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INTERNATIONAL CONFERENCE
CONTAMINATED SITES 2018

BANSKÁ BYSTRICA | SLOVAKIA, 08 – 10 OCTOBER 2018

CONFERENCE PROCEEDINGS

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MINISTRY
OF ENVIRONMENT
OF THE SLOVAK REPUBLIC

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DISTRIBUTION, MINERAL FORMS, AND BIOAVAILABILITY OF HEAVY METALS IN SOILS, THEIR IMPACTS ON SOIL BIOGEOCHEMICAL PROPERTIES (ANGREN-ALMALYK MINING-INDUSTRIAL AREA, UZBEKISTAN)

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KEYWORDS

Heavy metals in soil, distribution, mineral forms, bioavailability, soil microorganisms, bioindicators, soil microorganisms, Angren-Almalyk industrial area, Uzbekistan

ABSTRACT

The present study examined air pollution effects on soil health applying microbiological parameters. It was carried out near the Angren-Almalyk mining and industrial area in a semiarid region of Uzbekistan. This area was selected in order to establish a national monitoring program for assessing environmental condition of areas remote but downwind from greater emission sources. Moreover, little information exists about how air pollution affects microbiological functioning of soils in semiarid and arid regions of the world, and especially those of Central Asia. The soil samples, which are heavily impacted by aerial emissions from the coal burning and metal-processing industry of the Angren-Almalyk industrial area, were the main subject of our intensive investigation (Fig 1).

Knowledge of chemical mobility of heavy metals is fundamental to understanding their toxicity, bioavailability, and geochemical behavior. Mineralogical means and sequential extraction were employed to analyze the total contents, existing states, and chemical forms of heavy metals in soil. The aims of our studies were (i) to assess the relationship between distance from the emission sources and heavy metal concentrations in soil and to analyze the depth distribution of the metals as indication of their mobility along the downwind transect; (ii) to evaluate the mobile and immobile metal forms, and (iii) to analyze the composition of heavy metals mixtures by means of statistical methods to get hints of common sources of different metals. The second part of our intensive studies was focused to determine the influences of heavy metals (Cu, Pb, Zn, Cd and As) on soil microbial and nematode characteristics in Angren-Almalyk mining industrial area along the two deposition transect. Nematode population, community structure, ecological indices, pollution tolerance and other indicators including microbial biomass, metabolic quotient were studied in soil samples. Soil microbial biomass, nematode population and community ecological indices response to heavy metal pollution in Angren-Almalyk mining industrial area were evaluated. Metal pollution indicators and tolerance species are established and recommended for developing biomonitoring and bioremediation measures which planned in future for this region. Microbiological ecosystem properties were assessed by biological indicators such as basal respiration (R_B), microbial biomass related C and N contents, and microbial community functioning coefficients like the metabolic quotient qCO_2.

Soil samples were collected along the two 20-km down-wind transects in the Akhangaran river valley, nearby the industrial complexes. In the laboratory, all samples were sieved through a 2 mm mesh sieve and separated into two parts. The first part was stored in a refrigerator at 4ºC for the biological studies, the second part of the soil samples (n=176) were used for chemical and mineralogical studies. These samples were air-dried, grounded in an agate mortar, and homogenized for sequential chemical extraction (AAS, ICP-MS) and preparation of powder pellets for XRF and XRD analyses. QA/QC was performed on basis of certified reference materials (CRM). We have completed the analyses of the total metal concentrations (Cu, Pb, Zn, Cd, Ni, Cr and Mn) and metal forms (mineralogy and chemistry) in all soil samples. Were quantified the mineralogical characteristics, morphology, and chemistry of air-borne spheroids to characterize the mineralogical sources of the soil contamination by heavy metals using JEOL scanning electron microscope (SEM). Sub-samples for mineralogical studies were separated by gravity and size. Particle-size fractionation was carried out by sieving and by sedimentation in aqueous media. The fine-grained fraction was subjected to gravity separation and

fractionated into (A) the heavy mineral fraction (ore minerals and spherical airborne metal-rich particles) and (B) the light mineral fraction (parent rock minerals). The heavy mineral fraction separated from the fines were embedded in epoxy resin. Element mappings were performed with the polished and carbon-coated thin sections using a JEOL microprobe.

