



# Heavy metals in soils:

*distribution, forms, bioavailability, impacts to soil microorganisms*  
(Angren-Almalyk mining industrial area, Uzbekistan)

*N. Shukurov\**, *M. Kersten\*\**, *W. Wilcke\*\**, *Y. Steinberger\*\*\**, *S. Pen-Mouratov\*\*\**

\*Institute Geology and Geophysics, Academy of Sciences of Uzbekistan

\*\*Institute of Geosciences, Johannes Gutenberg University Mainz, Germany

\*\*\* Soil-Ecology Lab., faculty of life Sciences, Bar-Ilan University, Israel

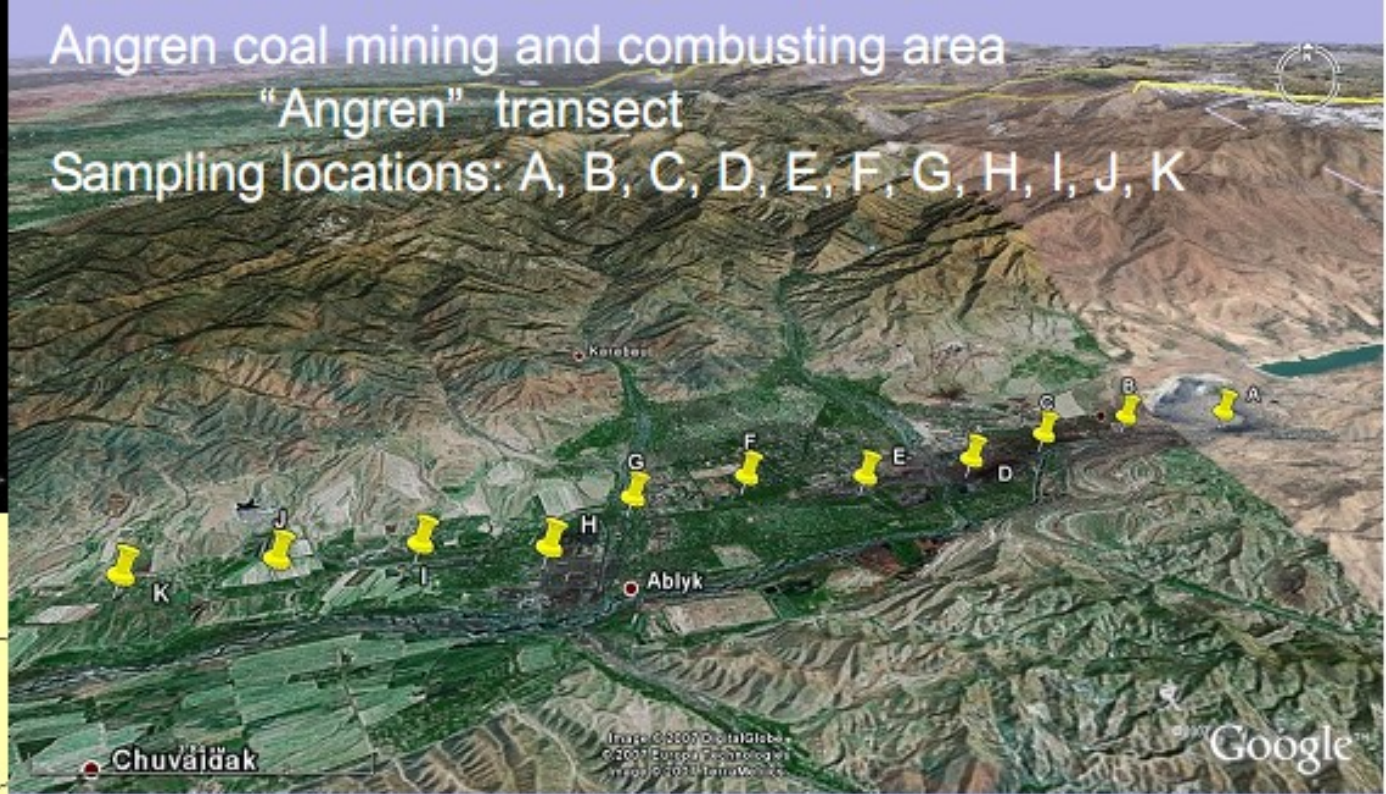




Angren coal mining and combusting area

“Angren” transect

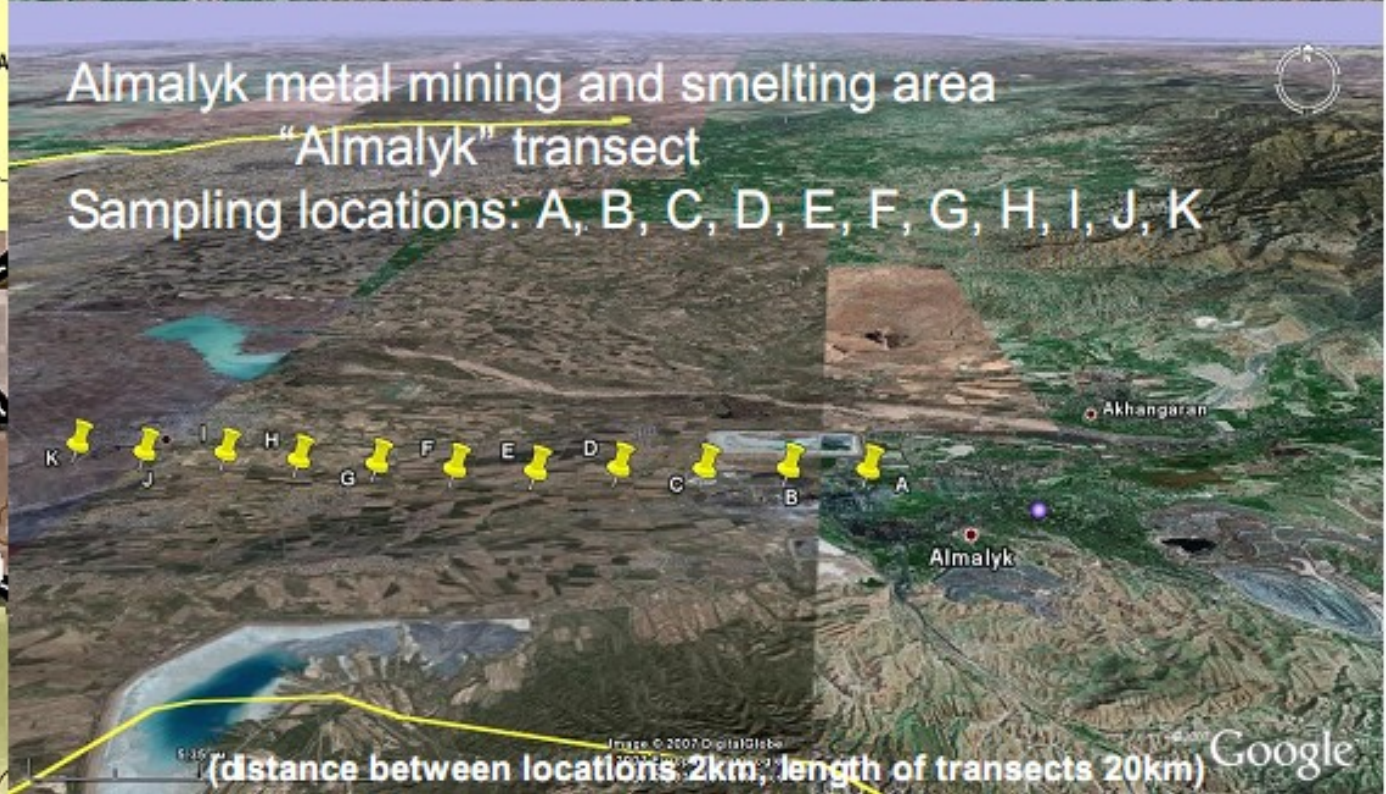
Sampling locations: A, B, C, D, E, F, G, H, I, J, K



Almalyk metal mining and smelting area

“Almalyk” transect

Sampling locations: A, B, C, D, E, F, G, H, I, J, K



(distance between locations 2km, length of transects 20km)

# 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 (<math><0,125+0,063\text{mm}</math>) and silt (<math><0,063\text{mm}</math>) fractions.

Fraction (<math><0,125+0,063\text{mm}</math>) subjected to gravity separation (bromoform).

