NEUTRON ACTIVATION ANALYSIS AT IFIN-HH BUCHAREST AND JINR DUBNA - COLLABORATIVE STUDIES

A. Pantelica[1], M.V. Frontasyeva[2], O.A. Culicov[2,3]

[1] Horia Hulubei National Institute for Physics and Nuclear Engineering (IFIN-HH), PO Box MG-6, 077125 Magurele, Ilfov county, Romania, apantel@nipne.ro

[2] Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Moscow Region, Russia, E-mail: marina@nipne.ro

[3]National Institute for R&D in Electrical Engineering (ICPE-CA), 313 Splaiul Unirii, 030138 Bucharest, Romania, E-mail: culikov@jinr.ro

21th International Seminar on Interaction of Neutrons with Nuclei (ISINN-21), Alushta, Ukraine, May 20-25, 2013

Introduction

This paper presents an overview of the collaborative studies performed, during about 15 years, at IFIN-HH in Bucharest-Magurele, Romania and JINR at Dubna, Russia, based on instrumental neutron activation analysis (INAA).

The common researches were developed in the frame of bilateral Russia-Romania collaborative projects, as well as international projects with a larger number of participating countries.

Our collaborative projects were focused on INAA application in environmental pollution studies.

INAA at JINR Dubna

Neutron irradiation in Russia was carried out at the radioanalytical complex REGATA at the IBR-2 reactor of JINR Dubna.

Pulsed fast reactor IBR-2 provided activation with the whole fission spectrum: thermal, epithermal and fast neutrons.

Thermal NAA takes advantage of the high intensity of neutrons available from the thermalization of fission neutrons and the large thermal neutron cross-sections for most isotopes.

The irradiated samples were measured for short and long half lives radionuclides at the NAA Frank Laboratory of JINR, using gamma-ray spectrometers based on HPGe detectors.

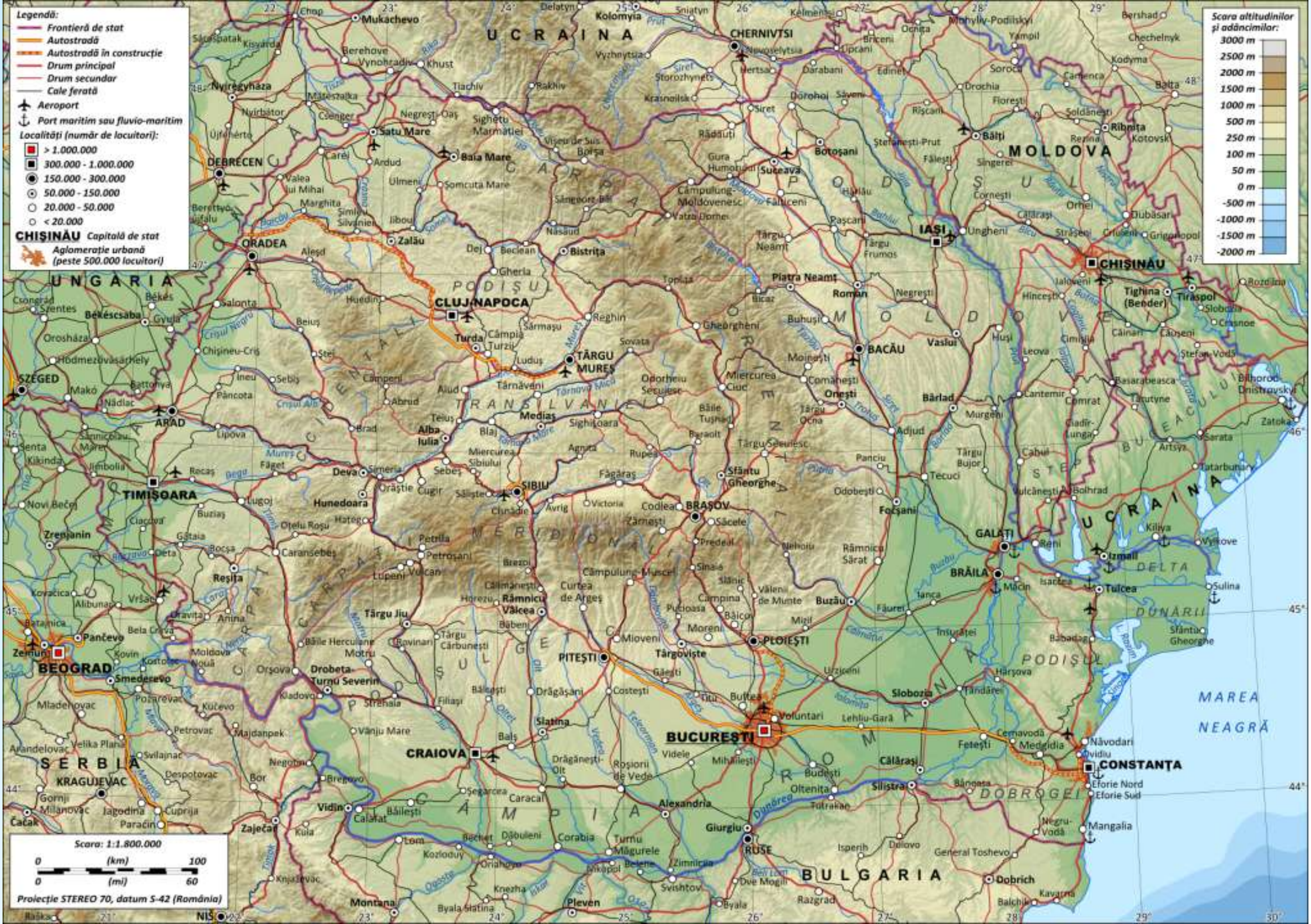
INAA at IFIN-HH in Bucharest

Neutron irradiation in Romania was carried out at the VVR-S reactor of IFIN-HH in Bucharest-Magurele until December 1997, then at TRIGA reactor of RAAN-SCN Pitesti at about 100 km far from Bucharest, by using a thermal neutron flux.

At the VVR-S reactor in Bucharest, short and long term irradiation of samples allowed to measure both short and long-lived radionuclides produced.

By neutron irradiations at the TRIGA reactor in Pitesti, only long-lived radionuclides could be measured ($T_{1/2}$ > 12.36 h, of ^{42}K).

The irradiated samples were measured in the low background NAA laboratory of IFIN-HH in Bucharest-Magurele.



Legendă:
Frontieră de stat
Autostradă
Autostradă în construcție
Drum principal
Drum secundar
Cale ferată
Aeroport
Port maritim sau fluvio-maritim
Localități (număr de locuitori):
> 1.000.000
300.000 - 1.000.000
150.000 - 300.000
50.000 - 150.000
20.000 - 50.000
< 20.000
CHIȘINĂU Capitală de stat
Aglomerație urbană (peste 500.000 locuitori)
Scara altitudinilor și adâncimilor:
3000 m
2500 m
2000 m
1500 m
1000 m
500 m
250 m
100 m
50 m
0 m
-500 m
-1000 m
-1500 m
-2000 m
Scara: 1:1.800.000
(km)
(mi)
Proiecție STEREO 70, datum S-42 (România)
UCRAINA
MOLDOVA
UNGARIA
SERBIA
BULGARIA
MAREA NEAGRĂ
PODIȘUL TRANSILVANIEI
DELTA DUNĂRII
PODIȘUL DOBROGEI
CÂMPIA ROMÂNĂ
BUCUREȘTI
CHIȘINĂU
BEOGRAD
CLUJ-NAPOCA
TIMIȘOARA
IAȘI
CONSTANȚA
CRAIOVA
GALAȚI
BRAȘOV
PLOIEȘTI
ORADEA
BRĂILA
ARAD
SIBIU
BACĂU
PITEȘTI
TÂRGU MUREȘ
CHERNIVTSI
DEBRECEN
SZEGED
KRAGUJEVAC
Baia Mare
Satu Mare
Suceava
Botoșani
Piatra Neamț
Bistrița
Zalău
Deva
Hunedoara
Alba Iulia
Reșița
Drobeta-Turnu Severin
Târgu Jiu
Râmnicu Vâlcea
Slatina
Alexandria
Giurgiu
Călărași
Slobozia
Tulcea
Focșani
Buzău
Târgoviște
Vaslui
Bârlad
Sfântu Gheorghe
Miercurea Ciuc
Ruse
Vidin
Pleven
Dobrich
Bălți
Tiraspol
Tighina (Bender)
Izmail
Ungheni
Cahul
Comrat

Elements determined by INAA

Long-lived radionuclides

As, Au, Br, Ca, Cd, K, La, Mo, Na, Sb, Sm, U, W from the counting runs I and II (cooling times of 4-5 and 7-8 days);

Ag, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Lu, Ni, Rb, Sb, Sc, Se, Sr, Ta, Tb, Th, Yb, Zn, Zr of long half-lives from the counting run III (cooling time of about 30 days).

