Joint Institute for Nuclear Research

Frank Laboratory of Neutron Physics sector of Neutron activation analysis and applied research

The Accumulation Features of Plants and Bivalves Near the Natural Sources of Strontium (Tula Region, Russia)

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Importance of geochemical levels for human health



Kashin-Beck or Urov disease

The excess of Sr cause the osteoarthrosis for children

- » The differentiated polyelement microelementosis with an excess of Sr, Mn, Cr, Ni, in some cases P, Ba, As, Zn and deficiency of Se, Cu, and Mo is typical or low in Urov biogeochemical provinces of Eastern Transbaikalia against the background territories
- » Parameters of migration of chemical elements in the soilplant complex reflected on their content in wheat, hair cover of animals and milk cows. The hay crops contain $72.8 \pm 31.6 \text{ mg/kg Sr}$
- » The sources of this imbalance are soil-forming rocks, specific conditions of soil formation (accumulation of organic matter in freezing soils of narrow valleys with a high degree of moisture and low flow, and selective concentration by plants)
- » The main reason is the ingestion of cereal grain grown in these areas and infected with the fungus, Fusaria sporotrichiella

Idea and Tasks of the study

• The aim was to find the specific elemental patterns in different substrates and biota organisms in the case of natural Sr excess

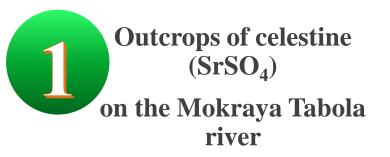
<u>Tasks:</u>

- To find a sites with Sr excess (Tula region, Russia)
- To choose the biomonitors and appropriate substrates
- To analyze the levels of the Sr and important elements
- To make a suggestions about such sites with the highest levels and appropriate objects for future monitoring



Three natural key zones with Sr sources

Samples: water, substrate (soil, sediment), biota (vegetation, mollusc shells)