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

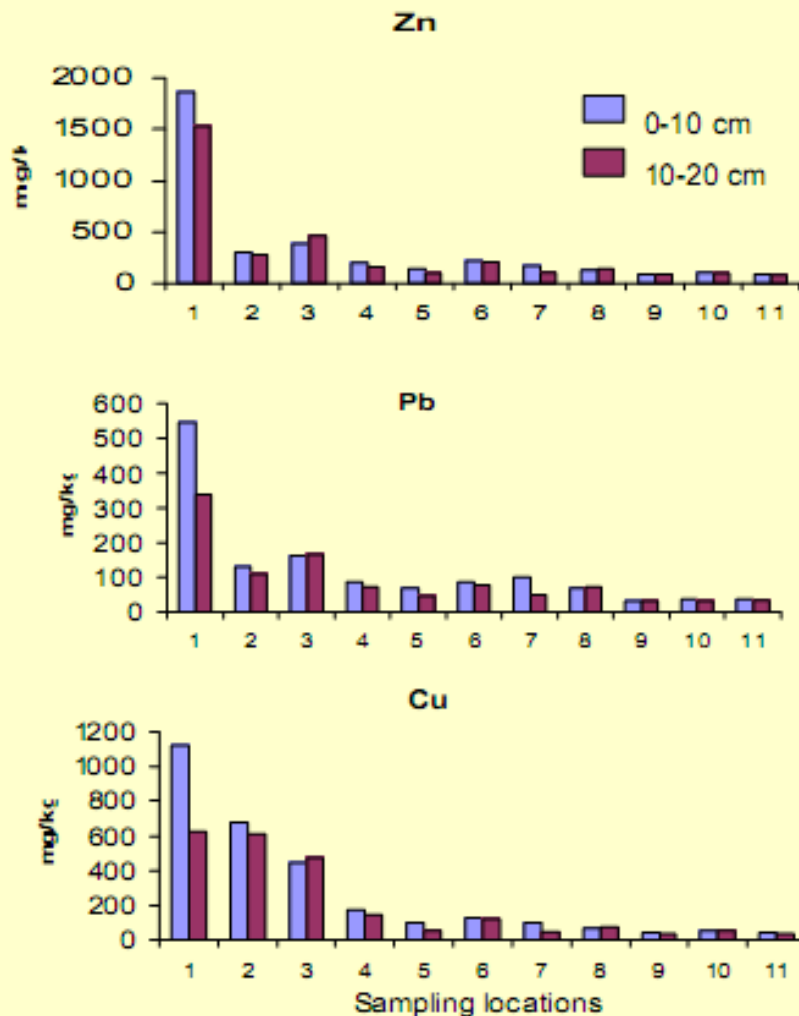
Scanning and element mapping of atmospheric particles and ore minerals (JEOL Superprobe microzond).

Some clay minerals were identified by using XRD.

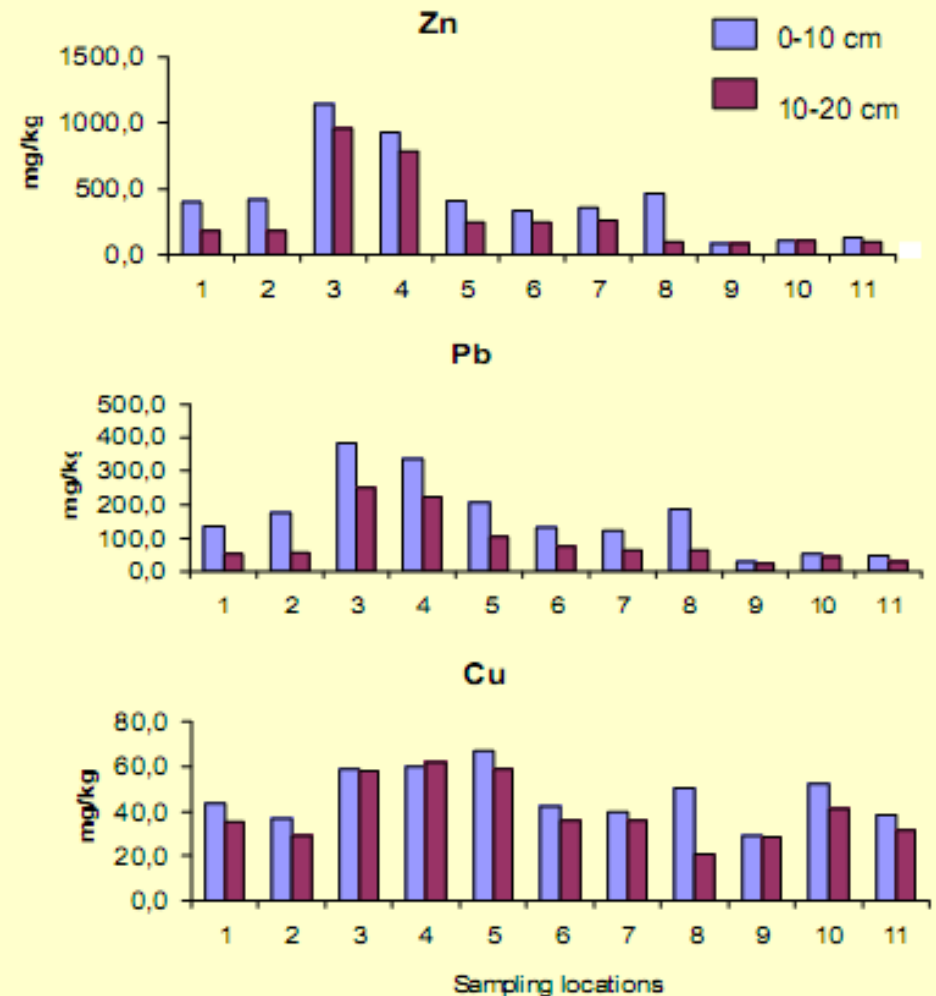


Distribution of heavy metal (total) concentrations in soil along the deposition gradients in Angren-Almalyk mining industrial area (mg/kg).

**Almalyk**  
(metal mining and smelting)



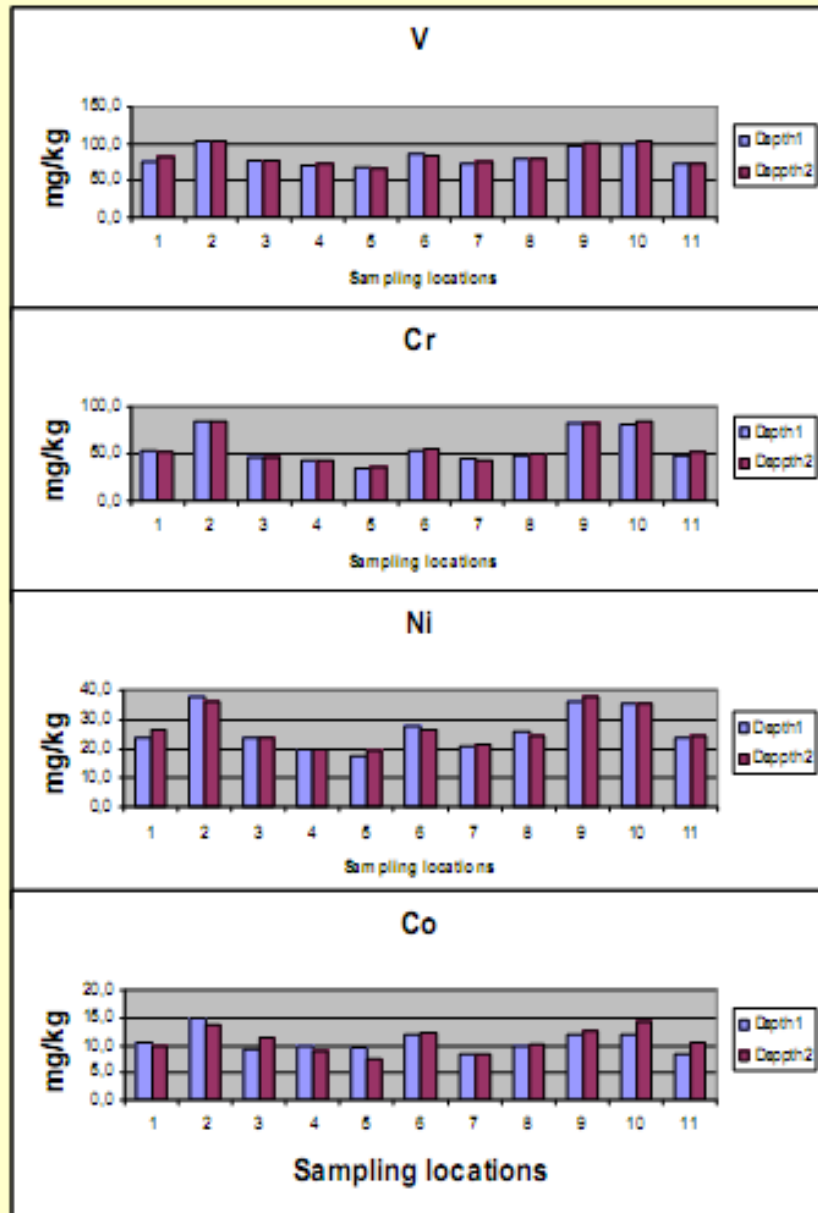
**Angren**  
(coal mining and combusting)



