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## BANSKÁ BYSTRICA, SLOVAK REPUBLIC, 8 – 10 OCTOBER 2018

*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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# COMBINING SELECTIVE SEQUENTIAL EXTRACTIONS AND X-RAY ADSORPTION SPECTROSCOPY FOR Cu SPECIATION IN SPOLIC TECHNOSOLS

Tatiana Minkina

Southern Federal University, Russia

tminkina@mail.ru

*The activity has been implemented within the framework of national project*
***Information and providing advice on improving the quality of environment in Slovakia***.
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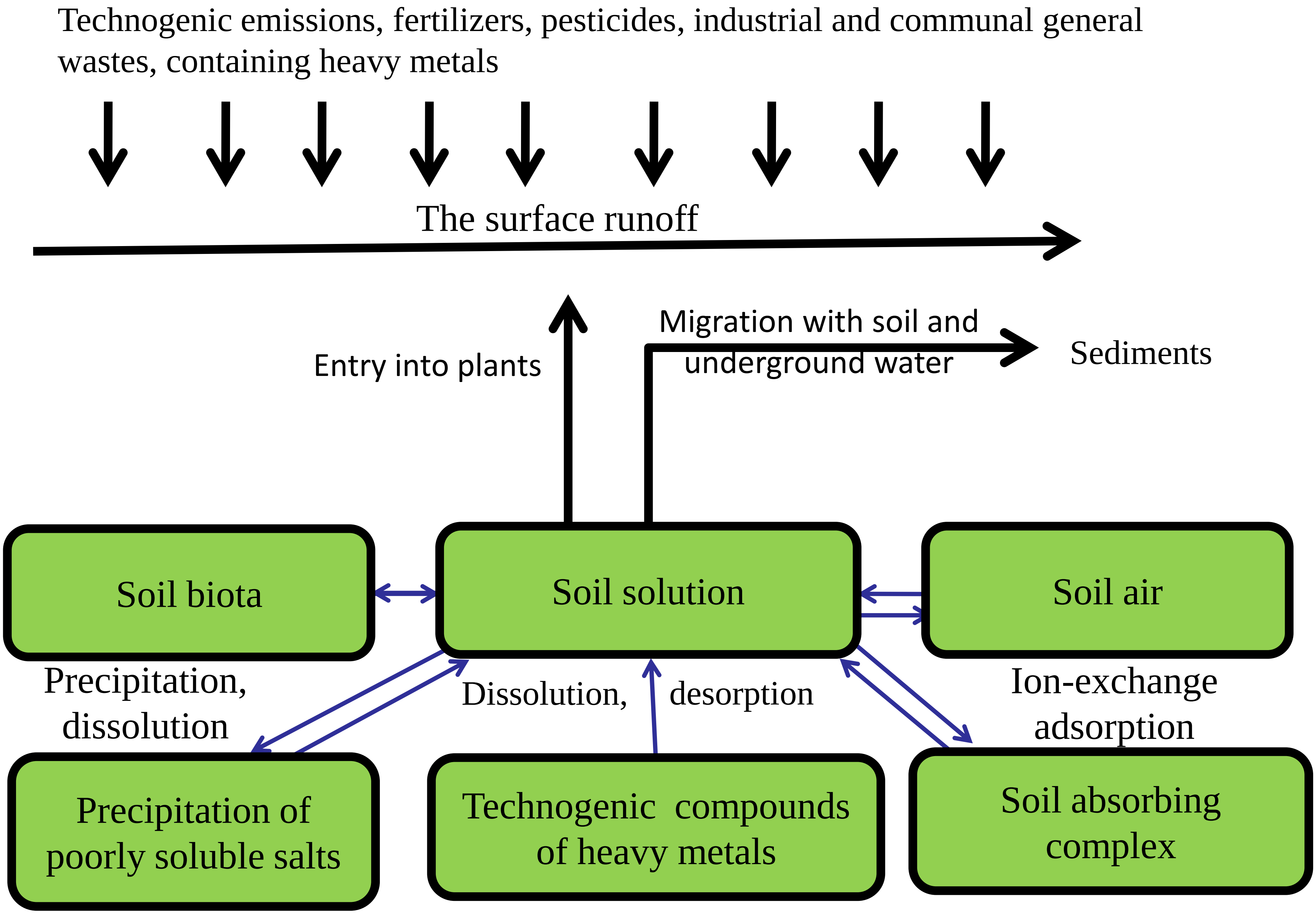


Technogenic emissions, fertilizers, pesticides, industrial and communal general wastes, containing heavy metals

The surface runoff

Entry into plants

Migration with soil and underground water

Sediments

Soil biota

Soil solution

Soil air

Precipitation, dissolution

Dissolution, desorption

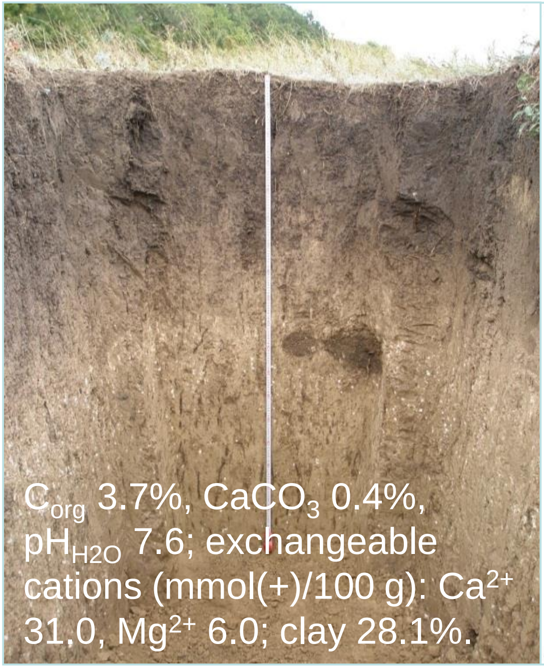
Ion-exchange adsorption

Precipitation of poorly soluble salts

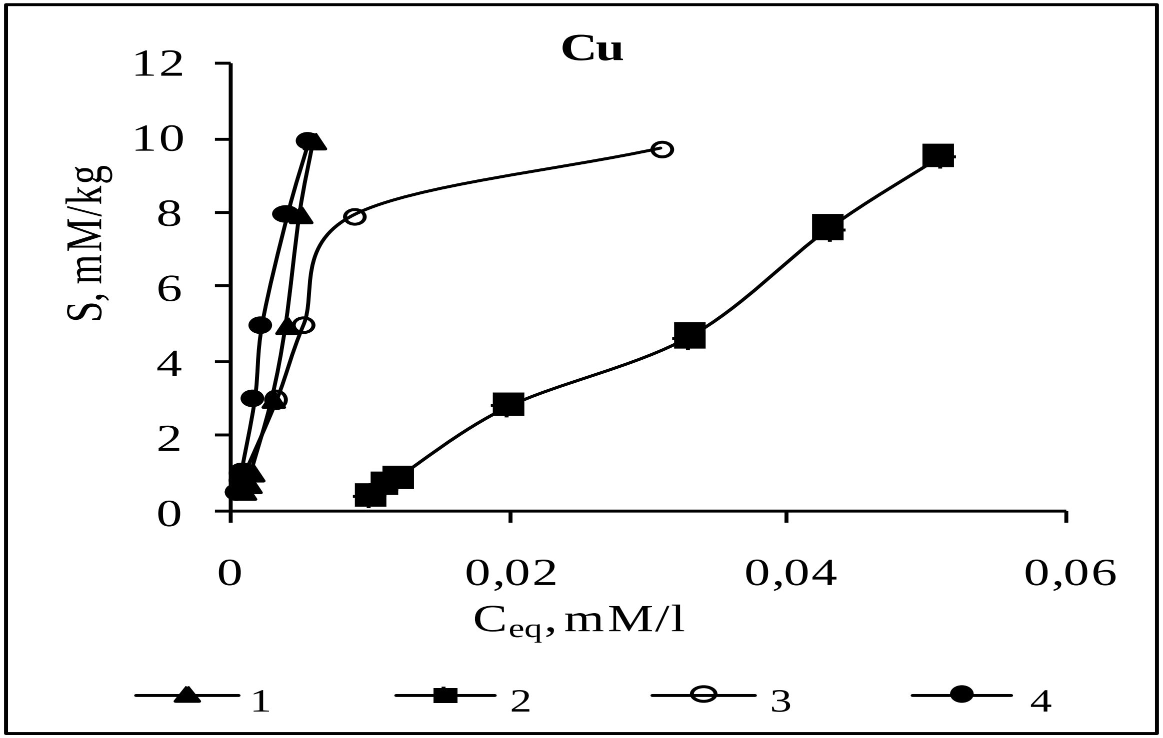
Technogenic compounds of heavy metals

Soil absorbing complex

**Pinskii, 1999**



$C_{org}$ 3.7%, $CaCO_3$ 0.4%, $pH_{H2O}$ 7.6; exchangeable cations (mmol(+)/100 g): $Ca^{2+}$ 31,0, $Mg^{2+}$ 6.0; clay 28.1%.



