Atomic and Nuclear Techniques in Environmental Studies

Octavian G. Duliu
University of Bucharest
JINR Dubna

Project and its Main Aims

It is a long lasting project involving researchers from more countries of which main goals consisted of getting and interpreting the experimental data prone to characterize the actual status of diverse environments such as recent unconsolidated sediments, soils, biota or to evidence and numerically characterize the anthropogenic influence

Methods

For a complex characterization we have used more Analytical Methods such as Alpha, Beta and Gamma ray Spectrometry, ICP – AAS, Computed Tomography, Neutron Activation Analysis, or X-ray Diffraction to which we have included Statistical Data Analysis e.g. Time Series or Principal Component, Discriminant and Cluster Analysis

Materials/Samples

- - Mosses and lichens from Livingstone Island, Antarctica, Moldova and Western Tajikistan
- River sediments and adjacent soils from Nile River (Egypt), Varzob, Sioma and Zarafshon (Tajikistan)
- - Black Sea euxinic sediments
- - Soil from Moldova

What we have investigated

- 38 to 41 major and trace elements including seven REE, Th and U
- Five Presumably contaminating elements V, Cr, Mn, Ni, Zn, As, Sb by INAA and Cu, Cd and Pb by ICP-AAS
- Sedimentary cycles

What we have investigated

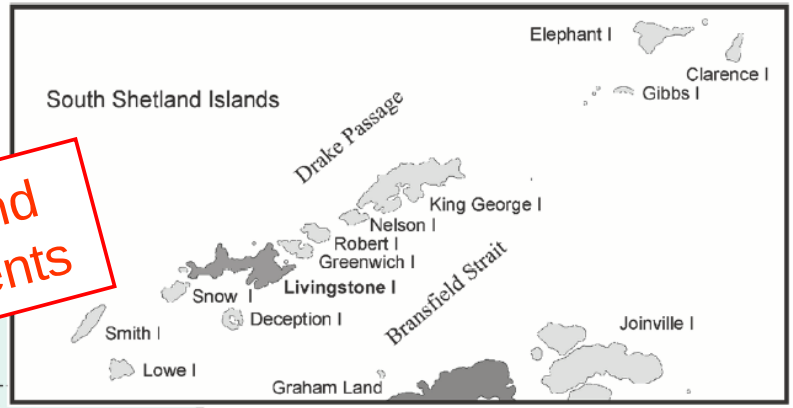
- 38 to 41 major and trace elements including seven REE, Th and U
- Five Presumably contaminating elements V, Cr, Mn, Ni, Zn, As, Sb by INAA and Cu, Cd and Pb by ICP-AAS
- Sedimentary cycles

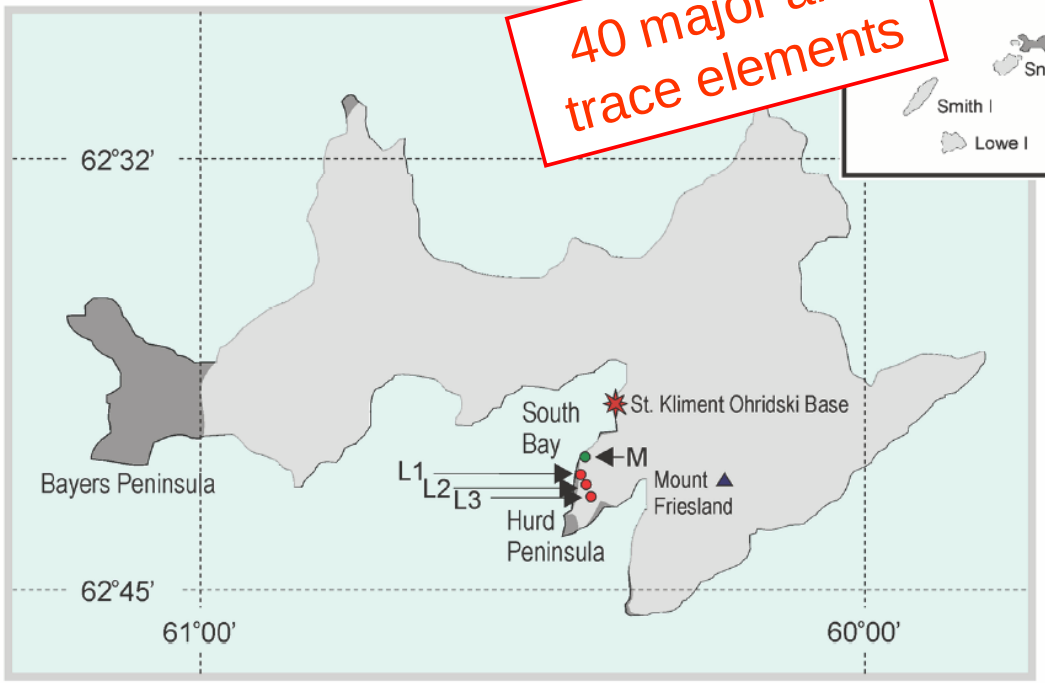
Results and Discussion
Environmental contamination

Livingstone Island, Antarctica

30 mosses (*Polytrichastrum alpinum, Pohlia cruda, Sanionia georgico-uncinata, Syntrichia filaris*) **INAA**

40 major and trace elements





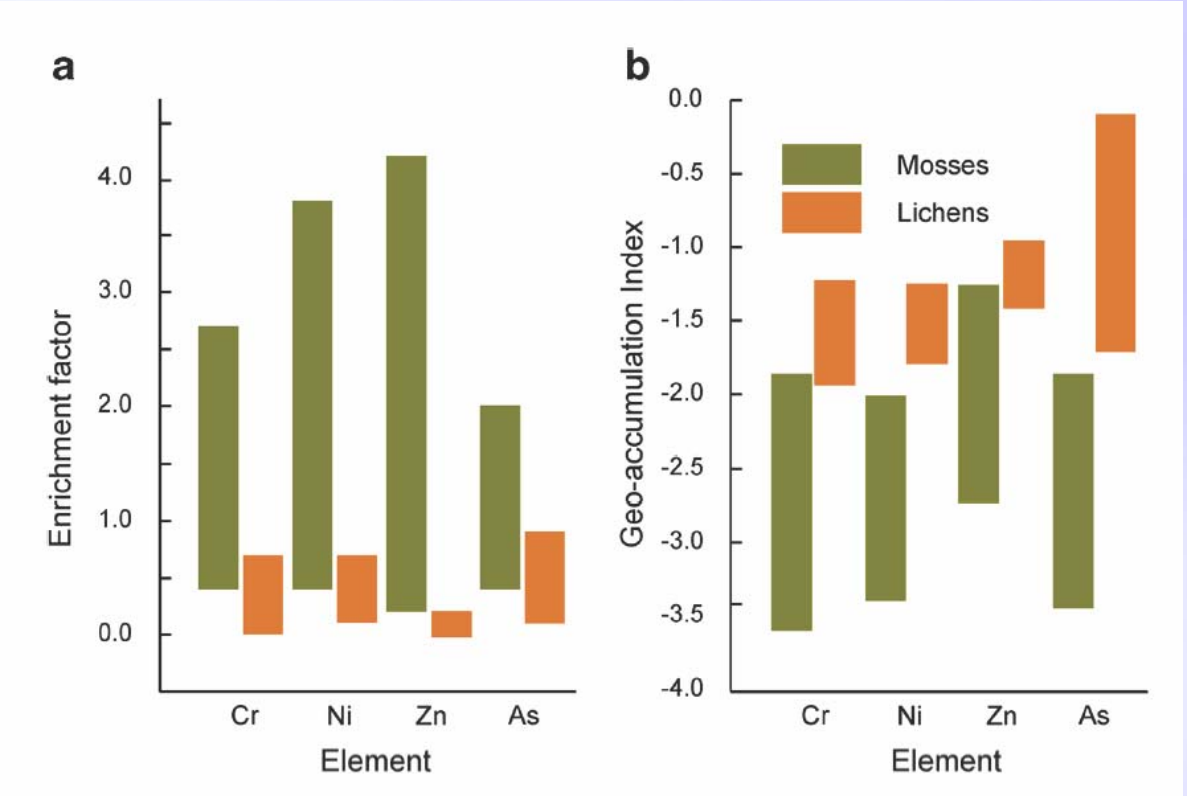
6 lichens (*Usnea antarctica and Usnea aurantiaco-atra*) **INAA**

Results and Discussion

Environmental contamination

Livingstone Island, Antarctica

Two indices : Enrichment factor and Geo-acumulation index, both of them pointed towards a quasi-absence of any anthropogenic influence on the Livingstone Island environment, mosses showing a higher capacity of retention



Results and Discussion

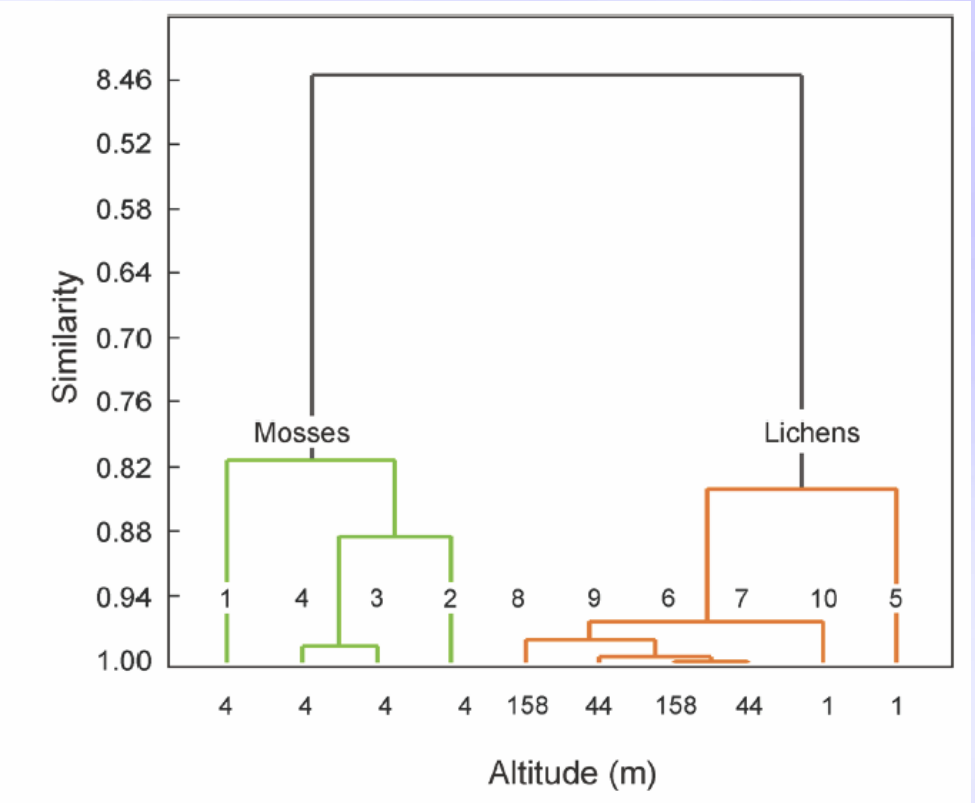
Environmental contamination

Livingstone Island, Antarctica

Different behaviors concerning the distribution and accumulation of presumably contaminating elements.