Short-lived radionuclides

Al, Ca, Cl, Cu, I, Mg, Mn, Sr, and V of short half-life (2.25 min of ^{28}Al – 2.58 h of ^{56}Mn).

Workplace monitoring and occupational health-related studies

In the framework of the EU INCO-Copernicus project (2002-2004) «Workplace monitoring and occupational health-related studies at some selected phosphate fertilizer plants in Russia, Uzbekistan, Poland, and Romania», acronim "Fertilizers and Health", possible hazardous effects of the fertilizer plant TURNU in Turnu Magurele were examined.

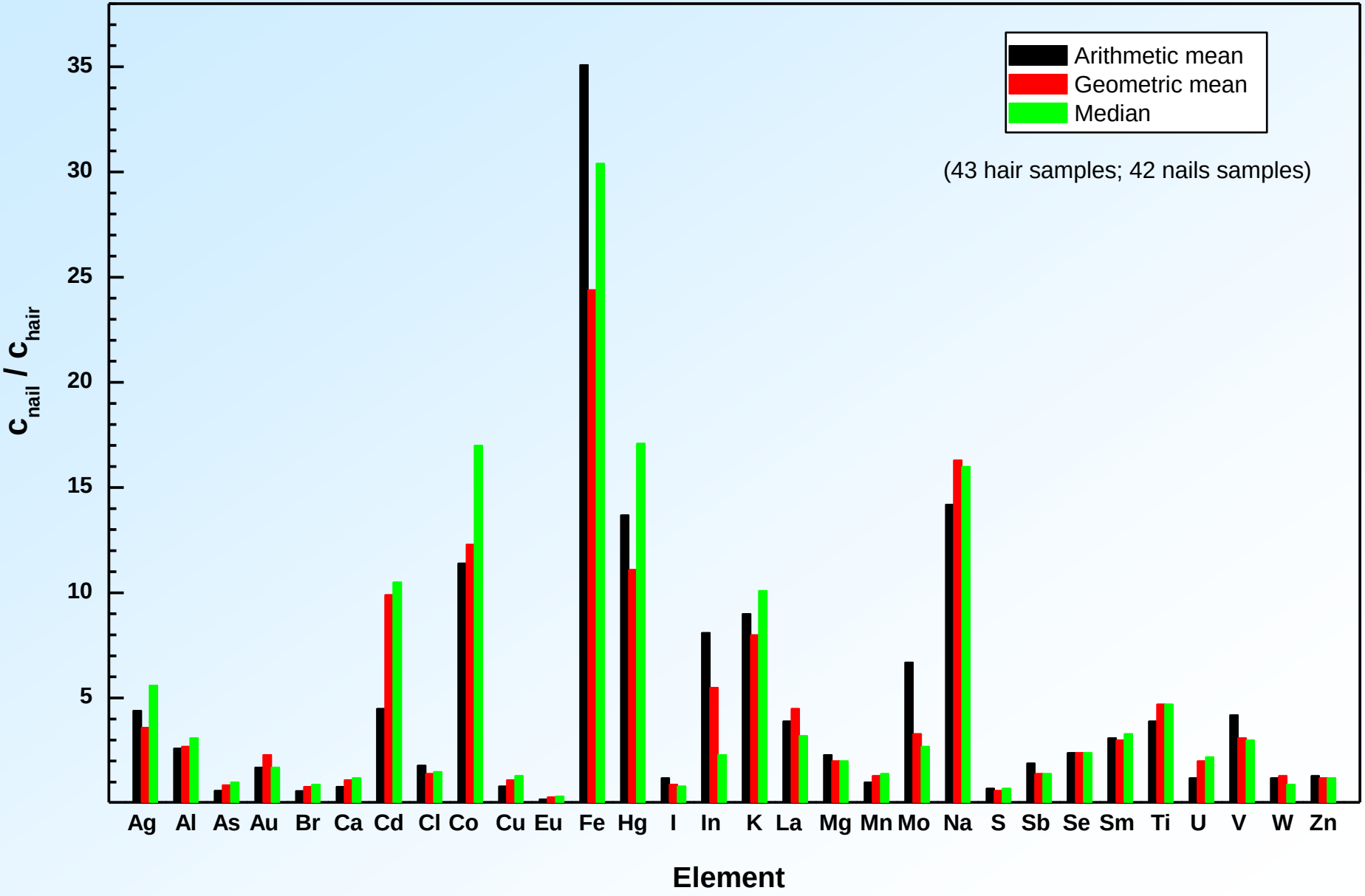
This research was based on an experience previously obtained in similar studies in Russia.

Environmental impact of a phosphate fertilizer plant was investigated on soil and vegetation (tree leaves, potato, carrot, and corn) collected at different distances to the plant, as well as workplace air and tap water samples; the impact on the health was examined on workers biosubstrates (hair and nails).

