Mercury and trace element contents of Donbas coals and associated mine water in the vicinity of Donetsk, Ukraine.

1. Introduction

Metal-enriched coals are present in the Donets Basin of eastern Ukraine and adjacent portions of Russia. Within Ukraine, approximately 10 billion tons of coal has been extracted during the 200 years of mining in the Donbas region, primarily in the Donetsk-Makeevka and Central mining districts (Panov et al,, 1999). Mineralization of the region has resulted in metal enrichment of these coals, and formation of sedimentary-hosted mercury deposits, in the Nikitovka ore field. Use of indigenous mercury-enriched coal in the coking by-product industry, metallurgical plants, coal-fired electric-generating stations, as well as its use in households, has led to widespread contamination by mercury, arsenic, lead, and other toxic substances (Panov et all, 1999; Kizilshtein and Kholodkov, 1999). The Donets Basin presents a good opportunity to study the contribution of mercury to the environment from anthropogenic sources, a topic that is especially important in light of its behavior as a global pollutant.

In order to assess the environmental and potential human health impact of present-day coal use in and around Donetsk, we sampled coal and associated mine waters in active Donbas mines. While many of the mines which produced the most metal-enriched coal have been closed, coal exceeding U.S. and western European averages for mercury and other metals is currently being extracted and used by utilities and other industrial applications in the region, as well as for domestic heating where heating is not centralized. The present study concentrates on coals from mines active at the time of sampling (2000-2005). In addition, we sampled coal from abandoned mercury mine workings at the Nikitovka mining camps in Corlovka, formerly produced as a byproduct of the mercury operation, and surface waters in catchment or mine tailings ponds exposed on the former mercury workings. The major goals of the study are first, to characterize trace element contents of coals from active mines, and secondly, to assess the potential for dispersion of toxic elements such as mercury, especially, in the vicinity of the former mercury mine workings. Results on trace constituents of Donbas coals presented here complement recent studies of the structural/tectonic, thermal/ coalification, and paleoecologic /paleoclimatologic history of the Donets Basin.

2. The Donets Basin

The Donets Basin (Donbas) is located in the southeastern portion of the Eastern European craton, within Ukraine and the Rostov area of Russia (Fig. 1). The Donbas occupies the southeastern segment of the Dniepr-Donets Basin, a Late Devonian rift structure extending in a WNW to F.SE direction and covering some 60,000 km^2 (Stovba et al., 1996; Panov, 1997). A thick sequence of Paleozoic and Mesozoic strata accumulated within the paleorift, including a Carboniferous section in excess of 12 km, as shown by seismic reflection data (Stovba et al, 1996; Maystrenko et al., 2003). Deformation of the sedimentary sequence within a portion of the Donets Basin known as the Donbas Foldbelt, takes the form of regionally extensive folds, thrust faulting, and inversion (Stovba and Stephenson, 1999; Spiegel etal., 2004). This portion of the Donbas is characterized by a

WNW-ESE trending Main Anticline that occupies the central portion of the Basin, paralleled by synclines to the north and south. Dips of beds steepen inward towards the center of the Basin as the Main Anticline is approached, and become more gradual at the margins of the Basin.

3. Donbas coal

Economic coal beds in the Donbas occur primarily in Serpukhovian (Upper Mississippian), Bashkirian (Lower Pennsylvanian), and Moscovian (Middle Pennsylvanian) strata. More than 330 coal beds are present, of which 130 are more than 0.45 m thick; the thickness of coal beds worked ranges from 0.7 to 1.2 m (Panov et al, 1999; Sachsenhofer et al, 2003). Carboniferous lithostratigraphic divisions are designated by English letters in alphabetical order from bottom to top in the section. Major lithologic divisions are designated by capital letters whereas coal zones are designated by lower case letters (Lazarenko et al, 1975; Sachsenhofer et al,, 2003). Sub-divisions within these zones have number designations that also increase upward. Coals determined in this study include Serpukhovian (c,), Bashkirian (g2), and Moscovian (K3fleft, b.5.7 m_H,3) samples (Fig. 2). This stratigraphic range, c,, to m3 encompasses all but the uppermost Moscovian and lowermost Serpukhovian coal beds produced in the region.

