgS), is found in coals only near sulfide ores, and occurs as thin cleats and layers, usually at the bottom of the coal beds and lenses. The latter probably served, as simple shields impeding the flow of ore-bearing solutions. In anthracites, cinnabar appears in late cleats, with chlorite occurring along the cleavage-oriented scales. The dispersed cinnabar accumulations color the chlorite bright pink. More often, cinnabar was not observed in coals, but rather in pyritic lenses and nodules with evident epigenetic features, such as cross-cutting cleats in pyrite, or as pyritic breccia cementation (Dvornikov, 1981). Cinnabar is sometimes not only a concentrator of Hg, but also a carrier of Hg in such mineralized coals. The Hg content of sphalerite and galenite may reach up to tens of ppm (Dvornikov and Kirikilitza, 1987).

Notably, clausthalite (PbSe) can contribute to the Hg content of coal. Proton microprobe study of a clausthalite grain from a Pennsylvanian age Manchester coal from Eastern Kentucky, shows a very high Hg concentration: as much as 47 ± 22 ppm Hg. Therefore, enhanced Hg contents in a near-roof bench mineralized by pyrite (0.52 ppm Hg) may be supplemented by the 10- μ m diameter clausthalite grains (Hower and Robertson, 2003). An additional study of sulfides in the Manchester coal indicated that not all Fe-sulfides contained equal amounts of Hg, strongly suggesting that simple correlations between Hg and pyritic sulfur are inherently flawed (J.D. Robertson and J.C. Hower, 2004, personal communication, in Sakulpitakphon et al., 2004).

6.2. Organic form

An Hg_{org} form can be indicated by where the Hg content of maceral concentrates is substantially higher than the Hg content of the whole, parent coal. However, such results should be interpreted cautiously because an apparent organic Hg enrichment of a maceral concentrate may result from micro-sulfide inclusions. For example, comparison of the Hg content of 12, handpicked vitrinite concentrates (nine from the

eastern United States, two from South Yorkshire, Great Britain, and one from the Sydney Basin, Australia) with the mercury content of the parent bituminous coals showed that in the USA vitrinites a Hg_{min} form dominates, but an Hg_{org} form may dominate the English and Australian coals. Statistical analysis of the major, minor, and trace element data further indicated that Hg is usually correlated with Fe (probably from pyrite) as well as with Co and Sm (Lyons et al., 1989).

According to Belyaev et al. (1989), in Jurassic Kansk-Achinsk basin brown coals, only 5% of the total Hg is bonded with organic matter, whereas for Kuznets basin coals organic form Hg makes up 81% (Khrustaleva et al., 2001, p. 38, 40).

Stepped leaching using a sequence of four solutions (1N CH₃COONH₄, 3N HCl, 48% HF, then 2N HNO₃) for 18 h at room temperature, and with a solid/liquid ratio of 1:7 was applied to 9 typical USA coals and seven concentrates crushed to minus 60 mesh (–0.25 mm). The results showed that 50% of the total Hg was removed by the HNO₃ for 12 of the 16 samples (Palmer et al., 1998). Although HNO₃ soluble Hg is attributed to Hg_{pyr}, HNO₃ can also oxidize both elemental (Hg⁰) and organic mercury (Hg_{org}) to the soluble, Hg²⁺ form. In a subbituminous coal from the Powder River basin that has a low Hg content (0.08 ppm Hg), the mercury is not entirely leachable and is interpreted to be Hg_{org} (Palmer et al., 1998).

Two-stepped Hg leaching of a lignite from North Dakota and Pennsylvanian-age bituminous coal (acidified water with a pH of 2 to 5, at room temperature, followed by concentrated HCl, at 80 °C) resulted in 60% to 90% removal of the initial Hg content. Seemingly, only the Hg_{org} and other forms, rather than sulfide form Hg, are leached by this process (Dronen et al., 2004). The practical significance of this study (lower Hg emissions from combustion by burning “Hg-cleaned” coal) is uncertain because disposal of Hg-bearing acid leachates poses a new problem.

Although the *concentration* of Hg_{org} is usually lower than Hg_{sulf}, the *contribution* of the organic form of mercury can be greater than sulfide form mercury. For example, Table 3 shows that Hg_{org} can contribute from 3% up to 100% of the total Hg, without a clear relation to the coal mineral content.

Evidently, the lower the sulfur content of the coal, the greater the potential contribution of Hg_{org} to the

Table 3

The contribution of organic form mercury (Hg_{org}) to the total Hg content in coal (mercury “organic affinity values”); compiled after data from Fiene et al. (1979, p. 37–40)

| Coal seam, U.S. state-of-origin | Low temperature ash (%) | Hg, ppm in coal | Organic form Hg (%) |
|---------------------------------|-------------------------|-----------------|---------------------|
| Herrin No. 6, Illinois | 20.37 | 0.23 | 100 ^a |
| Pittsburgh No. 8, West Virginia | 12.87 | 0.13 | 47 |
| Blue Creek, Alabama | 12.67 | 0.39 | 100 ^a |
| Rosebud, Montana | 14.49 | 0.06 | 3 |

^a The value is reported as more than 100% in the original paper, which is theoretically impossible and indicates limited analytical precision; a value of 100% is assumed and presented here.

total Hg. For example, the organic mercury contribution to Kentucky bituminous coal is assessed as 78%, at the gross Hg content of 0.44 ppm. In coal hydrogenation, mercury produces volatile products, which seem to be present as mercury–organic compounds (Filby et al., 1977).

An epigenetic origin of Hg_{org} is possible because sorption of Hg vapor is quite probable at elevated temperature, and both chemical and physical sorption have been experimentally proven (Khairtdinov, 1971, p. 678). For example, at a coal/intrusion contact, the Hg contents in natural coke and in the nearest 42 cm bench of thermally altered coal were much higher than the Hg content of the coal bed distant from the contact (Finkelman et al., 1992). High Hg contents in coal-derived graphites provide indirect evidence of such sorption processes. From 104 graphite samples studied, Hg contents are 1 to 9 ppm (15 samples), 10 to 99 ppm (6 samples), and 100 to 1000 ppm (13 samples; Janda and Schroll, 1960). Such phenomena are not universal, as Stewart et al. (2003) noted a depletion of Hg in coked coal adjacent to a peridotite intrusion into a high volatile bituminous, high-sulfur Illinois Basin coal.

6.3. Elemental form

Metallic Hg^0 was first discovered in a study of Hg-forms in the Donbas coals (Scherbakov et al., 1970). It was further discovered that the Hg^0 form dominates in Hg-aureoles adjacent to the Donbas ore bodies. The Hg^0 concentrations in the coals decline with distance from the ores and the Hg_{org} contribution increases (Dvornikov, 1981).

6.4. Distribution of Hg forms (based on complex procedures)

In the last decade, the procedure of sequential (stepped) coal leaching, which has been actively promoted by the U.S. Geological Survey (Finkelman et al., 1990b; Palmer et al., 1993), has been widely adopted. However, practitioners of this procedure do not always use the same technique; leaching steps may be skipped or different reagent concentrations used. For example, two samples were sequentially leached: a subbituminous coal from the Black Thunder seam, Power River Basin ($A^d=5.94\%$; $Hg=0.099$ ppm), and a cleaned bituminous Pittsburgh No. 8 coal ($A^d=7.58\%$; $Hg=0.11$ ppm). Bool and Helble (1995) observed that the Hg solubility partitioning (percent of total Hg) for the sequence, 1N $NH_4C_2H_3O_2$, 1:3 HCl, 48% HF, and 10% HNO_3 , was: 28%, 26%, 0%, and 34% with 12% insoluble Hg for the subbituminous coal, and 15%, 22%, 0%, and 27%, with 35% insoluble Hg for the bituminous coal. Therefore, in both coals, mercury is rather uniformly distributed between exchangeable, carbonate, sulfide, and organic forms.

The Hg content of nine, Triassic-age coal samples collected from coal bunkers in southwestern Guizhou province, China range from 0.34 up to 10.5 ppm, (average 1.04 ppm). The Hg distribution in the coal bed (in situ) seems to be even more variable. Selective leaching of the oxidized coal from a small mine (details are not reported) yields the following Hg-form partitioning (% of total Hg): 27.8% water-soluble Hg, 9.6% organic-bound Hg, 28.9% carbonate-bound Hg, 8.6% clay-bound Hg, and 24.0% sulfide-bound Hg (Zhang et al., 1999).

Two P_2 anthracites and two T_3 bituminous coals from the Qianxi Fault Depression Area, southwestern Guizhou province, China, were studied by sink–float, and sequential leaching methods. In addition, one fraction was ashed prior the analysis. Besides sulfide-bound Hg, a wide variety of Hg-bearing phases were detected using these methods (Table 4). The accumulation of Hg (and As) in these coals is probably influenced by low-temperature Carlin-type Au-mineralization (Zhang et al., 2003, 2004).

