Analytical techniques in environmental studies and nanotechnology

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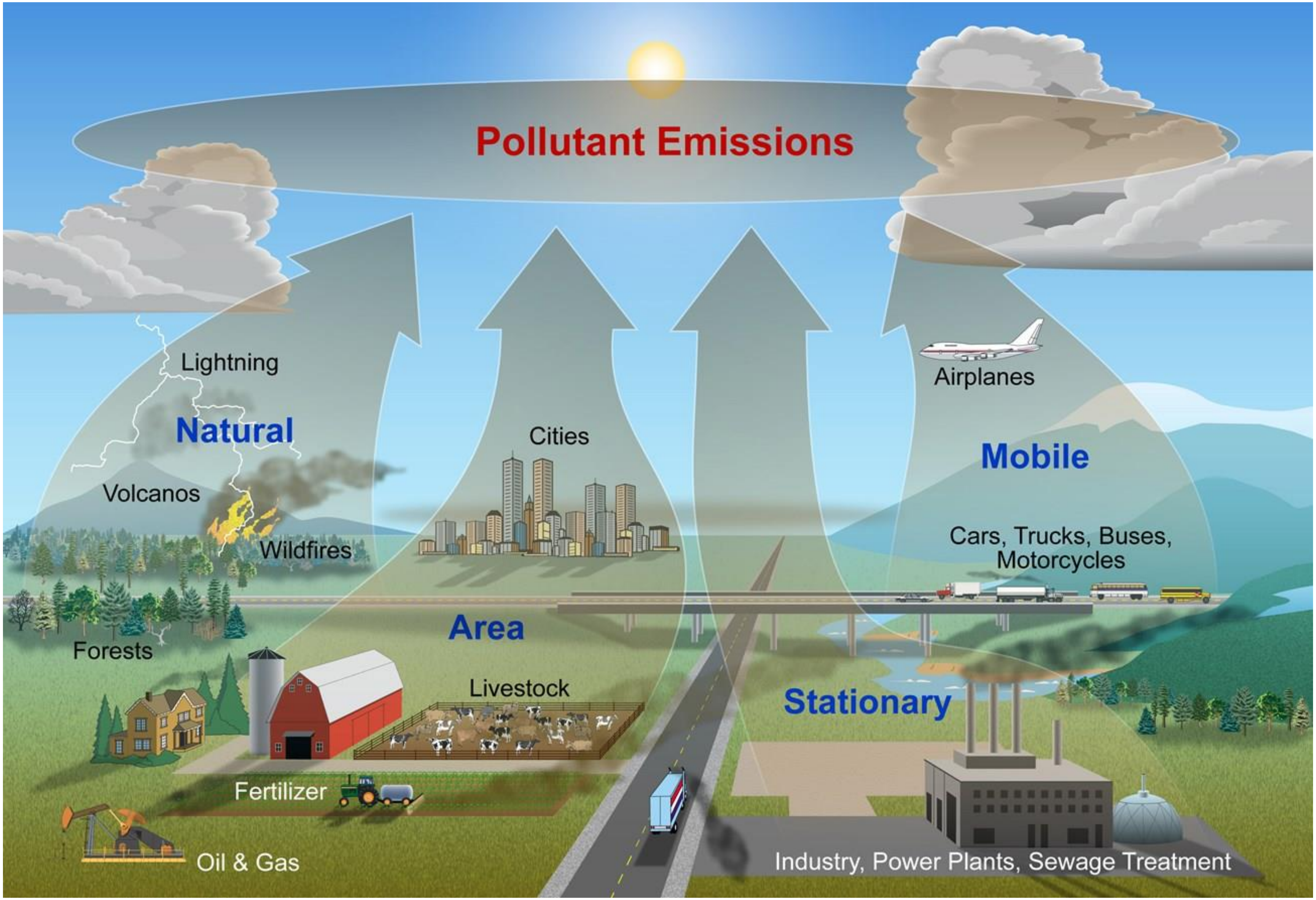
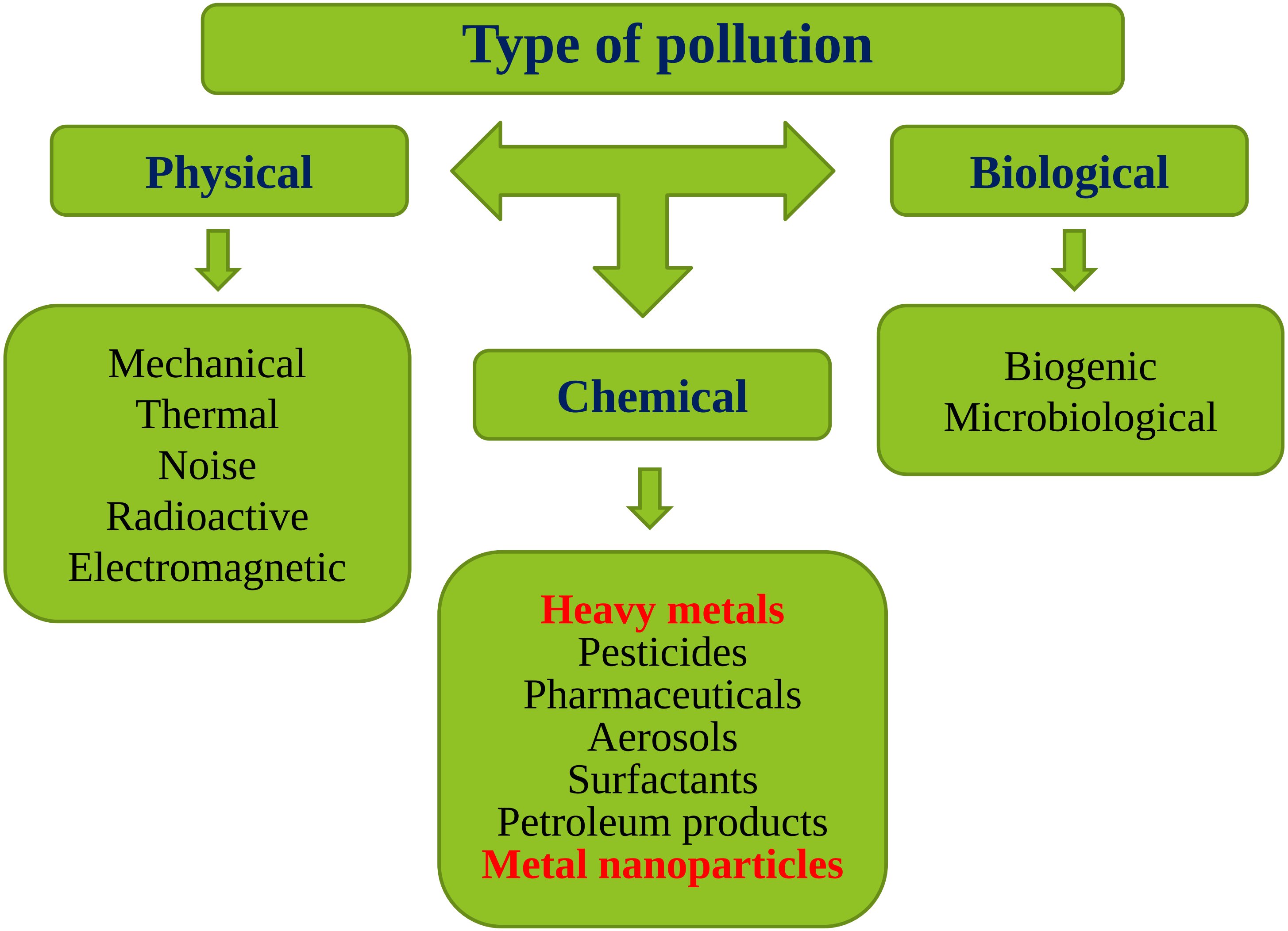
Environmental science is an interdisciplinary field that integrates *physics, biology, geography, ecology, chemistry, plant science, zoology, mineralogy, oceanography, limnology, soil science, geology, and atmospheric science* to the study the environment, and the solution of environmental problems.

Environment pollution

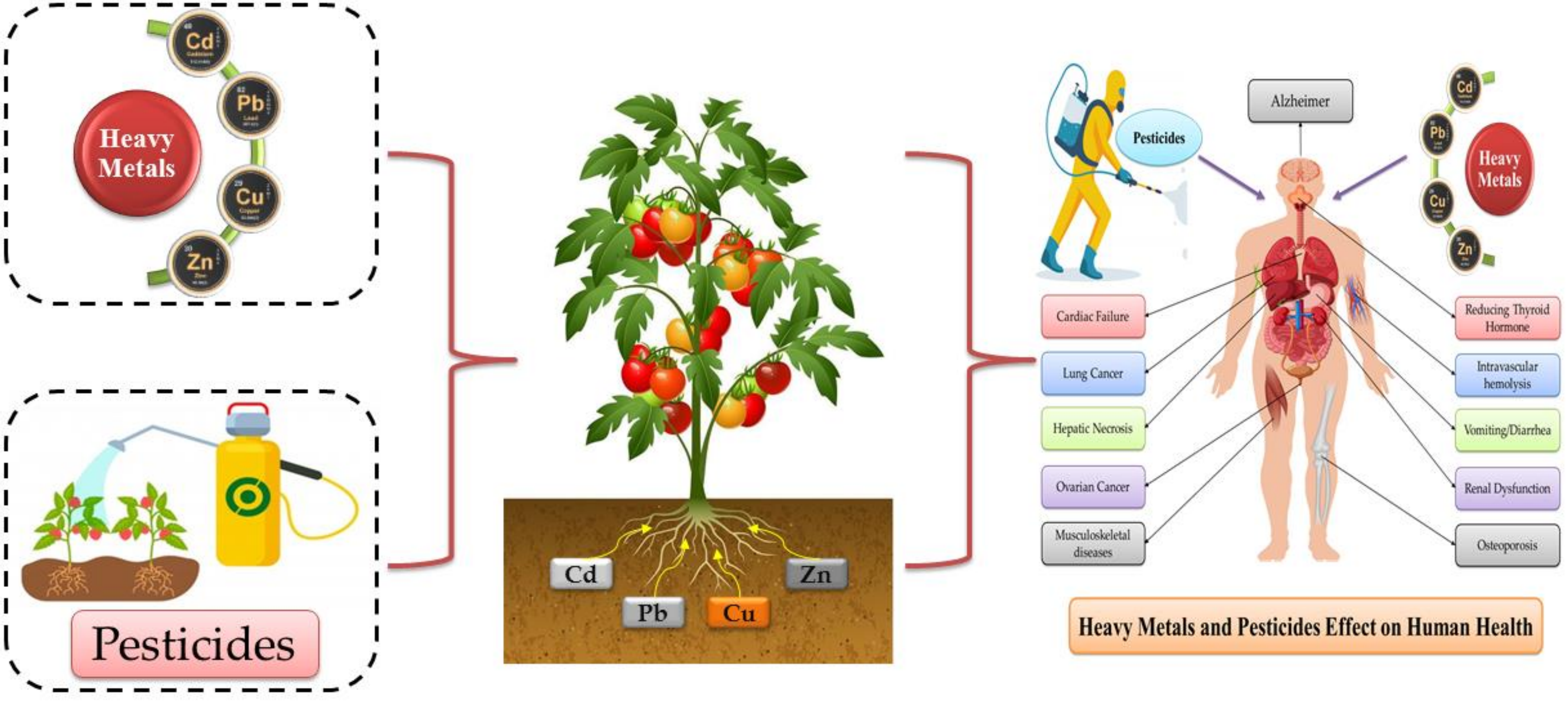
Sources of pollution



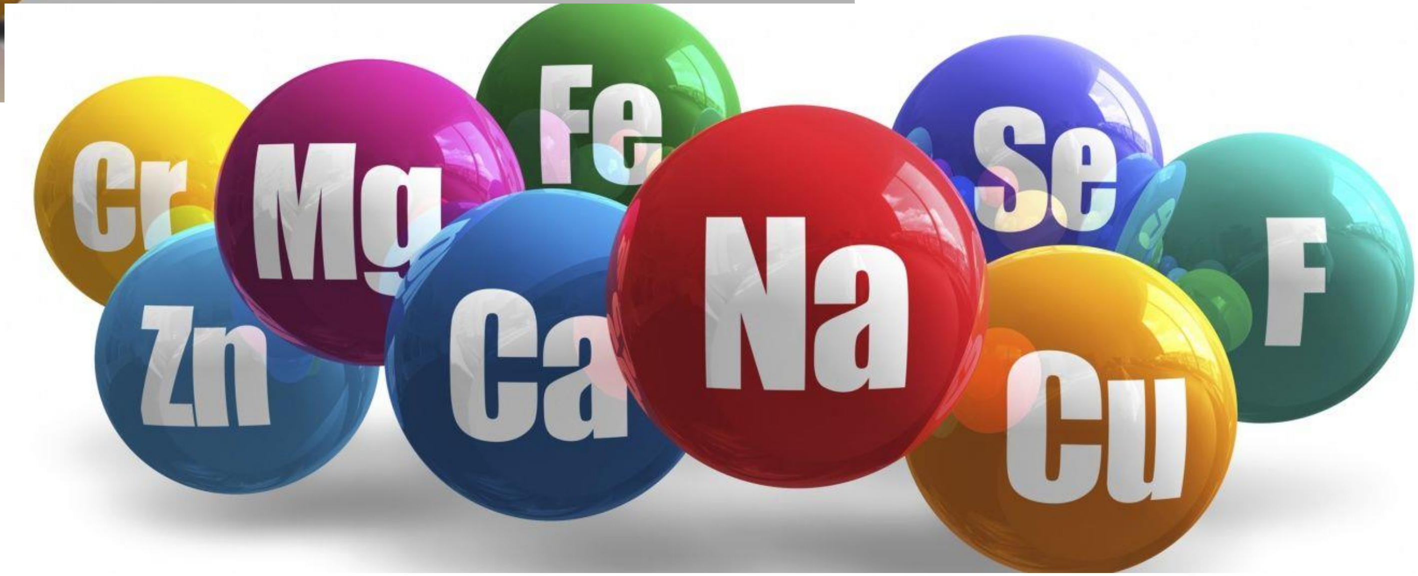
https://www.nps.gov/subjects/air/sources.htm

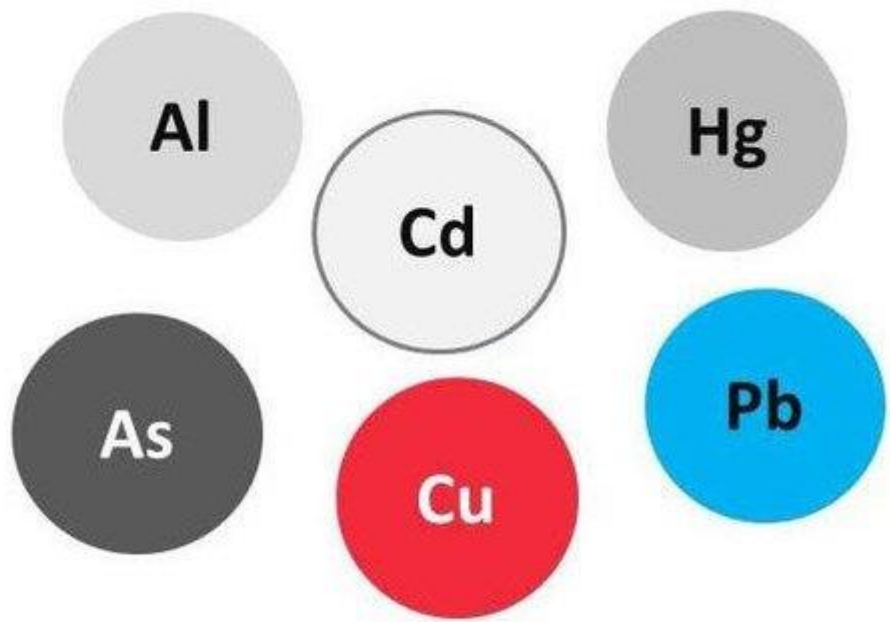

Type of pollution
Physical
Biological
Mechanical
Thermal
Noise
Radioactive
Electromagnetic
Chemical
Biogenic
Microbiological
Heavy metals
Pesticides
Pharmaceuticals
Aerosols
Surfactants
Petroleum products
Metal nanoparticles

Effect of chemical pollutants on living organisms



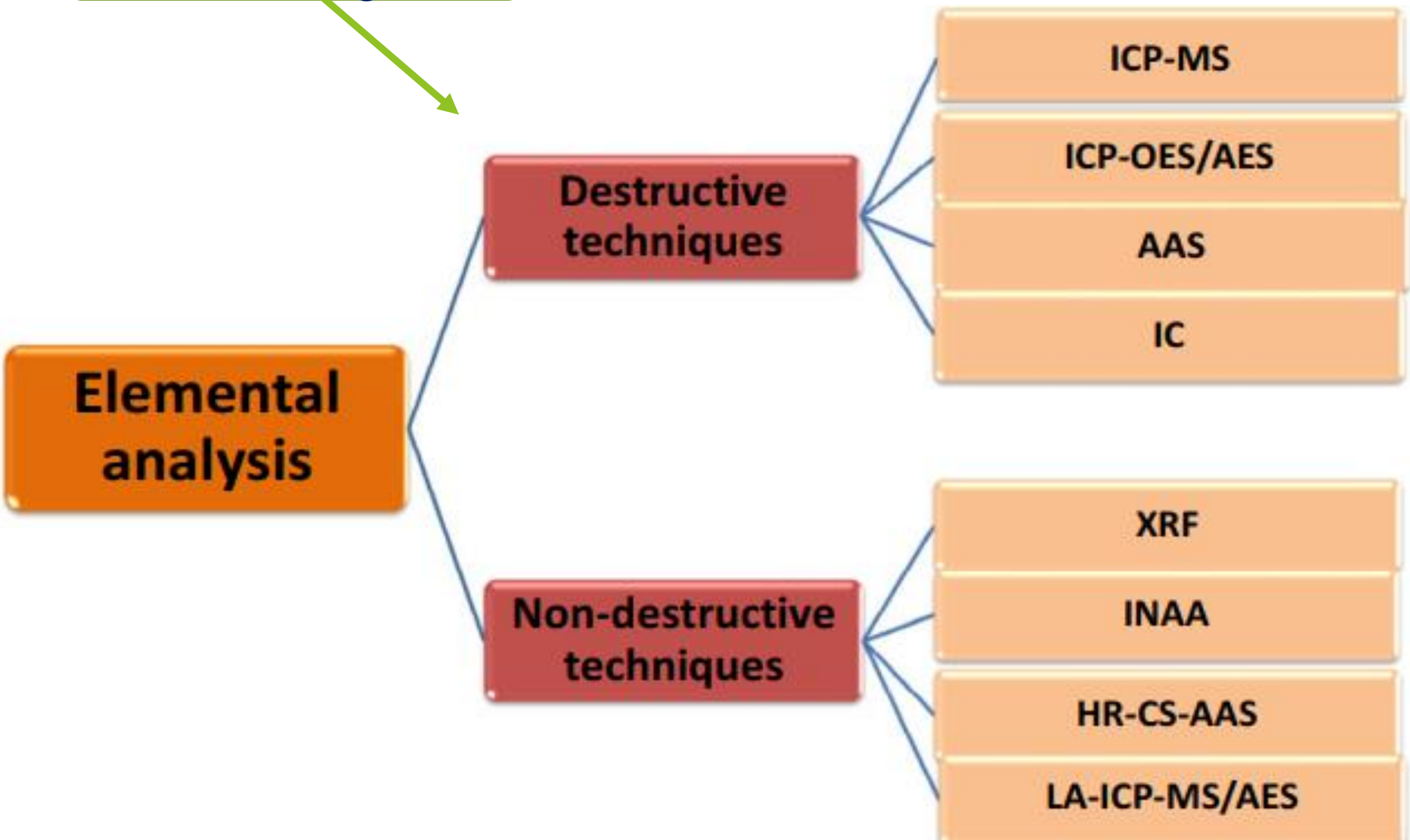
https://doi.org/10.3390/toxics9030042


Cr
Mg
Fe
Se
Zn
Ca
Na
F
Cu


Al
Cd
Hg
As
Cu
Pb

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

Destructive techniques

ICP-MS	ICP-OES	AAS
Principle: measures elemental concentrations by ionizing the atoms in a sample using an inductively coupled plasma source and then separating and detecting the ions based on their mass-to-charge ratios. ICP-MS offers superior sensitivity, lower detection limits, and excellent resolution, making it ideal for trace elemental analysis and isotopic ratio determination	***Principle:*** measures elemental concentrations by exciting atoms in a sample using an inductively coupled plasma source and then detecting the emitted light at characteristic wavelengths. ICP-OES excels in the rapid analysis of elements at higher concentrations, making it suitable for routine analysis in various industries.	***Principle:*** free atoms in the ground state can absorb light of a certain wavelength. AAS provides accurate quantitative results for individual elements, making it suitable for analyzing specific elements with high precision.
Detection Limits: ppm to ppt	***Detection Limits:*** ppm to ppb	***Detection Limits:*** ppm to ppb
Elemental Range: Li to U (75 elements)	***Elemental Range:*** Li to U (75 elements)	***Elemental Range:*** Li to U (70 elements)
Limitations: interferences, high equipment cost, complete samples digestion, highly-qualified personnel	***Limitations:*** interferences, high equipment cost, complete samples digestion, low sensitivity	***Limitations:*** interferences, single-element analysis, low sensitivity complete samples digestion.

