Intergovernmental International Organization
Joint Institute for Nuclear Research
Dubna, Moscow Region, Russian Federation

NUCLEAR ANALYTICAL TECHNIQUES USED TO STUDY BOTTOM SEDIMENTS

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SEDNET-7, April 3-6, Dubrovnik, Croatoa

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International Intergovernmental Organization

Armenia
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Romania
Russian Federation
Slovakia
Ukraine
Uzbekistan
Vietnam

Participation of Egypt, Germany, Hungary, Italy, the Republic of South Africa and Serbia in JINR activities is based on bilateral agreements signed on the governmental level.

The work is carried out in the framework of the following programs:

"Geochronology and retrospective study of pollution of unconsolidated sediments from oxygenated and anoxic territories of the Western Black Sea (*Grant of the RFBR – Romania Academy of Sciences, 2008-2009*)

"Control of Land Degradation in the Eurasian Region“ (*Grant of the RFBR, 2015-2017*)

Grants of Plenipotentiaries of the JINR Member-state (*Romania, 2011-2018)* and Associated Member state (*Egypt, 2012-2019*)

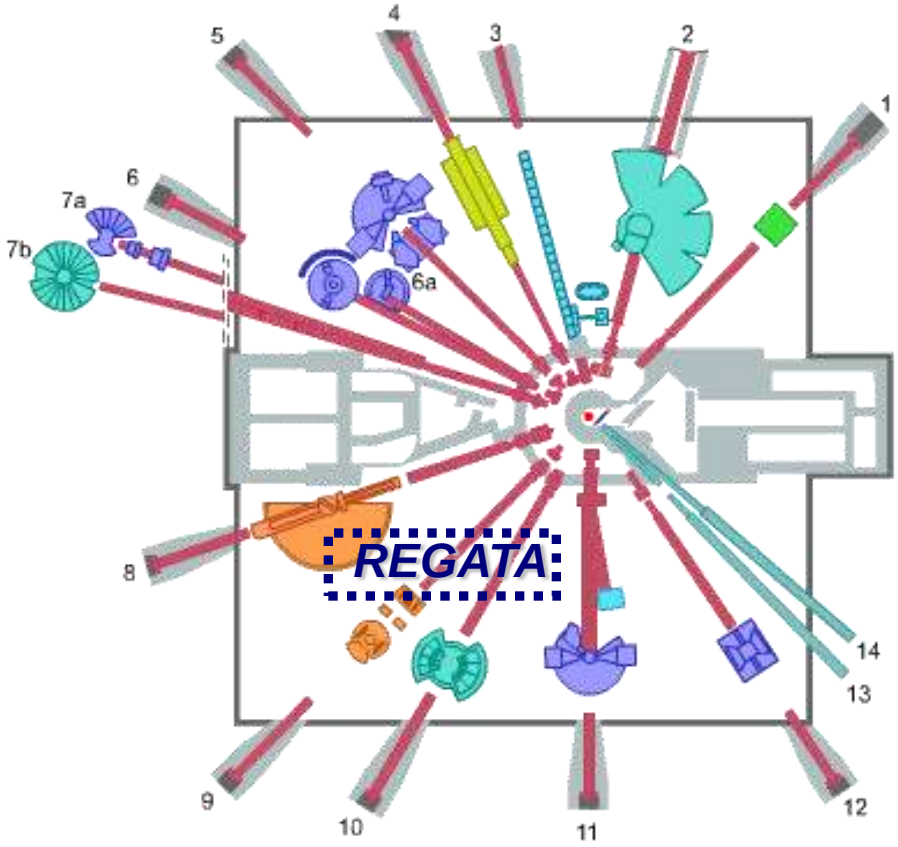
CONTENT

Long-term experience in applying **instrumental epithermal neutron activation analysis** for elemental determination in bottom sediments in aquatic ecosystems in various parts of the world, as well as **gamma-spectrometry of radionuclides** is described.

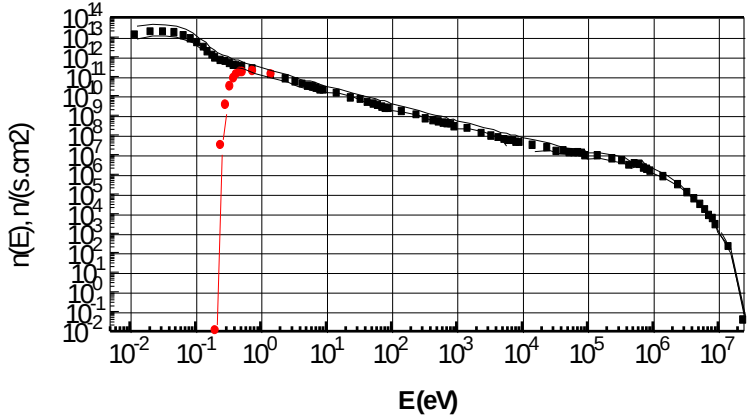
In spite of many other analytical techniques, **reactor activation with epithermal neutrons** is continuing to be most powerful method of muli-element determination with high precision and accuracy. **High-resolution gamma-spectrometry is a non-alternative technique** for tracing natural and man-made radionuclides [2].

NAA at reactor IBR-2
FLNP JINR

Radioanalytical complex REGATA



irradiation channels



Neutron energy spectra in irradiation channels CH1(■) and CH2 (curve)

The main characteristics of the irradiation channels at 1.5 MW

Irradiation site	Neutron flux density (n/cm^2 s) 10^{12}			T ^{0}C	Channel diam., mm	Channel length, mm
	Thermal	Resonance	Fast			
Ch1	Cd-coated	3.31	4.32	70	28	260
Ch2	1.23	2.96	4.1	60	28	260
Ch3	Gd-coated	7.5	7.7	30-40	30	400
Ch4	4.2	7.6	7.7	30-40	30	400

NAA + AAS

H																He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	*Cu*	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	*Cd*	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	*Pb*	Bi	Po	At	Rn
Fr	Ra	Ac**											Rf	Db	Sg	Bh	Hs
	*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
	**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw		

NAA ~ 55 elements

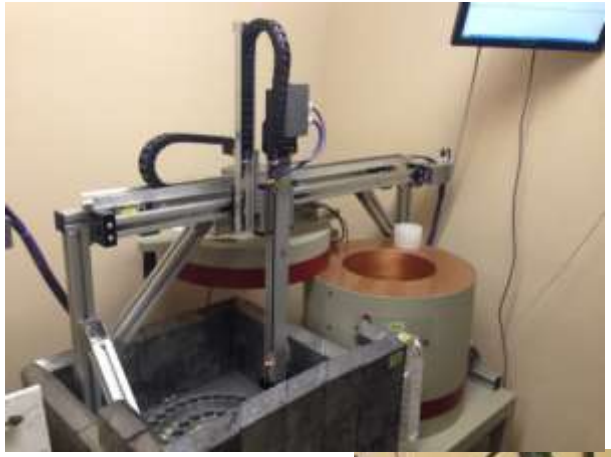
IAEA
International Atomic Energy Agency

TITLE OF RESEARCH CONTRACT:

Automation of Reactor Neutron Activation Analysis

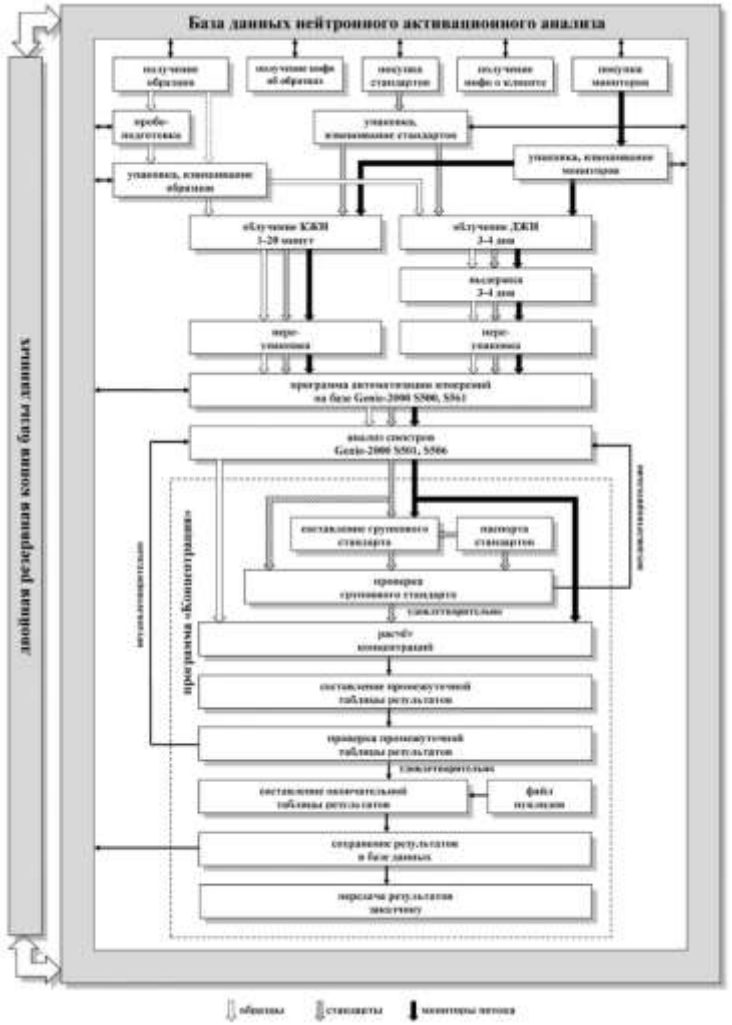
Part of the IAEA's Coordinated Research Project (CRP):

Development of an Integrated Approach to Routine Automation of Neutron Activation Analysis
(Ref. F1.20.25 / CRP1888)



NAA DATABASE

Software package for NAA at IBR-2

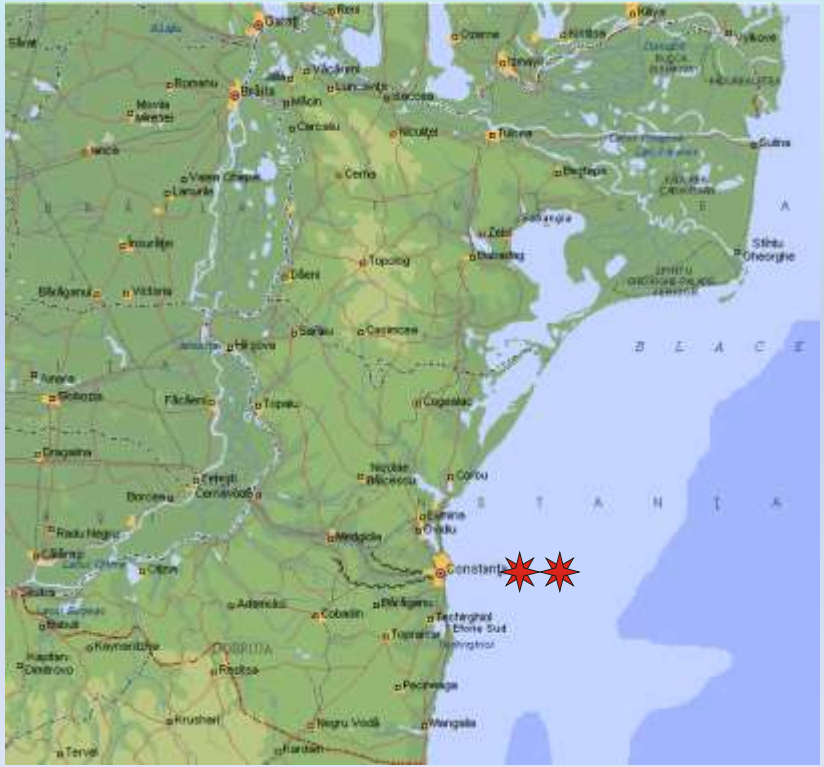


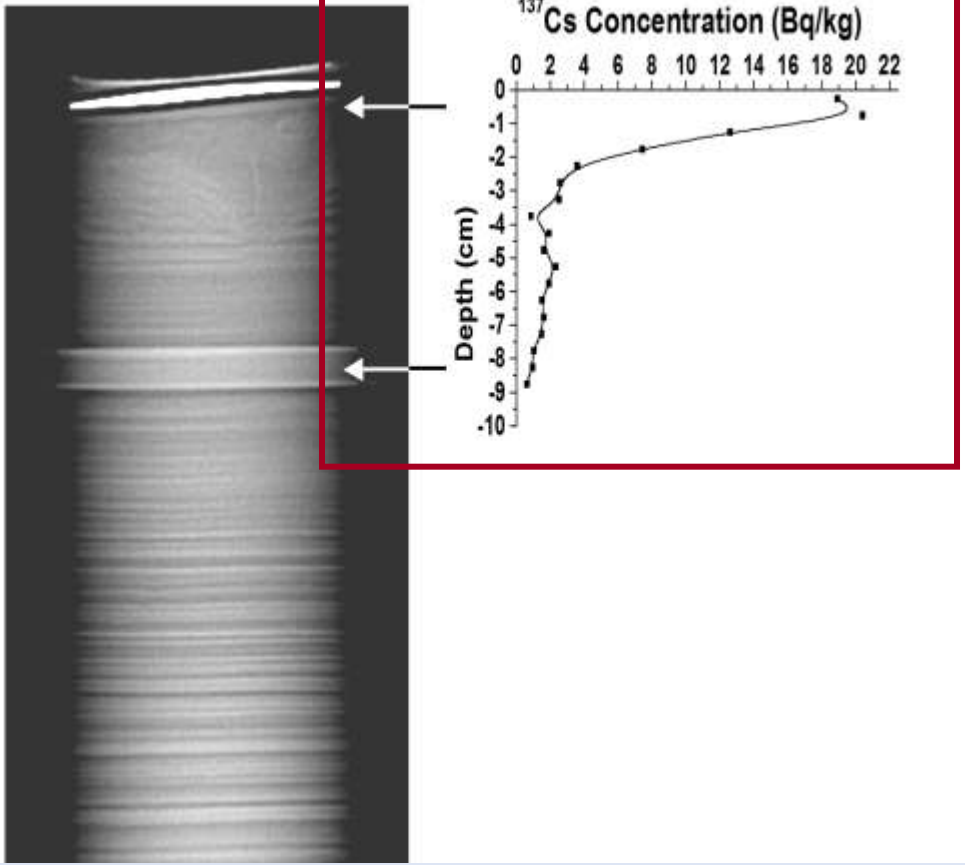
Inspection visit of IAEA representative, Mr. Danas Ridikas,
coordinator of IAEA CRP “Development of an Integrated Approach to Routine Automation of Neutron Activation Analysis”