**Adsorption isotherms of Cu by Haplic Chernozem at the application of chlorides (1), nitrates (2), acetates (3) and sulphates (4) of metal**

**The isotherms of the Cu adsorption from acetate and nitrate solutions are very good described by the Langmuir equation:**

$$S_{ads} = S_{max} \cdot kC/(1 + kC),$$

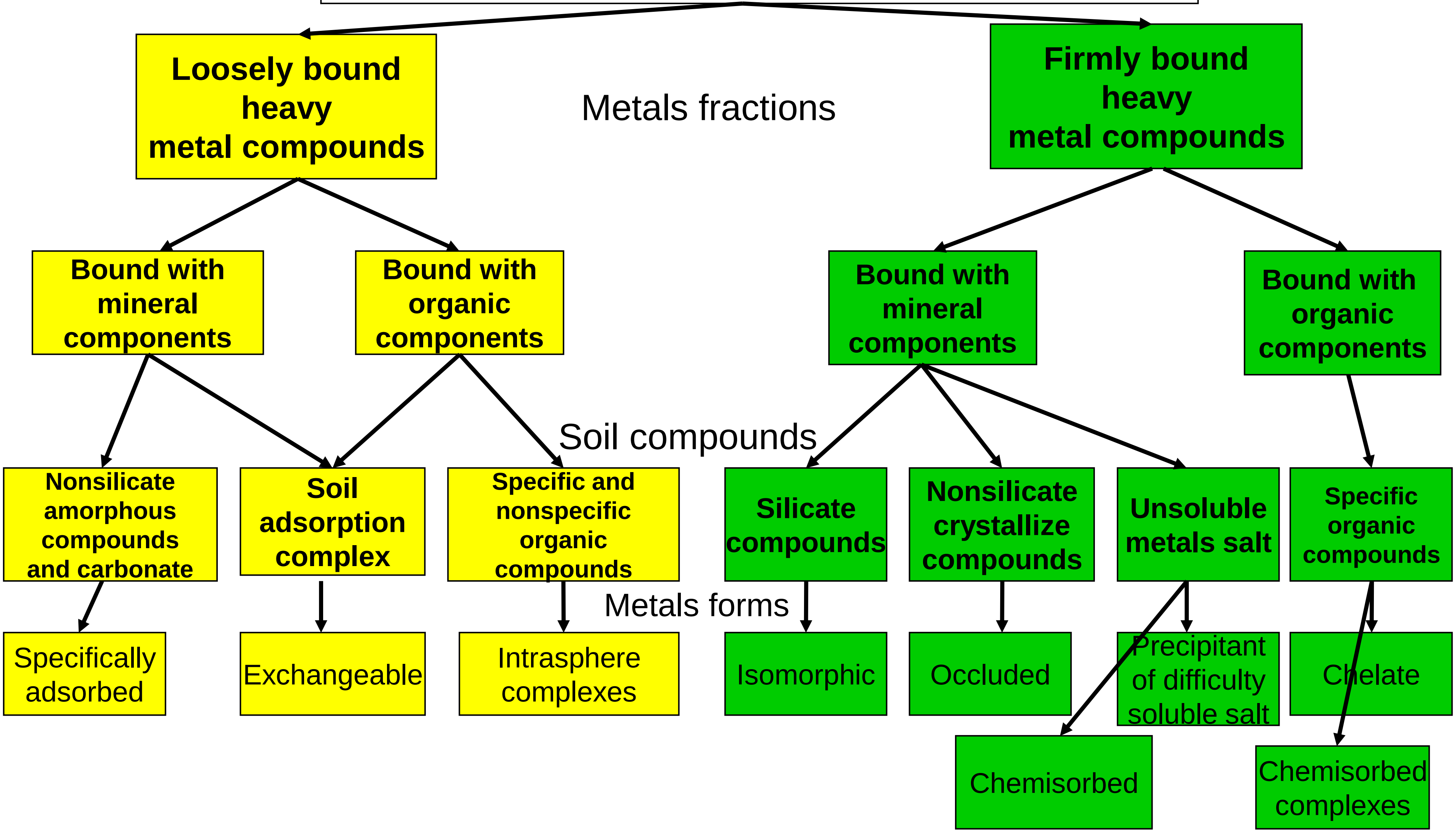
$S_{ads}$ - the content of the adsorbed cations;
$S_{max}$ - the maximum adsorption of the HM, mmol/100 g of soil;
$k$ - the constant of the affinity;
$C$ - the HM concentration in the equilibrium solution, mmol/L.

**Linearized form of Langmuir equation:**

$$1/S_{ads} = 1/\,S_{max} + 1/\,S_{max} \cdot kC$$

| Nitrate | | | Acetate | | |
|---|---|---|---|---|---|
| $S_{max}$, mmol/100 g | $k$ | $R^2$ | $S_{max}$, mmol/100 г | $k$ | $R^2$ |
| 1.3±0.1 | 93.7±20.7 | 0,94 | 1.2±0.1 | 159.2±0.6 | 0.82 |

# Distribution of heavy metals compounds in soil



Metals fractions

**Loosely bound heavy metal compounds**

**Firmly bound heavy metal compounds**

**Bound with mineral components**

**Bound with organic components**

**Bound with mineral components**

**Bound with organic components**

Soil compounds

**Nonsilicate amorphous compounds and carbonate**

**Soil adsorption complex**

**Specific and nonspecific organic compounds**

**Silicate compounds**

**Nonsilicate crystallize compounds**

**Unsoluble metals salt**

**Specific organic compounds**

Metals forms

Specifically adsorbed

Exchangeable

Intrasphere complexes

Isomorphic

Occluded

Precipitant of difficulty soluble salt

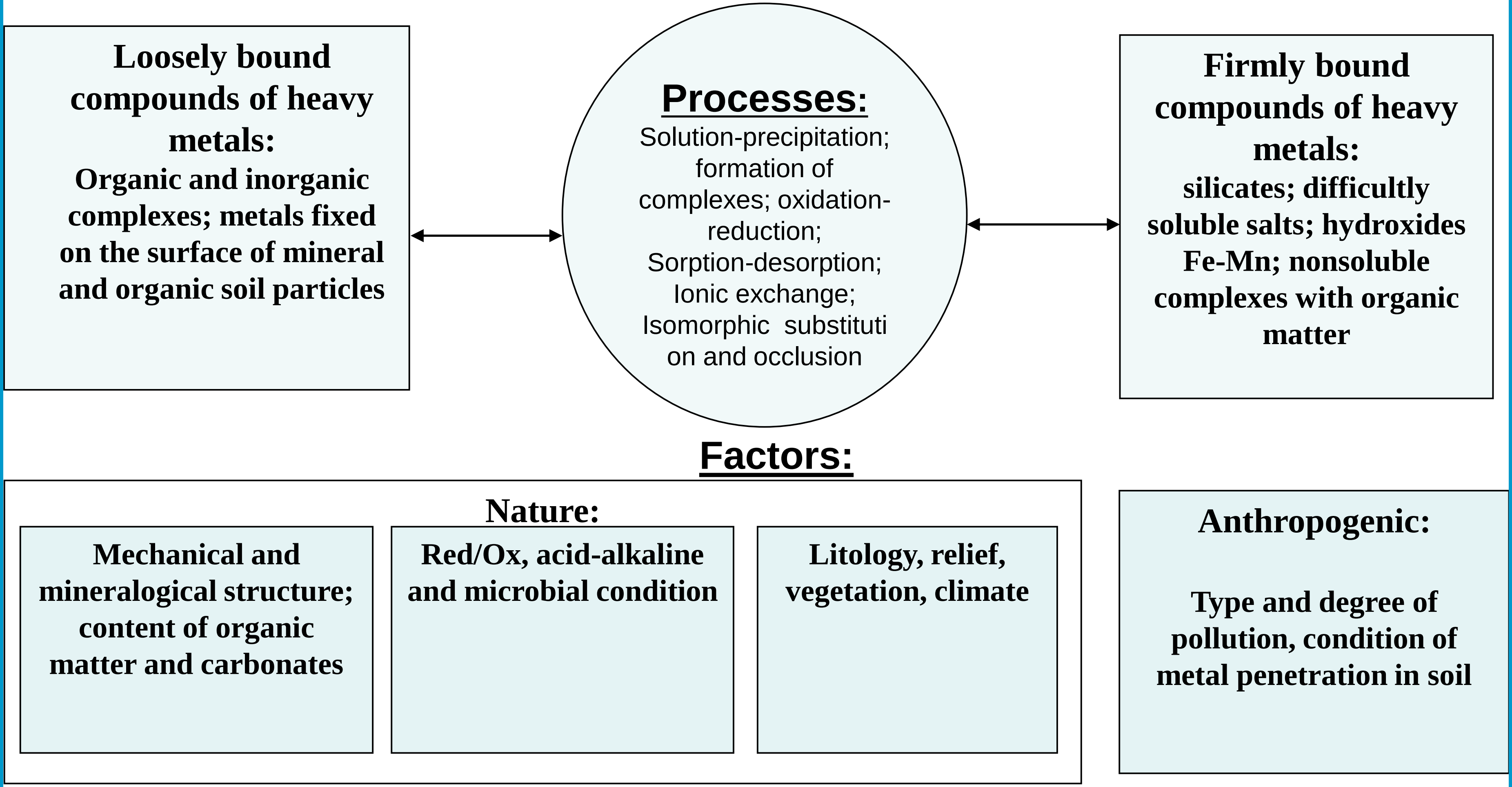
Chelate

Chemisorbed

Chemisorbed complexes

**Loosely bound metal compounds are particularly important from the ecological point of view, because these compounds can be consumed by plants and migrate into adjacent media.**

# METAL TRANSFORMATION IN SOIL



**Loosely bound compounds of heavy metals:**
**Organic and inorganic complexes; metals fixed on the surface of mineral and organic soil particles**

**Processes:**
Solution-precipitation; formation of complexes; oxidation-reduction; Sorption-desorption; Ionic exchange; Isomorphic substitution and occlusion

**Firmly bound compounds of heavy metals:**
**silicates; difficultly soluble salts; hydroxides Fe-Mn; nonsoluble complexes with organic matter**

**Factors:**

**Nature:**

**Mechanical and mineralogical structure; content of organic matter and carbonates**

**Red/Ox, acid-alkaline and microbial condition**

**Litology, relief, vegetation, climate**

**Anthropogenic:**

**Type and degree of pollution, condition of metal penetration in soil**

Metals distribution between the pools of the firmly bound and loosely bound compounds are controlled by complex of transformation processes.