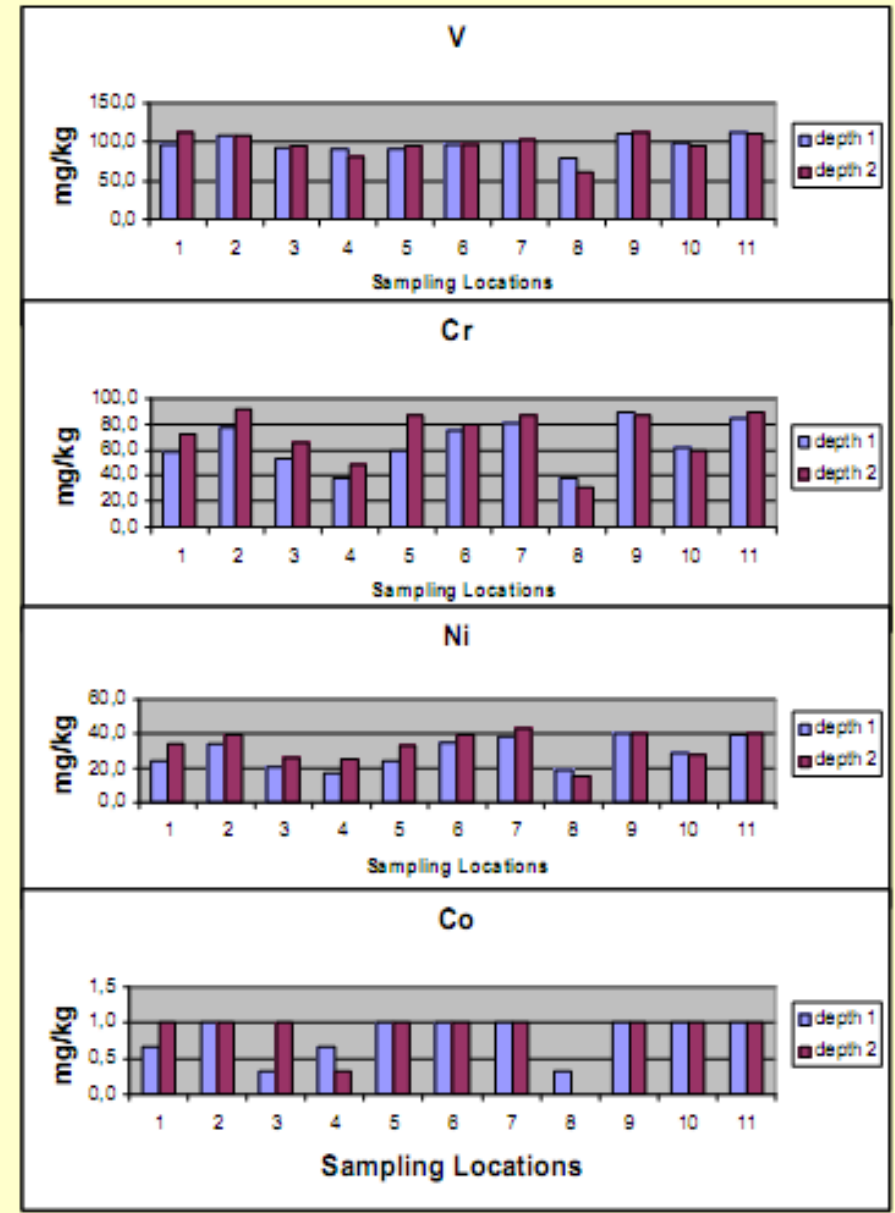
Note: Sampling location No. 1 is the nearest point to Smelter factory in Almalyk transect. Sampling points No 3 and No 4 are within the Angren power station, No 8 Resin factory along the Angren transect. Length of transects 20 km each, distance between locations 2 km

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

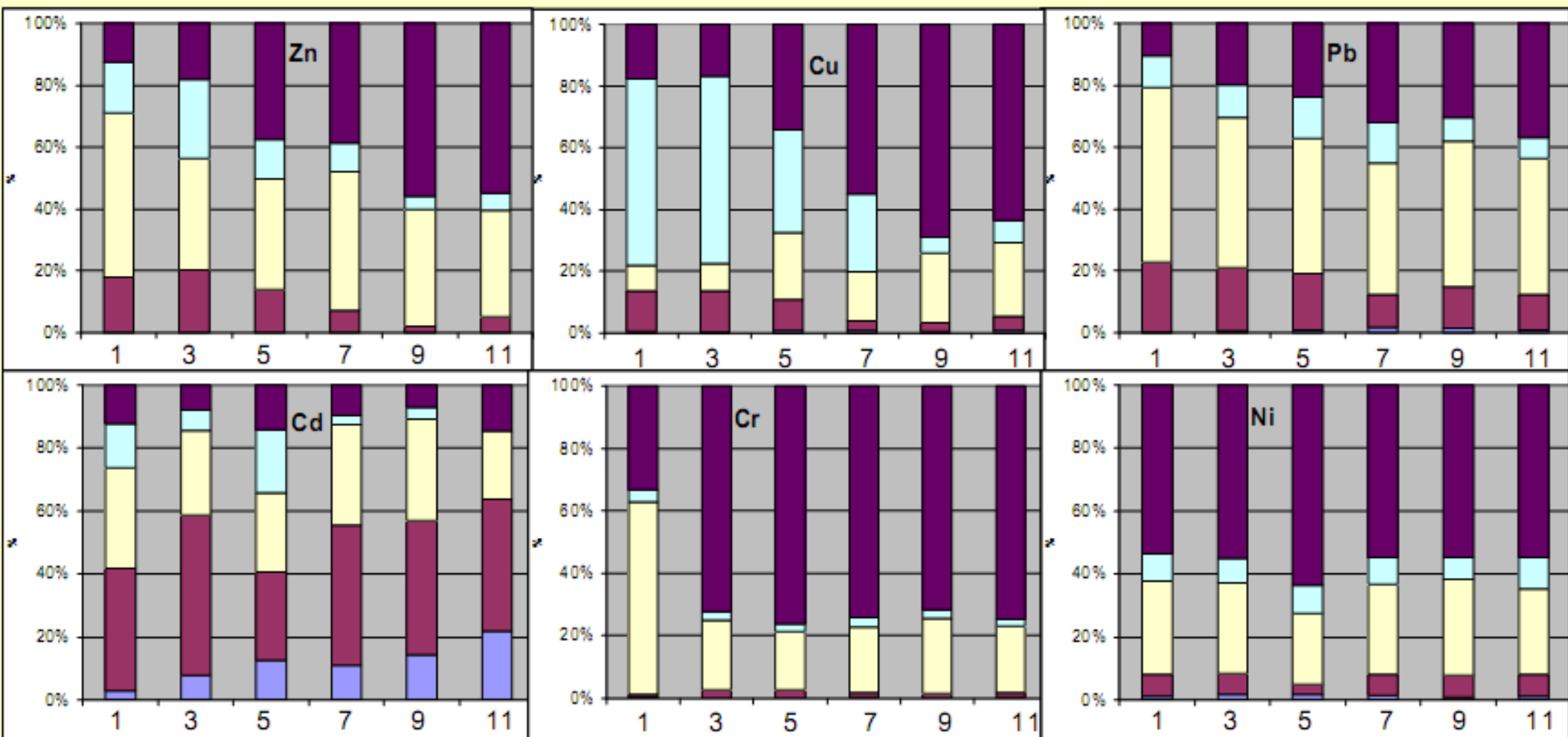
## Almalyk (metal mining and smelting)