Recent studies have focused on the coalification and thermal history of the Donets Basin (Sachsenhofer et al, 2002; Spiegel et al, 2004). and the implications of maceral and biomarker indicators for Carboniferous paleoecology and paleoclimatology (Sachsenhofer et al, 2003; Izart et al. 2006). Vitrinite reflectance patterns indicate that coalification along the Main Anticline is syn-deformational, but displacement of reflectance isoclines along thrusts indicates that these later structures postdate coalification (Sachsenhofer et al, 2002).

4. Methods (water samples)

To determine contents of mercury and other metals in mine water associated with coal production, mine water samples were taken from the three underground mines noted above. Mine drainage water was sampled underground from flowing collection ditches along working drifts, and/or at central water collection systems, either undei ground or at surface discharge points. In addition, surface water from mercury-mine catchment or tailings ponds at the Nikitovka mine site were collected to determine its water quality and the potential for uptake of mercury and other metals in fish caught by local residents. For comparison, lake-water from a residential part of Gorlovka was sampled, as well as water from a natural spring emanating nearby the Nikitovka mines and periodically consumed by local residents at times when their tap water is unavailable.

Field measurements for mine waters included water temperature, pi I, and conductivity. Filtered samples (0.2 um) for major anion analysis were collected in 50 ml plastic bottles. Samples (filtered and unfiltered) for major cation analysis (by 1CP-0ES) and trace element analyses (by ICP-MS; Hg by cold vapor atomic absorption spectroscopy) were collected in 60 ml teflon bottles and acidified in the field (0.5 ml to -1% v/v) with concentrated nitric acid. The total (soluble + recoverable from particulates) concentration of trace elements was obtained from the unfiltered, acidified samples which were completely digested using concentrated, double-distilled nitric and hydrofluoric acids. Filtered, unacidified samples were used foranion analysis by ion-chromatography. Alkalinity was determined in the laboratory by titration. Water sampling quality assurance included collection and analysis of field and laboratory blanks as well as analysis of field replicates. To determine the amount and type of potential contamination, field and field filter blanks were collected under the same ambient conditions as the collection of samples.

5. Water chemistry

Trace element data, both dissolved and total, are given in Appendix A, along with Ukrainian and U.S. (U.S. Environmental Protection Agency, 200S) water quality standards. These results are summarized in Table 3 for some elements of interest.

Mercury concentration in all the mine drainage water samples is less than 0.1 ug/L, well below U.S. drinking water standards (2 ug 1., Mercury in Gorlovka surface waters is also below the drinking water standard, with the highest value (1.7 ug/L) for a marshy area near the Nikitovka mercury plant. The relatively low dissolved mercury values reflect the very limited solubility of cinnabar, the primary host of mercury in the Nikitovka deposits. The surface waters show significantly greater values for arsenic (60-285 ppm), compared to ground waters including the coal mine waters and the Corlovka natural spring.

For the coal mine waters, partitioning of Co, Ni, Zn, and Pb to suspended solids was evident, even though overall levels were low. Among these samples the concentrations of trace elements were somewhat higher in the most saline water sampled, from the Glubokaya mine (Appendix A). The neutral to alkaline pH values seen throughout may reflect the use of lime and other agents on mine walls for dust control.

6. Discussion

Mine waters samples from the Glubokaya, Oktyabrskaya, and Artema Mines have concentrations for most trace elements that fall within ranges typically seen in natural waters (Hem, 1985), reflecting the fact that pyrite, the primary carrier of metals, is stable at subsurface conditions. Even in water from a Gorlovka spring emanating within a few hundred meters of the mercury mines, concentrations of trace metals such as Hg, As, Cd, Se, and Pb are well below drinking water standards. Surface waters collected in Gorlovka, including catchment or tailings ponds on the Nikitovka mine site show acceptable mercury levels, even meeting drinking water standards. This is consistent with cinnabar-hosted mercury, as its solubility under aqueous conditions is very low (but is enhanced in the presence of dissolved organic matter; Waples et. al., 2005). High levels of arsenic in surface waters, coal, and soils, suggest that it may be a confounding health factor when considered with elevated mercury levels in the area, if arsenic is found to be present in drinking water.