Sink–float and sequentially leaching methods were also used to study Hg partitioning in two coals from Australia and one coal from the United States (Table

Table 4

Mercury mode of occurrence in arsenic- and mercury-bearing coals from the Guizhou Province, China; compiled using data from Zhang et al. (2003)

| Mode of Hg occurrence and analytical method | Percent of the Hg reporting to the fraction | Comment |
|---|---|---|
| Water-leachable Hg: coal (10 g) is treated with 30 ml deionized distilled water at room temperature for 24 h. | 6.4 to 13.1 | The maximum water-leachable Hg value is for a T ₃ coal |
| Ion-exchangeable Hg: the coal is subsequently treated with 1N NH ₄ C ₂ H ₃ O ₂ at room temperature for 24 h. | 14.5 to 20.0 | The maximum ion-exchangeable Hg value is for an anthracite |
| Organic-bound Hg: a float fraction (<1.47 g/cm ³) of the treated coal is ashed at 650 °C, and the ash is treated by HNO ₃ +HClO ₄ | 30.6 | Assay for one Triassic coal only |
| Carbonate-bound Hg: a float fraction (<1.47 g/cm ³) is treated with 10 ml 0.5% HCl | 9.7 to 23.1.9 | The maximum carbonate Hg values is for an anthracite |
| Silicate-bound Hg: a float fraction (<2.8 g/cm ³) is treated with HF+HNO ₃ | 16.1 to 26.3 24.6 to 31.4 | Higher values are observed for anthracites |
| Sulfide-bound Hg: a sink fraction (>2.8 g/cm ³) is treated with HNO ₃ | 22.7 to 26.4 | The maximum sulfide Hg value is for a T ₃ coal |

5). As is shown in Table 5, the percentage contribution of Hg_{org} is nearly the same for all three coals (37% to 39% of total Hg), irrespective of coal ash, sulfur, or Hg values.

A Hg content of 0.08 ppm was observed for the low-sulfur, low-ash subbituminous coal from the Antelope mine, in the Powder River basin, Wyoming. Sequential leaching analysis showed that 50% of the Hg was in pyrite, 5% was in silicates, and 45% was in the organic matter. The large contribution of Hg_{org} is noteworthy (Palmer et al., 2000, p. 23).

Sequential leaching analysis applied to four typical USA coals (3 bituminous and 1 subbituminous) using NH₄C₂H₃O₂, HCl, HF, and finally HNO₃ showed that most of the Hg in the bituminous coals was associated with sulfide minerals, whereas an organic association

was indicated for nearly all of the Hg in the subbituminous coal. Notably, the bituminous coals contained from 0.1% to 1.5% pyritic sulfur whereas the subbituminous coal only contained 0.01% pyritic sulfur (Table 6; after Senior et al., 2000, p. 233).

7. Factors controlling Hg distribution

Two coal properties usually control the Hg distribution: the ash yield and the pyritic sulfur content. The relative importance of these properties is sometimes difficult to determine, especially for low-ash coals where increasing ash values may be caused by increasing pyritic sulfur contents.

Table 5

Semi-quantitative estimation of Hg distribution in three coal samples; compiled using data from Querol et al. (2001)

| Coal bed | Hg (ppm, dry coal) | Distribution of Hg in the coal (%) | | Distribution of Hg in the mineral matter fraction (%) | | |
|--|--------------------|------------------------------------|----------------|---|------------|---------------------|
| | | Organic matter | Mineral matter | Sulfides | Carbonates | Others ^a |
| Gascoine Wood, Australia (ash _{dry} =15.9%, S _{dry} =1.21%) | 0.06 | 37 | 63 | 75 to 100 | – | – |
| Herrin No 6, Illinois, USA (ash _{dry} =10.2%, S _{dry} =3.27%) | 0.10 | 37 | 63 | 75 to 100 | – | – |
| Wyee, Australia (ash _{dry} =23.1%, S _{dry} =0.36%) | 0.01 | 39 | 61 | 0 to 25 | – | 50 to 75 |

^a Mainly clay minerals.

Table 6
Distribution of Hg forms in typical U.S. steam coals (percent of total Hg); compiled using data from Senior et al. (2000, p. 233)

| Coal seam | Hg-bearing phases | | |
|----------------|-------------------|-----------------------|--|
| | Pyrite | HCl-leached sulphides | Organic matter or micro-minerals in organic coatings (“shielded minerals”) |
| Pittsburgh | 60 | 25 | 15 |
| Illinois No 6 | 65 | 20 | 15 |
| Elkhorn/Hazard | 20 | 40 | 40 |
| Wyodak | 0 | 0 | 100 |

7.1. Influence of ash yield

The distribution of sample points on plots of the ash yield vs. the Hg content of coal is influenced by the genetic (virtual) Hg fractions balance. If terrigenous Hg dominates, the relationship is linear. However, if an authigenic (sorbed) Hg fraction is present, this linear relationship is weakened. In such instances, the influence of the authigenic Hg is complicated by the “sorption optimum” for an element (Yudovich, 1978, p. 88), and a negative correlation can appear on plots of the ash yield vs. the Hg content expressed on an ash basis. The data presented in this section are for the coals from Russia, Kazakhstan, Belgium, Greece, the United States, and Canada (Kizilstein, 2002; Belyaev et al., 1989; Block and Dams, 1975; Georgakopoulos et al., 1995; Hatch, 1987; Goodarzi and Goodarzi, 2004).

7.1.1. Russia: Pennsylvanian age bituminous coals and anthracites, East Donbas

In a random sample of East Donbas coals ($n=736$), the following regression equation was calculated: $Hg = 3.093 \exp(0.028 A + 0.095 s)$ where Hg is ppm mercury (dry basis); A is wt.% ash, S is wt.% total sulfur, and all variables are expressed on a dry basis. However, the average Hg value calculated using this equation (6.78 ppm) corresponds poorly to the analytically determined average value ($n=240$, 9.39 ppm) (Kizilstein, 2002, p. 111–112). Moreover, both of these values are substantially higher than is typical for East Donbas coals.

7.1.2. Kazakhstan: Jurassic brown coals

Three coal horizons of the Shubarkol deposit had Hg contents in the range of 0.005–0.17 ppm and a

significant correlation between “Hg in coal–ash content” (Belyaev et al., 1989). More data are not given.

7.1.3. Belgium: Pennsylvanian bituminous coals and anthracites

Average ash values for raw coals from Belgium classified according to use were 3.7% (domestic coal), 5.4% (coking coal), 6.0% (industrial) and 32.5% (power plant coal); respective mercury values were 0.5, 0.5, 0.6, and 0.6 ppm Hg on a whole coal basis (Block and Dams, 1975, p. 148), and 14, 9, 10, and 2 ppm Hg calculated to an ash basis. The amount of mercury in the coals shows no relationship with the ash yield, but the amount of mercury calculated on an ash basis is inversely related to ash yield. This observation is illustrated in Fig. 3, and indicates a significant authigenic (Hg_{org} or Hg_{pyr}), rather than allogenic (Hg_{clast}), origin for mercury in these coals. Finally, it is worth noting that the Hg values calculated on an ash-basis and shown in Fig. 3 are substantially greater than the Hg assay values for the real coal ashes. Block and Dams (1975) attributed this difference to the volatility and subsequent loss of Hg in combustion gases during incineration.

7.1.4. Greece: Miocene lignites

The ash content of the Lava deposit coals of southwestern Greece, increases in the order: xylites, raw coals, xylitic lignites, lignites, and interbedded marls. As shown on Fig. 4, Hg contents expressed on a coal-basis show no relationship with ash but Hg contents expressed on an ash basis are high for low-ash coals and decrease with increasing ash yields

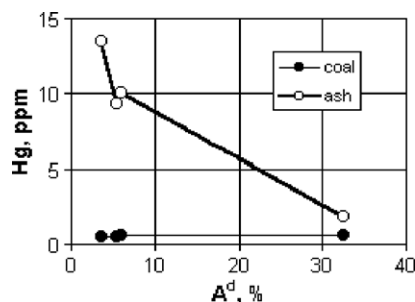


Fig. 3. Plot of Hg content in coal and ash (calculated), Belgium feed coals. Plotted from the data: (Block and Dams, 1975, p. 148).

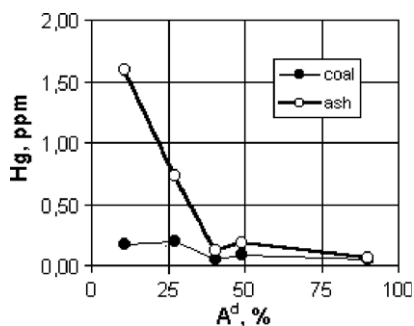


Fig. 4. Plot of Hg content in coal and ash (calculated), Greece lignites. Plotted from the data: (Georgakopoulos et al., 1995).

(Georgakopoulos et al., 1995). A “coal affinity” (coal-ophile property) of Hg is evident: Hg contents of most samples calculated on an ash basis are 3 to 10 times greater than the mercury content of the high-ash marls.

7.1.5. USA: Eocene lignites

Fig. 5 shows the relationship between the Hg content and ash yield is complicated for seven samples from the Vermillion Creek coalfield, Green River basin, Wyoming (Hatch, 1987). No relationship is observed for Hg expressed on a coal basis but a relationship between ash yield and Hg expressed on an ash basis is typical for all coal-ophile elements. High ash-basis Hg values are shown for low-ash coals with a complicating intermediate maximum Hg values shown for medium-ash coals (see Yudovich, 1978; or Yudovich and Ketris, 2002, for details).