## Angren (coal mining and combusting)



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

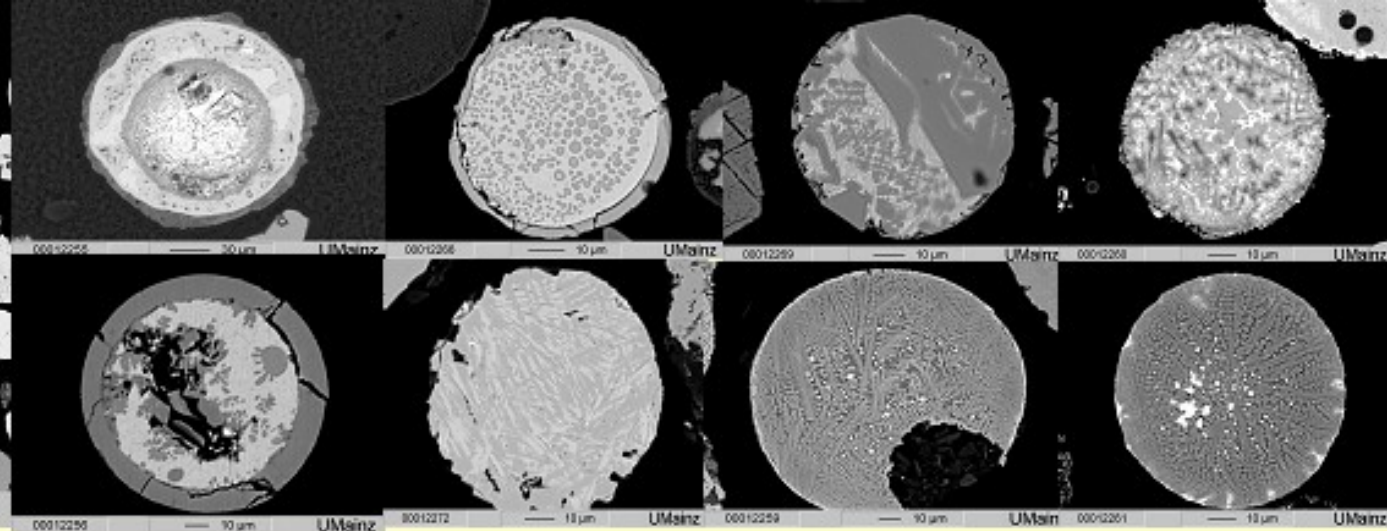
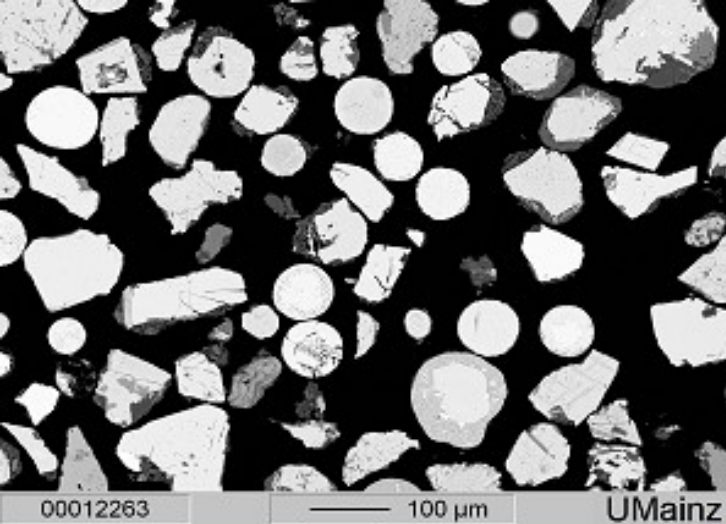


### Sampling locations:

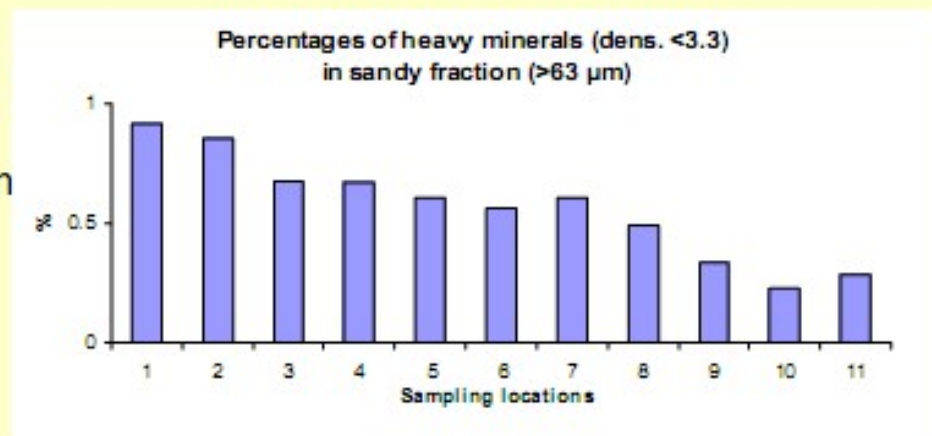
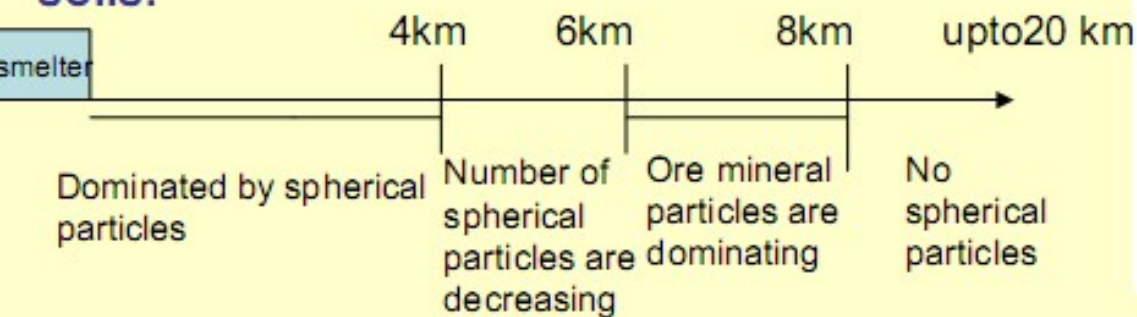
- 1- L1 (100 m distance from the Smelter)
- 3- L3 (4km distance from the Smelter)
- 5- L5 (8 km)
- 7- L7 (12 km)
- 9- L9 (16 km)
- 11- L11 (20 km)

