# Neutron activation analysis and complementary techniques in environmental studies

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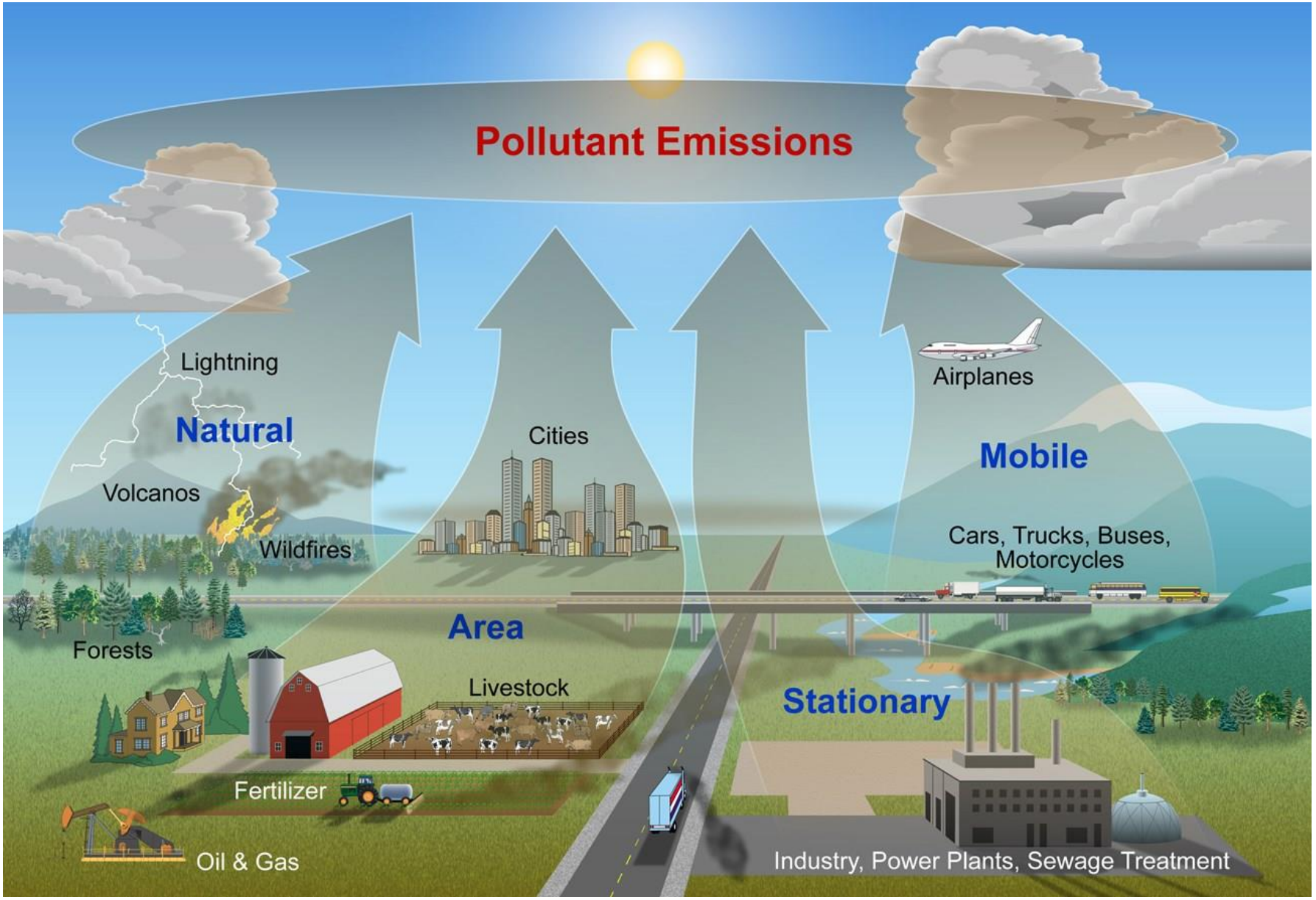
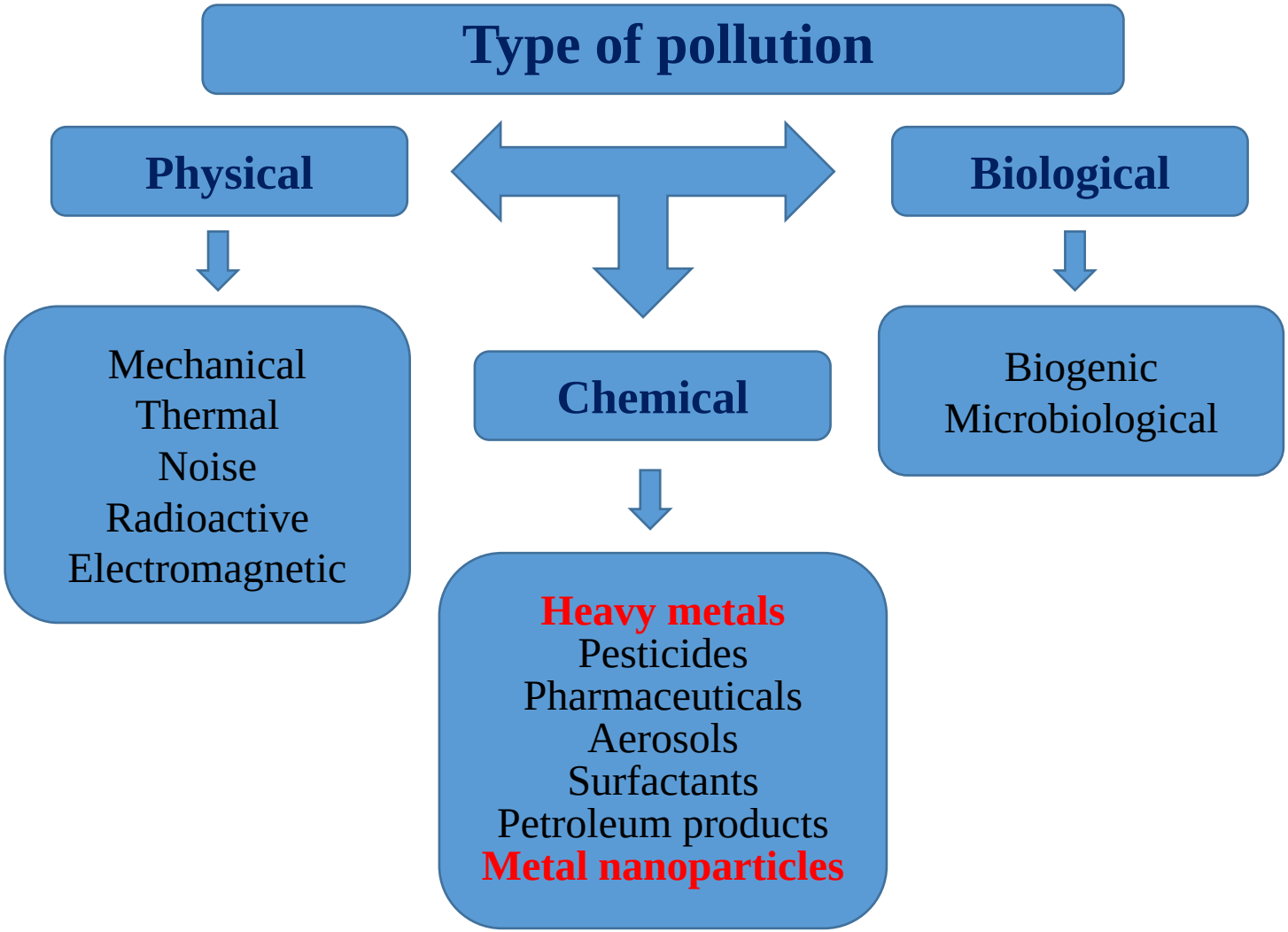
# Environment pollution

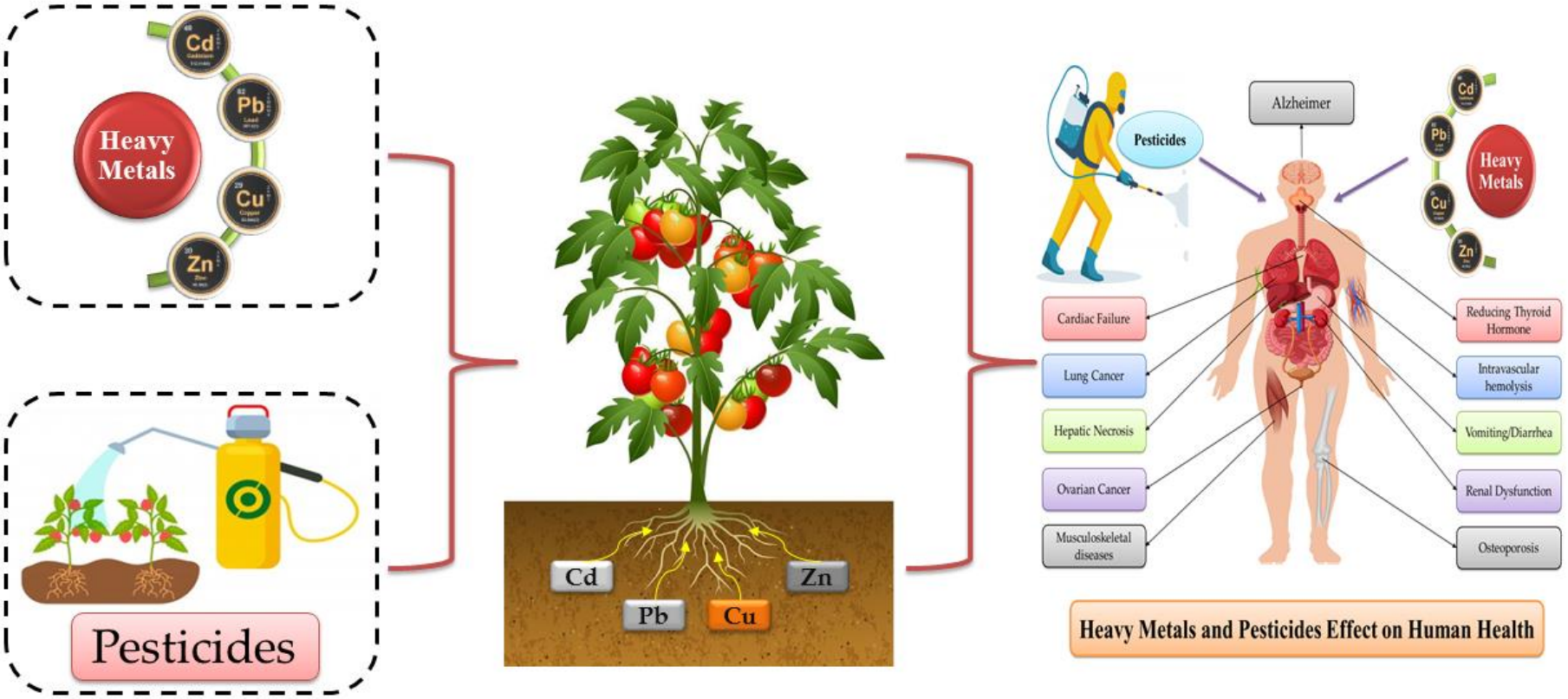
# Sources of pollution




https://www.nps.gov/subjects/air/sources.htm


Type of pollution
Physical
Biological
Chemical
Mechanical
Thermal
Noise
Radioactive
Electromagnetic
Biogenic
Microbiological
Heavy metals
Pesticides
Pharmaceuticals
Aerosols
Surfactants
Petroleum products
Metal nanoparticles

