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Distribution, mineral forms, and bioavailability of heavy metals in soils and their impacts on soil biogeochemical properties (Angren-Almalyk mining-industrial area, Uzbekistan)

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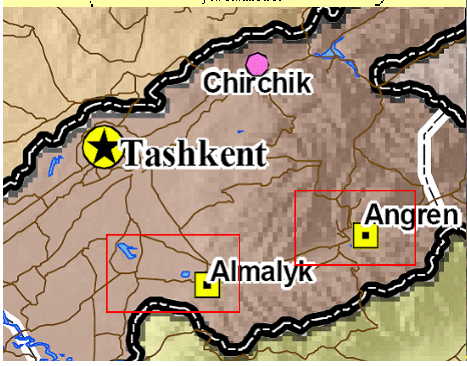
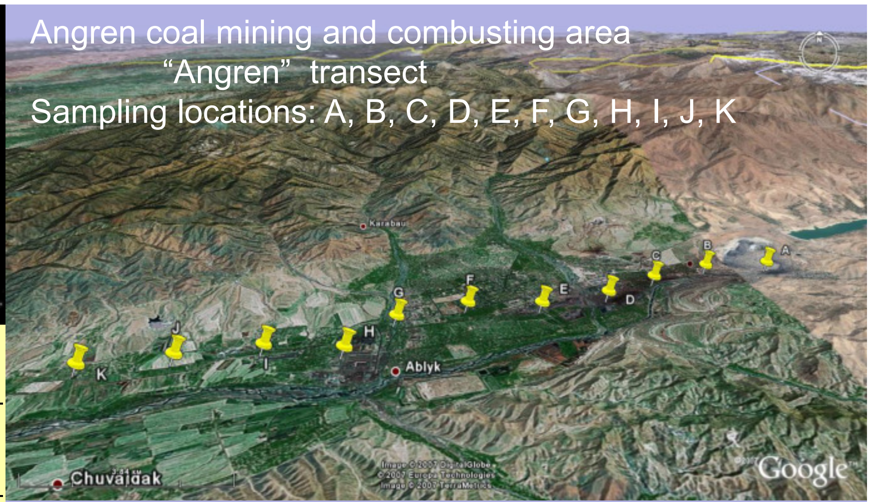
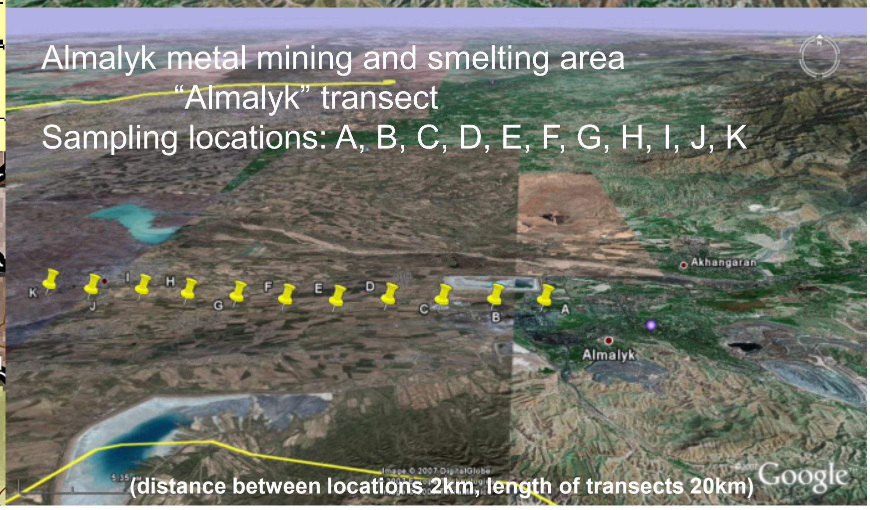






Chemical and mineralogical analyses

Total content of heavy metals (XRF spectrometer)

Chemical forms of heavy metals (5 step sequential extraction, Tessier et al.) measured by AAS.

Size separation into fine-grain sand (<0,125+0,063mm) and silt (<0,063mm) fractions.

Fraction (<0,125+0,063mm) subjected to gravity separation (bromoform).

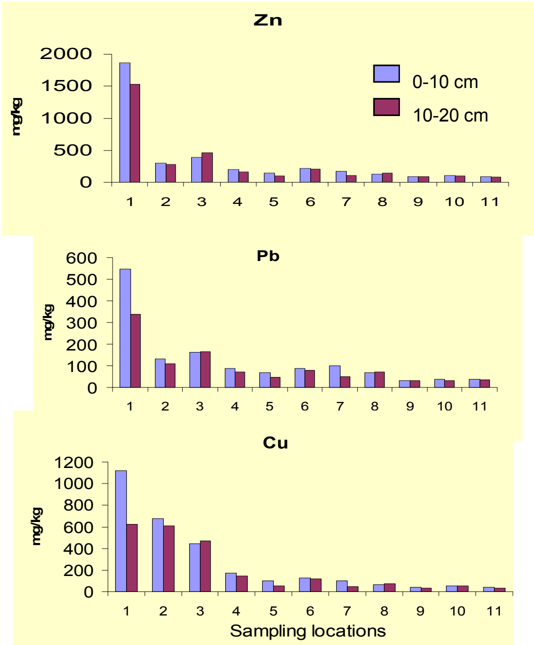
Thin sections were from heavy mineral fraction by using epoxy resin.

Scanning and element mapping of atmospheric particles and ore minerals (JEOL Superprobe microzond).

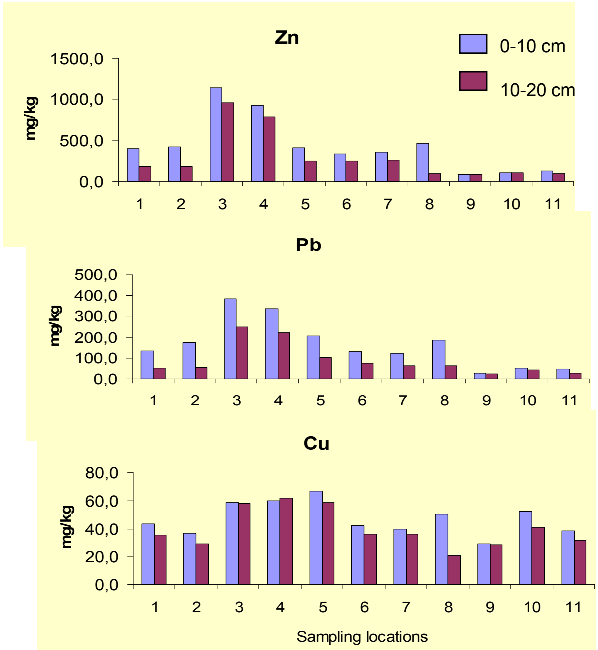
Some clay minerals were identified by using XRD.

Distribution of heavy metal (total) concentrations in soil along the deposition gradients in Angren-Almalyk mining industrial area (mg/kg).