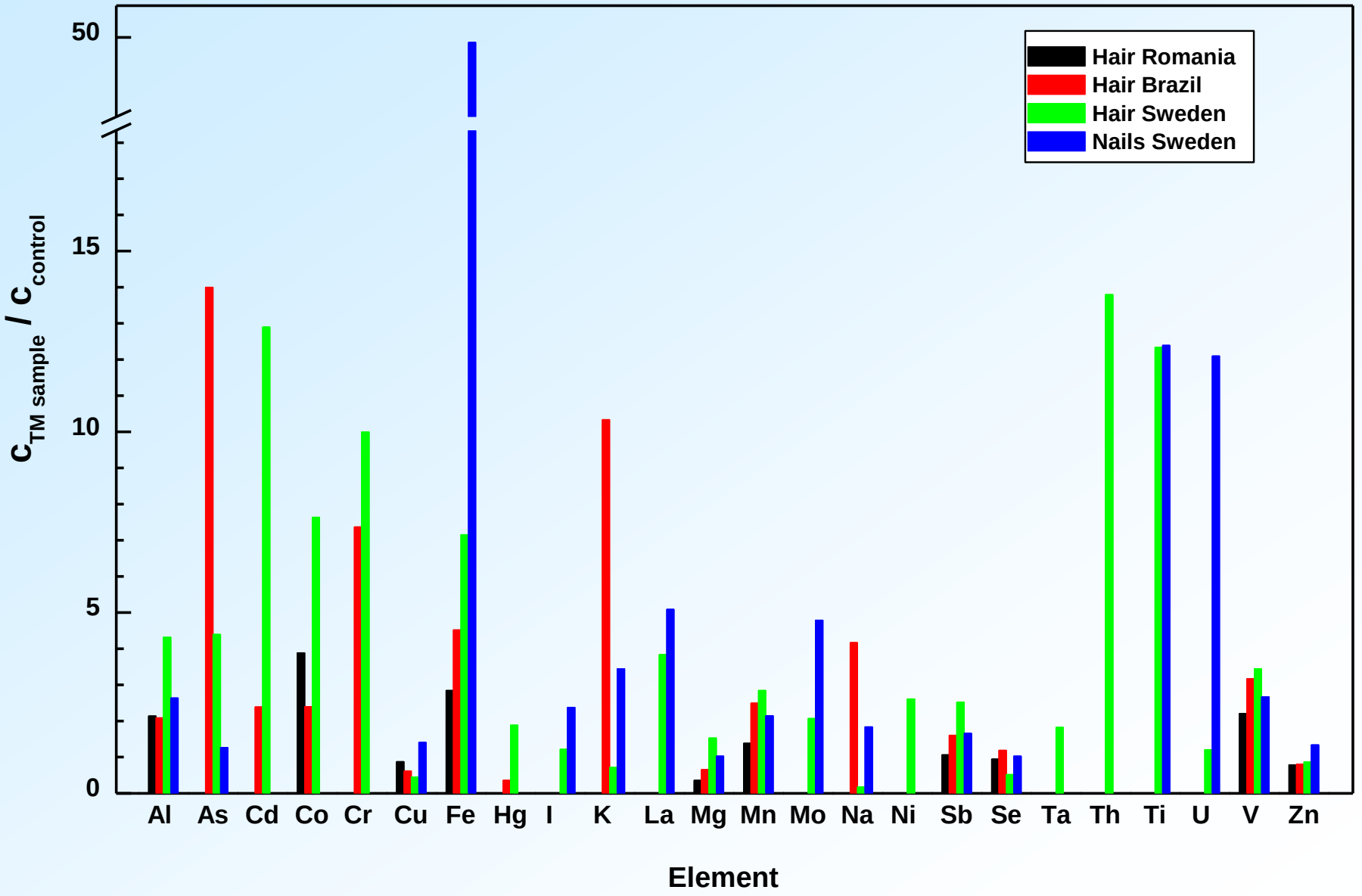
Hair and Nails biosubstrates

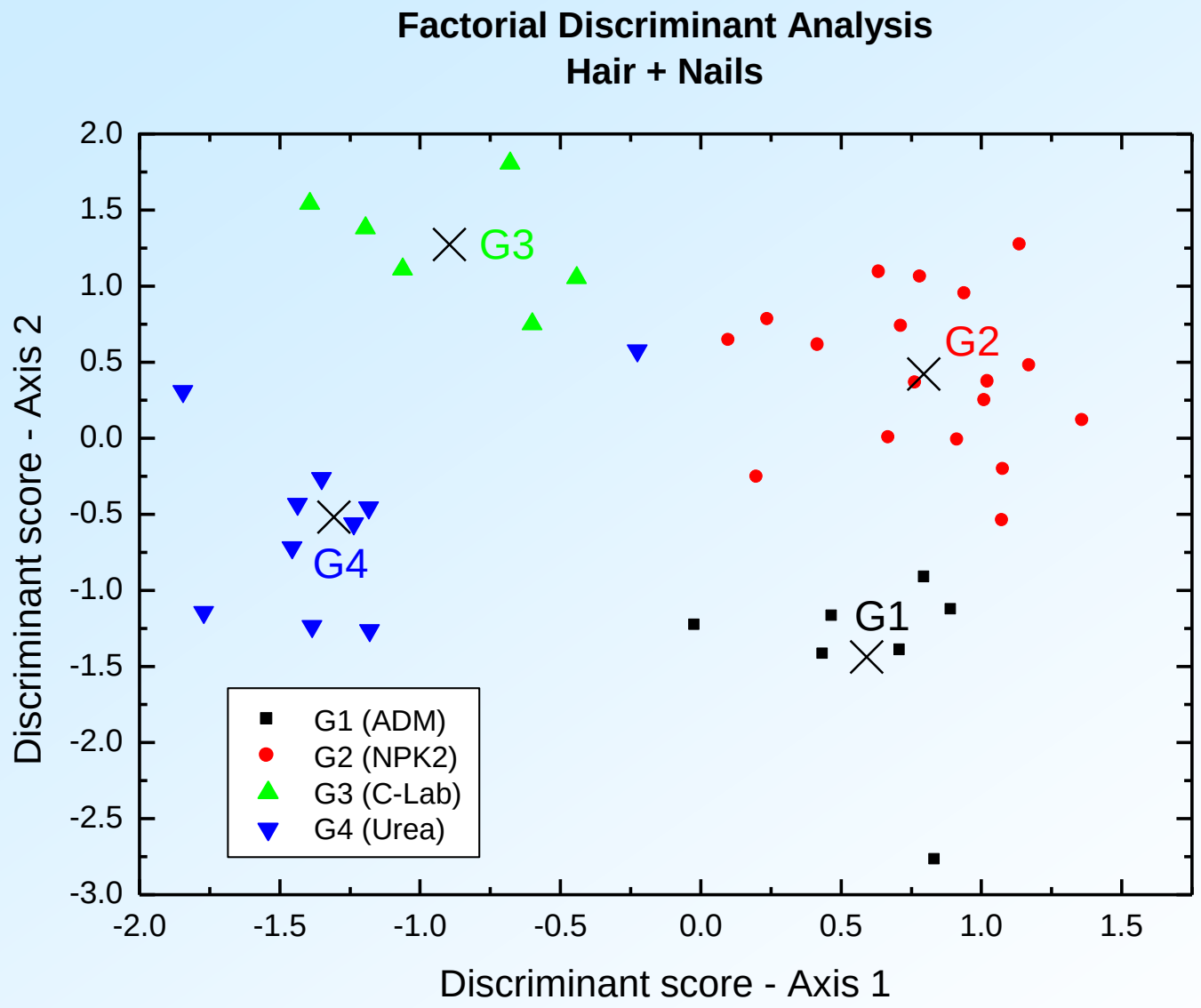
- **Hair and nails are biological materials generally used in the environmental pollution studies, particularly occupational exposure, based on the property to retain trace elements during their growth.**
- **By means of INAA occupational exposure effect was put in evidence on hair and nails samples collected from fertilizer industry workers in Romania, by a comparison with literature analytical data for unexposed subjects from Romania, Brazil and Sweden.**
- **As controls, samples collected from employees of the administrative staff of the plant not directly involved in the technological activities were taken. In addition, previous data on control hair samples in Bucharest and some literature data were considered.**

Ratios of element concentrations in nails and hair samples from TM fertilizer plant workers