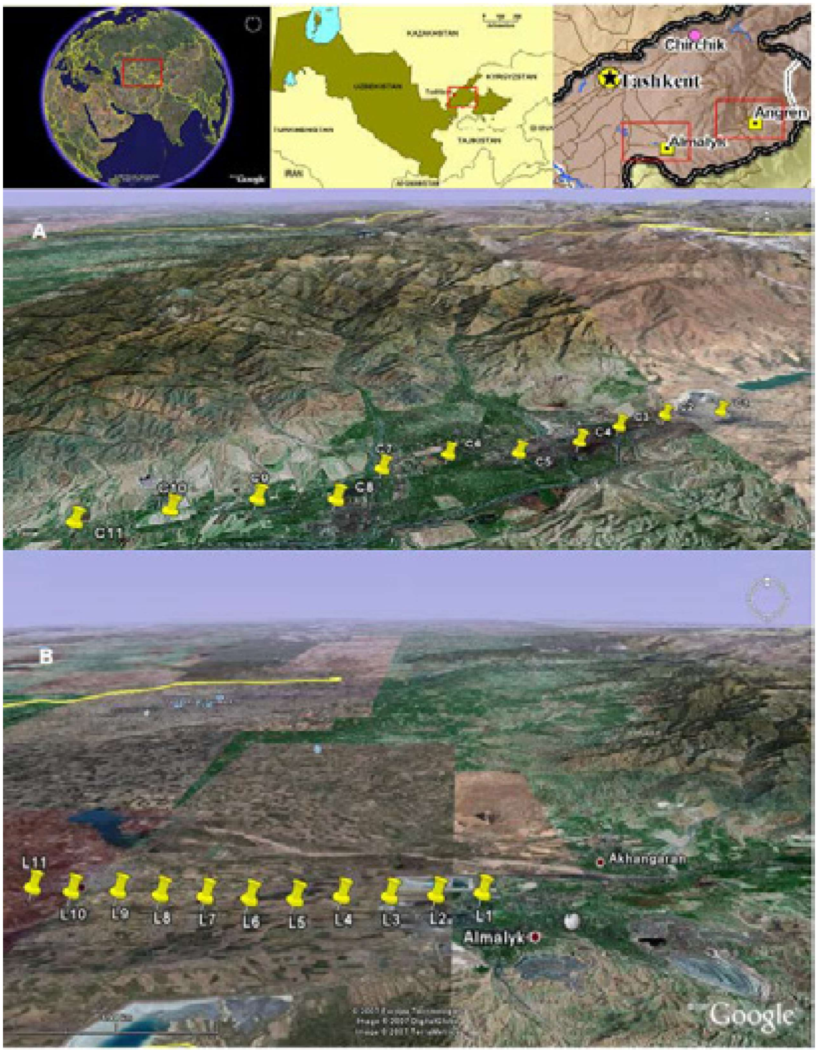
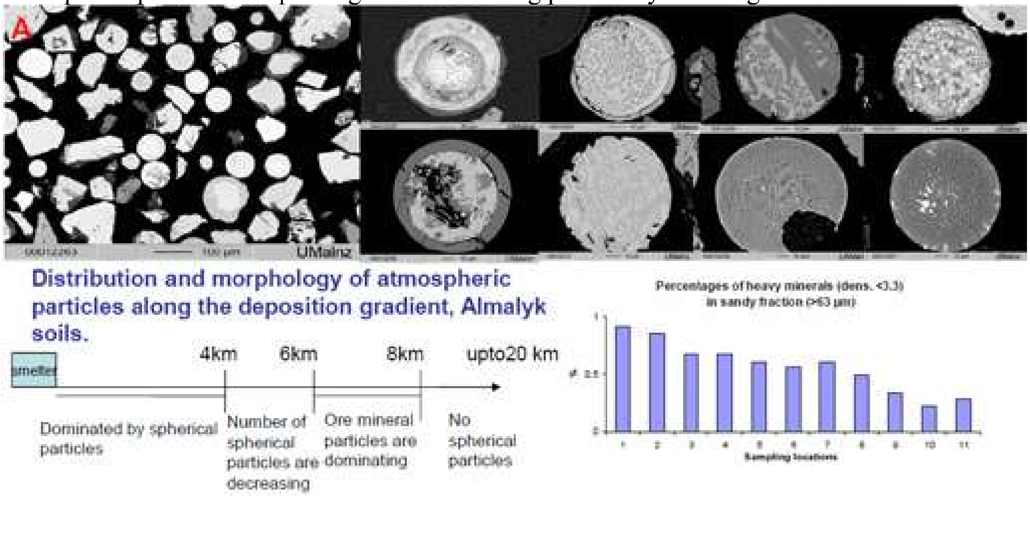


Fig. 1 Soil sampling locations in Angren-Almalyk mining industrial area (A – Angren; B – Almalyk).