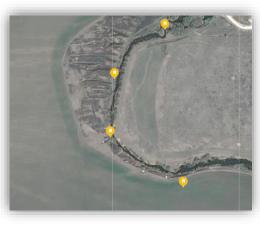


Bolsheberezovskoe swamp on the Nepryadva river



Special protected area

st. 1-4



Natural monument of regional significance

st. 5-9

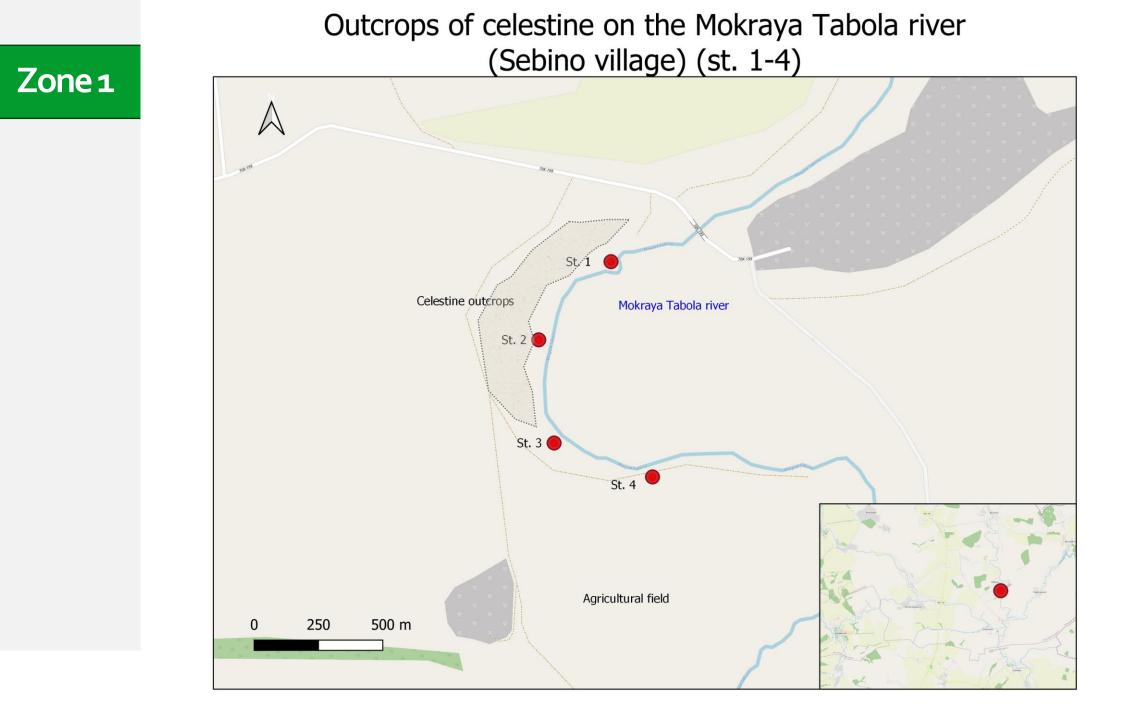


Protected area st. 10-12



Zone 1

Outcrops of celestine (SrSO₄) on the Mokraya Tabola river (Sebino village) (st. 1-4)