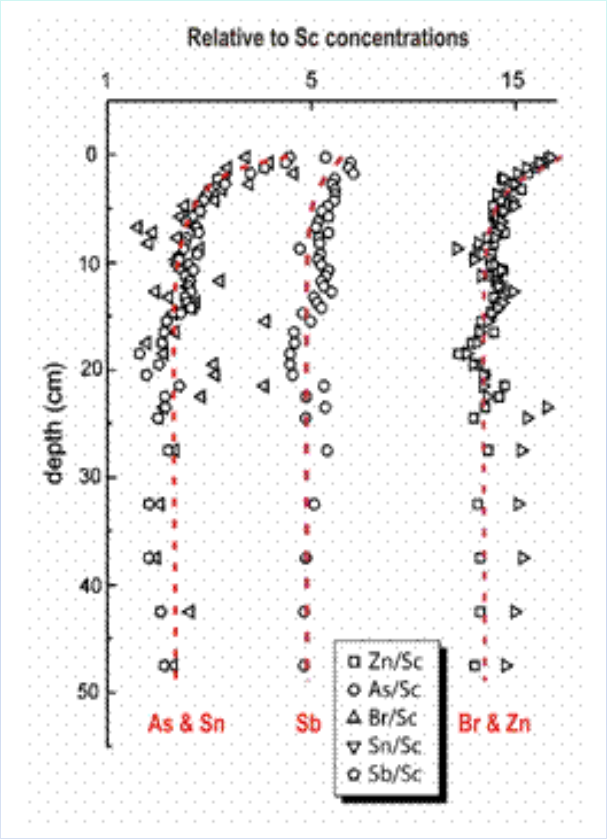
(he is coming to BioMAP-8 in July 2018)

Romania

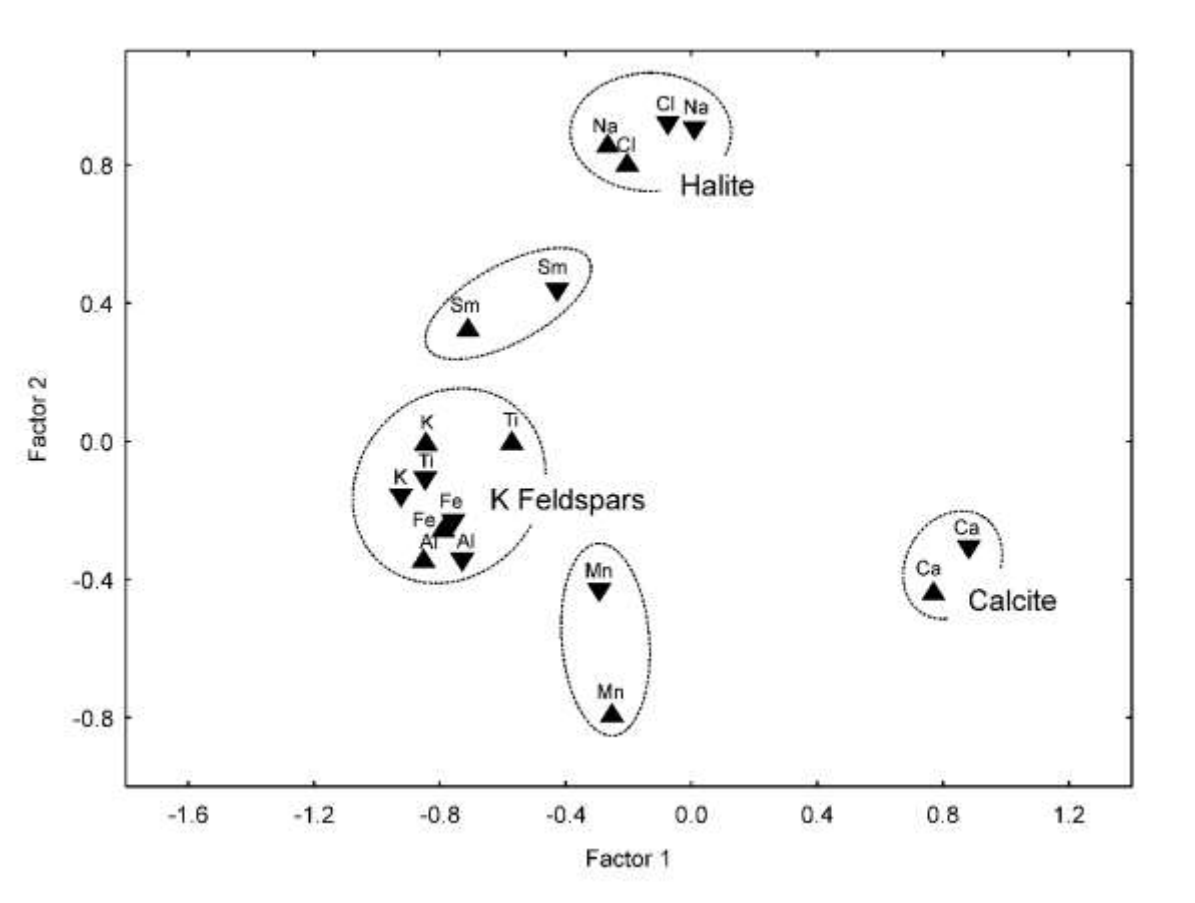
Geochronology and retrospective study of pollution of **unconsolidated sediments** from oxygenated and anoxic territories of the Western Black Sea




^{137}Cs Concentration (Bq/kg)
0 2 4 6 8 10 12 14 16 18 20 22
Depth (cm)
0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10


Relative to Sc concentrations
1 5 15
depth (cm)
0 10 20 30 40 50
As & Sn
Sb
Br & Zn
Zn/Sc
As/Sc
Br/Sc
Sn/Sc
Sb/Sc

