



Preliminary data on organic bounded heavy metals in sites affected by mining activity in Chiprovtsi district, NW Bulgaria

Предварителни данни за органичните комплекси и свързаните с тях тежки метали в почви, засегнати от минната дейност в Чипровския район, СЗ България

Tanja Stoilkova¹, Vassilka Mladenova¹, Tsvetan Kotsev², Zornitza Cholakova³, Ralf-Thomas Schmitt⁴

Таня Стоилкова¹, Василка Младенова¹, Цветан Коцев², Зорница Чолакова³, Ралф-Томас Шмит⁴

¹ Sofia University "St. Kliment Ohridski", 1504 Sofia, Bulgaria; E-mail: tstoilkova@gea.uni-sofia.bg; vassilka@gea.uni-sofia.bg

² Institute of Geography, Acad. G. Bonchev Str., Bl. 3, 1113 Sofia, Bulgaria; E-mail: tsvetankotsev@mail.bg

³ Department of Landscape Ecology and Environmental Protection, Sofia University "St. Kliment Ohridski", 15 Tzar Osvoboditel Blvd., 1504 Sofia, Bulgaria; E-mail: cholakova@gea.uni-sofia.bg

⁴ Museum fuer Naturkunde, Humboldt-Universitaet, Invalidenstrasse 43, D-10115 Berlin, Germany; E-mail: ralf-thomas.schmitt@rz.hu-berlin.de

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The three major mines in NW Bulgaria (Chiprovtsi Ag-Pb, Martinovo Fe and Govezhda Au (arsenopyrite) mines) and the ore processing carried out in the two ore-dressing plants near the town of Chiprovtsi from 1950 to 1999 have caused pollution of surface waters, channel sediments, soils, plants with heavy metal and metalloids (HMM). Because of the discharging of mine tailings in the Ogosta River channel before 1979 pollution of the alluvial soils in the floodplains many kilometers far from the mining area is established.

HMM are concentrated in grains of preserved primary ore minerals, in secondary minerals, sheet silicates with adsorbed pollutants.

Organic compounds with biogenic and anthropogenic origin have the potential to form complexes with heavy metals what may affect heavy metal desorption, solubility and mobility.

The aim of this study is to investigate the behaviors and interaction of heavy metals pollution and organic compounds in 3 soils profiles.

Sampling and description of the sampling sites

The sampling has been carried out in 2005 and 2006. Three sites differing in their position and therefore metal concentration were sampled.

The first one (A) is background reference point 500 m SW from Golyam Bukovetz mine tailings im-

poundment. It was sampled to a depth of 30 cm from three soil horizons in the following depths: A1 (0–2 cm), A2 (2–12 cm), A3 (12–27 cm).

The second one (B) is located at the water shed 100 m NE from the Golyam Bukovetz impoundment. The sampling was performed to a depth of 46 cm from four soil horizons in meadow without indication of tilling at least several decades. The following depth intervals have been studied: B1 (0–13 cm), B2 (13–23 cm), B3 (23–44 cm).

The third sampling site (C) is situated 35 km downstream from the Chiprovtsi mining area in agricultural land in floodplain of the Ogosta River left bank near the Gorno Tserovene village. The sampling was performed to 104 cm depth in intervals C1 (0–25 cm), C2 (25–43 cm), C3 (43–59 cm), C4 (59–104 cm).

Geochemistry

The fractions <63µm were analysed by X-ray fluorescence spectrometry (XRFS) and by ICP-AES for their major-, minor and trace-element contents. The organic components were analysed by GC-MS.

The soils in the region have high As, Pb, Zn and Cu background contents because of the rocks and ore deposits. The main pollutants in Chiprovtsi mining area are As and Pb.

In the background site all pollutants are under MPL (maximum permissible levels).

In the second sampling site As and Pb are over MPL at the surface and near surface levels, and Cu and Zn are under MPL.

In the third sampling site As and Pb concentrations exceed the MPL up to 600 and 17 times, respectively. Cu and Zn are slightly exceeded or vary around the MPL.

In order to characterize and identify the organic complexes and organic bounded metals 5g of each sample (fractions <63µm) was extracted by adding a mixture of methylene chloride/methanol (40 ml; v/v = 3:1), ultrasonicated for 20 min, and then was filtered to extract collection. Each extract was concentrated under argon before GC-MS analysis.

The extractable organic matter consist mainly of mixture of n-alkanes, n-alkanoic acids, sterols, alkanols.

The homologs of n-alkanes – heptadecane (C₁₇H₃₆), octadecane (C₁₈H₃₈), eicosane (C₂₀H₄₂), heneicosane (C₂₁H₄₄), tricosane (C₂₃H₄₈), tetracosane (C₂₄H₅₀), octacosane (C₂₈H₅₈), triacontane (C₃₀H₆₂) and the following acids – octanoic (C₈H₁₆O₂), azelaic (C₉H₁₆O₄), undecanoic (C₁₁H₂₂O₂), dodecanoic (C₁₂H₂₄O₂), tetradecanoic (C₁₄H₂₈O₂), hexadecanoic (C₁₆H₃₂O₂), octadecanoic (C₁₈H₃₆O₂) are dominant in all samples.

Steroids comprising 6-homoholesten-3-one, ergost-8-en-3-ol, and lanosten-3-on and the androsta furan (sterol) were also detected in C3 and C4 of the third sampling site.

n-Alkanes, n-alkanoic acids, steroids have high concentration (40–50%) in all samples. Their presence indicate decomposition of cellulose, waxes, resins, hormones and the presence of viable microbiota such as bacteria and fungi.

Traces of norcodein (alkaloid), 2-furanmethaneamine, tetrahydro with plant origin were also detected.

The presence of compounds like 1,3- and 1,4-bis(1-methylethyl)benzene; 1,1-(1,2-ethanediyl)bisbenzene; dibutyl phthalate; esters of phthalic acid – isobutyl undecyl ester, 2-ethylhexyl tetradecyl ester,

2-ethylhexyl ester, neopentyl nonyl ester, isohexyl isopropyl ester, 2-methylpropyl ester) is result of decomposition of plastics or pesticides. They are water insoluble but are concentrated in the humos.

Lauric acid, 2-(hexadecyloxy)-3-(octadecyloxy) propyl ester have been detected in the most samples from the surface. Their presence is due to anthropogenic pollution. Lauric acid and its derivatives are main part of surface active agents, used in the human life style.

1,3-Dioxane, 5-(hexadecyloxy)-2-pentadecyl have been isolated in the surface part of third sampling point C1. This toxic compound normally is formed by decomposition of herbicides.

In samples A3 and C5 Co-, Ni- and Fe- complexes have been detected. These complexes are Co, bis[eta-5-(1-cyclohexylmethyl)indenil], Ferrocene, 1,2,3,4,5-pentamethyl and Ni, [dimethyl[5-methyl-2-(1-methylethyl) cyclohexyl] phosphine] methyl [(1,2,3-eta)-2-pentyl] organic-metal compounds. The XRFS and ICP analyses reveal Co and Ni concentration between 20 and 40 ppm, while Fe content in all samples are several percents.

GC-MS has detection limit for analysing of heavy metals organic complexes, therefore the main pollutants in the region As-, Pb-, Cu- and Zn have not been detected.

Conclusions

This study shows that the dissolved organic matter has natural biogenic as well as anthropogenic sources. Co, Fe and Ni- organic bounded compounds indicate interaction between metal pollutions and dissolved organic compounds.

Further work is required to complete the analysis of the data obtained.

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