In the case of lichens, the mass fractions of

almost all elements decreases with altitude pointing towards a local origin of identified elements

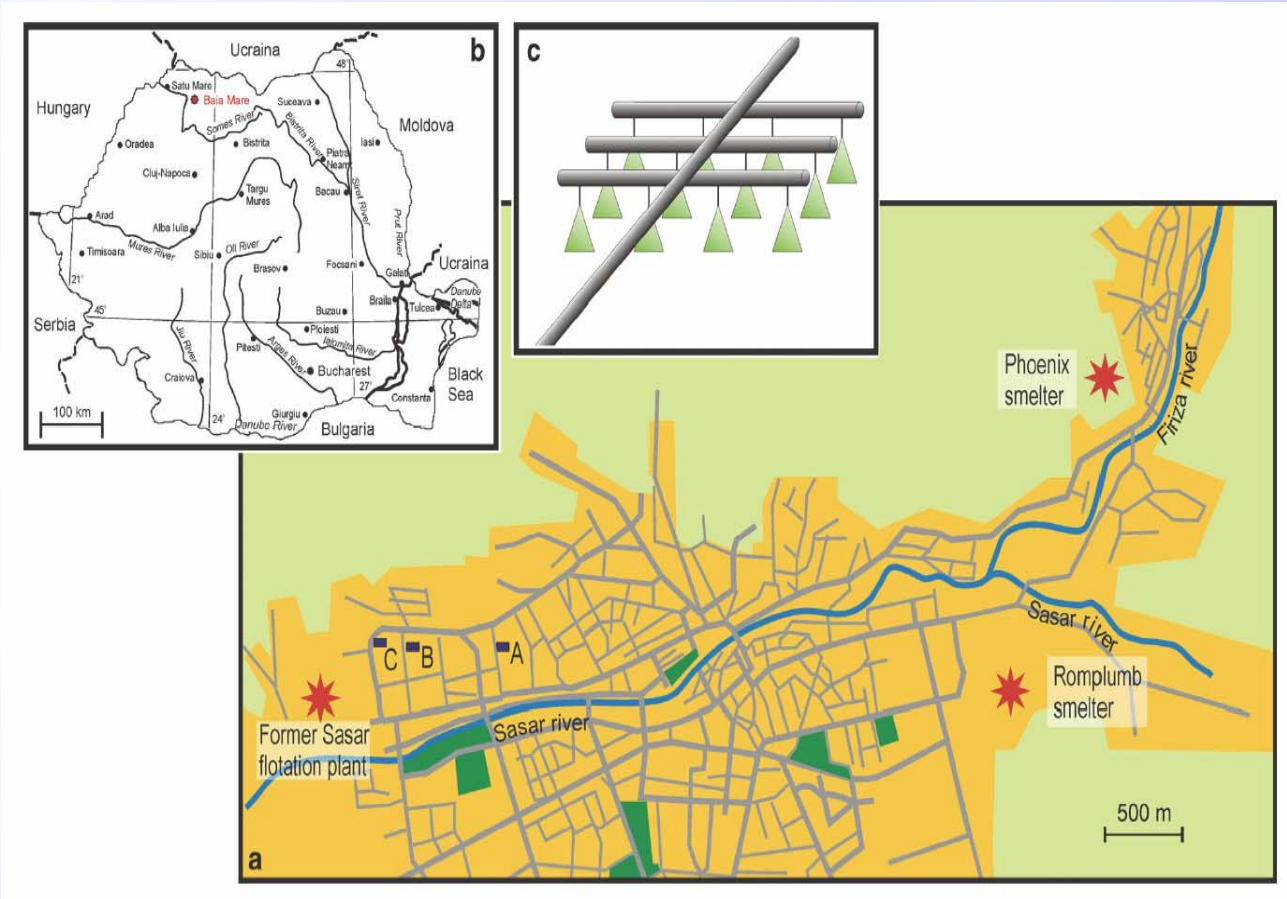


Results and Discussion

Environmental contamination

Former industrial area, Baia Mare, Romania

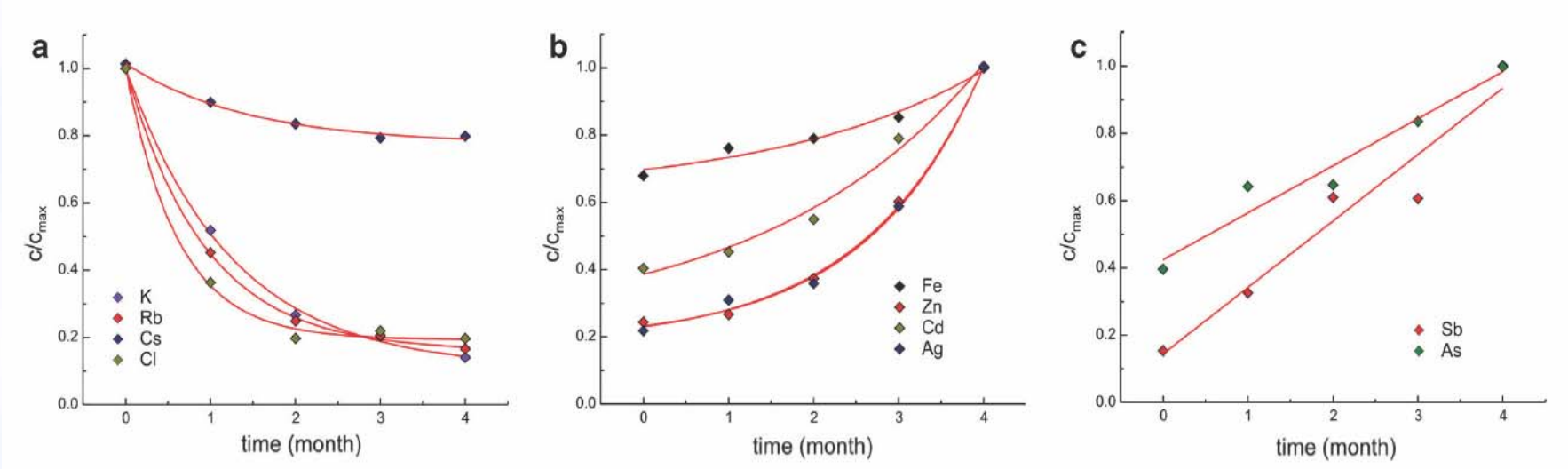
Active biomonitoring using the moss-bag transplant technique to investigate the kinetics of 38 elements in *Sphagnum girgensohni* moss samples placed in different places and at different height.



Results and Discussion

Environmental contamination

Former industrial area, Baia Mare, Romania



Apparently our contradictory results show the existence of thwo processes – accumulation of some presumably contaminating elements e.g. Fe, Zn, As, Sb, Cd and g, and the leaking of alkaline elements as well as of the Cl which, in spite of four months experiment, are fare from reaching the equilibrium.

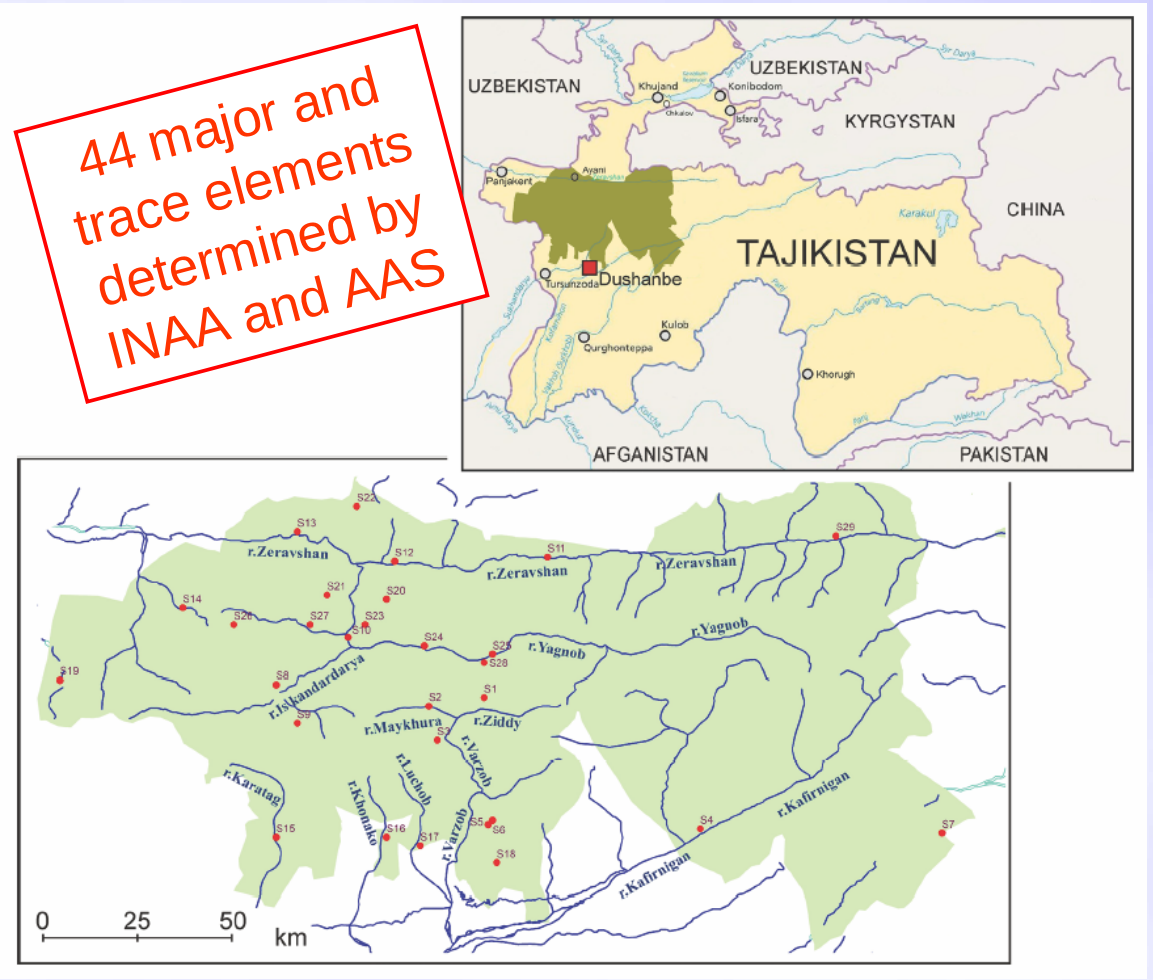
Results and Discussion

Environmental contamination

Western Tajikistan

A mountainous area of approximately 7000 sq. km of Western Tajikistan, *i.e.*, Turkestan, Zeravshan, Hissar, and Karateghin ridges characterized by complex geological settings to determine at which extent *Hylocomium splendens* can give confident information on environmental contamination.