Almalyk
(metal mining and smelting)



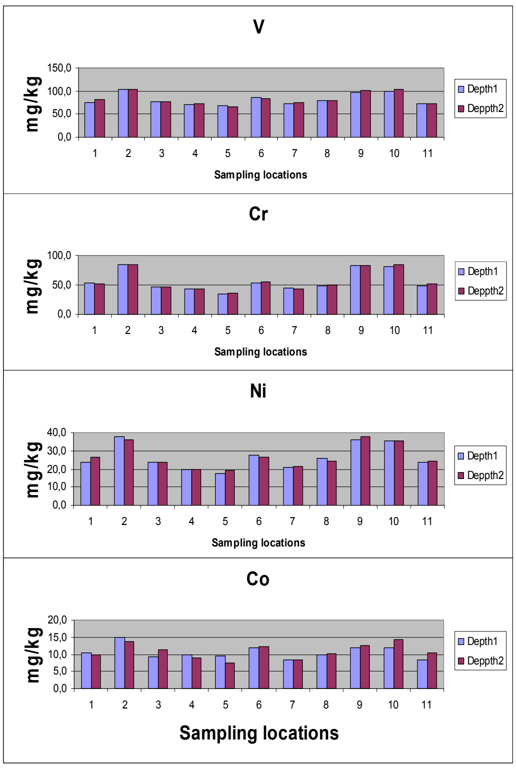
Angren
(coal mining and combusting)



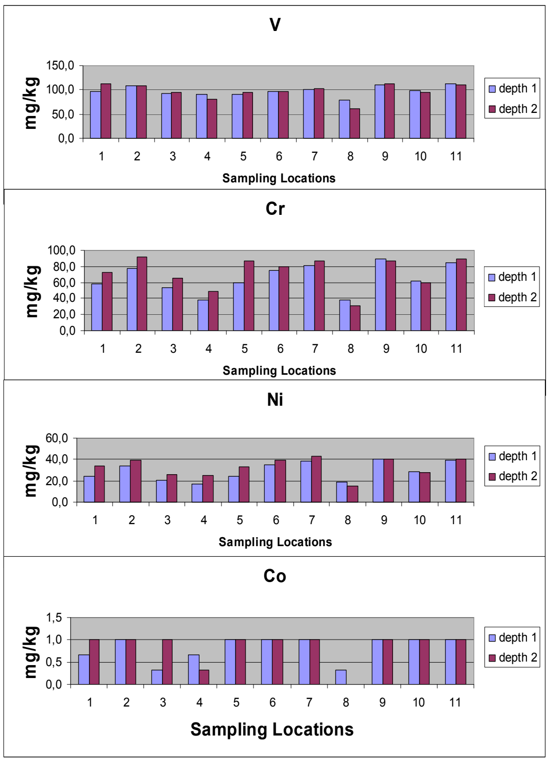
Note: Sampling location No. 1 is the nearest point to Smelter factory in Almalyk transect. Sampling points No 3 and No 4 are within the Angren power station, No 8 Resin factory along the Angren transect. Length of transects 20 km each, distance between locations 2 km

Distribution of heavy metal (total) concentrations in soil along the deposition gradients in Angren-Almalyk mining industrial area (mg/kg).

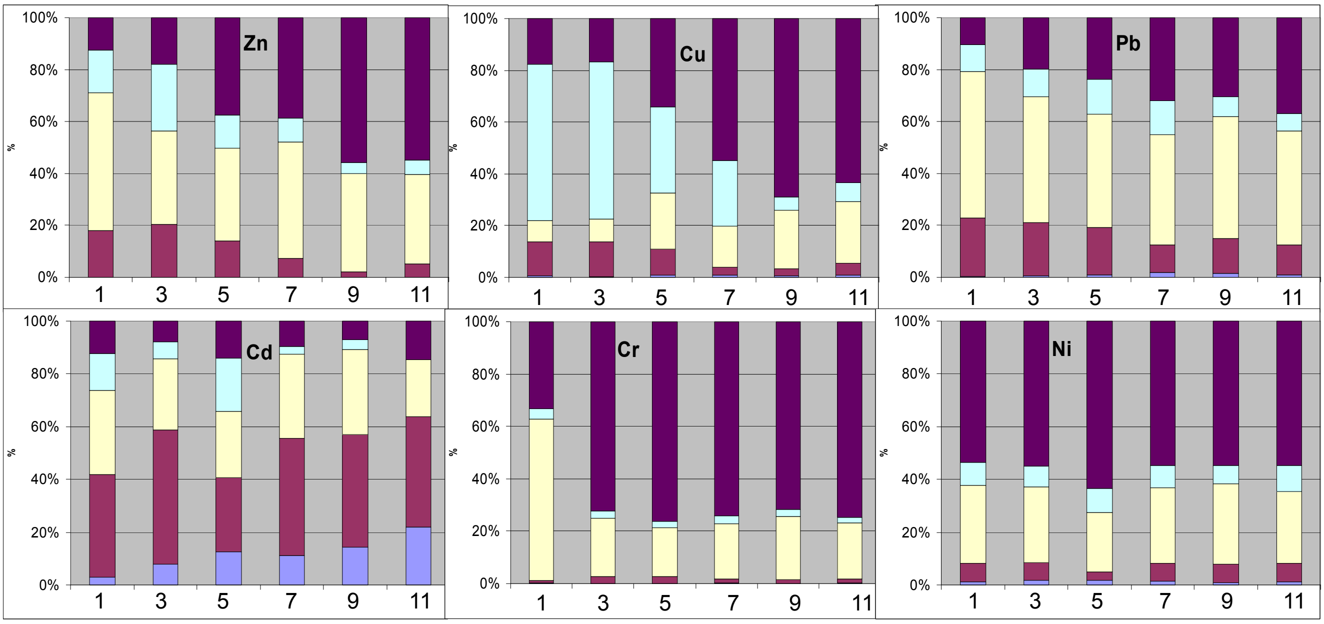
Almalyk
(metal mining and smelting)



Angren
(coal mining and combusting)

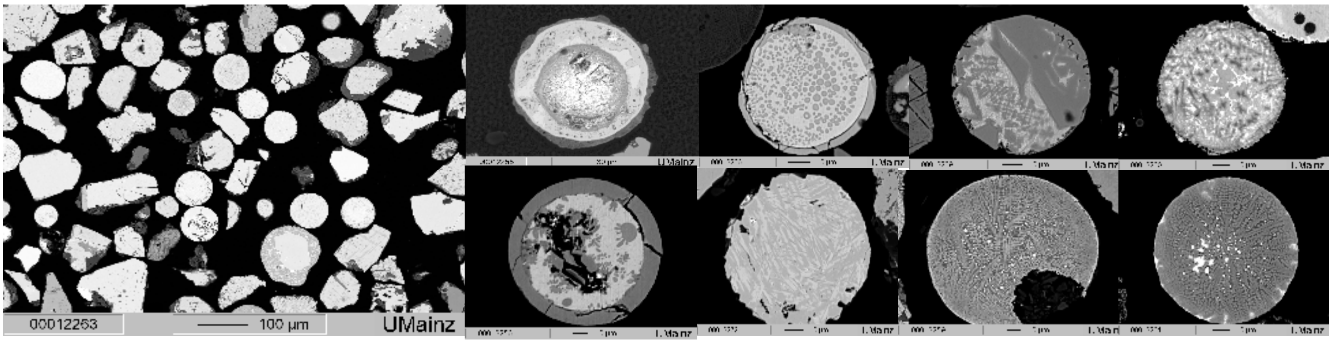


Percentage of the 5 metal fractions, % of total concentration (Almalyk)