Black Sea sediments: PCA of ENAA



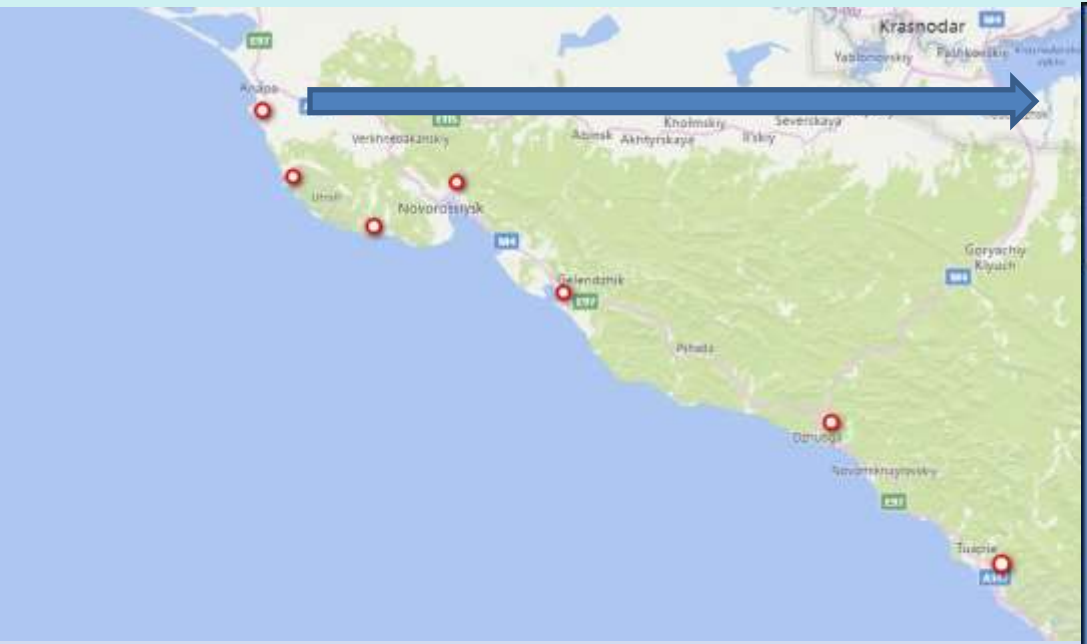
Russian Federation

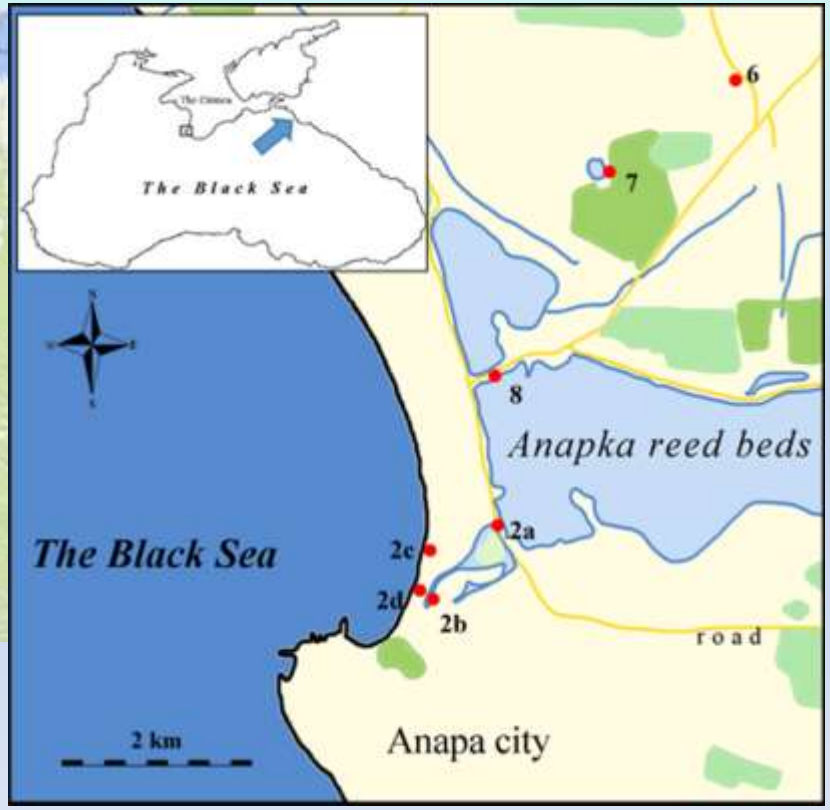
JINR Award (II PRIZE of 2017) for the cycle of papers in the field of applied research

Neutron activation analysis for ecological state assessment of the coastal ecosystems of the Black Sea

“

Study area: north-eastern part of the Black sea (RF)


Krasnodar
Anapa
Novorossiysk
Gelendzhik
Goryachiy Klyuch
Tuapse


The Black Sea
6
7
8
Anapka reed beds
The Black Sea
2a
2c
2d
2b
road
2 km
Anapa city

Sampling

- hydrophytes
- **bottom sediments**
- water
- coastal soils

➢ at a distance of 20, 40, 60 and 100 meters from the coast in three replications.

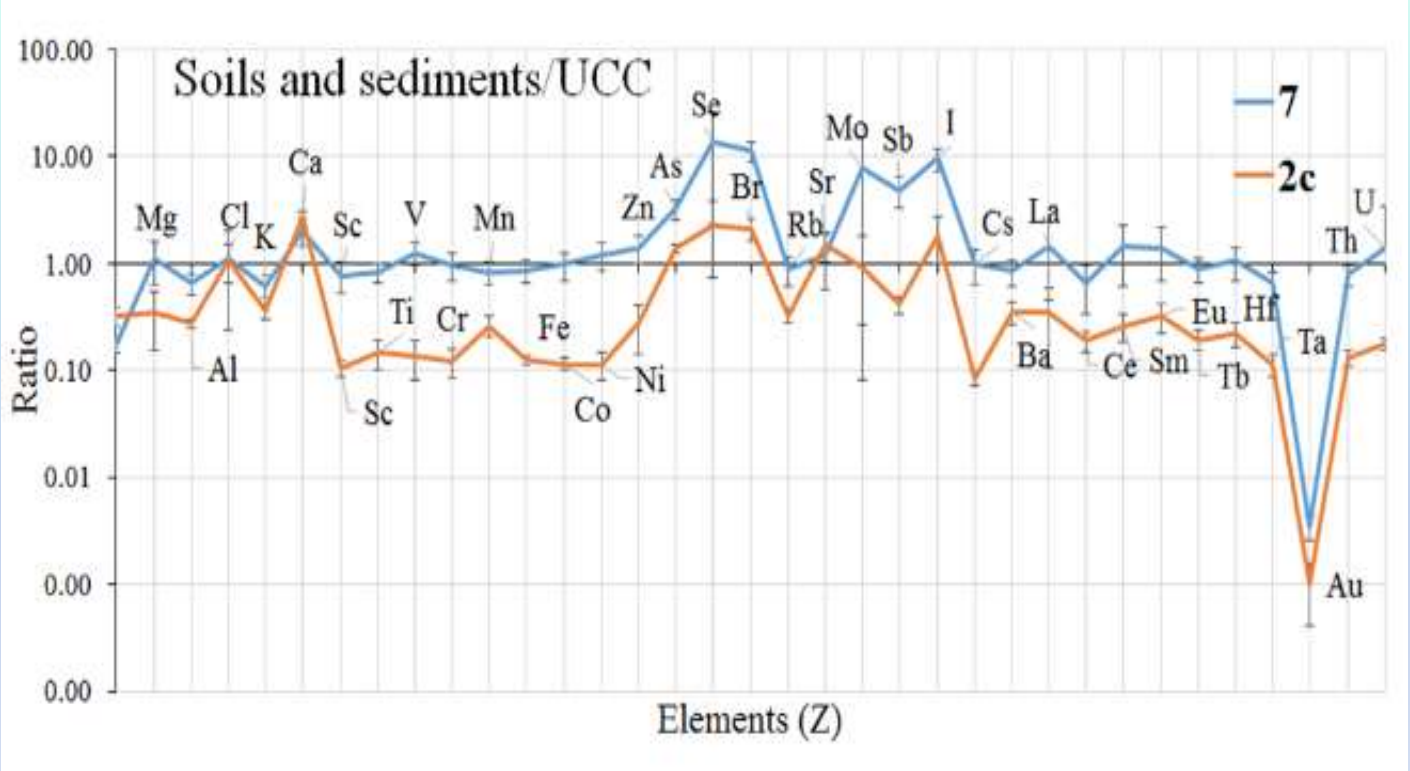
Factors of anthropogenic pollution. Anapa city dump