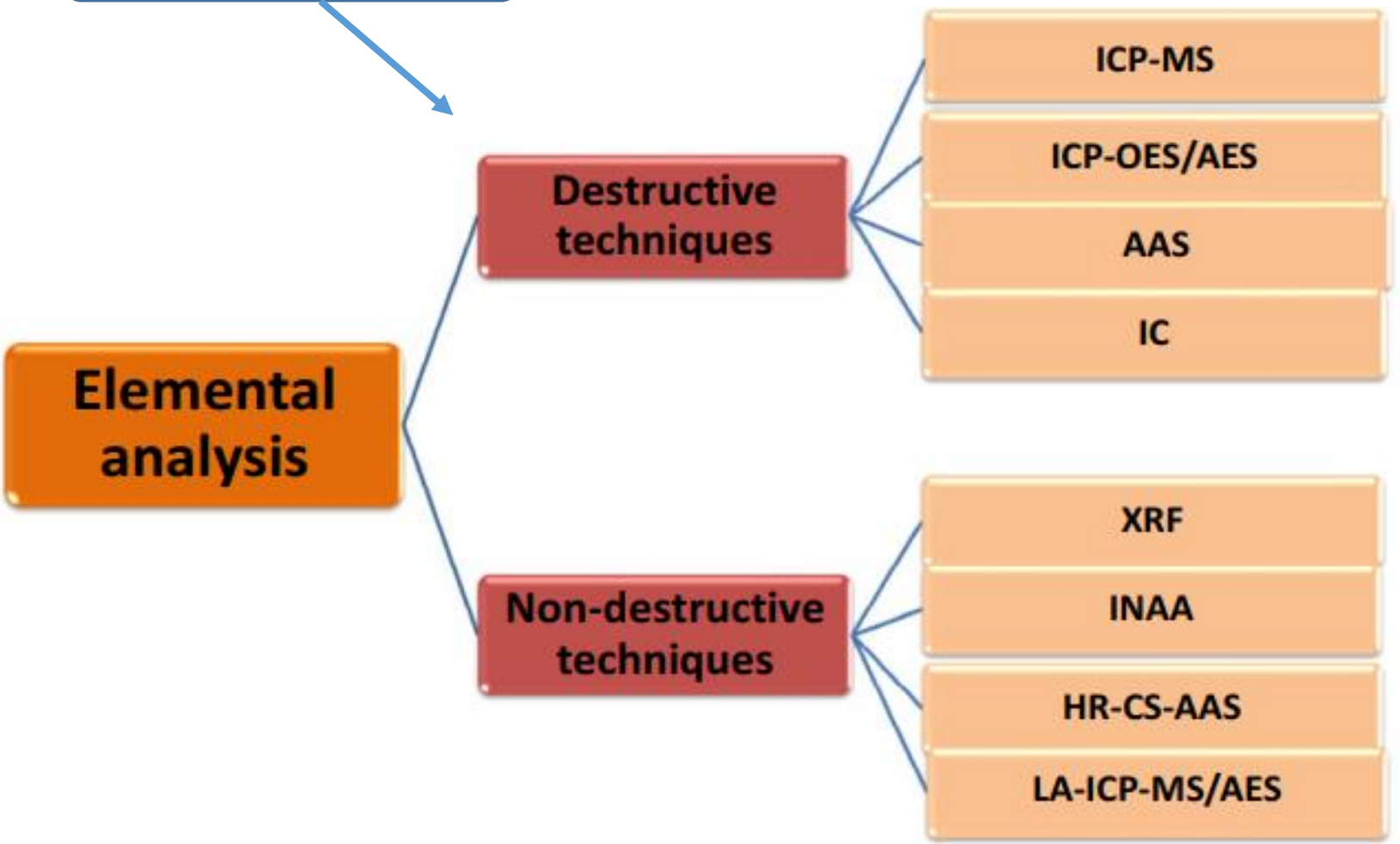
# Effect of chemical pollutants on living organisms




https://doi.org/10.3390/toxics9030042

# Analytical techniques used for elemental analysis

Sample preparation is a critical stage!!!




N. Mketo et al. https://doi.org/10.1016/j.trac.2016.09.002

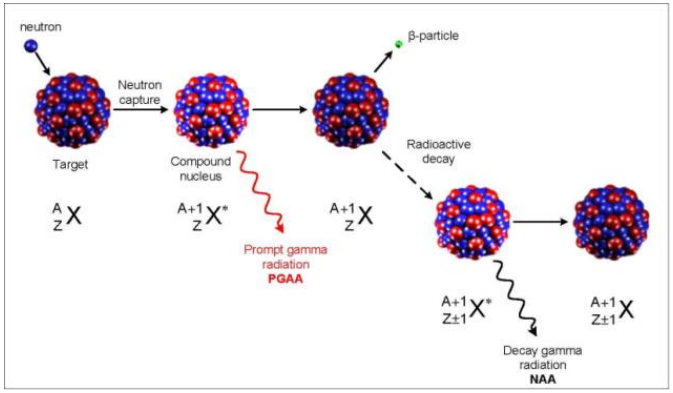
# Comparison of elemental analysis techniques

| Method | Detectable elements | Sensitivity* |
|---|---|---|
| **ICP-OES/MS/SFMS** | Li to U | ppm to ppt |
| **NAA** | H to U | ppm to ppt |
| **AAS** | Mainly metallic elements, up to 70 elements | ppm |
| **CHNOS** | C, H, N, O, S | 0.05–0.1 wt% |
| **XRF** | Be to U | 10 ppm–1 at% |
| **SEM-EDX** | All except H, He, and Li | 0.1–1 at% |
| **ERDA** | H to U | 0.1–0.5 at.% |
| **RBS** | Be to U | 0.1 at% |

https://measurlabs.com/blog/elemental-analysis-applications-and-method-comparison/

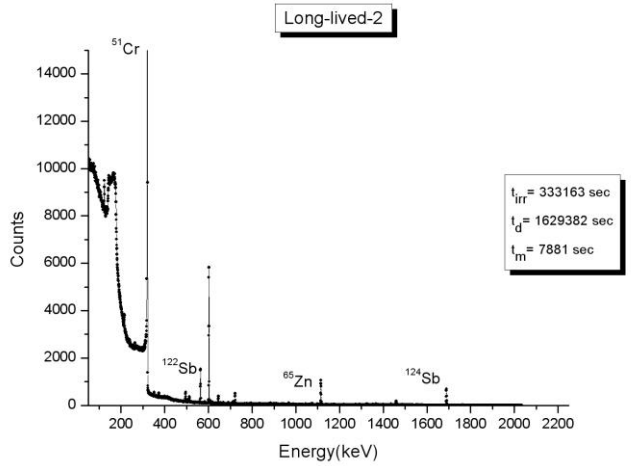
# Main steps of neutron activation analysis

## Irradiation




## Measurement


## Specta processing




## Results

| Na | | | Mg | | |
|---|---|---|---|---|---|
| Conc, µg/g | Err, % | MDC, µg/g | Conc, µg/g | Err, % | MDC, µg/g |
| 420 | 9 | 3.65 | 760 | 16 | 19.9 |
| 230 | 9 | 2.68 | 790 | 14 | 13.4 |
| 272 | 9 | 2.15 | 440 | 17 | 13.9 |
| 340 | 9 | 2.79 | 730 | 12 | 16.8 |
| 206 | 9 | 2.2 | 370 | 13 | 14.7 |
| 163 | 9 | 1.98 | 600 | 14 | 10.8 |
| 240 | 9 | 2.29 | 930 | 14 | 12 |
| 990 | 9 | 6.06 | 620 | 17 | 21.3 |
| 360 | 9 | 3.31 | 710 | 12 | 14.6 |
| 440 | 9 | 1.26 | 530 | 12 | 15.5 |

# Neutron activation analysis

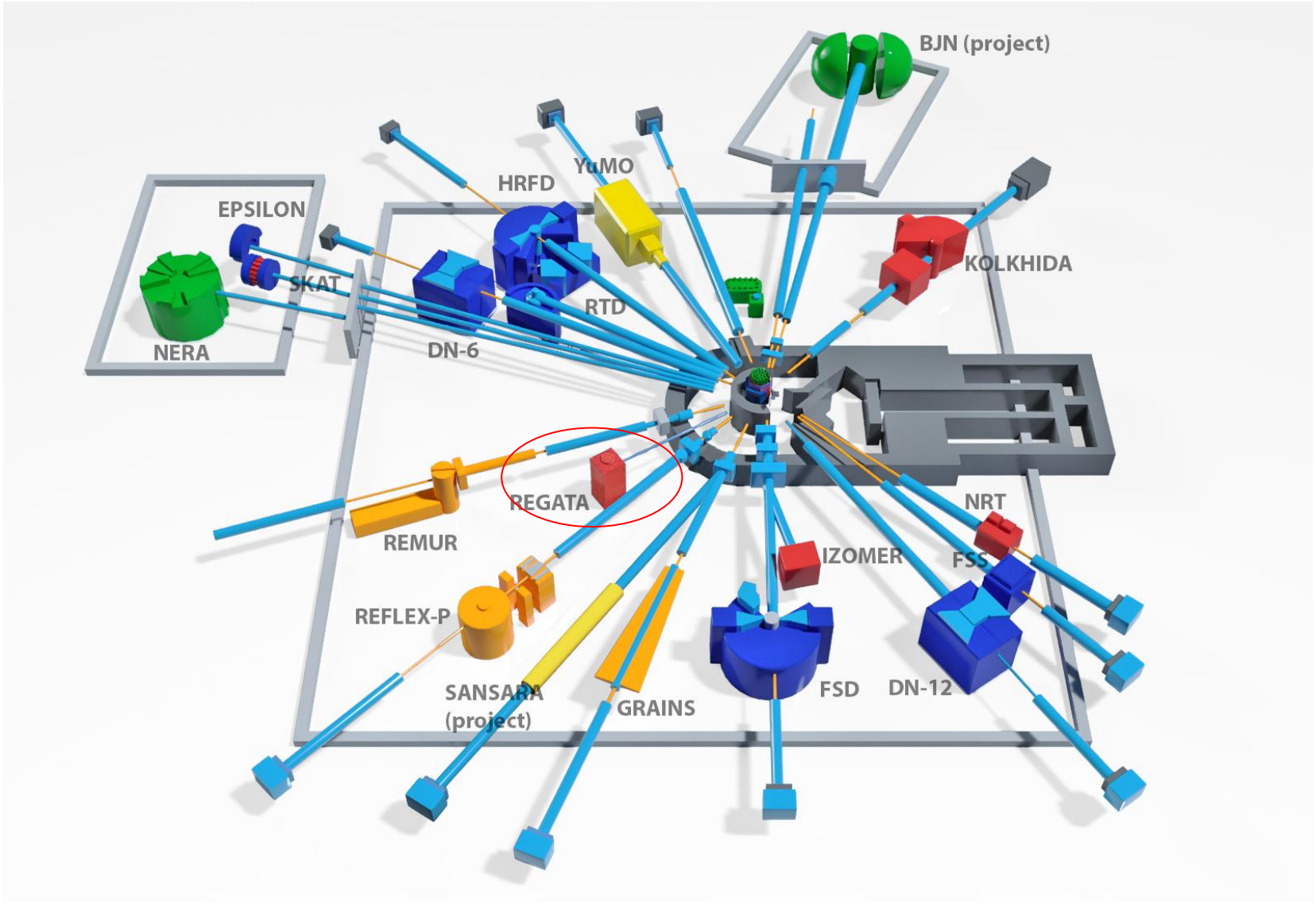
## Advantages

- ✓high sensitivity to a majority of elements;
- ✓good selectivity;
- ✓a possibility of simultaneously determining a large number of elements;
- ✓The method works for a very wide concentration range, from percent level down to the ppt and even sub-ppt level.
- ✓independence of the results on the form of chemical compounds;
- ✓NAA is in an unbeatable position in analysis of the rare earth elements (REE)
- ✓A nondestructive nature, which allows avoiding the risk of contamination of samples with reagents or their incomplete dissolution;
- ✓easy procedure for preparation of samples for analysis.

## Limitations

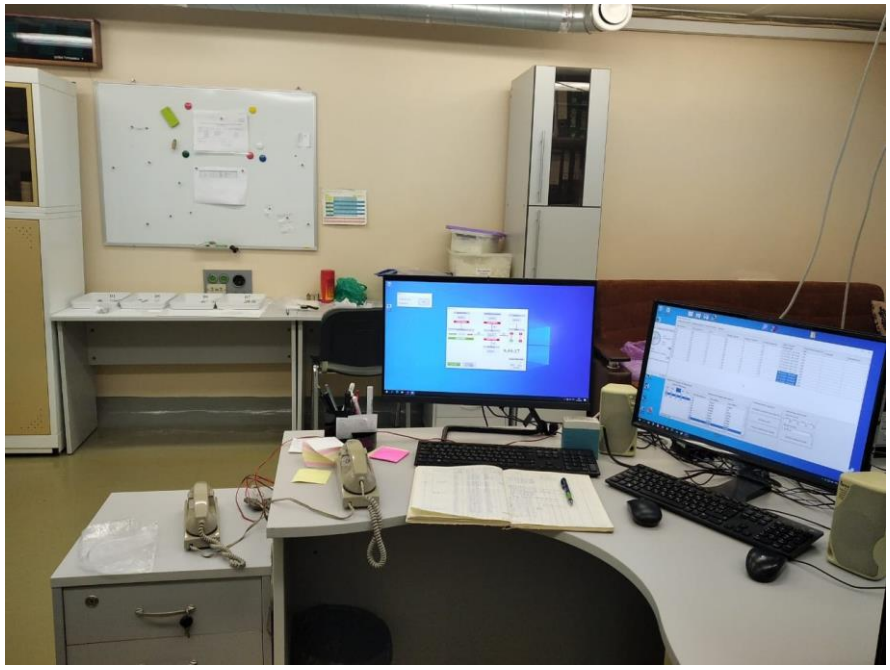
- ➢ necessity of using nuclear reactors;
- ➢ problems arising from storage and disposal of nuclear waste;
- ➢ time required for analysis.