Comparison of elemental analysis techniques

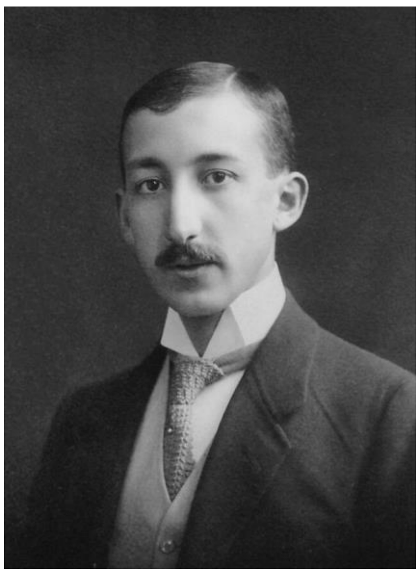
Method	Detectable elements	Sensitivity*
ICP-OES/MS/SFMS	Li to U	ppm to ppt
NAA	H to U	ppm to ppt
AAS	Mainly metallic elements, up to 70 elements	ppm
CHNOS	C, H, N, O, S	0.05–0.1 wt%
XRF	Be to U	10 ppm–1 at%
SEM-EDX	All except H, He, and Li	0.1–1 at%
ERDA	H to U	0.1–0.5 at.%
RBS	Be to U	0.1 at%

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

Neutron activation analysis

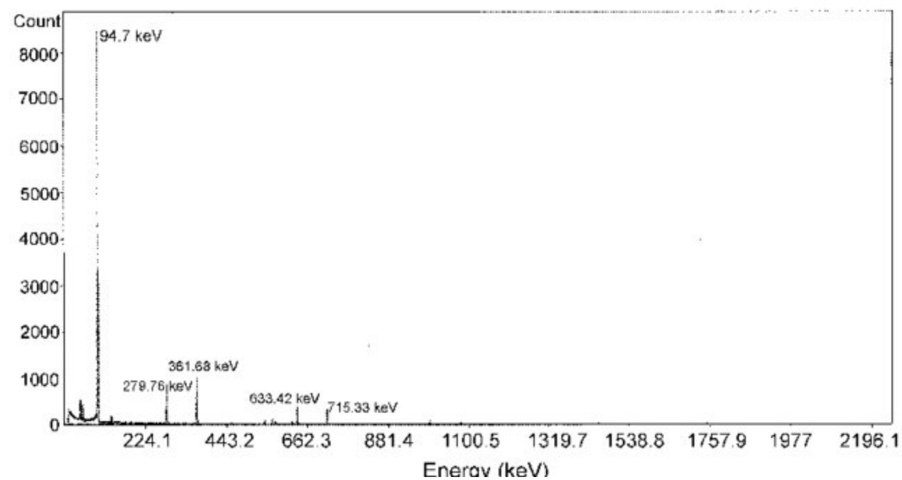
Neutron activation analysis was first developed by G. Hevesy and H. Levi in 1936. They used a neutron source (226Ra + Be) and a radiation detector (ionization chamber) and promptly recognized that the element Dy (dysprosium) in the sample became highly radioactive after exposure to the neutron source.

$$^{4}He+^{9}Be\rightarrow^{12}C+^{1}n$$



George de Hevesy

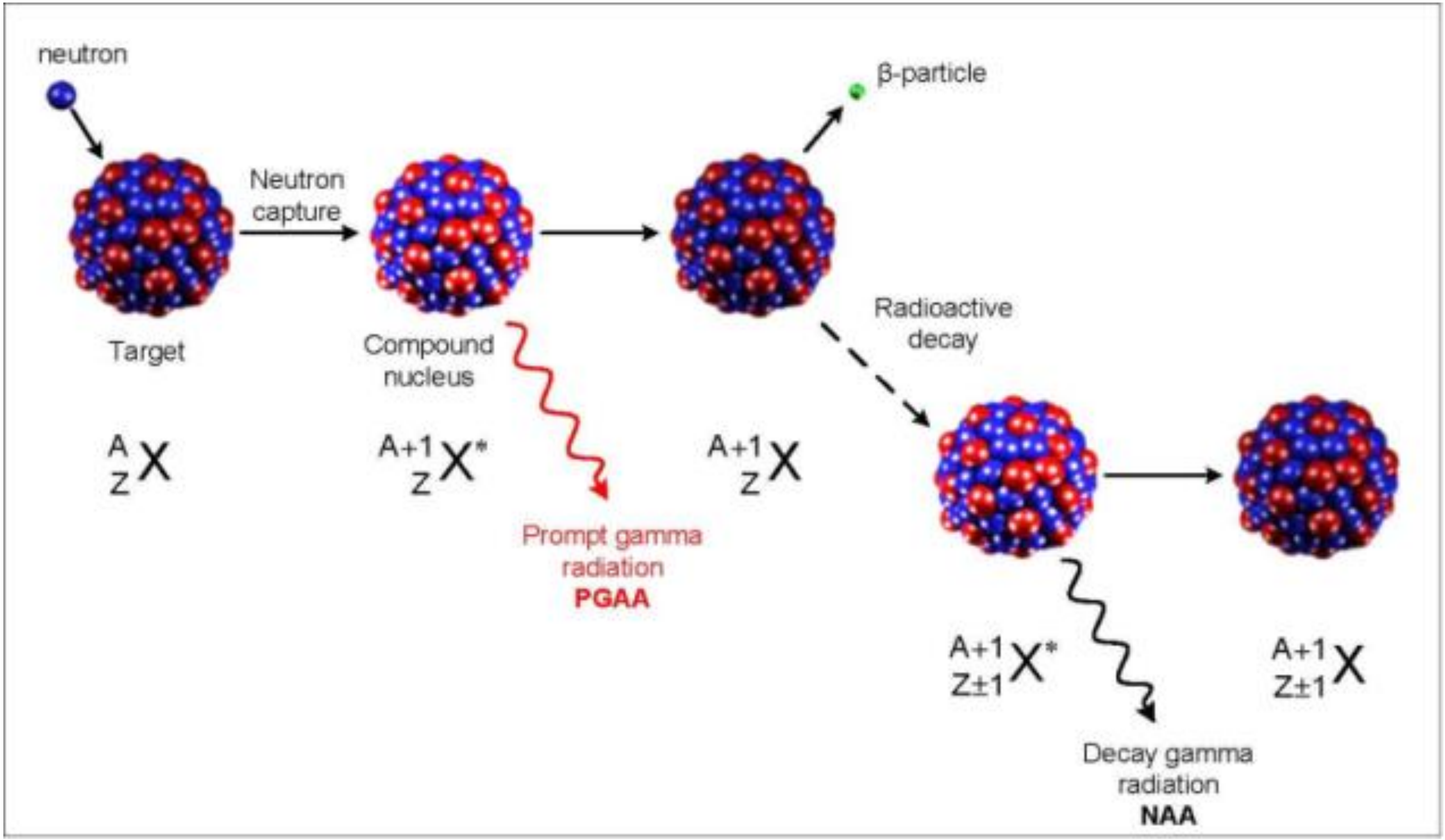
Hilde Levi



Gamma spectrum of dysprosium-165

G. Hevesy, Hilde Levi, The Action of Neutrons on the Rare Earth Elements, Det. Kgl. Danske Videnskabernes Selskab, Mathematisk-fysiske Meddelelser XIV, 5 (1936) 3–34

Diagram illustrating the process of neutron capture by a target nucleus followed by the emission of gamma rays



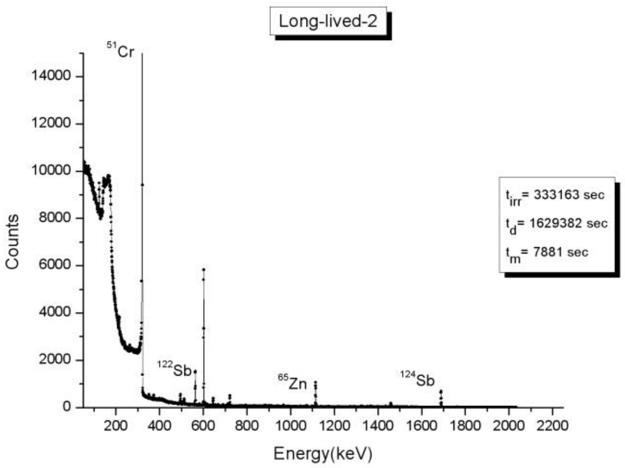
Main steps of neutron activation analysis

Irradiation

The most common reaction occurring in NAA is the (n,γ) reaction, but also reactions such as (n,p), (n,α), (n,n′) and (n,2n) are important.

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

Classification according to the time of measurement

(1) **prompt gamma-ray neutron activation analysis** (PGNAA), where measurements take place during irradiation. The PGAA technique is most applicable to elements with extremely high neutron capture cross-sections (B, Cd, Sm, and Gd)

(2) **delayed gamma-ray neutron activation analysis** (DGNAA), where the measurements follow radioactive decay. The latter operational mode is more common; thus, when one mentions NAA it is generally assumed that measurement of the delayed gamma rays is intended. About 70% of the elements have properties suitable for measurement by NAA

Classification according to chemistry involved

- Instrumental NAA (INAA): no chemical treatment of sample is involved.
- Radiochemical NAA (RNAA): chemical separations are done after irradiation to remove interferences or to concentrate the radionuclide of interest.
- Chemical NAA (CNAA): pre-irradiation chemical separations are employed.
- Molecular activation analysis: specific molecular components are determined.

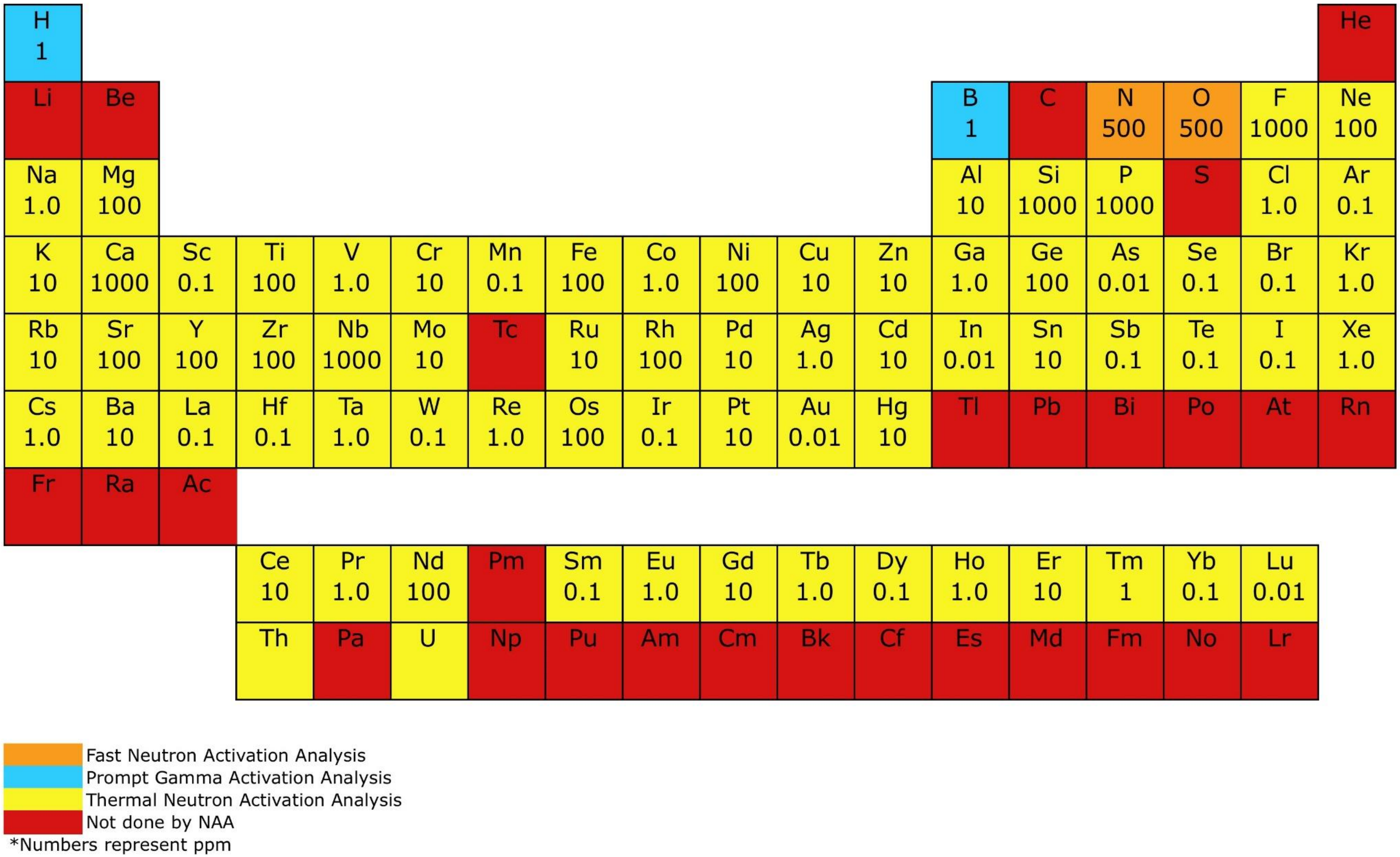
Neutron sources

- **Radioisotopic neutron sources**

Two-component sources based on (α,n) reactions: α decay from ^{239}Pu, ^{241}Am, ^{210}Po then $^{9}Be(\alpha,n)12C$

- Two-component sources based on (γ,n) reactions: ^{24}Na, ^{124}Sb then $^{9}Be(\gamma,n)2\ ^{4}He$
- **Spontaneous fission sources**, e.g. ^{252}Cf
- **Neutron generators**
- 2.4 MeV neutrons $D(d,n)^{3}He$
- 14-MeV neutrons $D(t,n)^{4}He$
- **Cyclotrons**, e.g. d shot at Be target.
- **Spallation neutron sources** e.g. heavy elements such as W, Pb, U irradiated with high-energy protons or other particles are spalled into two or more fragments and many neutrons are released.

- **Neutron reactors** (mostly used, they allow for determinations using different neutron reactions – reactor neutron spectrum).



https://www.nist.gov/laboratories/tools-instruments/instrumental-neutron-activation-analysis-inaa

Neutron activation analysis

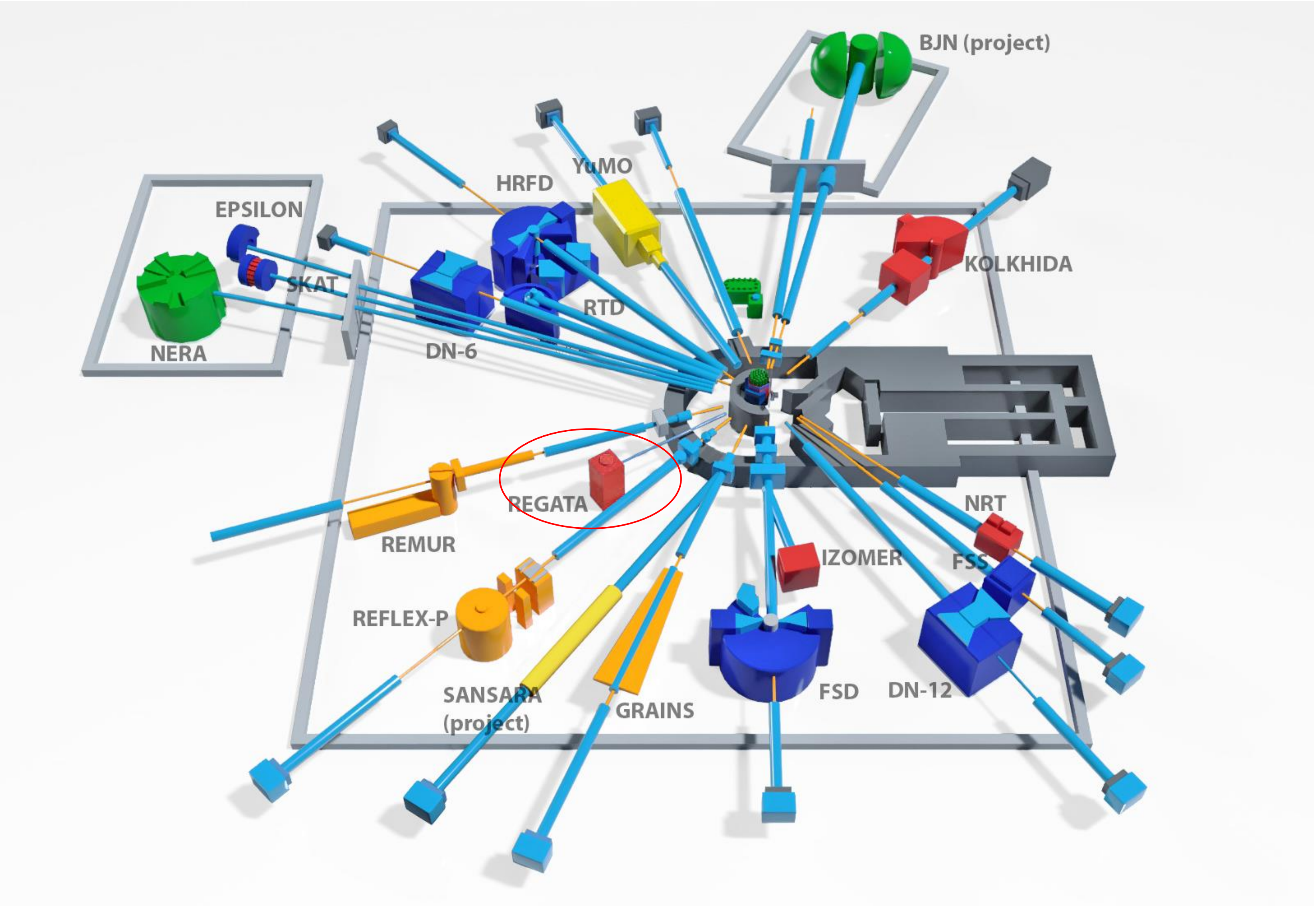
Advantages

- ✓ 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

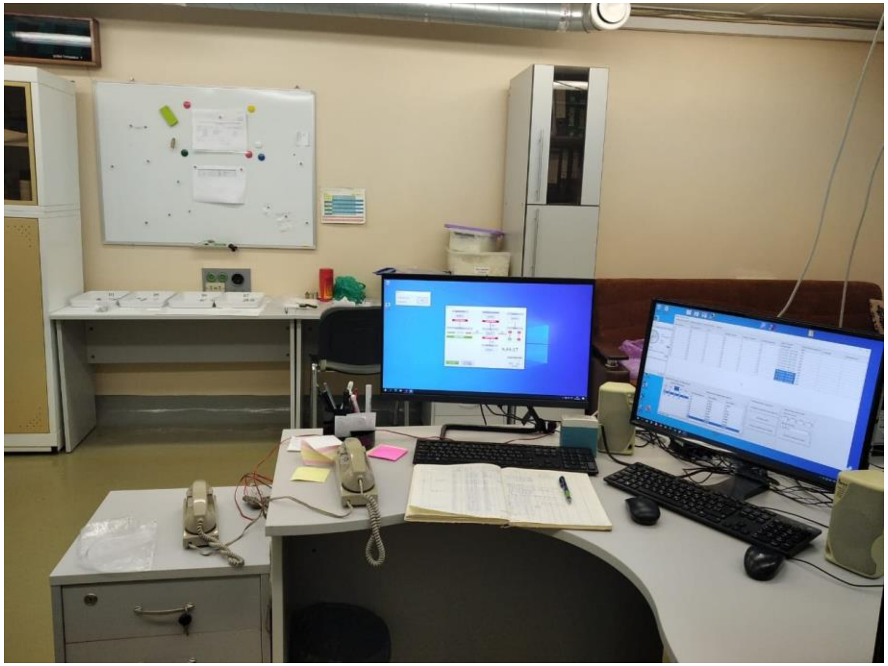
- ➢ necessity of using nuclear reactors;
- ➢ problems arising from storage and disposal of nuclear waste;
- ➢ time required for analysis.

