

THE DISTRIBUTION OF COAL-RELATED ORGANIC POLLUTANTS IN ENVIRONMENT FROM UPPER SILESIAN INDUSTRIAL REGION

Ádám Nádudvari¹, Monika J. Fabiańska²

¹ Institute for Ecology of Industrial Areas, Poland; ² University of Silesia, Poland

Introduction

The aim of the study was to identify polycyclic aromatic hydrocarbons (PAHs) in coal wastes of several types such as fresh, water-washed, self-heated, together with river water and river sediments from the Bierawka and Ruda Rivers polluted by coal dust, and rain water from erosion gullies of coal wastes dumps. For the research 190 samples were selected as a large representative group. The sample sets were compared to each other and also with published data. The another aim was to find a pattern in distribution relating to water washing, biodegradation, self-heating (called as secondary processes) in case of coal waste materials.

The extracts were not separated into different compound groups for GC–MS analyses due to the very low extractability of some of the samples. All extracts (water, coal waste and sediments) were analyzed on an Agilent 7890A gas chromatograph with, DB-5, DB-35 and DB-17MS columns coupled to a 5975C XL MDS mass spectrometer.

Results

The following substances were studied in detail: (a) 2 rings-compounds: indene and biphenyl; (b) with 3 rings: fluorenone, fluorene and its methyl derivatives, acenaphthylene, acenaphthene, retene; (c) with 4 rings: methylpyrenes, methylfluoranthenes, benzo[a]fluorene, benzo[b+c]fluorene, methylchrysenes, methylbenzo[a]anthracenes); (d) with 5 rings: picene, benzo[b]triphenylene, dibenzo[a,h]anthracene, benzo[b]chrysene; (e) with 6 rings: dibenzo[def,mno]chrysene (anthanthrene), dibenzopyrenes (a,h; a,l; a,i, a,e); (f) with 7 rings: coronene; and sulphur compounds such as 1,2,4-tritriolane, dibenzothiophene, benzo[b]tiophene, benzo[b]naphtho[2,1-d]thiophene, benzo[b]naphtho[1,2-d]thiophene, and benzo[b]naphtho[2,3-d]thiophene. Generally these compounds are present in petroleum products, crude oil, coal, and some of them are also formed by incomplete combustion. For evaluation of results these compounds were divided into groups according to their rings and types, i.e. sulphur containing PAHs.

Analyzing fresh coal waste samples most these compounds were found, except acenaphthylene, acenaphthene, 1,2,4-tritriolane, and benzo[b]tiophene. The most frequent substances were 4 rings PAHs and typically high relative percentages biphenyl, retene, 3-methylchrysene, benzo[a]fluorene and benzo[b+c]fluorene showed. In addition, this type of coal waste had elevated (because of lacking water-washing) naphthalene, methylnaphthalene relative contents (Nádudvari and Fabiańska, 2016a). Also C2- and C3-phenols presence indicates the absence of water-washing and bacterial/fungal degradation and oxidation of vitrinite particles which could release phenols (Nádudvari et al., 2016). In coal wastes from erosion gullies most of the studied compounds could be identified, except acenaphthylene, acenaphthene and benzo[b]tiophene. Typically retene, 4-methylpyrene, benzo[a]fluorene, benzo[b+c]fluorene and 3-methylchrysenes showed elevated contents. Also the typical

features was of low amounts (or absence) of naphthalene, methyl – and dimethylnaphthalenes and phenols in this sample group (Nádudvari and Fabiańska, 2016a; Nádudvari et al., 2016).

The self-heated coal wastes contained generally most of studied compounds, except acenaphthylene and low relative percentage of acenaphthene. Elevated relative percentages showed biphenyl, fluorenone, and retene. The presence of benzo[b]tiophene in several samples is related to the thermal cracking of organic material and expelled bitumen generated, which bitumen also contains abundant phenols, naphthalenes (Nádudvari and Fabiańska, 2016b). Furthermore, benzo[b]tiophene was mostly identified in crude oil (Valla et al., 2006) and that's why it was absent in fresh coal wastes and erosion gullies samples.

The most river sediments contained all compounds studied, with 4-ring PAHs dominating. Typically acenaphthylene, retene, benzo[a]fluorene and benzo[b+c]fluorene had high relative percentages. In these sediments coal dust occurs as dark layers, where PAHs diagnostic ratios indicated their pyrogenic origin (Nádudvari and Fabiańska, 2015). Also these river sediments contained C1- and C2-phenols (Nádudvari et al., 2016). In river water elevated relative contents of fluorenone, 2-methylfluorene, benzo[a]fluorene and benzo[b+c]fluorene were found. Several compounds could be identified in river water which are not water soluble e.g. indene, fluorenone, acenaphthylene. Probably they have industrial origin or come from air particulate matter. Rain water from erosion gullies did not contain the studied compounds.

The presence of 1,2,4-trithiolane (organosulfur compounds) in coal wastes from gullies, self-heated coal wastes and river sediments is related to mushroom flavour or fungi, which is result of ongoing decay of organic matter (<http://www.hmdb.ca/metabolites/HMDB39433>; Morita and Kobayasi, 1967).

Conclusions

In case of environmental aspects the presence of these harmful and carcinogenic organic compounds can increase more attention for coal waste dumps or coal dust pollution in environment. The presented research is in initial stage, however the achieved results are promising and it can be concluded, that secondary processes can influence and generate other compounds e.g. 1,2,4-trithiolane, or benzo[b]tiophene.

References

- Morita, K, Kobayashi, S., 1967. Isolation, structure, and synthesis of lenthionine and its analogs. *Chemical and Pharmaceutical Bulletin* 15(7), 988-993.
- Nádudvari, Á., Fabiańska, M.J., 2015. Coal-related sources of organic contamination in sediments and water samples of Bierawka River (Poland). *International Journal of Coal Geology* 152, 94-109.
- Nádudvari, Á., Fabiańska, M.J., 2016a. The impact of water-washing, biodegradation and self-heating processes on coal waste dumps in the Rybnik Industrial Region (Poland). *International Journal of Coal Geology* 154-155, 286-299.
- Nádudvari, Á., Fabiańska, M.J., Misz-Kennan, M., 2016. Distribution of phenols related to self-heating and water washing on coal-waste dumps and in coaly material from the Bierawka River (Poland). *Mineralogia Polonica* 46, No 1-2, 29-40
- Nádudvari, Á., Fabiańska, M. J. 2016b. Use of geochemical analysis and vitrinite reflectance to assess different self-heating processes in coal-waste dumps (Upper Silesia, Poland). *Fuel* 181, 102–119.
- Valla, J.A., Lappas, A.A., Vasalos, I.A., 2006. Catalytic cracking of thiophene and benzothiophene: Mechanism and kinetics. *Applied Catalysis A: General* 297, 90–101.