



Analytical challenges in chemical characterization of medicinal and aromatic plants

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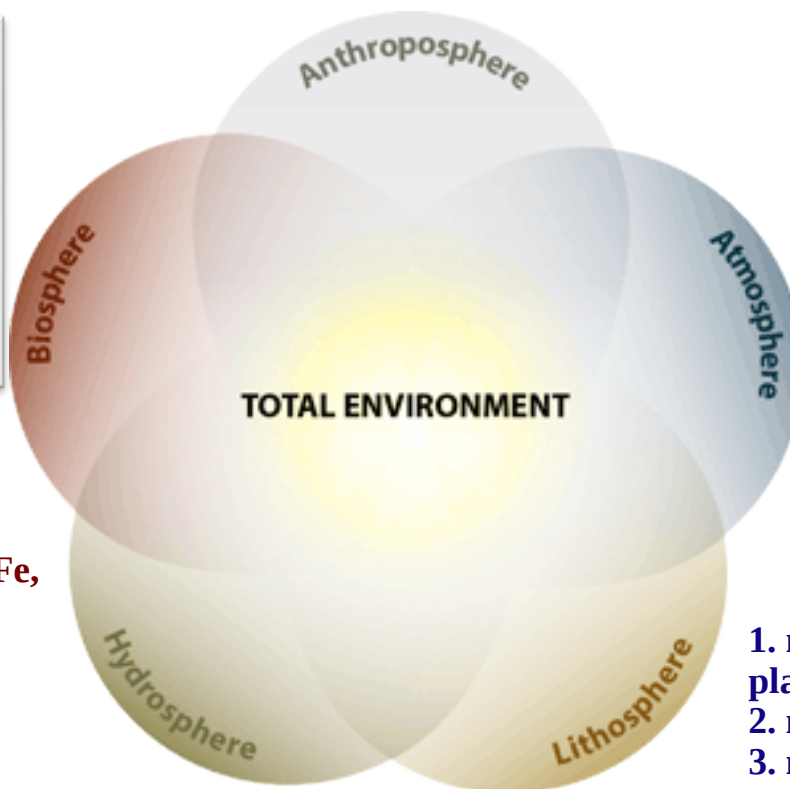
Faculty of Agriculture, Goce Delčev University, Krste Misirkov No. 10-A, 2000
Štip, Republic of North Macedonia



CHEMICAL ELEMENTS IN ENVIRONMENT



Biologically effective elements:
Na, Mg, Si, P, S, Cl, Ca, Ti, V, Mn, Fe,
Co, Mo



1. municipal wastewater-treatment plants
2. manufacturing industries,
3. mining,
4. transportation
5. agricultural cultivation & fertilization.....



Biologically hazardous elements:
Bi, Be, Al, Cr, Ni, As, Ag, Cd, Sb, Ba, Hg, Pb, Zn

Metals in environment

complex environmental chemistry

transport patterns

As	Cd	Pb	Hg
arsenic	cadmium	lead	mercury
74.922	112.411	207.2	200.59

meteorological conditions

mixing of emissions from multiple sources

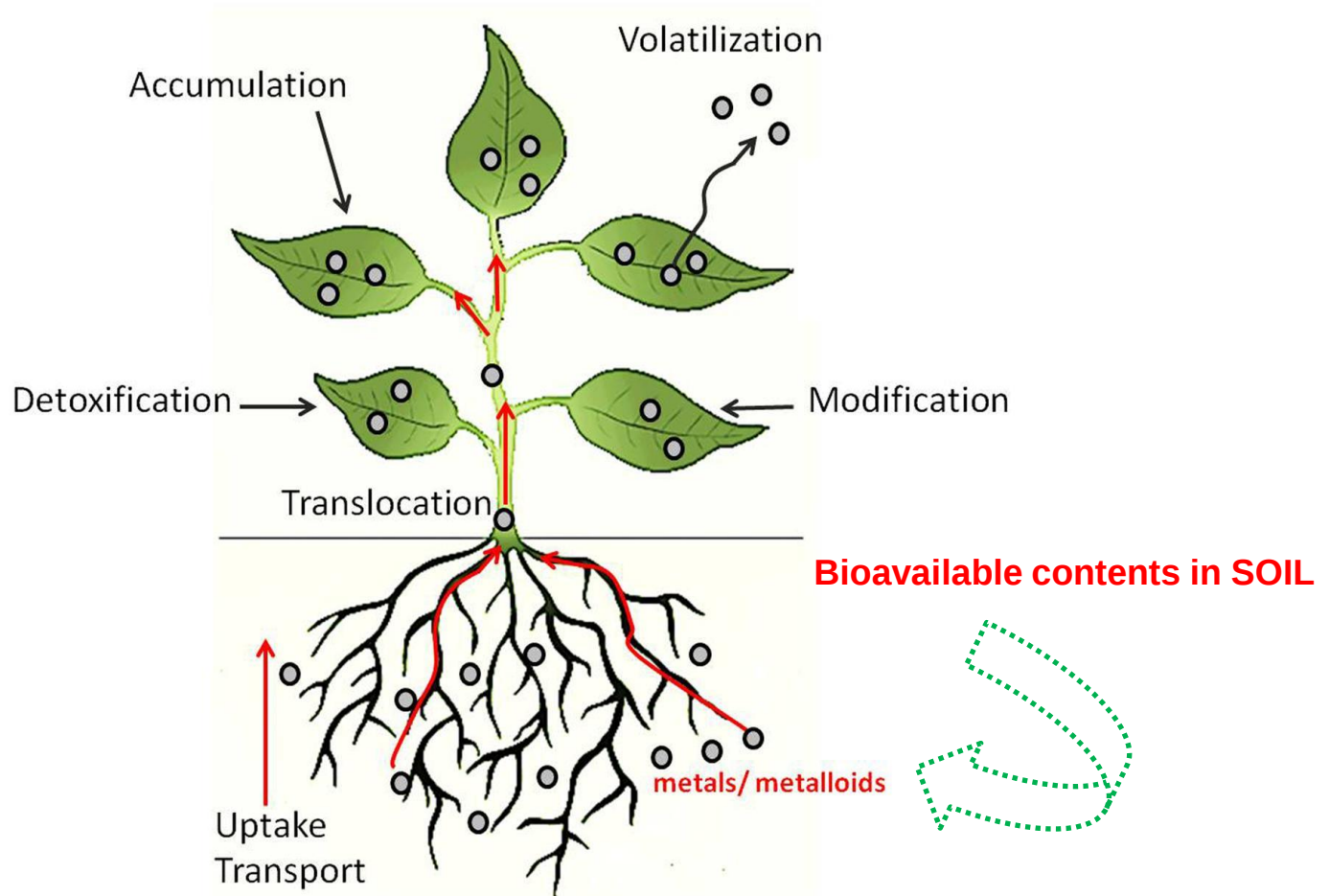
uncertainties associated with receptor modeling