Dynamics of increasing the area

2003 – 9 ha → **2013 – 26 ha**

Mineral composition of bottom sediments, dry matter (mg/kg)

Lithophilic							Chalkophilic					Siderophilic	
Na	Mg	P	K	Ca	Mn	Sr	S	Cu	Zn	As	Cd	Pb	Fe	Ni
20 m from the coastline (n=9)														
295.0 ±50.4	99.0 ±5.3	89.5 ±7.6	61.3 ±7.3	589.3 ±258.5	30.0 ±8.8	26.4 ±9.3	381.5 ±220.3	6.1 ±0.6	5.2 ±1.3	0.5 ±0.2	0.1 ±0.0	1.4 ±0.4	436.9 ±242.4	1.0 ±0.1
40 m from the coastline (n=9)														
278.0 ±68.5	62.3 ±25.9	49.7 ±19.4	45.3 ±18.1	413.7 ±93.1	24.4 ±4.9	34.5 ±9.1	314.0 ±70.9	5.6 ±0.5	4.0 ±1.1	0.4 ±0.1	0.1 ±0.0	0.8 ±0.4	328.8 ±74.1	0.9 ±0.3
60 m from the coastline (n=9)														
367.4 ±143.6	158.7 ±18.1	67.3 ±20.3	79.2 ±7.8	453.7 ±213.9	32.0 ±20.3	29.7 ±9.8	460.1 ±186.7	5.3 ±0.3	5.4 ±2.0	0.5 ±0.0	0.1 ±0.0	0.4 ±0.1	447.3 ±186.7	0.6 ±0.2
80 м from the coastline (n=3)														
228.0 ±7.2	61.0 ±1.5	732.4 ±17.7	54.0 ±1.1	205.0 ±4.6	20.7 ±0.6	77.6 ±4.5	43.6 ±1.5	4.7 ±0.2	4.2 ±0.2	1.2 ±0.1	0.1 ±0.0	20.4 ±0.0	290.0 ±13.1	0.4 ±0.0
100 м from the coastline (n=3)														
417.0 ±24.5	61.0 ±2.6	463.9 ±21.8	74.5 ±4.0	155.0 ±0.0	9.6 ±0.3	114.5 ±3.5	71.7 ±3.6	5.8 ±0.3	3.2 ±0.1	3.4 ±0.1	0.1 ±0.0	0.2 ±0.0	170.0 ±5.3	0.7 ±0.0
Mean concentration of elements at a distance of 20-100 m from the coastline (n = 33)														
315.1 ±99.2	98.4 ±43.7	165.1 ±216.4	62.4 ±17.1	430.00 ±222.6	26.3 ±13.1	42.2 ±28.4	325.6 ±204.0	5.6 ±0.6	4.6 ±1.5	0.8 ±0.9	0.1 ±0.3	0.8 ±0.5	372.6 ±180.4	0.8 ±0.3



Elemental content in soils and sediments normalized on UCC for two stations in the study area of the Russian Black Sea coastline

Nekhoroshkov et al. (2017) *American Journal of Analytical Chemistry* **8**(04):225-244

Conclusions

- The increase with the removal of the **Sr, As** and **P** content from the coastline suggests that their accumulation in the bottom sediments may be associated with biogenic processes
- The group of lithophilic and siderophilic elements is characterized by the highest dispersion, and chalcophilic elements (**S, As, Cd, Cu**) - by concentration (or its tendency)
- Shallow-water part of the Taman Bay in the area of the village of Sennoy as a conditionally pristine background area. It was shown that in this area a certain part of **Ca, S, Fe** and **Pb** enters the sea with the coastal runoff, but in the coastal zone some of these elements settle and accumulate in bottom sediments

- **how did your involvement in this project benefitted/increased the competencies of your work/laboratory so far**

M. Frontasyeva and A. Kamnev. Ecology and Society. Impacted ecosystems. Part 1. *Chemistry-Didactics-Ecology-Metrology*. Vol. 23, No. 1-2, 2018, p. 7-29; DOI: 10.1515/cdem-2018-0001 CHEM DIDACT ECOL METROL

Egypt

The effect of a rise in the sea level on the Nile Delta due to global warming

Why is this study so important?