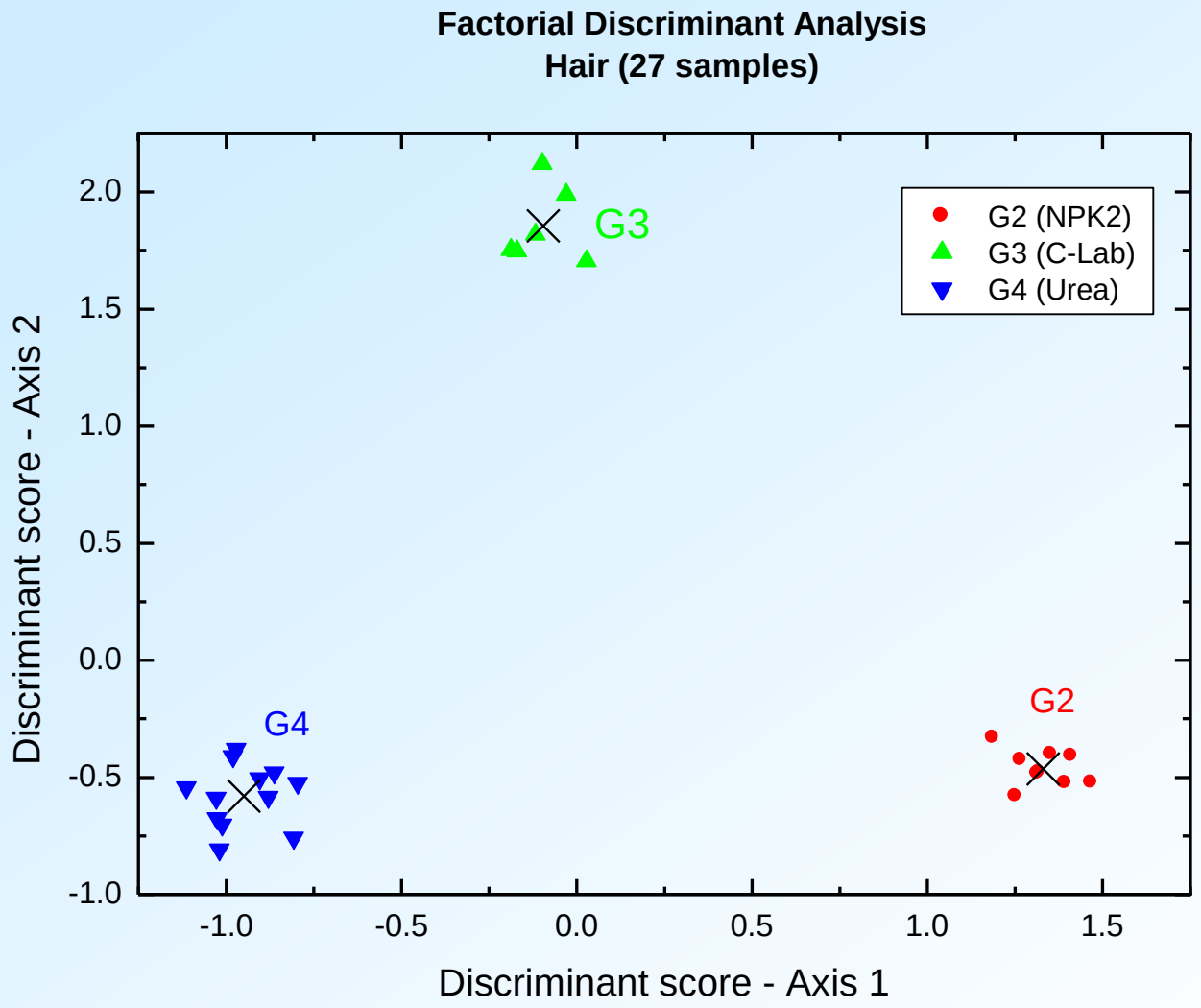


Comparison with literature data for the element concentrations in hair and nails samples from TM fertilizer plant





Factorial Discriminant Analysis (FDA) on hair and nails samples (41 pairs of samples, 28 variables).



Factorial Discriminant Analysis (FDA) on hair samples from 3 working shops of TURNU fertilizer plant (27 samples, 24 variables/elements).

Hair and Nails biosubstrates

Conclusions

- **Compared with the hair samples, higher element concentrations in nails were observed for Fe, Na, Co, Hg, Cd, K, In, Ti, La, Ag, Mo, V, Sm, Al, Se, Au, Mg, and U (ratios between 24 and 2, based on geometric averages).**
- **Higher than control concentration values were determined for Th, Cs, Cd, Ti, Cr, Co, Fe, As, Al, La, V, Mn, Ni, Sb, and Mo in hair samples.**
- **Relative to Sweden data (controls), ratios between 14 and 2, and for Fe, Ti, U, La, Mo, K, V, Al, I and Mn in hair samples, and between 49 and 2 in nails, based on median values were found.**
- **A higher number of elements could be determined by INAA in hair compared with nails samples.**

Hair and Nails biosubstrates

(continuation)

- **The degree of discrimination between groups of samples collected at different working shops was put in evidence by Factorial Discriminant Analysis (FDA) method.**

- **FDA was able to discriminate between three as well as four working groups of the fertilizer plant, using analytical data for 41 pairs of hair and nail samples (classification abilities higher than 80 %).**

References

Investigation of the occupational exposure in a Romanian fertilizer plant by instrumental neutron activation analysis of hair and nail samples, A. Pantelica, O.A. Culicov, M.V. Frontasyeva, C. Oprea, R. Georgescu, I.I. Georgescu, E. Pincovschi, Seventh International Conference On Radiochemistry (NRC-7), 24-29 August 2008, Budapest, Hungary.

Soil pollution around TM fertilizer plant

The elemental concentrations in surface soil collected in the vicinity of TURNU phosphate fertilizer plant in Romania, at different distances to the plant (0.5-15 km) on different cardinal directions were investigated by INAA and EDXRF techniques.

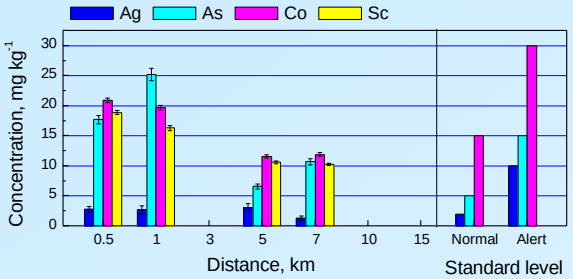
In general, the highest elemental concentrations in soils were put in evidence at 0.5 and 1 km distance to the plant.

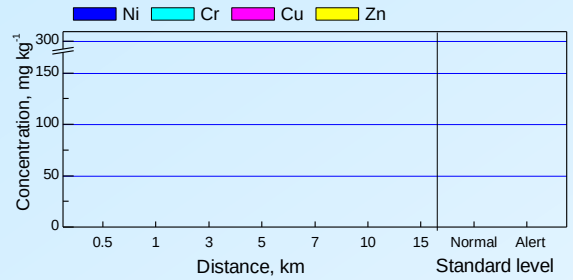
Variation with the distance to the plant of the element concentrations in soils were observed as follows:

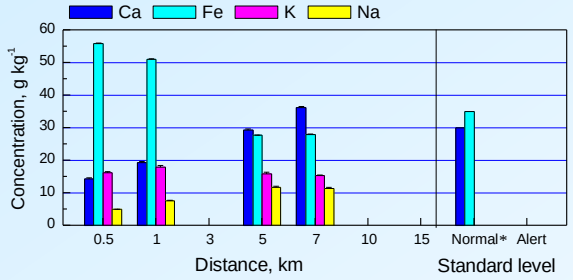
- **Decreasing of Ag, As, Au, Co, Fe, K, Ni, Rb, Sb, Sc, Se and Zn concentration;**
- **Increasing of Rare Earths, Sr and Zr concentration, with a maximum at 10 km;**
- **Increasing of Ca concentration on East and West directions, with no regular variation on Northeast and Northwest directions.**

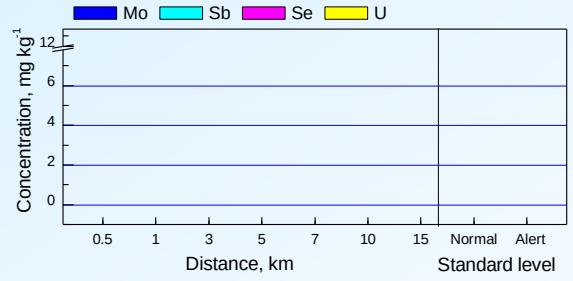
Elemental concentrations of soil in the vicinity of TURNU fertilizer plant