References

1.ASTM International (ASTM), 2007. ASTM D 4596-07. standard practice for collection 01 channel samples of coal in a mine. Annual Book of ASTM Standards 2007, Section /Petroleum Products. Lubricants and Fossil Fuels: V. 05.06. Caseous fuels: coal and coke. 3

pp.

2.Belkin. HE., Warwick, P.D.. Zheng. B.S., Zhou, DX. Finkelman. RJ3.. 1998. High arsenic coals related to sedimentary rock-hosted gold deposition in southwestern Gtiizhou Province. Pittsburgh Coal Conference. InCD-ROM. Pittsburgh. PA. 5 pp.

3.Bragg. Oman, K..Tewalt. S.J.. Oman. C.L. Rega. N.H.. Washington. P.M., Finkelman. R.B.,

199S. U.S. Geological Survey Coal Quality (COALQJJAL) Dathase: Version 2.0. U.S. Geological Survey Open-Kile Report 97-134. InCD-ROM.

4.Brownfleld. M.E.. Arbiter. R.H.,

Cathcart. J.D.. Johnson, S.Y.. Brownhcid. I.K.. Rice. 2005. Geologic setting and characterization of coals and the modes of occurrence ol selected elements from the Franklin coal zone. Puget Group, lohn IIenr\ No i mine. King County. Washington, USA. International journal of Coal Geology 63, 247-275.

5.Conko. KM. land* E.R., Kolker. A,, Koziov, K.. Gibb. H.J., 2007. Mercury and arsenic in the soil and water of Gorlovka, Ukraine: Society for Environmental Toxicology and Chemistry (SEfAC) Noith America 2Sth Annual Meeting, Milwaukee. Wl. November. 2007, abstracts, p. 226.

6.Dai, S., Sun. Y.. Zeng, R., 2006. Enrichment of arsenic, antimony, mercury, and thallium in a

Late Permian anthracite from Xingrcn. Guizhou. Southwest China, International journal of Coal Geology 66.217-226.

7.de Boorder. H.. Panov. B.S., Westerhof. A.B., Korchemagin. VA, 1995. Tectonic setting, deep

faults and mercury mineralization in Almaden, Spain, and Nikitovka, Ukrain affinities and contrasts: London. Transactions of the Institution of Mining and Metallurgy. Section B (Applied Earth Science), p. B66-B79.

8. Ketris, M.P., Yudovich, Ya.E., 2009. Estimations of Clarkes for Carbonaceous biolithes: world averages for trace element contents in black shales and coals. International Journal of Coal Geology 78,135-148.

9.Kiztlshtein, L.Y., Kholodkov, Y.I., 1999. Ecologically hazardous elements in coals of the Donets Basin. International Journal of Coal Geology 40,189-197.

10.Kolker, A, Bel kin, H.E., 2007. Characteristics of mercury-rich and extreme mercmy-rich coals in the Donbas region of Ukraine and Guizhou Province, China. Proceedings of the International Conference on Coal Science and Technology, Nottingham. UK. August, 2007. 6 pp.

11.Kolker. A., Panov, B.S.. Landa. E.R.. Panov, Y.B., Korchemagin. VA, Conko. KM. Shendrik T., 2O02. Trace-metal geochemistry and environmental implications of selected Donbas coals and associated mine water in the vicinity of Donetsk Ukraine, Proceedings, Nineteenth Annual International Pittsburgh Coal Conference, Pittsburgh, PA CD-ROM. 12 p.

12.Korchemagin, VA, 1977. Tektonik und geologische Entwicklund des Lagers fatten be-
zirkes von Nikitovka (Donez-Becken, UdSSR), Freiberger Forschungshefte, C 329.
Leipzig, pp. 69-82. in German.