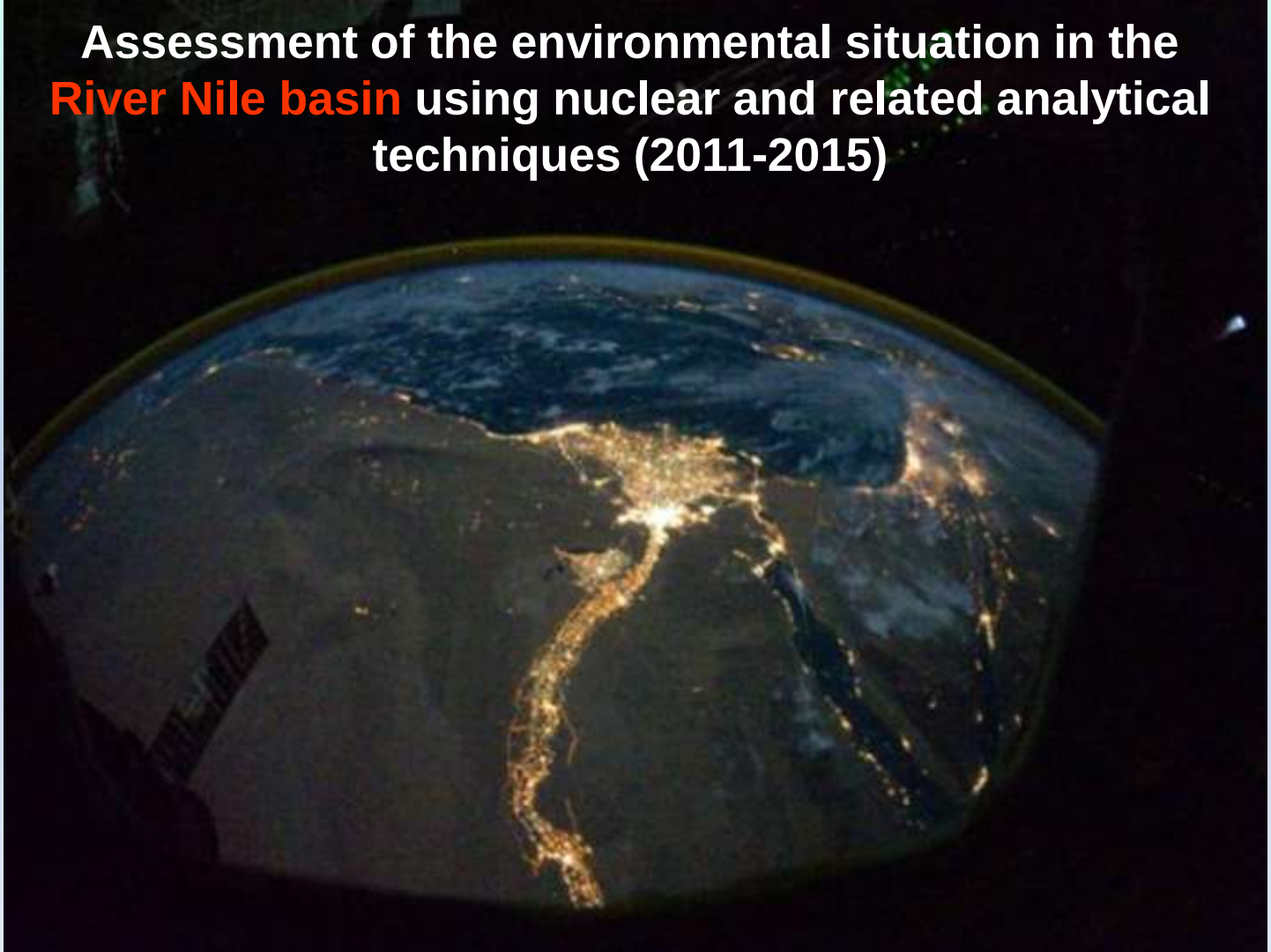
In case of global warming the Mediterranean sea water will be flooding new areas as shown in the previous slide. When finally soil surface will be cover by sea water, any metals fixed to the soil particles may be released for two reasons:

- high concentration of chloride may complex some metals and release them from soil particles, for example, Zn and Cd;
- the redox level in a newly formed sediments may decrease leading to reduction of some metals. Typical examples are reduction of Mn(IV) to Mn(II) and Fe(III) to Fe(II).

In both cases metals become more mobile. Change in redox level and ionic strength would also affect the chemical form of other metals. **When metals are released to sea water, they may become more available for uptake in aquatic organisms used for human food such as fish and other marine biota.**

Assessment of the present-day situation in the densely populated delta of the Nile river will provide **the base-line information for further predictions and actions**

Assessment of the environmental situation in the River Nile basin using nuclear and related analytical techniques (2011-2015)



Spokesman from JINR: Assoc. Prof., Dr. **Marina Frontasyeva**,
Department of Neutron Activation Analysis and Applied Research (NAA & AR), Division of Nuclear Physics,
Frank Laboratory of Neutron Physics

Co-spokesman from Egypt: Prof., Dr. **Hussein El Samman**,
Faculty of Science, Menoufia University Shibin El-koom, Egypt

Institutes of Egypt: *Menoufia University*, Shibin El-koom

South Valley University, Aswan

Tanta University, Tanta

Alexandria University

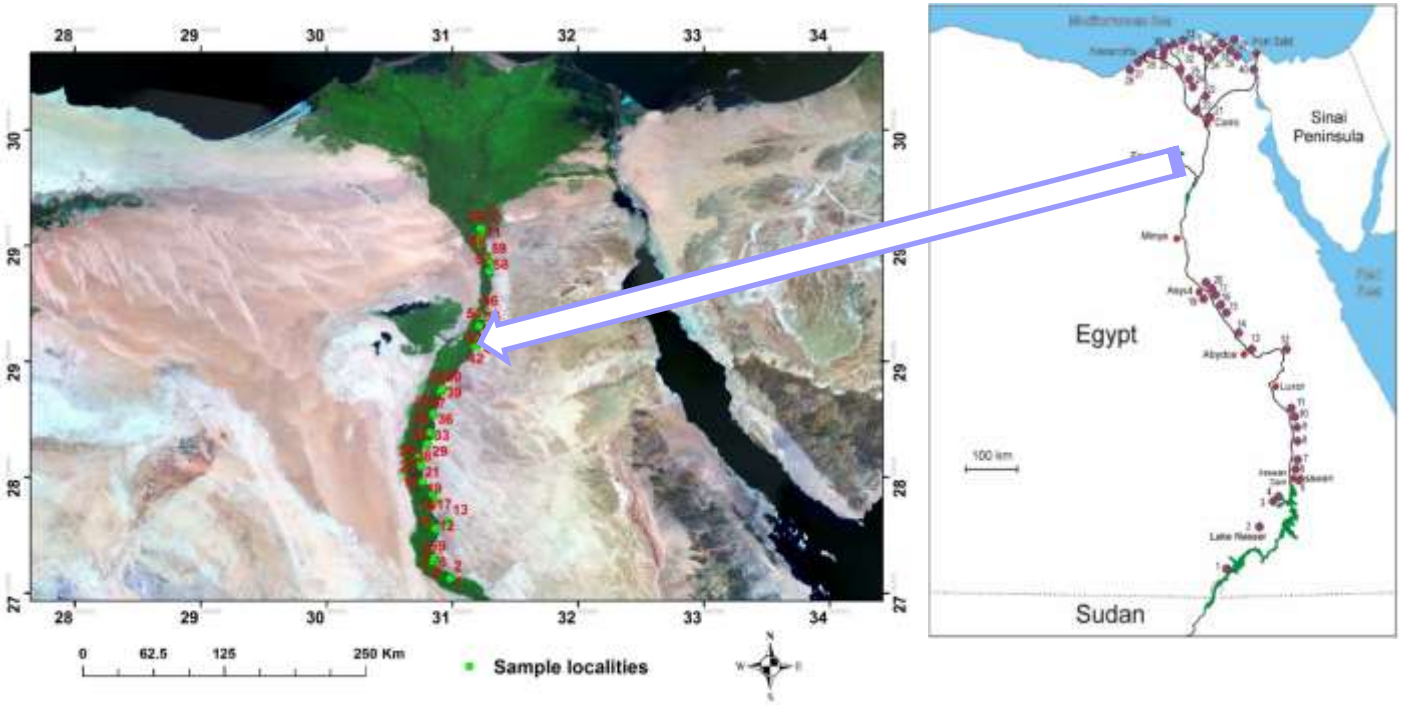
Egyptian Atomic Energy Authority

Academy of Sciences of Egypt
(Prof**. Tarek Hussein**)