44 major and trace elements determined by INAA and AAS

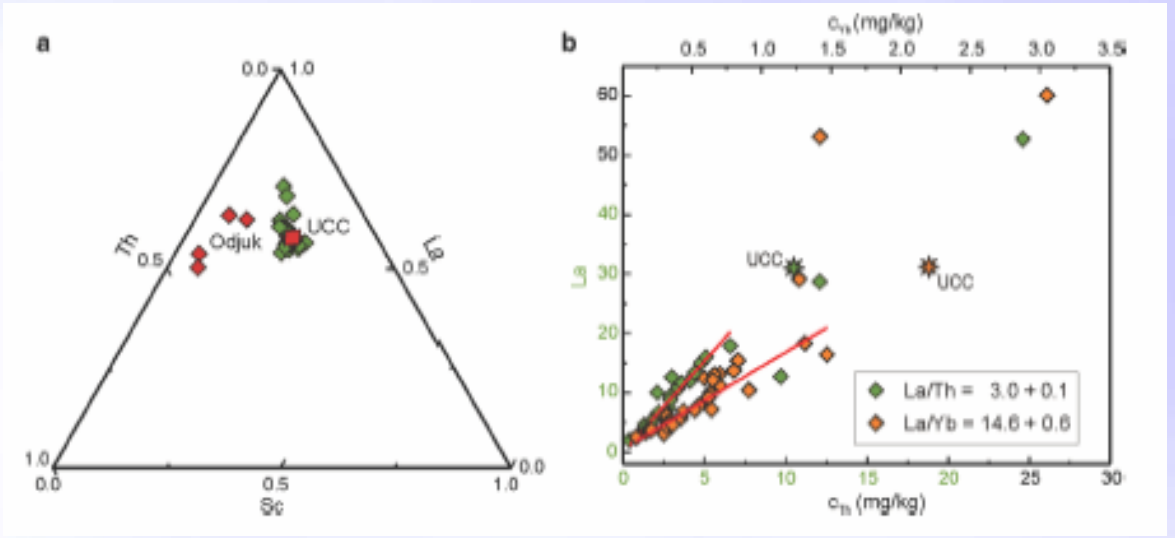


Results and Discussion

Environmental contamination

Western Tajikistan

Ternary Sc-La-Th and Lavs Th and La vs. Yb proved the Continental Crust origin of mineral debris acquired by the moss tissue excepting four samples collected in the vicinity of Odjuk pegmatite outcrop, of which position on both diagrams pointed towards an increased content of REE and Th.

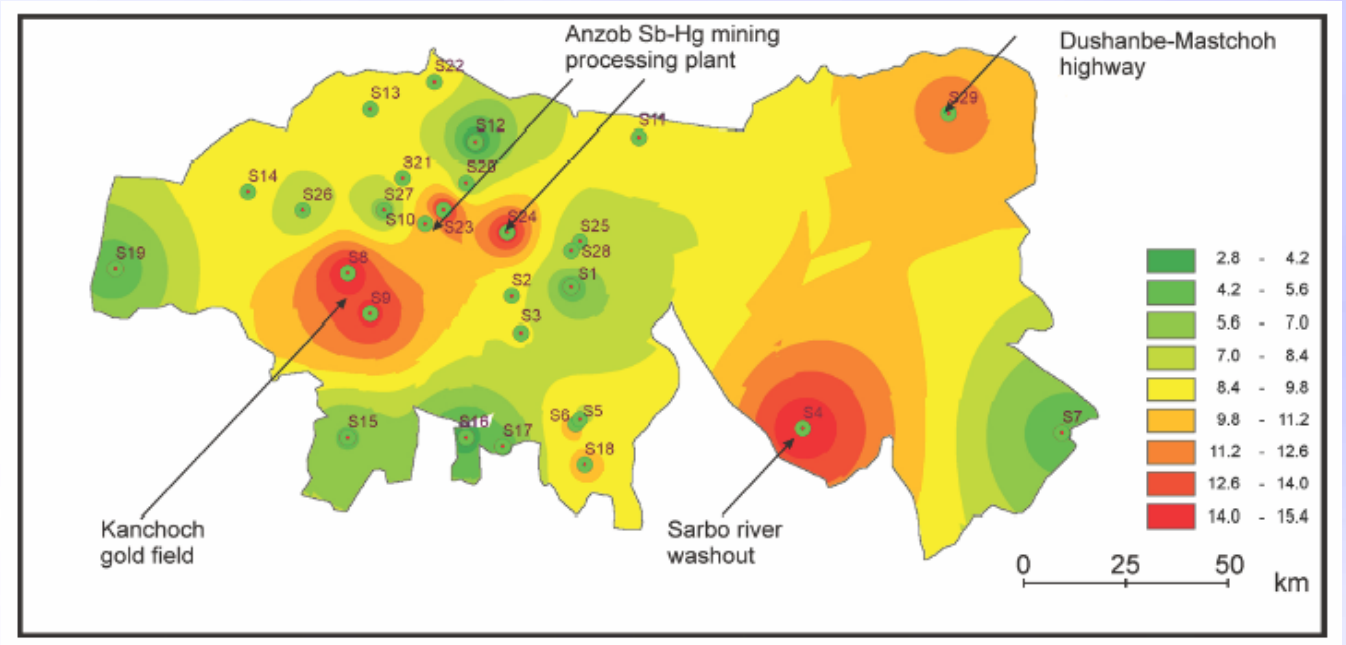


The La vs Th and La vs. Yb showed a perfect linear correlation characterized by a La/Th ratio of 3.2 ± 0.6 and La/Yb of 14.7 ± 3 very close to the UCC value of 2.95 and 15.5 respectively.

Results and Discussion

Environmental contamination

Western Tajikistan



The Contamination Factor and Pollution Loading used to quantify the level of contamination showed that despite a reduced industrial activity, both indices presented increased values. In our opinion, this finding could not be attributed only to mining activity, but most probably and to the geochemistry of the investigated area, rich in some places in felsic rocks, as in the case of Odjuk pegmatite deposit.

Results and Discussion

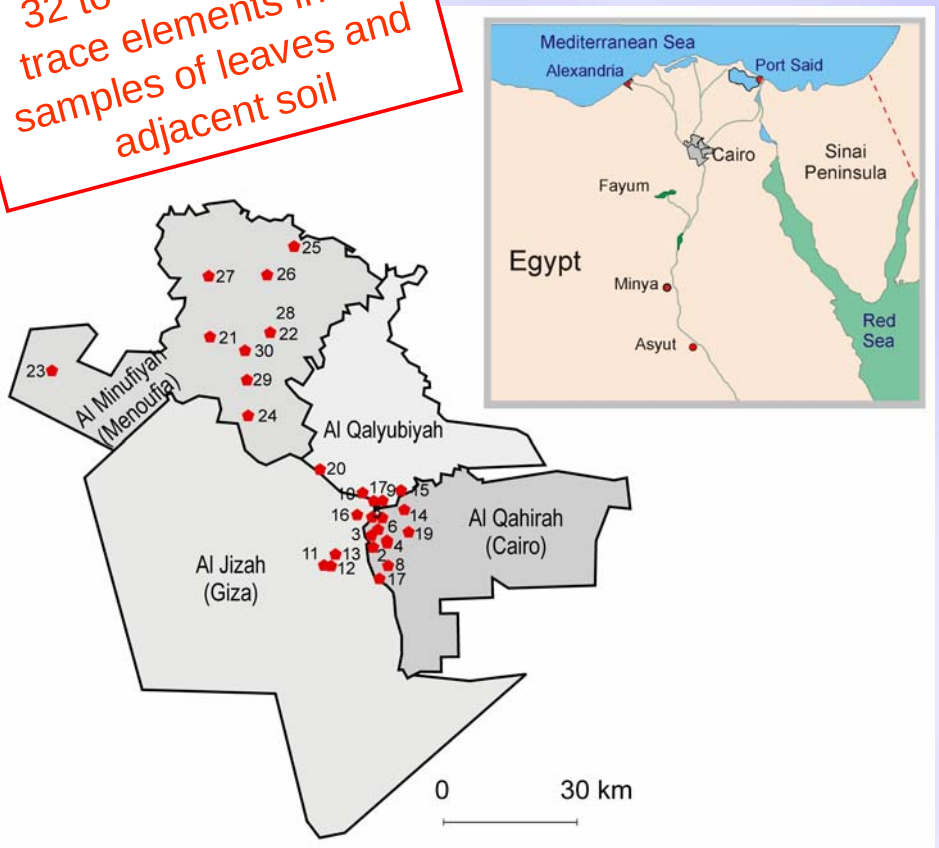
Environmental contamination

Mosses, which proved to be the best biomonitoring plants can not survive in dry climate, their role being taken by local evergreen vascular plant. In this regard, tree leaves, could retain through stomata the finest fraction of the atmospheric dust, showing to be reliable biomonitors.

Consequently, to asses the degree of local contamination we have used in the case urban Cairo and rural Menoufia the leaves of evergreen trees, *Eucalyptus globulus* Labill and *Ficus benjamina* L.

Egypt residential areas

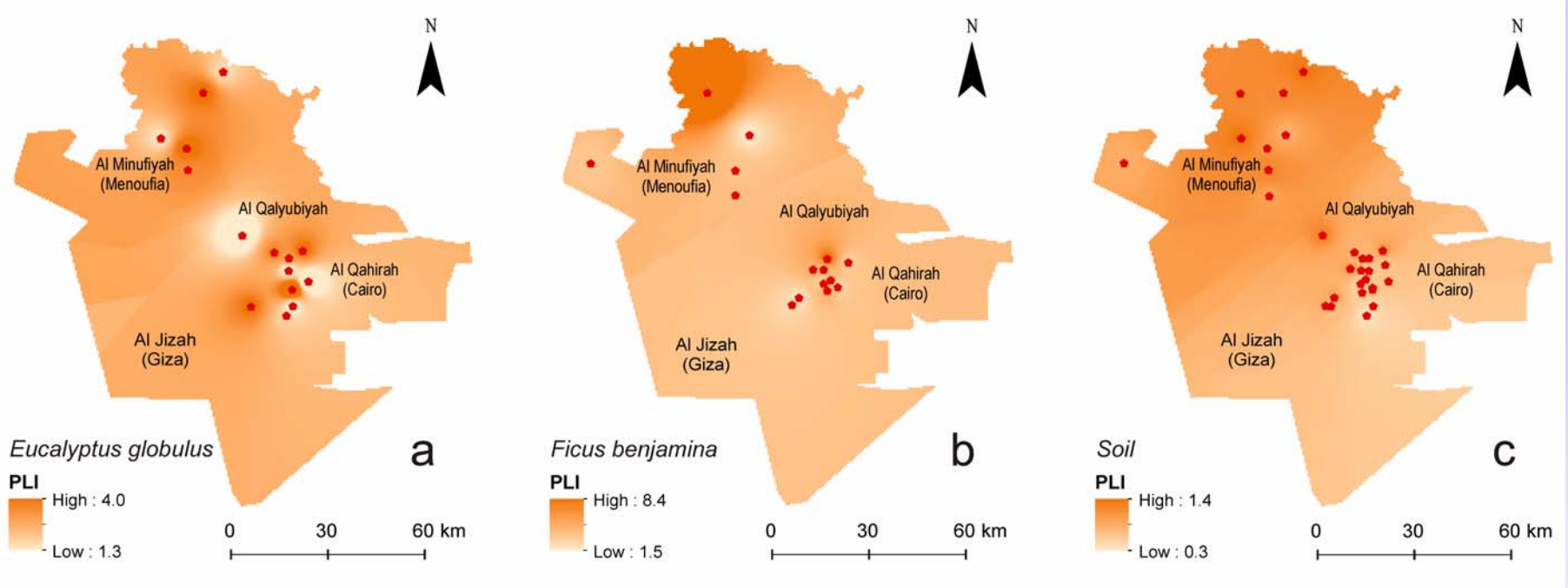
32 to 40 major and trace elements in 39 samples of leaves and adjacent soil



Results and Discussion

Environmental contamination

Egypt residential areas

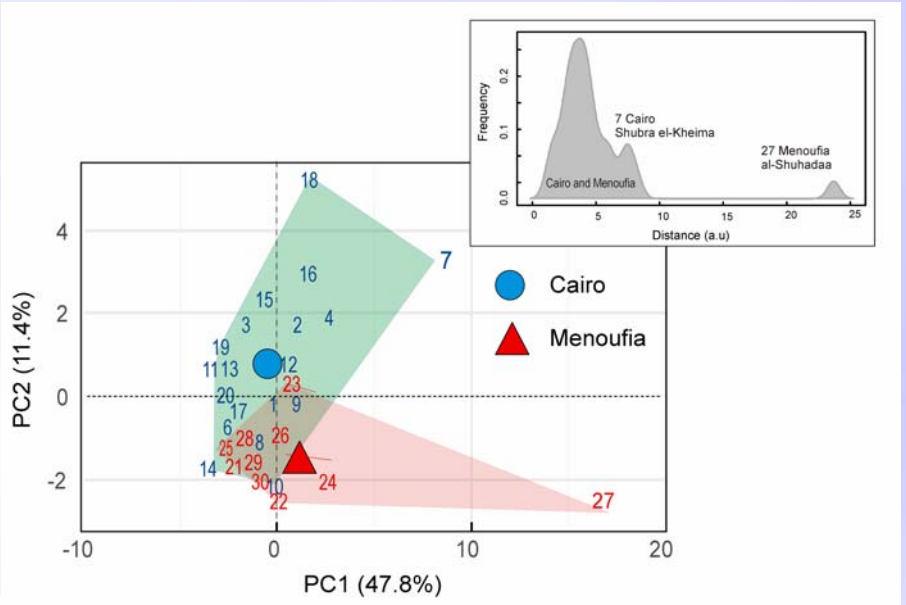


The distribution map of Pollution Load Index showed that paradoxically, the Menoufia rural area seems to be more contaminated that the urban Cairo, where only in some points PLI reached maximum values.

