Mode of occurrence of heavy metals in contaminated soils in the vicinity Almalyk mining and smelting complex

Nosir Shukurov[1] , Michael Kersten[2], Wolfgang Wilcke[2]
[1]Institute of Geology and Geophysics, Academy of Sciences of Uzbekistan,
700041 Tashkent, Uzbekistan
[2]University of Mainz, Institute for Geosciences, D-55099 Mainz, Germany

Objective:

- To characterize heavy metal binding forms of contaminated soils in the vicinity of a nonferrous metal mining and smelting complex
- Distribution of airborne particulate matter along the deposition gradient
- Identify the metal rich particles and study their interior structure

Material for this study:

- Soil samples from the Almalyk mining and smelting area, which are heavily impacted by atmospheric emissions from metal-processing activity.
- Resin based briquettes prepared from the heavy fraction of highly polluted soils

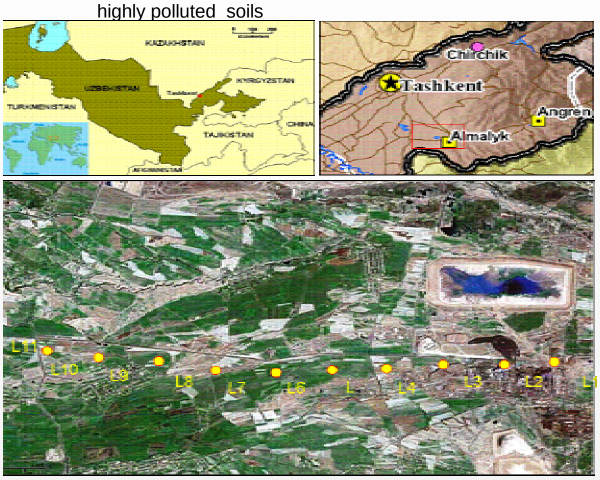

Fig.1: Sampling sites along the atmospheric deposition gradient in the vicinity of Almalyk mining and smelting complex, sites No.1 and No.4 located near the mining wastes, No.2 and No.3 located within the smelters, respectively.

Study area:

The Almalyk mining and smelting complex (AMSC) is the largest point-source emitter of sulphur and heavy metals in this area. Almalyk city was founded in 1951 from several settlements exploiting the rich nonferrous-metal resources of the Qurama Mountains. The city has become an important centre of nonferrous metallurgy and most important industrial center of Uzbekistan. As one of the largest mining companies in Uzbekistan, it has the capacity to mine and process about 25 Million ton of ore per year, with annual metal-producing capacity of Cu 130,000, Zn 40,000, and Pb 80,000 tons per year. The Almalyk complex emits about 100,000 tons of toxic substances (sulphur dioxide, carbons, nitrogen, oxides, sulphuric acid, heavy metals, arsenic, etc) per year, which is responsible for 13% of all of Uzbekistan's air emissions from stationary sources.

Sample preparation and analysis:

For studying in detail the binding forms of heavy metals in highly contaminated soils, samples were collected from the four sites in the vicinity of the metal mining and smelting area: sampling site No.1 located near the mine spoils, sampling sites No.2 and No.3 located near the Cu and Zn smelters, sampling site No.4 located near the tailings depository (Figure 1).

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) - heavy mineral fraction (ore minerals and spherical airborne metal-rich particles) and (B) – light mineral fraction (parents rock minerals). The heavy mineral fractions separated from the fines were embedded in epoxy-resin. Element mappings were performed with the polished and carbon-coated resin slabs using a JEOL microprobe.

Results:

A lot of grains and spherical particles with bright contrast appeared in the microprobe scans indicating metal-rich chemistry. Spherical particles dominated in 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).

Fe was abundant in most particles, 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 (Fig. 4).

Most of the spherical particles showed holes inside, or had Fe+Ti or Fe+Ti+Mn cores or rims, which indicates formation from a pre-existing molten phase. Occasionally, the hollow spheres contained bright particles composed primarily of Cu, Zn, Pb, and Si, with smaller amounts of Fe, Ti, and Ca (Fig. 6).

Fig.2. Morphology of heavy mineral particles from Almalyk soil, (a) of sampling site No.3, (b) small galena particle weathering to anglesite (scanned in sample from site No.1, (c) spherical pure Cu particle (>98%) from site No.3.

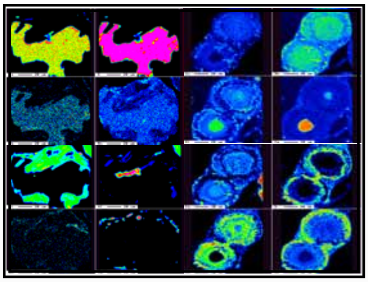

Fig.3: Element maps for typical heavy mineral particles.