### Chemical fractions:

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

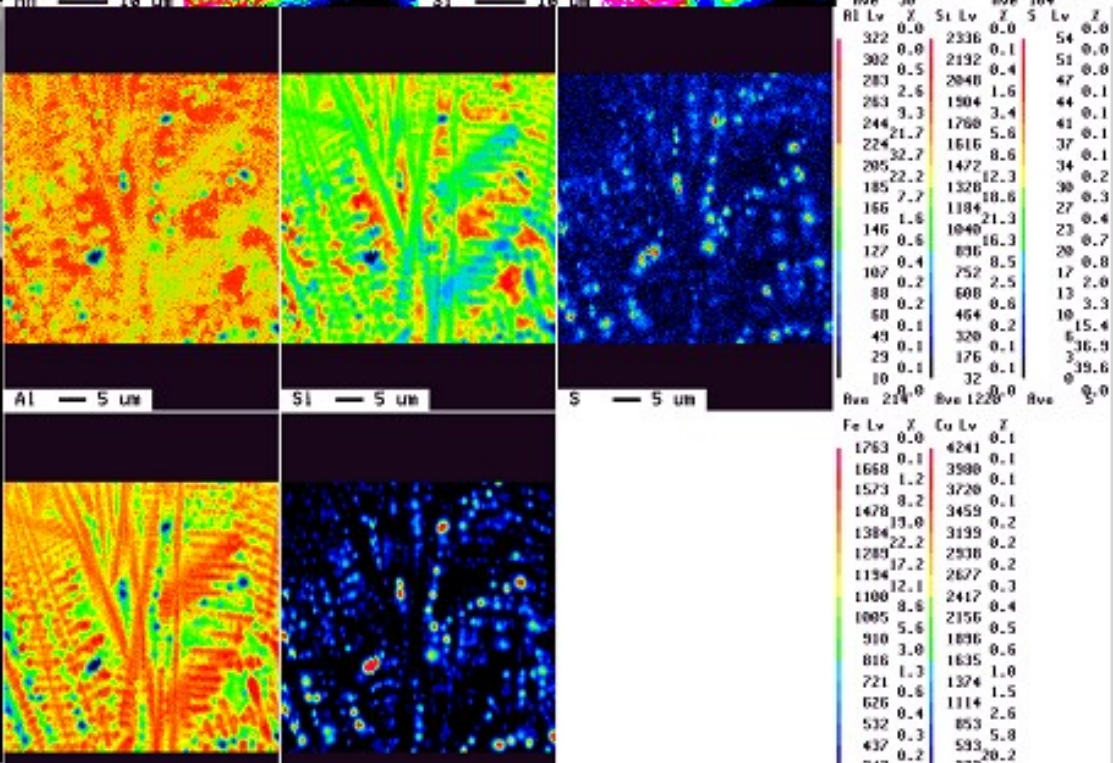
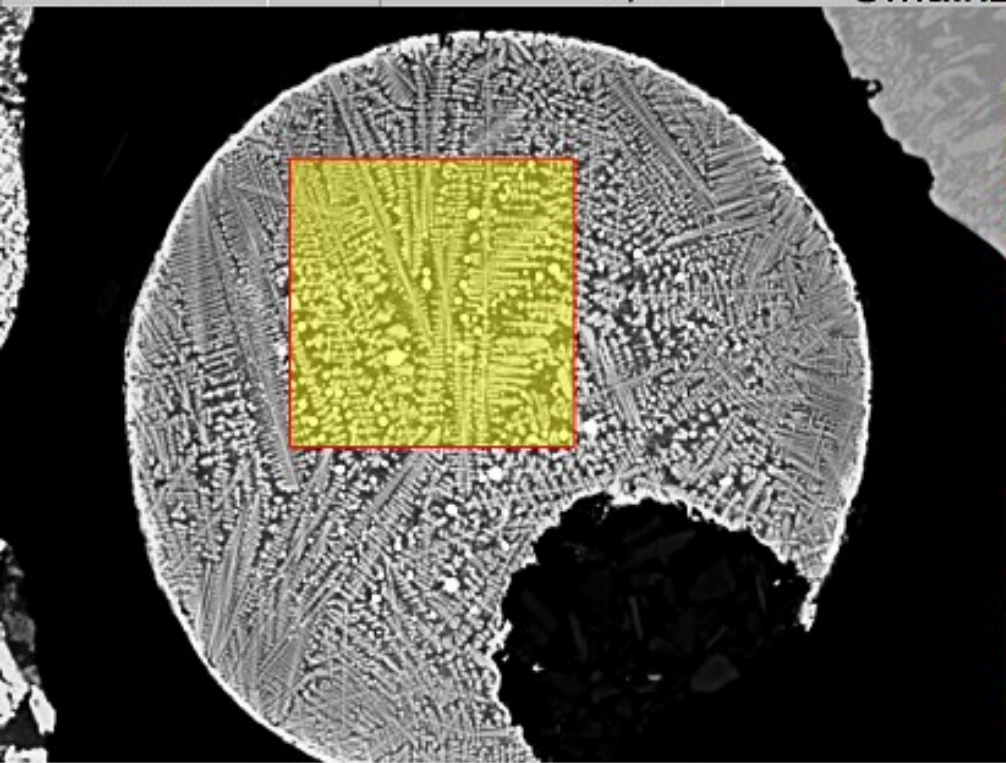
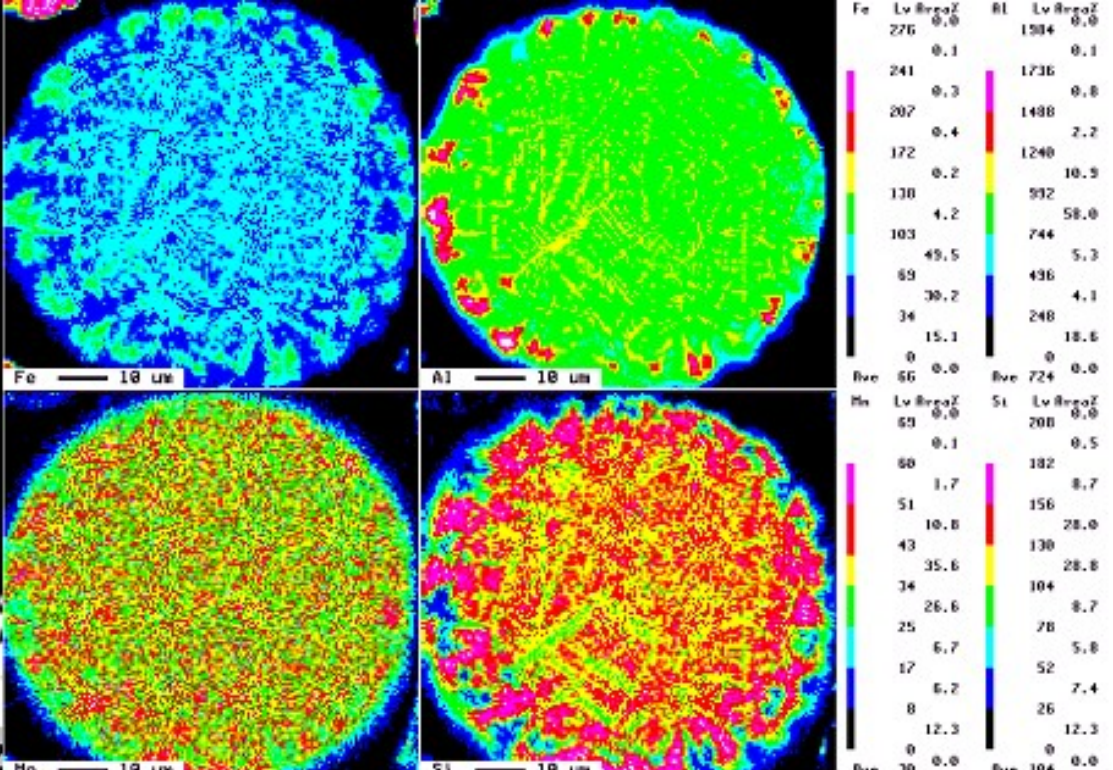
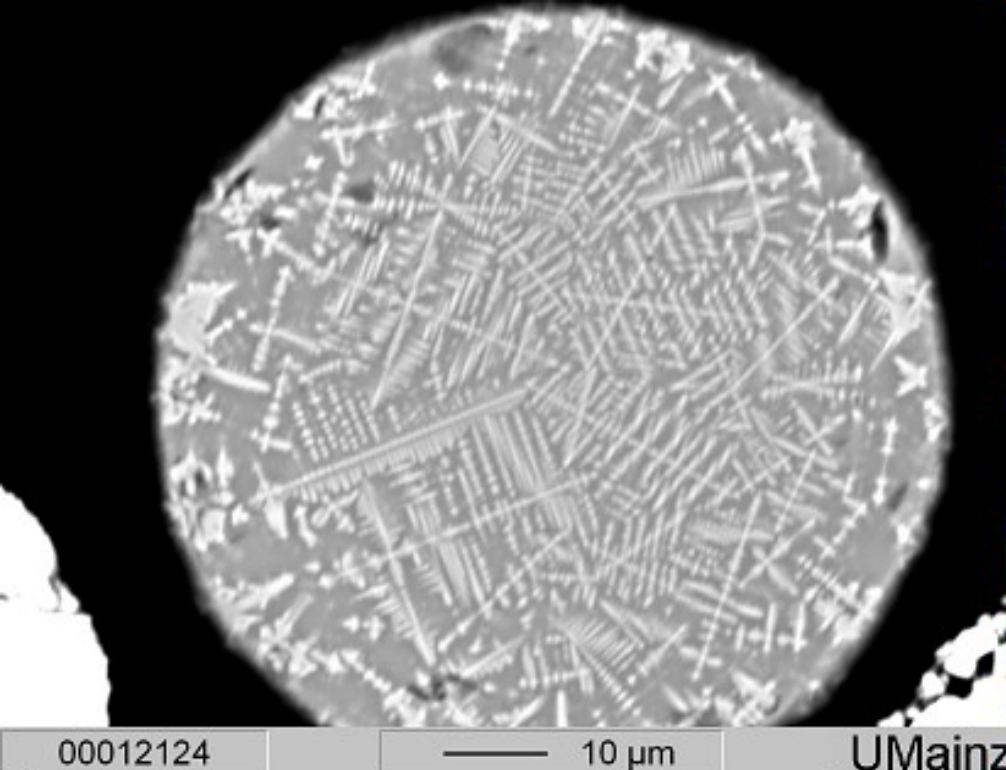


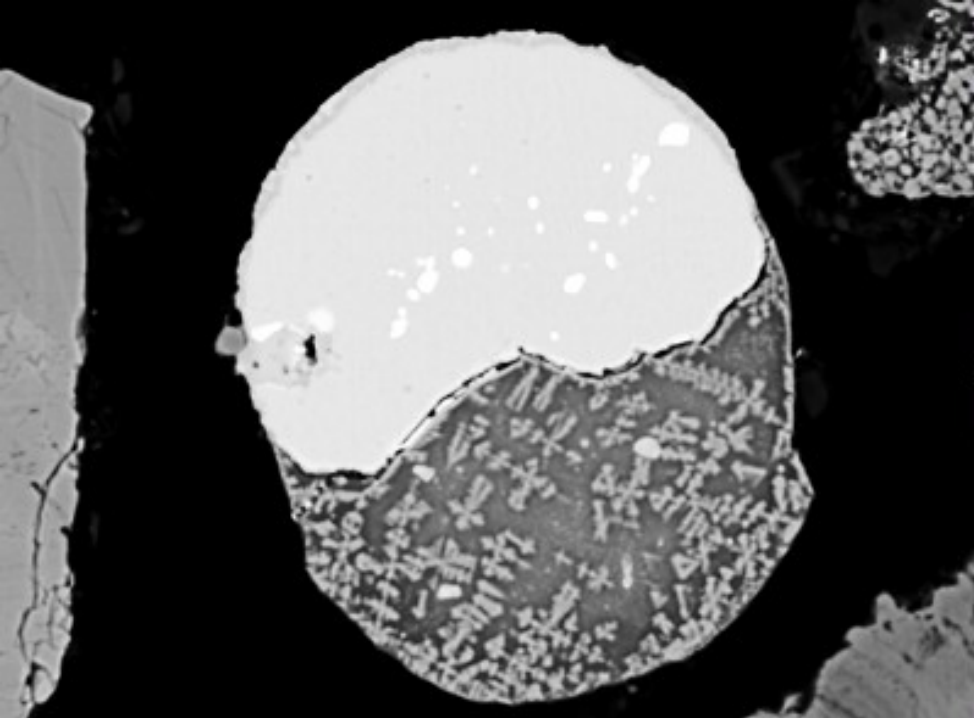
## Distribution and morphology of atmospheric particles along the deposition gradient, Almalyk soils.



### 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 be divided into: 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.