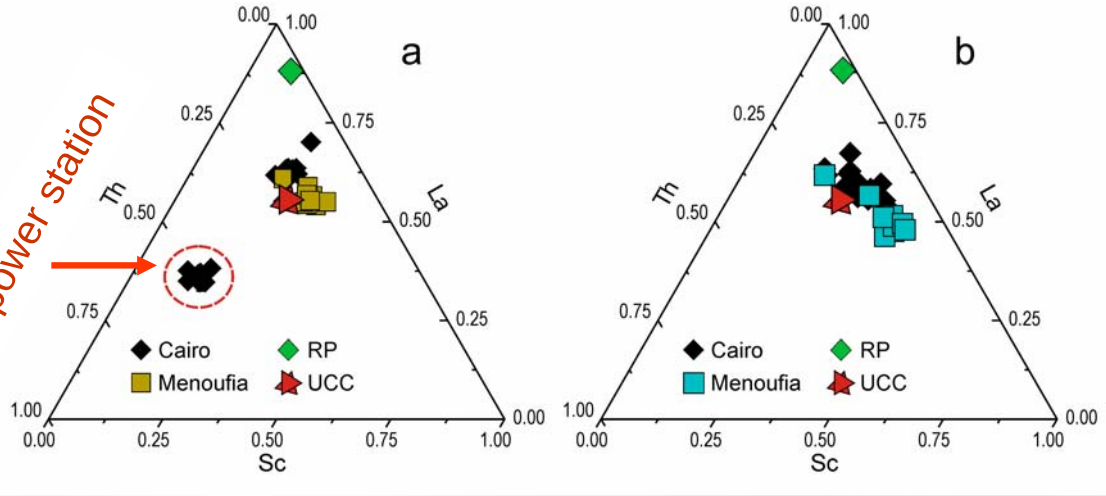
Results and Discussion
Environmental contamination

Egypt residential areas

Principal Component Analysis shows two distinct clusters completely distinct as Mahalanobis distance between centoids illustrates



Cairo power station



Ternary diagrams illustrating the origin of dust which represents the main vector of presumably contaminating elements.

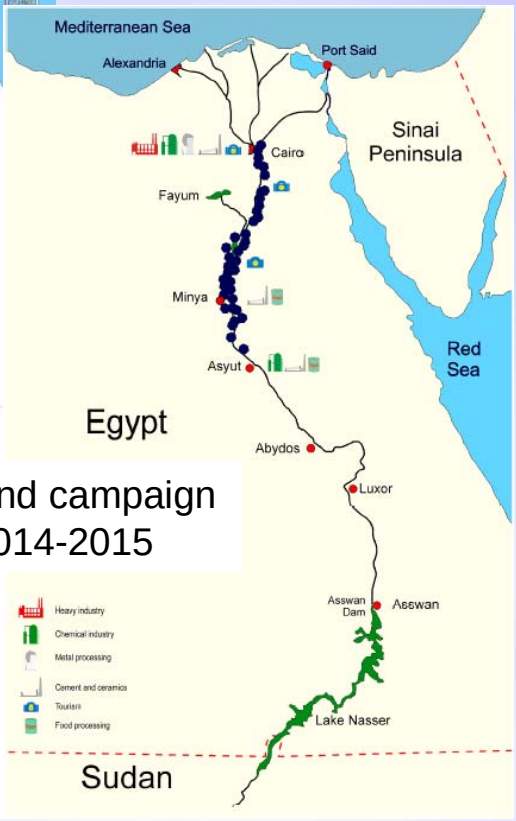
Results and Discussion

Environmental contamination

38 major and trace elements in more than 130 samples of sediments and soils practically covering entire Egyptian sector of Nile River collected in two campaigns between 2010 and 2015.

Relation between sediments and soils, origin of sedimentary material and the degree of anthropogenic contamination

Nile River, Egypt



38 major and trace elements in 130 samples

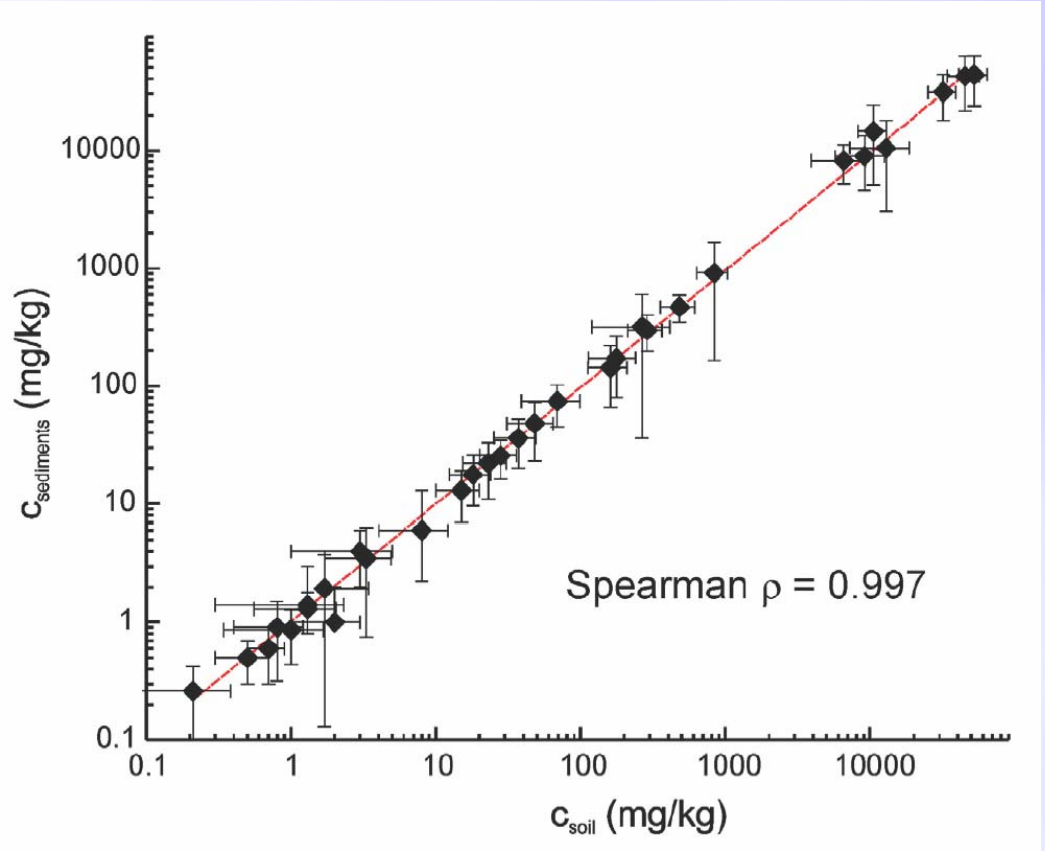
Results and Discussion

Environmental contamination

Nile River, Egypt

An excellent correlation between the distribution of mass fractions of all considered elements in sediments and soil.

Soil is mainly produced by the sedimentary material transported by Nile River and deposited during annual floods, our findings confirm this model

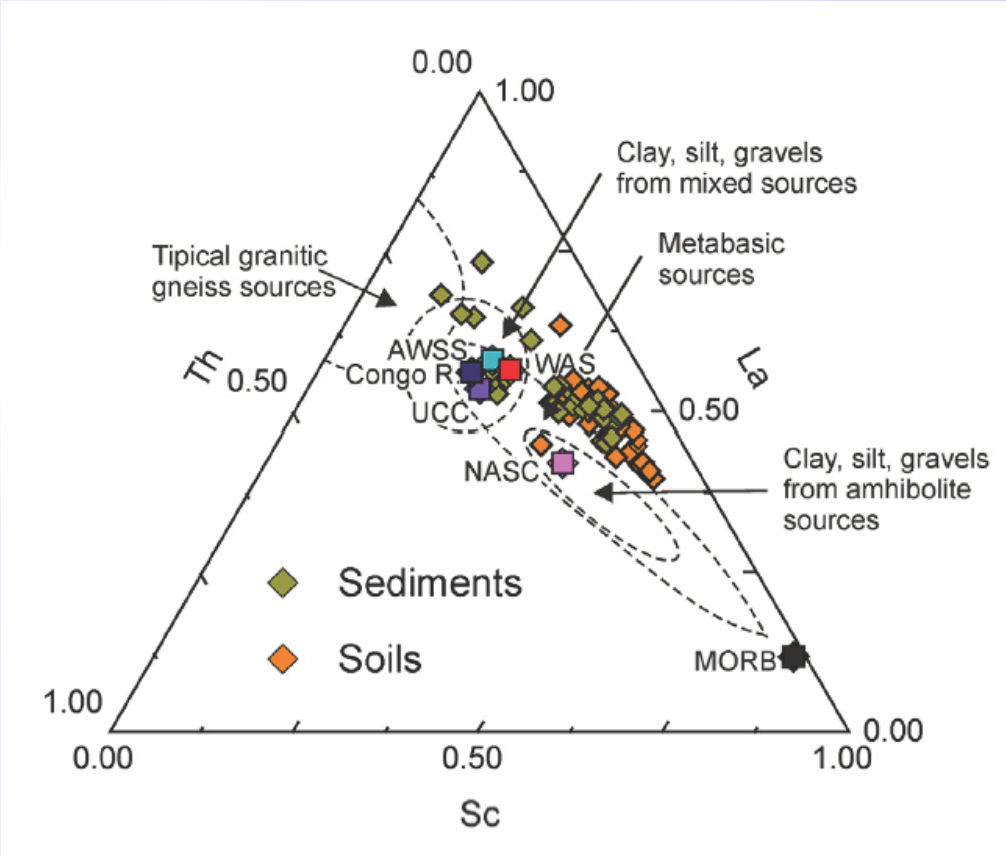


Results and Discussion

Environmental contamination

The ternary diagram of incompatible and insoluble elements Sc-La-Th points towards the presence of mafic material, most probable from Ethiopian High Plateaus, in good concordance with the source of Blue Nile which contribute with about 80% to the Nile River fluid debit.