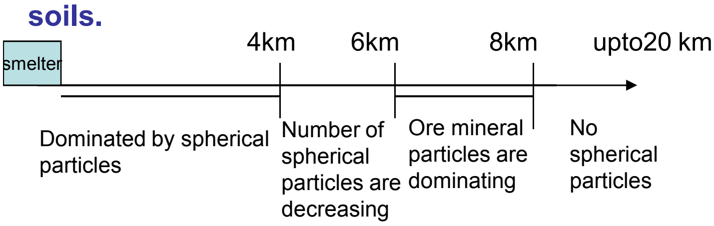


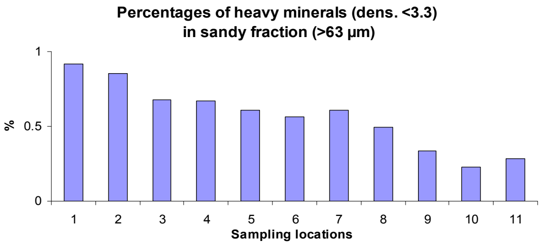
Sampling locations:
1- L1 (100 m distance from the Smelter)
3- L3 (4km distance from the Smelter
5- L5 (8 km)
7- L7 (12 km)
9- L9 (16 km)
11- L11 (20 km)

Chemical fractions:
F1- Exchangeable;
F2- Bound to Carbonates;
F3- Bound to Fe and Mn oxides;
F4- Bound to Organic Matter;
F5- Residual



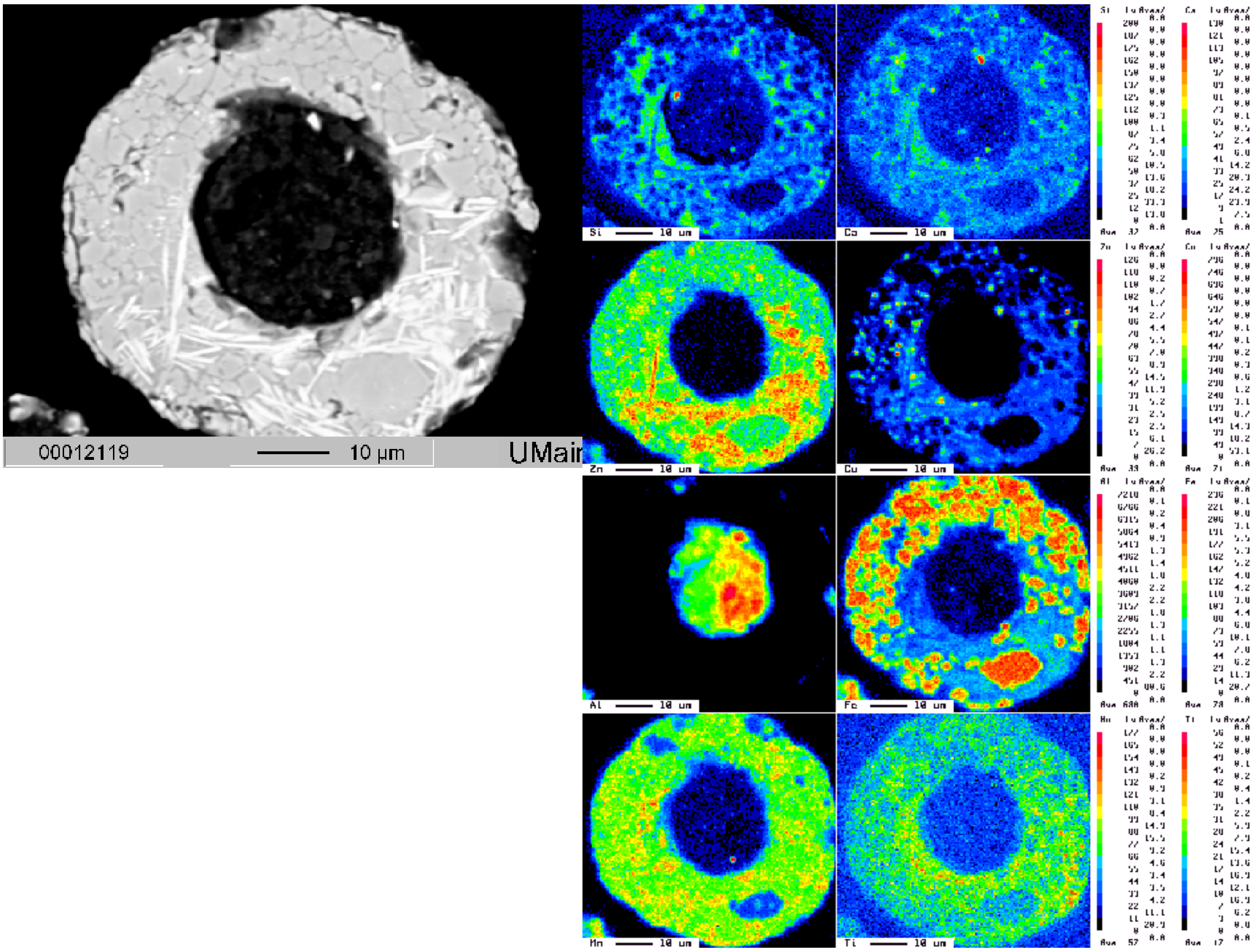
Distribution and morphology of atmospheric particles along the deposition gradient, Almalyk soils.





Emphases:

- The morphology and internal microstructure of the spherical particles in heavy mineral fraction of the soil samples from the Almalyk area indicates formation from a pre-existing molten phase, probably emitted by an inefficient air pollution control technique of the smelter.
- Spherical particles can 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.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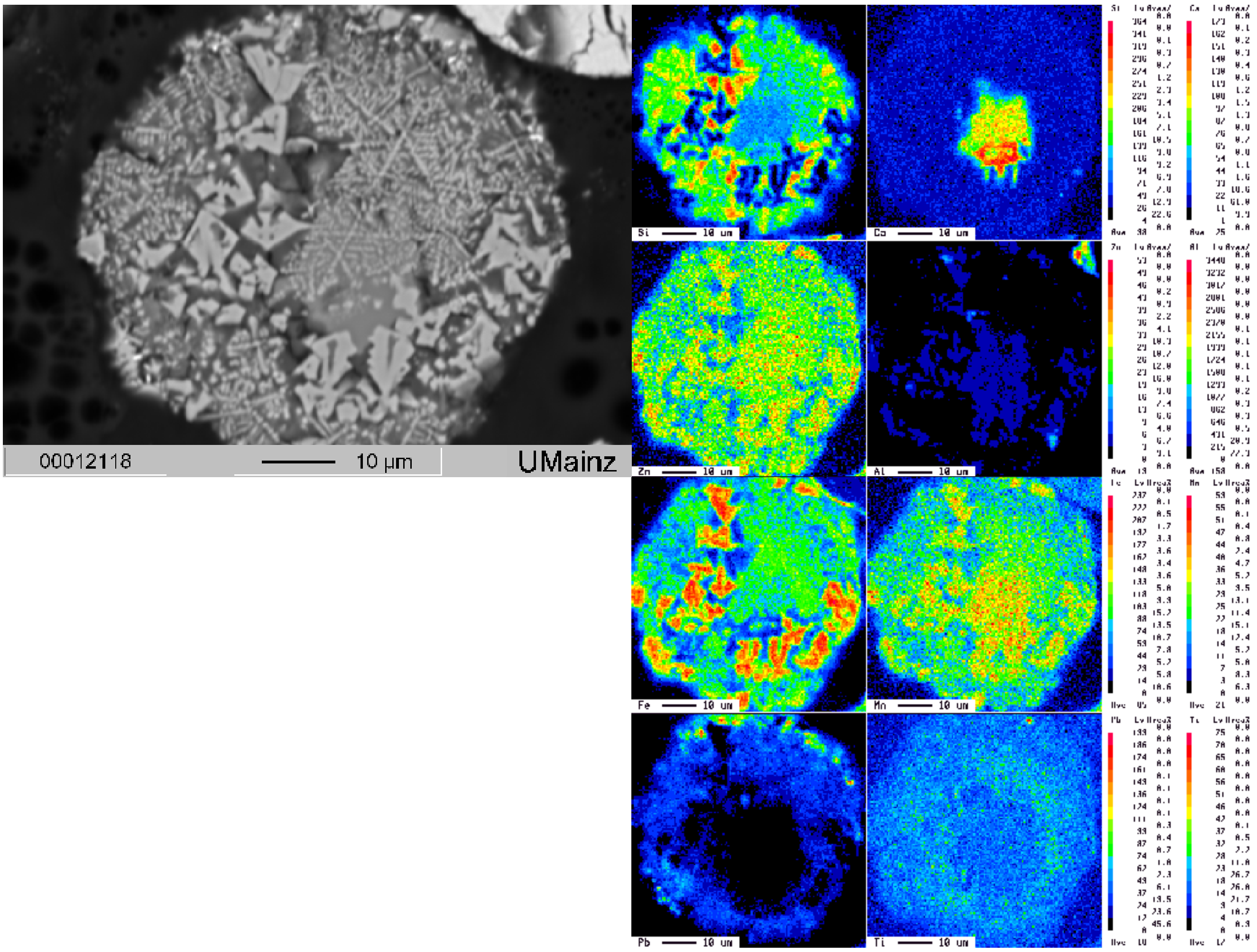
10 µm
UMain
Si
Ca
Zn
Cu
Al
Fe
Mn
Ti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10 µm