**Isotopic
“FINGERPRINTING”**

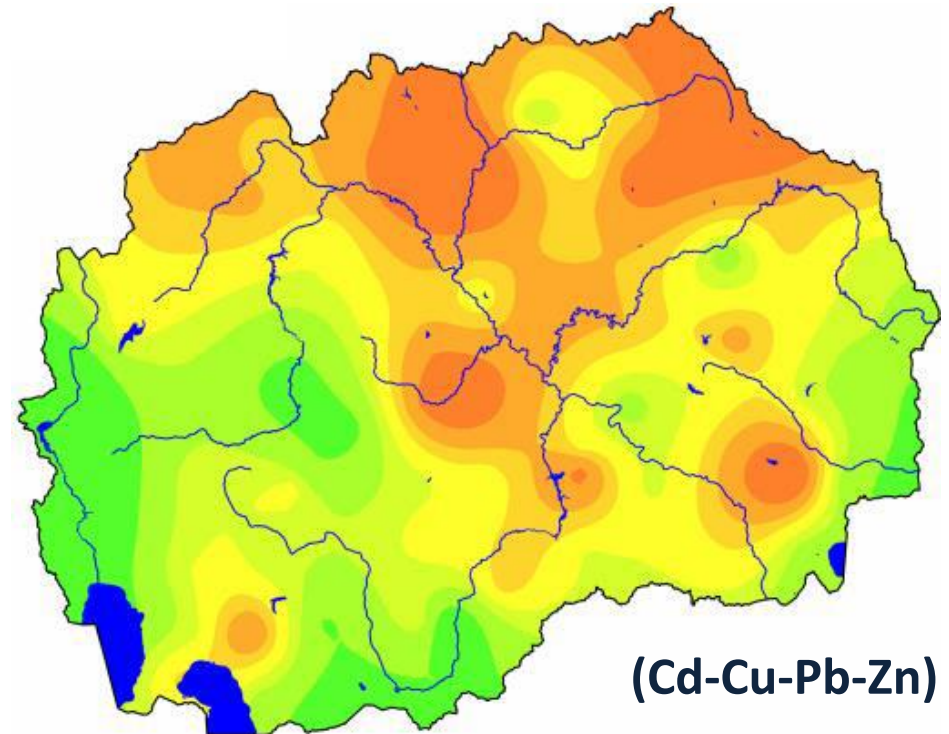
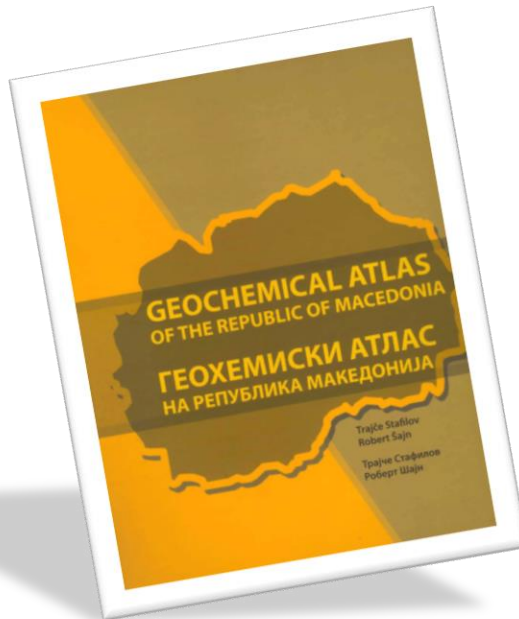
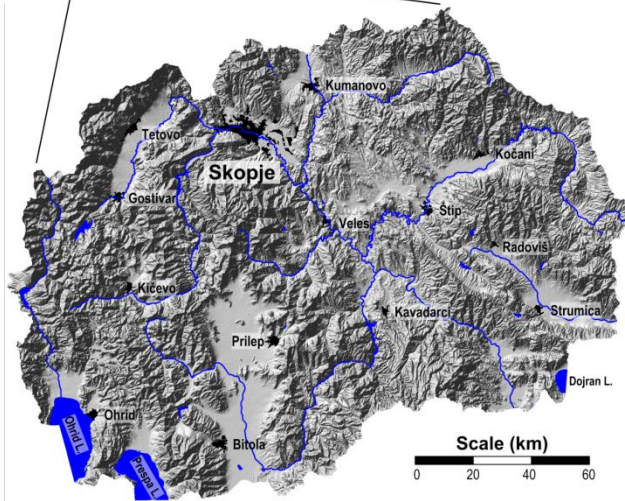


Artifacts
Precious metals
Foodstuffs.....