7.1.6. Canada: Cretaceous subbituminous coals

In four subbituminous Alberta coals, the weighted average Hg contents range from 0.036 up to 0.086 ppm, with a large variation in vertical bed columns. High Hg values (2 to 4 times more than the whole-bed average), are observed for benches of high-ash coals, coaly siltstones, shale partings, weathered coals, and in mineralized coals containing epigenetic pyrite. Consequently, a general, positive correlation between ash yield and Hg content is observed (Goodarzi and Goodarzi, 2004).

7.2. Influence of sulfur content

With few exceptions, the greater the sulfur content, the greater the Hg content of coal. As discussed above, this is because pyrite is both the main

concentrator, and the main carrier of mercury. For example, analyses of 75 bench samples of the Upper Freeport seam collected from 21 locations (Cecil et al., 1979, p. 235), confirmed the positive correlation between S_{pyr} and Hg. Such correlations are strong evidence that Hg_{pyr} is the dominant form of Hg in coal. Finkelman et al. (1990a) observed that more than half of USA coals with anomalously high mercury contents are also high-sulfur coals (which contain more than 3% total sulfur). Heavy fractions ($>2.90 \text{ g/cm}^3$), representing 3% to 9% by weight of sulfur-rich Illinois coals, contain 2.9 to 9.4 ppm Hg, whereas the raw, parent coals contain only 0.14 to 0.62 ppm Hg (Ruch et al., 1974). Such partitioning allows the production of low-ash, cleaned coal products with two to five times less Hg than the Hg in the raw coal. Ruch et al. (1971) concluded that pyritic Hg comprises up to 50% of the total Hg in these coals, with the remaining Hg apparently bonded with coal organic matter.

Shpirt noted that the lower the yield of the sulfide fraction, the higher the amount of Hg in the recovered sulfide minerals (Shpirt, 2002, p. 73). Such an observation appears rather strange. We suppose that, in this instance, Hg was redistributed from the organic matter to the sulfide minerals in the coal. For example, consider two hypothetical coals with the same Hg_{org} content (0.005 ppm) but different amounts of pyrite (0.1% and 1.0%). Redistributing Hg_{org} to Hg_{pyr} would result in 0.5 ppm Hg_{pyr} for the coal containing 1.0% pyrite, and 5 ppm Hg_{pyr} for the coal containing 0.1% pyrite.

The high-sulfur bituminous Springfield coal ($S_{\text{tot}}=5.45\%$, $A^d=12.91\%$) was sampled with five

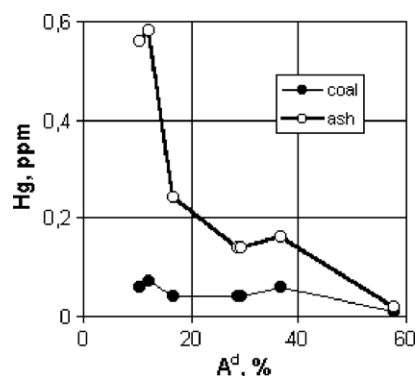


Fig. 5. Plot of Hg content in coal and ash (calculated) for seven Vermillion Creek coals. Plotted from the data: (Hatch, 1987).

benches along its full thickness of 149 cm (Mastalerz et al., 2004). The weighted average Hg content is 0.13 ppm. The highest Hg content (0.24 ppm) was in the fourth bench (83–114 cm from the roof), which also had the highest sulfur content ($S_{\text{tot}}=6.85\%$, $S_{\text{pyr}}=3.89\%$). The high volatile A bituminous Dean coal (Pennsylvanian) of southeast Kentucky was likewise sampled over its thickness of 112.5 cm with six benches (Mardon and Hower, 2004). The average Hg content for the whole seam was 0.243 ppm. However, the two uppermost benches account for much of the total mercury (0.428 and 0.125 ppm) and sulfur (4.94% and 2.21%), in the seam but only one third of the seam thickness (17.1 and 19.9 cm). The lower benches (75.5 cm) have Hg contents up to one order of magnitude less (0.006–0.099 ppm), with the maximum Hg content in the bottom bench ($S_{\text{tot}} 1.04\%$). The data from the six bench samples are plotted in Fig. 6. The S_{pyr} and Hg curves are concave, suggesting that pyrite is the only carrier of Hg.

This Dean coal feed to a 220-MW unit has ash, S, and Hg contents of 8.13%, 1.50% (and 0.65% S_{pyr}) and 0.113 ppm, respectively. During the pulverizing process, a “reject” is separated; that is, a pyrite-rich tailing is collected from the pulverizer. The “reject” has ash, S and Hg contents of 47.72%, 23.55% (and 23.20% S_{pyr}) and 2.387 ppm, respectively (Mardon and Hower, 2004). Thus, pyrite is the main site of Hg, and it probably contains about 10 ppm Hg.

7.3. Position of sample in the coal bed column

In Kizilstein's (2002) textbook, data are cited for four coal beds of East Donbas, each of which consists of two benches with different petrographic compositions.⁸ In addition, thin (1–2 cm) marginal coal layers were sampled near the bottom and roof of the beds. As seen in Table 7, ash, S, and Hg are nonuniformly distributed across the seam section with a distinct enrichment in the near roof layer. The Hg distribution corresponds well with sulfur, but not with ash content. Thus, there is a specific “marginal enrichment” in Hg and S (Yudovich, 1978, 2003).

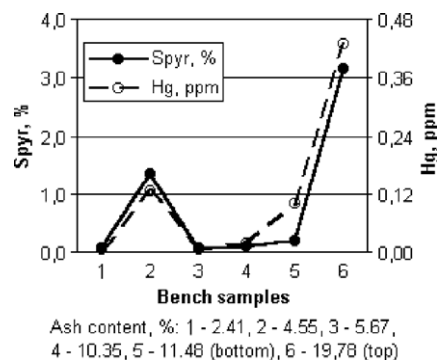


Fig. 6. Contents of S_{pyr} and Hg in the bench samples, Dean coal bed, Kentucky. Plotted from the data: (Mardon and Hower, 2004).

In the thickest lignite beds of the Kansk-Achinsk basin, some Hg enrichment occurs in near-roof benches (Russian Coal Base, 2002, p. 87).

Five channel samples of the Manchester coal from Clay County, southeastern Kentucky, have an average thickness of 0.65 m (range: 0.48 to 0.74 m) and an average ash yield of 5.4% (range: 3.79 to 7.11%). The average Hg content of the whole seam channel samples was 0.084 ppm, with 17 component bench samples ranging from 0.002 to 0.515 ppm Hg. The highest Hg value was from a near-roof bench, which also had the highest sulfur content ($S_{\text{tot}}=5.75\%$, with pyrite accounting for 46% of the mineral matter). However, three of highest Hg values were from bottom or middle benches, with the second highest Hg value (0.430 ppm) occurring in a middle bench sample containing little ash (1.88%) and sparse pyritic sulfur (0.09%; Sakulpitakphon et al., 2004). This suggests that Hg_{org} dominates the low-sulfur coal, and Hg_{pyr} dominates the high-sulfur coal. Clausthalite (PbSe) observed in the Manchester coal and may also be a Hg concentrator (Hower and Robertson, 2003).

8. General topics

As discussed above, syngenetic or epigenetic mercury accumulation is very possible in coal.

8.1. Syngenetic processes

Two situations may enrich Hg in peat bogs and their coals: (a) if thermal Hg-bearing waters or

⁸ The bench thicknesses were not given.

Table 7

Mercury distribution in the columns of four anthracitic beds, east Donbas, Shakhtisk-Nesvetayevsk geological–industrial region

| Bench | Bed i ₂ | | | Bed i ₃ ^{lower} | | | Bed i ₃ ^{upper} | | | Bed i ₆ | | |
|-----------------|--------------------|----------|-------------|-------------------------------------|-------|-------------|-------------------------------------|----------|-------------|--------------------|----------|-------------|
| | Ash (%, dry) | S (%) | Hg (ppm) | Ash (%, dry) | S (%) | Hg (ppm) | Ash (%, dry) | S (%) | Hg (ppm) | Ash (%, dry) | S (%) | Hg (ppm) |
| Near the roof | 18.0 | 2.5 | 10.6 | 21.4 | 3.0 | 5.1 | 25.5 | 2.5 | 3.5 | 30.2 | 3.5 | 4.8 |
| Upper | 11.0 | 2.1 | 2.8 | 18.2 | 1.9 | 1.5 | 16.6 | 2.4 | 3.1 | 15.3 | 2.5 | 1.5 |
| Lower | 7.5 | 1.1 | 0.9 | 14.2 | 2.9 | 3.4 | 12.5 | 1.5 | 1.3 | 13.2 | 1.5 | 1.1 |
| Near the bottom | 16.8 | 1.1 | 4.1 | 16.4 | 1.5 | 2.4 | 48.0 | 1.7 | 0.9 | 52.3 | 1.8 | 0.7 |

Compiled from: (Kizilstein, 2002, p. 63–64).

volcanic ash enter the peat bogs; (b) if syngenetic Hg-bearing pyrite is abundant in the coal.