East

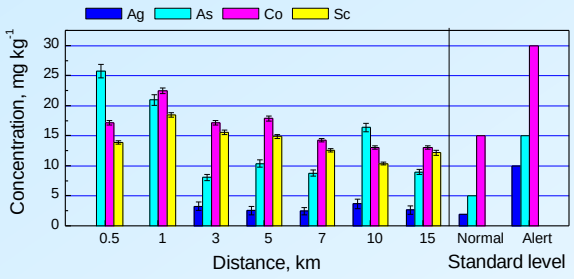


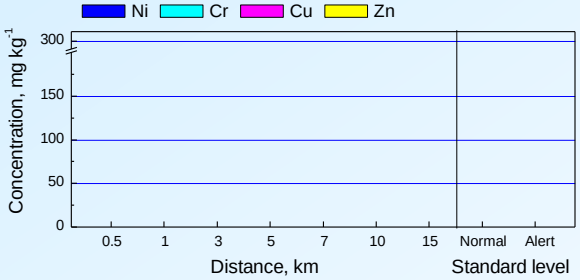


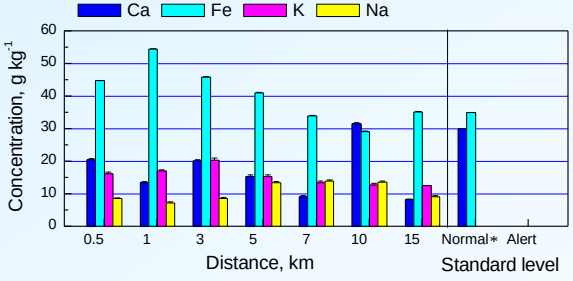


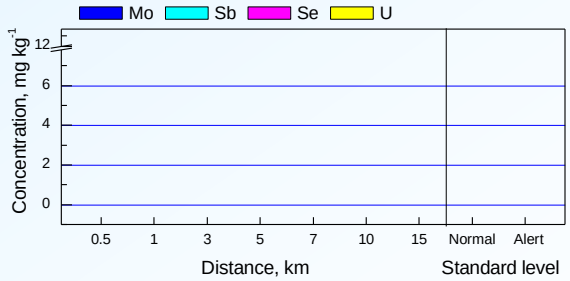


Nord-East

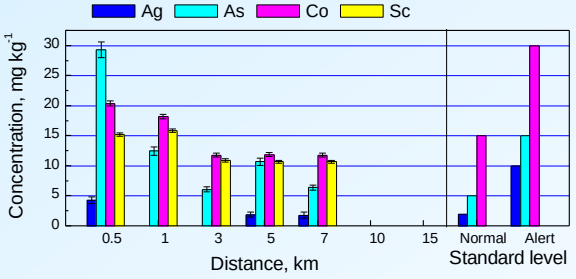


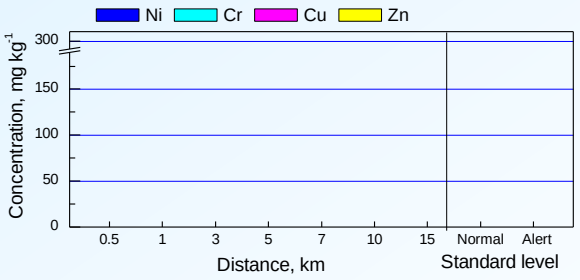


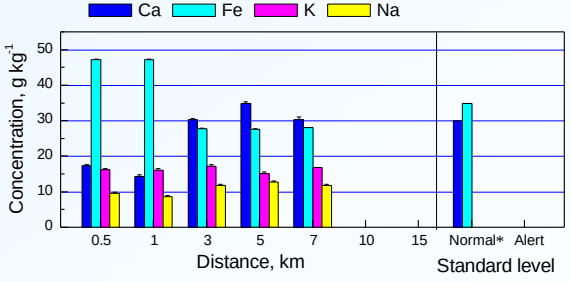


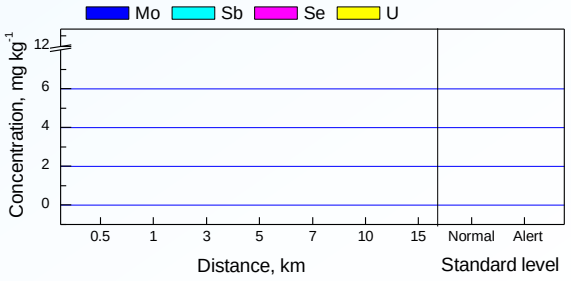


West









Standard level: Monitorul Oficial al Romaniei, Part.1, No. 303 bis/6.XI/1997; * Ontario Ministry of the Environment (USA), 1990; S.Dudka et.al./ Sci.Total Environ. 162 (1995) 161-171

Soil pollution around TM fertilizer plant

Higher element concentrations in Danube floodable soils downstream to the plant, by comparing with the upstream site (0.5-km to the plant) were determined.

The following downstream/upstream ratios (in parenthesis) were found: As (3.4), Au (4.4), Ca (2.4), Cd (> 5.2), Cr (1.8), Hf (1.9), Sb (5.6), Se (14.8), Sr (2.9), U (2.8), Zn (4.8), Zr (2.2), and REE (range from 1.1 to 2.0).

By comparing with the Romanian standards for normal and allert levels in soil, the following maximum ratios (in parentheses) were determined:

- **relative to the normal level: Ag (2.1), As (10.8), Ba (2.4), Co (1.4), Cr (3.9), Mo (2.3), Ni (3.7), Se (1.3), and Zn (2.0);**
- **relative to the low alert level: As (3.6), Ba (1.5), Cr (1.2), Cu (1.1), Ni (1.3), and V (5.3).**
- **relative to the high alert level: As (2.1) and V (2.6).**

Crop vegetation pollution around TM fertilizer plant

Crop samples from the agricultural areas in the vicinity of the plant (0.5 km distance) and a background (control) zone at Bucharest (130 - km Northeastern) were also investigated.

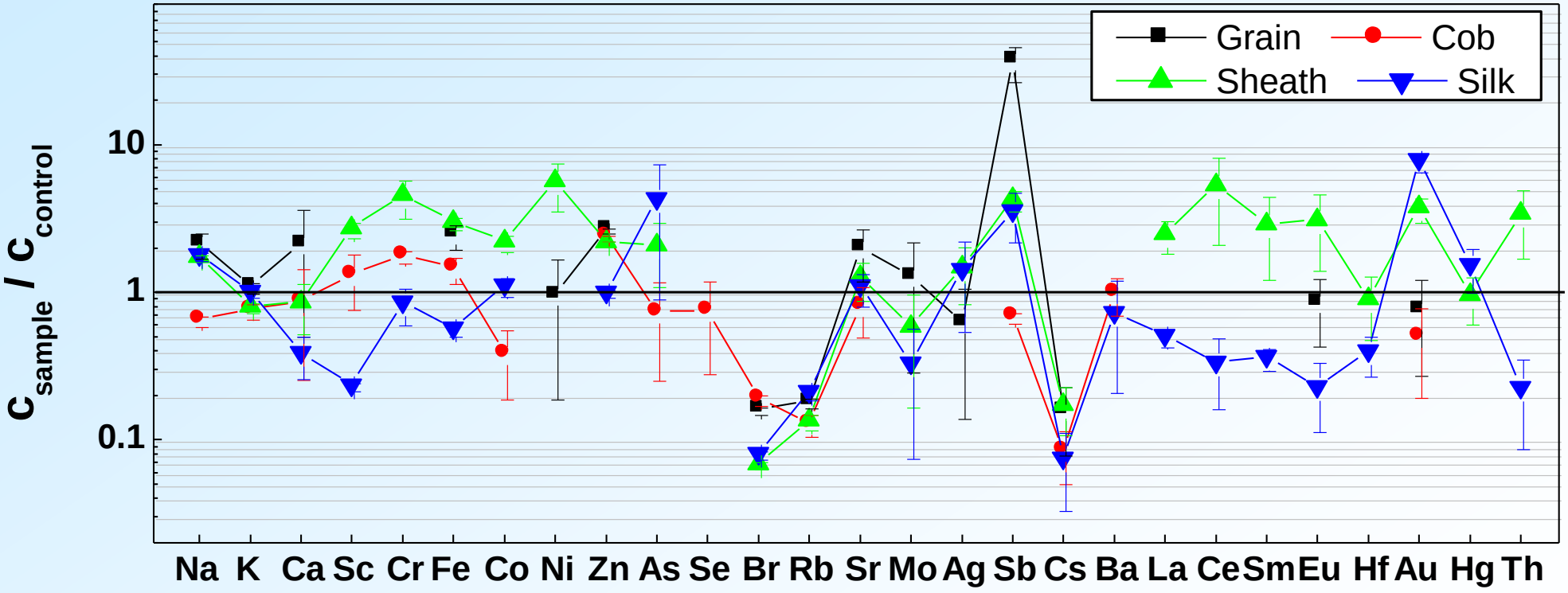
Potato (pulp and peal) and carrot (pulp and leaves) samples were collected from A3 (West) area, while ears of corn (grain, cob, sheath, and silk) from A7 and A8 (Northern) areas.