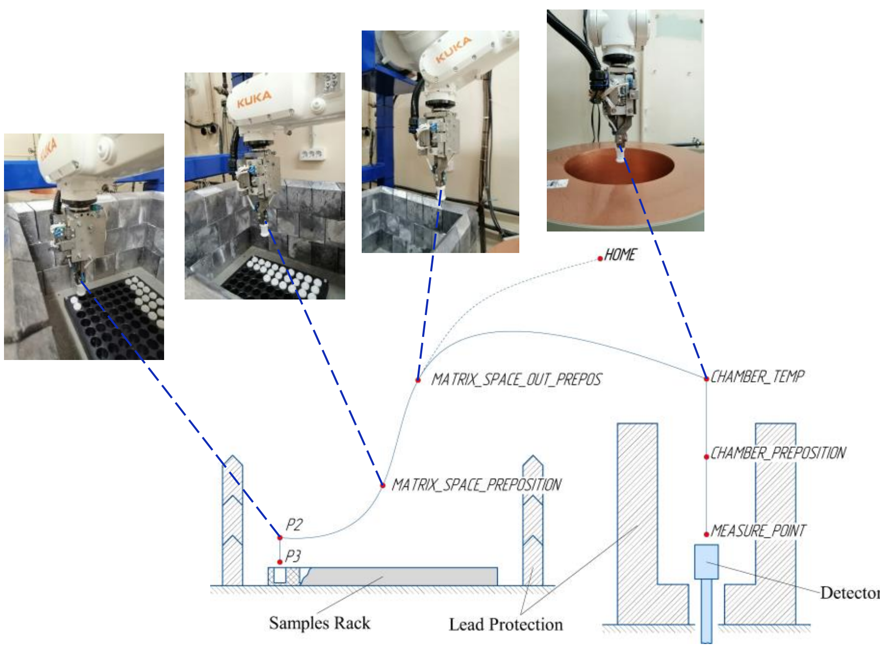
Reactor and Radioanalytical complex REGATA



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

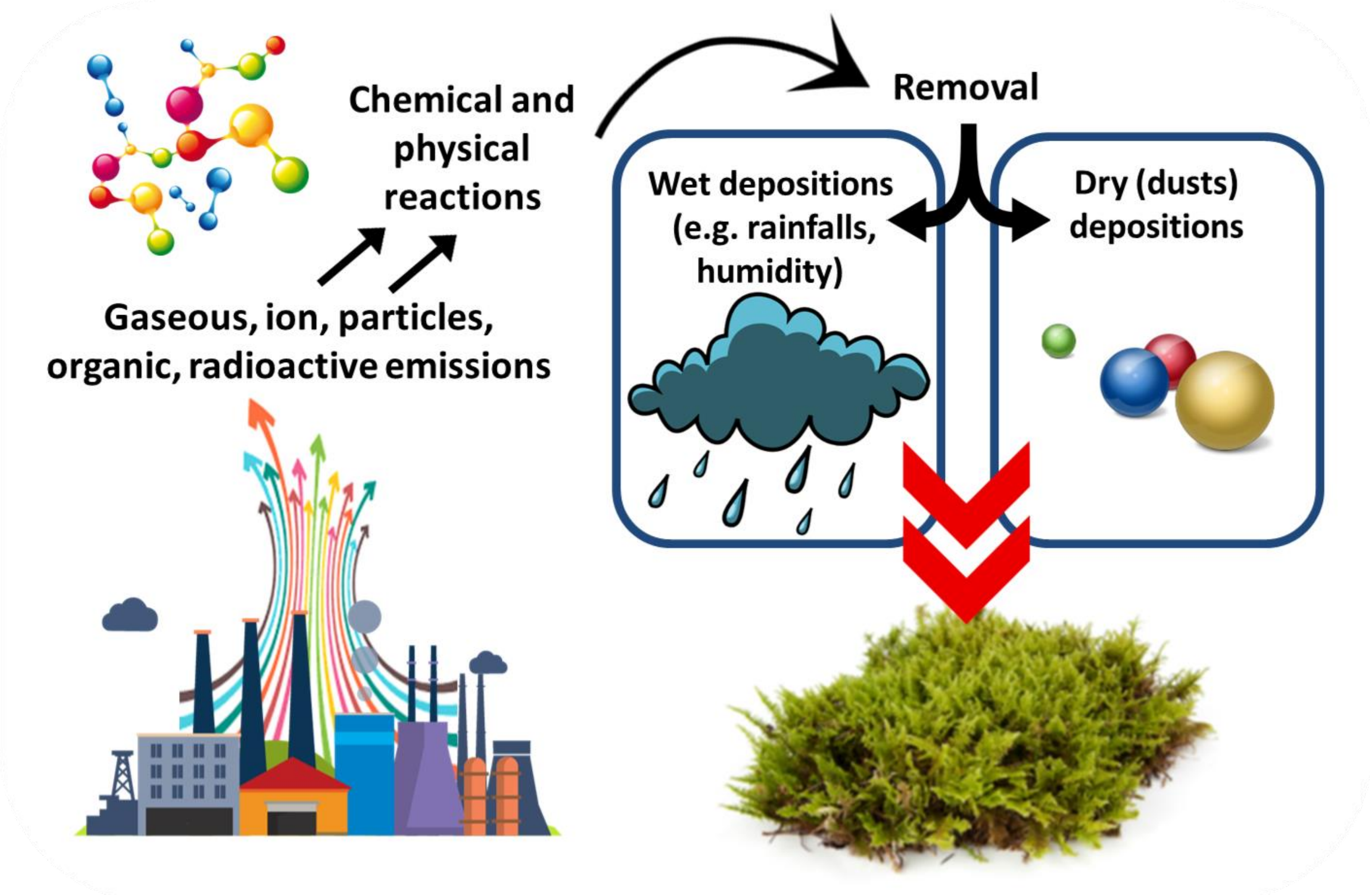
Long irradiation

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)

Scientific directions

Assessment of air pollution



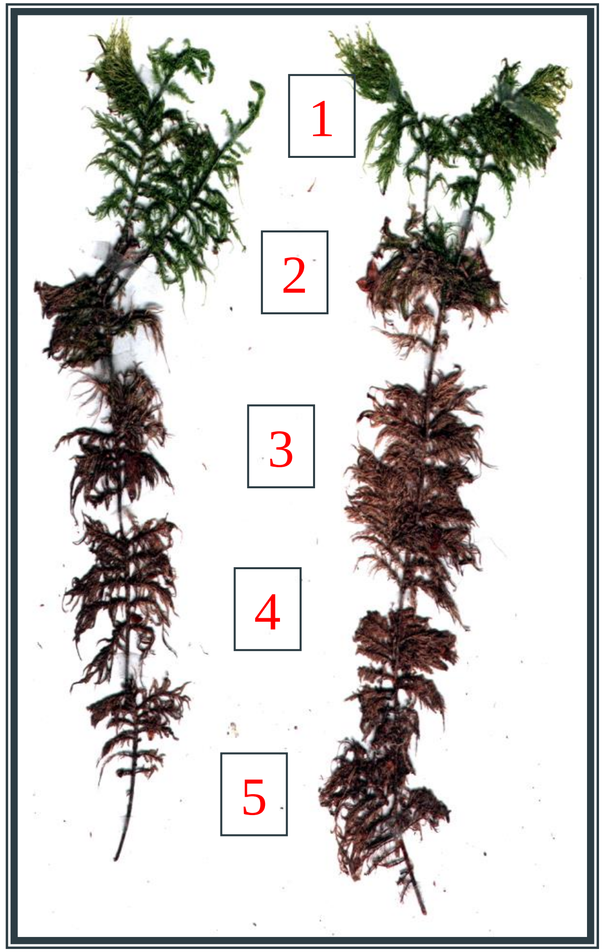
Passive biomonitoring

UNECE

United Nations Economic Commission for Europe

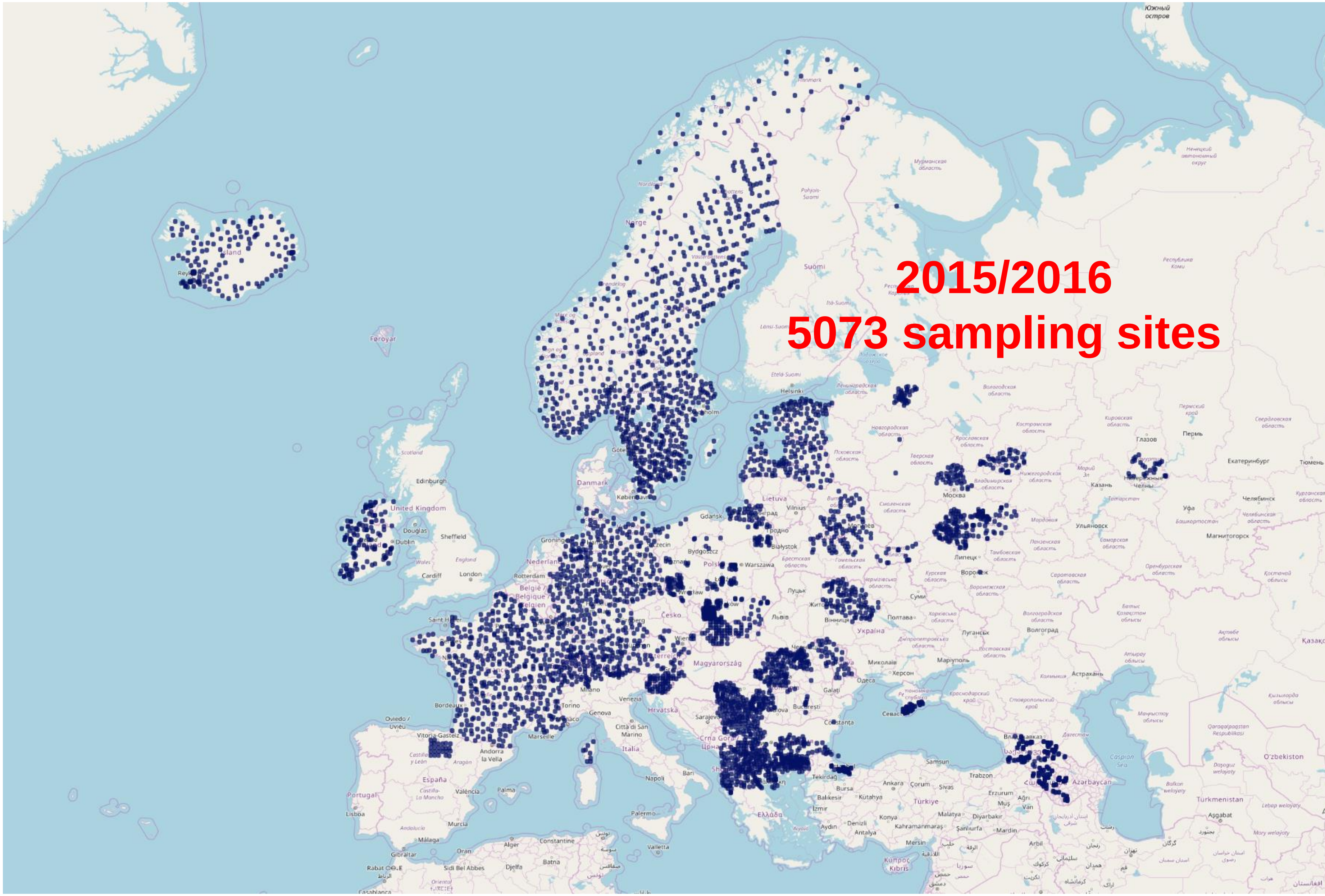
International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops

Working **G**roup on **E**ffects - 1981

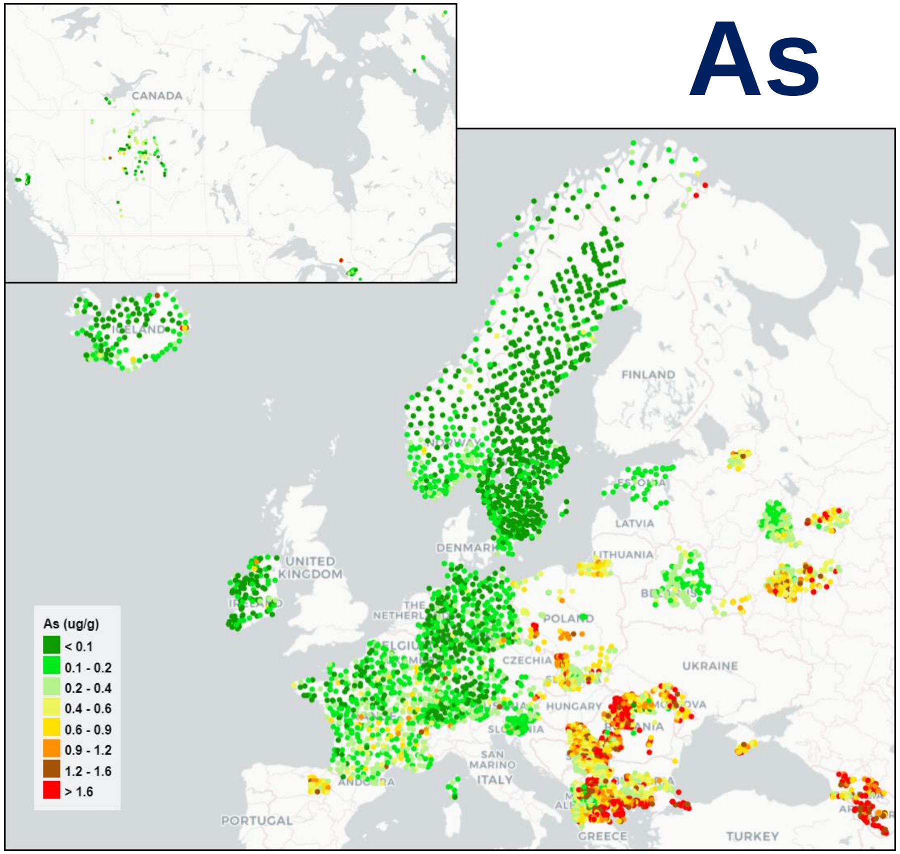


Pleurosium Schreberi

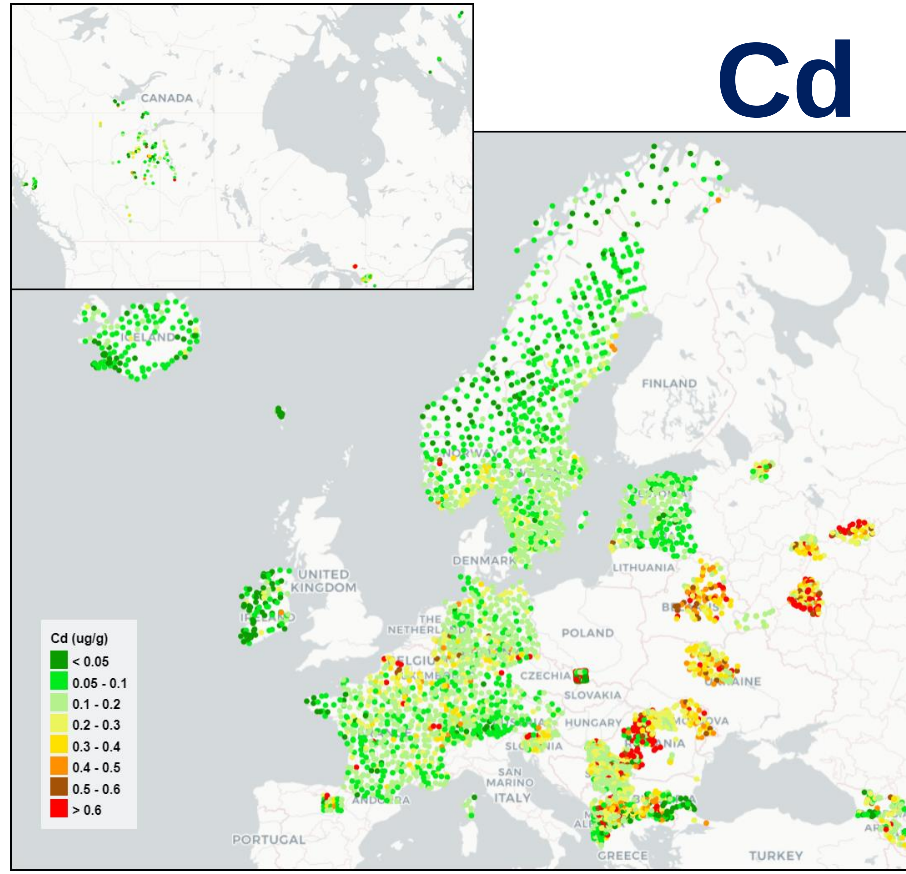
Segments

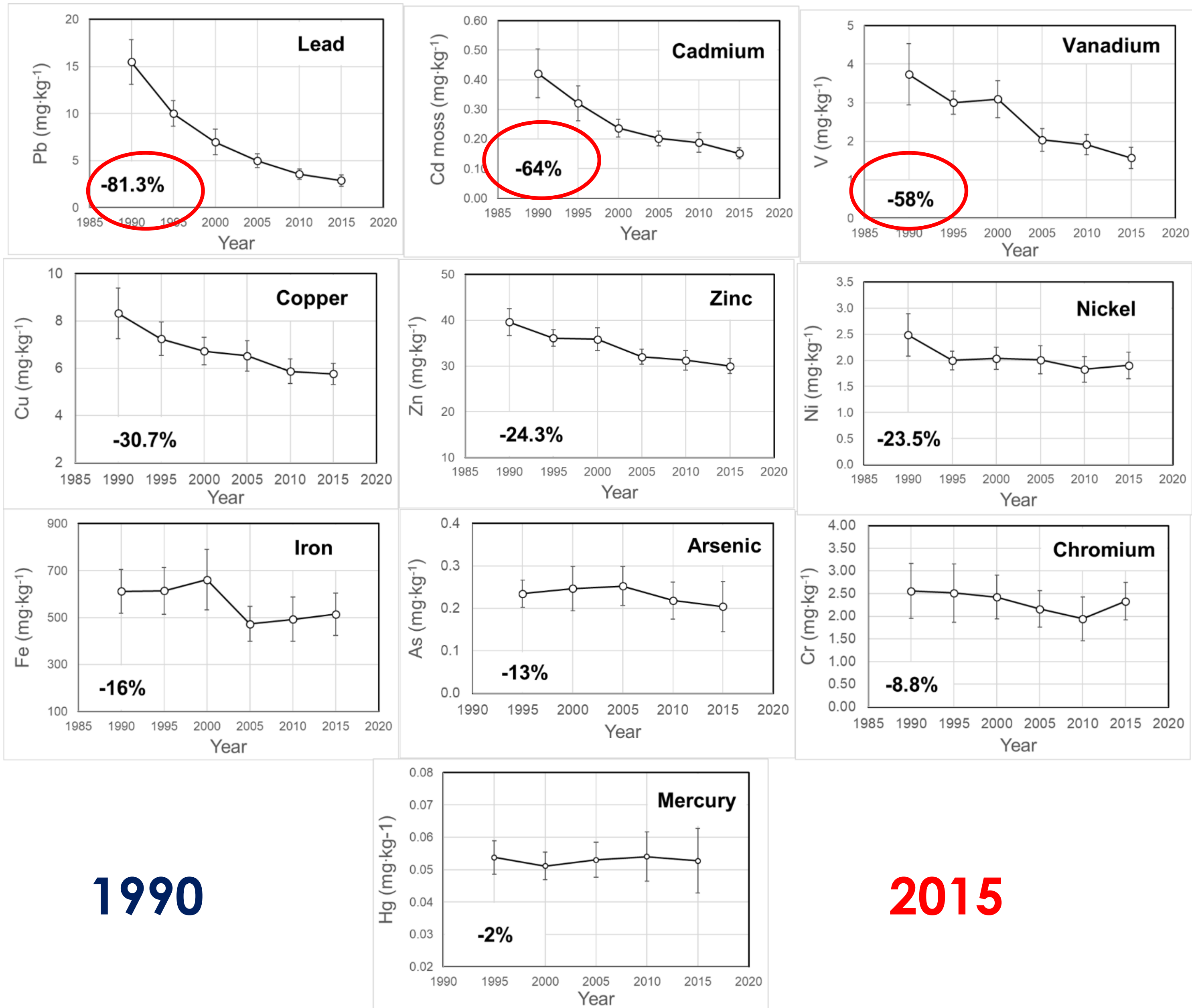

2015/2016
5073 sampling sites

As

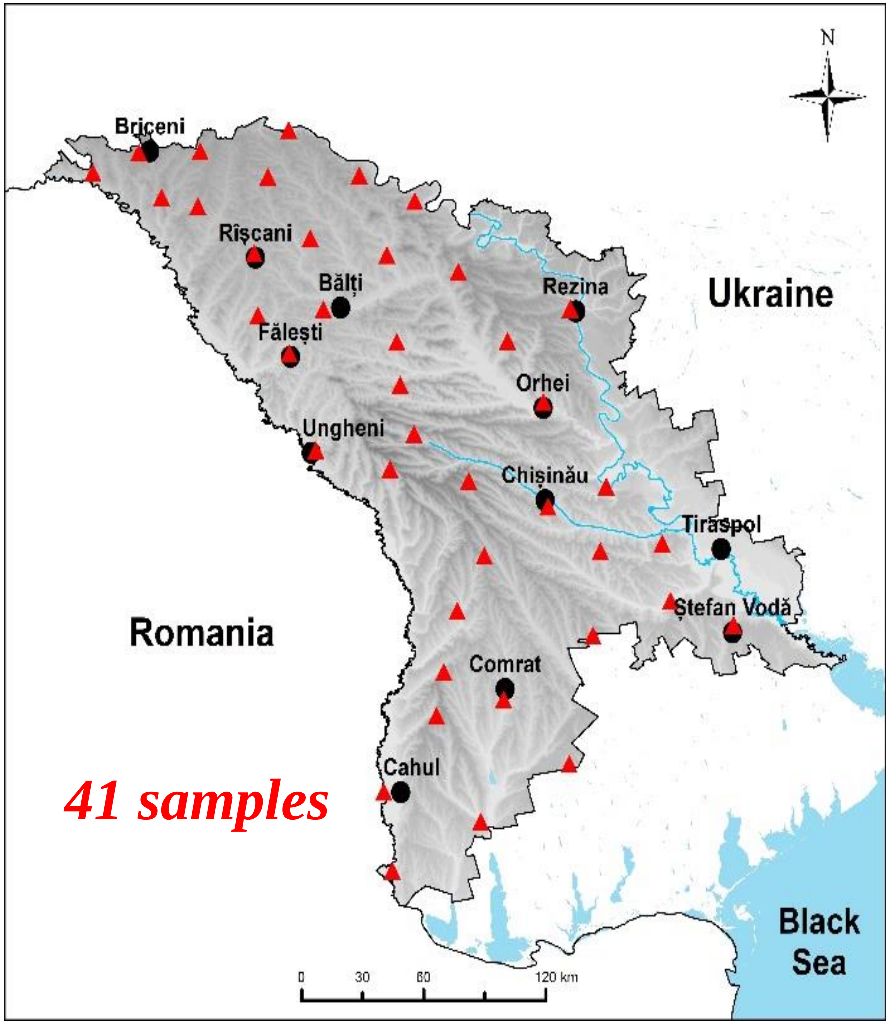

CANADA
ICELAND
FINLAND
NORWAY
ESTONIA
LATVIA
DENMARK
LITHUANIA
UNITED KINGDOM
IRELAND
THE NETHERLANDS
POLAND
BELGIUM
CZECHIA
UKRAINE
HUNGARY
MOLDOVA
SLOVENIA
ROMANIA
SAN MARINO
ITALY
ANDORRA
PORTUGAL
GREECE
TURKEY
As (ug/g)
< 0.1
0.1 - 0.2
0.2 - 0.4
0.4 - 0.6
0.6 - 0.9
0.9 - 1.2
1.2 - 1.6
> 1.6

Cd


CANADA
ICELAND
FINLAND
NORWAY
DENMARK
LITHUANIA
UNITED KINGDOM
THE NETHERLANDS
POLAND
CZECHIA
SLOVAKIA
UKRAINE
HUNGARY
MOLDOVA
SLOVENIA
SAN MARINO
ITALY
PORTUGAL
GREECE
TURKEY
Cd (ug/g)
< 0.05
0.05 - 0.1
0.1 - 0.2
0.2 - 0.3
0.3 - 0.4
0.4 - 0.5
0.5 - 0.6
> 0.6


Lead
Pb (mg·kg-1)
-81.3%
Year
Cadmium
Cd moss (mg·kg-1)
-64%
Year
Vanadium
V (mg·kg-1)
-58%
Year
Copper
Cu (mg·kg-1)
-30.7%
Year
Zinc
Zn (mg·kg-1)
-24.3%
Year
Nickel
Ni (mg·kg-1)
-23.5%
Year
Iron
Fe (mg·kg-1)
-16%
Year
Arsenic
As (mg·kg-1)
-13%
Year
Chromium
Cr (mg·kg-1)
-8.8%
Year
Mercury
Hg (mg·kg-1)
-2%
Year
1990
2015

Republic of Moldova



Location of sampling sites

- **Neutron Activation Analysis:**
  Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Br, Se, Rb, Sr, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, Th, and U.

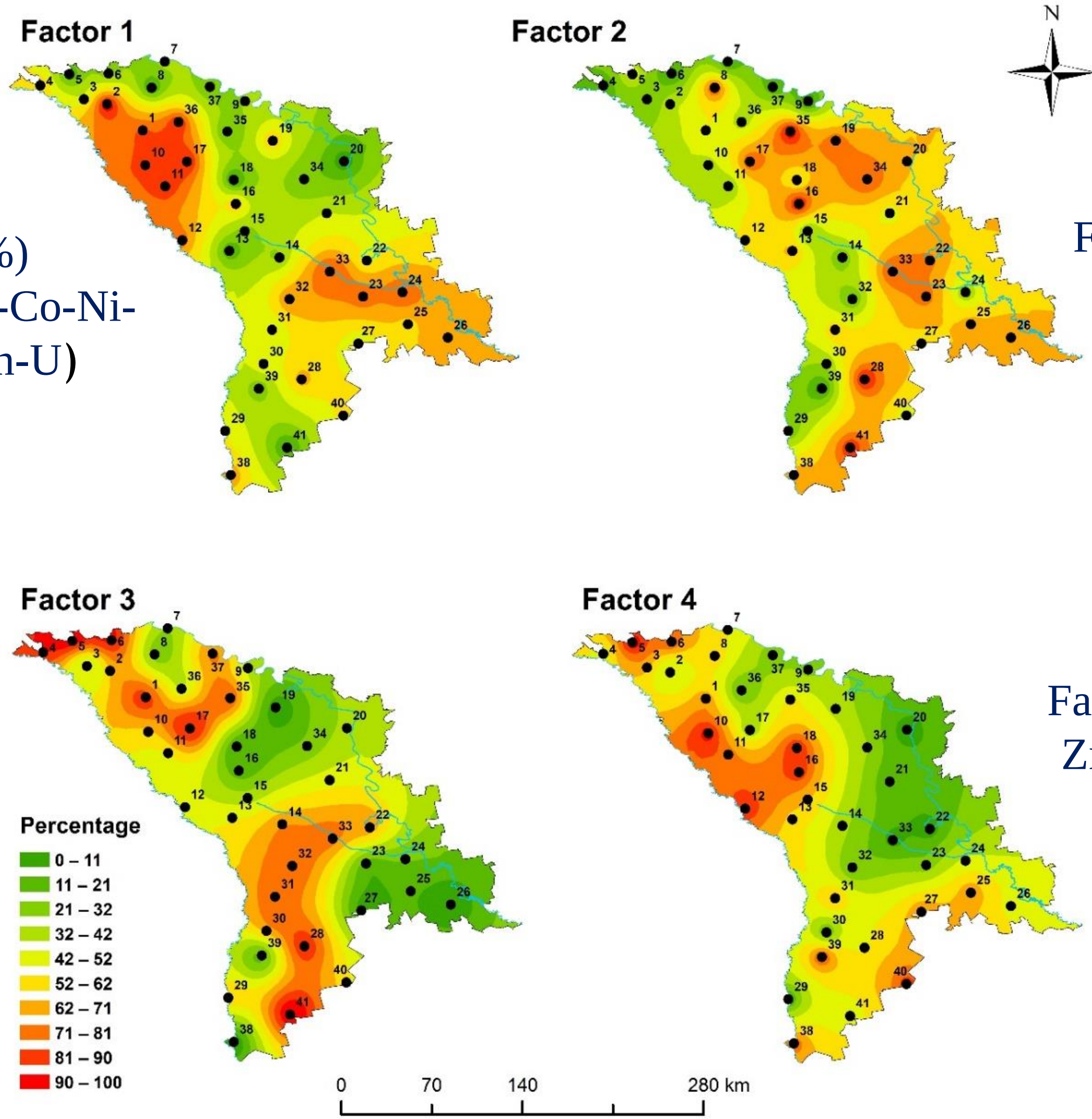
- **Atomic Absorption Spectrometry:**
  Cu, Cd, and Pb.

Factor 1 (47%)
Na-Al-Sc-Ti-Cr-Fe-Co-Ni-As-Rb-Sb-Cs-Th-U)

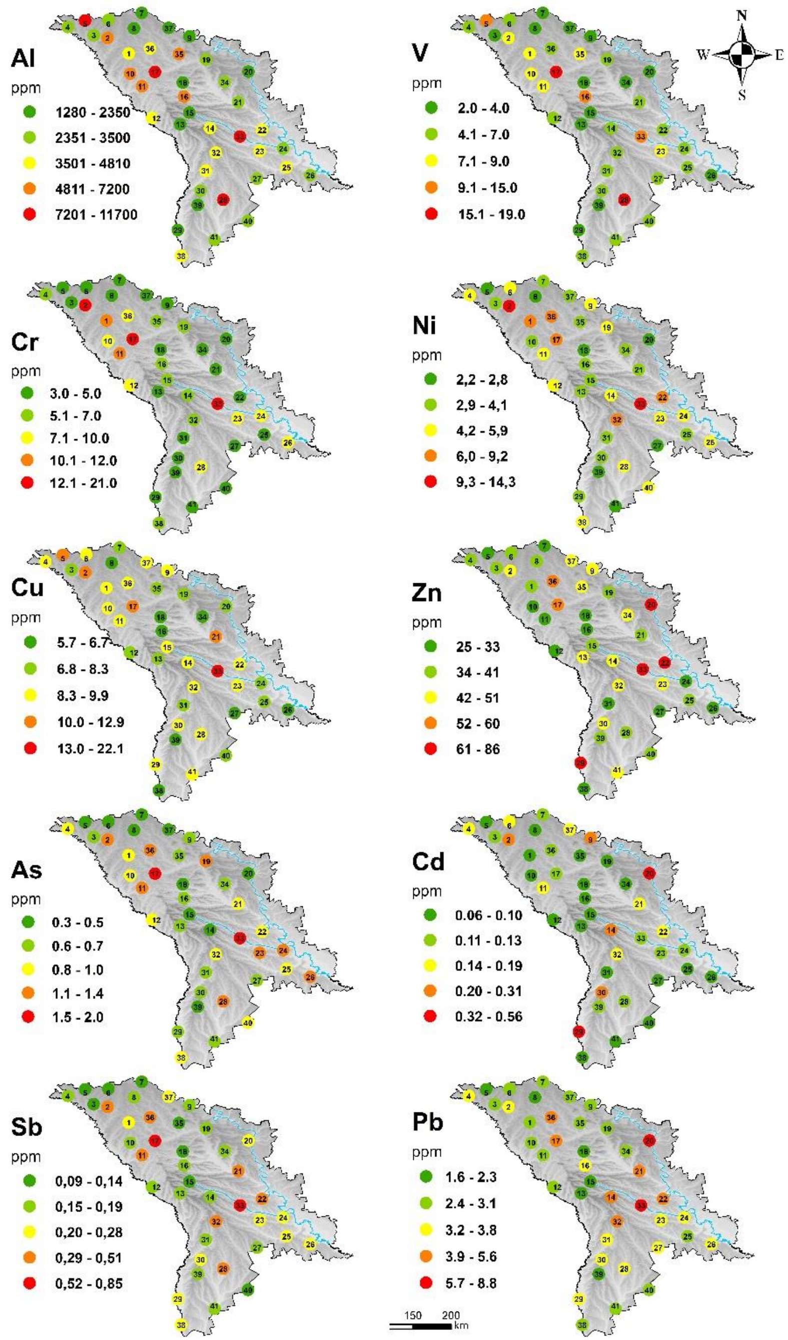
Factor 2 (14%)
Mg-Ca-Sr

Factor 3 (12%)
Cl-K-Br-Cu

Factor 4 (11%)
Zn-Sb-Cd-Pb

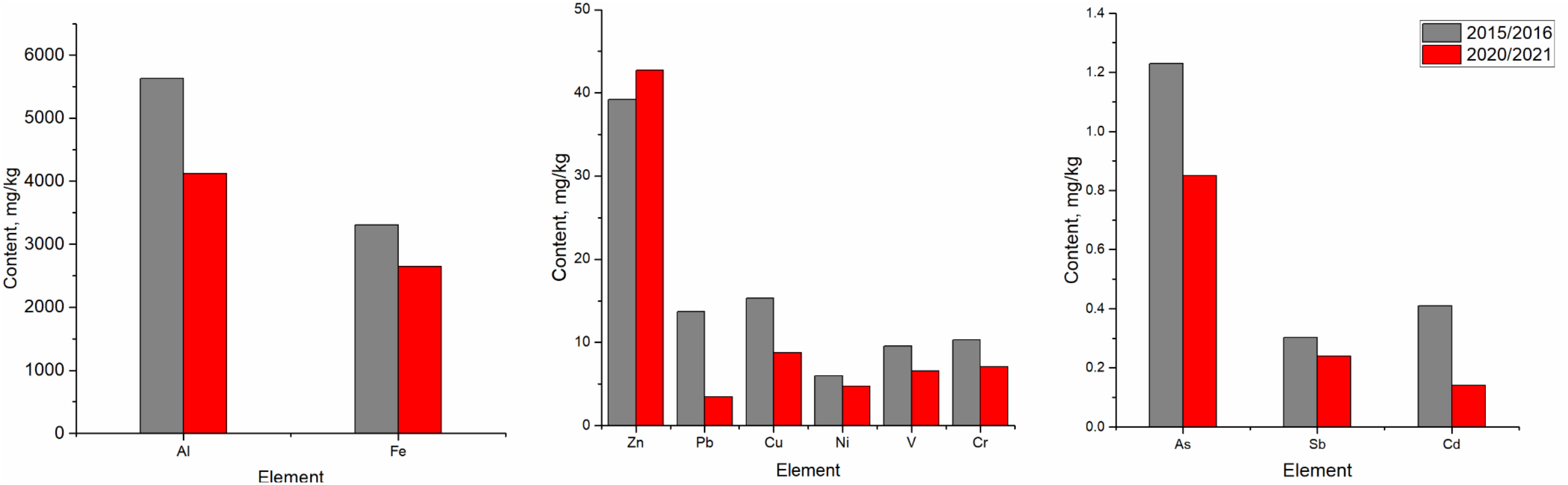


Map showing spatial distributions of Factors 1–4.