8.1.1. Volcanic enrichment

Until recently, Hg enrichment in coals from volcanism was unknown. However, Canadian data now show that this is very possible. On a generally positive correlated “ash yield vs. Hg content” plot for Alberta subbituminous coals (Goodarzi and Goodarzi, 2004), a sharp Hg anomaly was detected in a 3.5 cm bentonite parting within a 94.5-cm thick coal bed. While the weighted average Hg concentration of the coal without the parting was only 0.014 ppm, the bentonite contains as much as 1.270 ppm! Because this occurrence corresponds with strong Hg anomalies noted in tuff layers among marine black shales of the Pai-Khoi and Northern Urals (Yudovich et al., 1986), the anomaly is undoubtedly volcanogenic.

8.1.2. Hg-enrichment of high-sulfur coal benches

In the Section 6, examples were given of syngenetic Hg enrichment in the pyrites of sulfur-rich coal benches at the top and bottom of coal beds (Kizilstein, 2002; Mardon and Hower, 2004; Mastalerz et al., 2004; etc.). Such cases are probably very numerous. For example, an anomalously high Hg content (0.37 to 0.66 ppm) was observed near the top and bottom margins of the relatively high ash ($A^d=13.2$ to 39.9%), Paleocene coal bed of Wyoming (Wyodak, Roland); the mercury content is only 0.05 ppm in throughout the middle benches of this 21 m thick bed (Drever et al., 1977). Because sulfur is distributed in a similar manner throughout the bed, the marginal Hg distributions seem to be associated with sulfides that formed by diagenetic sulfate-reduction at the peat/sediment geochemical barrier.

8.2. Thermal epigenetic processes

It is assumed that thermal epigenetic Hg enrichment in coal occurs in three ways: (a) epigenetic Hg-bearing sulfides develop in coals (including proper Hg minerals); (b) vapor phase Hg is sorbed by earlier-formed syngenetic pyrite; (c) mercury in hydrothermal solutions is sorbed by coal organic matter.

As noted above, Hg anomalies are often associated with hydrothermal mineralization. Detailed studies have been performed on the Nikitov ore fields and on the south wing of the Donbas Northern Anticline. In this region it is likely that hydrothermal activity was synchronous with, and enhanced, coal metamorphism. An epigenetic origin for Hg is indicated where Hg occurs with other likely epigenetic sulfides (Pb, Zn, Sb, As and Ag sulfides) present in joint fissures. For example, in Lisichansk region, Donbas, there is a direct correlation between the concentration of Hg in the coal bed and the concentration of *secondary* pyrite and carbonate in the uppermost fractured benches of the coal bed. These concentrations vary laterally. In a distance of only 25 m along strike, Hg contents can vary by hundreds of times, and the amount of Hg in the coal is substantially greater where joint fissures are observed in the mines. Indeed, the highest Hg contents (up to 10 ppm) are not observed in coal, but in hydrothermal pyrites and hydrothermal breccia cementations associated with joints and fissures. In coal, the main Hg concentrator is late-stage hydrothermal pyrite (Tkach, 1966).

A detailed study identified no less than three stages of mineralization in the Donetsk basin (Dvornikov and Kirikilitza, 1987). *The earliest stage* is represented by fibrous and columnar quartz, with maximum development occurring between 360 and

380 °C. The second stage is represented by quartz, ankerite and calcite with disseminated sphalerite, galena and pyrite; maximum development occurring between 320–380 and 180–240 °C. The final (proper Hg-bearing) stage (60–120 °C) involved the formation of hydromica, dickite and chlorite with cinnabar (HgS) and millerite (NiS) impregnations and cleat fillings.

As a rule, the main carrier of epigenetic Hg in coal is pyrite. The average Hg content of such pyrite is 0.42 ppm, but individual values may reach tens of ppms. Only during the latest stage (which does not occur in all places!) do HgS and even native Hg⁰ sometimes make substantial contributions to the total Hg concentration. The Hg_{org} contribution can only be detected when Hg background contents are low. The most common mineral related to enhanced epigenetic Hg in coal is hydrothermal dickite, which is especially common in anthracites within anticlinal structures.

The Nikitov Hg-ore deposit is situated along the Gorlov anticline axis, which is a western branch of the main Donbas anticline structure. During its history, more than 30 kt of Hg have been mined from the Nikitov Hg-ore deposit (Kolker et al., 2002). This 15×1-km mineralized zone trends SE to NW and consists of two steeply-dipping ore zones. The host rocks are Pennsylvanian (Middle Carboniferous) coal-bearing cyclothems consisting of alternating coals, argillites, siltstones, and limestones. There are three ore-bearing sandstone horizons with a total thickness around 60 m: the Chigarniki, the Sofia, and the Cherny Kurgan (Black Tumulus). The ore field has a very complicated tectonic structure with additional faults and joint fissures. In general, Hg-ores (cinnabar and rarer stibnite, arsenopyrite, and pyrite) are controlled by the intersections of the latitudinal and longitudinal joint fissures. Wide primary Hg aureoles occur around ore bodies; they are distinguished in sandstones as well as in the coals.

Over a 75×60 km area where the Manchester coal bed and its stratigraphic correlatives are mined in adjacent Laurel and Clay counties of southeastern Kentucky, a total of 29 full-seam samples were collected. The Hg contents of the samples vary from 0.01 to 0.56 ppm with a clear increasing trend from northwest to southeast. Chlorine, As, Pb, and

vitrite R_{\max} values show similar trends, which further indicate structural control of the geochemical anomalies. For these reasons, it is very likely that metal-bearing solutions from the basement were introduced into coal-bearing strata through sheared zones. The process may be synchronous with coal metamorphism (thermal epigenesis). Additional evidence of epigenetic enrichment includes the association of coarse-grained Hg-bearing sulfides (pyrite and clausthalite) with inertinite (Sakulpitakphon et al., 2004).

An example from the Donbas (and also partially applicable to the Illinois Basin) shows that low-temperature hydrothermal processes (related or unrelated to coal metamorphism) are factors controlling the formation of epigenetic Hg-bearing mineralization in coals. Such a relation can be used to identify Hg-bearing coals in any region where Hg-mineralization is known in the host rocks (Kler and Nenakhova, 1981, p. 55). For example, in low-ash ($A^d=3.2\%$) Jurassic anthracites of the Nazar-Ailok deposit, Tadzhikistan, eight samples have high Hg concentrations—on average 115, and up to 254 ppm on an ash basis. The absence of a Hg–S correlation indicates the presence of Hg_{org}. In this case, Hg-enrichment in the coal also seems to be influenced by epigenetic hydrothermal processes. This is indirectly shown by the presence of telethermal Alpine-type ores in the Meso–Cenozoic strata of the mountains bordering the Tadzhik depression. In particular, the Kshert Sb–Hg ore deposit occurs near the Nazar-Ailok coal deposit (Valiev et al., 1993).

9. Conclusions

The global average Hg content of coal, expressed on a whole-coal basis (the Clarke value for Hg in coal), is 0.10 ± 0.01 ppm, and is the same for bituminous, subbituminous, and lignite rank coals. However, if mercury contents are expressed as a part of the ash, these contents greatly increase; on an ash-basis, bituminous and subbituminous A and B rank coals (hard coals) contain an average $0.87 (\pm 0.08)$ ppm Hg, whereas lignite and subbituminous C rank coals (brown coals) contain an average $0.62 (\pm 0.06)$ ppm Hg. Therefore, in general, Hg is a very *coalophile element*. It has a strong affinity for inorganic and

organic coal matter, but is obligatory authigenic (see monograph by Yudovich and Ketris, 2002 for details).

There are some coals enriched in Hg by one to two orders of magnitude above the Clarke value. Such coals are known in the Donbas (Ukraine), Russian Far East, parts of the Appalachian Basin (USA), Gulf Coast (USA), SW China, and in some other coalfields. Mercury in these coals is usually accompanied by other trace sulfophile elements (such as: As, Se, Pb, Cu, and Zn).

In low-sulfur coals, which are generally poor in Hg, only two Hg sites dominate: Hg_{org} and Hg_{sulfide} (commonly pyritic mercury, Hg_{pyr}). In more sulfur-rich coals, the Hg content is usually higher, and the Hg_{pyr} contribution also increases. In the unique Hg-enriched Donbas coals, both HgS and metallic mercury (Hg⁰) also occur.

Because Hg tends to concentrate in pyrite, the removal of pyrite tailings from coals results in lower Hg concentrations. Pyrite tailings are a potential feedstock for the industrial recovery of Hg and even more valuable elements.

Because of the extremely strong affinity of Hg²⁺ for humic matter, syngenetic (or early epigenetic) Hg accumulation in peats or lignites is theoretically possible. Indeed, some Hg accumulations in tropical and temperate zone peats are equal to or greater than those in coals. Until recently, such Hg accumulations in coals were unknown. However, syngenetic volcanogenic Hg accumulations in Canadian coals has been recently discovered.