Entrance of chemical elements in food chain



MULTI-ELEMENT DISTRIBUTION IN SOIL



(Cd-Cu-Pb-Zn)

Factor 2 (percentiles of distribution)



**Dominant geochemical association
In areas with anthropogenic
introducing of heavy metals**

Analytical challenges in chemical characterization

Multi-Collector Inductively Coupled Plasma with Mass Spectrometry (MC-ICP-MS)



High Resolution Inductively Coupled Plasma with Mass Spectrometry (ICP- HRMS)

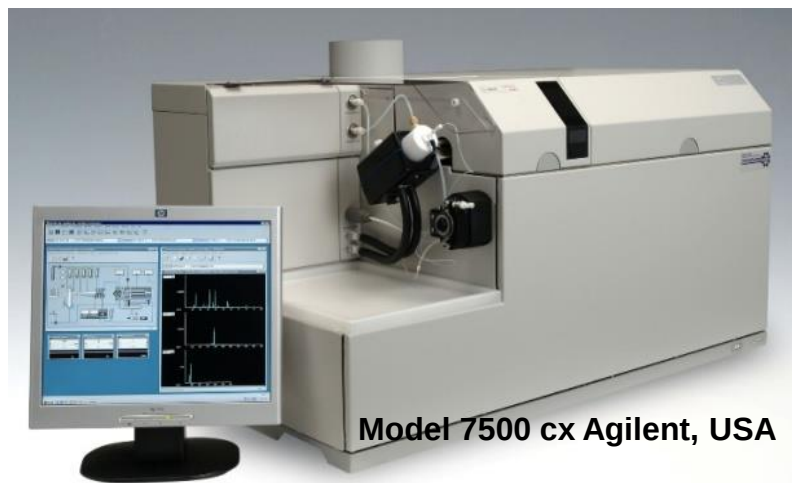


Thermal Ionization Mass Spectrometry (TIMS)

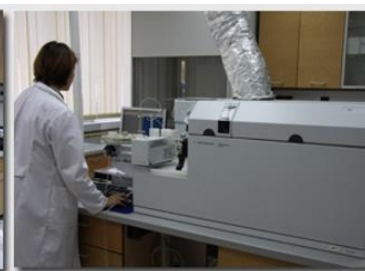
Isotopes measurements

DETERMINATION OF ISOTOPES

QUADROPOLE INDUCTIVELY COUPLED PLASMA WITH MASS SPECTROMETRY (Q-ICP-MS)



UNILAB
Faculty of Agriculture

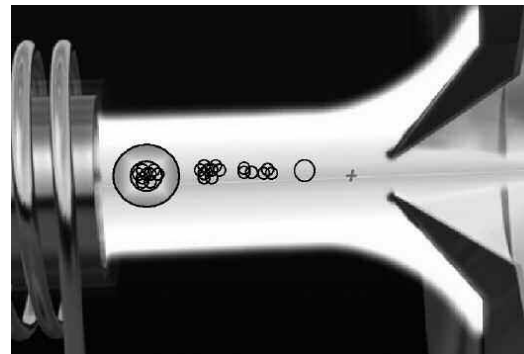
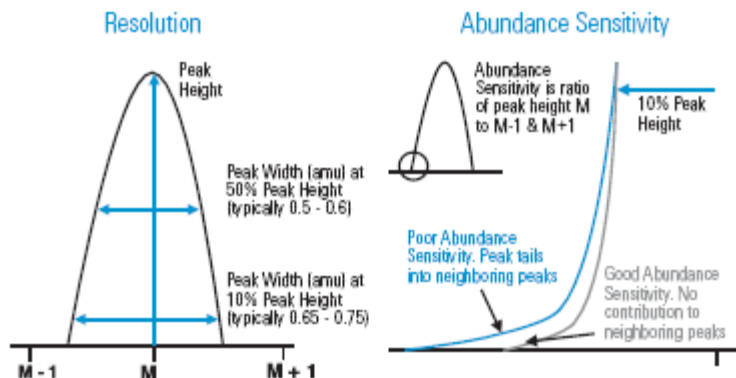
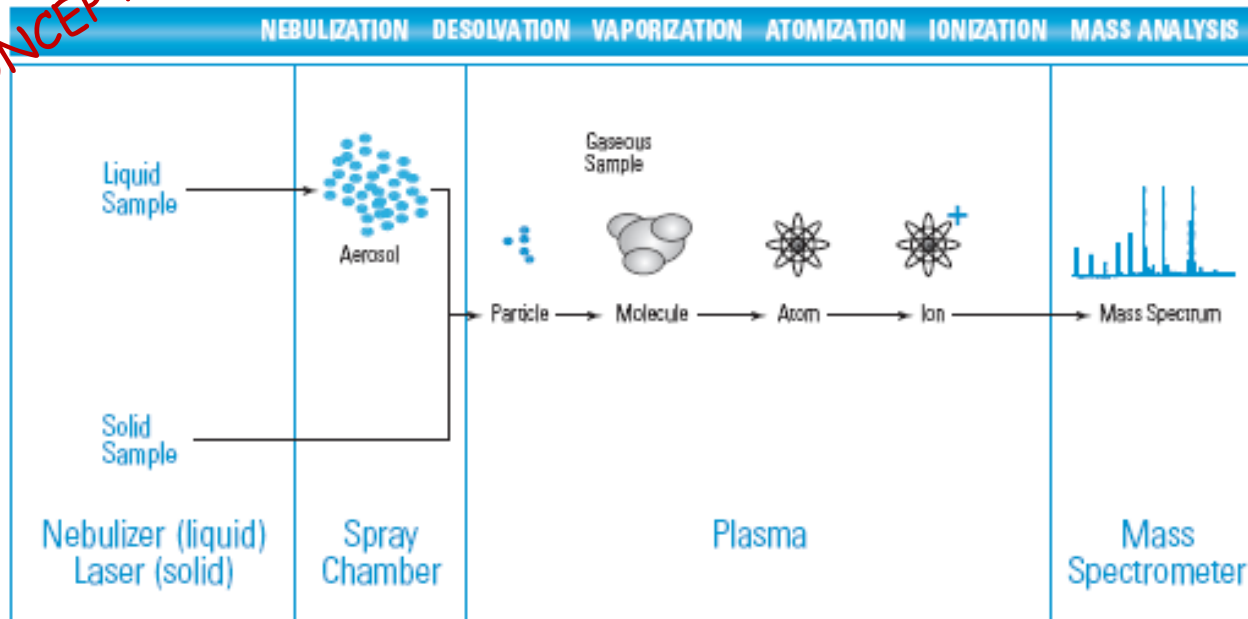