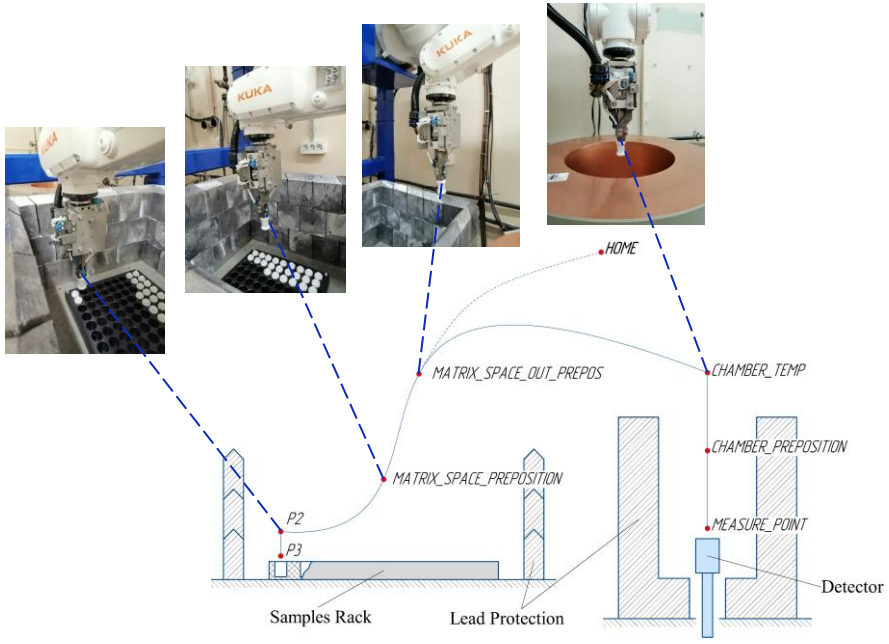
# Reactor and Radioanalytical complex REGATA



# Reactor and Radioanalytical complex REGATA

https://flnp.jinr.int/en-us/main/facilities/ibr-2/regata




KUKA
KUKA
KUKA
HOME
MATRIX_SPACE_OUT_PREPOS
CHAMBER_TEMP
CHAMBER_PREPOSITION
MATRIX_SPACE_PREPOSITION
P2
P3
MEASURE_POINT
Detector
Samples Rack
Lead Protection

# Procedures of samples irradiation

## Short irradiation

**Mg, Al, Si, Cl, I, Ti, V, Cu, Mn, Ca, S and Dy**

- ✓Irradiation channel: Ch 2 (full neutron spectrum)
- ✓Weight of samples: 0.1-0.5 gram
- ✓Irradiation time: 1- 30 min

## Long irradiation

**Na, K, Sc, Cr, Fe, Co, Ni, Zn, Ga, As, Se, Mo, In, Sn, Br, Rb, Sr, Zr, Sb, Cs, Ba, Ag, Cs, La, Ce, Sm, Tb, Hf, Ta, Nd, Nb, Y, Yb, W, Re, Ir, Hg, Au, Th and U**

- Irradiation channel: Ch 1 (Cd- screen, epithermal and fast neutrons)
- Weight of samples: 0.1-0.5 gram
- Irradiation time: 3- 5 days
- Cooling -3.5 days/ Repacking
- First measurement- 30 min.(live time), directly after repacking
- Cooling time – 20 days after the end of irradiation/ Second measurement – 1.5 hours (live time)

# Complementary techniques


The PlasmaQuant 9100 Elite


Thermo Scientific™ iCE™
3000 Series AA spectrometers


Milestone's DMA-80 Direct Mercury Analyzer

# Scientific directions

# Assessment of air pollution

Chemical and physical reactions

Gaseous, ion, particles, organic, radioactive emissions

Removal

Wet depositions (e.g. rainfalls, humidity)

Dry (dusts) depositions

# Passive biomonitoring


**UNECE**

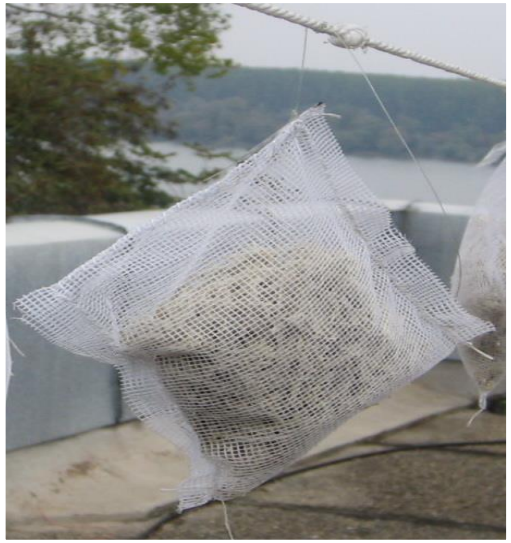
**United Nations Economic Commission for Europe**

**International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops**

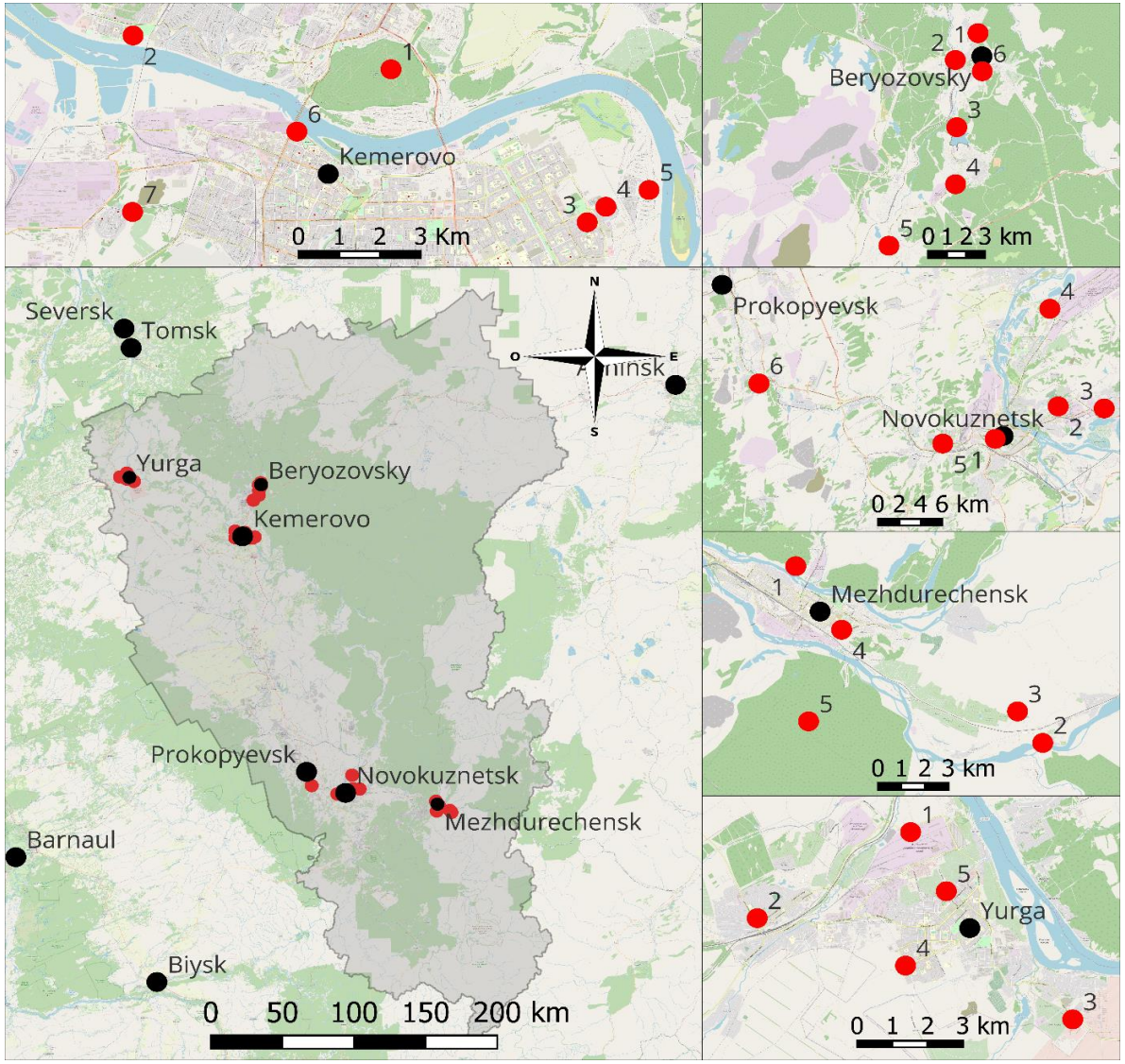
**W**orking **G**roup on **E**ffects - 1981