UMainz
Si
Ca
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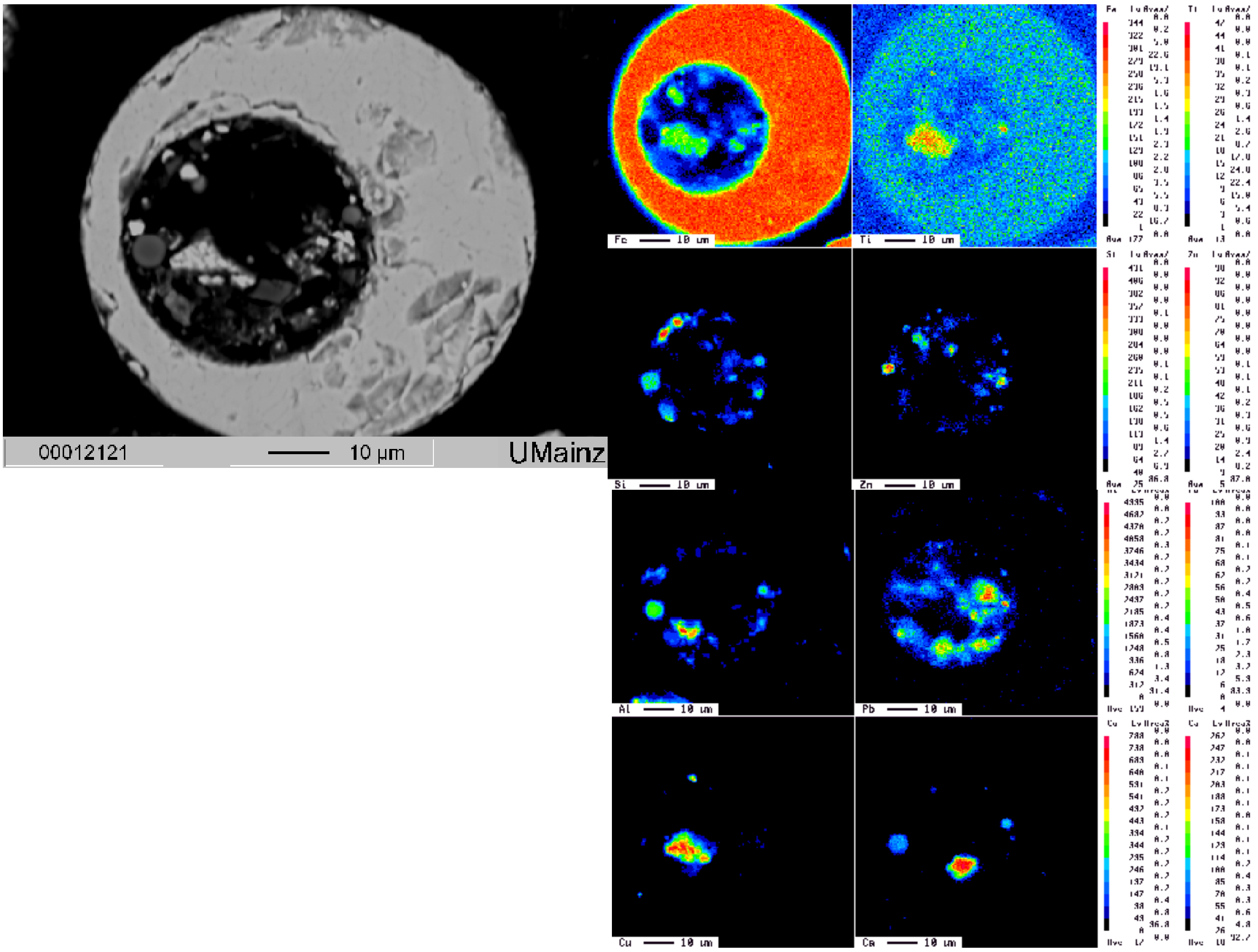
Pb
Ti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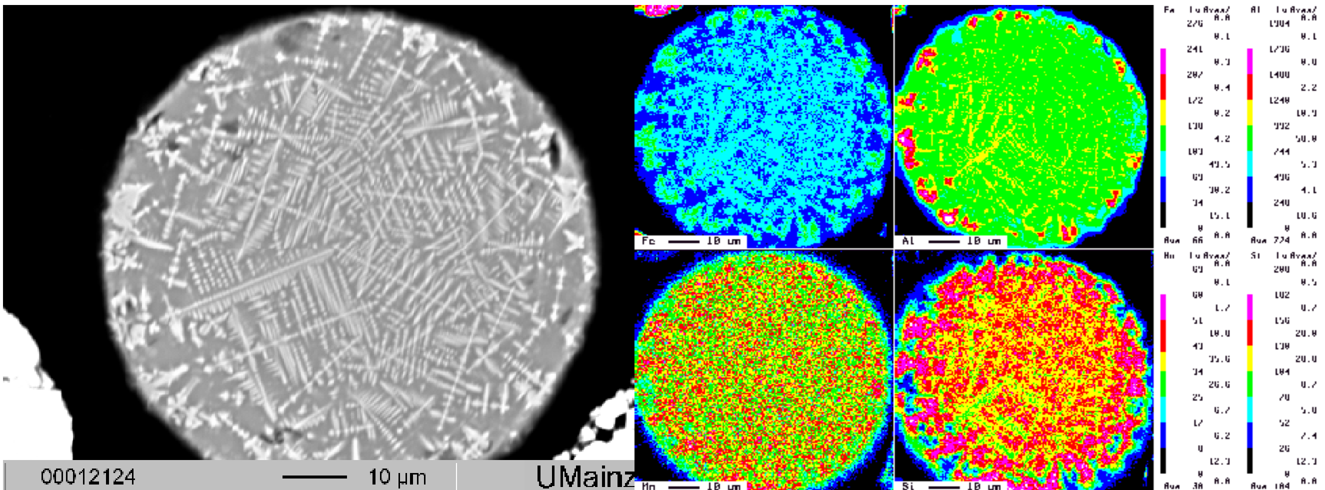
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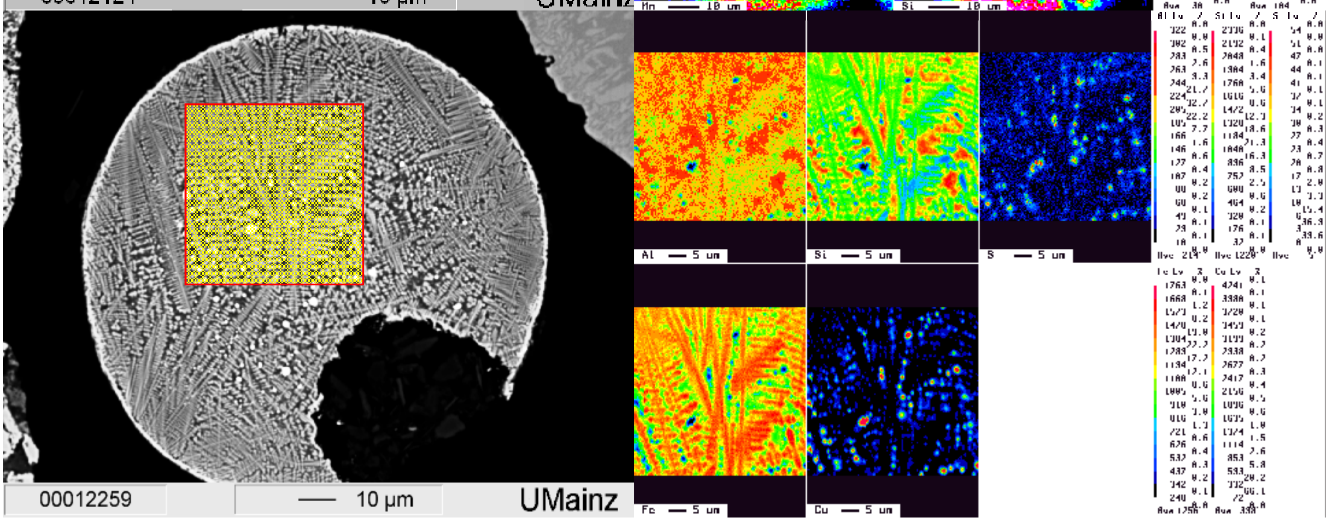
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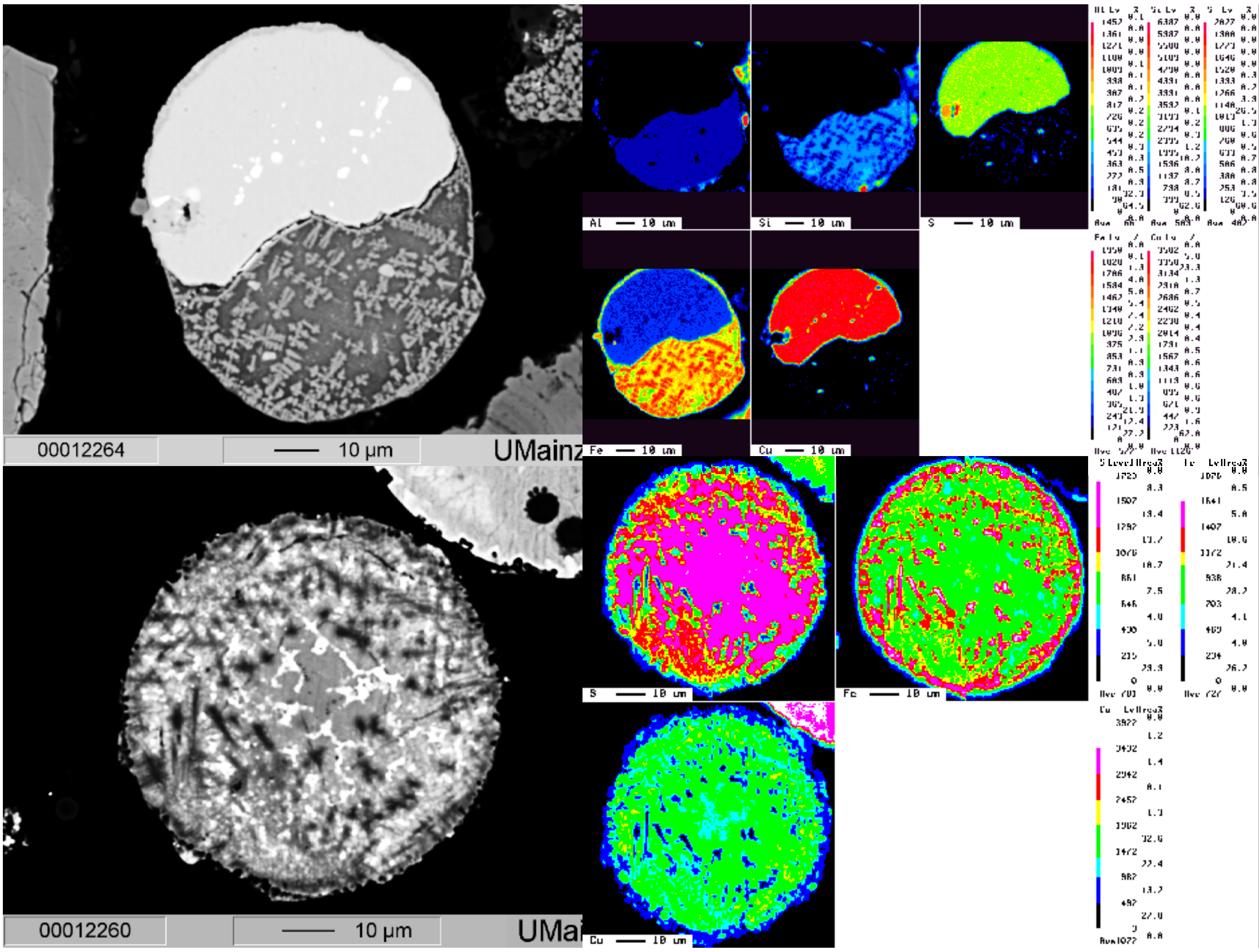
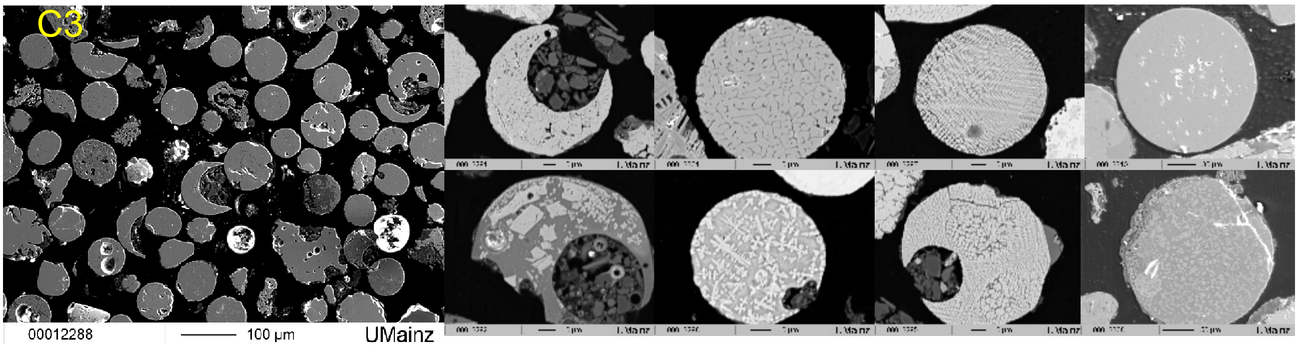
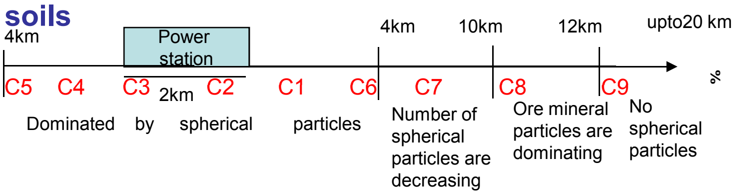
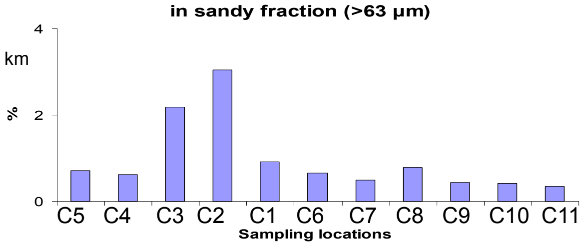