Predominance of one or another heavy metal compounds depends on soil composition and properties, and also from other natural and anthropogenic factors.

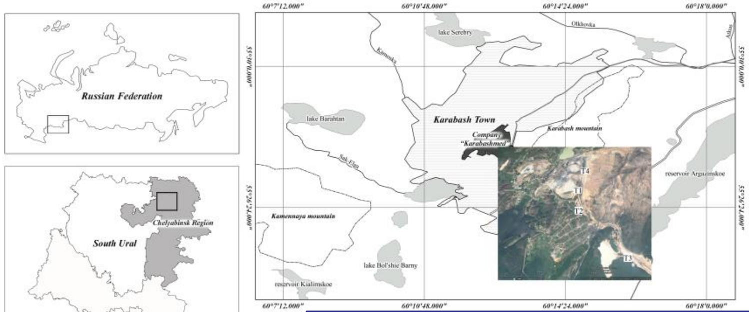
# Sequential extractions by Tessier's method (Tessier, Campbell, Bisson1979)

| FRACTION | **EXTRACTANT** | **Soil:solution ratio** | **Extraction conditions** |
|---|---|---|---|
| Exchangeable | **1M $MgCl_2$, pH 7.0** | **1:8** | The sample with extractant was shaken for 1 h at room temperature |
| Bound to carbonates | **1M $NaCH_3COO$, pH 5.0 (with $CH_3COOH$)** | **1:8** | The residue from the previous fraction with extractant was shaken for 5 h at room temperature |
| Bound to Fe-Mn oxides | **0.04M $NH_2OH{\cdot}HCl$ in 25% $CH_3COOH$** | **1:20** | The residue from the previous fraction digested 5 h with extractant by heating at 96 ± 3 °C under intermittent agitation |
| Bound to organic matter | **0.02M $HNO_3$+ 30% $H_2O_2$, pH 2.0 (with $HNO_3$), then 3.2M $NH_4CH_3COO$ in 20% $HNO_3$** | **1:20** | The residue from the previous fraction digested 5 h with extractant by heating at 85±2 °C under intermittent agitation |
| Residual | **$HF$+$HClO_4$, then $HNO_3$conc** | **1:25** | Evaporation |

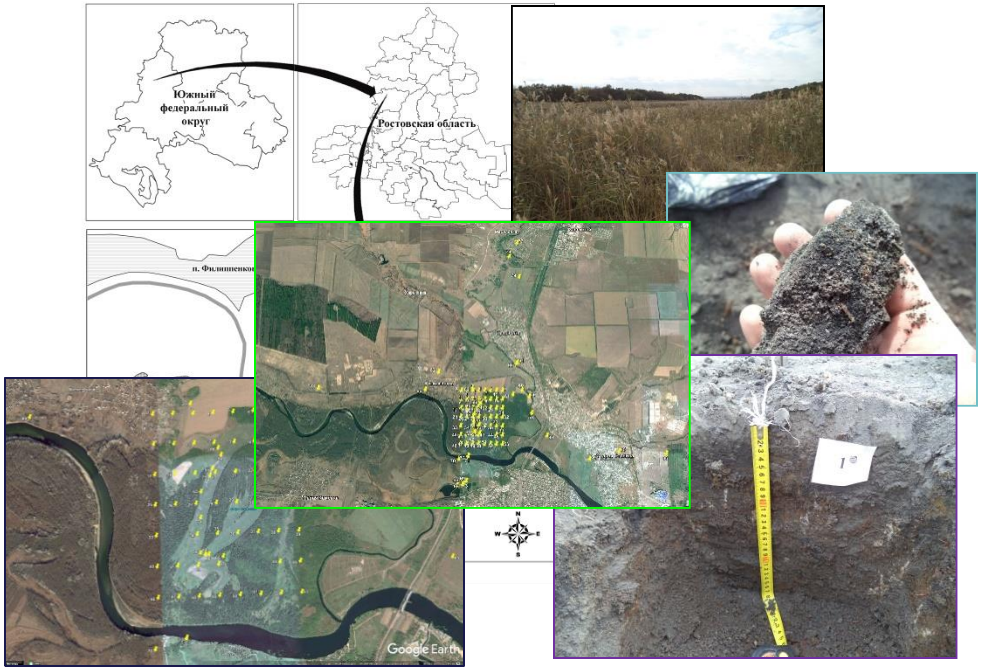
# SPOLIC TECHNOSOLS

Artificial pollution in a model experiment

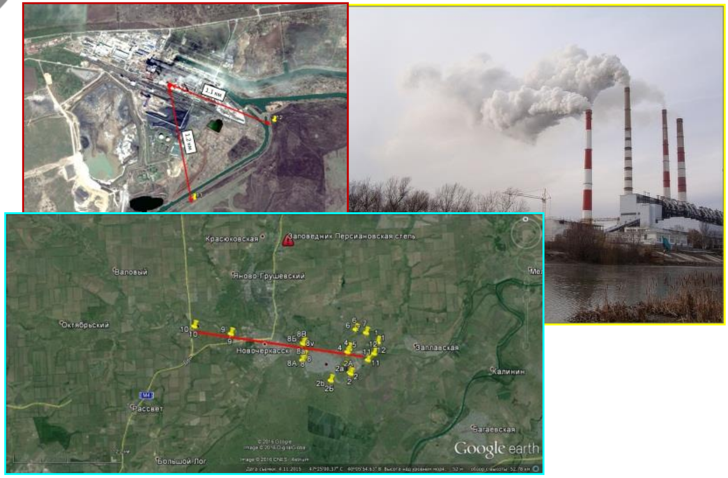
Karabash copper smelter, Southern Urals, Russia

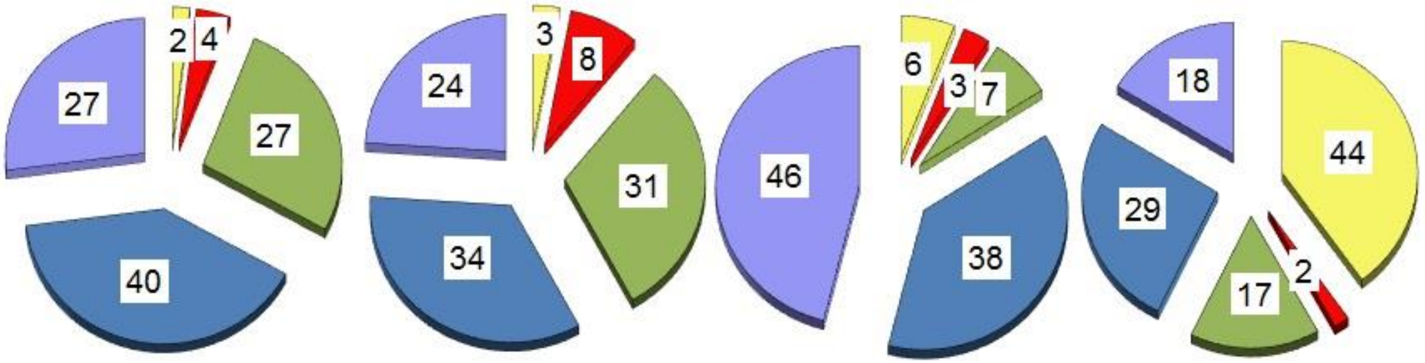


- The territory of sludge collectors of chemical plants in the Severskii Donets floodplain in Rostov oblast, South of Russia