# Active biomonitoring

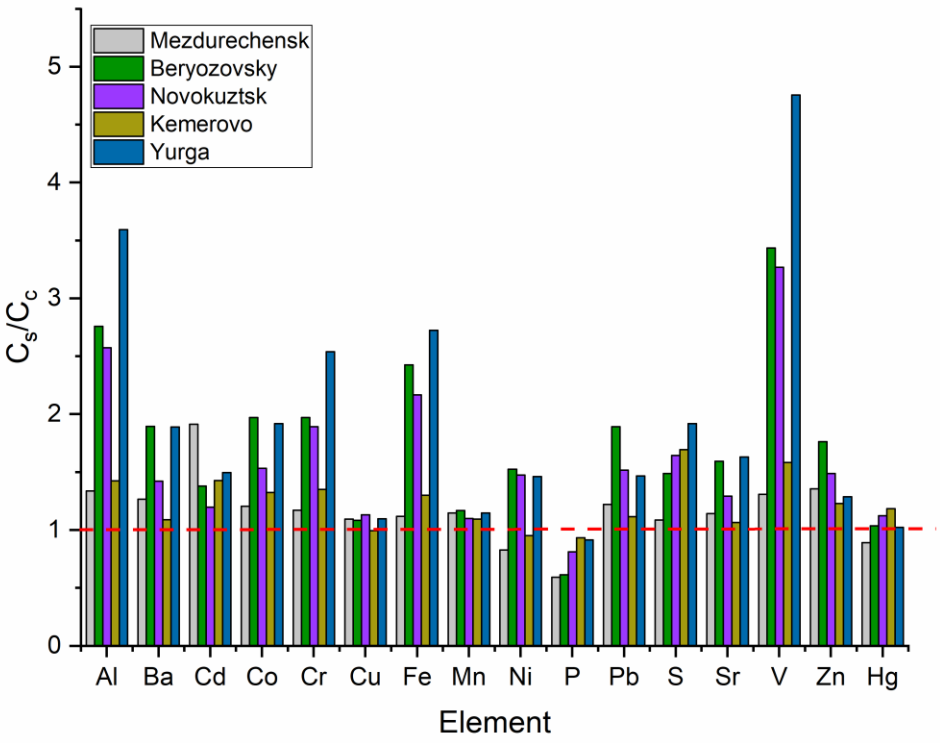
*Sphagnum girgensohnii* Russow



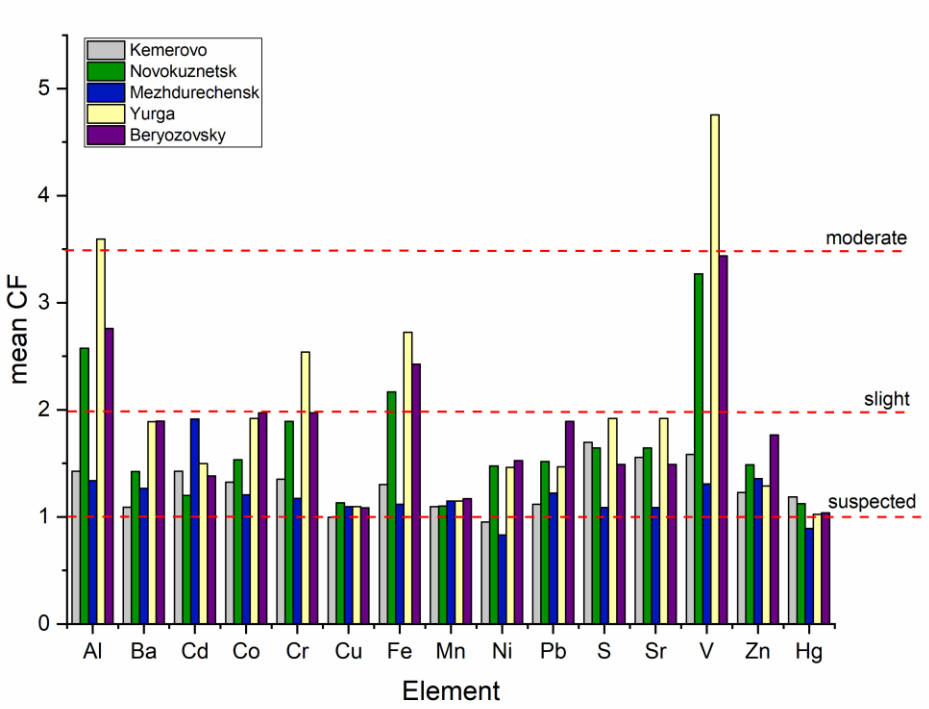
# Kemerovo region, Russia




## The map of moss bags exposur

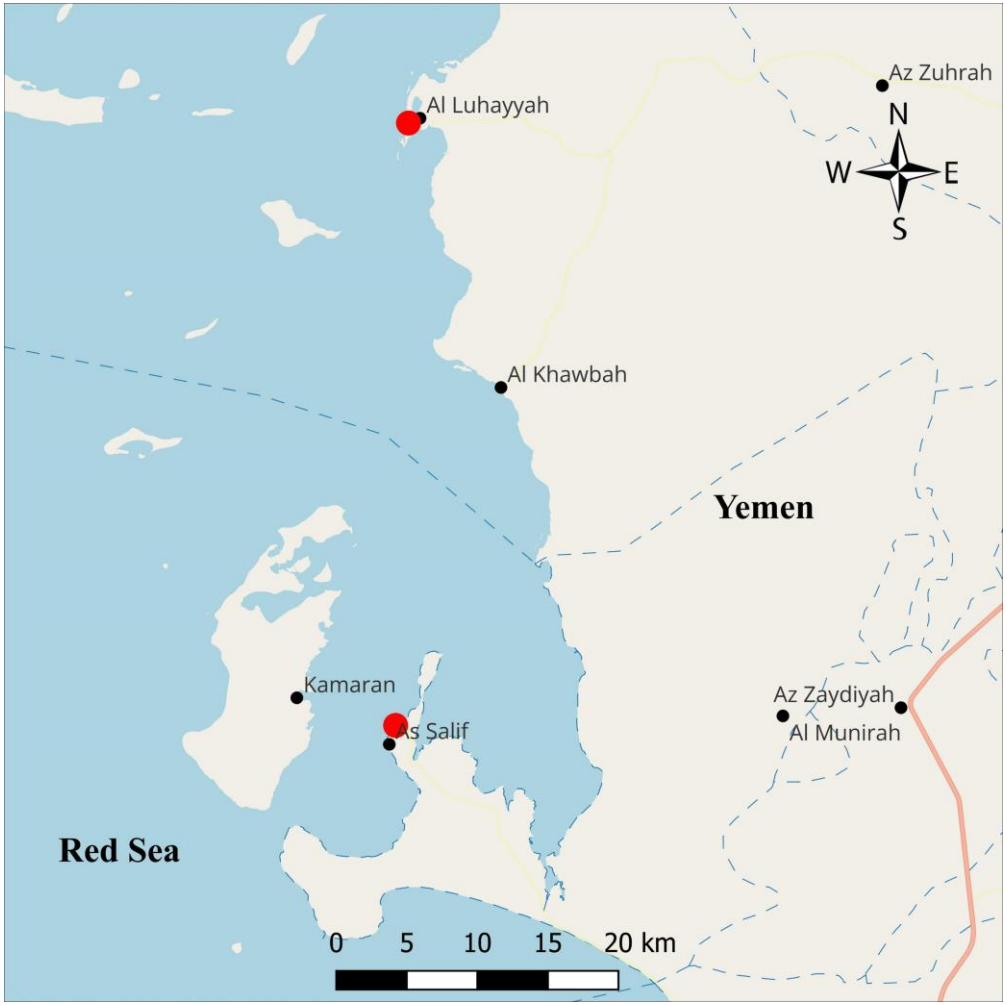



**Content of elements in samples in comparison with control**

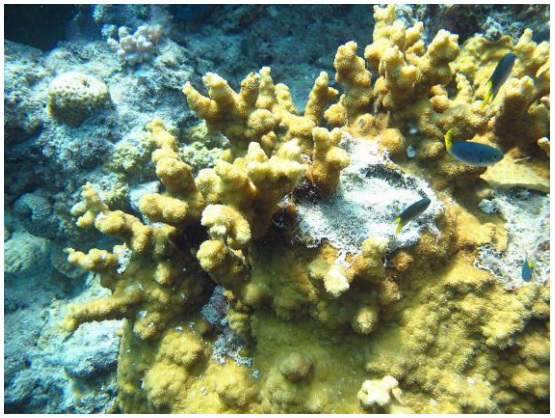



**The mean CF values for mosses samples exposed for two months in urban areas in Kemerovo region**

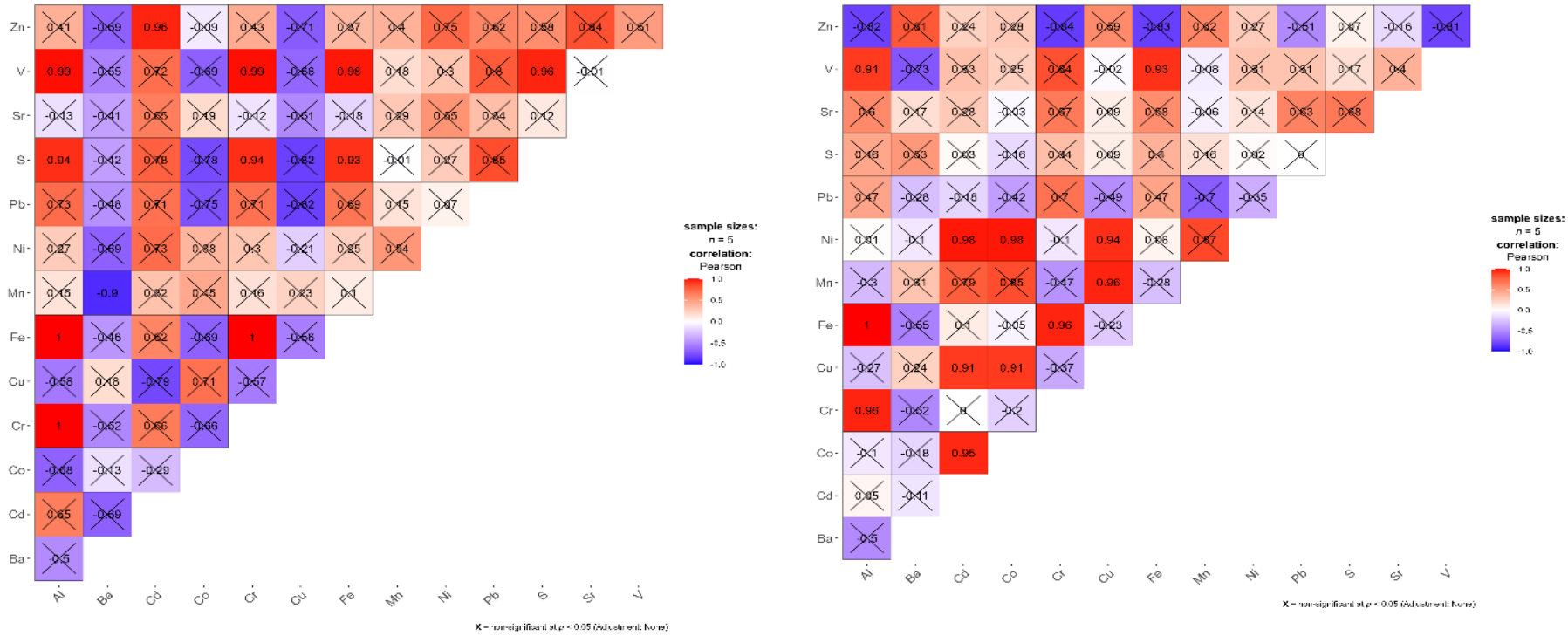
# Assessment of water pollution




**Corals sampling map (Al-Luhaya harbor and Al-Saleef harbor, Yemen).**



# Assessment of water pollution

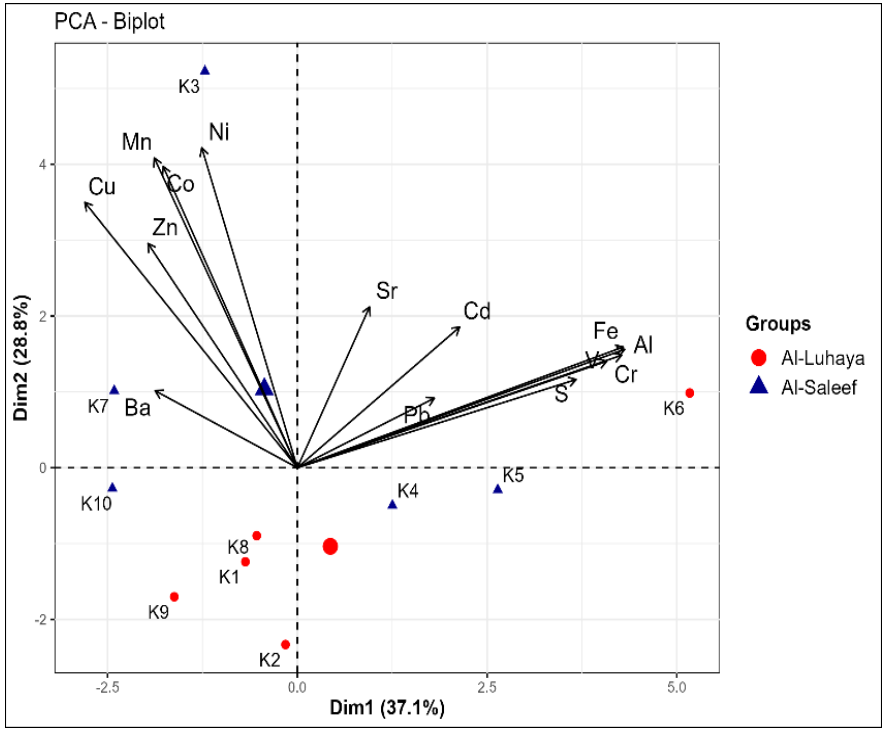



**Pearson correlation coefficient between element content in corrals collected from (a) Al-Luhaya and (b) Al-Saleef**

In corals collected from Al-Luhaya, a strong correlation was obtained between Al-Fe-Cr-S, Cd-Zn, Cr-V-Fe, Fe-V-S, and V-S

In corrals from Al-Saleef, a strong correlation was obtained between Al-V-Fe, Cr-Fe, Cd-Ni-Cu-Co, Co-Ni-Cu, Cu-Ni-Mn, and Fe-V.