- **Relative to the control zone Bucharest (130 km NE), significant higher element concentrations in vegetal samples grown in the vicinity of the fertilizer plant were put in evidence in vegetables (carrot and potato), and in a smaller degree in maize.**
- **Significant lower element concentrations in the vicinity of the fertilizer plant than of Bucharest area are noted for Br, Cs, and Rb in all crops samples (ratios between 2 and 15).**

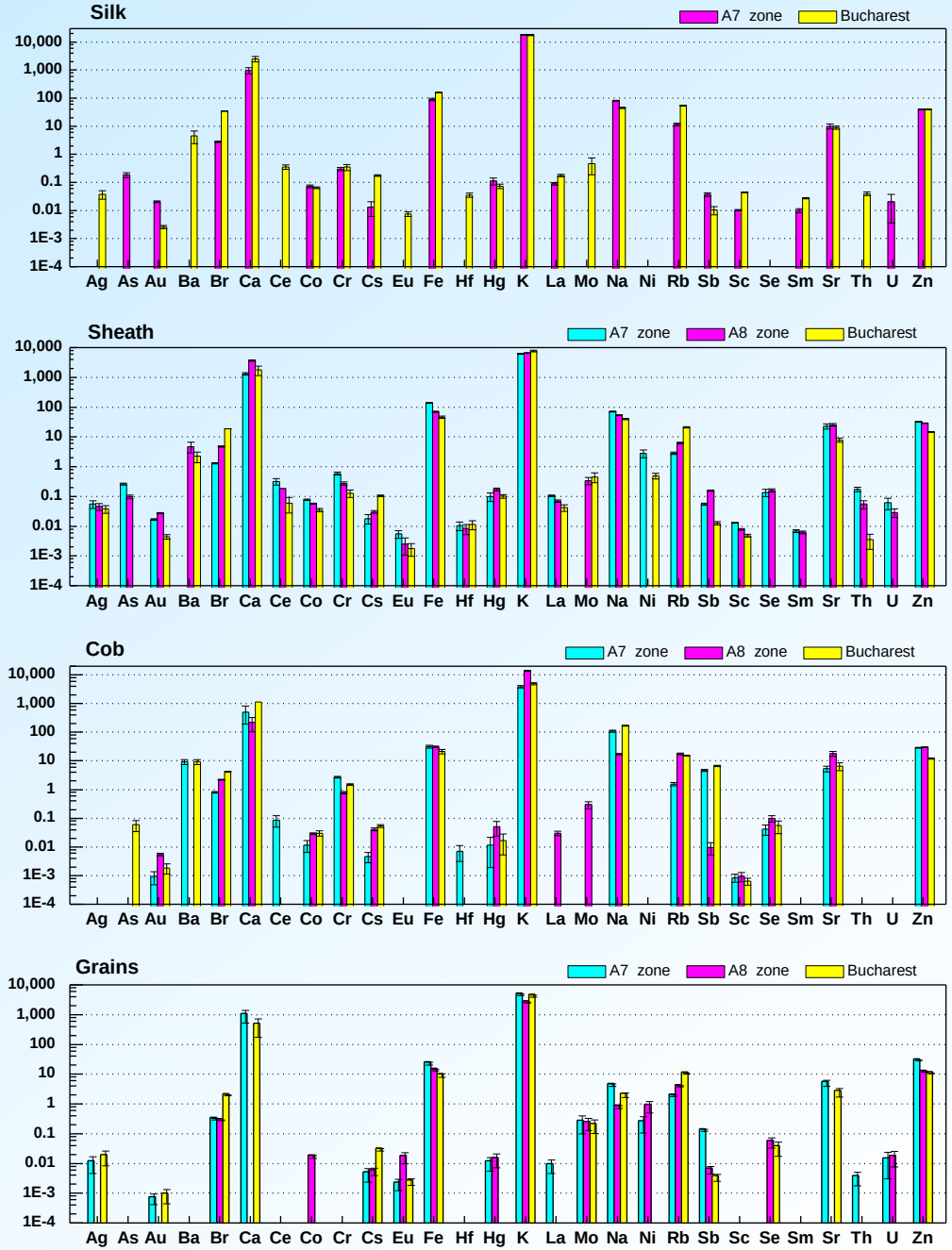
Crop vegetation pollution around TM fertilizer plant

- **Relative to the control zone, significant higher concentrations were found for various elements in carrot and potato, and to a lower degree also in the maize (ear of corn) grown in the vicinity of the fertiliser plant.**
- **Both potato and carrot pulp were found to accumulate Fe, Th, Ce, Cr, and Sb, their concentration ratio to control samples ranging between 2 and 10 for the potato and ranging between 50 and 113 for carrot samples. In addition, carrot pulp was found to accumulate As, La, Se, Zn, Sr and U (concentration ratios between 3 and 36).**
- **Fe, Mg, Mn, Ca, Cl, and K concentration values in carrot pulp, as well as Fe and Cl in potato pulp were found to exceed the normal levels, while those of As, Zn, and Hg were found to be lower than the maximum allowable levels in Romania.**
- **Significant lower element concentrations in the vicinity of the fertilizer plant than of Bucharest area are noted for Br, Cs, and Rb in all crops samples (ratios between 2 and 15).**

Ratio to control values for the ear of corn cultivated at 0.5 km to the fertilizer plant



Elemental concentrations in ears of corn in the vicinity of TURNU fertilizer plant (0.5 km N), mg kg $^{-1}$



Black Sea Economic Cooperation (BSEC) Project "Garden City"

The Black Sea Economic Cooperation (BSEC) Project "Garden City" (2008-2009), involving Bulgaria (coordinator), Romania, Russia, Serbia, Turkey and Greece, was aimed to study the accumulation of anthropogenically emitted toxic elements by different vascular plants (tree leaves) in order to select species able to accumulate the elements in excessive amounts being tolerant to them.

Besides INAA, applied at JINR Dubna, Proton Induced X-Ray Emmission (PIXE) at the Van de Graff Tandem accelerator of IFIN-HH was used to determine Al, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn and Sr in tree leaves (five species) collected from parks in Bucharest in accordance with the project protocol.

References

Revitalization of urban ecosystems through vascular plants: preliminary results from the BSEC-PDF project, Gorelova S. V., Frontasyeva M. V., Yurukova L., M. Coşkun, A. Pantelica, C.J. Saitanis, M. Tomašević, and M. Aničić, Agrochimica, 55 (2) (2011) 65-84

JINR Dubna - IFIN-HH collaborative projects

The JINR Dubna - IFIN-HH bilateral projects were focused on environmental pollution studies in Romania.

Of highest interest was to determine the level of the potentially toxic elements (e.g. As, Cd, Cr, Fe, Hg, Ni, Se, Zn) in vegetables grown in Romanian industrial sites using INAA technique.