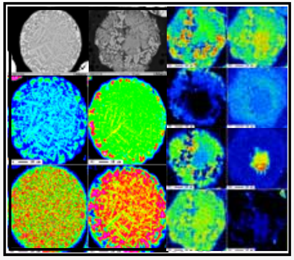

Fig.4: SEMs of spherical particles from the heavy mineral fraction showing metalliferous dendrites in a silicate matrix (from site No.2).

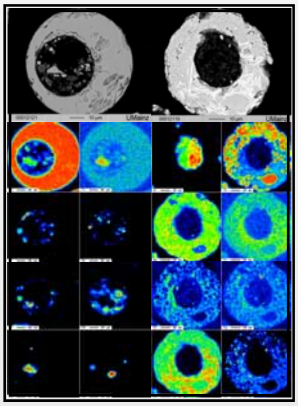

Fig.5. Microstructure and element maps of some spherical particles showing metalliferous cores with different core and rim structures.

Discussion:

Most of the heavy metals occur in the heavy mineral fraction of Almalyk Soils. Microprobe observations have shown that the studied heavy metals (Cu, Zn and Pb) are associated with two major binding forms in the contaminated soils. Sulfide-bound metals and those bound to 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. Spherical metalliferous particles can be found in smelter-impacted areas. Other particles related to the latter include (i) essentially pure metal particles (Cu, Zn, Al), (ii) metal-rich cores with silicate rims, and (iii) small spherical metal sulfide particles within larger, heterogeneous glassy particles. Morphology and internal microstructure of the spherical particles in the heavy mineral fractions of the soil samples indicates formation from a pre-existing molten phase, probably with the air pollution control process of the smelters. Abundance of such particles is critical in that they are known to easily release their metal inventory into the environment.

Corresponding author: michael.kersten@uni-mainz.de

Heavy metal distribution in soils along the atmospheric deposition plume of Angren coal processing area (Uzbekistan)

Nosir Shukurov[1], Wolfgang Wilcke[2] and Michael Kersten[2]

[1]Institute of Geology an Geophysics, Academy of Sciences of Uzbekistan, 700041 Tashkent, Uzbekistan
[2]University of Mainz, Institute for Geosciences, D-55099 Mainz, Germany

- ## OBJECTIVE:

To examine the effect of Angren industrial coal mining and combusting complex on heavy metal content in soils along the emission gradient.

- ## MATERIAL for this study:

Soil samples collected along a transect of 12 locations (2 km

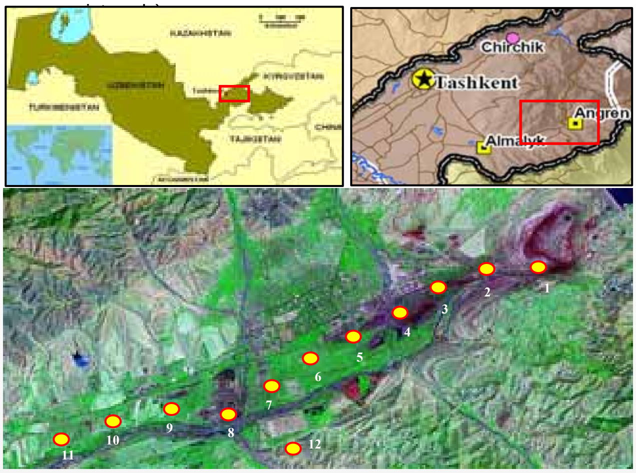

Fig. 1: Map of sampling sites along the atmospheric deposition gradient. Note that sites No. 4 and No. 8 are located within reach of the Angren power plant and rubber factory, respectively.

Study area: Angren city is the largest coal mining and power producing center in Uzbekistan, developed during and after World War II. The Angren power plant (250 MW capacity) works on basis of brown coal from the nearby Angren coal field (production capacity of 2.5 million tons/year, ash content 11-35 %). The coal mining and power generation industry in Angren uses old equipment that has not been upgraded since the 1990s. Air pollution control technology is in poor condition and several units need to be modernized. Emissions in the range of about 100000 tons/year over the last few decades have caused severe damage to natural ecosystems of the area, and dramatically increased impact of heavy metal rich dust and fly ash particles in this area.

Table 1. Summary of consumption and production figures for the two coal burning facilities in Angren industrial area based upon data obtained from the report of State Committee for Nature Protection of Uzbekistan (2001).

Facility	Angren	Novo-Angren
Energy production (MW)	205	1500
Coal consumption (million tons/year)	2.0	0.5
Fuel	Coal	Coal, gas
Technology	Conventional thermal	Conventional thermal
Ash production (million tons/year)	0.46	0.11
Annual atmospheric emission (thousand tons/year): Particulates Sulphur and nitrogen oxides	26 28	7 61

Sample preparation and analysis

Soil samples from two depths were collected in quadruplicate using a polypropylene shovel and subsequently transferred to clean polyethylene bags. In the laboratory, all samples were air-dried, sieved though a 2 mm mesh sieve, subsequently ground in an agate mortar, and homogenized before preparation of powder pellets (1.5 ml resin + 6 g soil) for XRF analyses. QA/QC was performed on basis of CRM's.