# Assessment of water pollution




**Principal component analysis for corrals collected from Al-Luhaya and Al-Saleef ports, Yemen.**

**Contamination factor and pollution load index values for corrals collected from Al-Luhaya and Al-Saleef ports, Yemen**

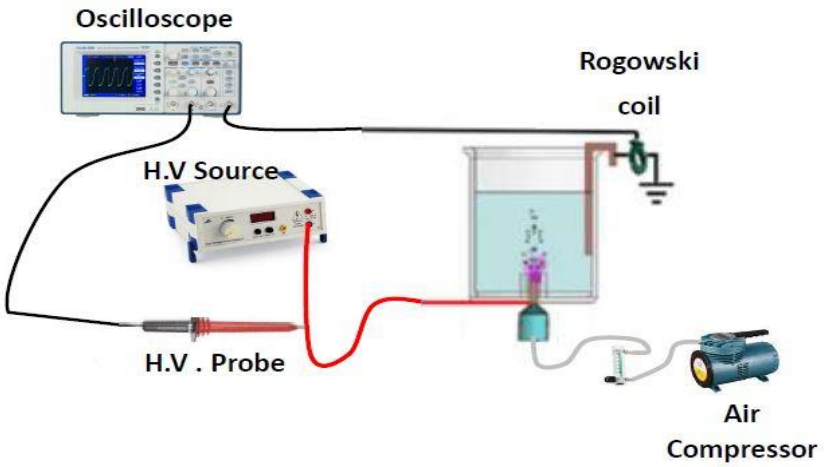
| | CF | |
|---|---|---|
| **Element** | Al-Luhaya | Al-Saleef |
| **Zn** | 0.65 | 1.73 |
| **Pb** | 0.26 | 0.52 |
| **Mn** | 0.31 | 0.54 |
| **Fe** | 2.86 | 3.43 |
| **Cr** | 0.38 | 0.49 |
| **Co** | 0.37 | 0.97 |
| **Ni** | 0.91 | 1.84 |
| **Cu** | 0.50 | 0.58 |
| **PLI** | 0.56 | 0.98 |

# Wastewater treatment


## Chemical composition of the leather tannery complex effluent

| Major ions | Concentration, mg/L | Element | Concentration, mg/L |
|---|---|---|---|
| Potassium | 17. 91 | Fe | 5.82 |
| Sodium | 236.6 | Cd | 0.36 |
| Magnesium | 0.5 | Cu | 0.10 |
| Calcium | 2.5 | Ni | 0.10 |
| Carbonates | 0.15 | As | 4.95 |
| Bicarbonate | 0.46 | Zn | 0.13 |
| Chlorine | 12.0 | | |
| Ammonia | 0.8 | | |
| Sulphates | 1000 | | |
| Phosphates | 7.3 | pH | 7.5 |

# First stage - cold atmospheric plasma treatment



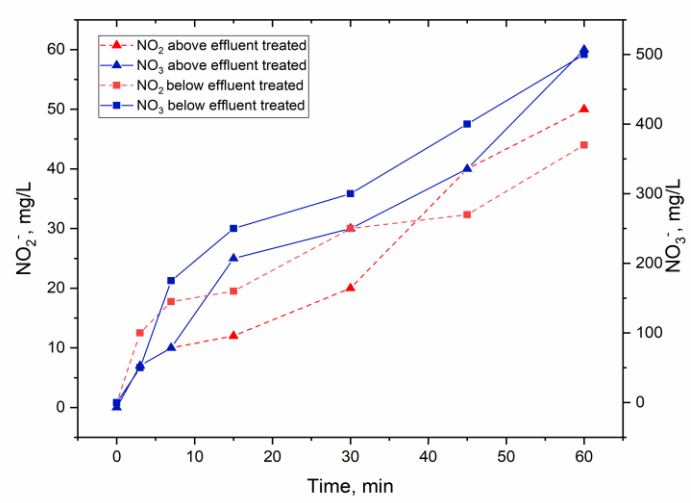

# Second stage - adsorption

time

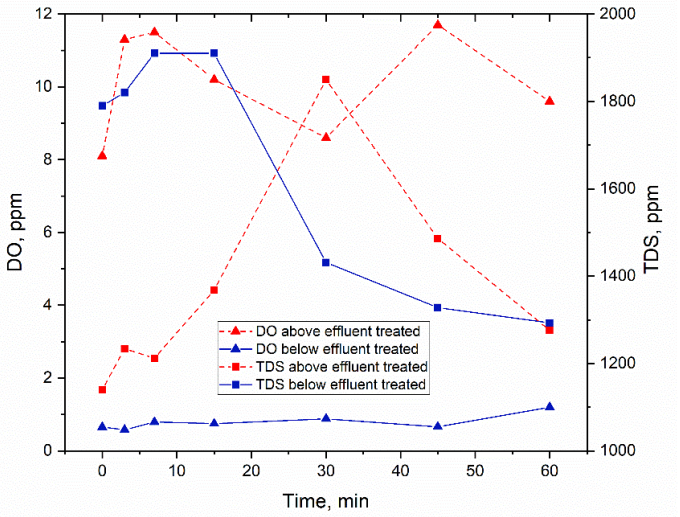
***Saccharomyces cerevisiae/ titanosilicate ETS-10***

ICP-OES
Fe, Cd, Cu, Ni, As, Zn

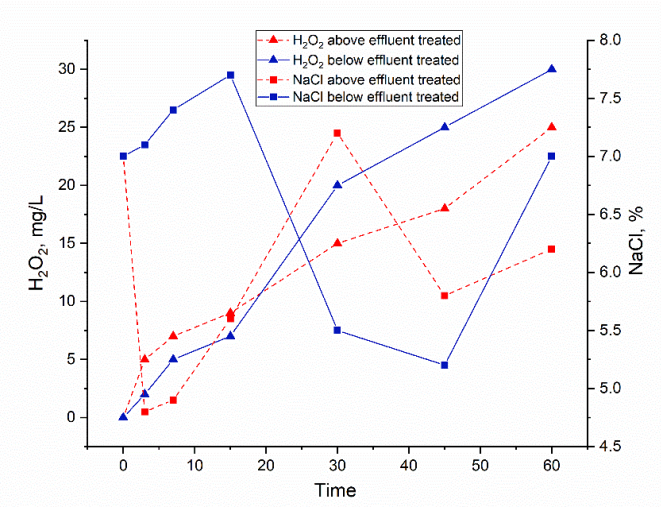
# First stage - cold atmospheric plasma treatment



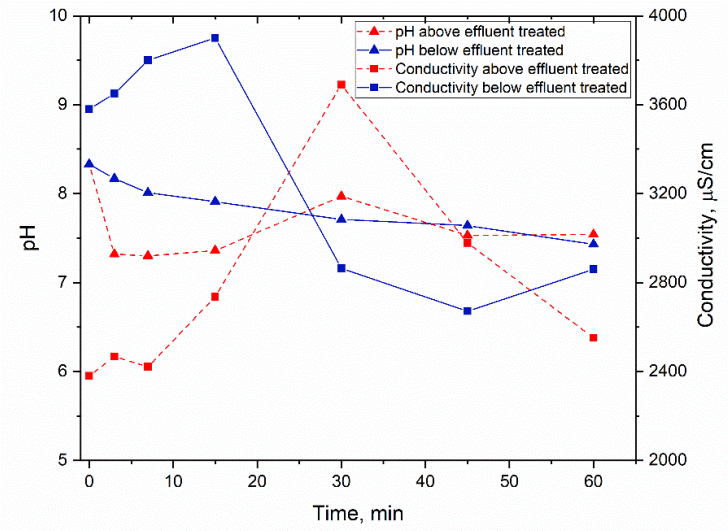

**Concentration of $NO_2^-$ and $NO_3^-$ in effluent treated with plasma**




**Concentration of DO and TDS in effluent treated with plasma**

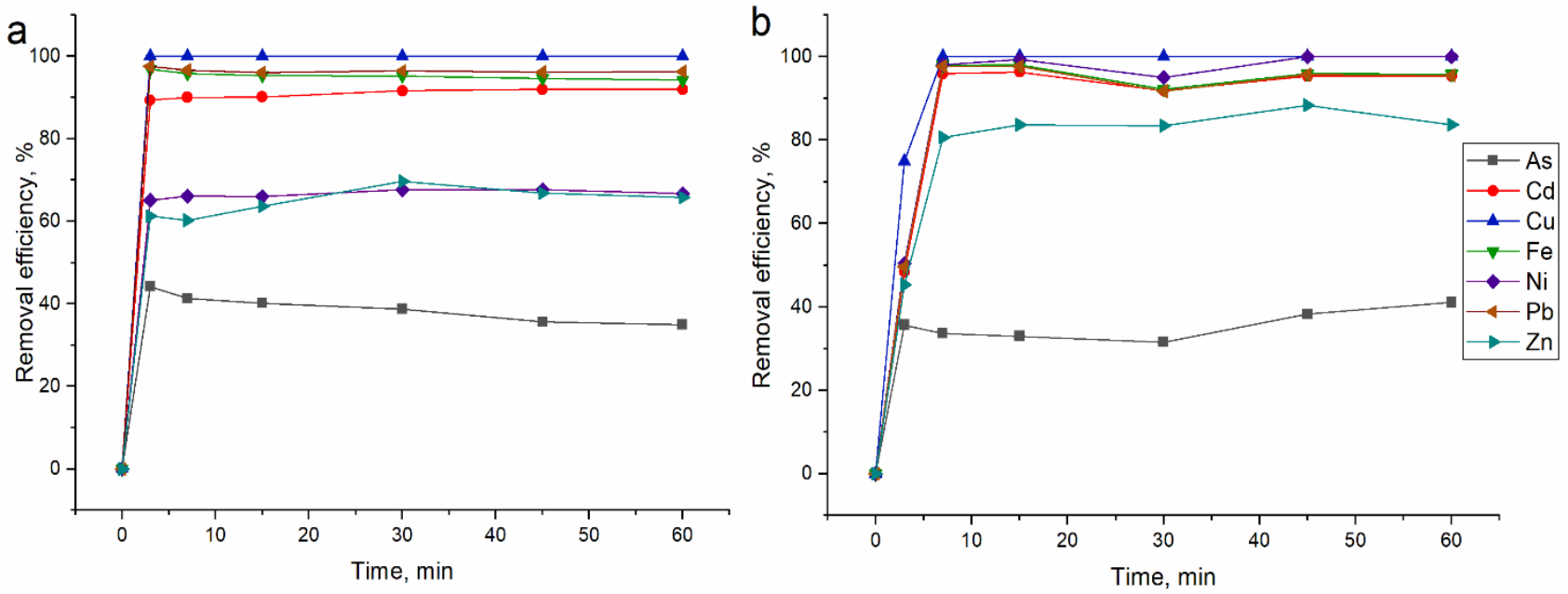



**Level of $H_2O_2$ and NaCl in effluent treated with plasma**




**pH and conductivity of effluent treated with plasma**

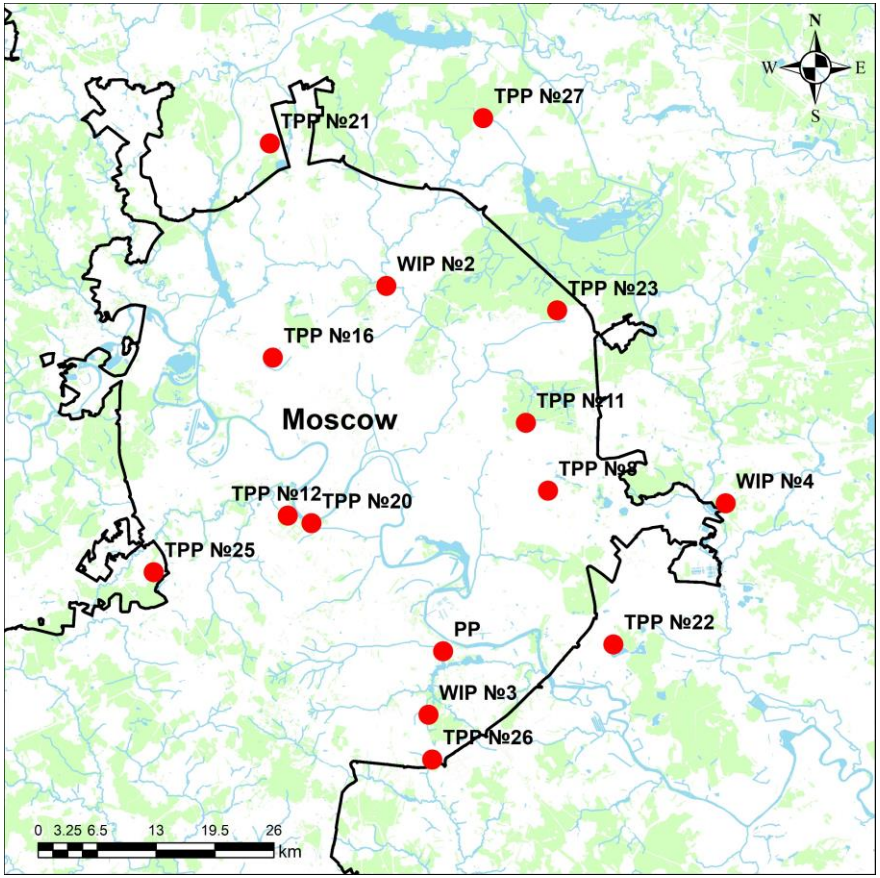
# First stage - cold atmospheric plasma treatment