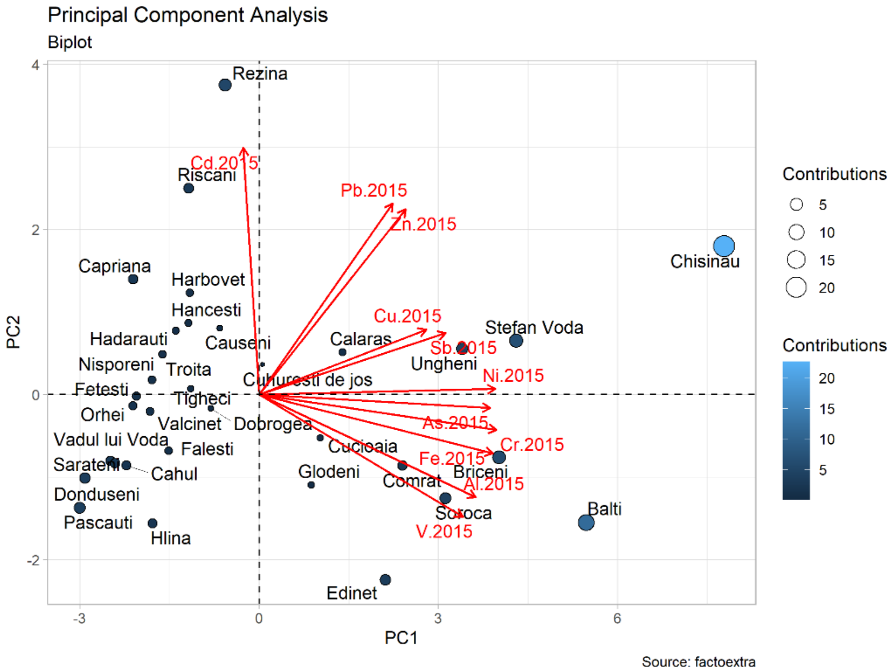
Hypnum cupressiforme

GIS maps of the distribution of elements in the Republic of Moldova

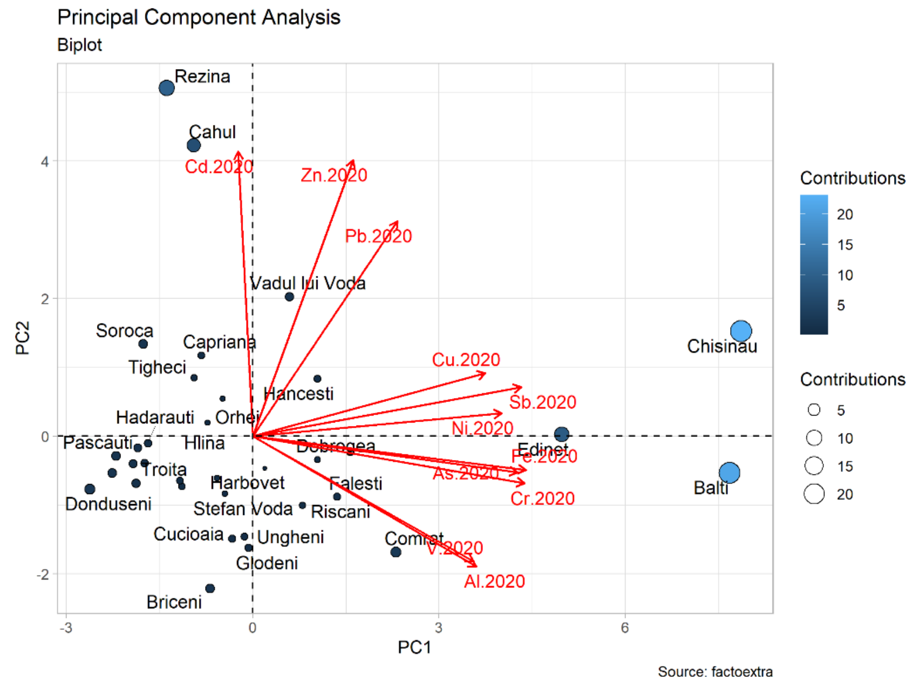


Comparison of the results from the 2020/2022 with values from the 2015/2016 moss survey

Significant differences $p < 0.05$ for Pb (by 75%), Cd (by 66%), Cu (by 43%) Cr (by 31%), As (by 30%), and Sb (by 30%).

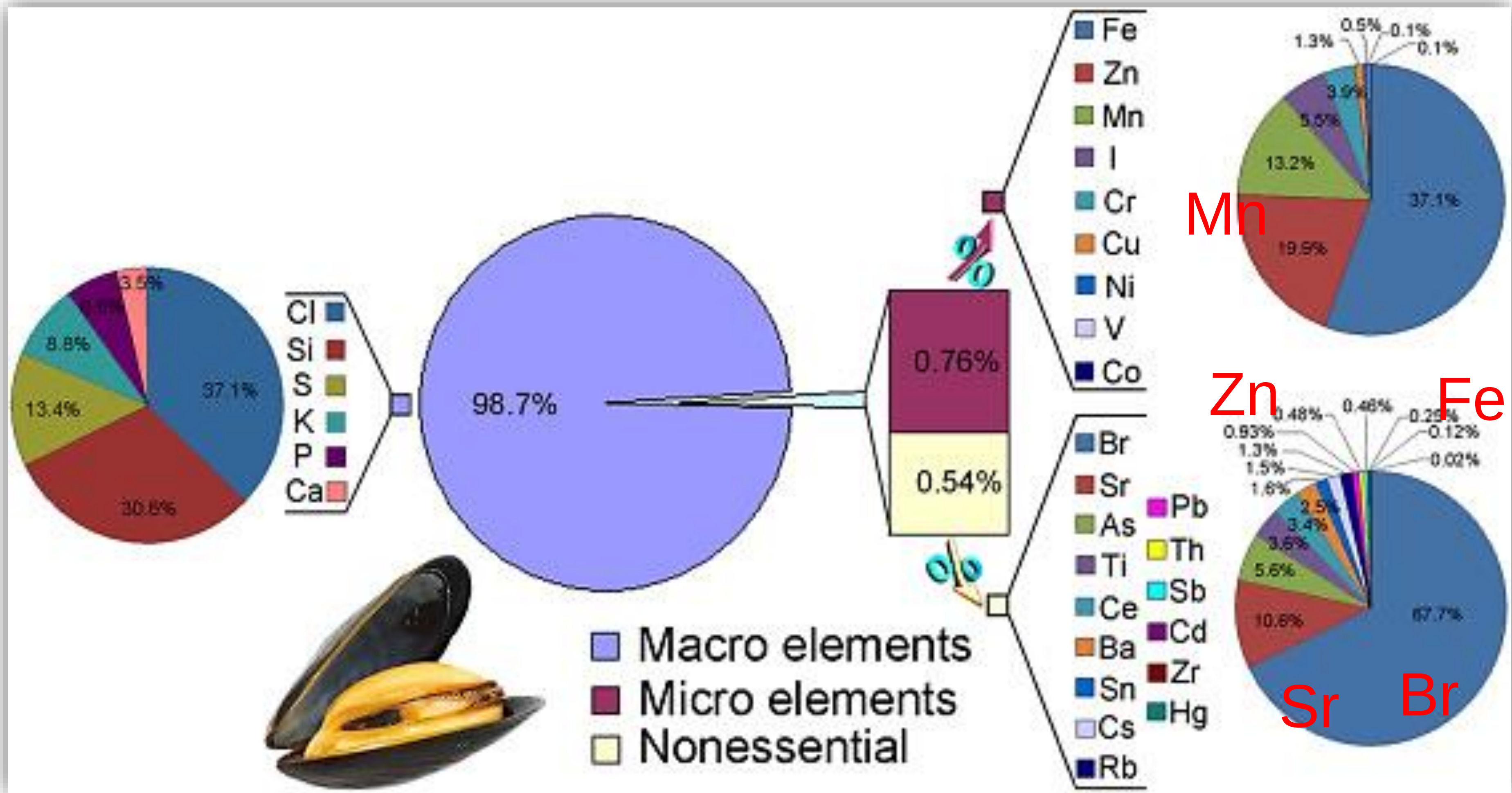


.Scatterplot of the component scores of individual sampling sites (the colour scale distinguishes the quality of the data representation in the graph) and plot of the Component Weights of individual elements for the **2015 survey**



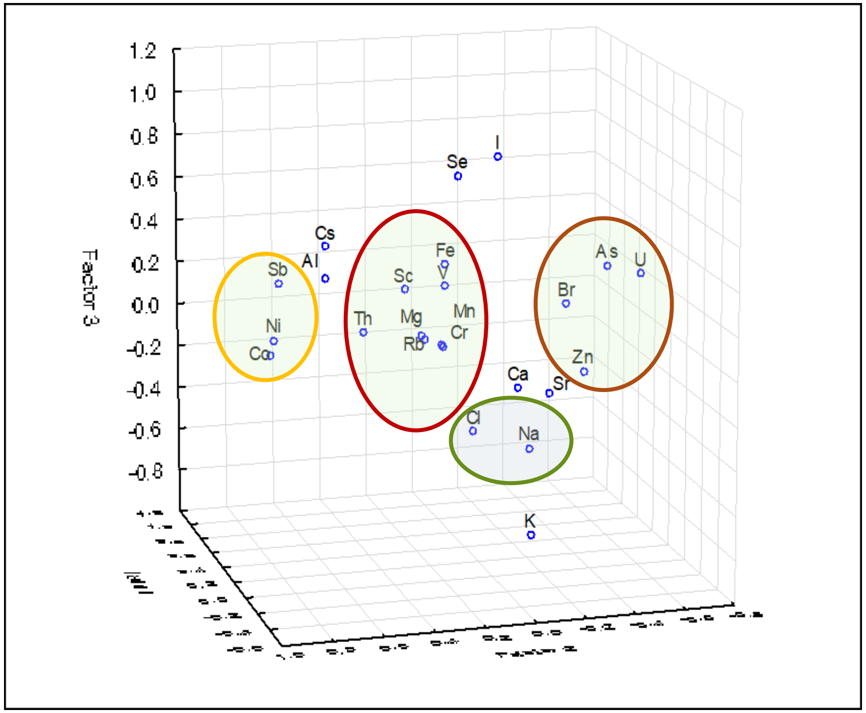
Scatterplot of the component scores of individual sampling sites (the colour scale distinguishes the quality of the data representation in the graph) and plot of the Component Weights of individual elements for the **2020 survey**

Assessment of water pollution



Assessment of water pollution

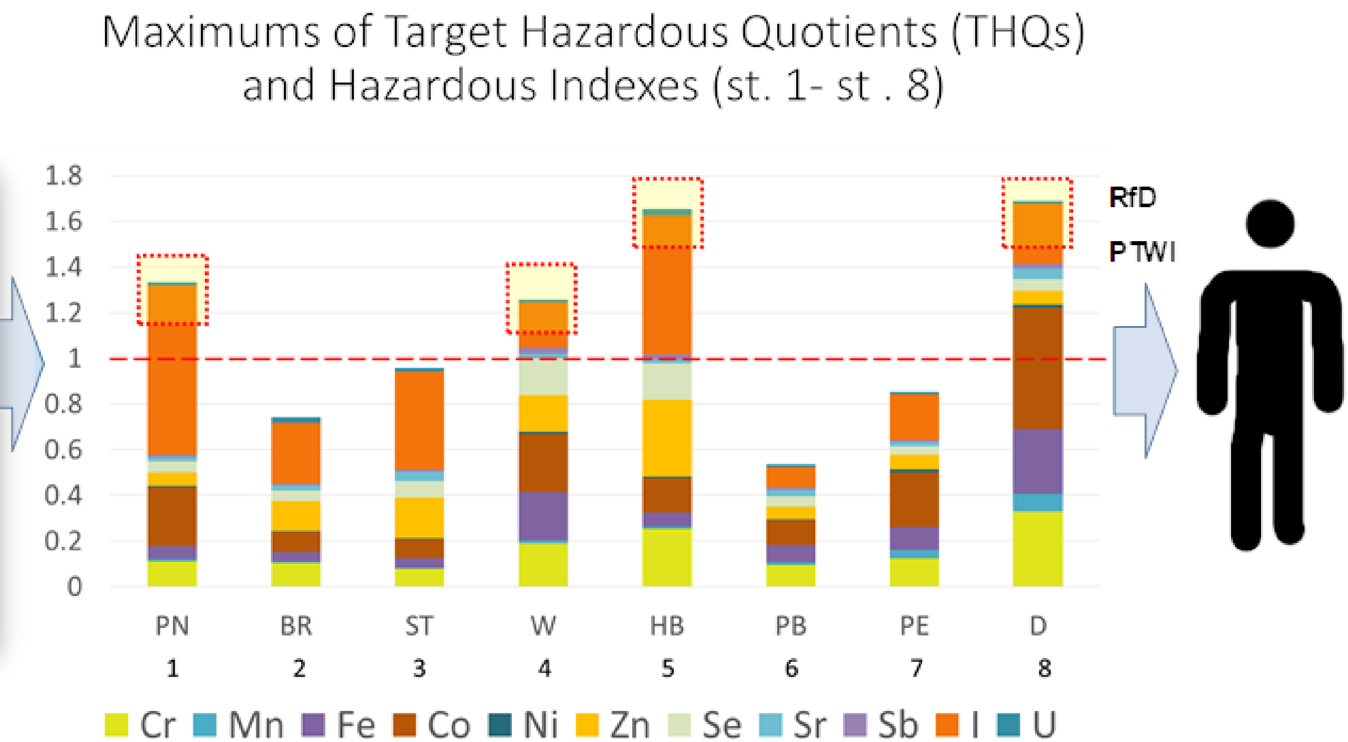
Typical groups of elements according to PCA



East Polluted stations (harbors at eastern coast of South Africa)

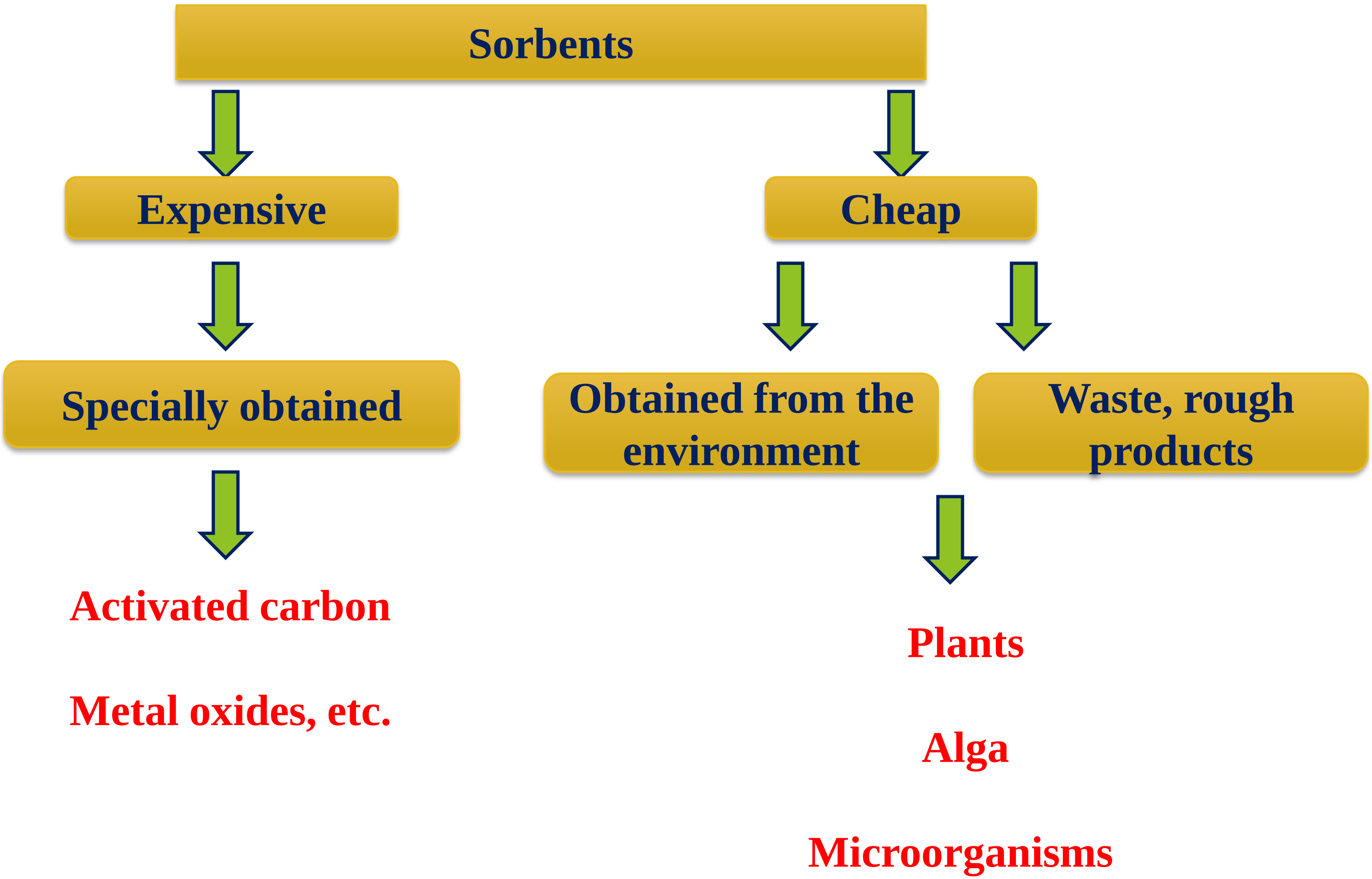
- **Al, Sc, V, Cr, Mn, Fe, Co, Th** were considered in pristine areas as terrigenous
- **Na, Mg, K, Cl, As, Br, I** were joined in one group that indicated the interlinking of this elements with the water salinity
- **Co, Ni, Sb, U** could be considered as anthropogenic in several events
- **Ca, Sr** interlinking with the deposition into shell and its construction
- **Na, Mg, Ca, As, Br, Sr, Cs** could be considered as terrigenous in cases of influence of storms (resuspension of bottom sediments)

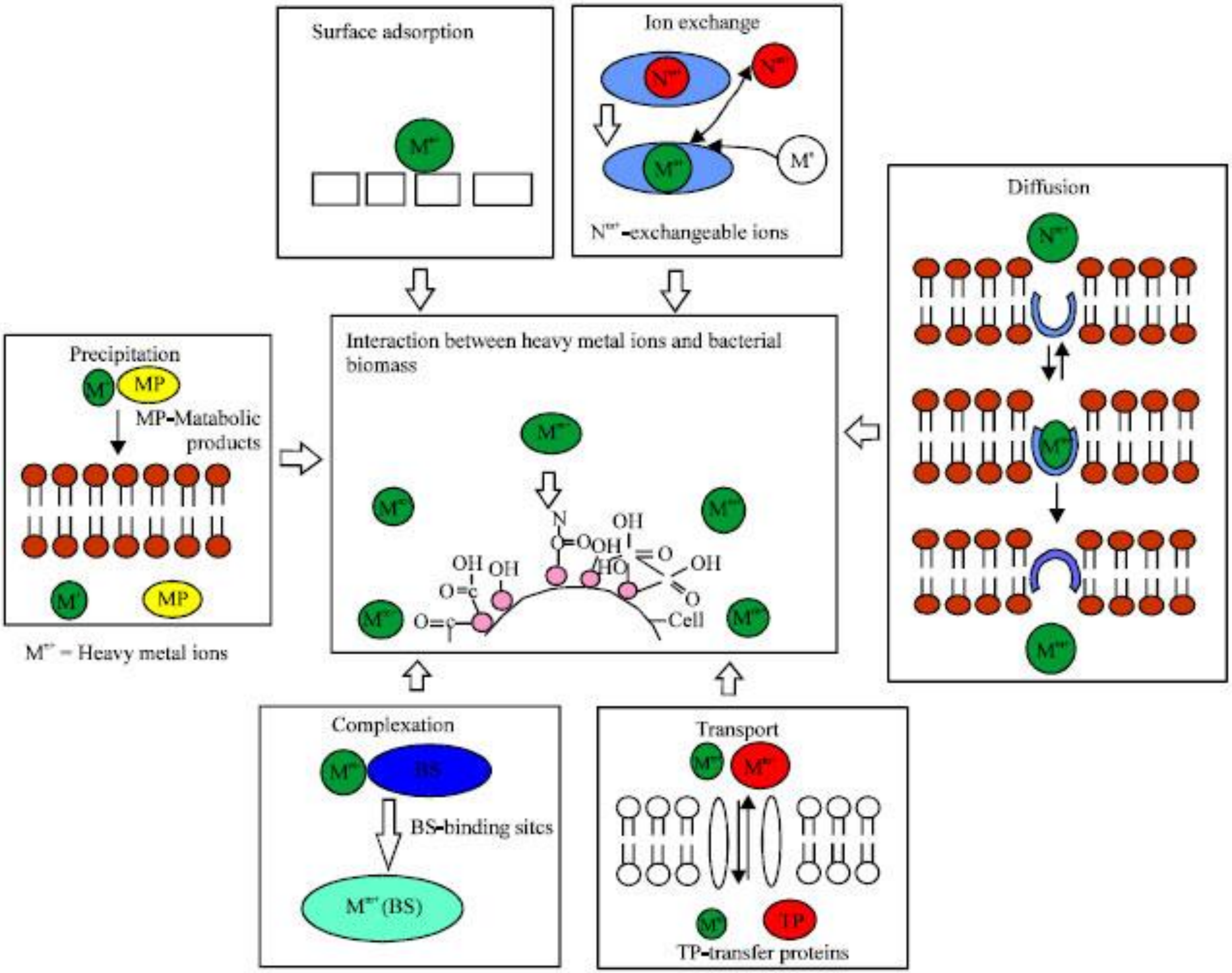
Hazard indices THQ and HI



In consumption of mussels:
Safe group: Na, Mn, Fe, Ni, Se, Sr, Sb, U
Risk group: Al, Cr, Co, Zn, As, and I

Wastewater treatment





Arti Hansda, Vipin Kumar, Anshumali. Research Journal of Environmental Toxicology, 9: 45-58.