Nile River, Egypt

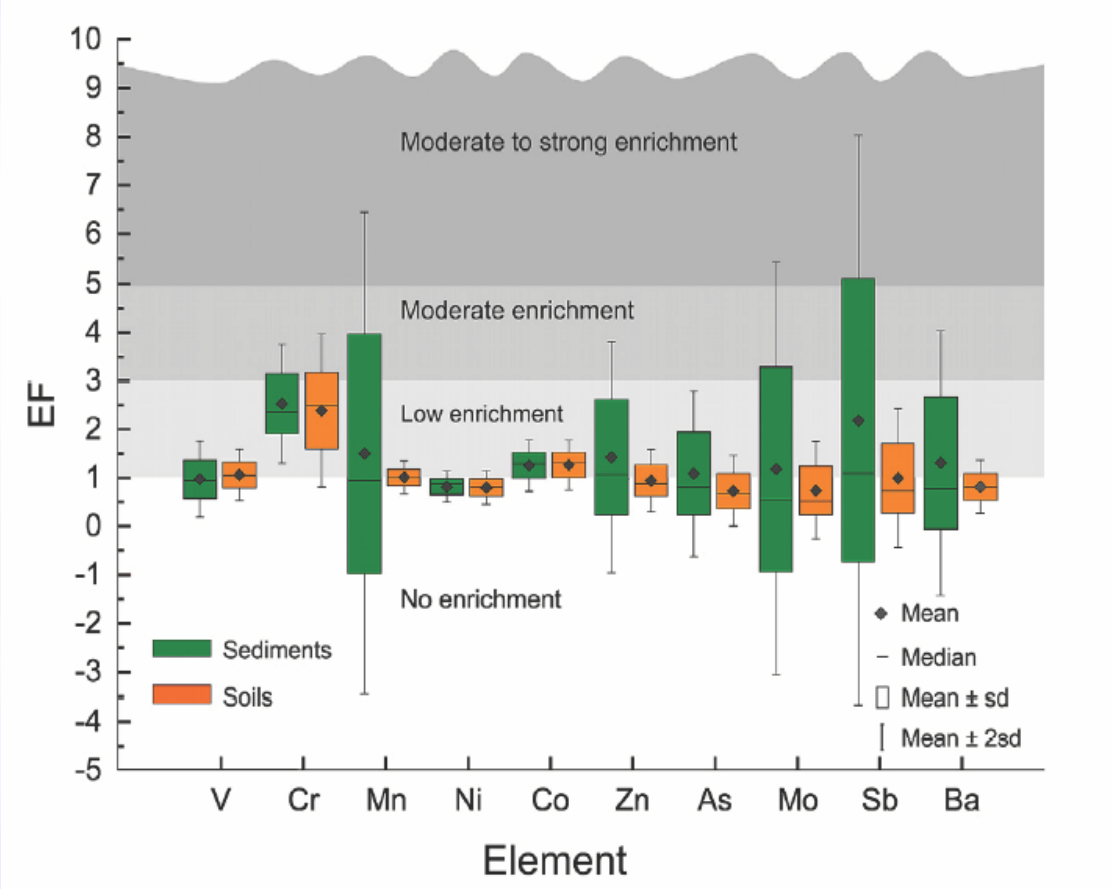


Results and Discussion

Environmental contamination

The same contamination indices, i.e. enrichment factor and Geo-accumulation index pointed towards to a very weak contamination of both sediments and soils, and this in spite of a human activity that lasted four millennia,

Nile River, Egypt



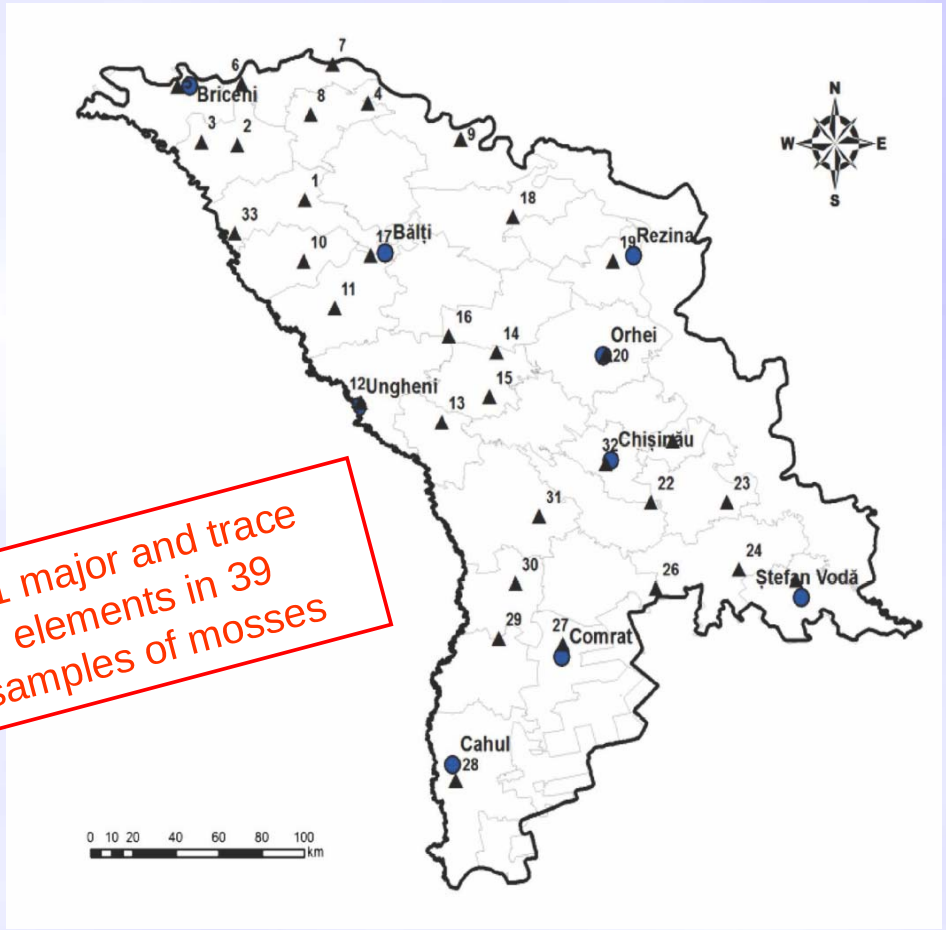
Results and Discussion
Environmental contamination

Moss biomonitoring using *Hypnum cupressiforme* (Hedw.) and *Pleurocarpous* sp as an alternative to *Hylocomium splendens* showed to be extremely useful in estimating the contamination level of Republic of Moldova.

As an alternative, to classical contamination indices, the distribution of Principal component analysis was used to identify and

characterize different pollution sources.

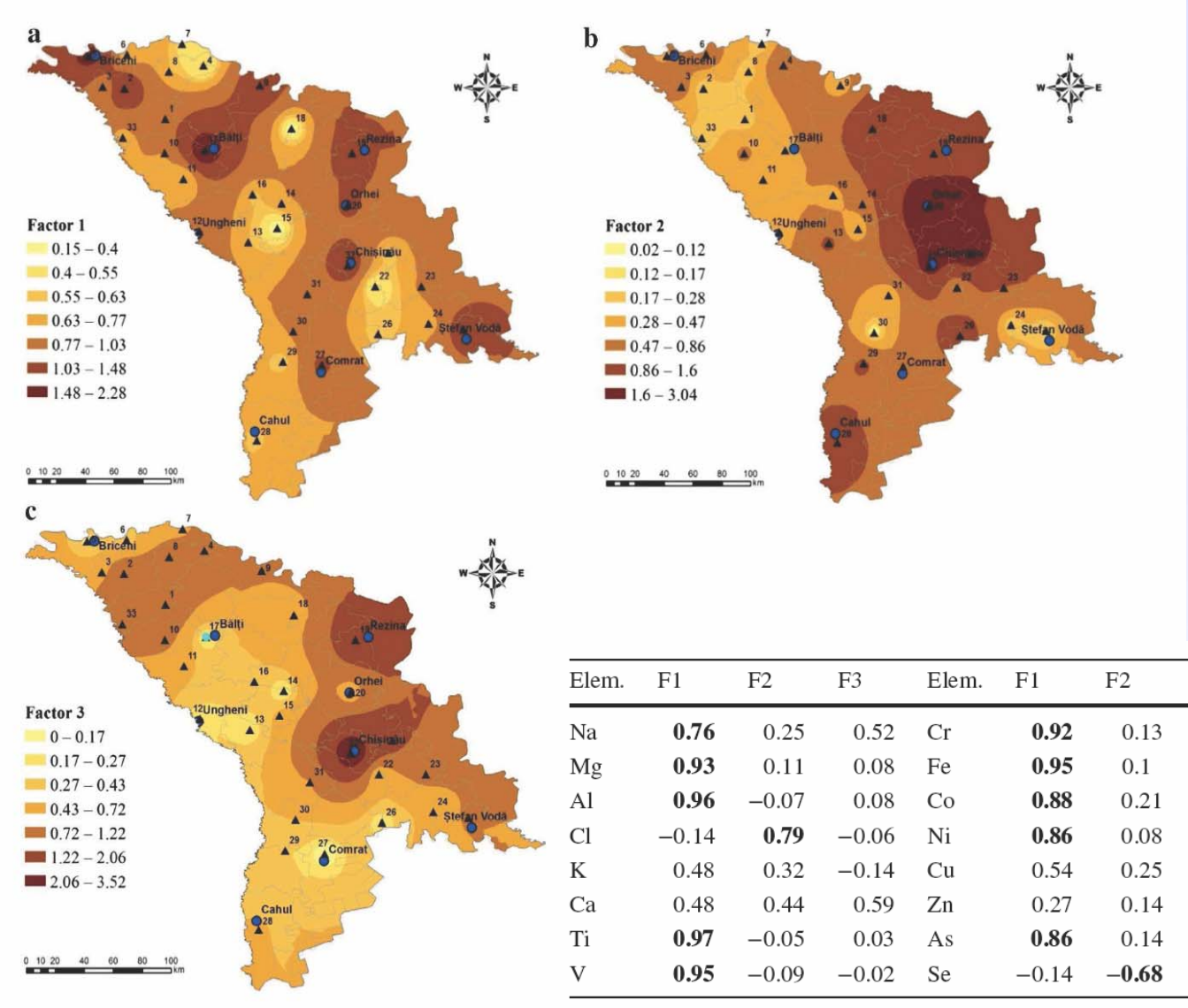
Republic of Moldova



41 major and trace elements in 39 samples of mosses

Results and Discussion

Environmental contamination



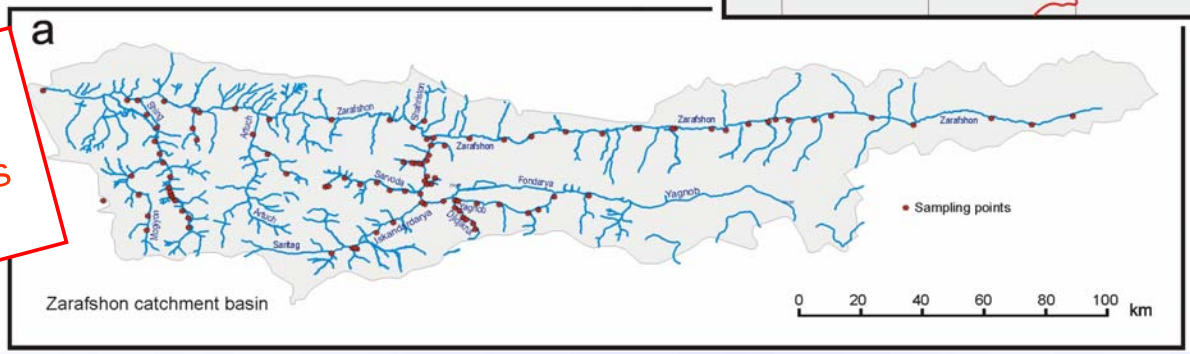
Republic of Moldova

Elem.	F1	F2	F3	Elem.	F1	F2	F3	Elem.	F1	F2	F3
Na	**0.76**	0.25	0.52	Cr	**0.92**	0.13	0.34	Sr	0.1	**0.71**	0.39
Mg	**0.93**	0.11	0.08	Fe	**0.95**	0.1	0.25	Cd	−0.25	−0.27	0.48
Al	**0.96**	−0.07	0.08	Co	**0.88**	0.21	0.40	Sb	0.55	0.13	**0.62**
Cl	−0.14	**0.79**	−0.06	Ni	**0.86**	0.08	0.46	Cs	**0.96**	0.09	0.20
K	0.48	0.32	−0.14	Cu	0.54	0.25	0.36	La	**0.90**	0.16	0.32
Ca	0.48	0.44	0.59	Zn	0.27	0.14	**0.77**	Pb	0.26	−0.13	**0.69**
Ti	**0.97**	−0.05	0.03	As	**0.86**	0.14	0.42	Th	**0.9**	0.18	0.36
V	**0.95**	−0.09	−0.02	Se	−0.14	**−0.68**	0.07	U	**0.82**	0.24	0.45