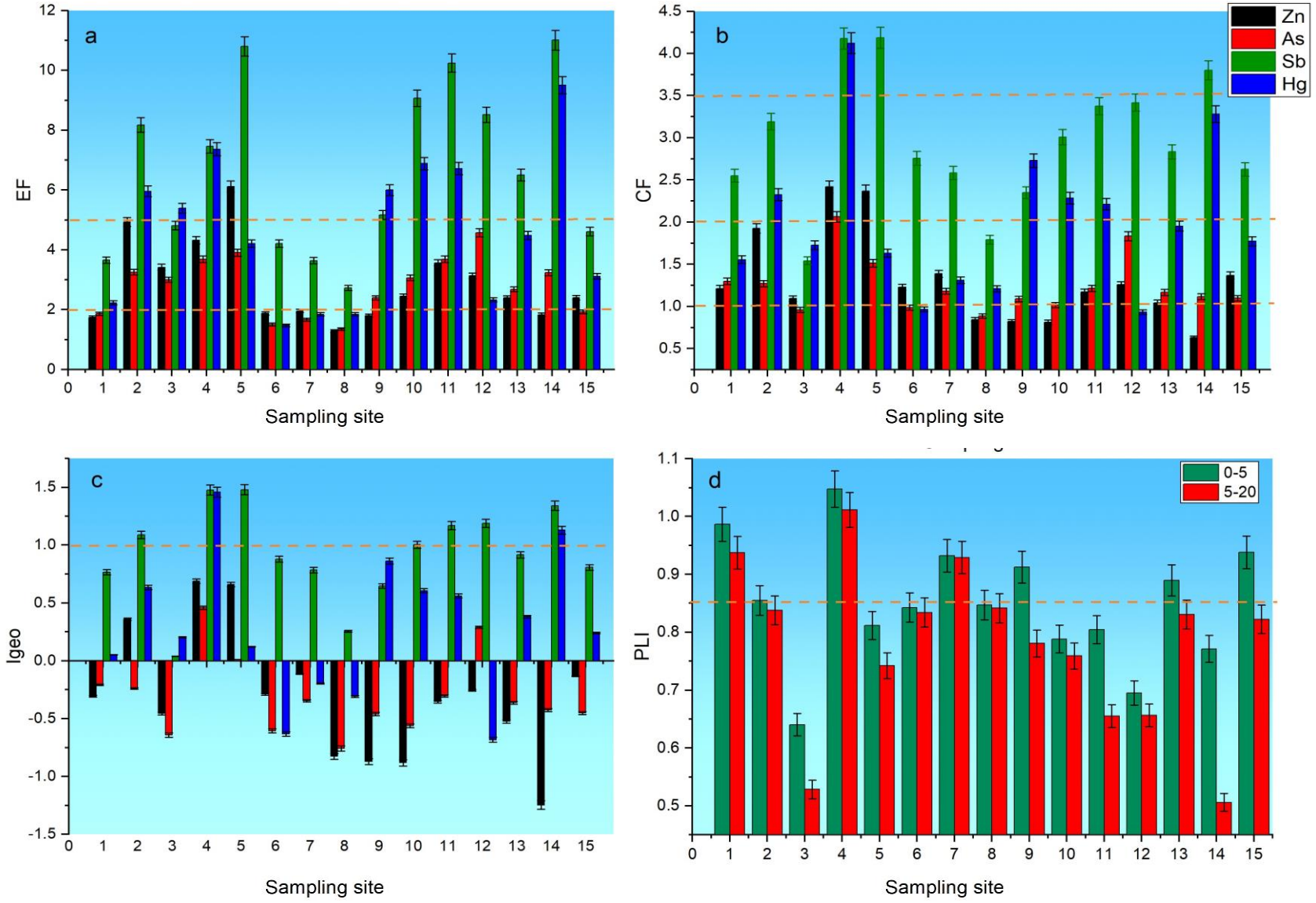

**Metal ion removal from tannery effluent on (a) *Saccharomyces cerevisiae* and (b) titanosilicate ETS-10**

| | Removal, % | |
|---|---|---|
| **Metal** | Titanosilicate ETS-10 | *Saccharomyces cerevisiae* |
| **Cu** | 100 | 100 |
| **Pb** | 95 | 94 |
| **Cd** | 96 | 96 |
| **Fe** | 95 | 96 |
| **Zn** | 88 | 66 |
| **Ni** | 100 | 67 |
| **As** | 41 | 44 |

# Assessment of soil pollution

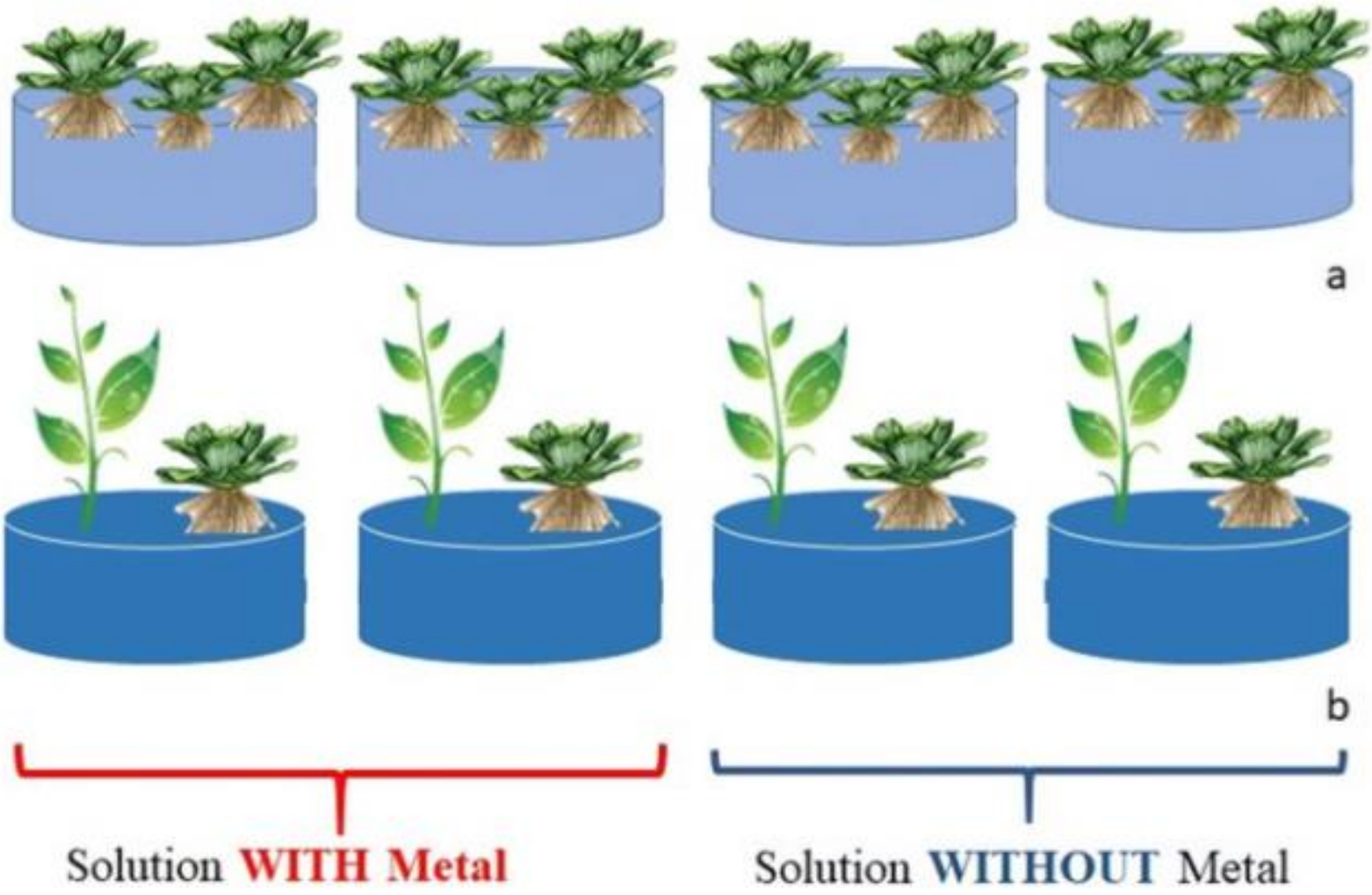



**Map of soil samples sampling locations. Black contour shows the City of Moscow metropolitan area.**

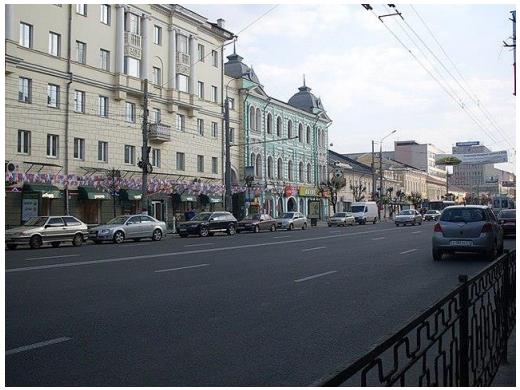



**The distribution of the average values ± corresponding uncertainties of EF (a), CF (b) and Igeo (d) of Zn, As, Sb and Hg, as well as the PLI (d) for each of the 15 investigated Moscow topsoil sampling sites.**

# Soil bioremediation



# Soil bioremediation



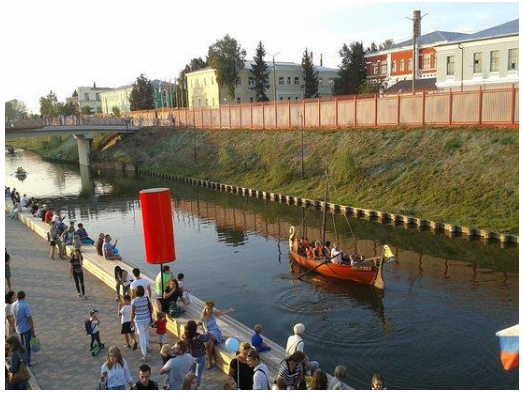
Lenin avenue

*Japanese millet

Kosogorsky Metallurgical Plant

Japanese millet*

Tulachermet



Embankment

# Soil bioremediation

## Characteristics of urban soils used in the study

| Soil sample | Background (Yasnaya Polyana) | KMP | Tulachermet | Highway (Lenina Ave.) | Embankment |
|---|---|---|---|---|---|
| **Soil type** | clay loam | clay loam | sandy loam | clay loam | sandy loam |
| **pH** | 6.20 | 7.26 | 7.35 | 7.29 | 7.31 |
| **Mn** | 900±87 | **6600±260** | 950±87 | 700±58 | **1600±156** |
| **Fe** | 39250±1960 | **45750±2290** | **116650±5830** | **45300±2260** | **97700±8754** |
| **V** | 65±3.2 | 55±4 | **145±7.2** | 59±2.9 | 91±5 |
| **Cr** | **116±8** | **137±12** | **117±4.5** | **70±2.8** | **1260±80** |
| **Ni** | 41±3 | 45±4 | **42±3.3** | 35±2.8 | **285±23** |
| **Cu** | 29±2 | 52±4 | 27±0.8 | 30±0.9 | **1188±89** |
| **Zn** | 23±2 | **192±9** | **71±3.6** | **106±5.3** | **4579±230** |
| **Pb** | 28±2 | **71±6** | 24±0.7 | 36±1.1 | **185±14** |
| **As** | 5.1±0.4 | **9.9±0.5** | 4.3±0.2 | 5.4±0.3 | **12.5±0.6** |

# Soil bioremediation

## Removal of elements from soils *Echinochloa frumentacea* in case of polyelement pollution, g/ha

| Element | KMP | TCh | Lenina Av. | Embankment | Background |
|---|---|---|---|---|---|
| **Pb** | 0.84 | 0.35 | 0.73 | 0.98 | 0.18 |
| **V** | 1.02 | 0.89 | 1.22 | 0.74 | 0.41 |
| **Cr** | 1.69 | 1.30 | **2.68** | **5.11** | 0.76 |
| **Ni** | 2.35 | 3.35 | **5.95** | **5.26** | 2.79 |
| **Cu** | **33.8** | 17.1 | **51.7** | **35.9** | 17.4 |
| **As** | 0.49 | 0.29 | 0.25 | 0.22 | 0.10 |
| **Fe** | **488** | **528** | **535** | **366** | **231** |
| **Mn** | **290** | 141 | **329** | 64 | 160 |
| **Zn** | **168** | 57.1 | **180** | **508** | 43.5 |

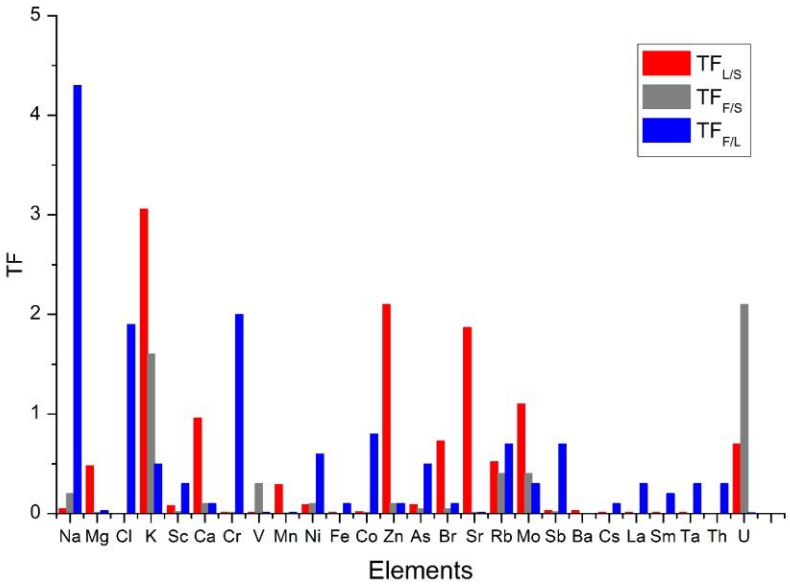
# Control of quality and safety of foodstuffs

*Golden Delicious*

*Record*

*Ialovenschii Ustoicivii*

# Apple




## Transfer factors in system soil-leaf-apple

Leaves-soil: K ($TF_{L/S}$=3.1), Zn ($TF_{L/S}$=2.1), Sr ($TF_{L/S}$ =1.9), and Mo ($TF_{L/S}$ =1.1) and Ca ($TF_{L/S}$=0.96).