Heavy metals were also fractionated by the sequential extraction procedure, in which the metal fractions were defined as exchangeable, carbonate-, Fe–Mn oxide-, organic matter-bound, and residual fractions. The sequential extraction scheme was developed from that of Tessier at al. (1979) and the same terminology is retained. Since this is the method that has given results about the possible bioavailability of the elements and their extractability or leachability, it is described in detail. Extraction was carried out progressively on an initial weight of 1.000 gram of soil sample. To measure the bioavailable heavy metal fraction were used diffusive gradients in thin films (DGT) at the maximum water holding capacity (MWHC) of the sub-samples. In particular, were separated the concentrations and effects of geogenic and smelter metals with the help of the stable isotopic signature.

The concentrations of a number of potentially toxic metals varied along the sampling transects, revealing a gradual decrease at increasing distance from the emission sources. The highest levels were found for the relatively volatile heavy metals (Cu: 457–871, Zn: 424–1695, and Pb: 163–441) in soils near the Almalyk metal smelter, and Zn (850–1051 ppm) and Pb (270–320 ppm) in soils near the Angren power plant suggesting that the metal pollutants probably derive from local stack emissions. Significant differences ($p<0.05$) were observed between the upper (0–10 cm) and deeper (10–20 cm) soil layers and among the particle size fractions for Cu, Zn, Pb, U, and Th, at most sampling locations of both study areas. The concentrations of a number of metals (Zn, Cu, Pb, Cd and As) were higher in the upper soil layer and in the clay fractions at all sampling sites. The distribution and concentrations of some other metals (Co, Cr, Ni, V, and Sc) showed an opposite trend, probably due to the native geochemical background. Furthermore, heavy metals were fractionated by a sequential extraction procedure, in which the metal fractions were defined as exchangeable, carbonate-, Fe-Mn oxide-, organic matter-bound, and residual fractions. Most of Cd was extracted with the exchangeable and carbonate-bound fractions. The highest concentrations of Ni and Cr were found in the residual fraction. The speciation of Cu, Pb, Zn, and Cd was related to distance from the emission source and soil depth. The mean contributions of Cu, Pb, Zn and Cd in the exchangeable fraction to the total concentrations were higher at the locations (nearest to the pollution sources) and decreased with increasing distance. Metals bound to carbonates and Fe–Mn oxides increased consistently with depth in first sampling location. There were almost no significant changes in the metal contents in all fractions after 12 km.

Several metal phases such as galena, chalcopyrite, sphalerite, pyromorphite, cerusite, hydrocerussite, leadhillite, and anglesite were identified by XRD. Of the crystalline metal phases, the presence of cerusite, malachite, azurite, hydrocerussite, and pyromorphite were identified as weathered forms of primary ore minerals at the first sampling location in Almalyk. A lot of grains and spherical particles with bright contrast appeared in the microprobe scans indicating a metal-rich composition. Spherical particles dominated in the soil samples collected near the metal smelters, whereas angular sulfide minerals (pyrite, galena, chalcopyrite, sphalerite) dominated in samples collected near the mine spoils and tailings depository (Fig 2). The morphology and internal microstructure of the spherical particles in a heavy mineral fraction of the soil samples from the Angren-Almalyk area indicate formation from a pre-existing molten phase, probably emitted by an inefficient air pollution control technique of the smelter in Almalyk and thermal power plant in Angren. Spherical particles can be divided in pure metal particles (Cu, Zn, Al), metal-rich cores with silicate rims, small spherical metal sulfide or oxide particles within larger heterogeneous glassy particles, well-organized particles with dendrite structure. Fine grains of sulfide ore minerals, covered with weathering rims of secondary ore minerals (sulfates or carbonates), can be related to contamination by mining activities. Fe was abundant in most particles from the Angren soils, associated with Ti, S or Pb, and Zn. A few bright grains showed a rim dominated by Si and K. Other associations found were Fe+S+Pb+Mn, or S+Pb+Zn+Mn+Fe, or pure Cu or Zn only. The absence of an O peak indicates that Cu, Zn, and Pb are largely associated with sulfides rather than sulfates. Numerous spherical particles showed distinct dendrite-like structures within a dark grey matrix. The matrix is composed largely of Si, Mn, Zn, Pb, Al and Fe or Fe alone, Ti, Cu, Si, and Ca, whereas the bright areas were formed mainly by Fe and Al, presumably in an oxide (spinel) form considering the strong O signal. Most of the spherical particles showed holes inside or had metalliferous rims around alumina cores, which indicates formation from a pre-existing molten phase. Occasionally, these technogenic spheres contained angular grains of primary ore minerals. Percentage of heavy minerals in Angren soils is more than in Almalyk's (1>4). Elemental composition of spherical particles very poor than Almalik's (almost all of them have elevated content of Fe oxide with less Si, Al, Mn, Ca content. In some particles fewer contents of Pb, Cu and S were observed. Spherical particles in Angren soils can be divided into 3 groups: a) well organized massive dendritic particles containing Fe oxide in light growing crystals and matrix containing Si, Al, Ca, Fe; b) homogenous spherical particles without any structures containing Fe oxide; c) small microscopic particles coated Fe oxide. Ore mineral particles mainly Hematite, titan-magnetite, magnetite and very fewer pyrite particles. Many of them covered with secondary ore minerals as Fe hydroxide and carbonates. The calcareous condition of soils in studied areas can stabilize atmospheric particles and prolong their weathering process by covering them with carbonate material (Fig 2).