Results and Discussion:

Levels for a number of potentially toxic metals varied along the sampling transect, revealing a gradual decrease at increasing distance from the emission sources (Fig. 2). The highest levels were found for the relatively volatile metals Zn (850-1051 ppm) and Pb (270-320 ppm) in soils near the power plant (locations 3, 4, 5, Fig. 1) and rubber factory (location 8), suggesting that the metal pollutants probably derive from local stack emissions.

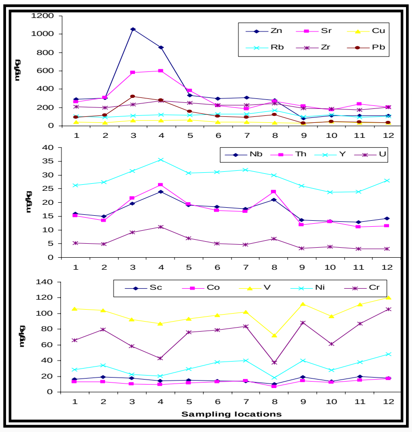

Fig. 2: Distribution of heavy metals along the atmospheric deposition gradient in Angren coal mining and combusting area.

Significant differences ($p<0.05$) were observed between the upper (0-10 cm) and deeper (10-20 cm) soil layers for Cu, Zn, Pb, Sr, U, and Th at most sampling locations (Table 2).

Table 2. Significant differences of heavy metal contents between upper and deeper soil layers (√ marking sampling sites with $p<0.05$)

	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	Pb	Th	U
1				√		√	√			√				√	√		√
2						√	√			√			√		√	√	√
3			√		√		√	√		√		√	√		√		√
4	√				√			√				√	√		√	√	√
5							√							√	√		
6						√	√			√					√		
7			√			√	√		√	√		√		√	√		
8	√	√				√	√		√	√	√	√	√	√	√		
9				√			√				√		√		√		
10						√						√		√	√		
11			√		√	√	√			√					√		
12						√	√							√	√		√

The contents for a number of metals (Zn, Cu, Pb, Ba, Sr, Nb, Zr, Y, U, Th) were higher in the upper soil layer at all sampling sites. Distribution and contents of some other metals (Co, Cr, Ni, V, and Sc) showed opposite behavior, probably due to a geochemical background (Fig. 3).

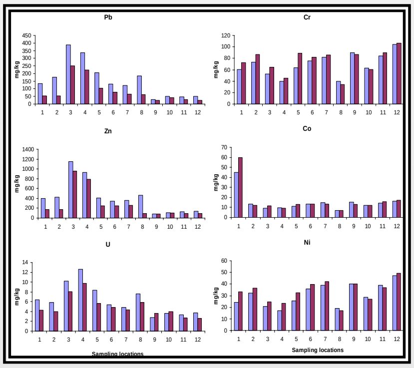

Fig. 3: Distribution of heavy metal concentrations along the deposition gradient in two soil layers (☐ 0-10cm; ■ 10-20 cm).

Conclusions: The Angren industrial coal mining and combusting complex is the major source for Pb, Zn, Cu, Sr, Zr, Ba, Nb, Y, Th, and U enrichment in soils. Highest contents were determined in the upper soil layer (0-10 cm). Distributions of only a few metals (Co, Cr, Ni, V and Sc) suggest lithogenic background. Therefore, we can divide enrichments of all studied heavy metals into two groups:
1) Anthropogenic (airborne) source: Pb, Zn, Cu, Sr, Zr, Ba, Nb, Y, Th, U
2) Lithogenic (geochemical) source: Ni, Cr, Co, V, Sc.