2nd Meeting Agriscience & Practice 2019, 12th April 2019 Štíp

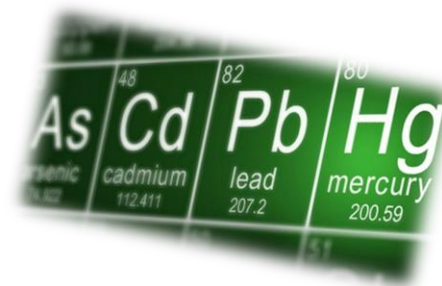
Isotopes measurements

As	Cd	Pb	Hg
arsenic	cadmium	lead	mercury
75	112.411	207.2	200.59

BASIC CONCEPT

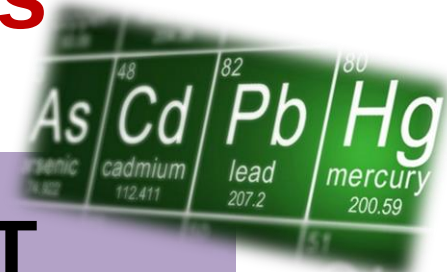


Isotopes measurements



INSTRUMENT	(ICP introduction system)
Sampler	Cu (standard)
Skimmer	Ni (standard)
Nebulizer	MicroMist (standard)
Plasma torch	Quartz, 2.5 mm (standard)
Integration Time	0.5 sec x 1 point
Replication	5
Tune parameters	
RF power	1500 W
Sample depth	7.5 mm
Carrier gas	1.06 L/min
Makeup gas	0.41 L/min
Extract lens 1	From -3 V to -5V
Extract lens 2	From -150 V to -161 V
Energy discriminator	2 V
Reaction gas	He 5.0 mL/min
CeO/Ce	0.58% (ref. value <0.65%)
Ce⁺⁺/Ce	2.05% ((ref. value <3%))

Isotopes measurements



SAMPLE PRETREATMENT

Microwave digestion system

- Closed-high-pressure decomposition
- Mixture of reagents (**5 mL HNO₃**, **3 mL H₂O₂**)

Organic matrix samples!!!!



Model MARS 5, CEM Corporation, USA

Step	Initial T (°C)	Final (°C)	Power (W)	Time (min.)
1	25	150	600	15
2	150	150	600	5
3	150	180	800	10
4	180	180	800	10

Internal standard elements:

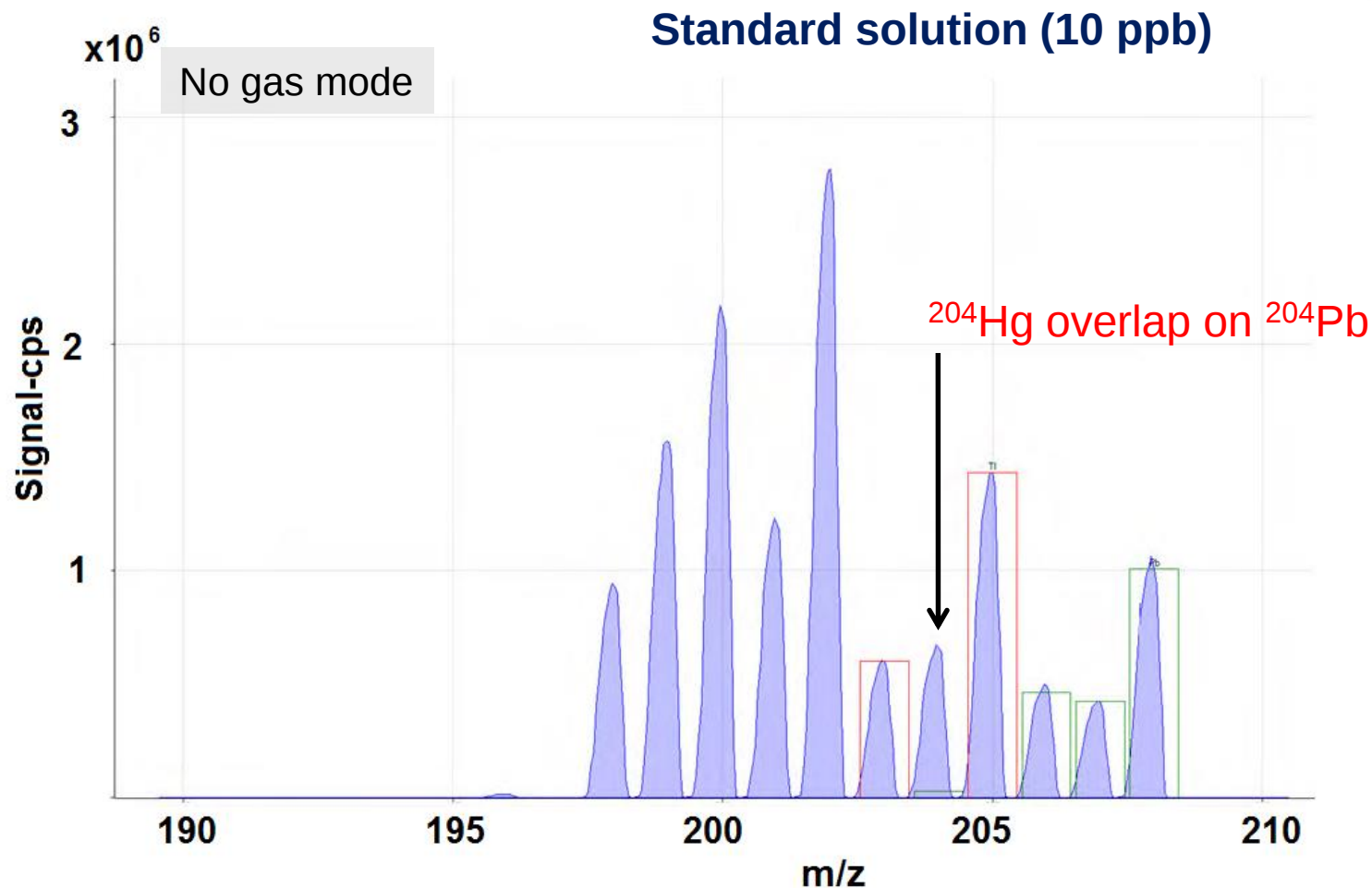
¹⁰³Rh, ¹⁹³Ir, ²⁰⁹Bi

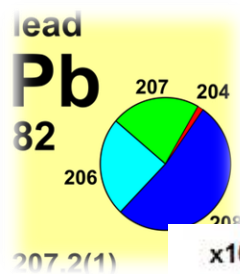
Ivanova,-Petropulos, V., Balabanova, B. et al., (2017) Food Analytical Methods.

Ivanova,-Petropulos, V., Balabanova, B. et al., (2016) Food Analytical Methods.

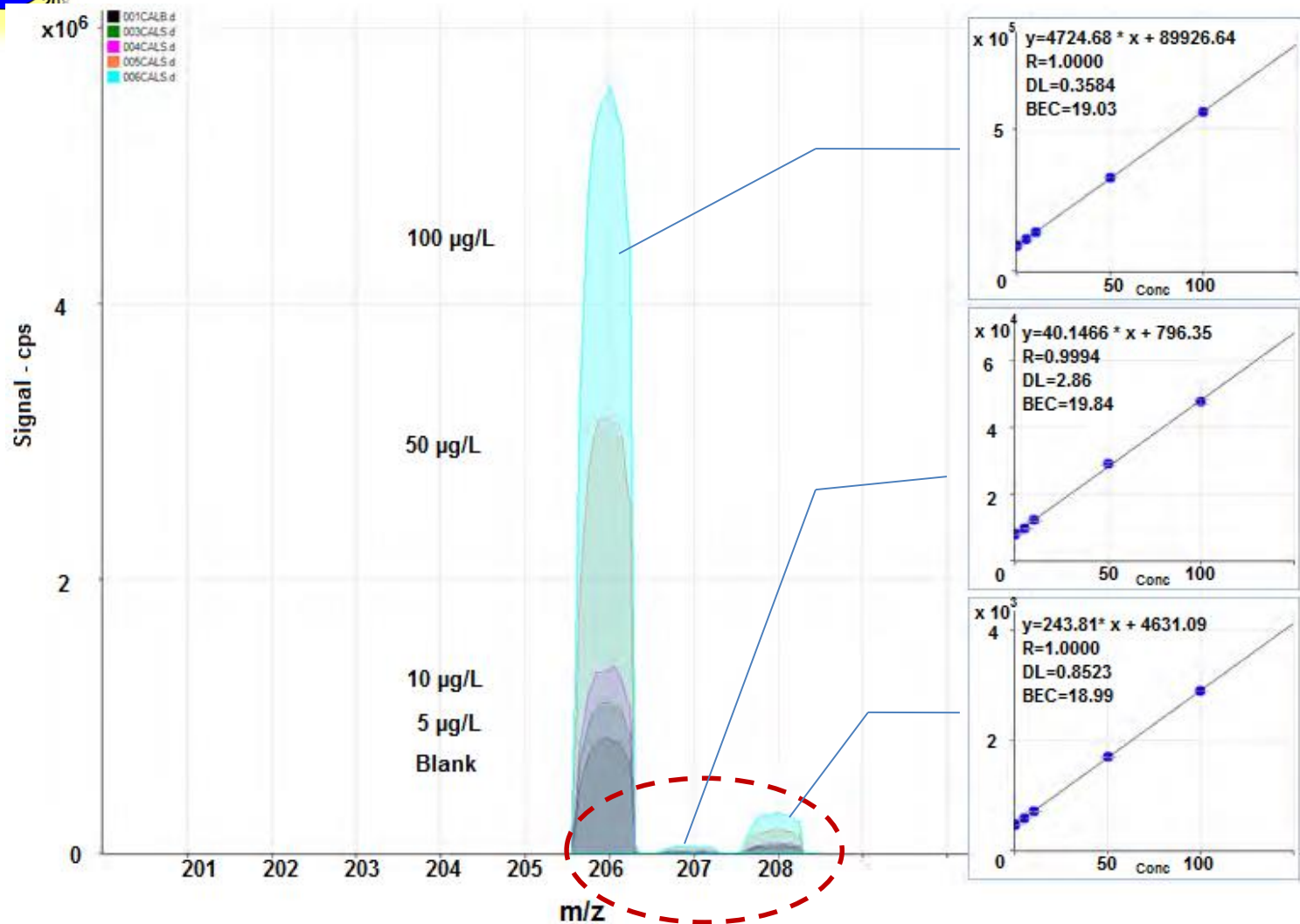
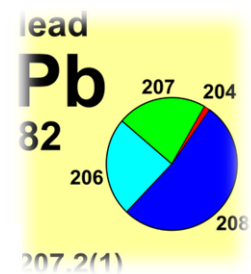
Mercury and lead isotopes measurements