The most important type of Hg enrichment in coals involves epigenetic, low-temperature hydrothermal processes. The Nikitovka (Ukraine), Warrior (USA), and Guizhou (China) basins provide good examples. In the two latter coal basins, the paragenetic association Hg–As–Au–Tl is similar to known Carlin-type Au deposits.

The most Hg-enriched coals are located in the Donbas–Donetsk coal basin, which is situated in the Ukraine and, in its eastern part, Russia. There are many coalfields in Donbas that are enriched in Hg by one order of magnitude above the coal Clarke level. The high concentrations of Hg in the Donbas coals are due to Hg-bearing hydrothermal mineralization. The long-term mining, combustion, gasification and coking of the Hg-bearing Donbas coals have created very serious environmental problems in the Ukraine.

Acknowledgements

James Hower kindly and selflessly edited the original Russian-to-English translation of this manuscript. Kevin R. Henke and Jeff Quick (the reviewers) presented us a lot of very important notes, corrections and references. We are very appreciative to our reviewers. James Hower, Kevin R. Henke, Alice Marksberry, Robert Finkelman, Aurora Rubel and Fariborz Goodarzi have supplied us with many references; many thanks for their kindly help. Prof. B.S.Panov (Donetsk city, Ukraine) has kindly informed us about average Hg contents in Donbas coal; many thanks for his friendly service.

References

- Alberts, J.J., Schindler, J.E., Miller, R.W., Nutter Jr., D.E., 1974. Elemental mercury evolution mediated by humic acid. *Science* 184, 895–897.
- Andersson, A., 1970. Något om kvicksilvrets geokemi. *Grundförbättring* 23. Specialnummer 5, 31–40.
- Arbuzov, S.I., Nikiforov, A.Yu., Rikhvanov, L.P., Ershov, V.V., 2000. Trace elements in lignites of Taldu-Dyurgun coal deposit (Altai Republic) and its utility problems. *Itogi i perspektivy geol. izuchen. Gornogo Altaya: Mater. nauch.-prakt. conf. Gornogo Altai: Altai-Geo*, pp. 52–56. [Summaries and Prospects of Geol. Studies of the Mountain Altai, Proc. Sci.-Econ. Conf.].
- Baskov, E.A., Surikov, S.N., 1989. *Hydrotherms of the Earth*. Nedra [Entrails Publ. House], Leningrad. 245 pp.
- Belyaev, V.K., Pedash, E.T., Ko, N.A., 1989. Minor elements in coal and host rocks at the Shubarkol coal deposit. *Razved. Ohr. Nedr [Exploration and Conservation of Mineral Resources]* 11, 12–16.
- Bernatonis, V.K., Arkhipov, V.S., Zadvizhkov, M.A., Preis, Yu.I., Tikhomirova, N.O., 2002. Geochemistry of the Great Vassyugan Bog plants and peats. *The Great Vassyugan Bog: Recent Status and Development Processes*. Tomsk: Inst. optiki atmosphery SO RAN [Atmosphere Optics Institute, Siberian Division of the Rus. Acad. Sci.], 204–217.
- Biester, H., Martinez-Cortizas, A., Birkenstock, S., Kilian, R., 2003. Effect of peat decomposition and mass loss on historic mercury records in peat bogs from Patagonia. *Environ. Sci. Technol.* 37, 32–39.
- Block, C., Dams, R., 1975. Inorganic composition of Belgian coals and coal ashes. *Environ. Sci. Technol.* 9, 146–150.
- Bool, L.E., Helble, J.J., 1995. A laboratory study of the partitioning of trace-elements during pulverized coal combustion. *Energy Fuels* 9 (5), 880–887.
- Bouška, V., Pešek, J., 1999. Quality parameters of lignite of the North Bohemian Basin in the Czech Republic in comparison with the world average lignite. *Int. J. Coal Geol.* 40, 211–235.

- Boylan, H.M., Cain, R.D., Kingston, H.M., 2003. A new method to assess mercury emissions: a study of three coal-fired electric-generating power station configurations. *J. Air Waste Manage. Assoc.* 11, 1318–1325.
- Bragg, L.J., Oman, J.K., Tewalt, S.J., Oman, C.L., Rega, N.H., Washington, P.M., Finkelman, R.B., 1998. Coal quality (COALQUAL) database - version 2.0. Open-File Rep. (U. S. Geol. Surv.), 97–134 (unpaginated CD-ROM).
- Brownfield, M.E., Affolter, R.H., Cathcart, J.D., 1994. Element characterization of coals from the Franklin coal zone, Puget Group, John Henry No. 1 Mine, King County, Washington. *Abstr. Programs - Geol. Soc. Am.* 26 (7), A-215.
- Bushell, A.J., Williamson, J., 1995. Trace element distributions and associations in UK coals, in coal science. In: Pajares, J.A., Tascon, J.M.D. (Eds.) *Proc. 8th Int. Conf. Coal Sci.* vol. 1. Oviedo, Sept. 10–15 1995. Elsevier, Amsterdam, pp. 167–170.
- Bykadorov, V.S., Vyalov, V.I., Podkamenny, A.A., Shibanov, V.I., 2002. Ulugkhem Basin and other basins of the Tyva Republik. *Ugol'naya baza Rossii. T. III.* [Russian Coal Base. Vol. III]. Geoinformmark, Moscow, pp. 270–363.
- Carpi, A., 1997. Mercury from combustion sources: a review of the chemical species emitted and their transport in the atmosphere. *Water Air Soil Pollut.* 98 (3–4), 241–254.
- Casagrande, D.J., Erchull, L.D., 1976. Metals in Okefenokee peat-forming environments: relations to constituents found in coal. *Geochim. Cosmochim. Acta* 40, 387–393.
- Cecil, C.B., Stanton, R.W., Allshouse, S.D., Finkelman, R.B., Greenland, L., 1979. Geologic controls on element concentrations in the Upper Freeport coal bed. *Prepr. - Am. Chem. Soc., Div. Fuel Chem.* 24 (1), 230–235.
- Chiardia, M., Cupelin, F., 2000. Gas-to-particle conversion of mercury, arsenic and selenium, trough reactions with traffic-related compounds (Geneva)? Indication from lead isotopes. *Atmos. Environ.* 34, 327–332.
- Diehl, S.F., Goldhaber, M.B., Hatch, J., Kolker, A., Pashin, J.C., Koenig, A.E., 2000. Mineralogic residence and sequence of emplacement of arsenic and other trace elements in coals of the Warrior Basin, Alabama. *Proc. 19th Ann. Int. Pittsburgh Coal Conf.* (23–27 Sept. 2002). Pittsburgh Pa., 14 pp. CD-ROM.
- Diehl, S.F., Goldhaber, M.B., Hatch, J., 2004. Modes of occurrence of mercury and other trace elements in coals from the warrior field, Black Warrior Basin, Northwestern Alabama. *Int. J. Coal Geol.* 59, 193–208.
- Ding, Z., Zheng, B., Zhang, J., Long, J., Belkin, H.E., Finkelman, R.B., Zhao, F., Chen, C., Zhou, D., Zhou, Y., 2001. Geological and geochemical characteristics of high arsenic coals from endemic arsenosis areas in southwestern Guizhou Province, China. *Appl. Geochem.* 16, 1353–1360.
- Drever, J.I., Murphy, J.W., Surdam, R.C., 1977. The distribution of As, Be, Cd, Cu, Hg, Mo, Pb and U associated with the Wyodak coal seam, Powder River Basin, Wyoming. *Univ. Wyo. Contrib. Geol.* 15 (2), 93–101.
- Dronen, L.C., Moore, A.E., Kozliak, E.I., Seams, W.S., 2004. An assessment of acid wash and bioleaching pre-treating options to remove mercury from coal. *Fuel* 83, 181–186.
- Dvornikov, O.G., 1967a. On the Hg occurrence in the Bokovo-Khrustal'ny depression anthracites (Donetsk basin). *Dopov. Akad. Nauk Ukr. RSR [Compt. Rend. Ukr. Sov. Social. Rep. Acad. Sci.]*, Ser. B 29 (4), 293–298.
- Dvornikov, O.G., 1967b. On the Hg occurrence in the high volatile bituminous coals, Small Folded Structure region (Donetsk basin). *Dopov. Akad. Nauk Ukr. RSR [Compt. Rend. Ukr. Sov. Social. Rep. Acad. Sci.]*, Ser. B 29 (9), 828–830.
- Dvornikov, A.G., 1967c. Some peculiarities of the Hg-bearing coals, East Donetsk basin (Rostov district). *Dokl. Akad. Nauk SSSR [Compt. Rend. USSR Acad. Sci.]* 172 (1), 199–202.
- Dvornikov, A.G., 1981. Mercury modes of occurrence in Donetsk basin coals. *Dokl. Akad. Nauk SSSR [Compt. Rend. USSR Acad. Sci.]* 257 (5), 1214–1216.
- Dvornikov, A.G., Kirikilitsa, S.I., 1987. Mercury in Donetsk basin coals. *Nedra [Entrails Publ. House]*, Moscow. 155 pp.
- Feng, X., Hong, Y., 1999. Modes of occurrence of mercury in coals from Guizhou, People's Republic of China. *Fuel* 78 (10), 1181–1188.
- Feng, X.B., Sommar, J., Lindqvist, O., Hong, Y.T., 2002. Occurrence, emissions and deposition of mercury during coal combustion in the Province Guizhou, China. *Water Air Soil Pollut.* 139, 311–324.
- Fiene, F.L., Kuhn, J.K., Gluskoter, H.J., 1979. Mineralogic affinities of trace elements in coal. In: Rogers, S.E., Lemmon Jr., A.W. (Eds.), *Symposium on Coal Cleaning to Achieve Energy and Environ. Coals Proc.* Vol. 1. EPA, Washington, DC, Rep. EPA-600/7-79-098a, pp. 29–58.
- Filby, R.H., Shah, K.R., Sautter, C.A., 1977. A study of trace element distribution in the solvent refined coal (SRC) process using neutron activation analysis. *J. Radioact. Anal. J. Radioanal. Chem.* 37, 693–704.
- Finkelman, R.B., 1980. Modes of occurrence of trace elements in coal. PhD thesis. College Park, University of Maryland. 302 pp.
- Finkelman, R.B., 2004. Potential health impacts of burning coal beds and waste banks. *Int. J. Coal Geol.* 59, 19–24.
- Finkelman, R.B., Dulong, F.T., Stanton, R.W., Cecil, C.B., 1979. Minerals in Pennsylvania coal. *Pa. Geol.* 10 (5), 2–5.
- Finkelman, R.B., Bragg, L.J., Tewalt, S.J., 1990a. Byproduct recovery from high-sulfur coals. *Processing and Utilization of High-Sulfur Coals*, vol. III. Elsevier, Amsterdam, pp. 89–96.
- Finkelman, R.B., Palmer, C.A., Krasnow, M.R., Aruscavage, P.J., Sellers, G.A., Dulong, F.T., 1990b. Combustion and leaching behaviour of elements in the Argonne Premium coal samples. *Energy Fuels* 4, 755–767.
- Finkelman, R.B., Bostick, N.H., Dulong, F.T., 1992. Influence of an igneous intrusion on the element distribution of a bituminous coal from Pitkin County, Colorado. *Ninth Ann. Meet. The Soc. Org. Petrology (University Park, PA, July 23–24)* *Abstr. Progr.*, pp. 112–114.
- Georgakopoulos, A., Fernández-Turiel, J.L., Filippides, A., Llorens, J.F., Kassoli-Fourmaraki, A., Querol, X., Lopez-Soler, A., 1995. Trace element contents of the lava xylite/lignite and Ptolemais lignite deposits, Macedonia County, Greece. In: Pajares, J.A., Tascon, J.M.D. (Eds.), *Coal Science, Proc. 8th Int. Conf. Coal Sci.* vol. 1. Oviedo, Sept. 10–15 1995. Elsevier, Amsterdam, pp. 163–166.