Corresponding author: michael.kersten@uni-mainz.de

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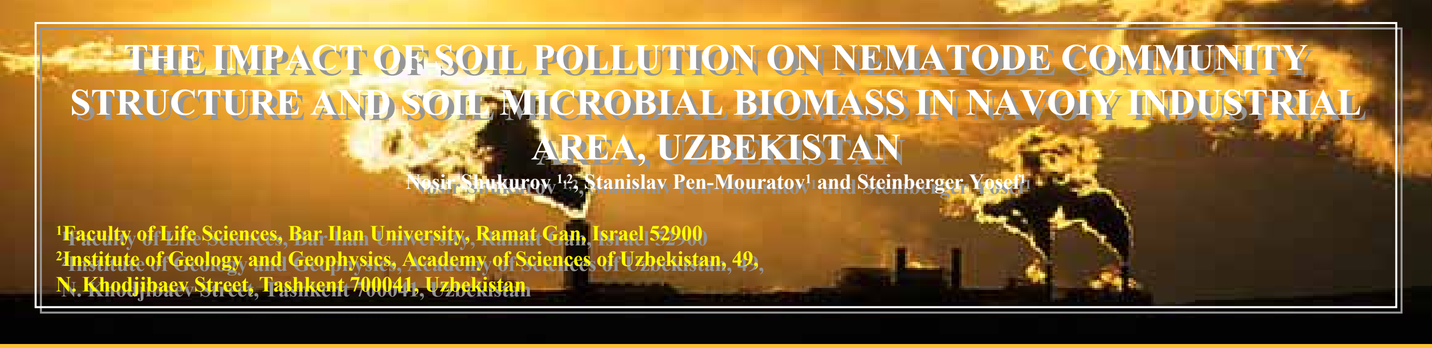


THE IMPACT OF SOIL POLLUTION ON NEMATODE COMMUNITY STRUCTURE AND SOIL MICROBIAL BIOMASS IN NAVOIY INDUSTRIAL AREA, UZBEKISTAN

Nosir Shukurov [1,2], Stanislav Pen-Mouratov[1] and Steinberger Yosef[1]

[1]Faculty of Life Sciences, Bar Ilan University, Ramat Gan, Israel 52900
[2]Institute of Geology and Geophysics, Academy of Sciences of Uzbekistan, 49,
N. Khodjibaev Street, Tashkent 700041, Uzbekistan

The effects of ammonium-rich and heavy-metal air pollution produced by the industrial enterprises at Navoiy (Uzbekistan) on soil free-living nematodes and microbial population activities was investigated in soil samples collected in a 5-km radius surrounding the industrial enterprises (A–NavoiAzot enterprises; B–NavoiGRES; C–Residential area; D–Agricultural area; E–Desert area) (Fig. 1). At each location, soil samples were collected (n=4) from the upper layer (0-10 cm) for determination of soil moisture (SM), total organic carbon (C_{org}), total soluble nitrogen (TSN), soil electrical conductivity (EC) and cations (Ca^{2+}, K^+, Na^+). Heavy metals (As, Cu, Pb, Zn), soil basal respiration (BR), microbial biomass (C_{mic}) and nematode population were determined.

Table 1. Main chemical characteristics of the soil samples (n=17)

Sampling sites	pH	Sm %	C_{org} %	EC $mS\ g^{-1}$	Ca^{2+} $mg\ kg^{-1}$	Na^+ $mg\ kg^{-1}$	K^+ $mg\ kg^{-1}$	Cu $mg\ kg^{-1}$	Pb $mg\ kg^{-1}$	As $mg\ kg^{-1}$
A	8.2	0.80	0.4	1.9	20	31	7	32	6.3	15
B	7.9	0.93	0.5	3.7	61	41	8	33	6.7	13
C	8.1	0.93	0.4	1.3	14	24	5	35	6.7	15
D	8.1	0.80	0.8	1.4	5	15	20	30	5.0	10
E	8.1	0.75	0.5	1.0	7	23	5	17	5.0	9

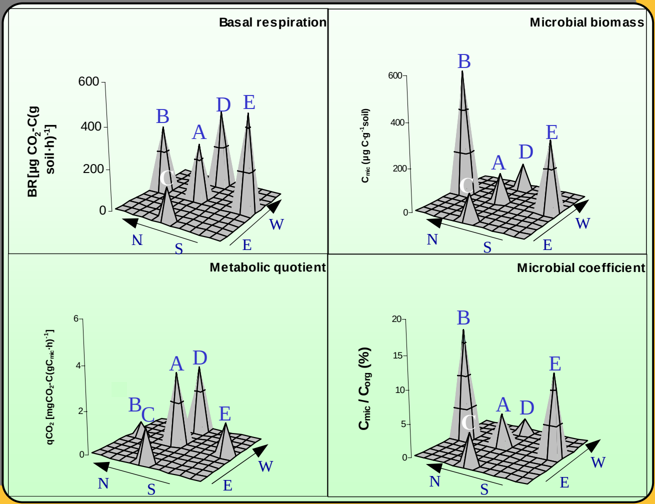


Fig. 2. Soil microbial biomass, basal respiration, metabolic quotient and microbial coefficient in soil samples taken at different sampling sites at the Navoiy industrial area.