Leaders of the project**,** Prof. **Hussein El Samman** (Egypt), Dr. **Marina Frontasyeva** (JINR, RF) and associates discussing the project (first on the right is **Khaled Ali Mohanned** who will come to Dubna in December 2011 to participate in NAA of the Egyptian samples

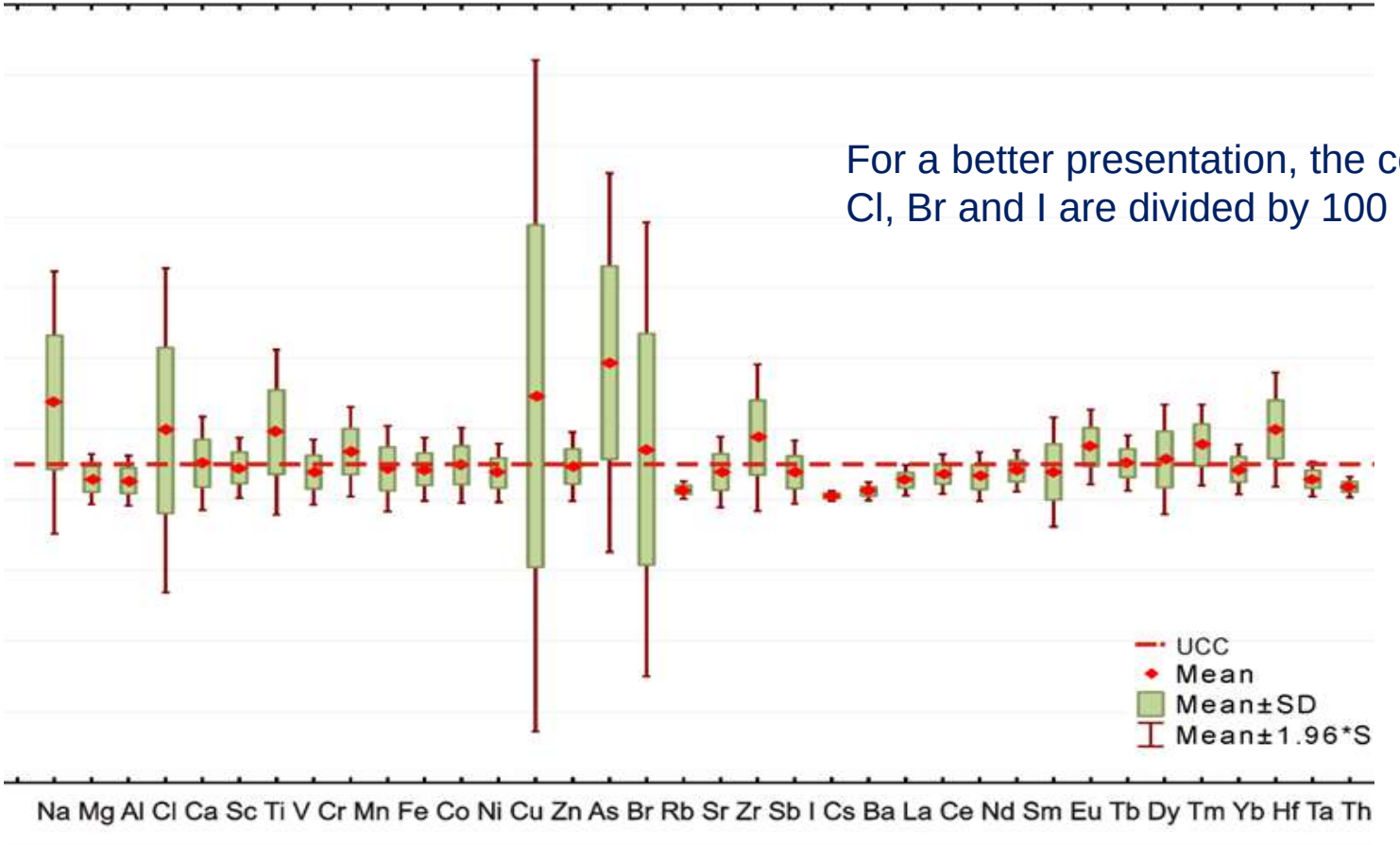

6N
5N
3N
17N
8N
10N
2N
4M
3M
2M
1M
21S
20S
18S
24S
19S
27S
E61
E4
E55
E63
E62
E32
E34
E38
E21
E28
E35
E23
E25
E3
E5
E1
11w
10w
9w
12w
13w
14w
15w
15k
11k
12k
17k
7K
6K
13k
10k
2K
1K
4K
9k
8K
Google

Extension of the study in 2015-2016



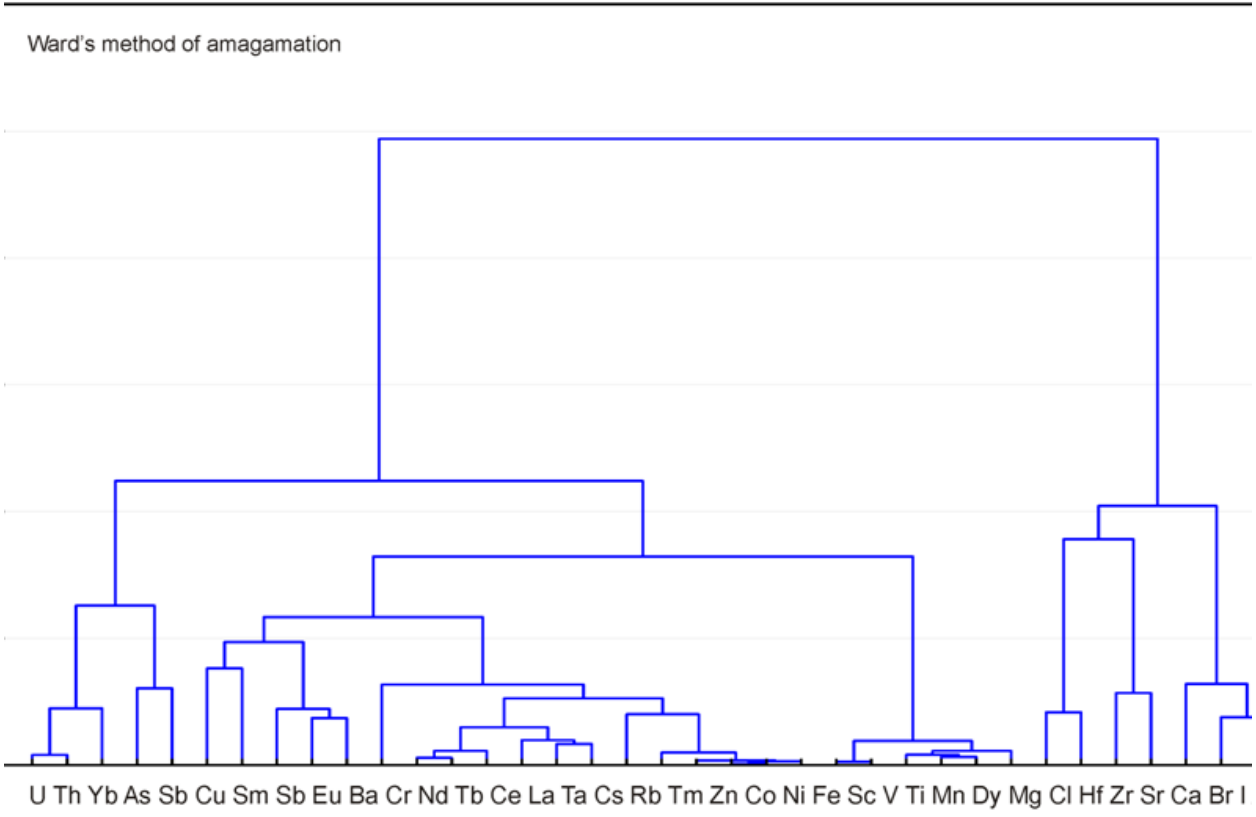
Published in the same Journal “African Soil Science”