- Ghosh, S.B., Das, M.C., Roy, R.R., Banerjee, N.N., 1994. Mercury in Indian coals. *Indian J. Chem. Technol.* 1, 237–240.
- Gluskoter, H.J., Ruch, R.R., Miller, W.G., Cahill, R.A., Dreher, G.B., Kuhn, J.K., 1977. Trace elements in coal: occurrence and distribution. *Illinois Geol. Surv. Circ.* 499 (154 pp.).
- Goetz, L., Springer, A., Pietra, R., Sabbioni, E., 1981. Mobilization of heavy metals from fossil-fueled power plants, potential ecological and biochemical implications: III. Heavy metal content in coals burnt in European power plants. *Rep. EUR-6998*, pt. III. 56 pp.
- Goodarzi, F., Goodarzi, N.N., 2004. Mercury in western Canadian subbituminous coal—a weighted average study to evaluate potential mercury reduction by selective mining. *Int. J. Coal Geol.* 58, 251–259.
- Greeson, P.E., 1970. Biological factors in the chemistry of mercury. *Mercury in the Environment. Prof. Pap. - U.S. Geol. Surv.* 713, pp. 32–34.
- Hatch, J.R., 1987. Element geochemistry. Geological investigations of the Vermillion creek coal bed in the Eocene Niland Tongue of the Wasatch Formation, Sweetwater County, Wyoming. *Prof. Pap. - U.S. Geol. Surv.* 1314-G (7), 121–131.
- Horvat, M., Nolde, N., Fajon, V., Jereb, V., Logar, M., Lojen, S., Jacimovic, R., Falnoga, I., Liya, Q., Faganelli, J., Drobne, D., 2003. Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. *Sci. Total Environ.* 304, 231–256.
- Hower, J.C., Robertson, J.D., 2003. Clausthalite in coal. *Int. J. Coal Geol.* 53, 219–225.
- Janda, J., Schroll, E., 1995. Geochemische Untersuchungen an Grafitgesteinen. *Int. Geol. Congr., 21st Sess. Pt. 1 Copenhagen.* pp. 40–53.
- Joensuu, O.I., 1971. Fossil fuels as a source of mercury pollution. *Science* 172 (3987), 1027–1028.
- Karabulut, S., Karabakan, A., Denizli, A., Yurum, Y., 2001. Cadmium (II) and mercury (II) removal from aquatic solutions with low-rank Turkish coal. *Sep. Sci. Technol.* 36, 3657–3671.
- Karasik, M.A., Dvornikov, O.G., 1963. On the Hg occurrence in the southern-eastern Donetsk basin. *Mineral. i geokhim. Pivden.-skhidn. chast. Donbasu [Mineralogy and Geochemistry of the Southern-Eastern Donetsk Basin]*. Kiev: AN URSR [Acad. Sci. Ukraine Soviet Socialist. Rep.], 53–67.
- Karasik, M.A., Dvornikov, A.G., 1968. Mercury content of the Donetsk basin coals and their industrial derivatives. *Moscow: ONTI VIEMS [Sci.-Techn. Dep., All-Union Inst. Econom. Geol.]*, 48 pp. (Ser.: *Geol. mestorozhd. polezn. iskop. Region. Geol.*, No. 6) [Ser.: *Geol. Depos. Mineral Resources. Regional Geology*, issue 6].
- Keeler, G.J., Glinsorn, G., Pirrone, N., 1995. Particulate mercury in the atmosphere: its significance, transport, transformation and sources. *Water Air Soil Pollut.* 80, 159–168.
- Kennedy, E.J., Ruch, R.R., Gluskoter, H.J., Shimp, N.F., 1971. Environmental studies of mercury and other elements in coal and lake sediments as determined by neutron activation analysis. *Nucl. Methods Environ. Res., Proc. Am. Nucl. Soc. Top. Meet. Columbia*, 205–215.
- Kerndorff, H., Schnitzer, M., 1980. Sorption of metals on humic acid. *Geochim. Cosmochim. Acta* 44, 1701–1708.
- Ketris, M.P., Yudovich, Ya.E., 2002. Method of calculation of the coal Clarke values. *Tr. - Inst. Geol.* 104, 111–117 [Trans. Geol. Inst., issue 104].
- Khairtdinov, I.A., 1971. On the mercury gas aoreols. *Geokhimiya [Geochemistry]* 6, 668–683.
- Khrustaleva, G.K., Andrianova, T.P., Medvedeva, G.A., Kvochkina, L.V., Ulanov, N.N., 2001. Geological aspects of coal conversion to liquid fuels: a review. *Geoinformmark, Moscow*. 55 pp.
- Kirkby, W.A., 1927. Mercury from coal tar. *J. Soc. Chem. Ind.* 46, 422R.
- Kizilstein, L.Ya., 2002. *Ecogeochemistry of Trace Elements in Coals. - Rostov-na Donu [Rostov-on the Don river]. SK NZ VSh [North-Caucasus Sci. Center of High School]*. 296 pp.
- Kizilstein, L.Ya., Kholodkov, Yu.I., 1999. Ecologically hazardous elements in coals of the Donets Basin. *Int. J. Coal Geol.* 40, 189–197.
- Kizilstein, L.Ya., Peretyat'ko, A.G., Gofen, G.I., 1989. Concentration of trace elements in coals in light of hard–soft acid–base concept. *Khim. Tverd. Topl. [Chem. Solid Fuels]* 2, 132–138.
- Kler, V.R., 1988. Minor element concentrations in the coals and coal-bearing formations. In: Kler, V.R., Nenakhova, V.F., Saprykin, F.Ya., Shpirt, M.Ya., Rokhlin, L.I., Kulachkova, A.F., Iovchev, R.I. (Eds.), *Metallogeny and geochemistry of coal-bearing and oil shale-bearing strata of the USSR: the regularities of the element concentrations and methods of their study*. Nauka [Science Publ. House], Moscow, pp. 67–142.
- Kler, V.R., Nenakhova, V.F., 1981. *Paragenetic Complexes of Mineral Resources of the Oil-Shale- and Coal-Bearing Strata*. Nauka [Science Publ. House], Moscow. 175 pp.
- Kolker, A., Finkelman, R.B., 1998. Potentially hazardous elements in coal: modes of occurrence and summary of concentration data for coal components. *Coal Prep.* 19, 133–157.
- Kolker, A., Panov, B.S., Landa, E.R., Panov, Y.B., Korchemagin, V.A., Conko, K.M., Shendrik, T., 1974. Trace-metal geochemistry and environmental implications of selected Donbas coals and associated mine water in the vicinity of Donetsk, Ukraine. *Proc. 19th Ann. Int. Pittsburgh Coal Conf. (23–27 Sept. 2002)*. Pittsburgh Pa., 12 pp. CD-rom.
- Kowalevski, A.L., 1974. *Biogeochemical Prospecting of Ore Deposits. Nedra [Entrails Publ. House]*, Moscow. 144 pp.
- Kuzubova, L.I., Shuvaeva, O.V., Anoshin, G.N., 2000. *Methyl Mercury in the Environment. Occurrence, Natural Origin, and Determination Methods. An Analytical Review*. Novosibirsk: GPNTB SO RAN (State Public Sci.-Res. Library, Siberian Division of the Rus. Acad. Sci.). 82 pp. (Ser.: *Ecologiya [Ecology]*, vyp [issue] 59).
- Lyons, C., Palmer, C.A., Bostick, N.H., Fletcher, J.D., Dulong, F.T., Brown, F.W., Brown, Z.A., Krasnow, M.R., Romankiw, L.A., 1989. Chemistry and origin of minor and trace elements in vitrinite concentrates from a rank series from the Eastern United States, England and Australia. *Int. J. Coal Geol.* 13, 481–527.
- Madsen, P.P., 1981. Peat bog records of atmospheric mercury deposition. *Nature* 293, 127–130.
- Mantoura, R.F.C., Dickson, A., Riley, J.P., 1978. The complexation of metals with humic materials in natural waters. *Estuar. Coast. Mar. Sci.* 6, 389–408.