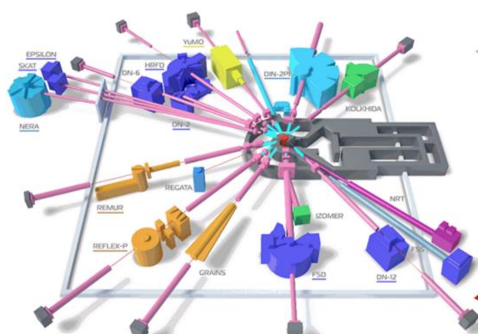
Beer production

Waste *Saccharomyces cerevisiae*

T, t, C, pH

AAS: Cu

NAA: Zn, Ni, Sr, Ba



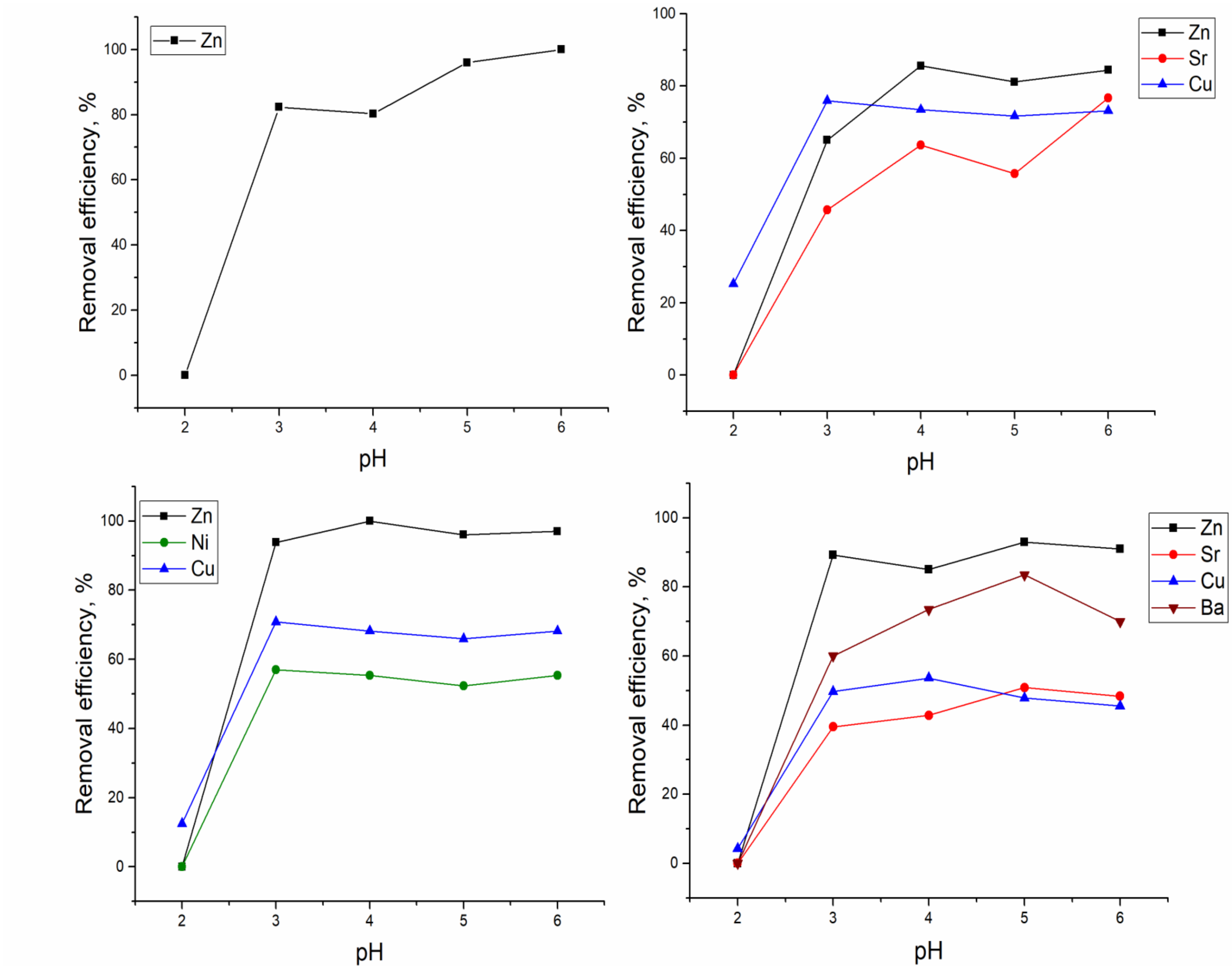
Studied systems:

Zn(II)

Zn(II)-Sr(II)-Cu(II)

Zn(II)-Ni(II)-Cu(II)

Zn(II)-Sr(II)-Cu(II)-Ba(II)



Removal of metal ions at different initial pH (at T 20 ^{0}C; sorbent dosage 0.5 g/L; adsorption time 1 h).

Elemental composition of industrial effluent

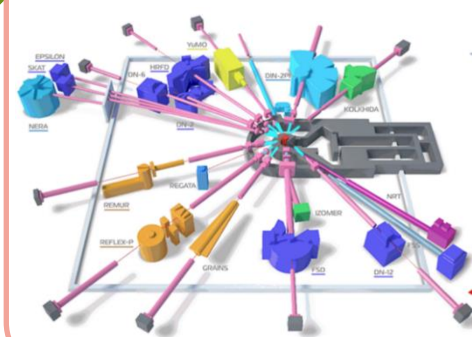
Element	Sr	Ni	Cu	Zn	Ba	pH
Concentration, µg/L	340	839	58	49843	35	6.0

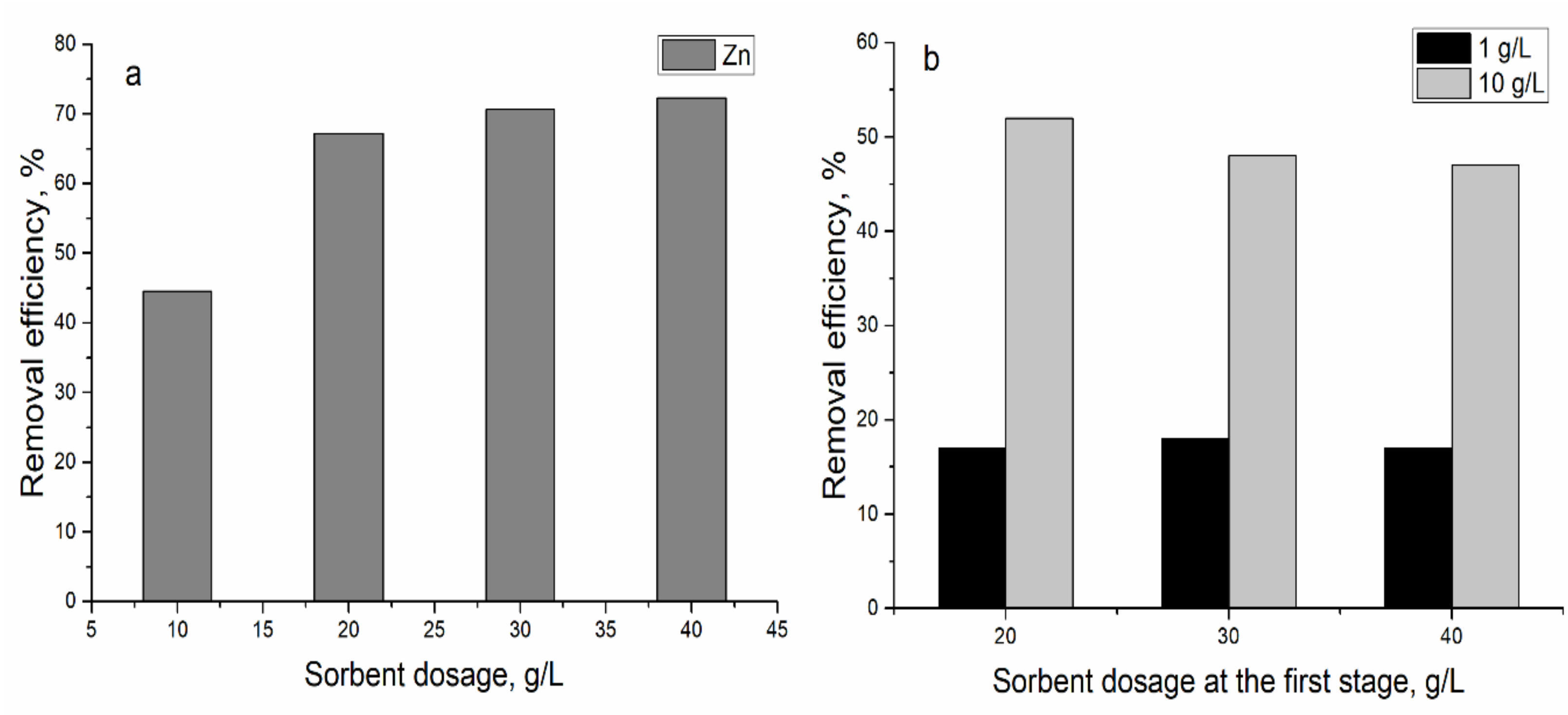
Saccharomyces cerevisiae

C, pH

AAS: Cu

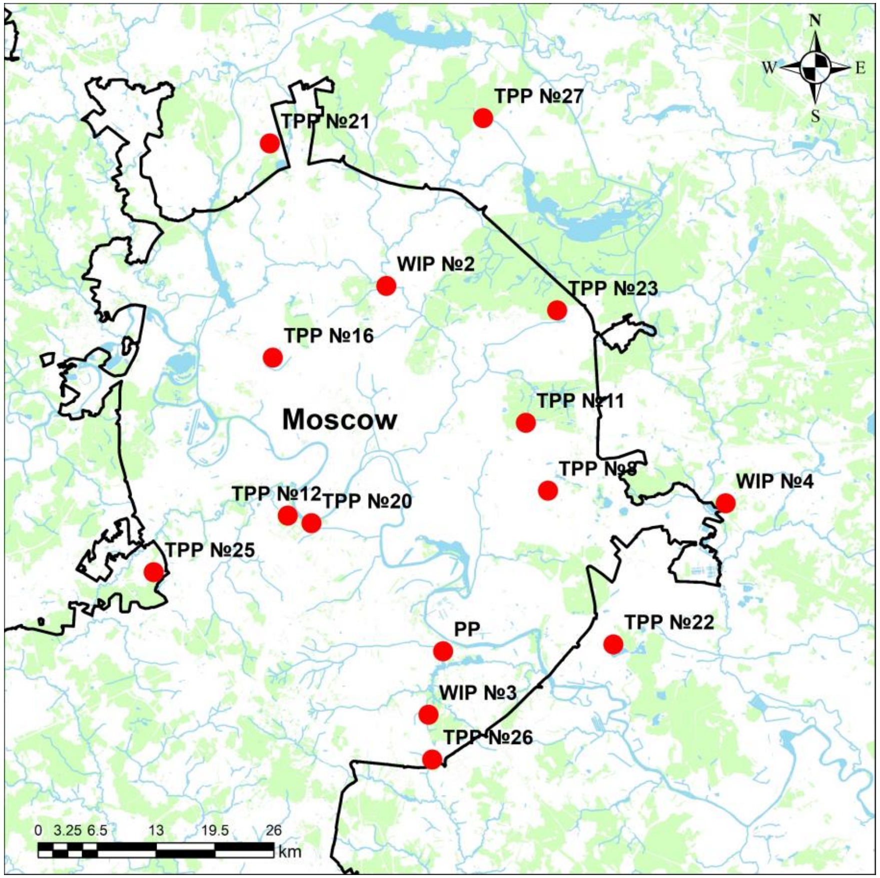
NAA: other elements



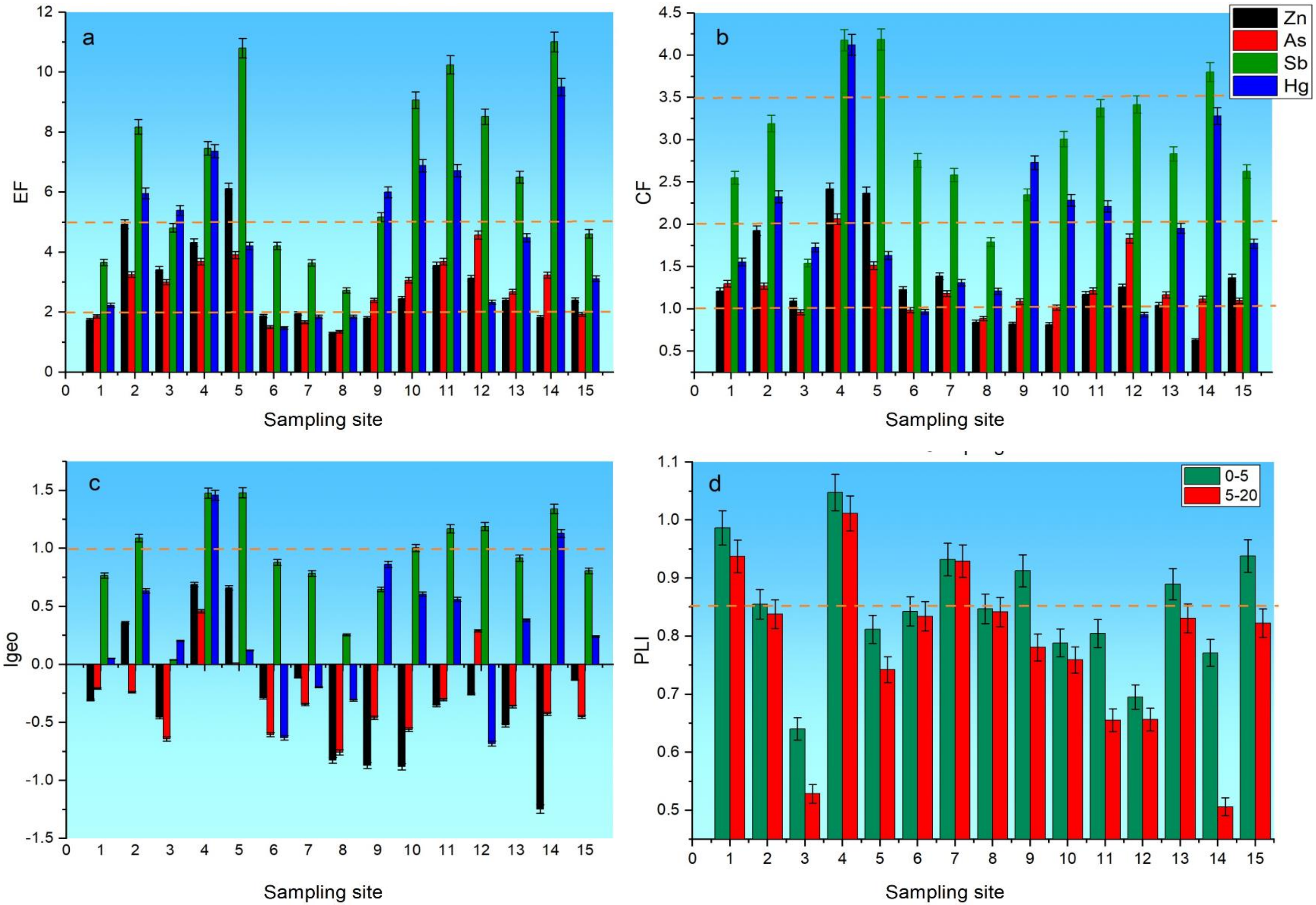


Removal of zinc ions from industrial effluent at different sorbent dosage (at T 20 ºC; adsorption time 1h)