Results and Discussion
Environmental contamination

Zarafshon (Golden) River Tajikistan

With an area of 17700 km^2. the Zarafshon catchment basin covers diverse geological formations spread from the alpine zone 3200-3500 m above sea level to less than 150 m in the Kyzyllcum



38 major and trace elements in 112 samples of sediments and soil

Zarafshon River rises at an altitude of 2775 m, flows through a 300 km narrow and deep valley, reaches the city of Panjakent, crosses the Tajikistan-Uzbekistan border, passes the cities of Samarkand and Bukhara and finally is lost in the Kyzyllcum desert.

Results and Discussion

Environmental contamination

Zarafshon (Golden) River Tajikistan

The geological diversity of the mountainous Tajikistan is well represented along the Zarafshon valley and its numerous tributaries.

Here there is a multitude of ore deposits consisting of antimonite, cinnabar and metacinnabarite pyrite, marcasite, realgar, auripigment, sphalerite as well as and hematite.

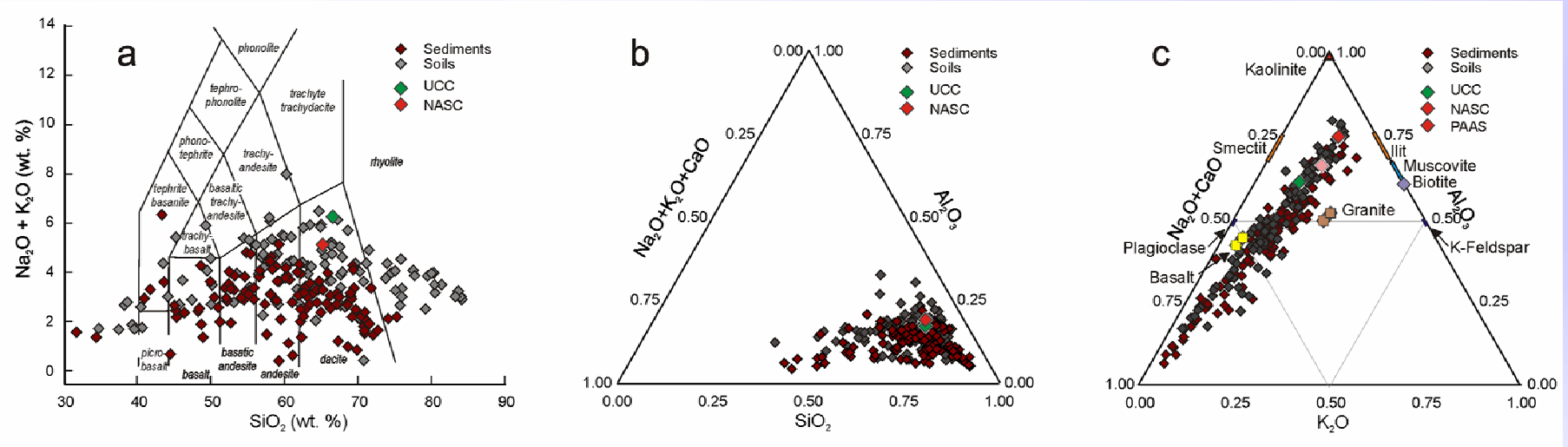
On the northern slope of the Gissar range, operates the Anzob Hg-Sb mining and processing plant contaminating neighboring areas.

Moreover, the Mogiyon River, the largest Zarafshon tributaries is located the Taror ore field of which mineralization is predominantly represented by a silver-tin-polymetallic association spatially combined with sulphide showing the closest correlation between Ag and Sb.

Results and Discussion

Environmental contamination

Zarafshon (Golden) River Tajikistan

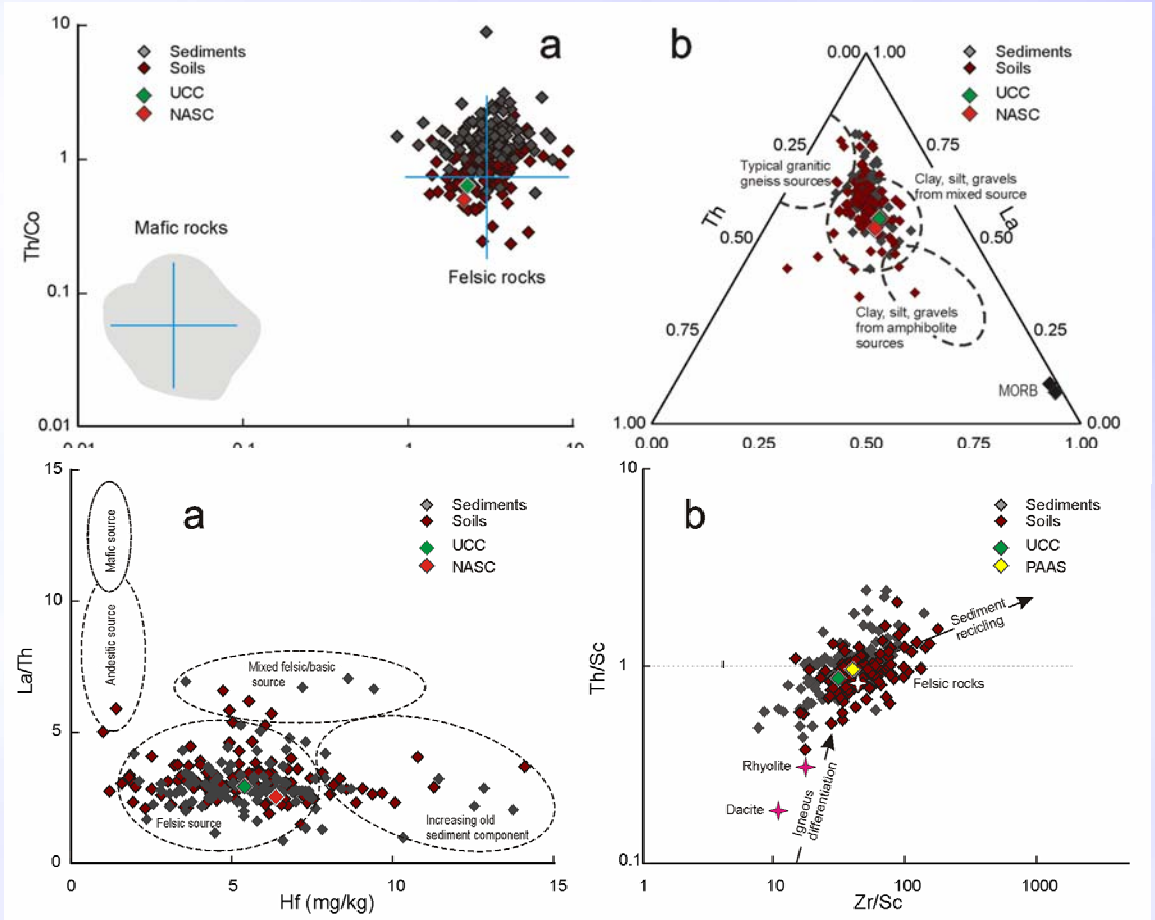


Discriminating total alkali metal oxides vs. SiO_2 biplot (a), ternary SiO_2-Al_2O_3-Na_2O+K_2O+CaO (b) and K-A-CN (c) illustrating the preponderance of felsic material in Zarafshon sediment and soils as well as the significant presence of weathered material.

Results and Discussion
Environmental contamination

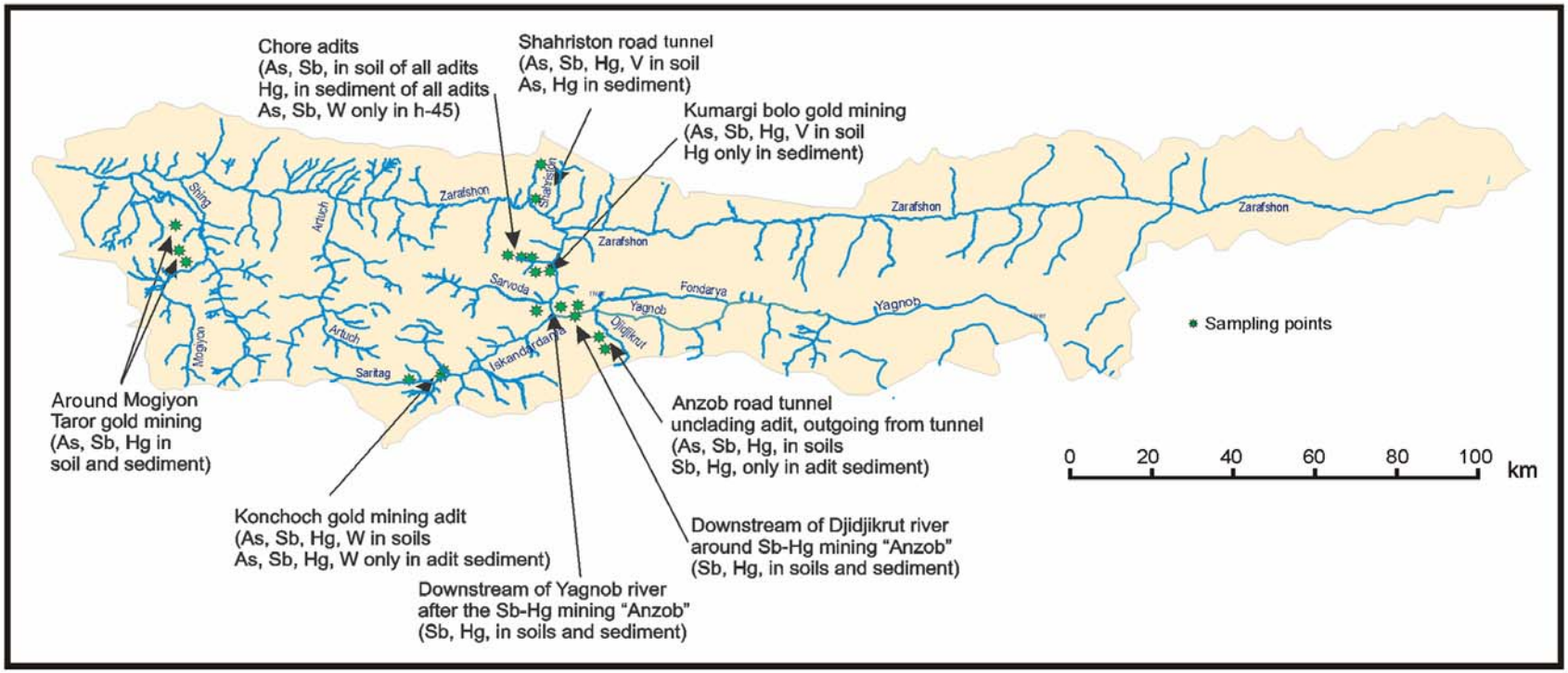
Zarafshon (Golden) River Tajikistan

Discriminating bi-plot Th/Co vs. La/Sc (a) and ternary Sc-La-Th diagram (b) (upper figure) as we as the discriminating bi-plots La/Th vs Hf (a) and Th/Sc vs. Zr/Sc (b) (lower figure) proving a perfect concordance concerning the incompatible elements of Zarafshon river soil and sediments of