- Mardon, S., Hower, J.C., 2004. Impact of coal properties on coal combustion by-product quality: examples from a Kentucky power plant. *Int. J. Coal Geol.* 59, 153–169.
- Martínez-Tarazona, M.R., Vega, J.M.G., García, A.B., 1997. Pyrite and trace elements in high-rank coals. In: Ziegler, A., et al. (Eds.), *Proc. 9th Intern. Conf. Coal. Sci.*, 7–12 Sept. 1997, vol. 1. DGMK, Essen, pp. 397–400.
- Mason, B., Moore, C.B., 1982. *Principles of Geochemistry*. Wiley, New York. 344 pp.
- Mastalerz, M., Hower, J.C., Drobniak, A., Mardon, S., Lis, G., 2004. From in-situ coal to fly ash: study of coal mines and power plants from Indiana. *Int. J. Coal Geol.* 59, 171–192.
- Meij, R., Vredenburg, L.H.J., Winkel, H.T., 2002. The fate and behavior of mercury in coal-fired power plants. *J. Air Waste Manage. Assoc.* 52 (8), 912–917.
- Meytov, E.S., 2001. Metal-bearing coals. *Ugol'naya baza Rossii. T. IV [Russian Coal Base. Vol. IV]*. Geoinformmark, Moscow, pp. 293–301.
- Palmer, C.A., Krasnow, M.R., Finkelman, R.B., d'Angelo, W.M., 1993. An evaluation of leaching to determine modes of occurrence of selected toxic elements in coal. *J. Coal Qual.* 12 (4), 135–141.
- Palmer, C.A., Mroczkowski, S.J., Finkelman, R.B., Crowley, S.S., Bullock Jr., J.H., 1993. The use of sequential leaching to quantify the modes of occurrence of elements in coal. 15th Ann. Intern. Pittsburgh Coal Conf. Proc. (Pittsburgh: Sept. 14–18 1998). Pittsburgh, 28 pp., CD-rom, PDF166.
- Palmer, C.A., Mroczkowski, S.J., Kolker, A., Finkelman, R.B., Bullock, J.H., Jr., 2000. Chemical analyses and modes of occurrence of selected trace elements in a Powder River Basin coal and its corresponding simulated cleaned coal. *U.S. Geol. Surv. Open-File Rep.* 00-323, 52 pp.
- Pavlova, L.S., Timofeev, A.A., 2000. Accompanying mineral resources in coals. *Ugol'naya baza Rossii. T. I. [Russian Coal Base. Vol. I]*. Geoinformmark, Moscow, pp. 120–121.
- Pentari, D., Foscolos, A.E., Perdikatis, V., 2004. Trace element contents in the Domeniko lignite deposit, Ellassona basin, Central Greece. *Int. J. Coal Geol.* 58, 261–268.
- Porritt, R.E., Swaine, D.J., 1976. Mercury and selenium in some Australian coals and fly-ash. *Aust. Inst. Fuel. Conf.*, Sydney, NSW, Preprint, Pap. 18, pp. 18.1–18.9.
- Querol, X., Fernández-Turiel, J.L., López-Soler, A., 1995. Trace elements in coal and their behaviour during combustion in a large power station. *Fuel* 74, 331–343.
- Querol, X., Klika, Z., Weiss, Z., Finkelman, R.B., Juan, R., López-Soler, A., Plana, F., Kolker, A., Chenery, S., 2001. Determination of element affinities by density fractionation of bulk coal samples. *Fuel* 80, 83–96.
- Ren, D., Zhao, F., Wang, Y., Yang, S., 1999. Distribution of minor and trace elements in Chinese coals. *Int. J. Coal Geol.* 40, 109–118.
- Roos-Barraclough, F., Martínez-Cortizas, A., García-Rodeja, E., Shotyk, W., 2002. A 14500 year record of the accumulation of atmospheric mercury in peat: volcanic signals, anthropogenic influences and a correlation to bromine accumulation. *Earth Planet. Sci. Lett.* 202, 435–451.
- Rösler, H.J., Beuge, P., Schrön, W., Hahne, K., Bräutigam, S., 1977. Die anorganischen Komponenten der Braunkohlen und ihre Bedeutung für die Braunkohlenerkundung. *Vorträge zum Berg- und Hüttenmännischen Tag 1976 in Freiberg*. Freiberg, 53–70 (Freib. Forschungsh., C331).
- Ruch, R.R., Gluskoter, H.J., Kennedy, E.J., 1971. Mercury content of Illinois coals. III. *State Geol. Surv. Environ. Geol. Notes* 43 (15 pp.).
- Ruch, R.R., Gluskoter, H.J., Shimp, N.F., 1974. Distribution of trace elements in coal. EPA, Washington, DC. *Environ. Protect. Technol. Ser. EPA-650-2-74-118*. 49 pp.
- Russian Coal Base, 2002. Coal basins and coal fields of the eastern Siberia. Southern part. *Geoinformmark, Moscow*, pp. 363–475.
- Sabbioni, E., Goetz, L., Springer, A., Pietra, R., 1983. Trace metals from coal-fired power plants: derivation of an average data base for assessment studies of the situation in the European Communities. *Sci. Total Environ.* 29, 213–227.
- Sakulpitakphon, T., Hower, J.C., Schram, W.H., Ward, C.R., 2004. Tracking mercury from the mine to the power plant: geochemistry of the Manchester coal bed, Clay County, Kentucky. *Int. J. Coal Geol.* 57, 127–141.
- Saukov, A.A., 1946. *Geochemistry of Mercury*. Moscow, 1946. 80 pp. (Proc. Inst. Geol. Sci. Acad. Sci. USSR, 78, No. 17).
- Scherbakov, V.P., Dvornikov, O.G., Zakrenichna, G.L., 1970. New data about mercury modes of occurrences in Donetsk basin coals. *Dopov. Akad. Nauk Ukr. RSR [Compt. Rend. Ukr. Sov. Social. Rep. Acad. Sci.]*, Ser. B 2, 126–130.
- Sedykh, A.K., 1997. *Uglovsk coal basin. Ugol'naya baza Rossii. T. V. Kn. 1 [Russian Coal Base. Vol. V, issue 1]*. Geoinformmark, Moscow, pp. 115–174.
- Senior, C.L., Zeng, T., Che, J., Ames, M.L., Sarofim, A.F., Olmez, I., Huggins, F.E., Shah, N., Huffman, G., Kolker, A., Mroczkowski, S., Palmer, C., Finkelman, R., 2000. Distribution of trace elements in selected pulverized coals as a function of particle size and density. *Fuel Process. Technol.* 63, 215–241.
- Seredin V.V., 1998. New type of Au-PGE mineralization in the Late Cenozoic coal-bearing strata of the Pacific coast. *Tes. dokl. godichn. ses. VMO (Mosc. otd.)*. [Abstr. Annual Ses. All-Russian Mineral. Soc. Moscow Divis.], Moscow, 80–81.
- Seredin, V.V., Danilcheva, J.A., 2000. Hazardous elements in metalliferous coal deposits of the Russian Far East. *International Geological Congress. 31st Session, Rio de Janeiro, Brazil (6–17 Aug., 2000)*. Congress Program. *Geol. Surv. Braz.*, Rio de Janeiro, p. 3950.
- Seredin, V.V., Povarennykh, M.Yu., 1995. First finding of the platinum minerals in coals. *Dokl. Ross. Akad. Nauk* 342 (6), 801–803.
- Seredin, V.V., Shpirt, M.Y., 1995. Metalliferous coals: a new potential source of valuable trace elements as by-products. In: Pajares, J.A., Tascón, J.M.D. (Eds.), *Coal Science, 8th ICCS Proc.*, vol. II. Elsevier, Amsterdam, pp. 1649–1652.
- Seredin, V.V., Povarennykh, M.Yu., Shpirt, M.Ya., 1994. Platinum mineralization in Russian coal deposits. 7-y Mezhdunarod. platinovyi symposium (Moscow: 1–4 Aug. 1994). *Tes. docl. Moscow: Moscow contact, 102*. [7th Int. Platinum Sympos. Abstr.].