As arsenic 74.922	Cd cadmium 112.411	Pb lead 207.2	Hg mercury 200.59
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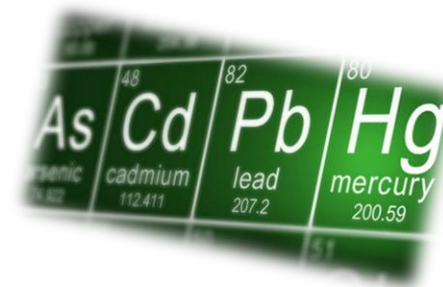




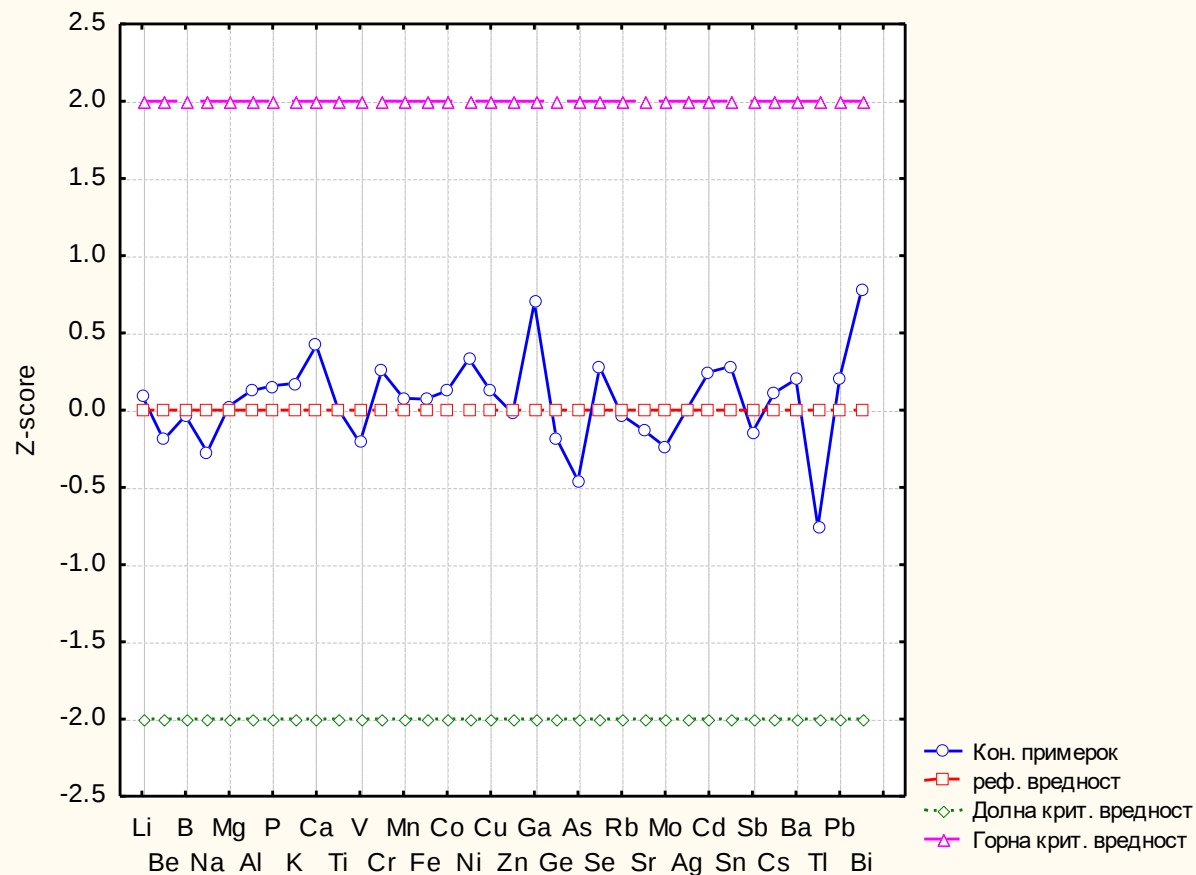
Lead isotopes measurements



QA/QC Accuracy

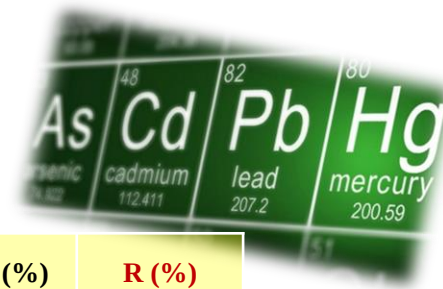


Element	Unit	Isotope	Analytical range
Li	µg/L	7	0,5-50
Be	µg/L	9	0,1-50
B	µg/L	11	10-1000
Na	mg/L	23	100-1000
Mg	mg/L	24	100-5000
Al	mg/L	27	10-500
P	mg/L	31	50-5000
K	mg/L	39	500-10000
Ca	mg/L	42	500-10000
Ti	mg/L	48	50-500
V	µg/L	51	1-100
Cr	µg/L	53	1-100
Mn	mg/L	55	10-100
Fe	mg/L	56/57	10-500
Co	µg/L	59	0,1-50
Ni	µg/L	60	1-100
Cu	mg/L	63	5-500
Zn	mg/L	64	10-500
Ga	µg/L	69	0,5-50
Ge	µg/L	72	0,1-50
As	µg/L	75	0,1-50
Se	µg/L	77	0,1-50
Rb	mg/L	85	1-100
Sr	mg/L	88	1-500
Mo	µg/L	95	0,1-50
Ag	µg/L	107	1-50
Cd	µg/L	111	0,1-100
Sn	µg/L	118	0,1-50
Sb	µg/L	121	0,1-10
Ba	mg/L	137	1-100
Hg	µg/L	202	0,1-50
Tl	µg/L	205	1-100
Pb	µg/L	206/207/208	5-5000
Bi	µg/L	209	1-50



Element	Unit	Isotope	Analytical range
Li	µg/L	7	0,5-50
Be	µg/L	9	0,1-50
B	µg/L	11	10-1000
Na	mg/L	23	100-1000
Mg	mg/L	24	100-5000
Al	mg/L	27	10-500
P	mg/L	31	50-5000
K	mg/L	39	500-10000
Ca	mg/L	42	500-10000
Ti	mg/L	48	50-500
V	µg/L	51	1-100
Cr	µg/L	53	1-100
Mn	mg/L	55	10-100
Fe	mg/L	56/57	10-500
Co	µg/L	59	0,1-50
Ni	µg/L	60	1-100
Cu	mg/L	63	5-500
Zn	mg/L	64	10-500
Ga	µg/L	69	0,5-50
Ge	µg/L	72	0,1-50
As	µg/L	75	0,1-50
Se	µg/L	77	0,1-50
Rb	mg/L	85	1-100
Sr	mg/L	88	1-500