The following industries were considered:

- **phosphorous fertilizer production at Turnu Magurele,**
- **non-ferrous metallurgy at Copsa Mica,**
- **iron and steel metallurgy at Targoviste.**

Vegetables collection

Vegetal species:

- parcel (*Petroselinum hortense*),
- dill (*Anethum graveolens*),
- lovage (*Levisticum officinale*),
- celery (*Apium graveolens*),
- kale (*Brassica oleracea*).

Control zones:

Magurele (Ilfov county)

Crevedia (Dambovita county)

Polluted zones:

Turnu Magurele (phosphorous fertilizer industry)

Târgoviste (iron and steel industry)

Copsa Mica (non-ferrous industry)

Industrial impact on vegetables

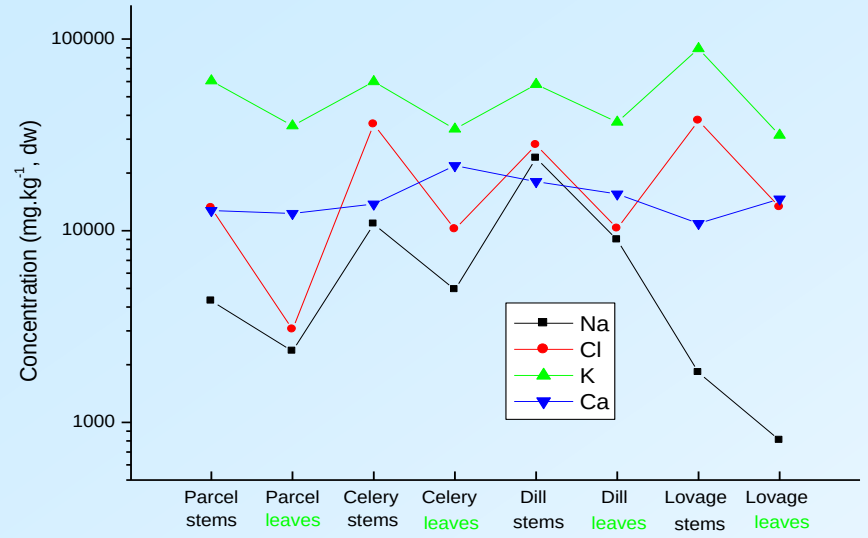
Comparing the leaves and stems morphological parts of five vegetable species (parcel, dill, lovage, celery, and kale):

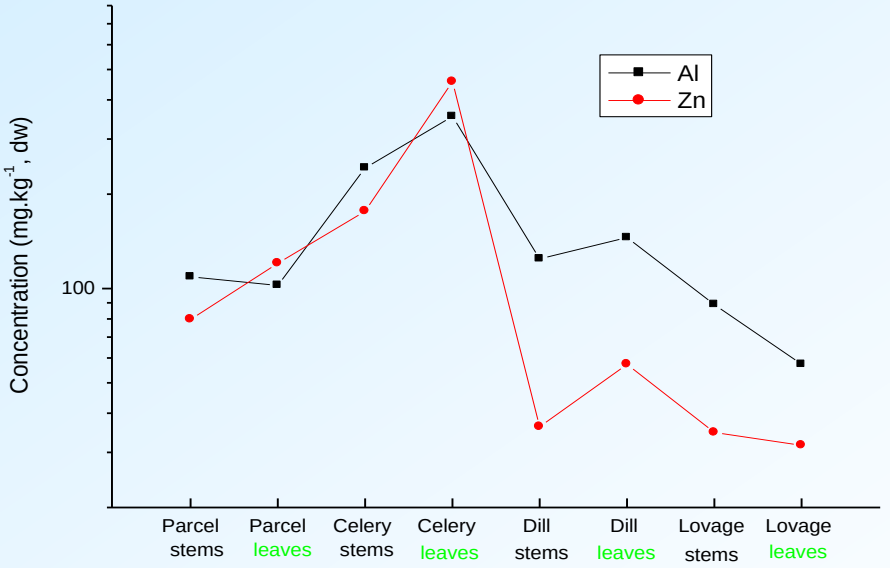
- higher concentrations in stems (d.m.) were observed in all species for Na, Cl, K, Br, Rb, and Sr;
- higher concentrations in stems were also observed for Ba in all species except celery.

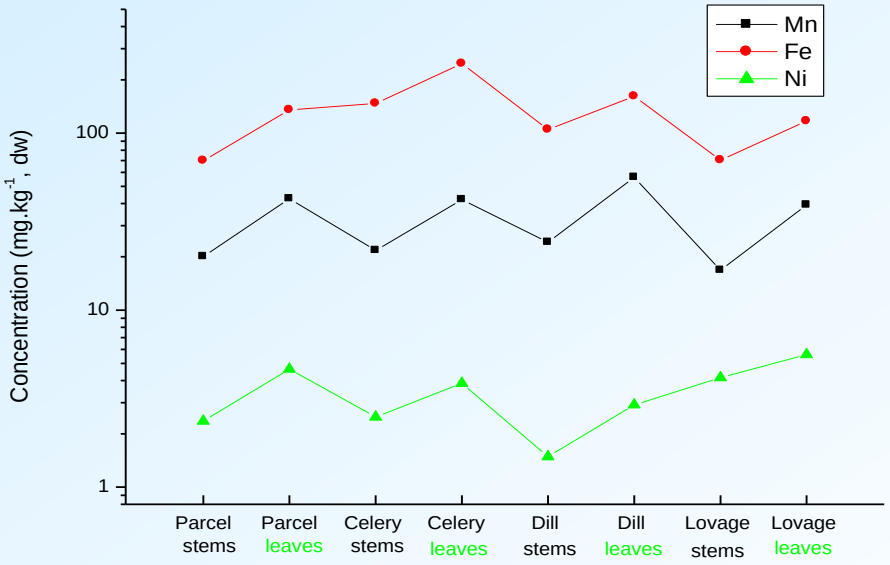
- higher concentrations in leaves (d.m.) were observed in all species for Mg, Mn, Fe, Ni, Mo, Sb, and Au;
- higher concentrations in leaves were also observed for Sc, Zn and Se in all species except lovage, for Cd, Hg and U in celery, and for Co, As, Ag, Cd, Ce, Sm, Hg and Th in kale.

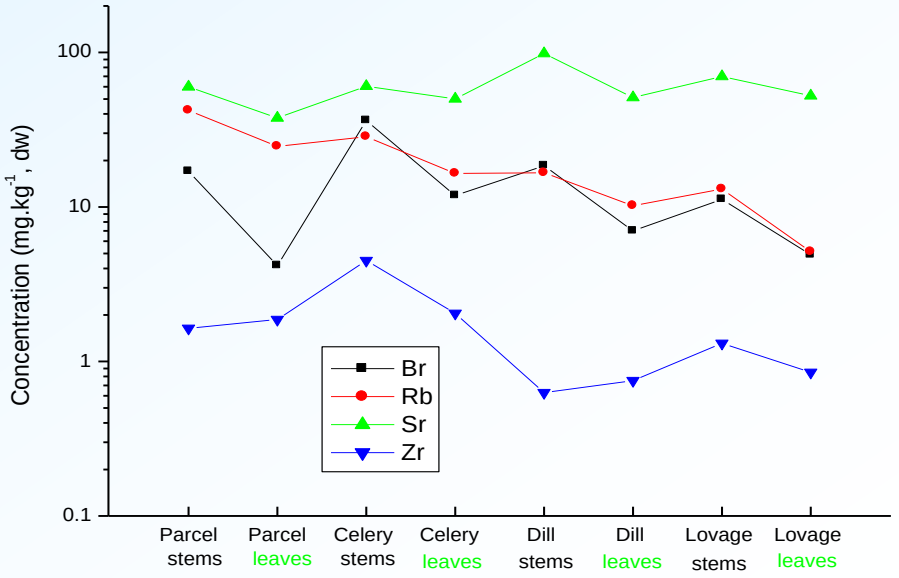
Cl, K, Ca, and Fe concentrations in the investigated vegetables were found to be similar with the normal values in Romania.