Novocherkassk Power Station





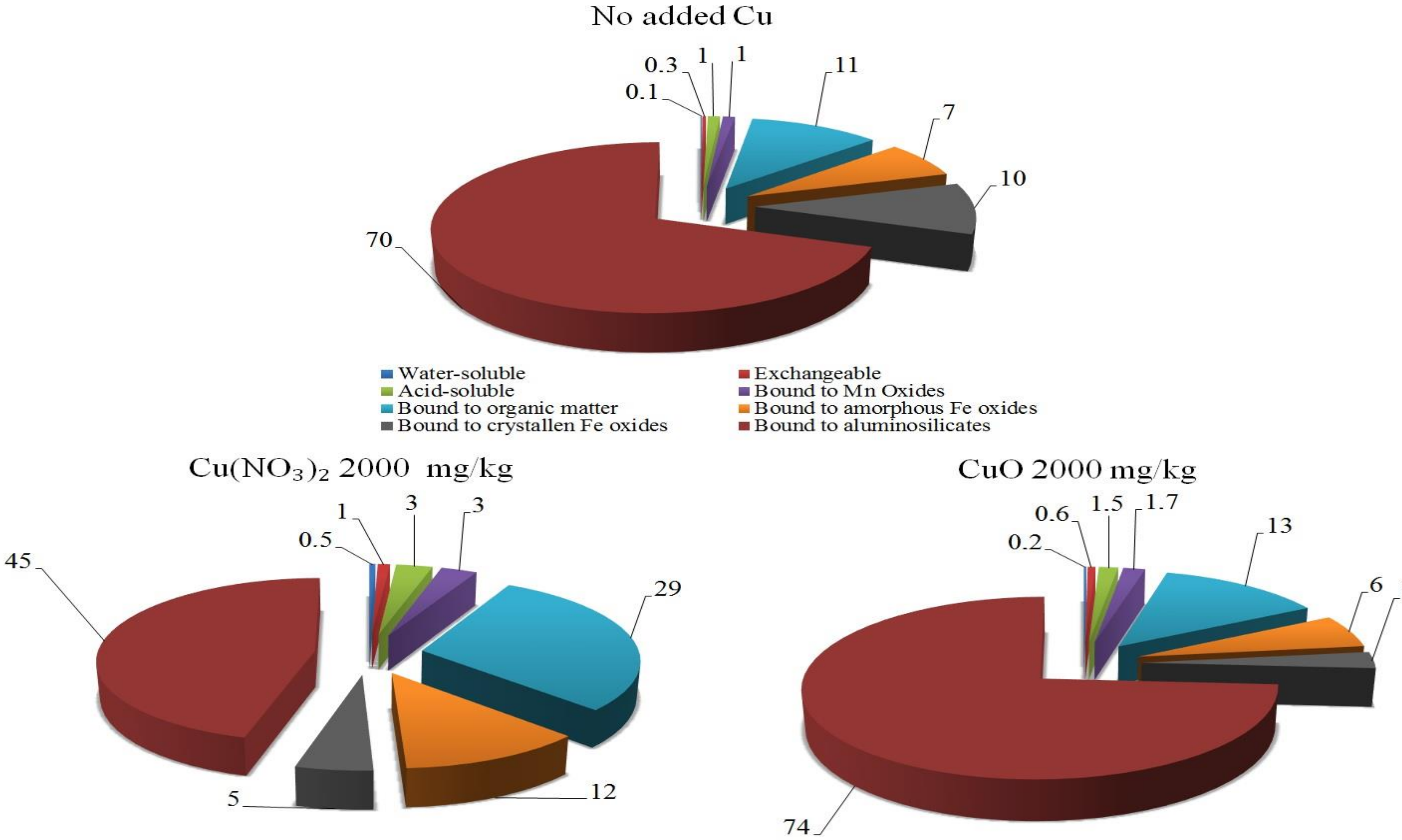
| | Artificial pollution in a model experiment 2000 mg/kg Cu | The territory of Novocherkassk Power Station, Russia | The sediment ponds of chemical plants in the city of Kamensk-Shakhtinskii, South of Russia | Karabash copper smelter, Southern Urals, Russia |
|---|---|---|---|---|
| 🟨 Exchangeable | 52.0±5.7 | 2.3±0.2 | 33.1±2.2 | 466.2±73.0 |
| 🟥 Bound to carbonates | 72.7±4.1 | 6.0±1.4 | 17.1±1.5 | 21.3±6.7 |
| 🟩 Bound to Fe–Mn oxides | 561.0±19.1 | 23.4±3.3 | 37.8±4.7 | 182.9±24.5 |
| 🟦 Bound to organic matter | 819.0±27.6 | 25.2±3.8 | 219.0±18.4 | 204.5±36.0 |
| 🟪 Silicate-bound (residual) | 562.9±24.7 | 18.3±3.1 | 269.8±20.9 | 466.2±73.0 |
| Total (47 mg/kg*) | 2067.6±48.3 | 72±11.8 | 375.0±47.7 | 1066.9±123.8 |

(*) lithosphere clark of Cu (Vinogradov, 1957)

# Cu speciation in Spolic Technosols

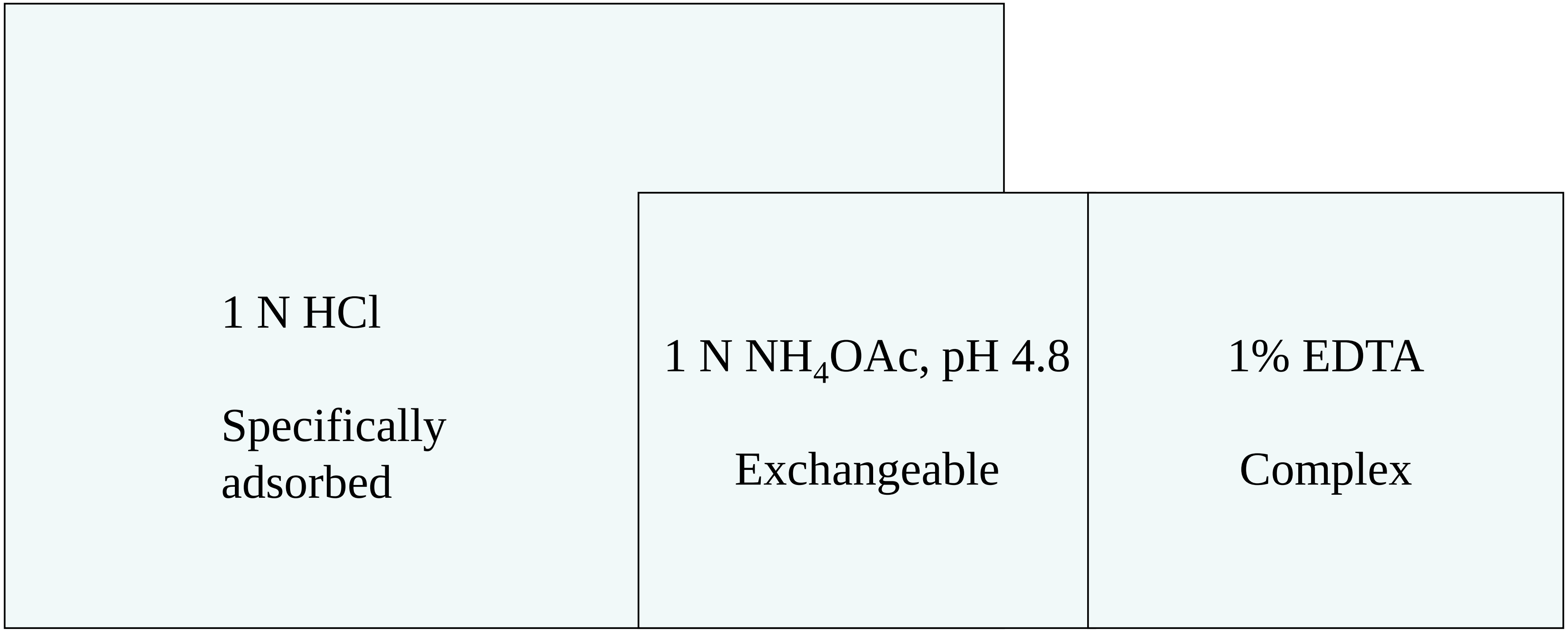
# Sequential fractionation of heavy metals by the Miller scheme (Miller et al., 1986) modified by Berti and Jacobs (1996)

| Fraction | Soil : solution ratio | Extraction conditions | Extractant |
|---|---|---|---|
| Water-soluble | 1 : 10 | Shaking at room temperature for 16 h | Distilled water |
| Exchangeable | 1 : 10 | Shaking at room temperature for 8 h | 0.5 M $Ca(NO_3)_2$<br>pH 7.0 |
| Acid-soluble | 1 : 10 | Shaking at room temperature for 8 h | 0.44 M $CH_3COOH$<br>pH 2.5 |
| Bound to Mn oxides | 1 : 14 | Shaking at room temperature for 30 min | 0.1 M $NH_2OH \cdot HCl$ +<br>0.01 M $HNO_3$ |
| Bound to organic matter | 1 : 14 | Shaking at room temperature for 24 h | 0.1 M $Na_4P_2O_7$ |
| Bound to amorphous Fe oxides | 1 : 14 | Shaking in the dark for 4 h | 0.175 M $(NH_4)_2C_2O_4$ +<br>0.1 M $H_2C_2O_4$ |
| Bound to crystalline Fe oxides | 1 : 14 | Placed in a boiling water bath under periodical shaking for 5 h | 0.175 M $(NH_4)_2C_2O_4$ +<br>0.1 M $H_2C_2O_4$ |
| Connected with silicates (residual) | 1 : 25 | Evaporation | Extract of HF + $HClO_4$ from the residual fraction |



A more significant increase in the content of Cu bound to amorphous Fe forms compared to that bound to crystalline Fe forms can indicate a technogenic input of the metal into the soil .