The box and whiskers diagram of the content of all 37 considered elements from Nile valley sediments and soils normalized to **Upper Continental Crust** (UCC).

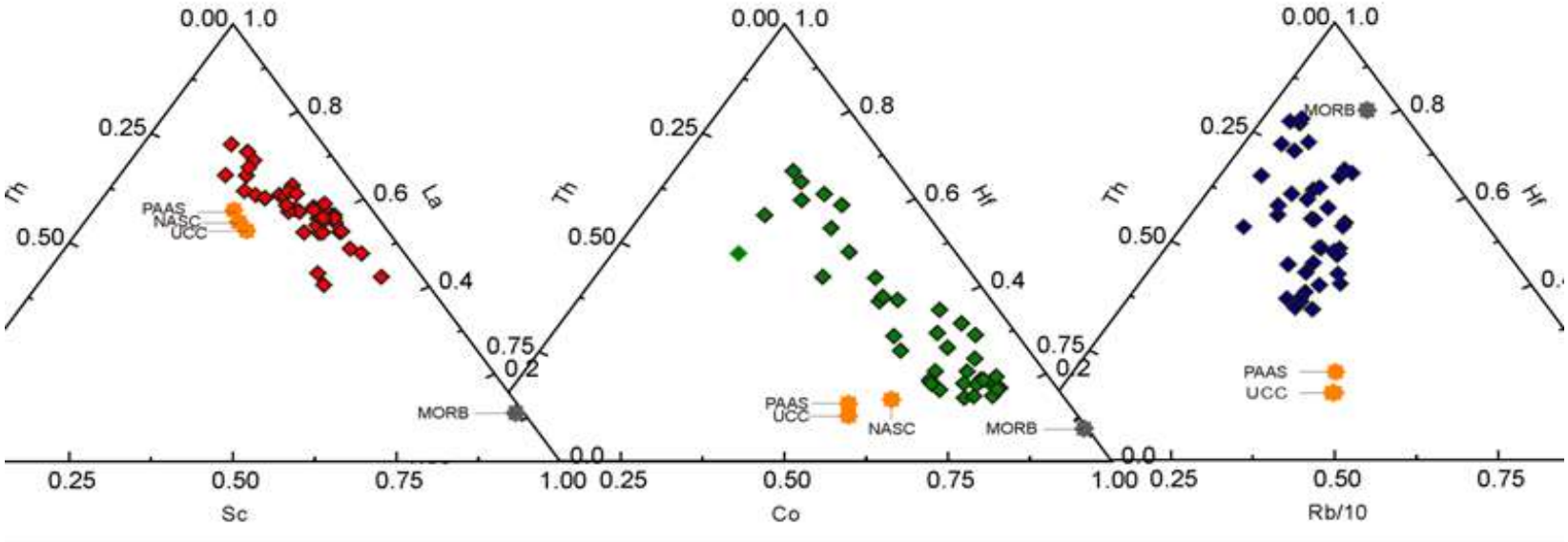


For a better presentation, the content of Cl, Br and I are divided by 100

The tree diagram (r Pearson correlation coefficient) regarding all 37 investigated elements



The ternary diagrams La-Sc-Th, Co-Hf-Th and Rb/10-Hf-Th illustrating the existing differences between Nile sediments and soils and sedimentary **Upper Continental Crust** (UCC), **North American Shele Composite** (NASC) and **Post Archean Average Shale** (PAAS), as well as igneous **Mid-Ocean Ridge Basalt (**MORB)



Wafaa M. Arafa, Wael M. Badawy, Naglaa M. Fahmi, Khaled Ali, Mohamed S. Gad, Octavian G. Duliu, Marina V. Frontasyeva, Eiliv Steinnes

Geochemistry of sediments and surface soils from the Nile delta and lower Nile valley studied by epithermal neutron activation analysis

African Earth Sciences. No. 107, **2015,** p. 57-64. Elsevier ***(Impact Factor 2.2)***

W.M. Badawy, E.H.Ghanim, O.G. Duliu, H.El Samman, M. V. Frontasyeva

Major and trace element distribution in soil and sediments from the Egyptian Central Nile valle

African Earth Sciences. No. 131, **2017**, p. 53-61. Elsevier ***(Impact Factor 2.2)***

Journal of
Computational and Theoretical Nanoscience
Vol. 14, 1357–1361, 2017

Modeling the Coordination Between Na, Mg, Ca, Fe, Ni, and Zn with Organic Acids

Ali Okasha[1], Diaa Atta[1], Wael M. Badawy[2,3], Marina V. Frontasyeva[3,*], Hanan Elhaes[4], and Medhat Ibrahim[1,*]

[1] *Spectroscopy Department, National Research Centre, 33 El-Bohouth Str. 12622 Dokki, Giza, Egypt*
[2] *Radiation Protection and Civil Defense Department, Nuclear Research Center, Egyptian Atomic Energy Authority (EAEA), 13759 Abu Zaabal, Egypt*
[3] *Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, str. Joliot-Curie, 6, 141980 Dubna, Moscow Region, Russian Federation, Russia*
[4] *Physics Department, Faculty of Women for Arts, Science, and Education, Ain Shams University, 11757 Cairo, Egypt*

Hydrogen bonding plays an important role in the coordination of metals with organic acids. Density Functional Theory (DFT) at B3LYP/6-31g(d,p) level is conducted to evaluate total dipole moment, HOMO/LUMO band gap energy and geometrical parameters of COOH. Na, Mg, Ca, Fe, Ni, and Zn were coordinated with COOH of acetic and benzoic acid in the presence of two water molecules. C=O is calculated at the same level of theory. Results indicate that the coordination is shifting the characteristic band of COOH and changing the bond distance and bond angles of COOH. The shift

Thank you for attention!