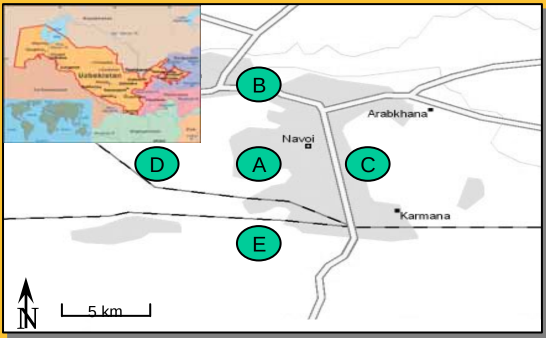


Fig. 1. Locations of sampling sites

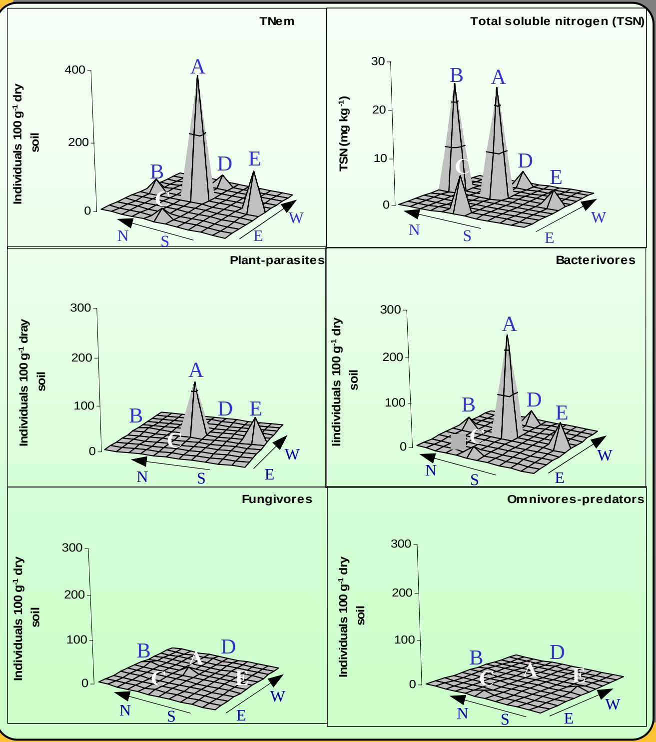


Fig. 3. Total soluble nitrogen contents, nematode population and trophic groups in the soil samples taken at the different sampling sites at the Navoiy industrial area.

Soil sample pH was found to be weakly alkaline, with levels ranging between 7.9 to 8.1. Mean soil moisture content varied from 0.75 to 0.93%, without any significant differences between the sampling stations. The heavy metals Cu, Pb and As were accumulated in the upper soil layer (table 1). A significant difference was found between soil heavy metal content for Cu ($p<0.0005$) and As ($p<0.02$). Basal respiration and microbial coefficient (C_{mic}/C_{org}) were found to be significantly negatively correlated with Cu and As soil content. A significantly positive correlation was found between the Cd concentration and the metabolic quotient (qCO_2) ($p<0.003$). The highest level of TSN was found near the industrial enterprises, with 23.8 and 24.0 mg kg^{-1} at NavoiAzot and NavoiGRES, respectively. No significant correlation was observed between the soil microbial population and total soluble nitrogen. Furthermore, the qCO_2, which is a known ecophysiological index for the soil microbial population, was found to be correlated with the total number of nematodes in general and with the bacterivore feeding group in particular. The nitrogen pollution significantly influenced the total number of nematodes and the distribution of nematode communities (Fig.2; Fig.3). Soil total nitrogen content was correlated with the total density of nematodes ($p<0.05$, $r=0.483$, $n=17$) and plant-parasites trophic group ($p<0.02$, $r=0.548$, $n=17$).

Conclusions: **Results of present study elucidate the direct and indirect effects of industrial pollution on soil microbial biomass and nematode community around the Navoiy industrial complex: 1). the plant-parasite population reached maximum values in the vicinity of NavoiAzot; 2). large number of bacteriovore abundance near the factory is based on stimulation of microbial community and 3). soil microbial population, fungivore and omnivore-predator trophic groups were very sensitive to pollution.**

Effect of heavy metals on soil chemical and biological activity in the vicinity of the Almalyk Mining and Metallurgical Complex, Uzbekistan

Nosir Shukurov[1,2], Stanislav Pen-Mouratov[1] and Yosef Steinberger[1]