**In accordance with the suggested systematization reagents for determine of metals compounds were chosen.**



1 N HCl

Specifically adsorbed

1 N $NH_4OAc$, pH 4.8

Exchangeable

1% EDTA

Complex

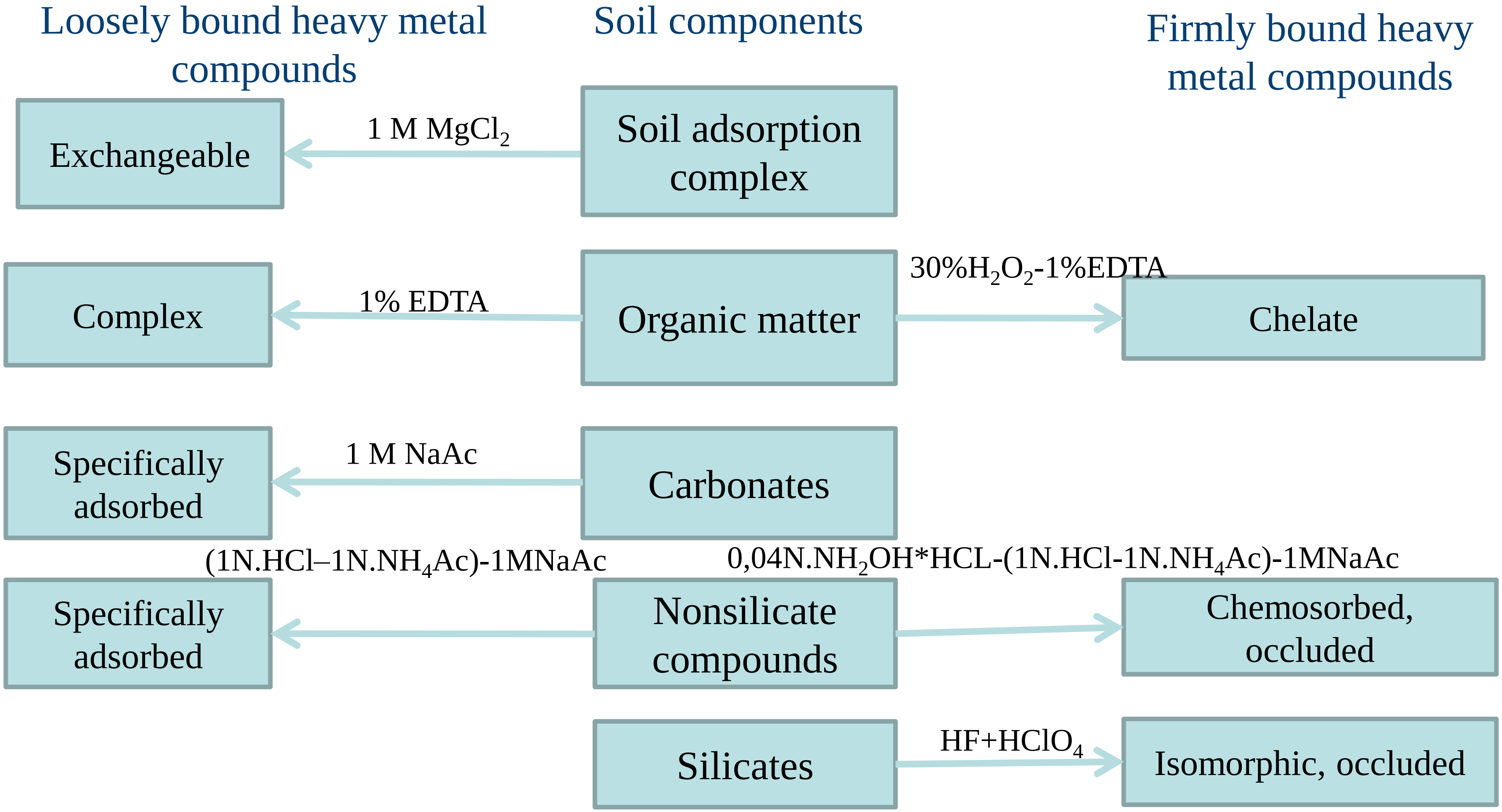
**Extracts of metal forms**

**These parallel extractants are recommended for determining of loosely bound compounds of metal in soils**

**The contents of firmly and loosely bound metal compounds fixed by the organic substances and nonsilicate minerals have been determined by this method.**

**This enables to establish the polyfunctionality of soil components and their participation in metals mobilization and immobilization.**

## Heavy metal compounds with soil particles and their determination



Loosely bound heavy metal compounds

Soil components

Firmly bound heavy metal compounds

Exchangeable ← 1 M $MgCl_2$ ← Soil adsorption complex

Complex ← 1% EDTA ← Organic matter → 30%$H_2O_2$-1%EDTA → Chelate

Specifically adsorbed ← 1 M NaAc ← Carbonates

Specifically adsorbed ← (1N.HCl–1N.$NH_4$Ac)-1MNaAc ← Nonsilicate compounds → 0,04N.$NH_2$OH*HCL-(1N.HCl-1N.$NH_4$Ac)-1MNaAc → Chemosorbed, occluded

Silicates → HF+$HClO_4$ → Isomorphic, occluded

# Relative contents of loosely and firmly bound metal compounds in Haplic Chernozem

| Application rate, mg/kg | Loosely bound compounds (LB), % of fraction within LB | | | | Firmly bound compounds (FB), % of fraction within the FB | | |
|---|---|---|---|---|---|---|---|
| | Exchangeable, $MgCl_2$ | Complex | Specifically adsorbed | | with organic matter | with Fe-Mn hydroxides | with silicates |
| | | | on carbonates | On Fe-Mn hydroxides | | | |
| **Cu** | | | | | | | |
| Blank | 13 | 8 | 71 | 8 | 10 | 2 | 88 |
| 2000 | 12 | 40 | 12 | 36 | 32 | 24 | 44 |

| Application rate, mg/kg | LB/FB, % of the total content |
|---|---|
| Blank | 5/95 |
| 2000 | 55/45 |

It is establish that the larger part of the metals was firmly fixed in the soils. The LB of the Cu in the natural soil is low (5%). The FB metals are mainly caused by the fixation of silicate minerals.

Upon the soil contamination organic substances and nonsilicate minerals become the main metal adsorbents.

# ***Is there a future for sequential chemical extraction?***

## The unique properties of X-ray absorption spectroscopy:

- very high intensity;
- spectr continuum;
- polarization;
- modulated beam. That allows the analysis in the polycrystalline and heterogeneous samples, for example – soils.

**XANES -** X-ray Absorption Near Edge Structure

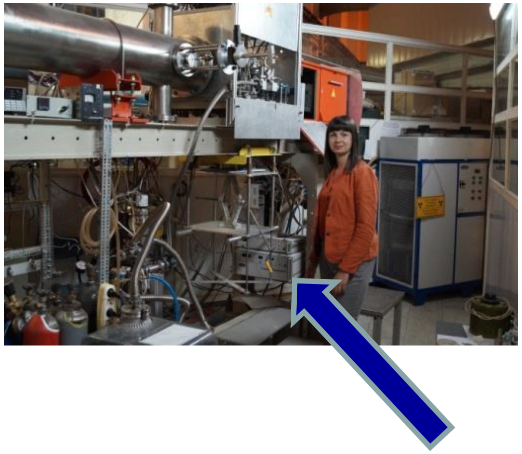
**EXAFS -** Extended X-Ray Absorption Fine Structure

**METHODS**

**XRD -** X-ray diffraction

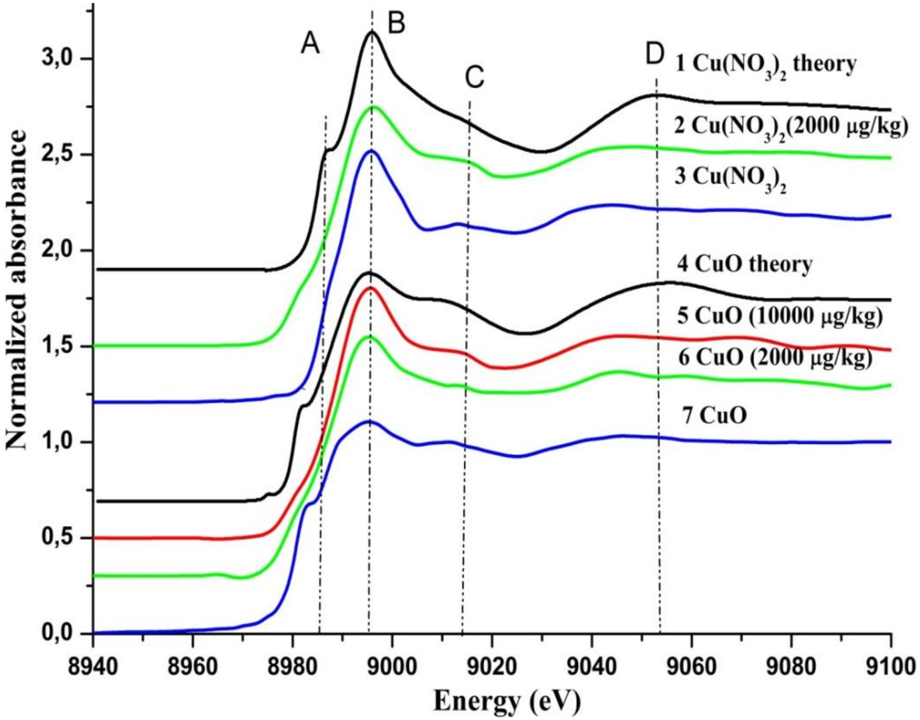
**Modeling** of molecular dynamics and quantum chemical (VASP)