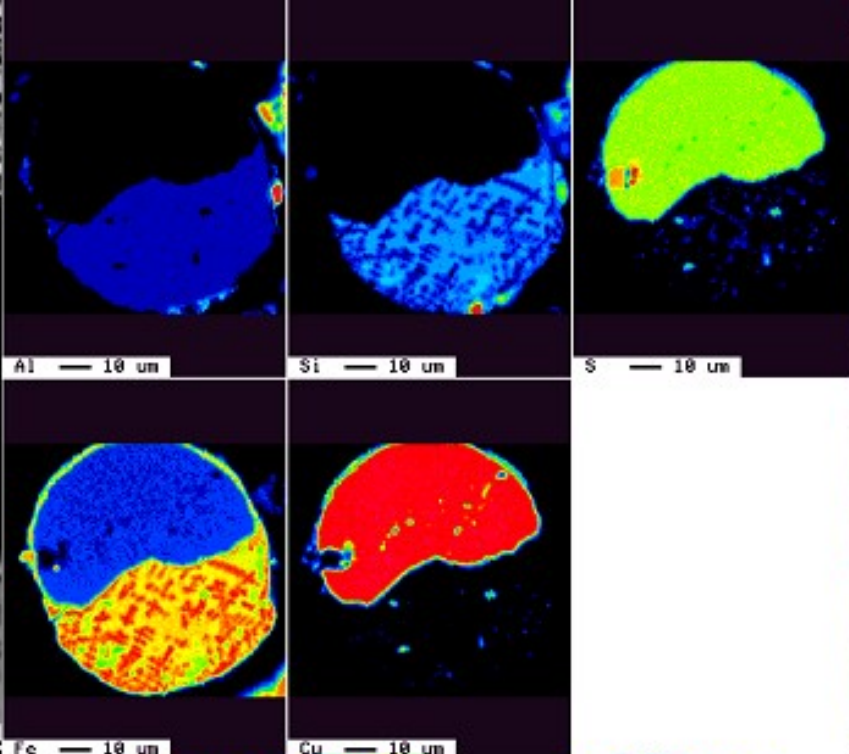




00012264

10 μm

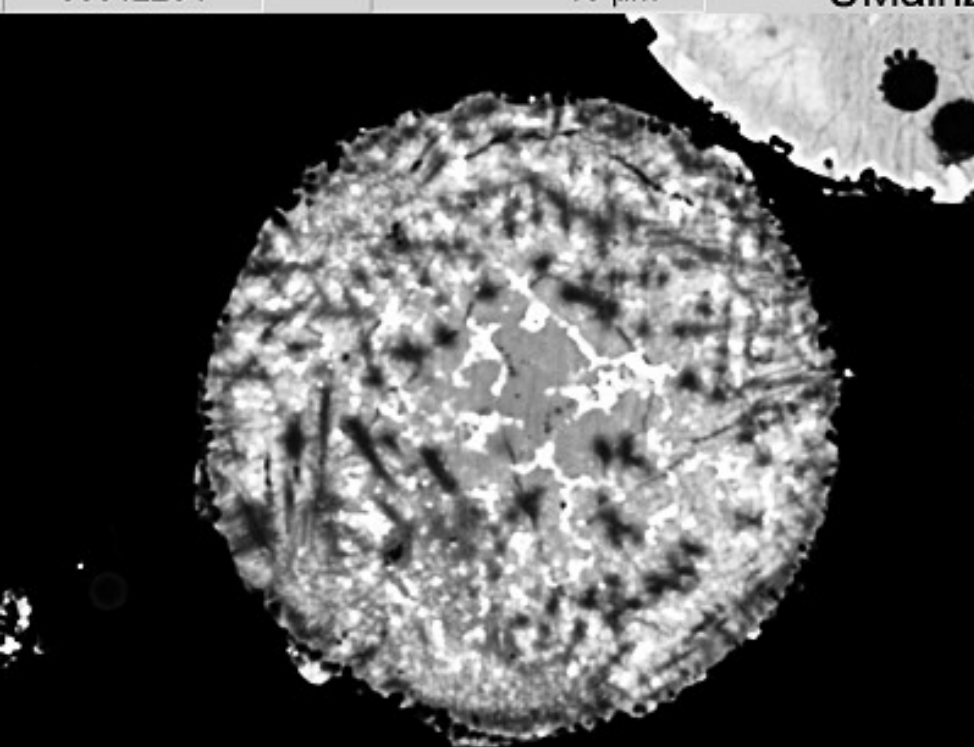
UMainz



Al	Si	S
1452	6387	2027
1361	5987	1900
1271	5588	1773
1180	5189	1646
1089	4790	1520
997	4391	1393
907	3991	1266
817	3592	1140
726	3193	1013
635	2794	886
544	2395	760
453	1995	633
363	1596	506
272	1197	380
181	798	253
90	399	126
0	0	62.6
0	0	0
Rve 66	Rve 593	Rve 462

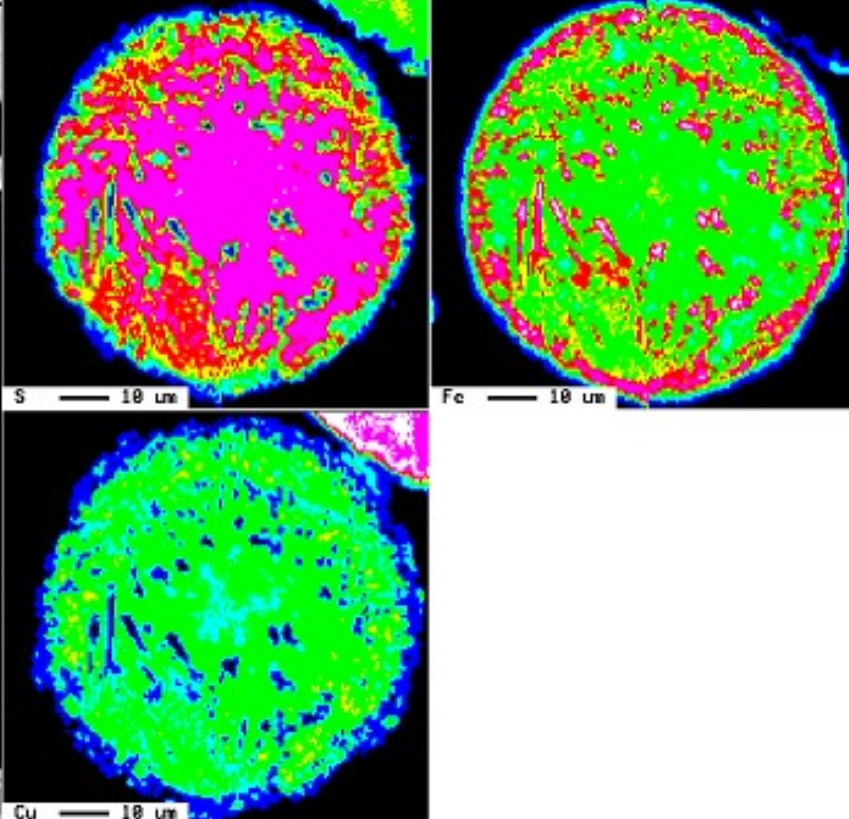
Fe	Cu
1950	3582
1828	3350
1706	3134
1584	2910
1462	2686
1340	2462
1218	2238
1096	2014
975	1791
853	1567
731	1343
609	1119
487	895
365	671
243	447
121	223
0	62.6
0	0
Rve 577	Rve 1125