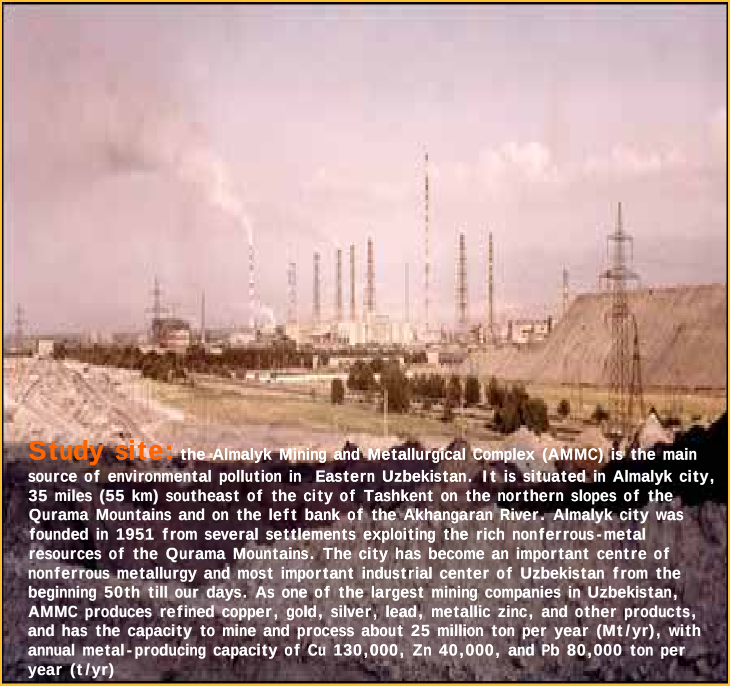
Faculty of Life Science Bar - Ilan University Ramat-Gan Israel 52900;
Institute of Geology and Geophysics, Academy of Sciences of Uzbekistan, 49, N. Khodjibaev Str., Tashkent 700041, Uzbekistan. E-mail: nosirsh@yahoo.com

Objectives: To evaluate the soil physics-chemical (pH, soil moisture (SM), total organic carbon (C_{org}), total soluble nitrogen (TSN), soil exchangeable cations (Ca^{2+}, K^+, Na^+), electrical conductivity (EC)) and biological properties (nematode population, microbial biomass, microbial indices) in response to heavy metal contamination along the deposition gradient.

Hypothesis: Nematode population density, microbial biomass and metabolic quotient will be influenced by heavy metal concentration in soil.

The aim of this project was to study the heavy metal impact on the soil microbial and nematode population along the emission gradient from the Almalyk industrial complex at 4 locations: 0, 5, 10, and 15 km along the downwind transect (Fig.1).

Details: At each location, soil samples were collected (n=5) from the upper layers (0-10 and 10-20 cm) and the soil environmental variables (SM, C_{org}, TSN, Ca^{2+}, K+, Na^+), level of heavy metals (Cd, Cu, Pb, Zn, As), and biological activities (nematode population, basal respiration and microbial biomass) were determined.



Study site: the Almalyk Mining and Metallurgical Complex (AMMC) is the main source of environmental pollution in Eastern Uzbekistan. It is situated in Almalyk city, 35 miles (55 km) southeast of the city of Tashkent on the northern slopes of the Qurama Mountains and on the left bank of the Akhangaran River. Almalyk city was founded in 1951 from several settlements exploiting the rich nonferrous-metal resources of the Qurama Mountains. The city has become an important centre of nonferrous metallurgy and most important industrial center of Uzbekistan from the beginning 50th till our days. As one of the largest mining companies in Uzbekistan, AMMC produces refined copper, gold, silver, lead, metallic zinc, and other products, and has the capacity to mine and process about 25 million ton per year (Mt/yr), with annual metal-producing capacity of Cu 130,000, Zn 40,000, and Pb 80,000 ton per year (t/yr)

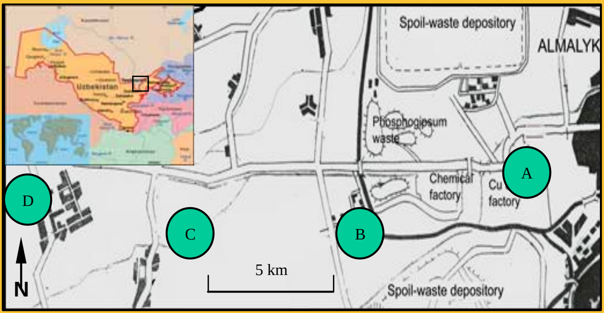


Fig.1. Location of the study sites along the transect from the Almalyk industrial complex (A - 0 km; B - 5 km; C - 10 km and D - 15 km from the complex).

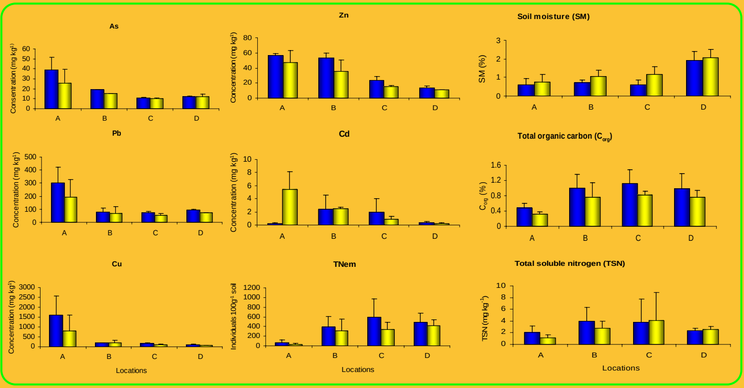


Fig.2. Distribution of heavy metals concentration, soil moisture, total organic carbon, total soluble nitrogen and total number of nematodes along the deposition gradient at two soil layers (🟦 0-10 cm; 🟨 10-20 cm)