- Seredin, V.V., Danilcheva, J.A., Cherepovsky, V.F., Vassianovich, A.M., 1999. Ge-bearing coals of Russian Far East deposits: an example from the Luzanovka openmine. In: Li, B.Q., Liu, Z.Y. (Eds.), *Prospects for Coal Science in 21st Century*. Sci. Technol. Press, Shanxi, pp. 137–140.
- Shotyk, W., Goodsite, M.E., Roos-Barracough, F., Frei, R., Heinemeier, J., Asmund, G., Lohse, C., Hansen, T.S., 2003. Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the ^{14}C “bomb pulse curve”. *Geochim. Cosmochim. Acta* 67, 3991–4011.
- Shpirt, M.Ya., 2002. Transformations of mercury and its compounds at the coal use. *Chim. tverd. topliva [Solid Fuel Chemistry]* 5, 73–86.
- Shvatsev, S.L., 1998. *Hydrogeochemistry of Hypergenesis Zone*. (2nd edition, revised). Nedra [Entrails Publ. House], Moscow. 366 pp.
- Skogerboe, R.K., Wilson, S., 1981. Reduction of ionic species by fulvic acid. *Anal. Chem.* 53, 228–232.
- Sokolov, V.A., Timofeev, A.A., Tereschenko, S.P., Logvinov, M.I., Faidov, O.E., Zhukovsky, N.T., Chernoviyants, M.G., 2000. Accompanying mineral resources in coals. *Ugol'naya baza Rossii*. T. I. [Russian Coal Base. Vol. I]. Geoinformmark, Moscow, pp. 82–83.
- Stewart, A.K., Massey, M., Padgett, P.L., Rimmer, S.M., Hower, J.C., 1934. Influence of a basic intrusion on the vitrinite reflectance and chemistry of the Springfield (No. 5) coal, Harrisburg, IL. Twentieth Annual Meeting of the Society for Organic Petrology, 21–24 September 2003, Arlington, VA, 59.
- Stock, A., Cucuel, F., 1934. Die Verbreitung des Quecksilbers. *Naturwissenschaften* 22 (22/24), 390–393.
- Stolzenburg, T.R., Stanforth, R.R., Nichols, D.G., 1986. Potential health effects of mercury in water supply wells. *J. Am. Water Works Assoc.* 78, 45–48.
- Stutzer, O., 1914. *Kohle (Allgemeine Kohlengologie)*. Gebr. Borntraeger, Berlin. 345 pp.
- Swaine, D.J., 1990. *Trace Elements in Coal*. Butterworths, London. 278 pp.
- Tkach, B.I., 1966. On the geochemical peculiarities of the mercury distribution in coal beds of the Lisichansk region (Donetsk basin). *Geokhimiya [Geochemistry]* 5, 610–616.
- Toole-O'Neil, B., Tewart, S., Finkelman, R.B., Akers, D.J., 1999. Mercury concentration in coal—unraveling the puzzle. *Fuel* 78, 47–54.
- Tuncali, E., Palmer, C.A., Finkelman, R.B., 2001. Characterization of Turkish coals: an example of international cooperation to develop a World Coal Quality Inventory (WoCQI). 26th Int. Tech. Conf. Coal Util. Fuel Systems Proc. (Sheraton Sand Key Clearwater, Florida, USA, March 5–8, 2001), pp. 647–658.
- U.S. Environmental Protection Agency, 1990. *The Clean Air Act Amendments of 1990, Section 114*. Washington, DC: Gov. Print. Office.
- U.S. Environmental Protection Agency, 1995. *Mercury Study Report to Congress*. EPA /600/ PYY/002 Aa.
- U.S. Environmental Protection Agency, 1996. *Study of hazardous air pollutant emissions from electric utility steam generating units - Interim Final Report*, EPA-453/R-96-013a.
- U.S. Environmental Protection Agency, 1997. *Mercury Study Report to Congress*. Vol. 1. Executive summary. Office of Air Quality Planning and Standards and Office of Research and Development; December. EPA-452/R-97-003.
- U.S. Environmental Protection Agency, 2000. *Method 7473. Mercury in solids and solutions by thermal decomposition, amalgamation and atomic absorption spectrometry*. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Update IVA. Washington, DC: Gov. Print. Office.
- U.S. Environmental Protection Agency, 2003. *Mercury*. <http://www.epa.gov/mercury> (Accessed December 2003).
- U.S. Geol. Survey, 1970. *Mercury in the environment*. Prof. Pap. - U.S. Geol. Surv. 713 (67 pp.).
- Valiev, Yu.Ya., Gofen, G.I., Pachadzhinov, D.N., 1993. Trace elements in Jurassic anthracites of the Nazar-Ailok deposit (Central Tadzhikistan). *Geokhimiya [Geochemistry]* 2, 243–251.
- Varshal, G.M., Koscheeva, I.Ya., Khushvakhitova, C.D., Velyukhanova, T.K., Tatsiy, Yu.G., Danilova, V.N., Tyutyunnik, O.A., Chkhetiya, D.N., Galusinskaya, A.Kh., 1999. Mercury complexing with humic acids as the most important stage of the mercury biosphere cycle. *Geokhimiya [Geochemistry]* 3, 269–275.
- Wang, Q., Shen, W.G., Ma, Z.W., 2000. Estimation of mercury emission from coal combustion in China. *Environ. Sci. Technol.* 4 (13), 2711–2713.
- Warwick, P.D., Crowley, S.S., Thomas, R.E., 1995. Distribution of HAPs trace elements in U.S. Gulf coast coals. Twelfth Ann. Int. Pittsburgh Coal. Conf. Proc. (Sept. 11–15), pp. 1146–1150.
- Yudovich, Ya.E., 1978. *Geochemistry of Fossil Coals*. Nauka [Science Publ. House], Leningrad. 262 pp.
- Yudovich, Ya.E., 2003. Notes on the marginal enrichment of germanium in coal beds. *Int. J. Coal Geol.* 56, 223–232.
- Yudovich, Ya.E., Ketris, M.P., 1988. *Geochemistry of Black Shales*. Nauka [Science Publ. House], Leningrad. 272 pp. (See also English short outline with a large bibliography: [Yudovich and Ketris, 1997](#)).
- Yudovich, Ya.E., Ketris, M.P., 1994. *Trace elements in black shales*. Nauka [Science Publ. House], Ekaterinburg. 304 pp.
- Yudovich, Ya.E., Ketris, M.P., 1997. *Geochemistry of Black Shales*. Prolog, Syktyvkar. 212 pp.
- Yudovich, Ya.E., Ketris, M.P., 2002. *Inorganic Matter of Coals*. URO RAN [Ural Division of the Russian Acad. Sci.], Ekaterinburg. 422 pp.
- Yudovich, Ya.E., Zolotova, V.V., 1994. Trace elements in the Pechora Basin coals. *Narodn Khoz-vo Resp. Komi [Nat. Econ. Rep. Komi.]* 3, 16–25.
- Yudovich, Ya.E., Ketris, M.P., Merts, A.V., 1985. *Trace elements in fossil coals*. Nauka [Science Publ. House], Leningrad. 239 pp.
- Yudovich, Ya.E., Ketris, M.P., Fridlender, N.G., Aldanazarov, R.A., 1986. *Geochemistry of mercury in the Pai-Khoi and North Urals black-shale formations*. *Geokhimiya [Geochemistry]* 6, 810–818.
- Zhang, J., Ren, D., Xu, D., 1999. Distribution of arsenic and mercury in Triassic coals from Longtoushan Syncline, Southwestern Guizhou, R. China. In: Li, B.Q., Liu, Z.Y. (Eds.), *Prospects for Coal Science in 21st Century*. Sci. Technol. Press, Shanxi, pp. 153–156.

- Zhang, M.Q., Zhu, Y.C., Deng, R.W., 2002. Evaluation of mercury emissions to the atmosphere from coal combustion, China. *AMBIO* 31 (6), 482–484.
- Zhang, J., Qui, Y., Ren, D., Liu, J., Zheng, C., 2004. Concentrations and occurrences of mercury and arsenic in coals from the Qianxi Fault Depression Area in Southwestern Guizhou, China. 12th Int. Conf. Coal. Sci. (2–6 Nov. 2003, Cairns, Australia), pap. No. 7B2. 9 pp.
- Zhang, J., Ren, D.Y., Zhu, Y.M., Chou, C.-L., Zeng, R., Zheng, B., 2004. Mineral matter and potentially hazardous trace elements in coals from Qianxi Fault Depression Area in Southwestern Guizhou, China. *Int. J. Coal Geol.* 57, 49–61.