**Fragment of a large ring of the Kurchatov synchrotron**

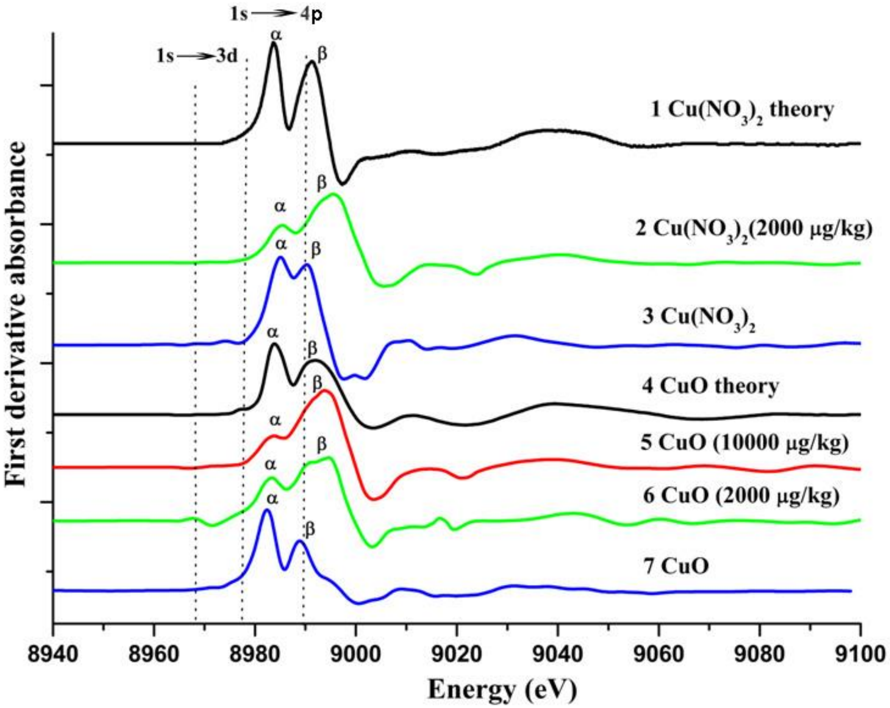


The experimental XANES and EXAFS spectra and X-ray diffraction measurements were performed at the Structural Materials Science beamline of the Kurchatov Center for Synchrotron Radiation (NRC “Kurchatov Institute”, Moscow).

# Experimental XANES spectra of chernozem samples contaminated with CuO and $Cu(NO_3)_2$



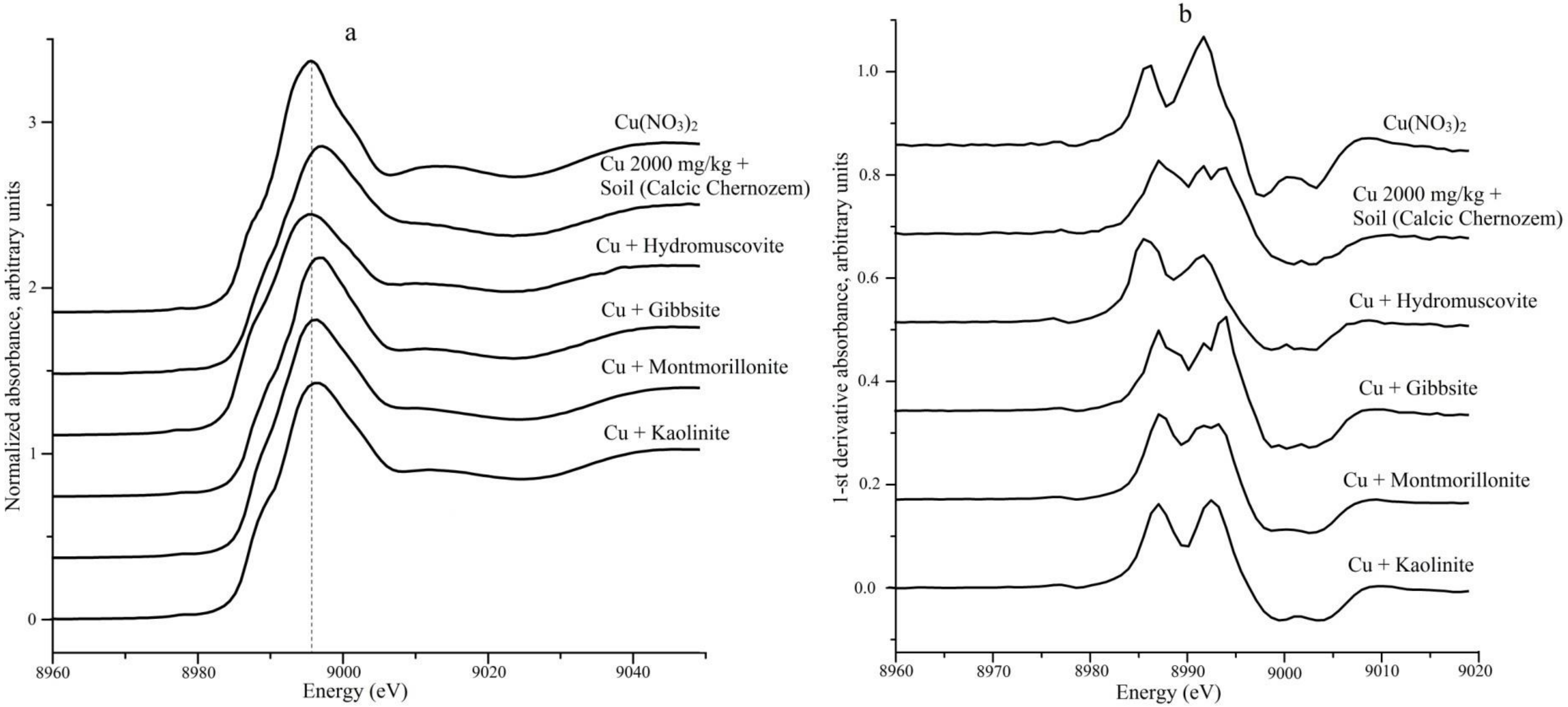
**Normalized Cu K-edge XANES spectra**



**First derivatives of XANES spectra**

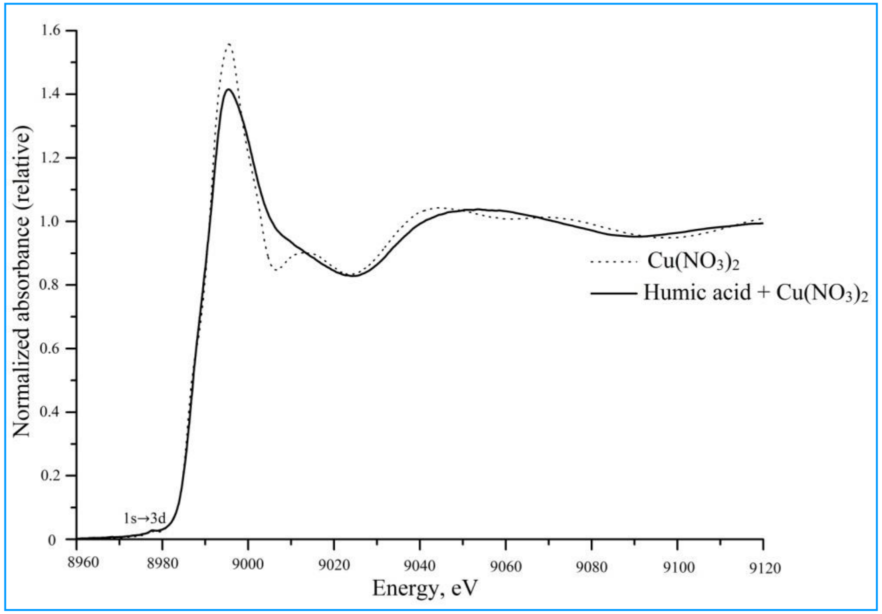
Application of this method demonstrated that the state of copper introduced in chernozem as CuO did not change after three year of incubation. After being introduced as $Cu(NO_3)_2$ the state of copper changed very much.