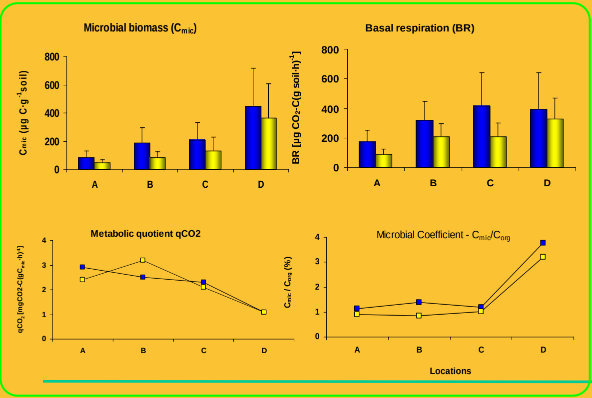


Fig. 3. Microbial biomass, basal respiration, metabolic quotient and microbial coefficients values obtained in soil samples contents along the deposition transect at 0 to 10(🟦) and 10 to 20 cm (🟨) soil layers

Results: Significant differences between soil chemical and biological properties were observed with the increase of distance from the source to downwind direction and depth. A significant difference was found in heavy metal concentrations, total number of nematodes, total organic carbon, and microbial biomass contents was found along sampling locations ($p<0.0001$) and depth ($p<0.01$). The highest number of nematodes and microbial biomass content were observed in soil samples from the distances 10-15 km (Fig.2; Fig.3). Respiration displayed similar results to the microbial biomass (Fig.2). The derived metabolic quotient - qCO_2 revealed significant differences by distance, confirming environmental stress in first and second locations. The microbial ecophysiological coefficient (C_{mic}/C_{org}) was lowest in soils with high heavy metal content (fig.3). This suggests that the immobilization of organic matter as microbial biomass can be more difficult in polluted soils than in unpolluted ones.

Conclusions: Thus, the emission of a copper smelter has resulted in a marked accumulation of heavy metals in soils near the smelter through atmospheric deposition. High heavy metal content in soils resulted in decrease in soil moisture, total organic carbon amounts in soil, and effect on total number of nematodes, soil respiration and microbial biomass content.

DISTRIBUTION OF SOIL MICROBIAL BIOMASS AND FREE-LIVING NEMATODES POPULATION IN TERRACE CHRONOSEQUENCES OF MAKHTESH-RAMON CRATER

Nosir Shukurov [1,2], Stanislav Pen-Mouratov[1] and Steinberger Yosef[1]

[1]Faculty of Life Sciences, Bar Ilan University, Ramat Gan, Israel 52900
[2]Institute of Geology and Geophysics, Academy of Sciences of Uzbekistan, 49,
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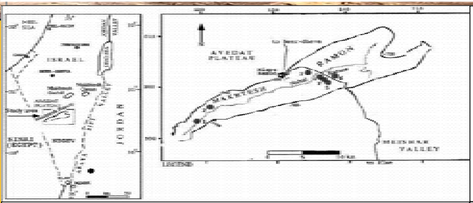