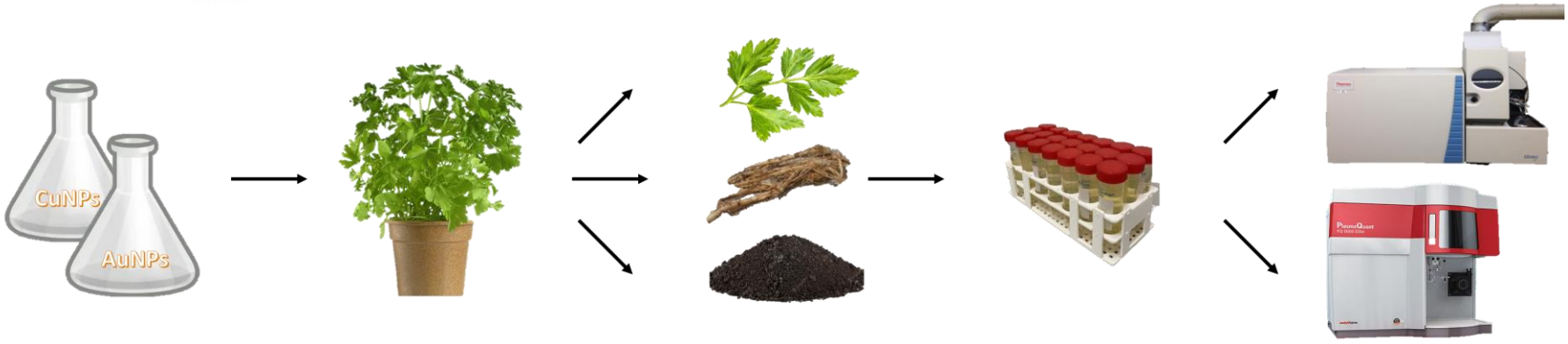
Fruits-soil: K ($TF_{F/S}$= 1.6) and U ($TF_{F/S}$ = 2.1).

Fruits- leaves: TF> 1.0 was obtained for Na, Cl, and Cr.

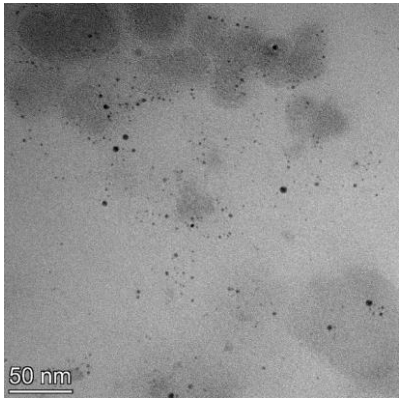
**Estimated daily intake of metal (DIM) and potential health hazards (HQ) from fruit**

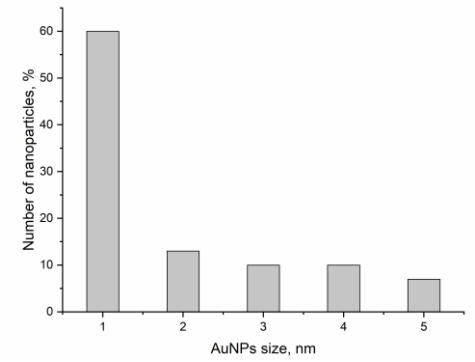
| | Apple | | | Plum | | | Grape | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Element** | C mg/kg f.w. | DIM, mg/day | HQ, mg/kg/day | C mg/kg f.w. | DIM, mg/day | HQ, mg/kg/day | C mg/kg f.w. | DIM, mg/day | HQ, mg/kg/day | $R_fD$, mg/day |
| **Cr** | 3.9 | 1.2 | 0.01 | 0 | 0 | 0 | 0.48 | 0.1 | 0.004 | 105 |
| **Co** | 0.5 | 0.1 | 0.05 | 0.7 | 0.2 | 0.07 | 0.6 | 0.2 | 0.06 | 3 |
| **Fe** | 78 | 23 | 0.4 | 151 | 45 | 0.75 | 8.8 | 2.6 | 0.04 | 10-60 |
| **Mn** | 8.1 | 2.4 | 0.5 | 2.2 | 0.6 | 0.1 | 1.7 | 0.5 | 0.1 | 0.5-5.0 |
| **Ni** | 6.7 | 2.0 | **1.4** | 1.4 | 0.4 | 0.3 | 1.8 | 0.2 | 0.2 | 1.4 |
| **V** | 0.6 | 0.2 | 0.1 | 0 | 0 | 0 | 1.3 | 0.4 | 0.3 | 1.8 |
| **Zn** | 33 | 9.9 | 0.7 | 25 | 7.5 | 0.5 | 6.4 | 1.9 | 0.1 | 15 |

# Effect of nanoparticles on plants

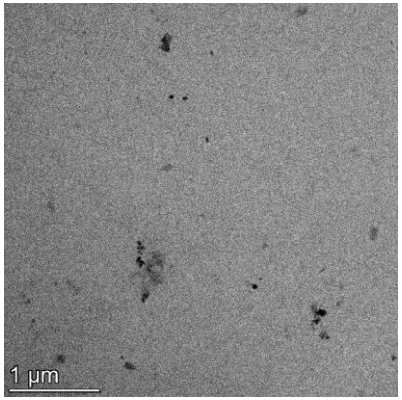


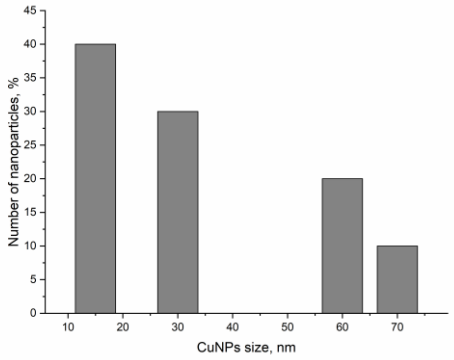

## AuNPs

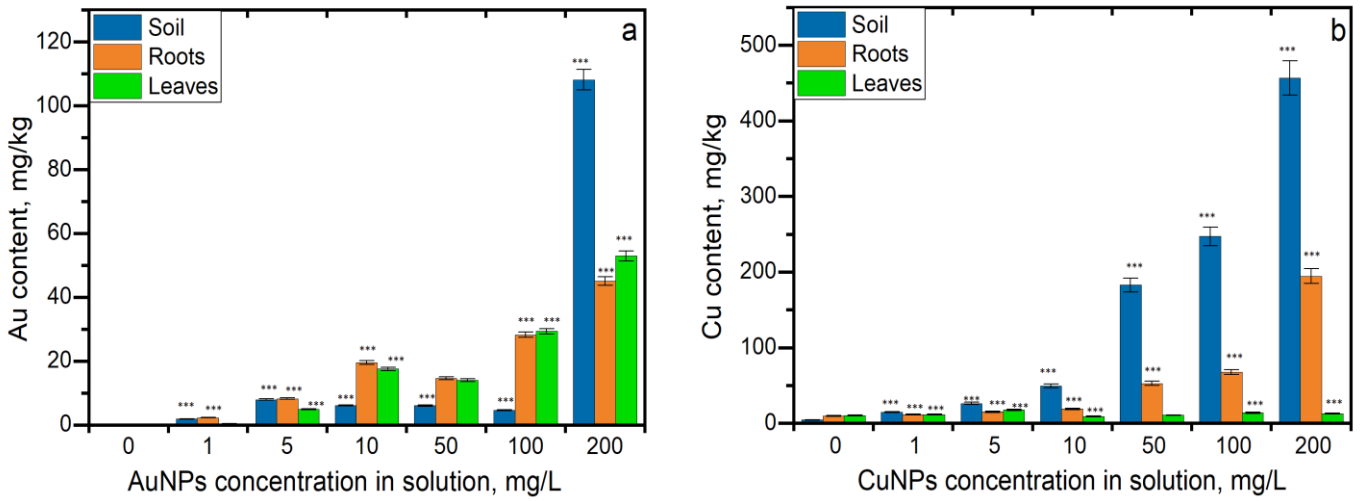


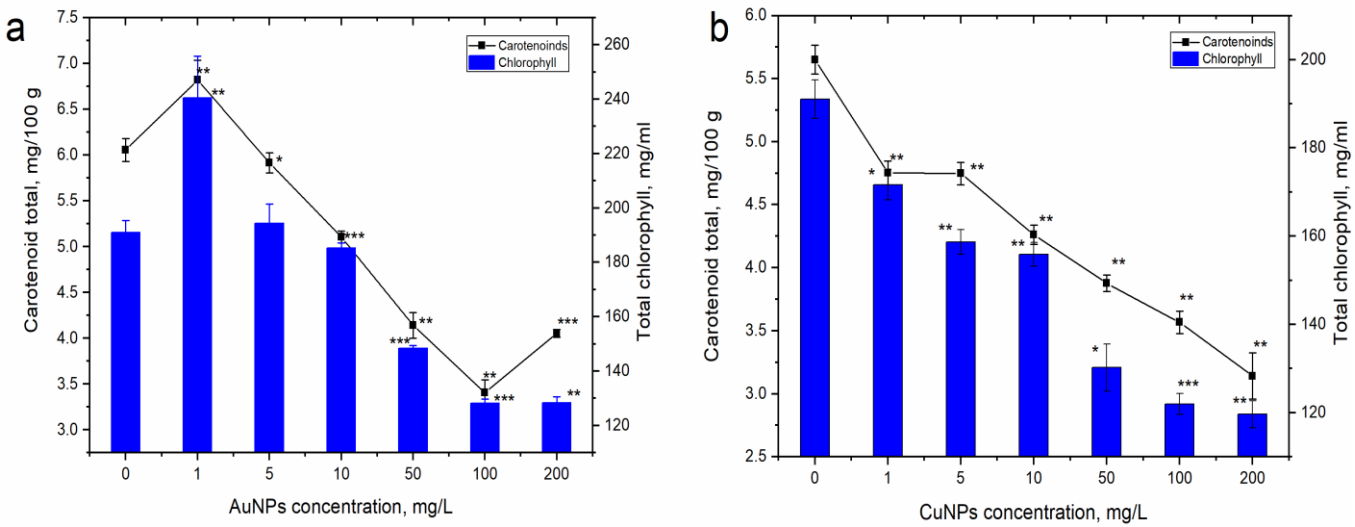

## CuNPs






**The content of copper and gold in parsley segments grown on soil watered with (a) AuNPs and (b) CuNPs determined by ICP-MS/OES techniques, (NPs concentrations 1-200 mg/L, duration of experiment 10 days**

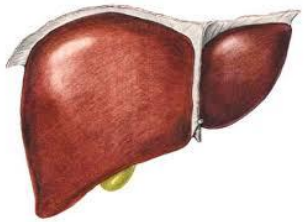



**Change in the content of carotenoids and total chlorophyll in the aerial parts of parsley grown on soil watered with (a) AuNPs and (b) CuNPs**

# Effect of nanoparticles on animals

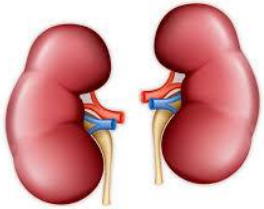
To study uptake of AgNPs (8.7 nm) both for mothers and the offspring experimental females were drinking the AgNPs solution with concentration of 25 µg/ml since one week before pregnancy and to the end of lactation (one month after birth).