# Experimental Cu K-edge XANES spectra for Chernozem and mineral phases at modification with a saturated $Cu(NO_3)_2$ solution

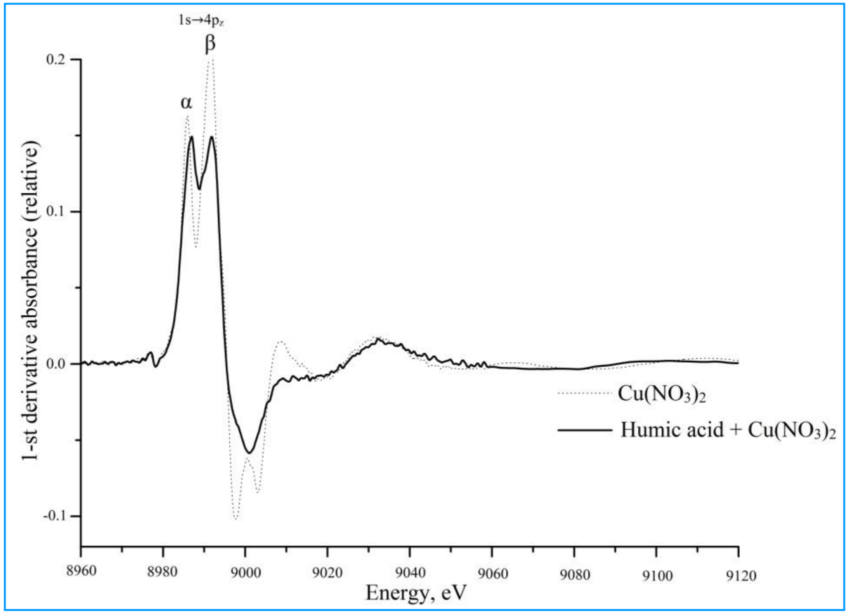


X-ray diagnostics revealed that copper ions are incorporated in the octahedral sites of minerals

# The experimental Cu K-edge X-ray absorption spectra (XANES) of organic phase from Chernozem



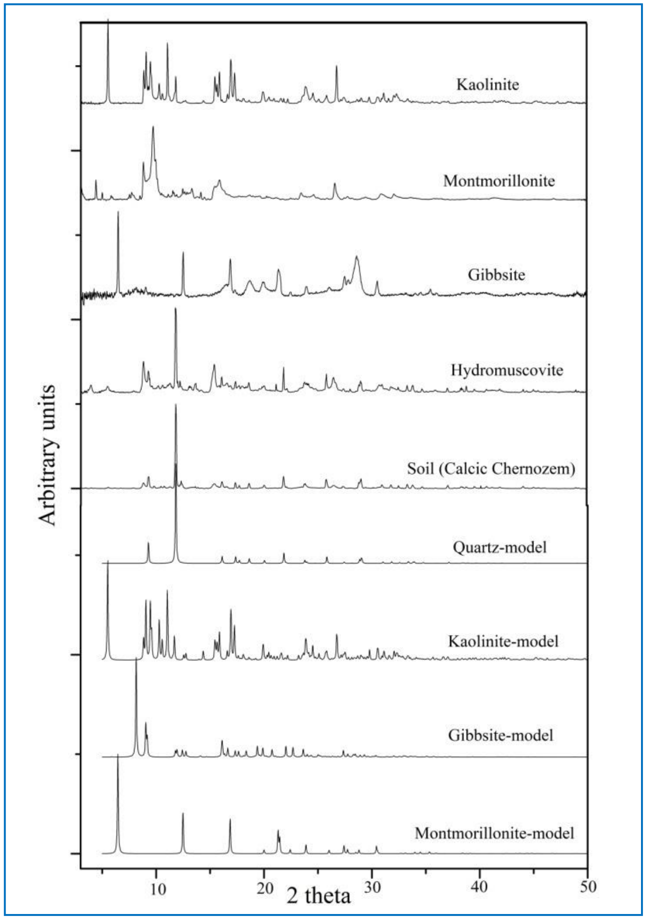
**Normalized Cu K-edge XANES spectra**



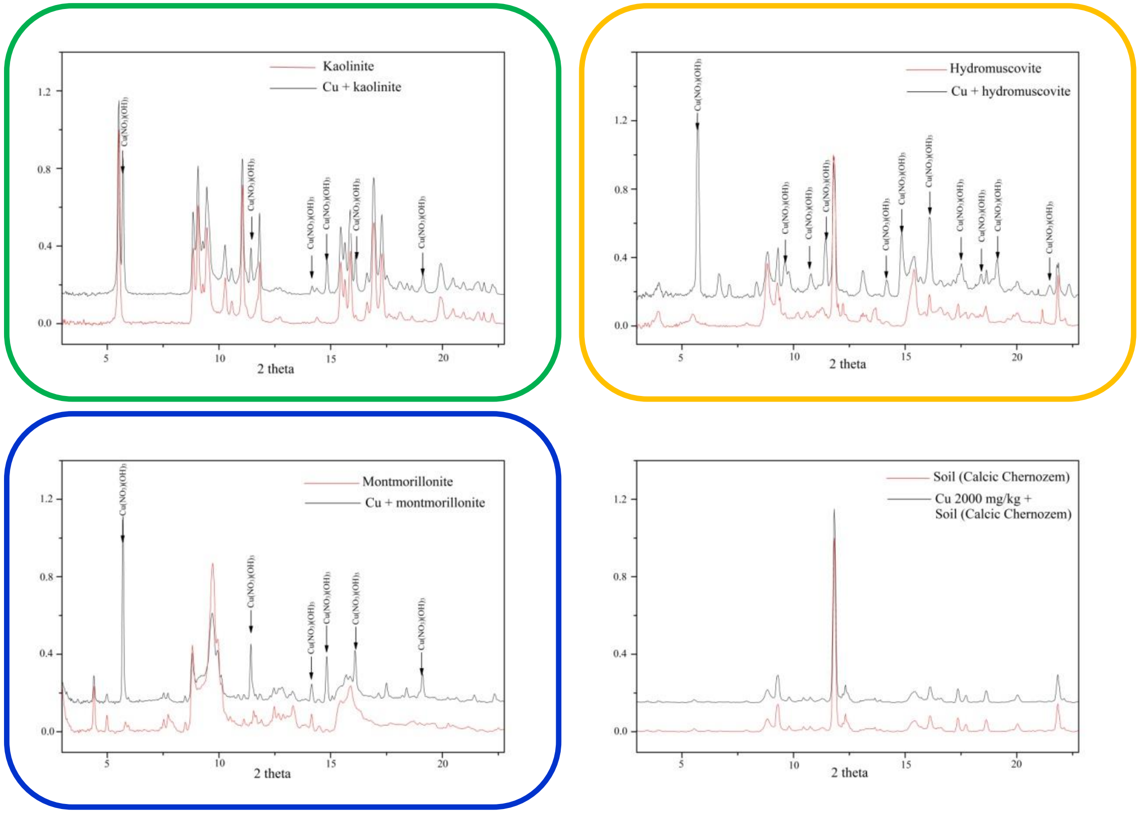
**First derivatives of XANES spectra**

Shown that $Cu^{2+}$ bonded with humic materials at the expense of covalent bond and forms octahedral inner-sphere chelate complexes.

# X-ray diffraction analysis (XRD)



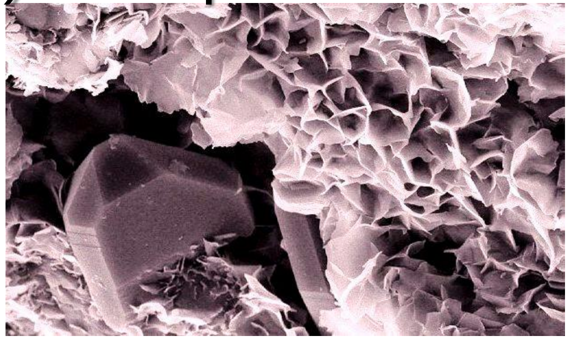
XRD patterns for the original soil samples and the mineral phases, and calculated models from the ICSD database

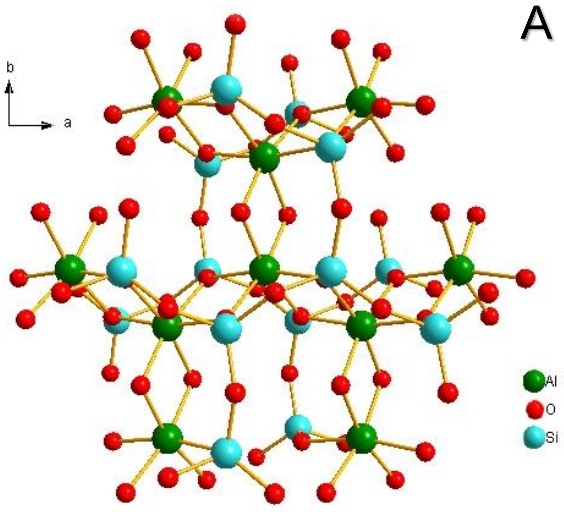


**Comparative analysis of X-ray powder diffraction patterns for soil samples and layered silicate phases before and after modification with a saturated $Cu(NO_3)_2$ solution**

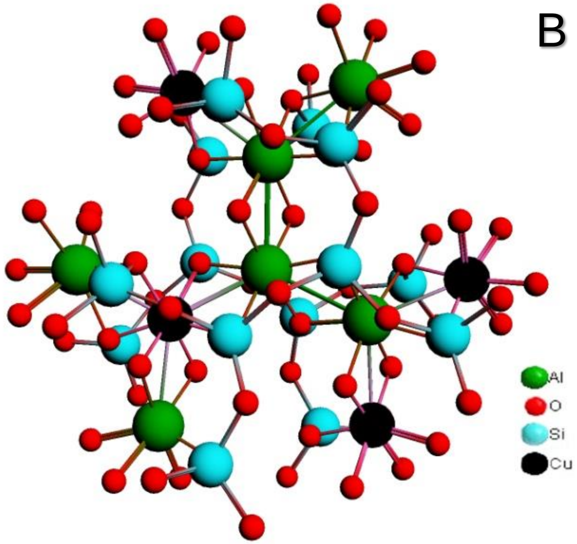
X-ray diagnostics revealed that excess Cu (II) ions are removed from the system due to the formation and precipitation of coarsely crystalline $Cu(NO_3)(OH)_3$.