Distribution and morphology of atmospheric particles along the deposition gradient, Angren soils



Percentages of heavy minerals (dens. <3.3) in sandy fraction (>63 µm)



Emphases:

- 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 less 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 less pyrite particles. Many of them covered with secondary ore minerals as Fe hydroxide and carbonates.
- Calcareous condition of soils in studied areas can stabilize atmospheric particles and prolong their weathering process by covering them with carbonate material.

Soil biological analyses

Soil moisture was determined gravimetrically (105oC, 48 h).

Soil pH was determined in H_2O (soil solution ratio 1:2.0) with a potentiometric glass electrode.

Soil salinity was determined in soil extracts and expressed as electrical conductivity (EC). Soluble cations (Ca^{2+}, K^+, Na^+) were determined by a flame photometer (Rhoades, 1982).

Total organic carbon (Corg) was determined using a modified method of Rowell (Rowell, 1994). The method is based on organic matter oxidation by K-dichromate.

Total soluble nitrogen (TSN) in soil was determined by using the method of Houba et al. (1987). The amounts of TSN in the soil extracts were determined using a Skalar Autoanalyzer unit (S.F.A.S., 1995).

Nematode population was determined by extraction from 100 g soil samples using the Baermann funnel procedure (Cairns, 1960). The recovered organisms were counted using a compound microscope and preserved in formalin (Steinberger and Sarig, 1993).

Soil microbial biomass (Cmic) was determined using a chloroform fumigation incubation (CFI) assay, according to Jenkinson and Powlson (1976). CO_2 concentration was measured in the head space of the glass jars using a Gas Chromatograph (GC) and Cmic was calculated as: *Cmic=[(CO_2-C from fumigated soil) – (CO_2-C from control sample)]/kc* A kc of 0.41 was used, as proposed by Anderson and Domsch (Anderson and Domsch, 1990).

Soil basal respiration (BR) as CO_2 evolution, was determined by GC (Sparling and West, 1990).

Metabolic quotient (qCO_2) was calculated as the ratio between basal respiration (BR) and microbial biomass (Cmic) (Anderson and Domsch, 1990). The qCO_2 is a specific parameter for evaluating the effects of environmental conditions on the soil microbial biomass.

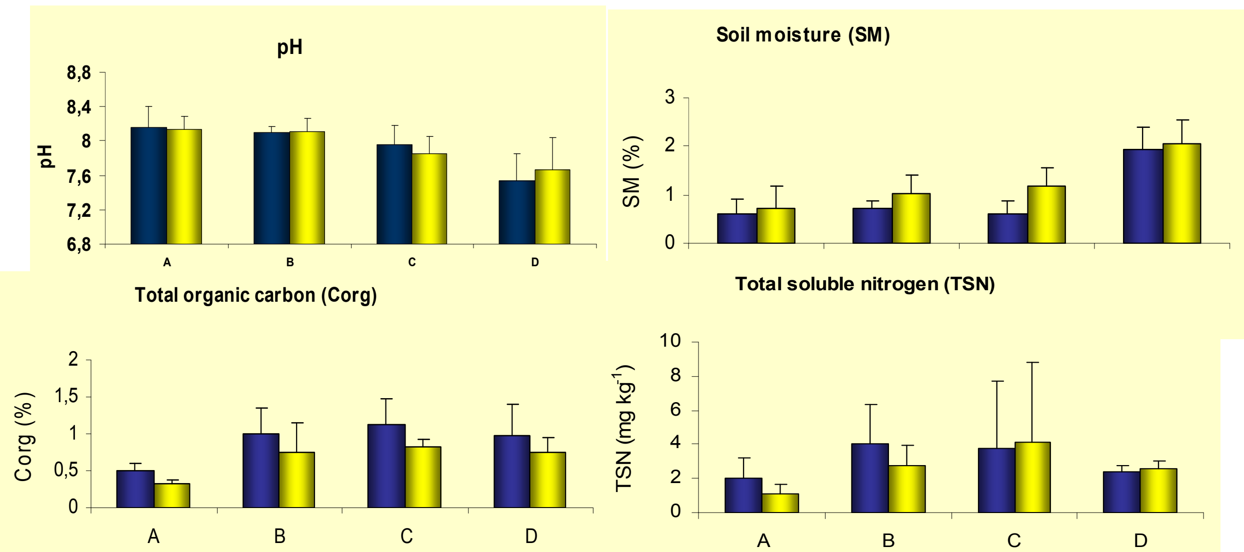
Microbial coefficient, known as substrate availability, was determined as the Cmic/Corg ratio.

All data were subjected to statistical analysis of variance using the SAS model (ANOVA, Duncan's multiple range tests and Pearson correlation coefficient) and were used to evaluate differences between separate means. Differences obtained at levels of $p<0.05$ were considered statistically significant.