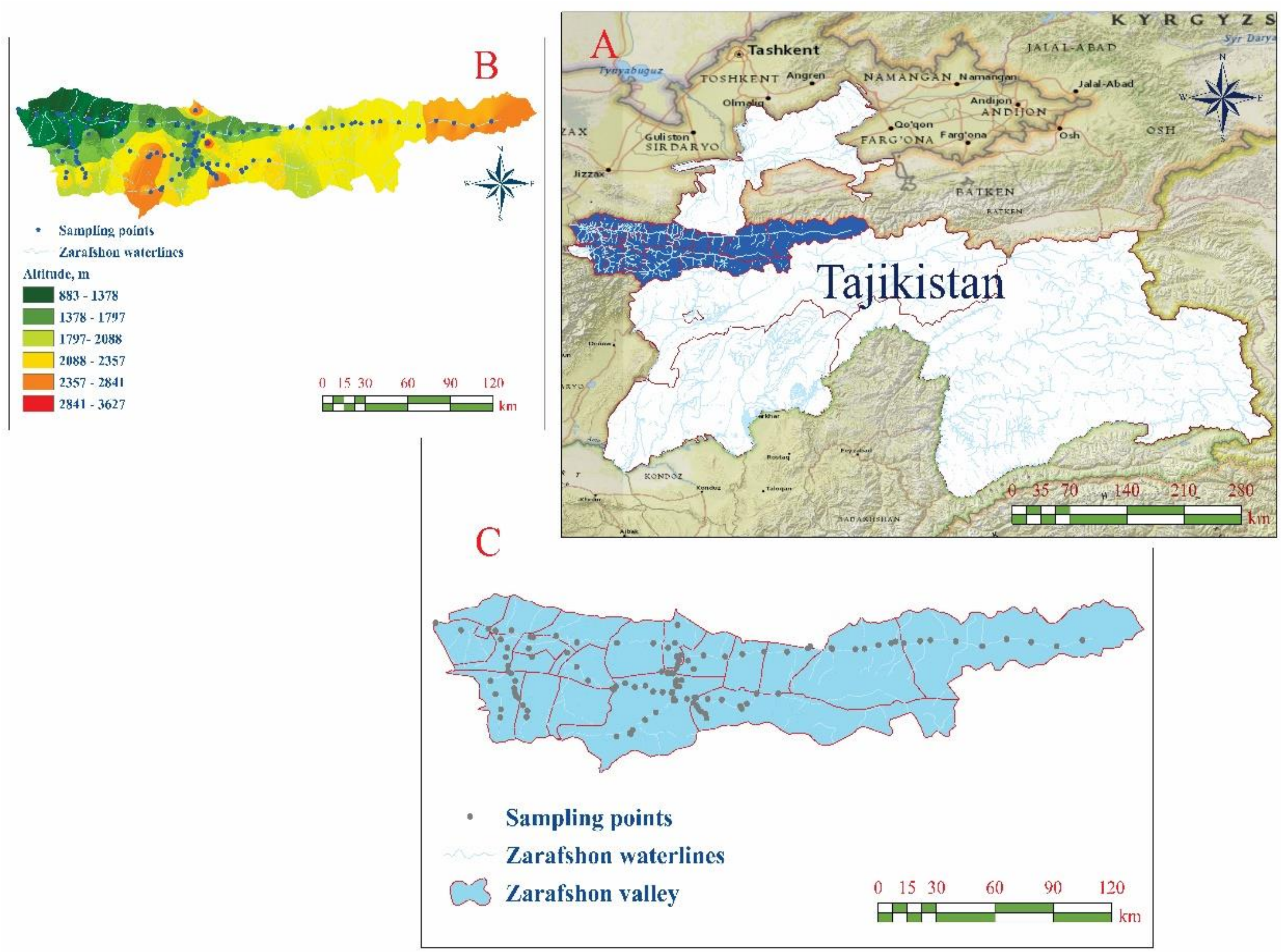
Assessment of soil pollution



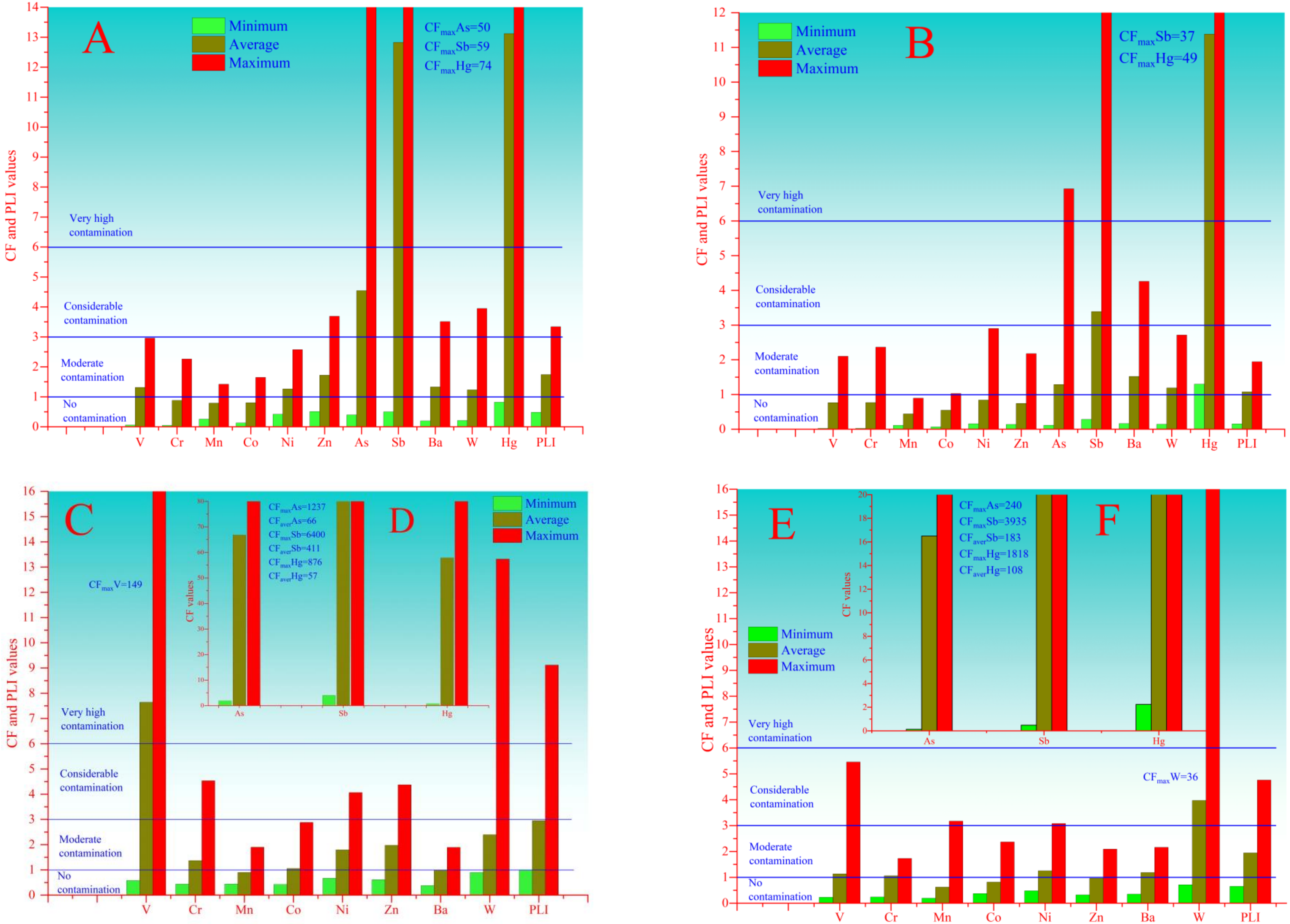
Map of soil samples sampling locations. Black contour shows the City of Moscow metropolitan area.



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.



Investigated area location in the Tajikistan map (A); Altitude (meter) of investigated area respectively by sampling points (B); soil and sediment sampling sites of Zarafshon valley (C)



Values of CF and PLI of unexposed soil (A) and sediments (B), as well as soils (C and D) and sediments (E and F) related to anthropogenic impact

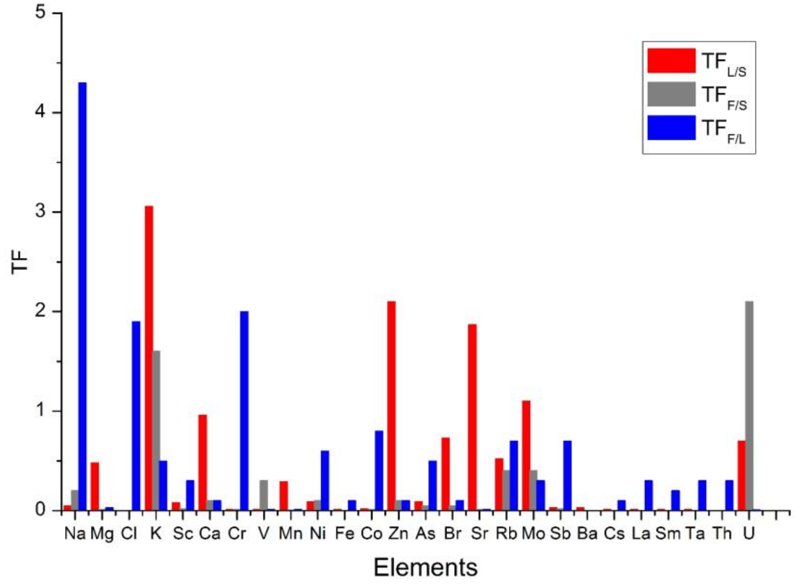
Control of quality and safety of foodstuffs

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

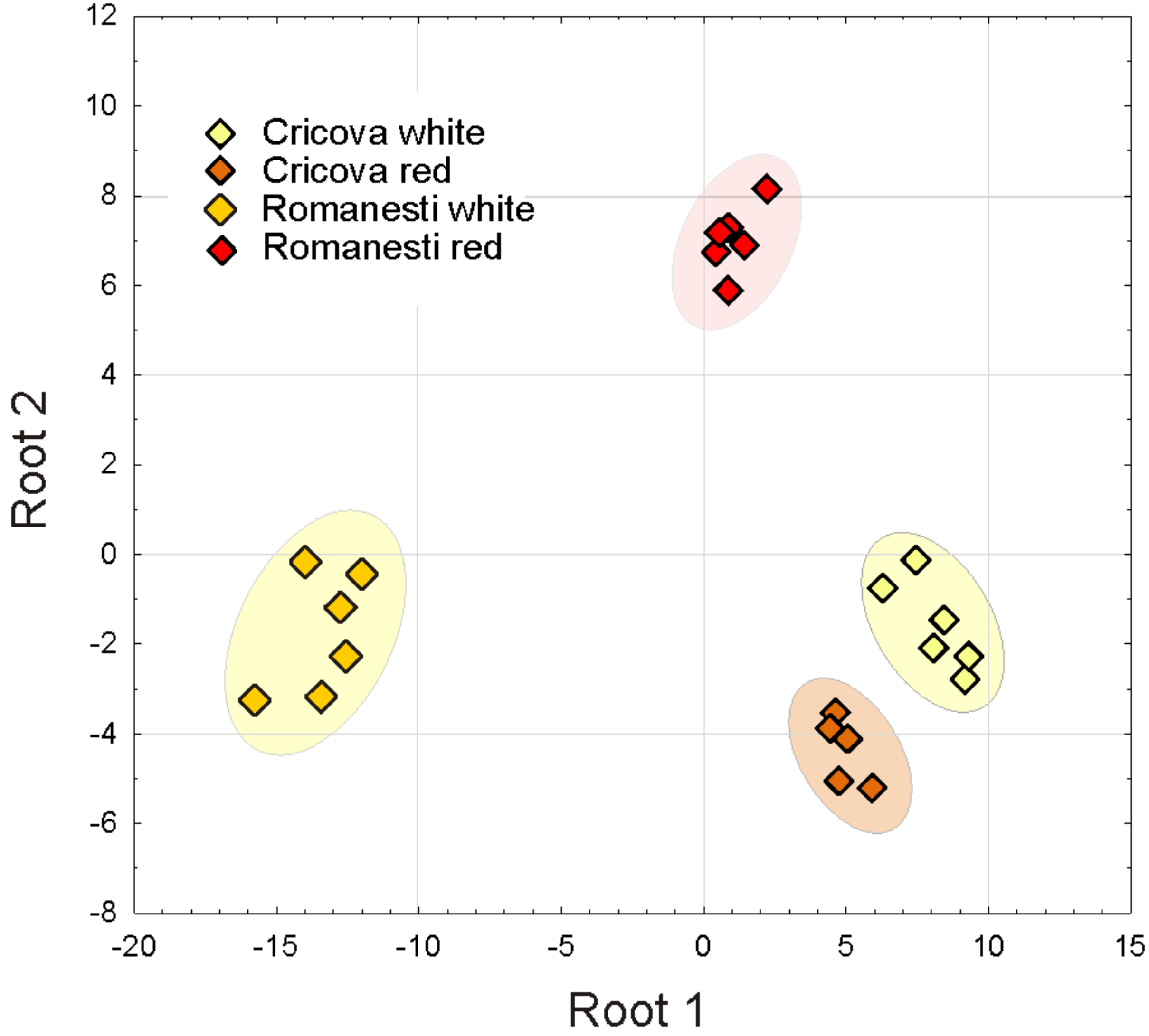
Control of quality of wine samples

Cabarnet, Regent, Pinot Noir, Nero, Syzar, Merlot, Malbec, Sauvignon, Riesling, Pinot Gris, Muscat, UniBlanc

Pinot, Chardonnay, Cabernet, Chardonney, Pinot Frank

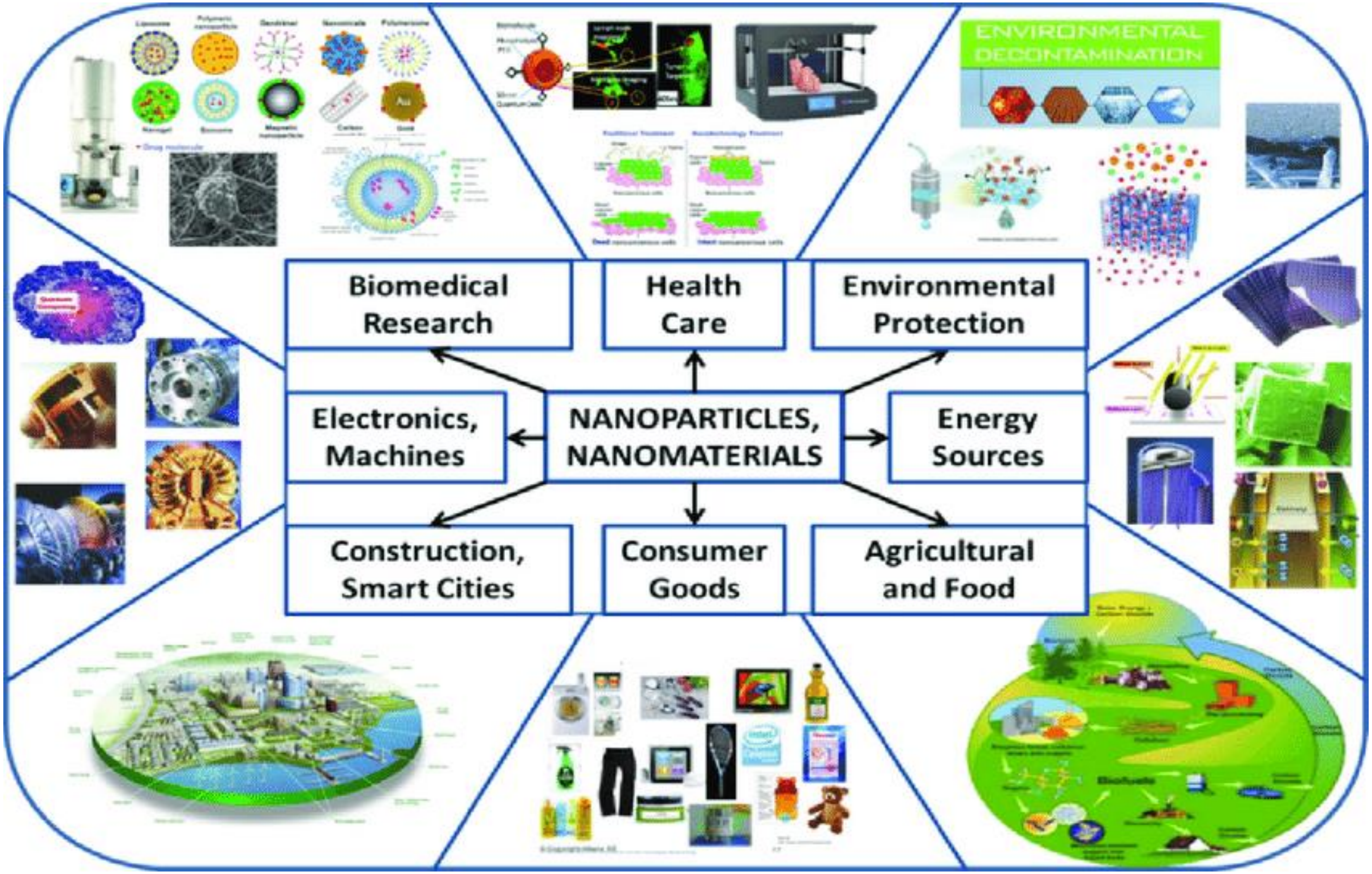
The experimental values (± S.D.) of the concentrations of 18 elements in investigated wines determined by NAA

Element	Romanesti red			Romanesti white			Cricova red			Cricova white		
Na	19	±	9	16	±	1	11	±	2	11	±	3
Mg	104	±	12	87	±	12	77	±	5	92	±	21
Al	1.4	±	1.0	1.9	±	0.5	1.4	±	1.0	1.5	±	0.7
K	690	±	80	380	±	230	460	±	80	550	±	100
Ca	54	±	14	75	±	24	66	±	13	68	±	21
Mn	1.35	±	0.14	1.22	±	0.25	0.93	±	0.14	1	±	0.2
Fe	3.5	±	3.3	2	±	1.9	1.1	±	0.7	0.7	±	0.4
Co	6.3	±	3.6	9.8	±	1.4	4.2	±	1.6	3.2	±	0.7
Ni	39	±	10	32	±	11	18	±	9	20	±	5
Zn	0.44	±	0.23	0.55	±	0.04	0.92	±	0.41	0.49	±	0.08
As	-	-	-	-	-	-	0.26	±	0.21	0.3	±	0.12
Br	280	±	90	92	±	92	69	±	25	104	±	44
Rb	1.7	±	0.2	1.1	±	0.5	1.6	±	0.3	1.6	±	10.3
Sr	1.01	±	0.23	0.64	±	0.19	0.84	±	0.32	0.75	±	0.15
Sb	0.48	±	0.18	0.41	±	0.13	0.59	±	0.37	0.53	±	0.26
Cs	3.3	±	0.8	3.1	±	2.5	7.5	±	2.8	6.1	±	1.1
Ba	276	±	270	110	±	30	70	±	41	87	±	27
U	0.12	±	0.06	0.20	±	0.06	0.13	±	0.04	0.13	±	0.01



The discriminating Root2 vs. Root 1 bi-plot illustrating the result of Discriminate Analysis of the 24 sets of wines. It can be remarked that the Romanesti wines are better discriminated with respect to Cricova ones.

Nanotoxicology



https://sciendo.com/it/article/10.2478/ebtj-2018-0019

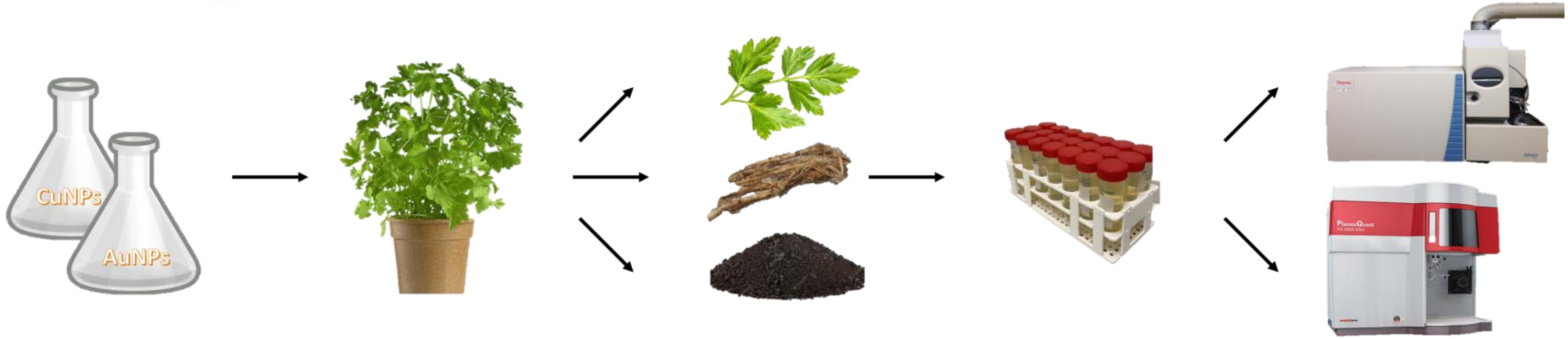

EVOLUT
ГЕЛЬ АНТИСЕПТИЧЕСКИЙ
с наночастицами серебра
8 ЧАСОВ ЗАЩИТЫ ОТ БАКТЕРИЙ


KREISEL
731
KLEJE • GIPSY • TYNKI
1-20mm
FUGA
SILVER
nanocząsteczki srebra
unikalna technologia
antybakteryjna
2 kg

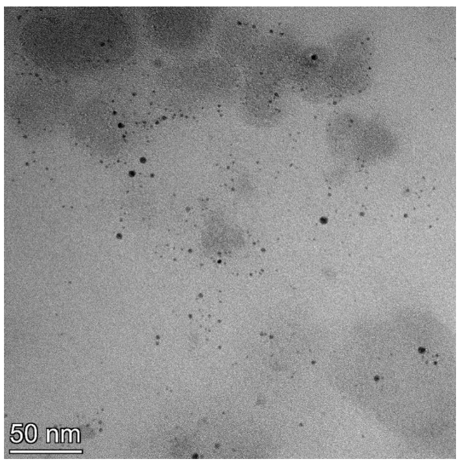

WRIGLEY'S
ЕСТЕСТВЕННАЯ БЕЛИЗНА ЗУБОВ
Orbit
white
Нежная мята
ДЛЯ ВАШИХ ВОПРОСОВ И ПОЖЕЛАНИЙ