Mo	µg/L	95	0,1-50
Ag	µg/L	107	1-50
Cd	µg/L	111	0,1-100
Sn	µg/L	118	0,1-50
Sb	µg/L	121	0,1-10
Ba	mg/L	137	1-100
Hg	µg/L	202	0,1-50
Tl	µg/L	205	1-100
Pb	µg/L	206/207/208	5-5000
Bi	µg/L	209	1-50

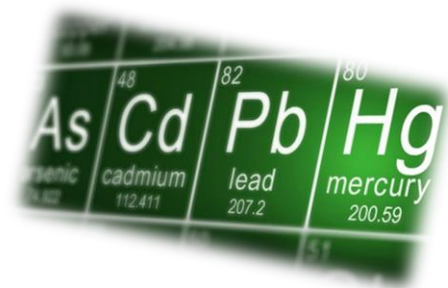
QA/QC Precision



Element	BCR-060 ^a (mg/kg)	BCR-060 ^b (mg/kg)	RSD (%)	R (%)
B	25	24,3	1,2	97
Na	9	9,81	1,7	109
Mg	10	10,3	0,7	103
Al	4180	4057	2,6	97
P	11,8	10,6	2,2	90
K	13,7	14,2	0,6	104
Ca	43,3	45,1	1,5	104
V	6	5,52	0,8	92
Cr	26	27,3	1,3	105
Mn	1760	1675	1,5	95
Co	4	3,70	1,3	93
Ni	40	38,6	1,1	97
Cu	51,2	52,4	2,7	102
Zn	313	317,8	1,5	102
As	8	8,12	1,9	102
Se	0,7	0,64	0,7	91
Rb	23	22,7	2,6	99
Mo	2	2,11	2,1	105
Ag	0,2	0,21	1,8	105
Cd	2,2	2,27	0,6	103
Sn	6	5,60	1,3	93
Sb	0,4	0,37	1,9	94
Cs	0,4	0,42	1,2	105
Tl	0,24	0,25	0,7	104
Pb	64	66,1	1,3	103

BCR-060: Aquatic plant - *Lagarosiphon major*

REGULATORY MEASURES



Reference

Schilcher et al. (1987, 1990)
German Ministry of Health 1991 (Schicher 1994)
Kabelitz (1998)
WHO (1999)
WHO (2007)
Pharmacopoea Europea Monograph Kelp (2007)
EC 1881/2006 and EC 629/2008
Herbal drugs monograph 1433 (2008)

Pb Cd Hg

10	0.5	-
5	0.2	0.1
10	0.5	-
10	0.3	-
10	0.3	-
5	4	0.1
3	1.0	0.1
5	0.5	0.1

content given in mg/kg

The safe use of medicinal and aromatic plants requires the absence of toxic heavy metals in the products



Foeniculi fructus



Valeriana radix



Menthae folium



Juniperi fructus



Liquiritae radix



Hyperici herba



Thyme (Serpylli herba)