# The modeling of montmorillonite structure after Cu (II) absorption of molecular dynamics methods





| Neighboring Atom | Distance, Å | Ange bond, $O_{eq}$-Al(Cu)- $O_{ax}$, ° |
|---|---|---|
| Montmorillonite, standard | | |
| Al-$O_{equatorial}$ | 1.929 ± 0.004 | 105.92 ± 18.25 |
| Al-$O_{axial}$ | 1.946 ± 0.007 | |
| Montmorillonite, the model with Cu (II) absorption | | |
| Cu-$O_{equatorial}$ | 1.916 ± 0.008 | 105.15 ± 18.10 |
| Cu-$O_{axial}$ | 1.931 ± 0.004 | |

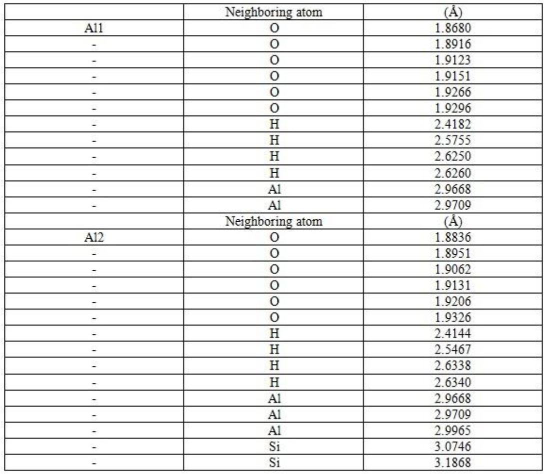


# Application of computer technologies for an estimation of influence atoms of Cu(II) in the kaolinite

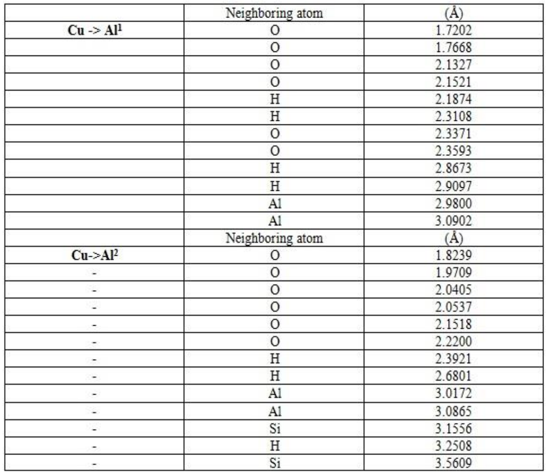
*High-performance computing cluster designed to solve quantum chemical problems*

*896-core desktop supercomputer accelerate scientific simulations*

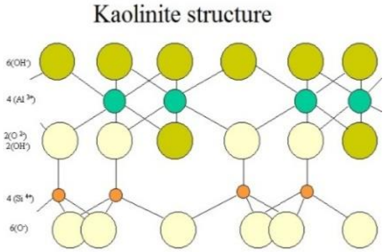
## Comparative results of the kaolinite structure by the method of quantum chemical modelling **VASP**, without and with Cu (II) ion model defects



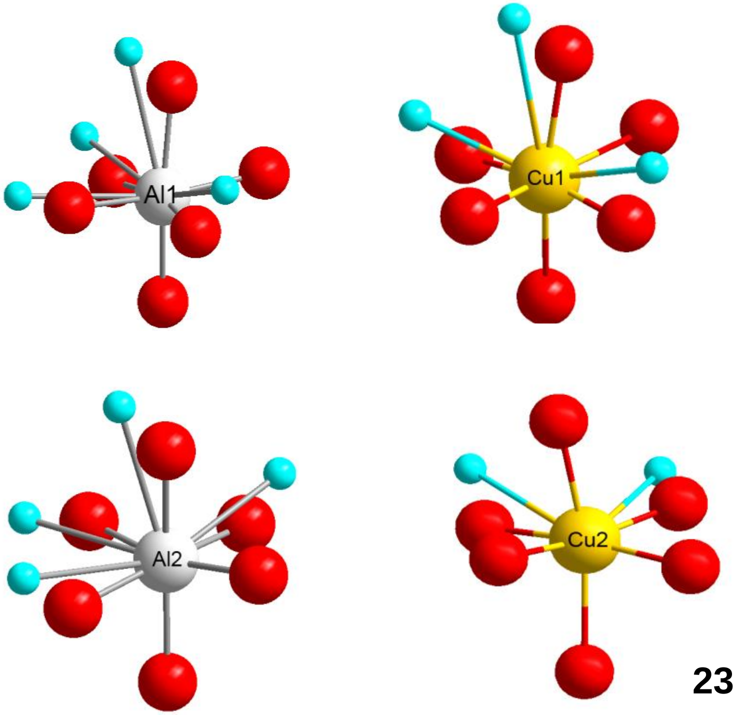
| | Neighboring atom | (Å) |
|---|---|---|
| Al1 | O | 1.8680 |
| - | O | 1.8916 |
| - | O | 1.9123 |
| - | O | 1.9151 |
| - | O | 1.9266 |
| - | O | 1.9296 |
| - | H | 2.4182 |
| - | H | 2.5755 |
| - | H | 2.6250 |
| - | H | 2.6260 |
| - | Al | 2.9668 |
| - | Al | 2.9709 |
| | Neighboring atom | (Å) |
| Al2 | O | 1.8836 |
| - | O | 1.8951 |
| - | O | 1.9062 |
| - | O | 1.9131 |
| - | O | 1.9206 |
| - | O | 1.9326 |
| - | H | 2.4144 |
| - | H | 2.5467 |
| - | H | 2.6338 |
| - | H | 2.6340 |
| - | Al | 2.9668 |
| - | Al | 2.9709 |
| - | Al | 2.9965 |
| - | Si | 3.0746 |
| - | Si | 3.1868 |



| | Neighboring atom | (Å) |
|---|---|---|
| **Cu -> Al$^1$** | O | 1.7202 |
| | O | 1.7668 |
| | O | 2.1327 |
| | O | 2.1521 |
| | H | 2.1874 |
| | H | 2.3108 |
| | O | 2.3371 |
| | O | 2.3593 |
| | H | 2.8673 |
| | H | 2.9097 |
| | Al | 2.9800 |
| | Al | 3.0902 |
| | Neighboring atom | (Å) |
| **Cu->Al$^2$** | O | 1.8239 |
| - | O | 1.9709 |
| - | O | 2.0405 |
| - | O | 2.0537 |
| - | O | 2.1518 |
| - | O | 2.2200 |
| - | H | 2.3921 |
| - | H | 2.6801 |
| - | Al | 3.0172 |
| - | Al | 3.0865 |
| - | Si | 3.1556 |
| - | H | 3.2508 |
| - | Si | 3.5609 |



**Without Cu** **Cu**



# CONCLUSION

**It is impotent to combine new instrumental physical methods with chemical extraction procedures to add and extend the knowledge about changes in the Cu speciation and mobility in contaminated soils and its effect by plants.**

# Thanks

# The combined fractionation scheme of metals

| **Characteristic** | Data obtaining method by | |
|---|---|---|
| | **Analitical** | **Calculation (by the difference between the heavy metal contents in the extracts)** |
| **1. Metals in exchangeable form** | | |
| - Easily exchangeable | 1M $MgCl_2$ | |
| - Difficultly exchangeable | | Difference 1N. $NH_4CH_3COO$ - 1M $MgCl_2$ |
| **2. Metals bound with carbonates and forming their own mineral forms** | | |
| -total | No method | |
| -loosely bound (specifically adsorbed) | 1M $NaCH_3COO$,<br>pH 5 | |
| -firmly bound (coprecipitated, occluded, chemisorbed, precipitations of difficultly soluble HM compounds) | No method | |
| **3. Metals bound with nonsilicate Fe-Mn compounds** | | |
| -total | 0,04 M $NH_2OH \cdot HCl$ | |
| -loosely bound (specifically adsorbed) | | Difference (1N. HCl –1N. $NH_4CH_3COO$) - 1M $NaCH_3COO$ |
| -firmly bound (occluded) | | Difference 0,04M $NH_2OH \cdot HCl$ - (1N. HCl -1N. $NH_4CH_3COO$- 1M $NaCH_3COO$) |
| **4. Metals bound with organic metal** | | |
| -total | 30% $H_2O_2$ | |
| -loosely bound (complexes) | | Difference 1% EDTA in 1N. $NH_4CH_3COO$– 1N. $NH_4CH_3COO$ |
| -firmly bound (chelates) | | Difference 30% $H_2O_2$ –1% EDTA |
| **5. Metals firmly fixed in silicate minerals** | Extract of HF + HClO4 from the residual fraction (after all the extractions) | Difference between the total content of the element in the soil and the total content of all the fractions (except for the residual fraction) |

# Solubility diagrams of $PbCO_3$ (1), $CuCO_3$ (2), $Pb(OH)_2$ (3), $Cu(OH)_2$ (4), $Zn(OH)_2$ (5) and the HM activity in ordinary chernozem equilibrium solution logarithm