Elemental concentrations in leaves and stems of green vegetables by INAA

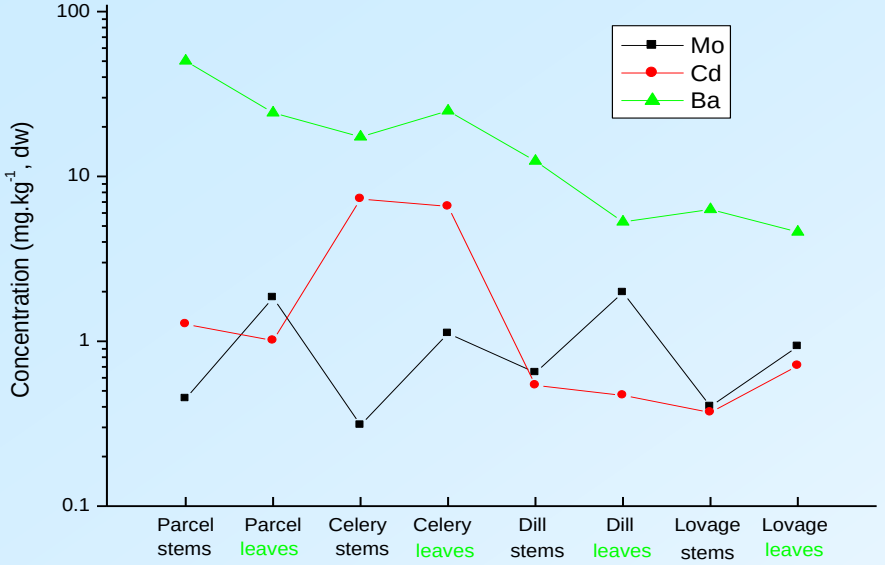


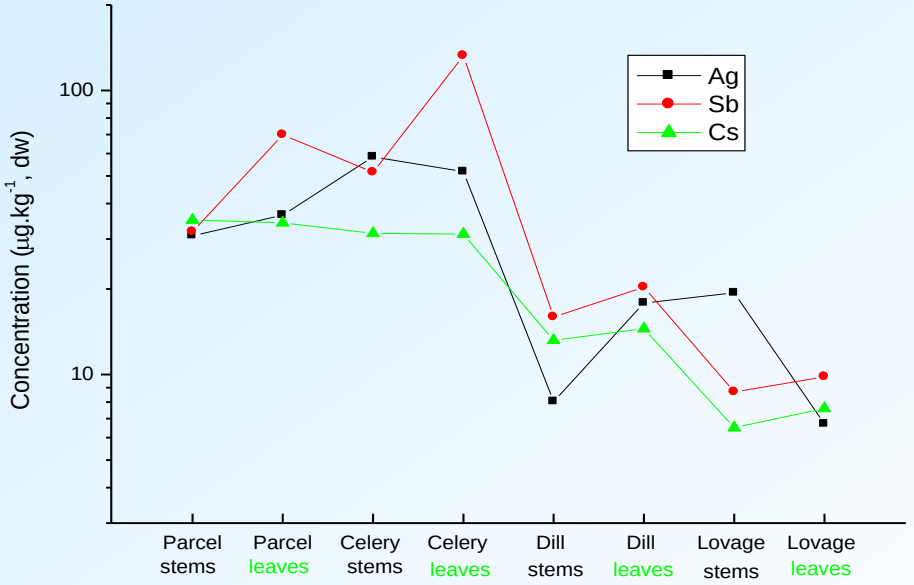


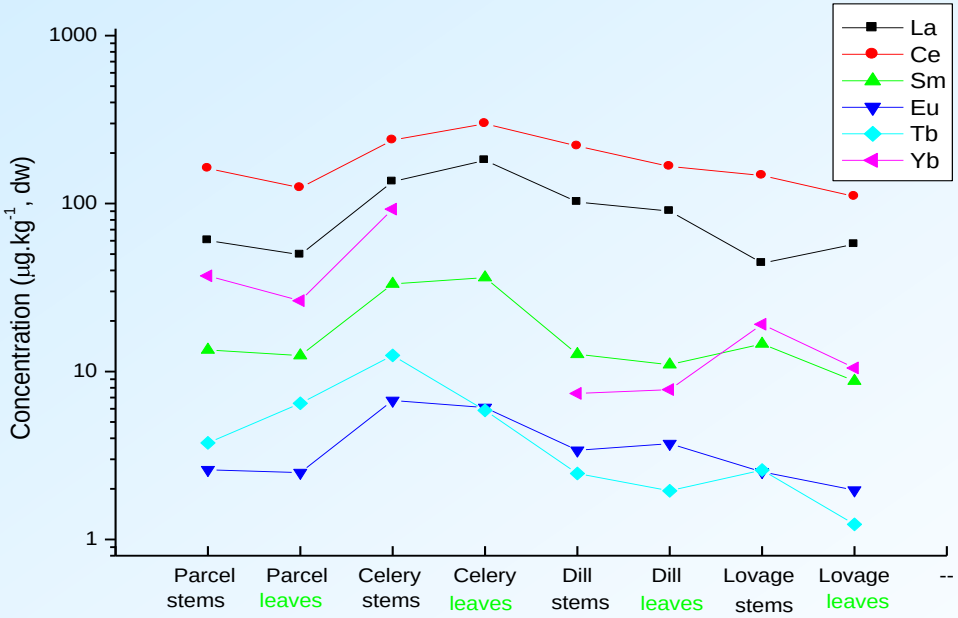


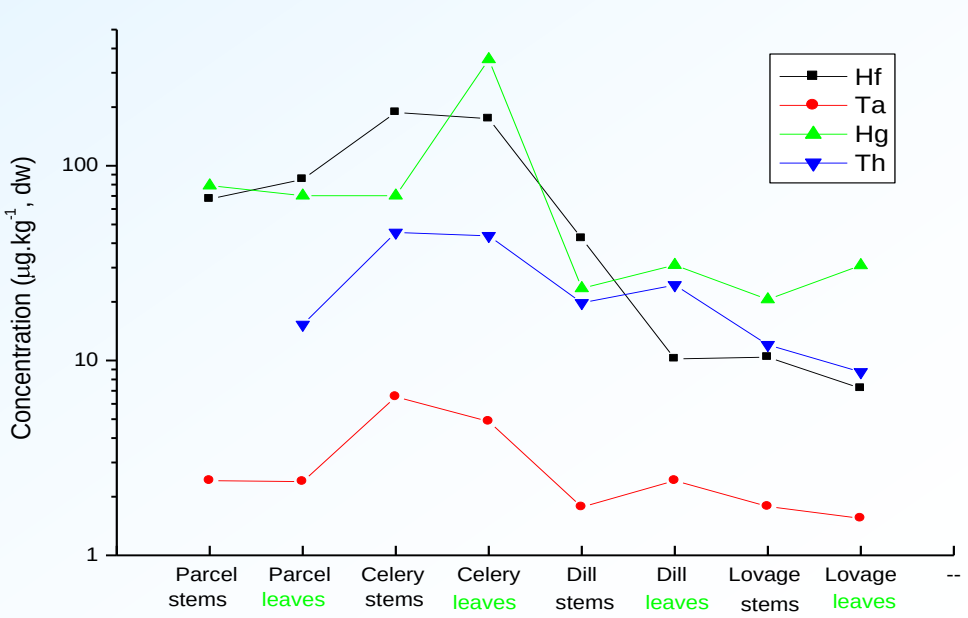


Elemental concentrations in leaves and stems of green vegetables by INAA









Acknowledgement

The authors are indebted to the nuclear reactor staff for the neutron irradiations in INAA.

Thank you for your attention !