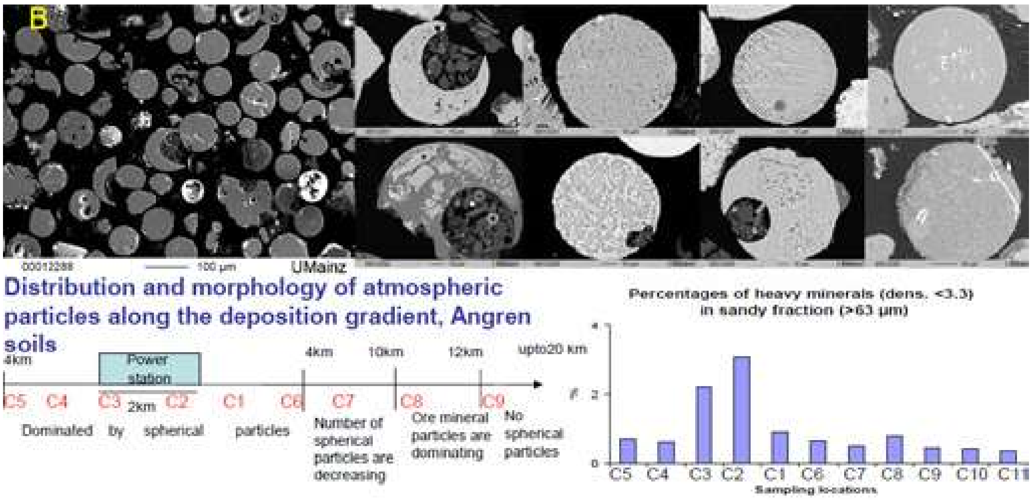


Fig. 2 The morphology and internal microstructure of the spherical particles in a heavy mineral fraction of the soil samples from the Angren-Almalyk area, and their distribution along the deposition gradient (A – Almalyk; B – Angren).