blood



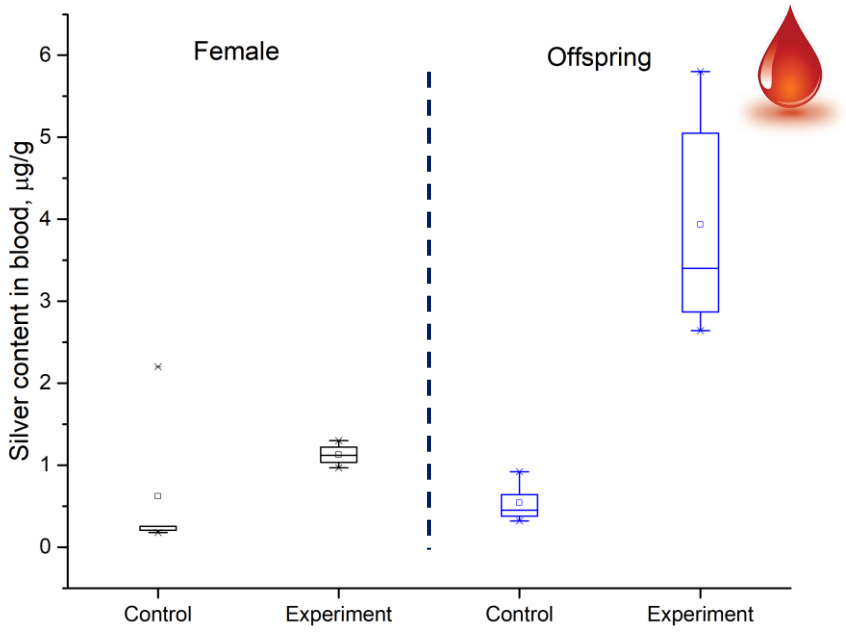
liver

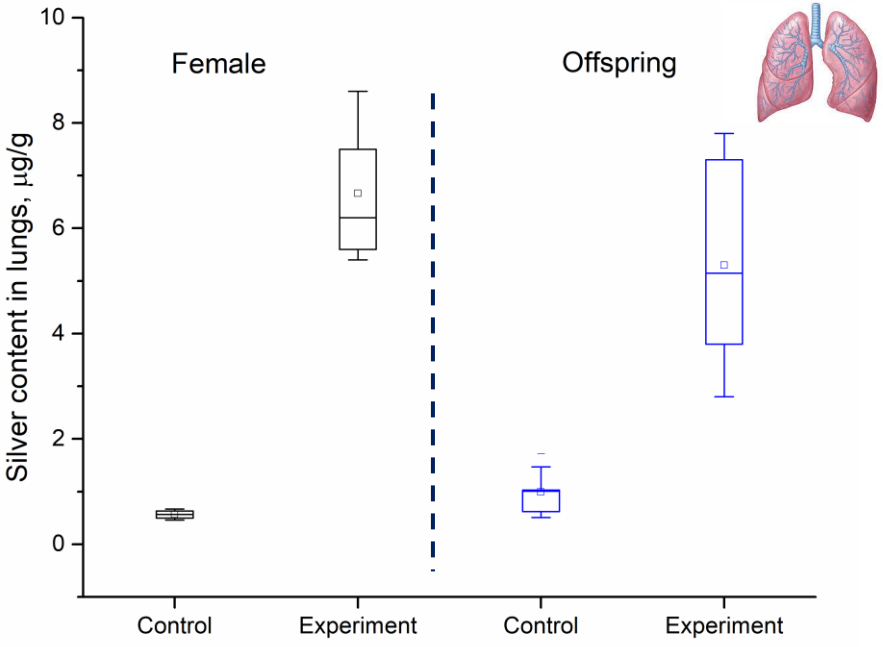
lungs

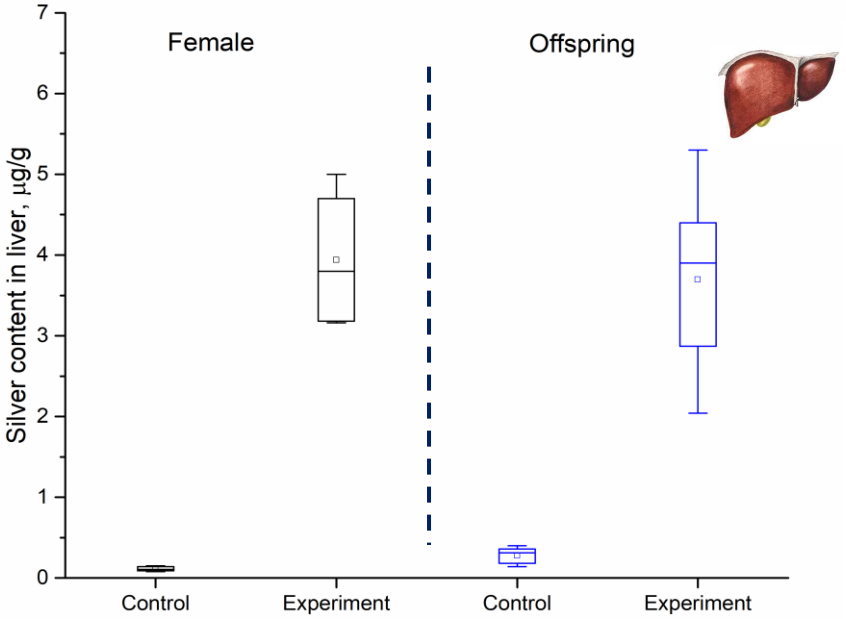


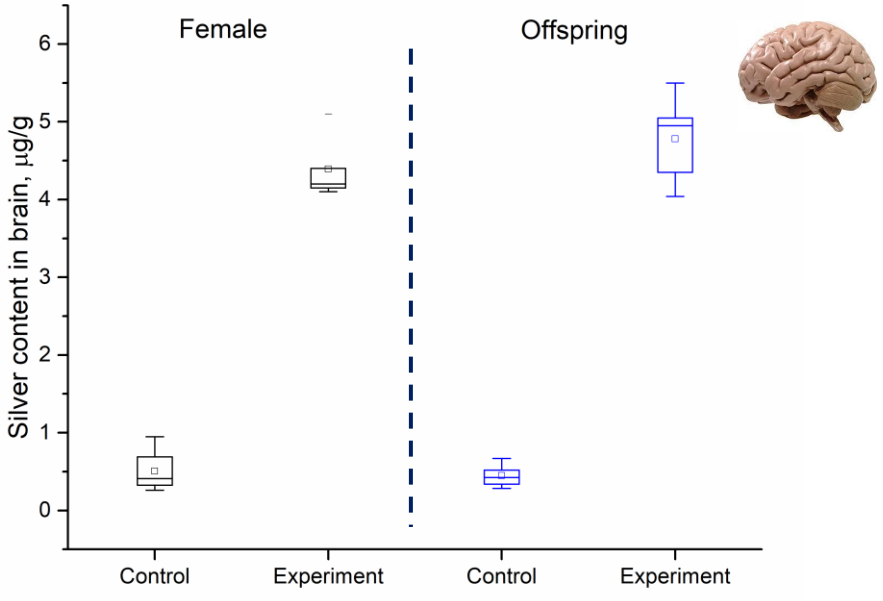
kidneys

brain

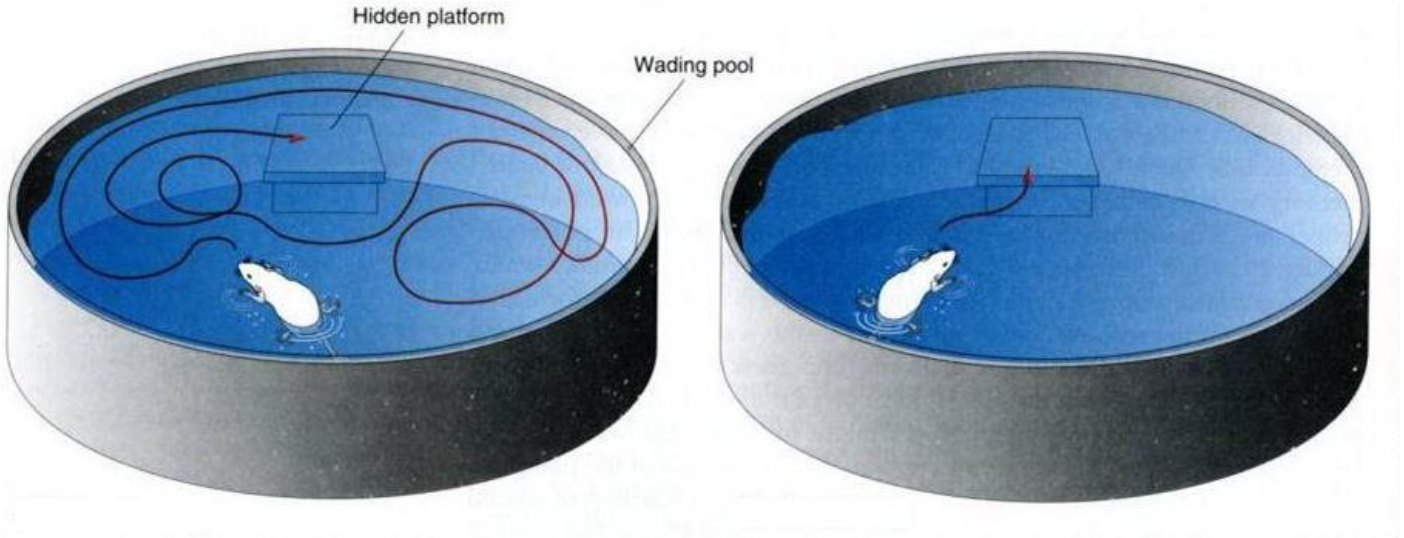


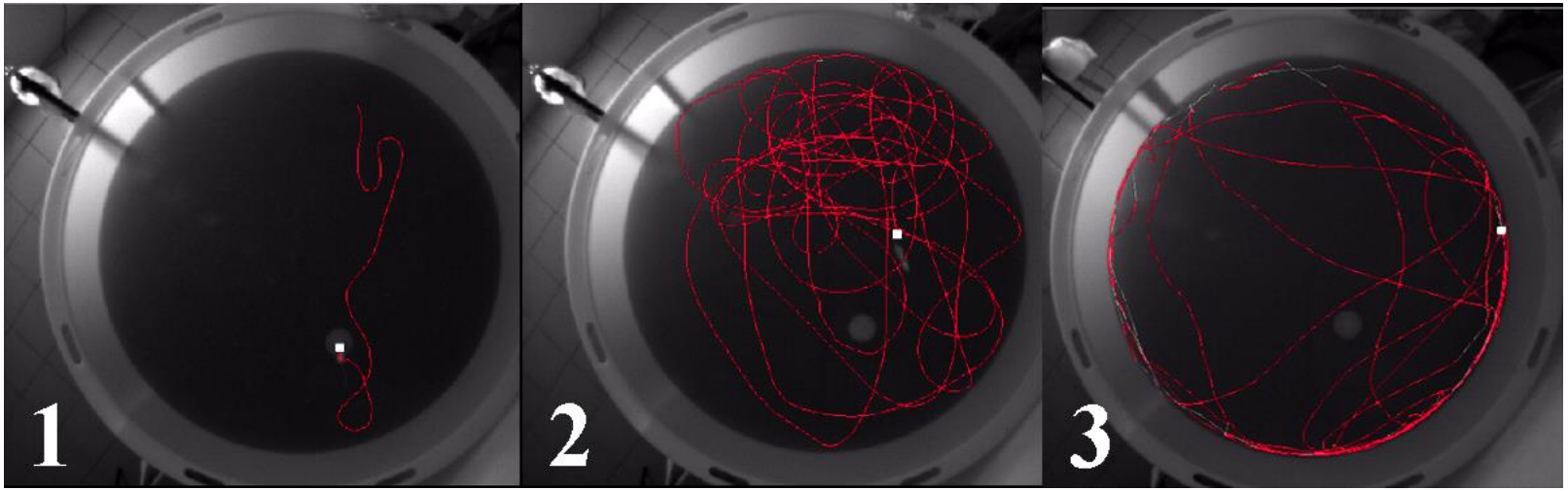




**Silver content in the mice and their offspring organs**




**Examples of movement pattern of animal with different types of behavior in the Morris test: 1 – directional search, 2 – random searching, 3 – thigmotaxis (strategy of incapable individuals).**


Thank you for attention!