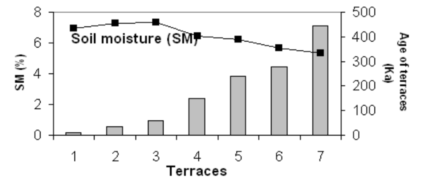

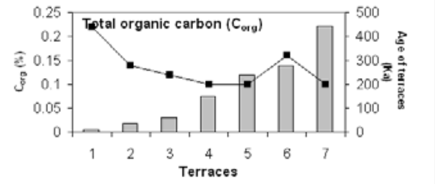

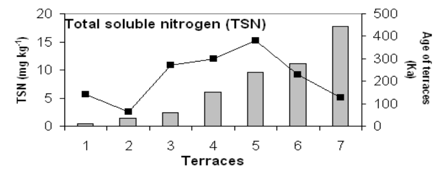

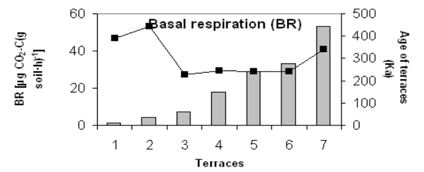

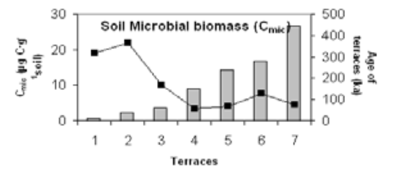

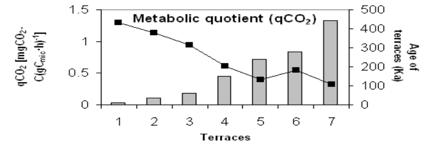

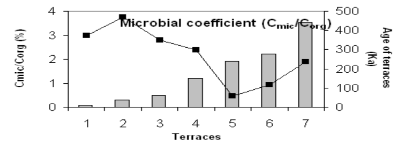

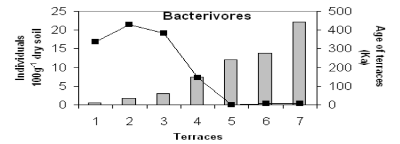

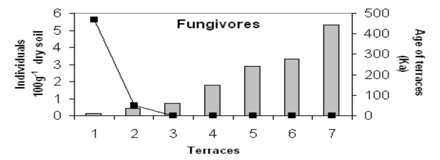

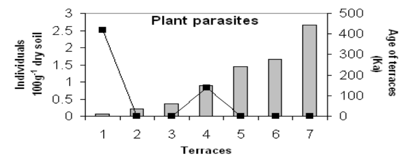

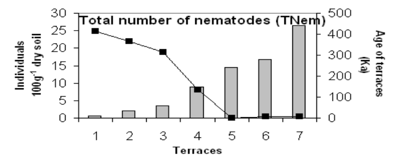

Makhtesh Ramon is a deep erosional "cirque" 40 km long and 12 km wide entrenched along an anticline axis and surrounded by steep walls. It is centered at 30º35'N, 34º50'E, the long axis running ENE to WSW. It has an area of 241 km^2. Altitudes range from 1.020 m on the western rim to 420 m a.s.l. near the outlet of the main wadi, Nahal Ramon. Nahal Neqarot, which flows east of the Ramon anticline towards the Dead Sea, serves as the local erosional base level of the Ramon Valley. The climate of the area is arid to extremely arid. The mean multi-annual rainfall is 85 mm at the northern rim and 56 mm at the "cirque" bed in the central part. A mean maximal daily temperature of 34ºC is measured in July, whereas a mean minimal temperature of 12.5ºC is measured in January. Seven terraces, dated by the RTL method, ages from 10 Ka to 500 Ka, were found in the Makhtesh Ramon crater and described by Plakht (2000): terrace I (aged as 10 Ka)- pebbles interbedded with thin bands of sand; terrace II (27-36Ka) - fine material with alternating calcic horizons of aeolian origin; terrace III (48-60Ka) - pebbles in the sandy matrix and buried gypsic paleosol; terrace IV (101-150Ka) - interbedded pebbles and sandy-loamy layers; terrace V (205-240Ka) - coarse gravel dominates the composition of this alluvium; terrace VI (220-278Ka) - interbedded layers of pebbles and sands; terrace VII (375-443Ka) - consisting mainly of a well-rounded conglomerate interbedded with layers of well-cemented carbonate sand. The effects of the age of these seven erosional fluvial terraces of Makhtesh Ramon in the central Negev Desert on soil chemical and biological properties were examined in this study. Five random soil samples were collected from the upper 0-10 soil layer of each of the seven erosion terraces in the early hours at the end of the rainy season of 2003-2004. Soil samples were sieved through a 2-mm mesh sieve in order to remove organic debris before biological and chemical analyses. The following soil physic-chemical and biological analyses were undertaken on each one of the samples collected at the study site: soil water content (SWC), total organic carbon (Corg),total soluble nitrogen (TSN), soil pH, soil salinity as electrolytic conductivity (EC), soluble cations (Ca2+, K+, Na+), soil microbial biomass (Cmic), soil basal respiration (BR), metabolic coefficient (qCO2), microbial coefficient as the Cmic/Corg ratio, nematode population and ecological indices. Obtained data were subjected to statistical analysis of variance (ANOVA). When significance at a level of $p<0.05$ was observed, Tukey's values were calculated for separation of the means.

There were significant effects of erosion age of these terraces on soil moisture, organic carbon, soil salinity, and electrical conductivity. It is known that soil biological activity in arid ecosystems is determined by well-known limiting factors such as soil moisture and organic matter. Significant ($p<0.002$) differences in total nematode population and microbial biomass [(22.0-3.4 Cmic (µg C·g-1 soil)] were observed between terraces. Biological activity of soils in lower and younger terraces was greater than in older and higher terraces. The ecophysiological status (qCO2) of the soil microbial community was found to decrease from a maximal value of 1.3 to 0.32 mg CO2-C (gCmic·h)-1 along the terraces (from younger to older ones). This study illustrates the integrated effect of age, altitude, and the morphostratigraphic position of terrace