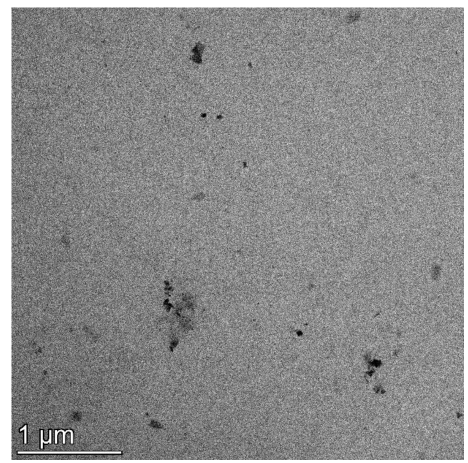

не содержит токсичных солей серебра
Аргенсепт
тоник
с наночастицами серебра
антисептический
очищающий
успокаивающий
50 мл
нанопродукция

Effect of nanoparticles on plants

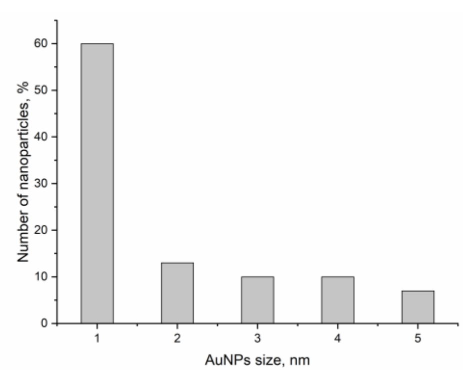


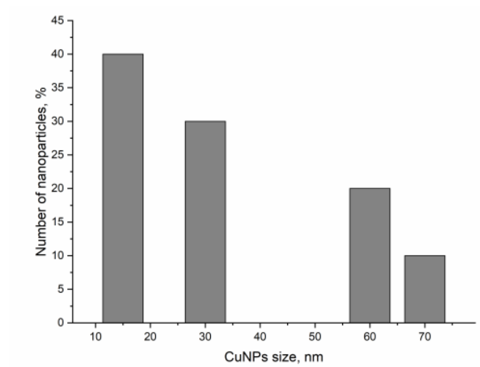
AuNPs

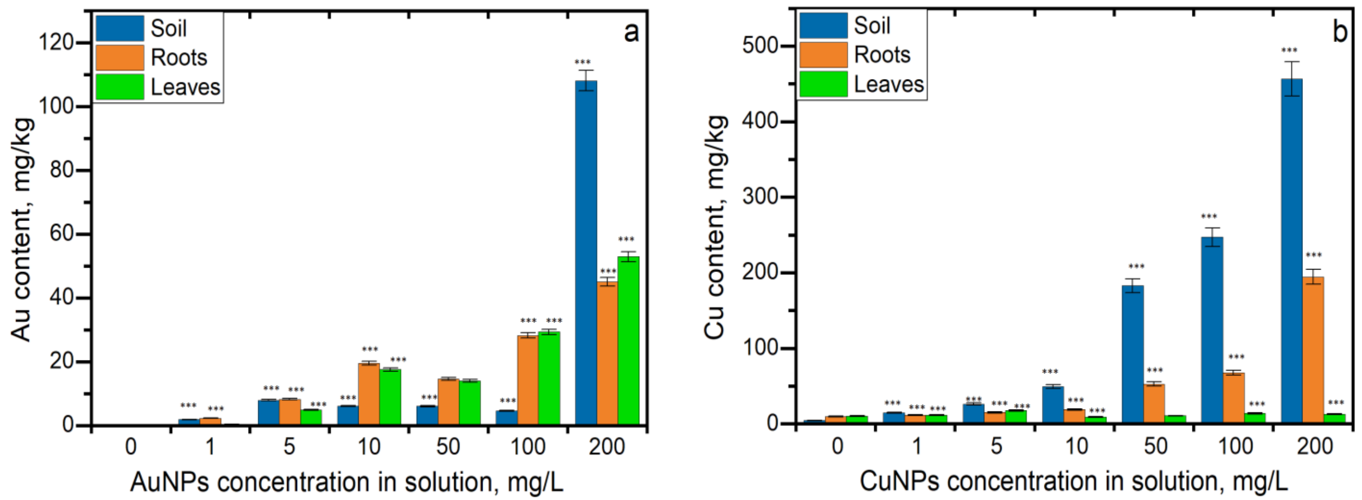




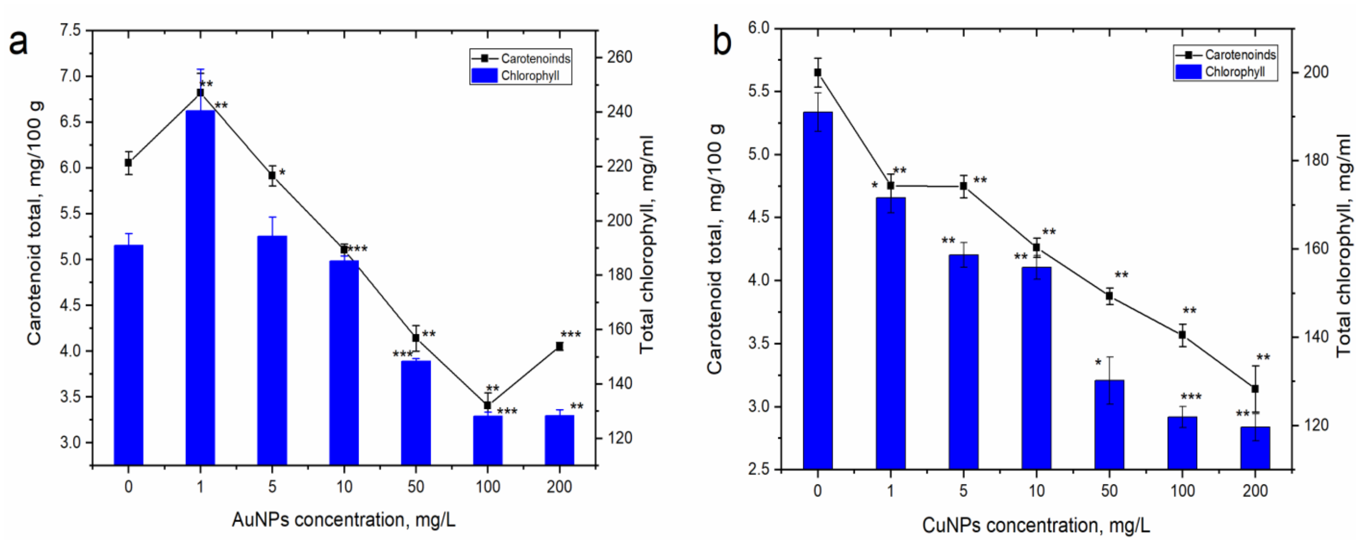
CuNPs







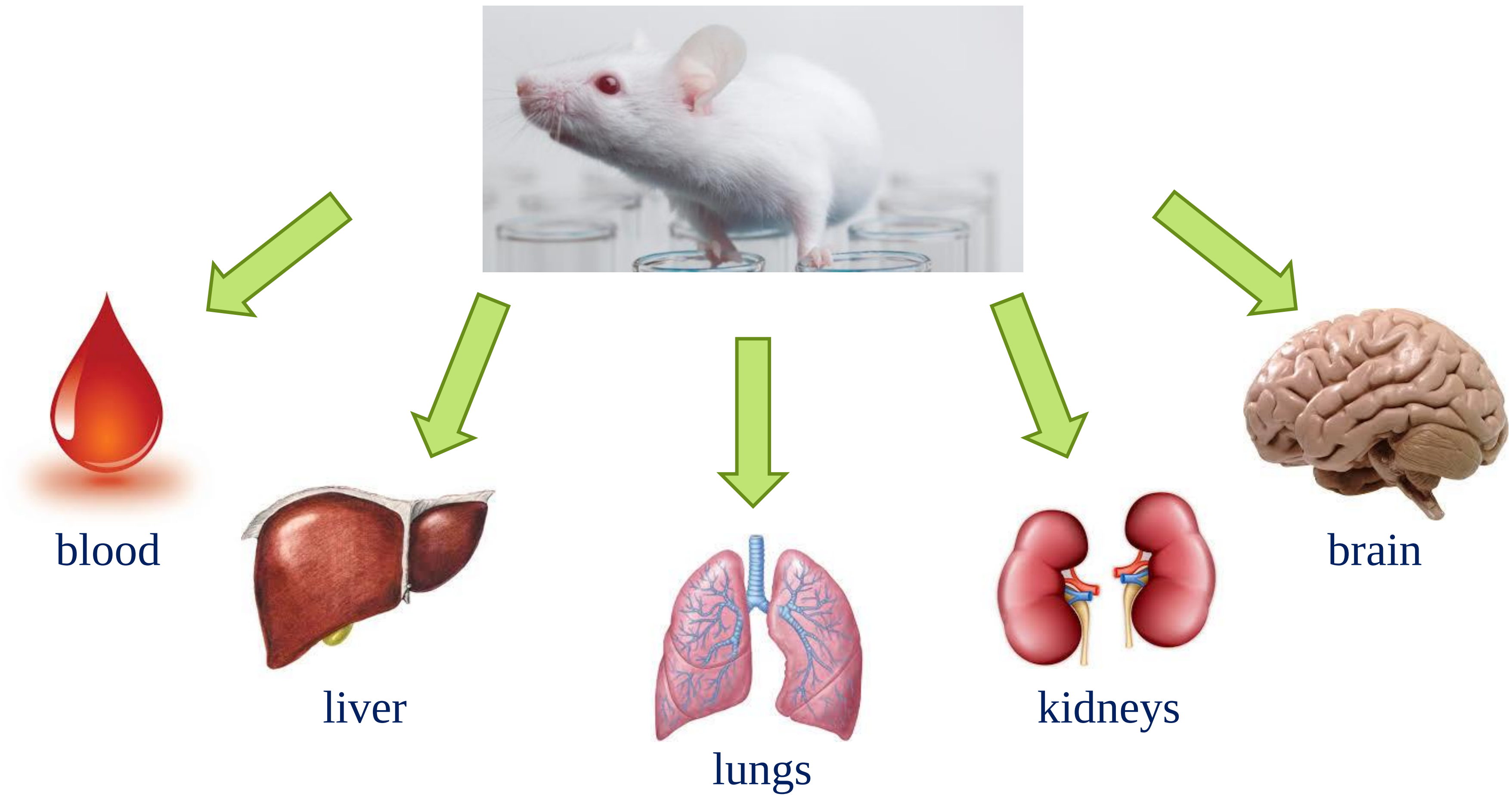
The content of copper and gold in parsley segments grown on soil watered with (a) AuNPs and (b) CuNPs determined by ICP-MS/OES techniques, (NPs concentrations 1-200 mg/L, duration of experiment 10 days

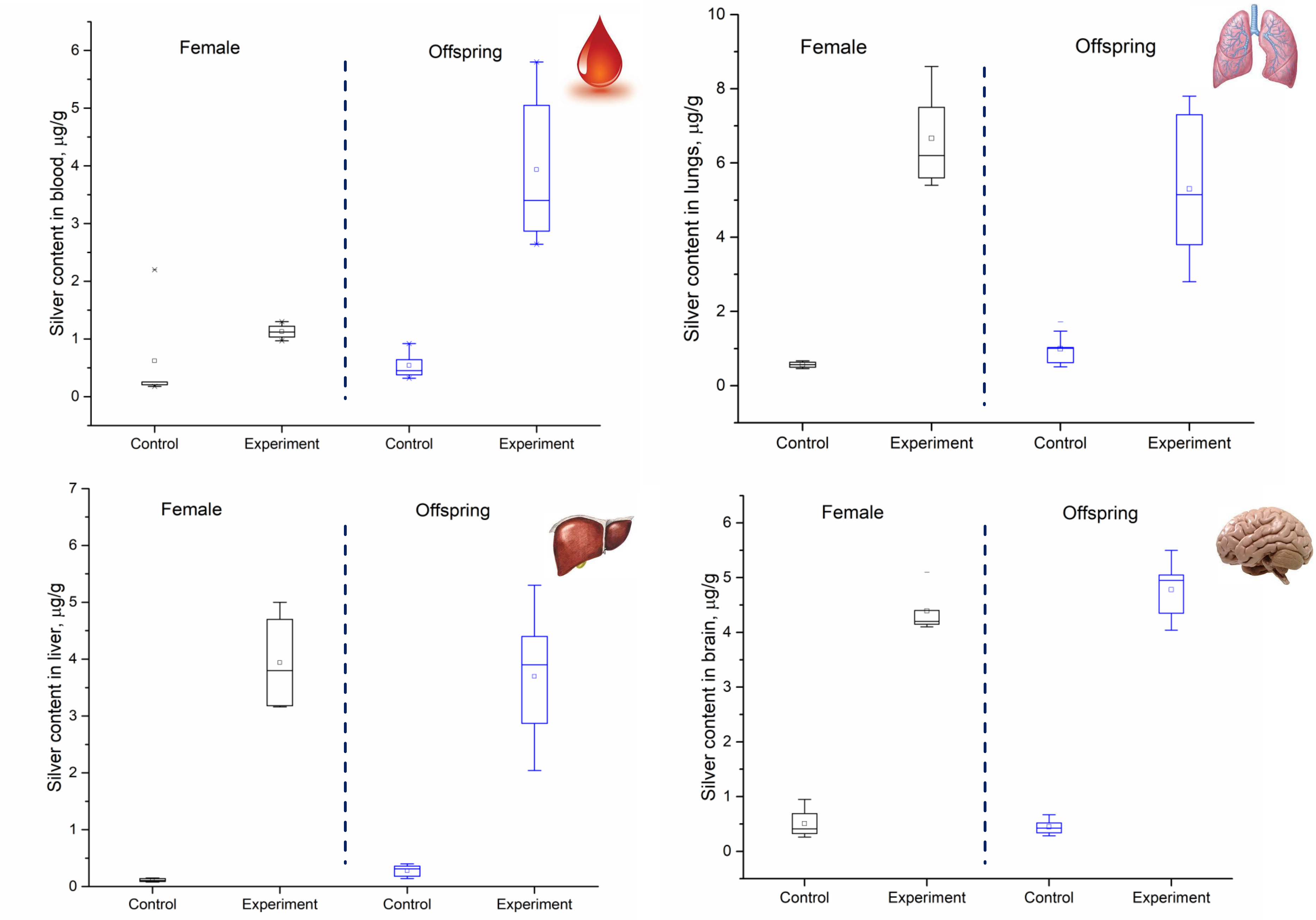


Change in the content of carotenoids and total chlorophyll in the aerial parts of parsley grown on soil watered with (a) AuNPs and (b) CuNPs

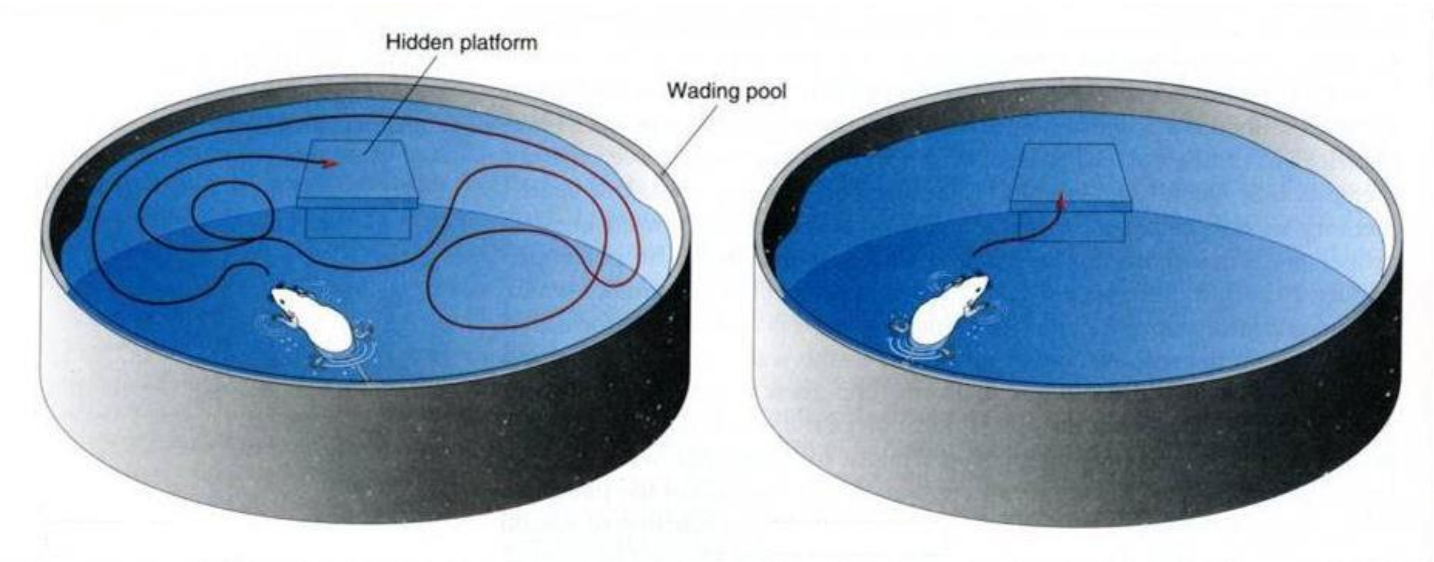
Effect of nanoparticles on animals

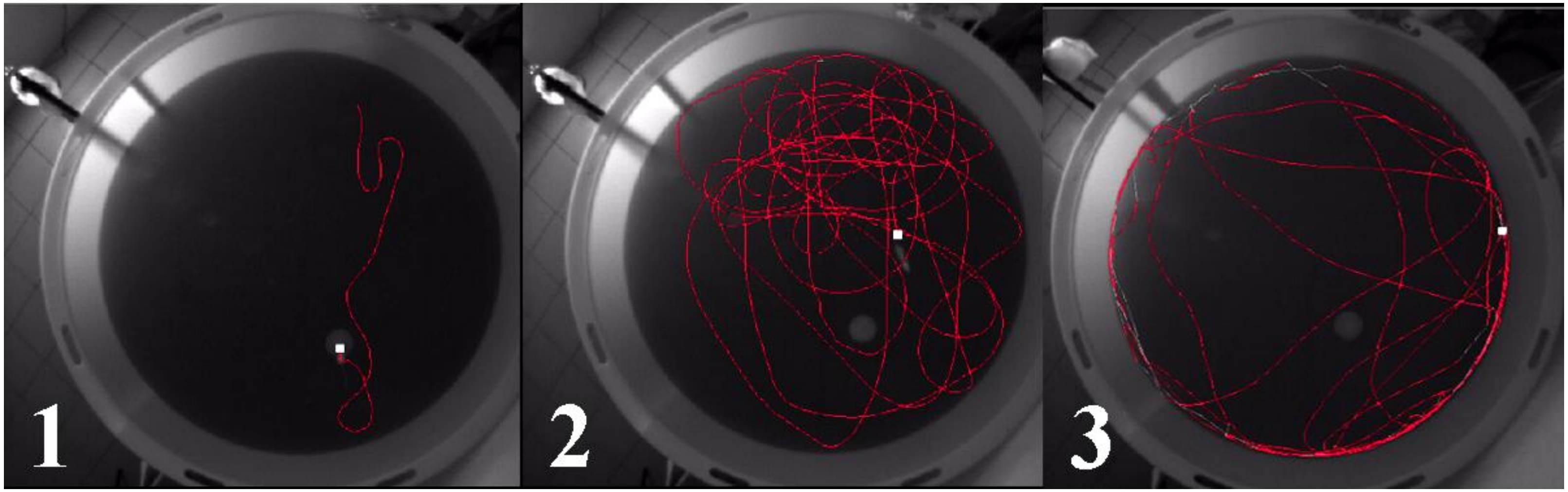
To study uptake of AgNPs (8.7 nm) both for mothers and the offspring experimental females were drinking the AgNPs solution with concentration of 25 μg/ml since one week before pregnancy and to the end of lactation (one month after birth).





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!