00012260

10 μm

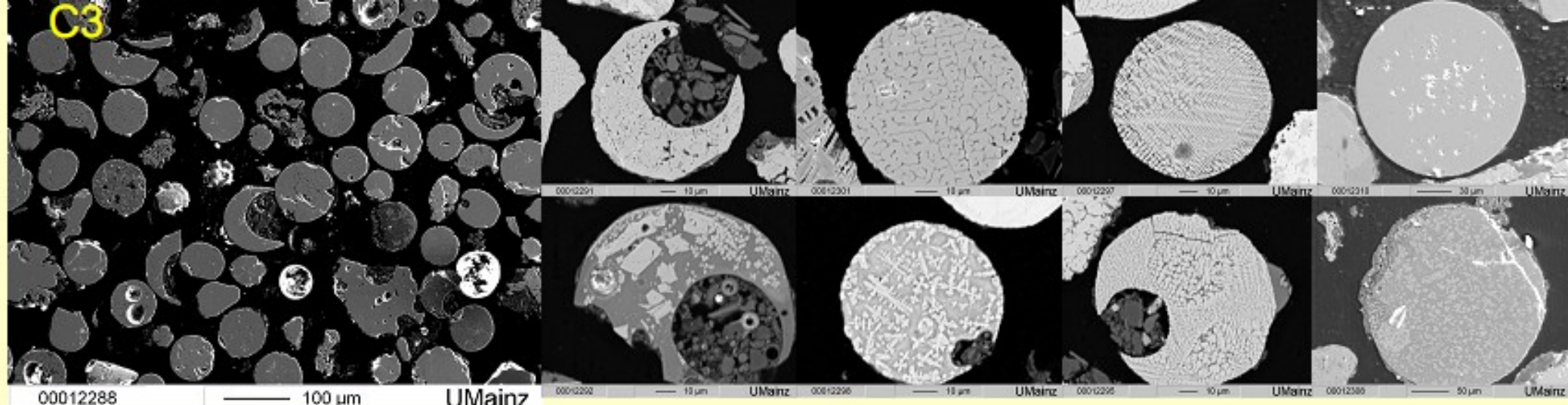
UMa



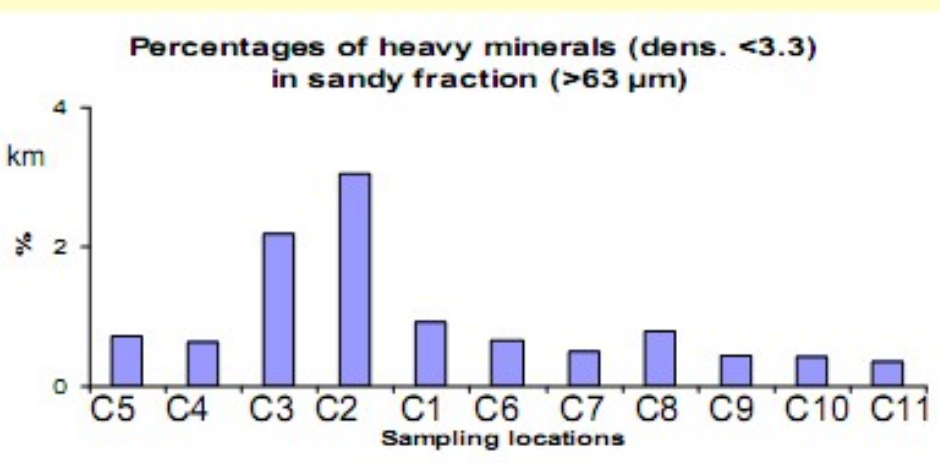
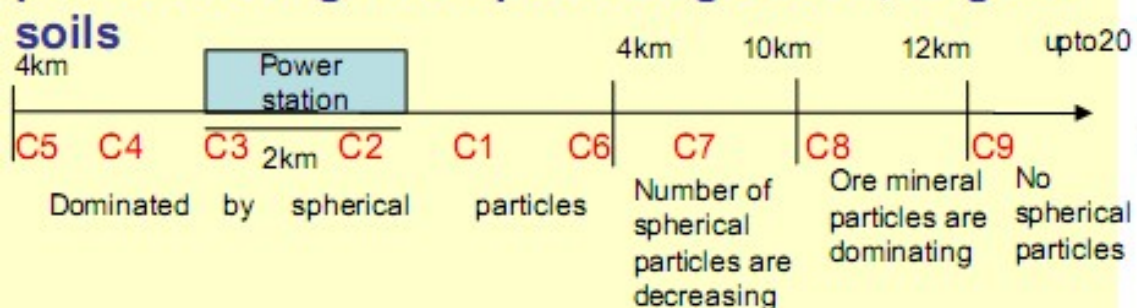
S	Fe
1723	1876
1507	1641
1292	1407
1076	1172
861	938
646	703
430	463
215	234
0	26.2
0	0
Rve 781	Rve 727

Cu
3922
3432
2942
2452
1962
1472
982
492
3
Rve 1072



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



### Emphases:

- Percentage of heavy minerals in Angren soils is more than in Almalik'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 (105°C, 48 h).

Soil pH was determined in H<sub>2</sub>O (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<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>) were determined by a flame photometer (Rhoades, 1982).

Total organic carbon (C<sub>org</sub>) 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 (C<sub>mic</sub>) was determined using a chloroform fumigation incubation (CFI) assay, according to Jenkinson and Powlson (1976). CO<sub>2</sub> concentration was measured in the head space of the glass jars using a Gas Chromatograph (GC) and C<sub>mic</sub> was calculated as:  $C_{mic} = [(CO_2-C \text{ from fumigated soil}) - (CO_2-C \text{ from control sample})] / k_c$ . A k<sub>c</sub> of 0.41 was used, as proposed by Anderson and Domsch (Anderson and Domsch, 1990).

Soil basal respiration (BR) as CO<sub>2</sub> evolution, was determined by GC (Spurling and West, 1990).

Metabolic quotient (qCO<sub>2</sub>) was calculated as the ratio between basal respiration (BR) and microbial biomass (C<sub>mic</sub>) (Anderson and Domsch, 1990). The qCO<sub>2</sub> 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 C<sub>mic</sub>/C<sub>org</sub> ratio.

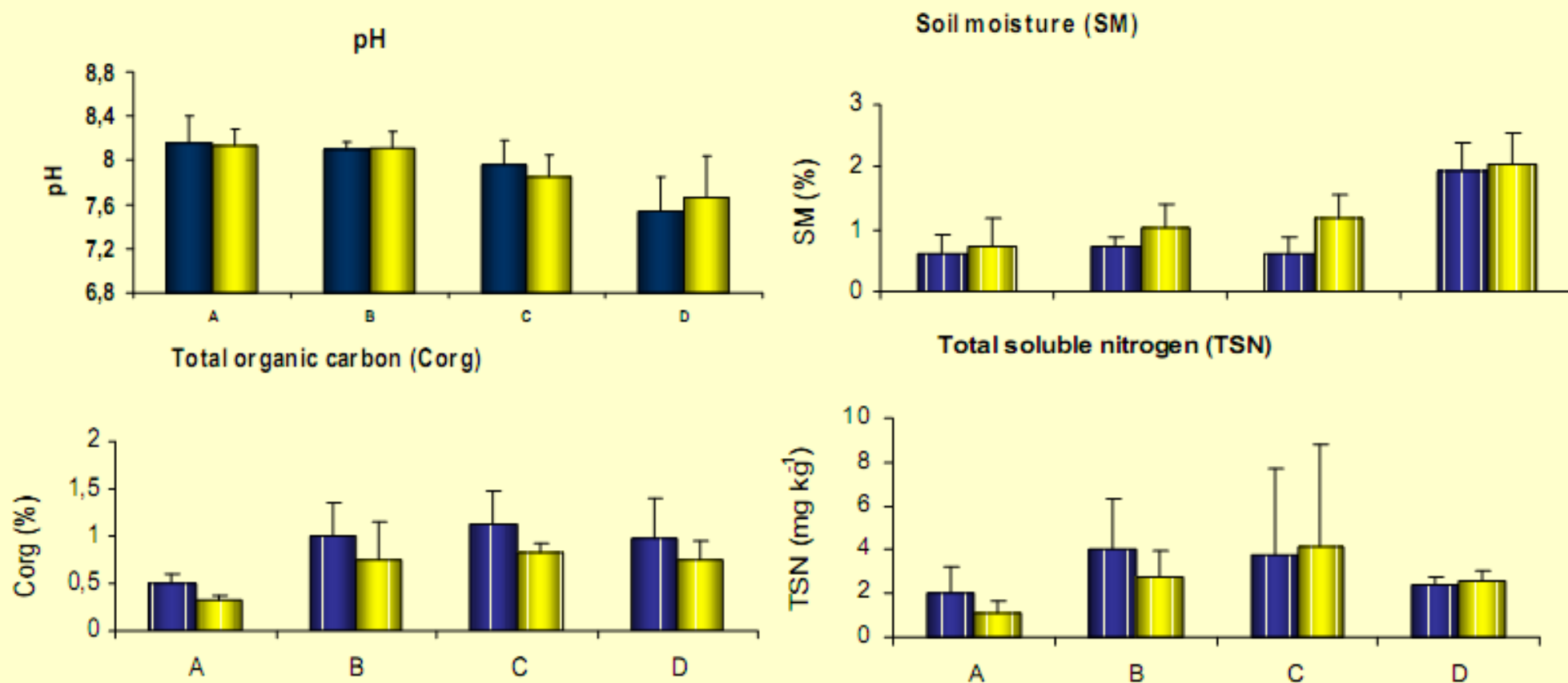
All data were subjected to statistical analysis of variance using the SAS model (ANOVA, Duncan's multiple range tests and Pearson correlation coefficient) and were used to evaluate differences between separate means. Differences obtained at levels of p < 0.05 were considered statistically significant.



