Transfer of Microelements Within the Chain “Soil – Water - Grass - Cow” at the Territory of Intensive Industrial Pollution and a Possibility to Produce Ecologically Safety Product

ISTC Project #1872 “Working out a Program of Remediation and Development of the City of Karabash by Implementing Technologies for Recovery of Its Technogenic Resources”

**Goals of the investigation**

- identification of physico-chemical mechanisms of chemical contamination of the territory of town Karabash due to the impact of the blister copper production plant;
- comparative statistical analysis of trace elements abundance in mineral (air, snow, soil, well water) and biological (grass, cow’s internal, milk) objects of the Karabash ecosystem;
- determination of microelements partitioning between entero-sorbent Bifezh® and internal of cows.

**Authors:**
Polyakov E.V.¹, Barysheva N.M. ², Aristarkhova L.N. ³, Malygina A.A. ³, Remez V.P. ⁴, Surikov V.T. ¹.

¹) Institute of Solid State Chemistry UB RAS, Ekaterinburg, Russia;
²) Russian Federal Nuclear Center VNIITF, Snezhinsk, Russia;
³) Sverdlovsk Science - Research Veterinary Institute, Ekaterinburg, Russia,
⁴) UNIHIM&EP, Ekaterinburg, Russia.
Internal and inter-laboratory quality control of primary analytical data collected on the territory of Karabash

- **Analytical methods:** ICP-MS (1) AAS(2);
- **Analytical Groups:**
  - (1) - Institute of Solid State Chemistry UB RAS, Ekaterinburg, Russia,
  - (2) - Sverdlovsk Science - Research Veterinary Institute, Ekaterinburg, Russia;
- **Objects (samples):** snow (74), drinking water (60), soil (21).
- **Elements analyzed:** Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sn, Sb, J, Te, Cs, Ba, La, Ce, Hg, Te, Pb, Th, U.

In the experiments with animals a groups of 14 milkers (milk producing cows) and 12 calves were selected from the farmer’s herds. The duration of the experiments was 5 months.

Each of the groups was divided into the experimental and control subgroups. Animals in the experimental group were fed by 100g (milkers) and 60 g (calves) of entero-sorbent in addition to the usual portion of daily forage.

The samples of blood, urine, milk were collecting for elemental analysis one time in 10 days; samples of internals (muscles, kidneys, liver, heart, lungs, bones) were collected after autumn animal slaughtering.
Location of place of researches (town Karabash, vest direction from Chelyabinsk city)
Physicochemical modeling of chemical contamination of the territory of the city due to the impact of the blister copper production plant.

- Principal stages of the smelting technology

Bath smelting process of blister copper production

Roasting of Cu-concentrate + flux (Si, Ca oxides)

autogenous smelting

1200-1300 °C

Light oxide slag

Sulfide matte

1200-1300 °C

Light oxide slag

Blister copper

O₂+air

Dust+SO₂

Volatile oxides, dust

Volatile metals

O₂
Vaporization of metal impurities at the final stage of blister copper melt formation as a factor of chemical pollution

Example of correlation between the abundance of minor metals in Karabash snow and calculated volatility (P) of the same pure metals at the temperature of blister copper formation (1260 °C).

Detected concentration of metal in snow, mkg/l

Calculated metal pressure at gas phase, (P) a.u.

- $b[0]=-0.639$
- $b[1]=0.628$
- $r^2=0.730$
Comparative statistical analysis of trace elements distribution between snow, soil and surface water on the territory of the city.

- Chemical elements partitioning between melted snow and soil at the same points (left fig.);
- Minor elements distribution between soil and well water at the same points of the territory. (right fig.).
- Zc is the total soil contamination index, r.u.
Mass transfer of the minor elements from grass (forage) collected at the territory of Karabas to the blood and urine of milkers

- Typical example of the chemical elements partitioning between grass (forage) and blood (upper figure), and grass and urine (lower figure) detected for the concrete animal;
- It is indicated that the correlation coefficients of correlations which describe chemical elements partitioning are more significant for the pair “blood – grass” ($r=0.850$) then for the pair “grass – urine” ($0.750$).

$C(\text{grass, blood, urine})$ – concentration of the elements in the sample of grass (forage), urine.
Abundance of microelements in the cow’s milk and their mass-transfer in the chain “milk - urine”

- Typical for Karabash cows abundance of chemical elements in the milk and urine (a);
- between samples correlation of chemical composition of cow milk (b)
- correlation of urine and milk chemical composition characteristic for cows at the territory of Karabash (c).

\( C(\text{milk, urine}) \) – concentration of the elements in the sample (“N” denotes number of the sample) of milk, urine.
Revealed low level of contamination of Karabash milk with regard to the abundance of toxic chemical elements

- Chemical composition of cow’s milk samples from Karabash in comparison with the data on milk from standard dairy farms (Calabria, Italy).


- Erdogan S., Celik S., Erdogan Z. Comparison of Selected Toxic Elements in Cow Serum and Milk Samples from Industrial and Rural Regions // Bull. Environ. Contam. Toxicol, 72(2004), 931–936
Generalized data on the efficiency of sorbent Bifezh as a bovine entero-sorbent

Distribution coefficients $K_d$ for microelements between entero-sorbent Bifezh and organs within experimental group of cows as a function of microelements concentration in organ of animal.

$K_d = \frac{\text{(mass of microelement in the sorbent, mkg/g)}}{\text{(mass of microelement in the organ, mkg/g)}}$
Resume

- Flows of microelements, the main source of which on the territory of town Karabash is cupper smelter plant, are determined to have logarithmic linear rule of partitioning within the chains “air (snow)-water-soil-grass-cow”.

- The elemental composition of cows’ milk at the contaminated territory doesn’t contain increased levels of all controllable microelements (above background level) even in the case the internal of the animals contain extremely high levels of the same chemical elements.

- Comparison of partitioning of more the 25 microelements between entero-sorbent Bifezh® and different organs of cows allowed to estimate general isotherm of selectivity of the given entero-sorbent toward the microelements.

- The role of medication Bifezh® as an effective protector against penetration of such microelements as Ni, As, Cd, Cr, Cu, Pb, Co in the internal of the cows is established experimentally.
Thank you very much for your attention! Muchos gracias!

- The research team (*from left to the right, with the Karabash plant as a background*):
  - Angelina Maligina,
  - Ludmila Aristarkhova,
  - Mikhail Remez,
  - Evgeny Polyakov,
  - Nina Barysheva,
  - Victor Remes,
  - Vladimir Surikov (off camera)