Results and Discussion
Environmental contamination

Zarafshon (Golden) River Tajikistan

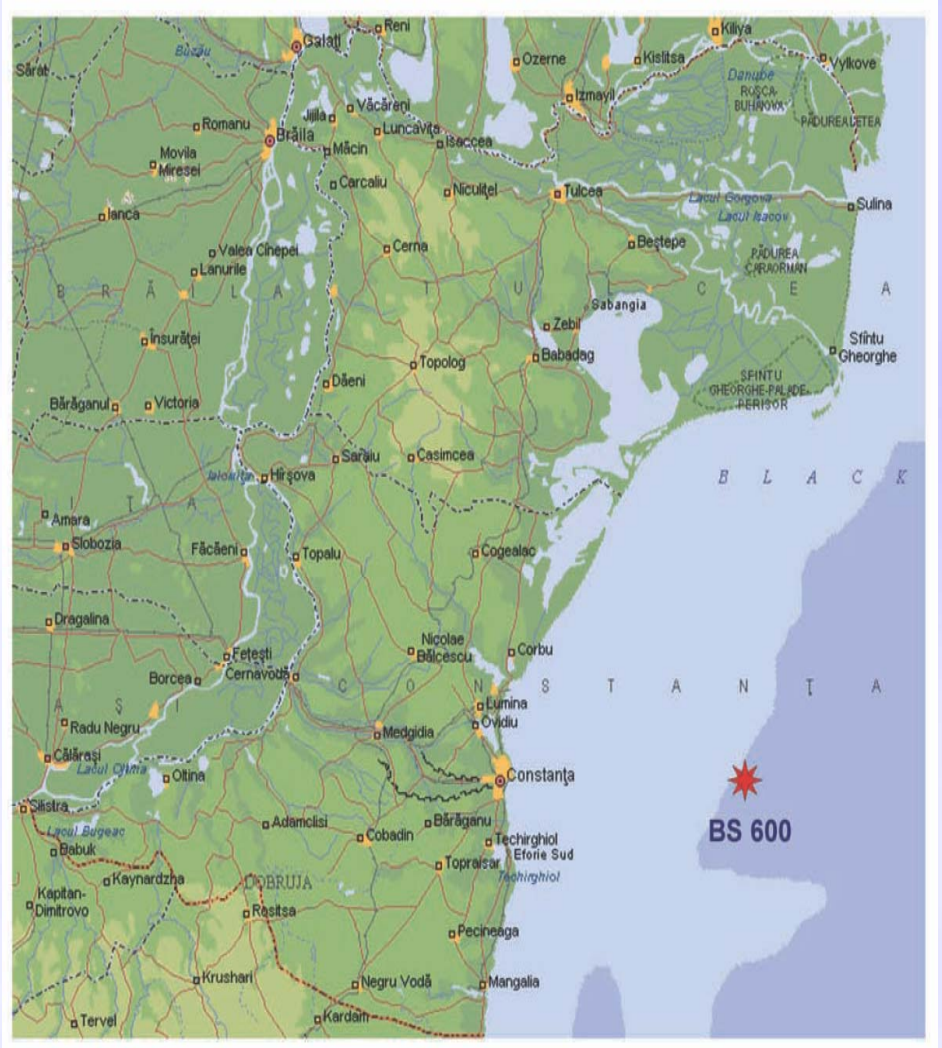


The distribution of geoaccumulation index, contamination factor and pollution load index evidenced more places mainly contaminated by As, Sb, Hg, and in rare cases, with V and W.

Results and Discussion
Environmental contamination

Black Sea euxinic sediments

At depths below 120 to 180 m, the Black Sea water column is completely devoid of oxygen and is saturated with hydrogen sulphide providing provide ideal conditions for the preservation of laminated sediments, which, in turn, represent a *sui generis* archive of the annual and multiannual climate changes



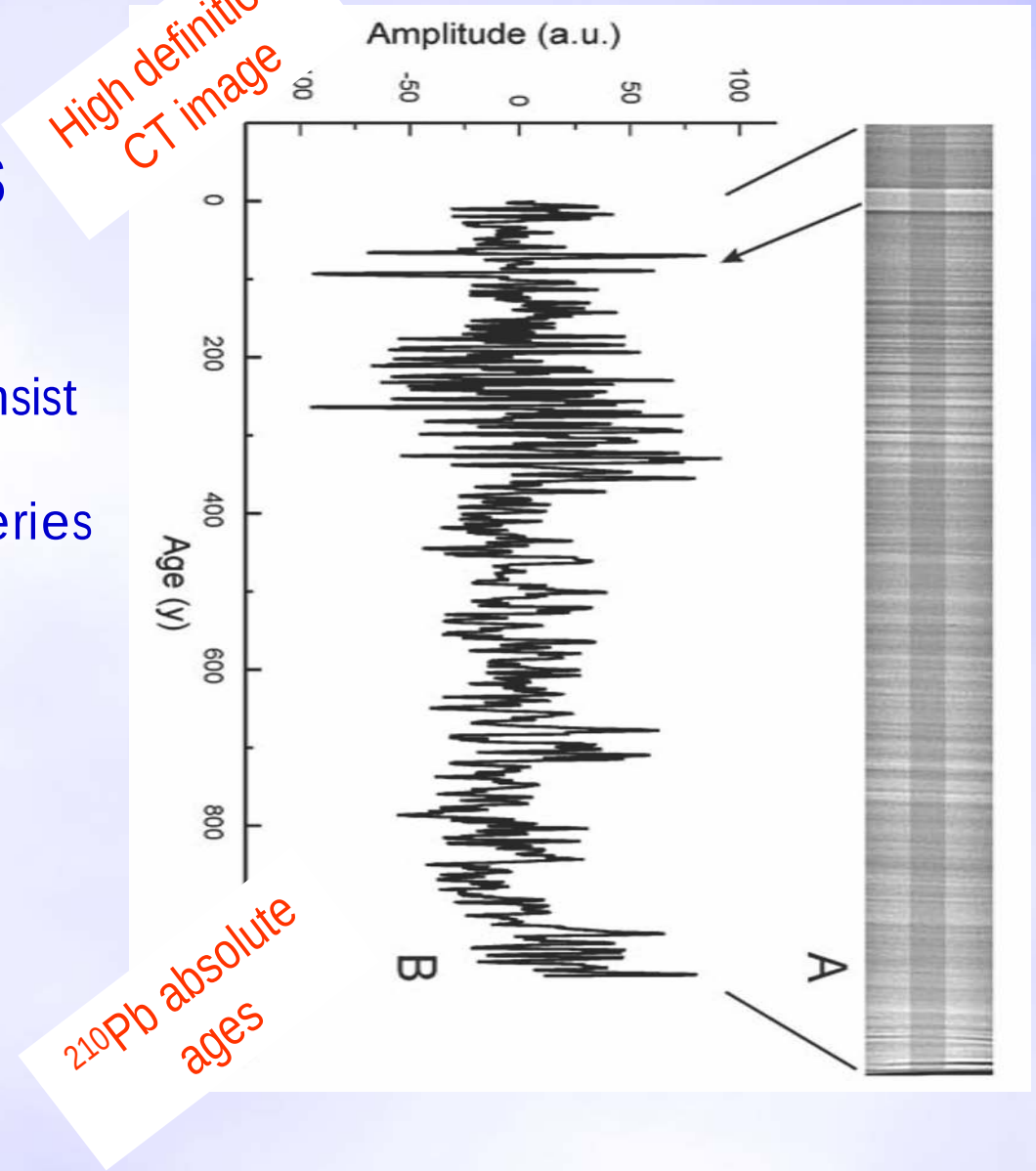
Results and Discussion

Enviromental contamination

Black Sea euxinic sediments

As a result of this, the recent sediments deposited under euxinic conditions, consist of alternating light and dark laminae which form a time series well preserved due to the absence of bioturbation,.

Consequently, knowing an absolute geochronology obtained by ^{210}Pb, it was possible to identify different depositional cycles.

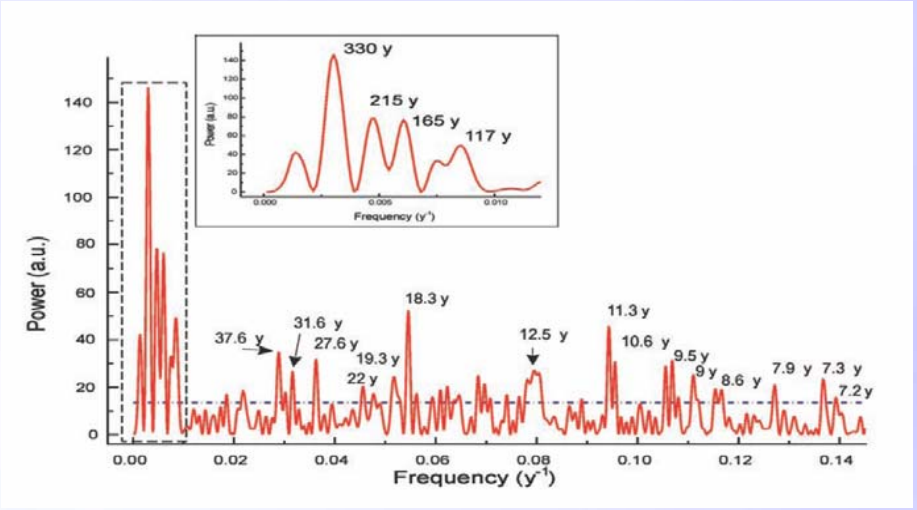


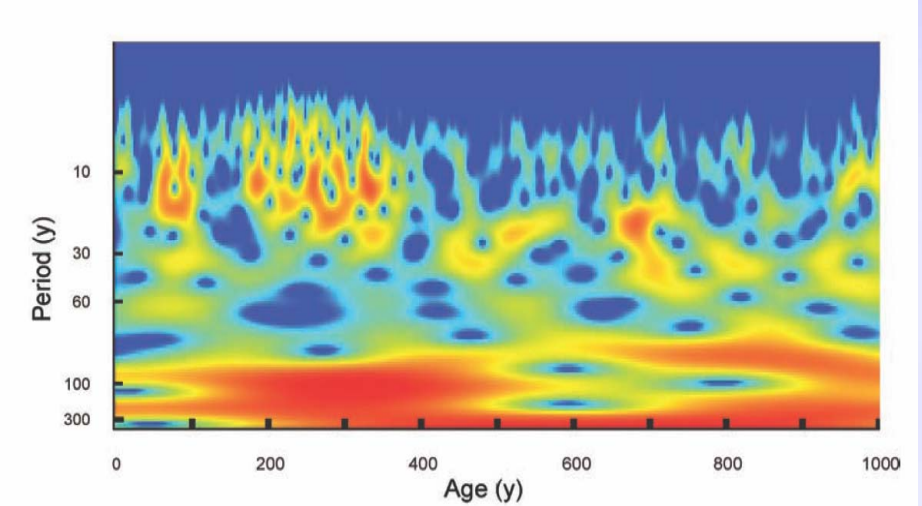
Results and Discussion
Environmental contamination

Black Sea euxinic sediments

Resulting time series is well described by corresponding Power as well as by Evolutionary wavelet spectra.