Lycium barbarum



Agrimonia herba



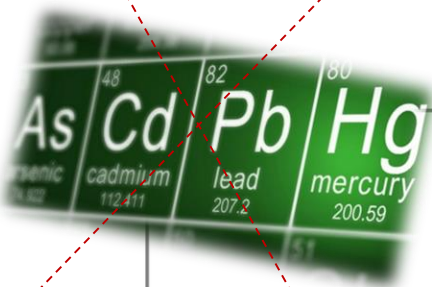
Origani vulgaris



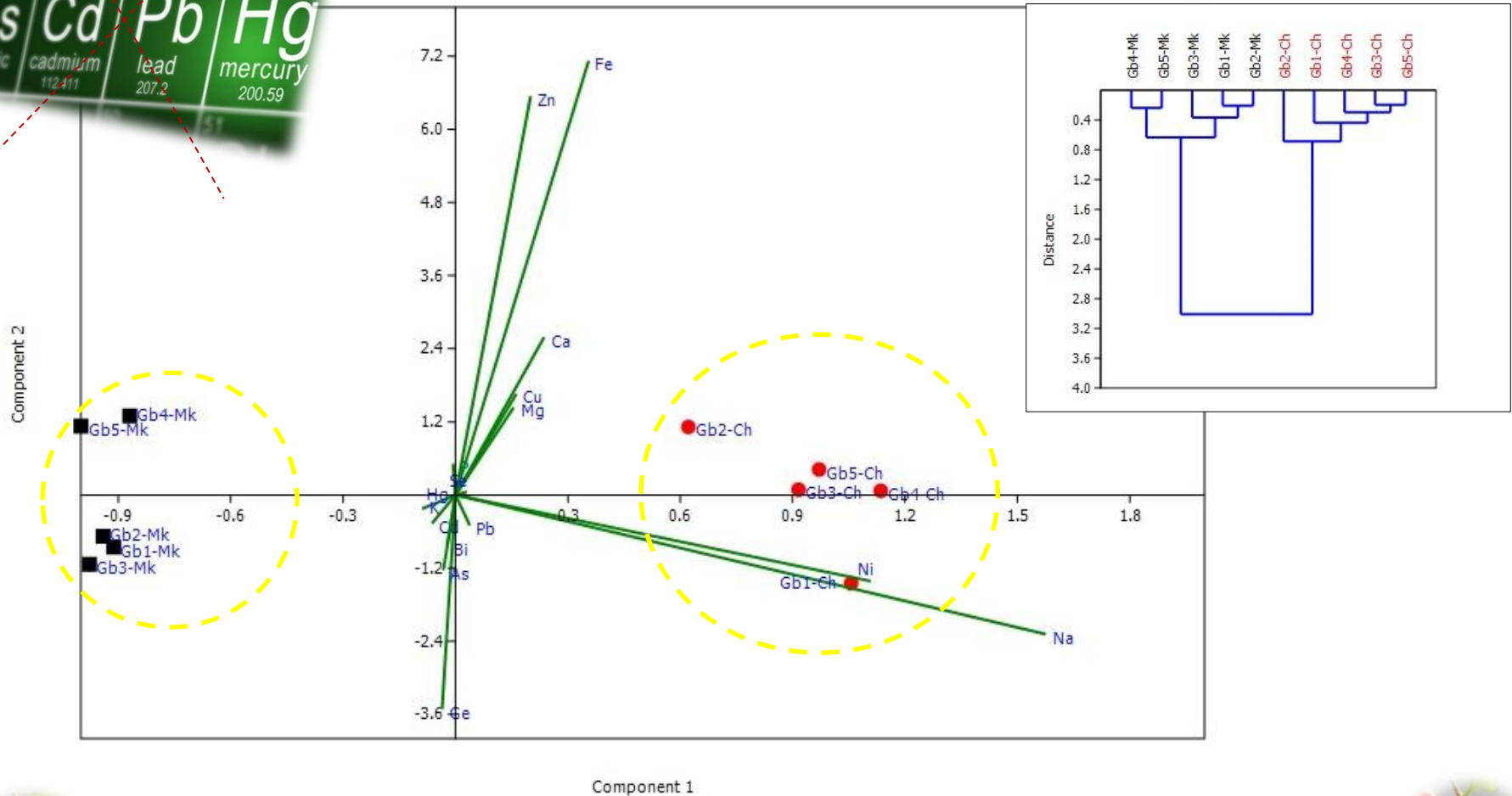
Rubi fruticosi folium



Multi-element characterization of *Lycium barbarum* Goji berries



As arsenic 74.922	Cd cadmium 112.411	Pb lead 207.2	Hg mercury 200.59
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CONCLUSIONS

Q-ICP-MS – sensitive method for simultaneous measurements using single tune mode.

- $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios can be very useful for improving isotopic characterization of ENVIRONMENTAL ISOTOPE STUDIES.
- Isotopic data often do not provide a *simple tracer* to identify and distinguish source emissions.
- Improved characterization of point source emissions could be achieved with additional isotopic ratios, such as isotopes of Sr and Hg.



PERSPECTIVES....

MULTI-DISCIPLINARY APPROACH

RARE-EARTH ELEMENT ANALYSIS

MULTI-ISOTOPE RATIO

METAL BINDING SCAN ANALYSIS

CHEMOMETRIC TOOLS:

Principal Component Analysis (PCA)
Cluster Analysis (CA)
Linear Discriminant Analysis (LDA)
Canonical Discriminant Analysis (CDA)
Artificial Neural Networks (ANN)

Research projects:

Characterization of multi-element profiles and multi-isotope ratios records as a tool for determination of the geographical origin of various plant species, foodstuffs and beverages

Bilateral project, Ministry of Education and Science-2018



Thank you for your attention!