Twenty-nine nematode taxa were identified in the present investigation for Almalyk downwind transect: twelve taxa belonged to the bacterivore trophic group, 5 were fungivores, 7 were planted parasites and 5 were omnivores-predators. The mean density of the soil free-living nematodes increased with distance from the pollution source in both soil layers. Moreover, nematode density in the upper (0–10) cm soil layer showed a gradual increase in T_{NEM} population between sampling locations, yielding significantly high $R^2 = 0.98$ values, a value which decreased to a level of $R^2= 0.69$ with the increase in distance (20 km). In the deeper (10–20 cm) soil layer, the R^2 values obtained for a similar distance were found to be similar ($R^2=0.8$). The nematode density was higher in the upper soil layer (from 1.2 to 2.0 times at the different sampling locations) than in the deeper soil layer ($p<0.02$). The percentage of each trophic group out of the whole population was found to be affected by the distance from the pollution sources. Trophic group density increased with distance; however, these increases were not always similar along the both transects. Bacterivores (BF) and plant-parasites (PP) in the deeper soil layer and omnivore- predators (OP) in both soil layers, increased consistently from the pollution source to the edge of the study area, whereas BF, PP and fungivores (FF) in the upper soil layer increased to first three locations and then decreased to other locations in Almalyk. Nematode data obtained from the Angren sampling site also show almost similar responses to pollution with small varieties because of the complicated nature of disturbance (coal ash, resin, and metalloorganic) and also the nonlinear distribution of pollutions sources along the transect. The effect of pollution on the density and biomass of soil free-living nematodes was found to be highest at the pollution source in Almalyk, with fungivores and plant parasites dominating at the upper and deeper soil layers next to the pollution source. These groups decreased along the transect, yielding domination to bacteria and fungi feeders. The females of the total soil free-living nematodes were found to be the most resistant to heavy metal pollution levels, while the juveniles were found to be sensitive to changes in heavy metals. The Maturity and modified maturity indices, that reflect the degree of disturbance of the soil ecosystem, were found to be the most sensitive indices.

Microbiological ecosystem properties were assessed by biological indicators such as basal respiration (R_B), microbial biomass related C and N contents, and microbial community functioning coefficients like the metabolic quotient qCO_2. There was a significant spatial dependence and differences for all soil chemical and microbiological parameters tested. The highest contents were found for the relatively volatile metals Zn (≤1,136 mg/kg) and Pb (≤373 mg/kg) in upper soil layers near the power station suggesting that the metal pollutants are derived from local stack emissions. Soil microflora was obviously affected by heavy metals. Significant positive correlations ($p\leq0.001$) were found between the metal content, RB, and qCO_2, while a negative one was found for the mineralizable N and C_{mic}/C_{org} ratio. A high total number of nematodes was found only most distant from the industrial emission sources. The results disclosed remarkable spatial dependence not only of the heavy metal impact onto the soil but also of microbiological soil properties in the study area. The latter suggests bioavailability of the anthropogenic metals in the soil affecting the soil microbial community. This is suggested by less biomass formation and higher qCO_2 values in heavy metal-contaminated compared to less-polluted soil plots. Knowledge of these spatial ecosystem functioning patterns and dependence could be very useful in determining and delineating specific land use and management programs that would be suited and feasible for the highly polluted area. Results of this study can be utilized to develop a monitoring program that may quantify the harmful effects on the soil health and impact of any future remediation activities. Studies on the relationship between soil biota and pollution levels have raised the question regarding the status of natural soil microbial health, stressing the importance of background data of environmental conditions, and elucidating the importance of this environmental monitoring approach even in semiarid and arid regions. Soil microbiological parameters, in particular, the metabolic quotient qCO_2 as one of the most sensitive bioindicators identified for that region, should clearly become part of the national environmental monitoring program.

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This publication has been prepared by the Slovak Environment Agency to support the International Conference CONTAMINATED SITES 2018, Banská Bystrica 8 – 10 October 2018. The conference was organised by the Slovak Environment Agency in close cooperation with the Ministry of Environment of the Slovak Republic during the Slovak Presidency 2018/2019 of the Visegrad Group.

25 YEARS SLOVAK ENVIRONMENT AGENCY

DYNAMIC VISEGRAD FOR EUROPE
SLOVAK PRESIDENCY 2018/2019 OF THE VISEGRAD GROUP

PUBLISHED BY:
Slovak Environment Agency
Tajovského 28
975 90 Banská Bystrica
SLOVAKIA
Tel.: + 421 48 4374 164
www.sazp.sk
contaminated-sites.sazp.sk

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ISBN: 978-80-89503-91-9
EAN: 9788089503919

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Document completed in September 2018.

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ACKNOWLEDGEMENT:
The editors of this document would like to thank all authors of papers and proofreaders for their contributions.

THIS DOCUMENT SHOULD BE CITED AS:
Slovak Environment Agency. International Conference Contaminated sites 2018, Banská Bystrica 8 – 10 October 2018. Conference Proceedings. Banská Bystrica, September 2018. ISBN: 978-80-89503-90-2.
Available on the Internet: http://contaminated-sites.sazp.sk/

The activity has been implemented within the framework of national project
Information and providing advice on improving the quality of environment in Slovakia.
The project is cofinanced by Cohesion Fund of the EU under Operational programme Quality of Environment.

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