The power spectrum evidenced with a 99% ($p < 0.01$), probability at least seven cycles having periods of 330, 215, 165, 117, 18.3, 11.3 and 7.3 years respectively.



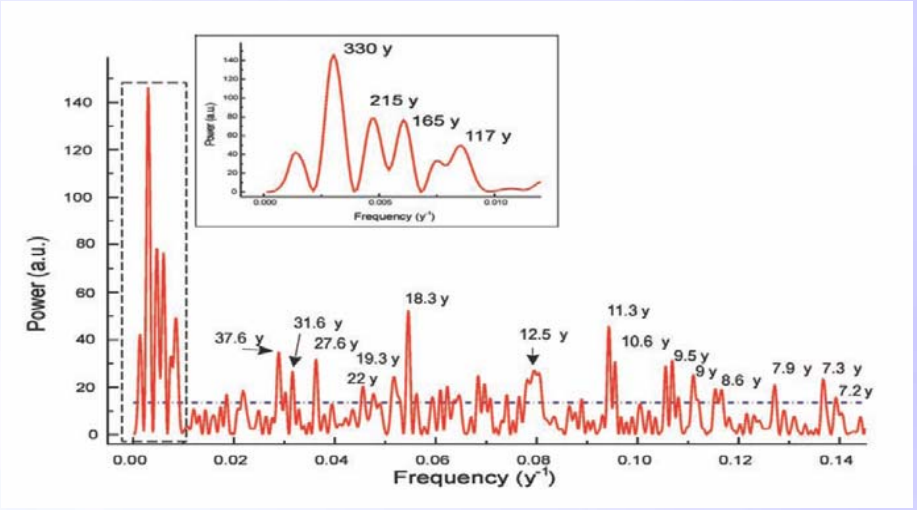


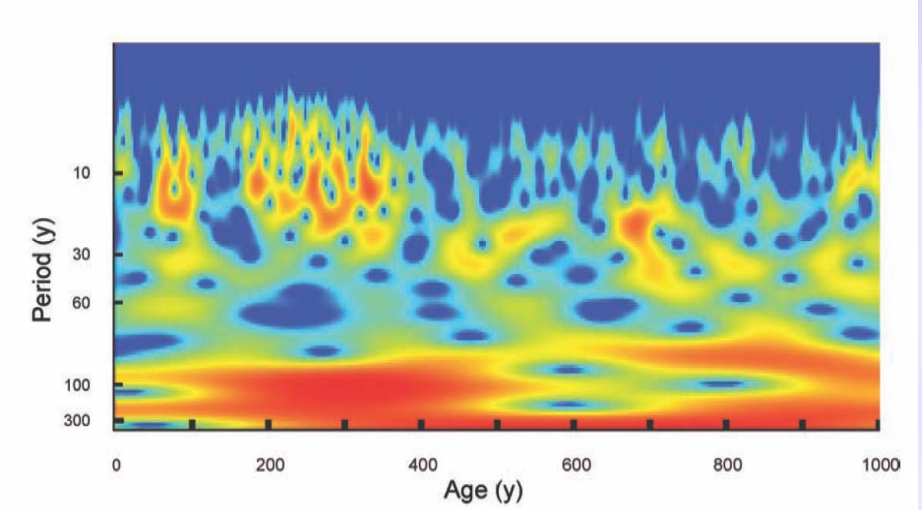
Results and Discussion
Environmental contamination

Black Sea euxinic sediments

The high amplitude, 330 years cycle present along the entire core was previously reported for some anoxic North America mid latitude reservoirs.

The second long time span 215 y cycle is closer to the de Vries solar activity cycle with a periodicity of about 200-210 years.



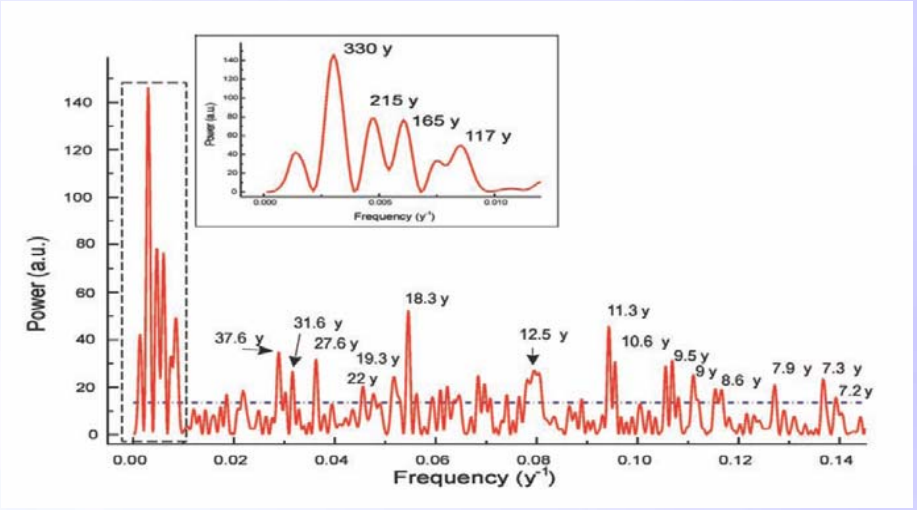


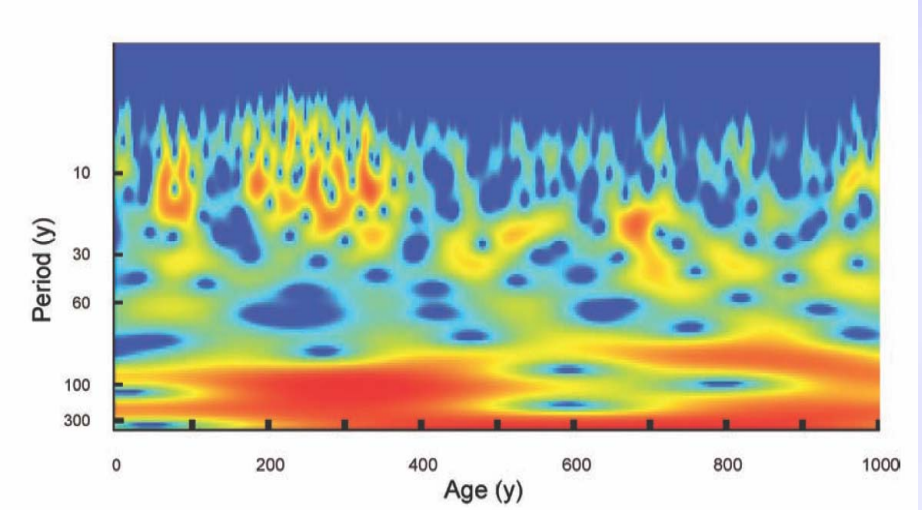
Results and Discussion
Environmental contamination

Black Sea euxinic sediments

The next 18.3 y cycle is close to ~17 y climatic one documented in the North America tree growth rings.

A couple of strong signals with periods of 11.3 and 10.6 y could be correlated with the 11 y solar cycle.

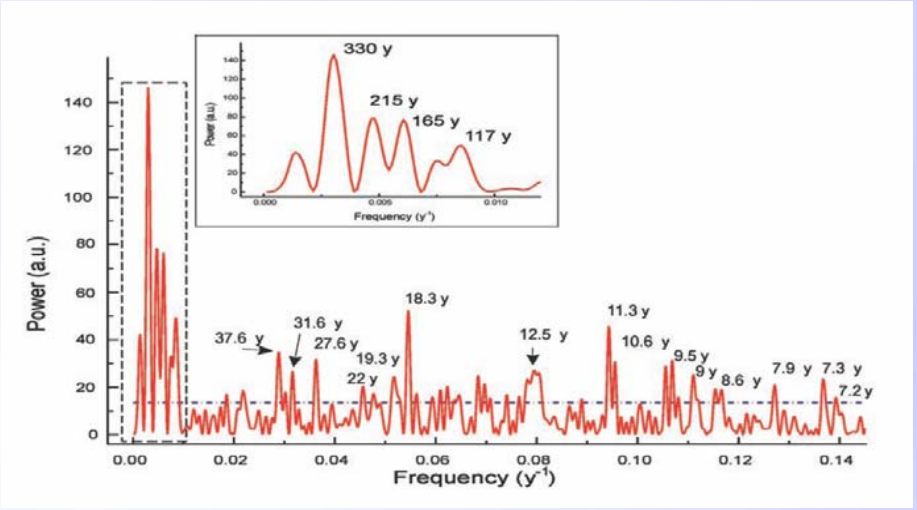


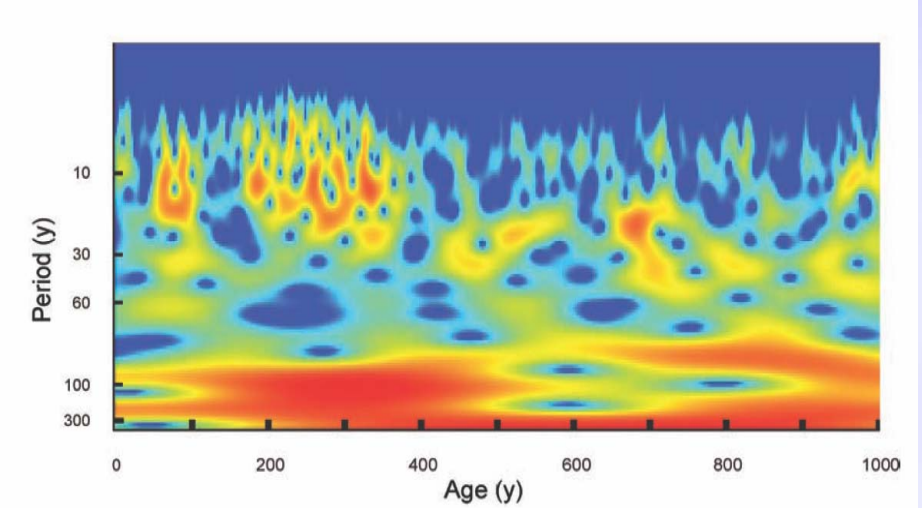


Results and Discussion
Environmental contamination

Black Sea euxinic sediments

The evolutionary wavelet spectrum shows more irregular short time cycles between about 1650 and 1820 AD which includes the Maunder and Dalton minima and coincides with the second part of the Little Ice Age as well as with the onset of Industrialization in Western Europe





Concluding Remarks

We have presented some of the most important results obtained in investigating diverse environmental systems by combining more elemental analytical techniques with appropriate statistical data analysis which significantly permitted a more complex description and understanding of considered systems

Contributors

I would evidence the contribution to this project of my colleagues and friends

Daler Abdusamadzoda, Djamshed Abdushukurov, Wael Badawy, Carmen Cristache, Otilia Culicov, Marina Frontasyeva, Dmitrii Grozdov, Svetlana Gundorina, late Gheorghe Oaie, Konstantin Vergel, Nikita Yushin, Inga Zinicovscaia

whom I express my gratitude

Thanks

Thanks You for attention and Organizers of this Seminary for the opportunity to meet and present our results in spite of Covid 19 pandemics