RESULS:

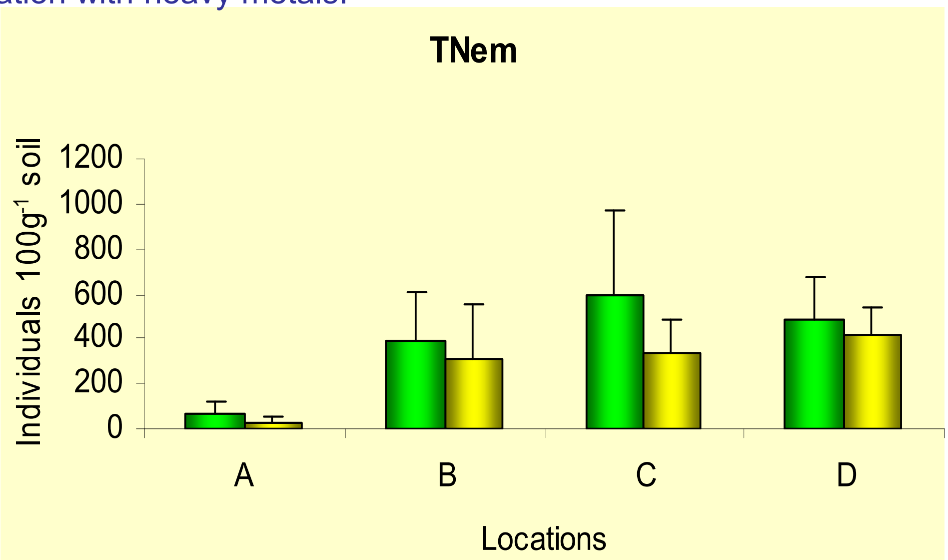
Significantly close relationships were observed between metal content and soil biological activity in both studied areas.

The decrease in heavy metal concentration along the transect was found to be an opposite trend to the changes in soil moisture availability, organic carbon and total soluble nitrogen.



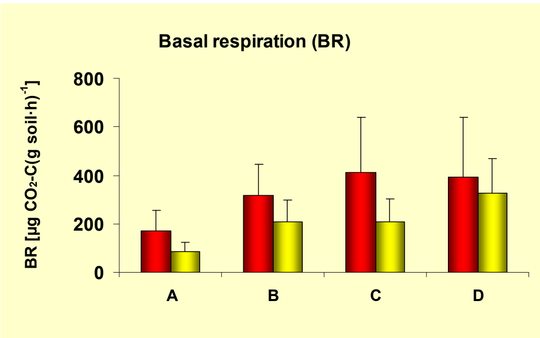
Soil pH, soil moisture, total organic carbon and total soluble nitrogen contents along the deposition gradient at two soil layers (0-10 cm; 10-20 cm)

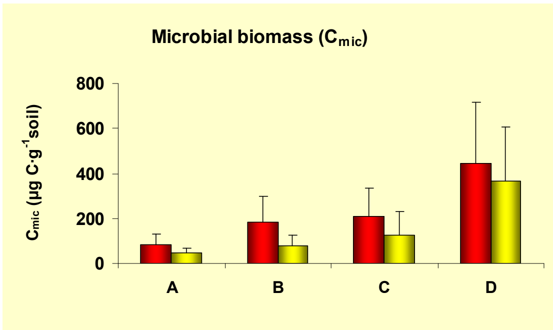
Total number of nematodes, basal respiration (Br) and microbial biomass total organic carbon ratio (Cmic/Corg) had a significantly negative correlation with heavy metals.



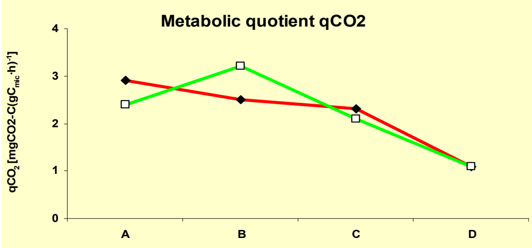
Distribution of number of nematodes along the deposition gradient at two soil layers (0-10 cm; 10-20 cm)

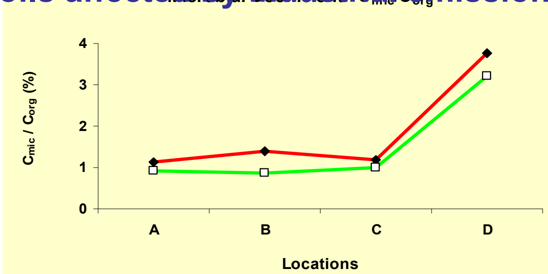
Soil microbial properties





assessment of PAH contamination in soils affected by industrial emissions;





Basal respiration, microbial biomass, metabolic quotient and microbial coefficients values obtained in soil samples contents along the deposition transect at 0 to 10( ) and 10 to 20 cm ( ) soil layers

THE IMPACT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AND THEIR OXYGENATED DERIVATIVES (OPAHS) ON MICROORGANISMS IN SOILS OF ANGREN INDUSTRIAL AREA

There was a significant spatial dependence and differences for all soil chemical and microbiological parameters tested. PAHs and OPAHs concentration (Fig. 1) in upper soil layers (0-10 cm) were highest near the power station (C and B) followed by A (near coal mine pit) suggesting that these pollutants are derived from local stack emissions. Areas far from these emission sources had progressively lower PAH/OPAH concentration except near rubber factory (F). Deeper soil layer (10-20 cm) had lower concentration than upper soil layer except in location (A) (data not shown). OPAHs followed similar trend as PAHs indicating that they are emitted together with PAHs. Soil micro-flora was obviously affected by PAHs and OPAHs near the pollution source. Highest total number of nematodes and number of plant parasite nematodes trophy group were found most distant from the industrial emission sources with comparatively lower PAH and OPAH concentrations (Fig.1). Positive correlations were found between PAHs and OPAHs concentrations, soil respiration, and metabolic quotient qCO2, while a negative one for the mineralizable N, Cmic/Corg and Cmic/Nmic ratios.