## RESULTS:

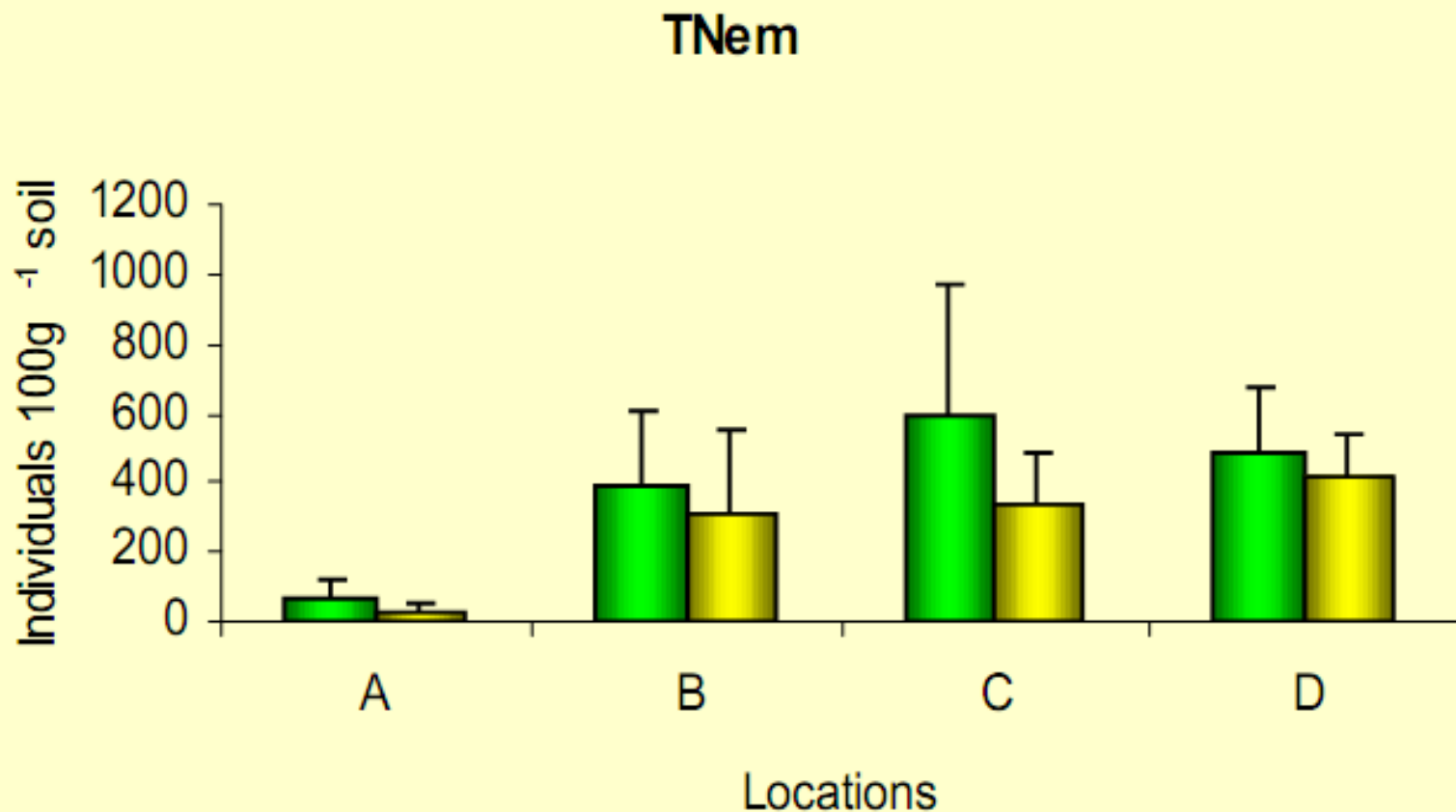
Significantly close relationships were observed between metal content and soil biological activity in both studied areas.

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)

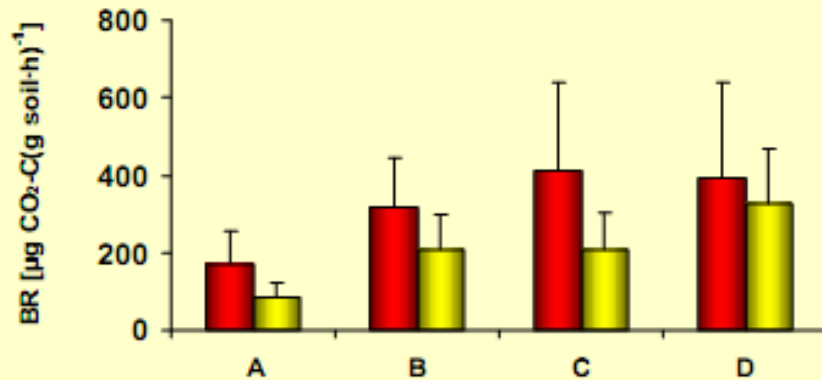
Total number of nematodes, basal respiration (Br) and microbial biomass total organic carbon ratio ( $C_{mic}/C_{org}$ ) had a significantly negative correlation with heavy metals.



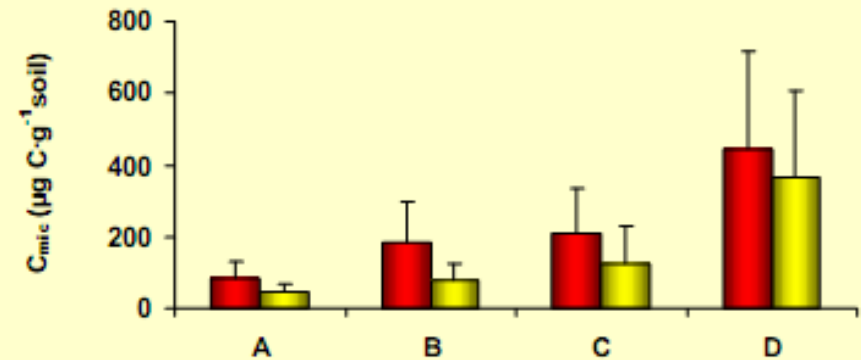
Distribution of number of nematodes along the deposition gradient at two soil layers ( ■ 0-10 cm; ■ 10-20 cm)

# Soil microbial properties

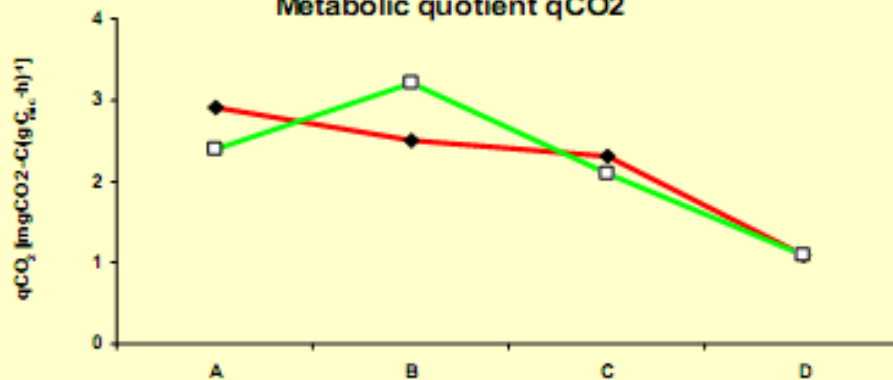
Basal respiration (BR)



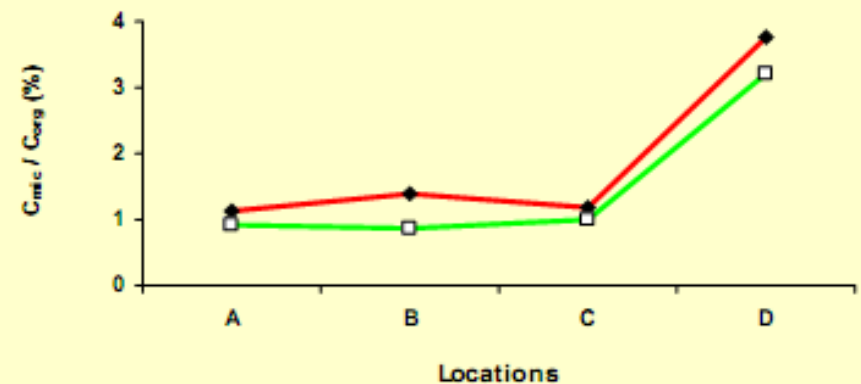
Microbial biomass ( $C_{mic}$ )



Metabolic quotient  $q_{CO_2}$




Microbial Coefficient -  $C_{mic}/C_{org}$



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 m ( ) soil layers

# 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., Wilcke 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., Wilcke 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-Almalyk mining industrial area). Conference Supplement to *Geochimica et Cosmochimica Acta*, Goldschmidt Conference 13-18 July, Vancouver, Canada. *Geochimica et Cosmochimica 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-Almalyk 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.

# Many Thanks!

These investigations were supported by **DAAD**, **INTAS** and **NATO SPS** to **Dr. Nosir Shukurov**.

The authors wish to express their appreciation to **Dr. Thomas Reischmann**, **Dr. Burkhard Schulz-Dobrick**, **Mrs. Nora Groschopf**, **Ms. Antije Friedrichsen** from the University of Mainz and to **Ms. Ginetta Barness** from Soil Ecology lab, Bar-Ilan University for their useful advices and kind technical assistance.