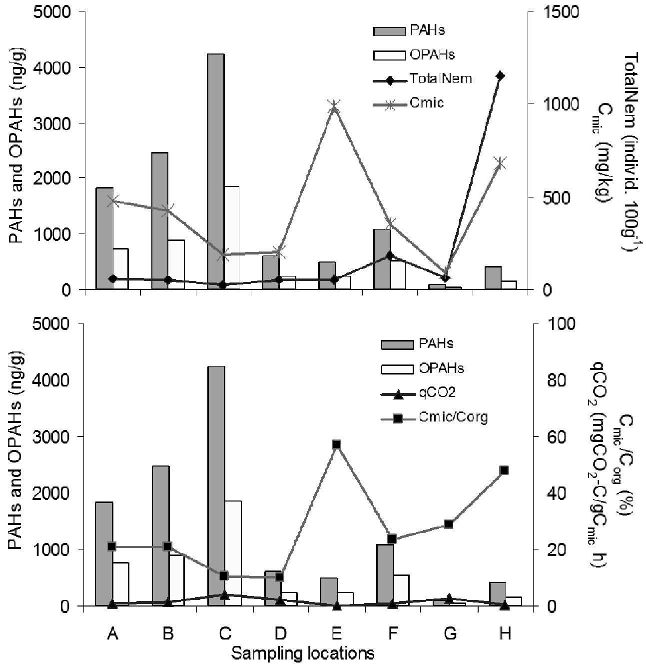
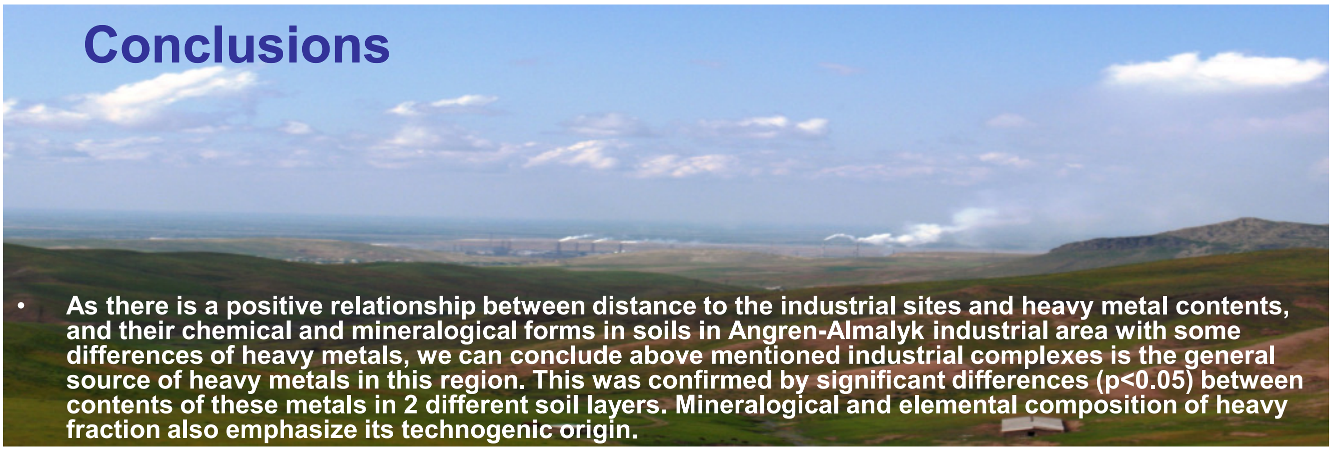


Fig. 1. PAHs, OPAHs concentration, total number of nematodes, microbial biomass, metabolic quotient, and Cmic/Corg ratio distribution along the 20 km downwind transect.



Conclusions

- **As there is a positive relationship between distance to the industrial sites and heavy metal contents, and their chemical and mineralogical forms in soils in Angren-Almalyk industrial area with some differences of heavy metals, we can conclude above mentioned industrial complexes is the general source of heavy metals in this region. This was confirmed by significant differences ($p<0.05$) between contents of these metals in 2 different soil layers. Mineralogical and elemental composition of heavy fraction also emphasize its technogenic origin.**

- **Data obtained during these investigations has shown intensive effect of mining industry to soil ecosystem. Results on 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 transects illustrate their negative response to heavy metal pollution.**

- **Obtained data on nematode population and community structure, ecological indices and other indicators including microbial biomass, metabolic quotient in soils of Angren-Almalyk mining industrial area show bright future of this techniques as tools for environmental biomonitoring and bioremediation.**

Articles in Scientific Journals:

- Shukurov, N., Pen-Mouratov, S. and Steinberger Y. (2005). The impact of Almalyk industrial complex on soil chemical and biological properties. Environmental Pollution 136:331-340.
- Pen-Mouratov, S., Shukurov, N., and Steinberger, Y. (2008) . Influence of industrial heavy metal pollution on soil free-living nematode population.. Environmental Pollution, Volume 152, Issue 1, March 2008, Pages 172-183.
- Pen-Mouratov S., Shukurov N., Steinberger Y. "Soil free-living nematodes as indicators of both industrial pollution and grazing activity in Central Asia", J. Ecological Indicators (submitted).
- Shukurov N., Pen-Mouratov S., Steinberger Y., Kersten M.. «Soil biogeochemical properties of Angren industrial area, Uzbekistan». J. Soils & Sediments (Submitted);

Papers presented at conferences and meetings:

- Pen-Mouratov, S., Shukurov, N., Plakht, J., and Steinberger, Y. (2005).Soil free-living nematode and microbial population in the anticline erosional cirque, Makhtesh Ramon crater, Israel. The Joint International Symposia for Subsurface Microbiology (ISSM 2005) and Environmental Biogeochemistry (ISEB XVII) Jackson Hole, Wyoming - August 14-19, 2005, the USA.
- Shukurov, N., Wilcke, W., Kersten, M.(2006) Heavy metal distribution in soils along the atmospheric deposition plume of Angren coal processing area (Uzbekistan)/ The 7th International Symposium on Environmental Geochemistry (ISEG), 25-30 September, 2006, Beijing, China.
- **Shukurov, N., Kersten, M., Wilcke, W. (2006) Heavy metal binding forms in contaminated soils impacted by the Almalyk mining and smelting complex / The 7th International Symposium on Environmental Geochemistry (ISEG), 25-30 September, 2006, Beijing, China.**
- **Shukurov N., Kersten M., Willcke W., Talipov R. (2007): Environmental Mineralogy of Contaminated Soils (Almalyk Metal Mining and Smelting Area, Uzbekistan. International Youth Scientific Conference (IYSC-2007) on "Mountain Areas - Ecological Problems of Cities", May 29-30, Yerevan, Armenia.**
- **Shukurov N., Kersten M., Willcke W., Kodirov O. (2007): Distribution of Heavy Metal Concentration in Soils Along The Atmospheric Deposition Gradient (Angren Coal Processing Area, Uzbekistan). International Youth Scientific Conference (IYSC-2007) on "Mountain Areas - Ecological Problems of Cities", May 29-30, Yerevan, Armenia.**
- **Shukurov N., M. Kersten, S. Pen-Mouratov, Y. Steinberger, W. Wilcke. Heavy metals in soils: Distribution, forms, bioavailability and their impacts on soil biota (Uzbekistan, Angren-Almalik mining industrial area).Conference Supplement to Geochimica et Cosmochemica Acta, Goldschmidt Conference 13-18 July, Vancouver, Canada. Geochemica et Cosmochemica Acta, Vol.72, No 12S, Page A-864.**
- **Shukurov N., Y. Steinberger, S. Pen-Mouratov, W. Wilcke, M. Kersten. Heavy Metals In Soils Of Angren-Almalik Mining Industrial Area: Distribution, Forms, Bioavailability, And Their Impacts On Nematode And Microbial Biomass. Abstracts proceedings. 33rd International Geological Congress (33rd IGC), 6-14 August, 2008, Oslo, Norway.**

Some research which are still seeking to be investigated for this area:

Isotope analyses, stable Pb isotope signature for separating anthropogenic (airborne) metals from geogenic (lithogenic) ones.

Assessment of PAH contamination in soils affected by industrial emissions

ultrafine nano-sized metal rich particles that appear to be more toxic than larger-size particles;

evaluation of potential remediation measures of sites contaminated by both heavy metals and PAH's.

INTAS | NATO OTAN Science for Peace and Security (SPS) North Atlantic Treaty Organization | DAAD Deutscher Akademischer Austausch Dienst German Academic Exchange Service

Many Thanks!

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