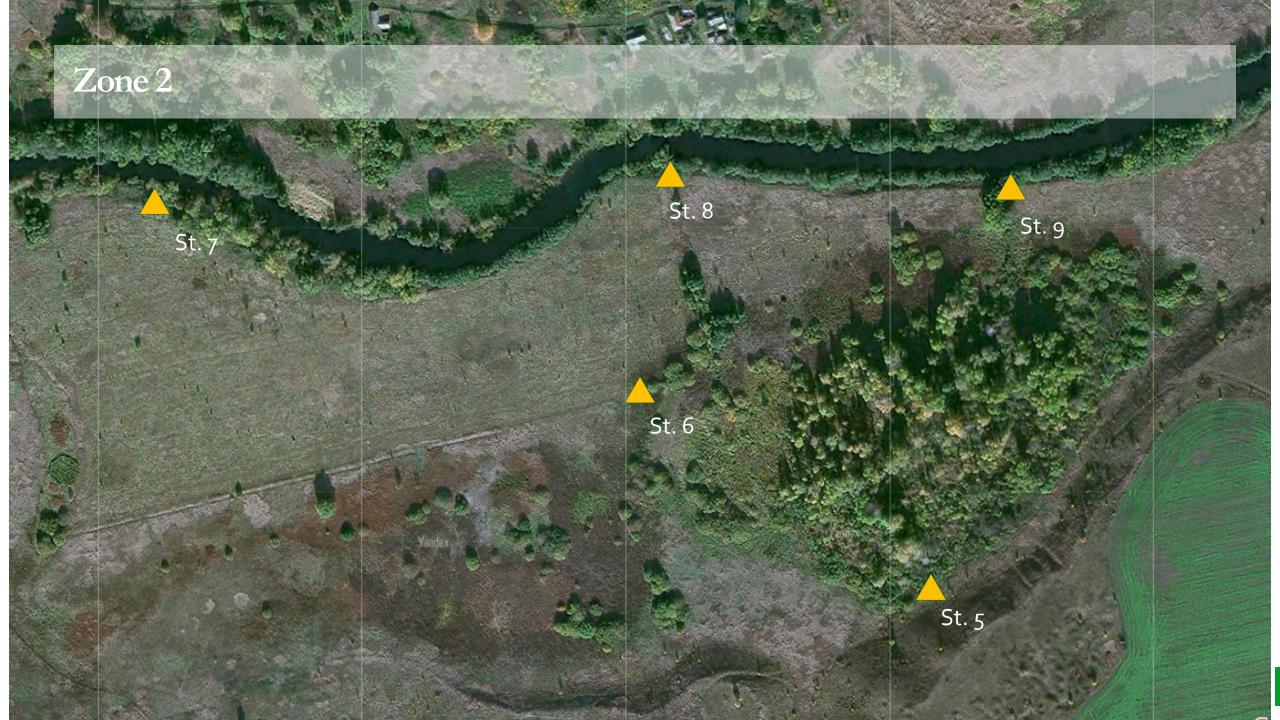
Celestine (SrSO₄) rock outcrops

St. 2

St. 4: Flushing from the agricultural field



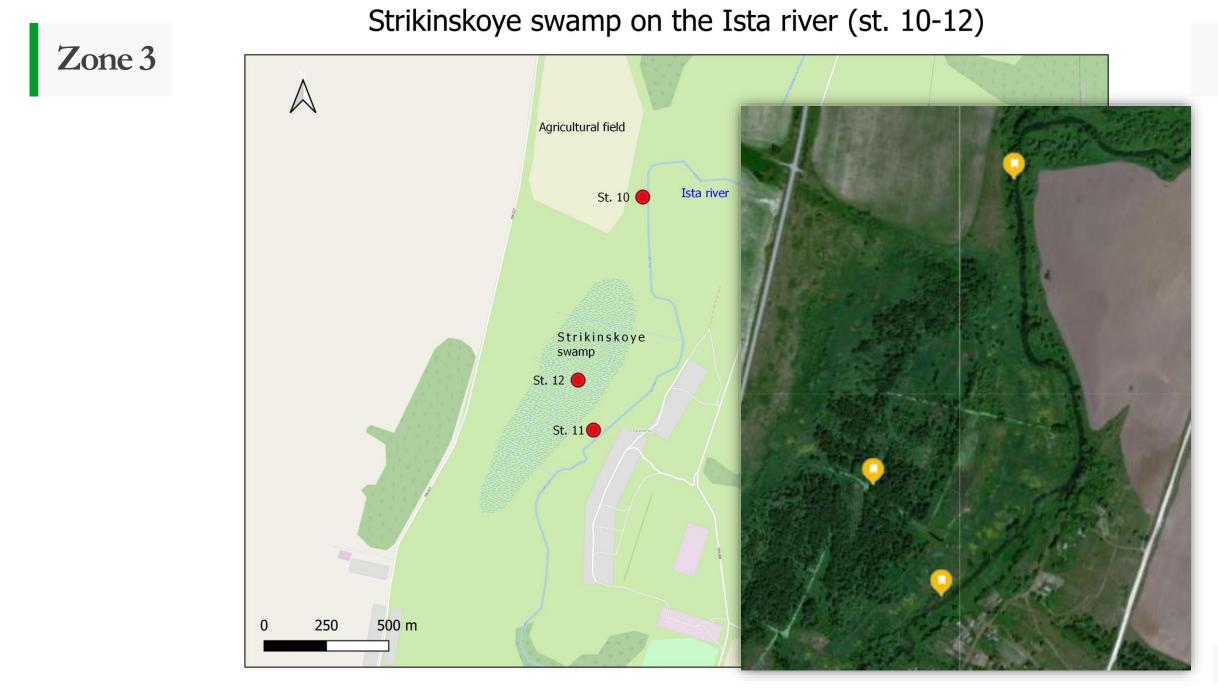




A Nepryadva river St. 9 St. 8 St. 7 Bolsheberezovskoye swamp St. 6a St. 6 St. 5 250 500 m 0 Agricultural field

Zone 2

Bolsheberezovskoye swamp on the Nepryadva river (st. 5-9)





Sampling

St. 1-12 + st. 0 and St. M as the background

- » Water with nitric acid
- » Two kind of substrate: soil and sediments
- » The common species of plants (buttercup *Ranunculus repens*)
- » The common filtrator organism: bivalvia freshwater molluscs (*Unio sp.*)
- In addition, for the background comparison the appropriate samples were collected from the Don river and Moskva river



AnalyticalTechnique

Sample preparation and measurements

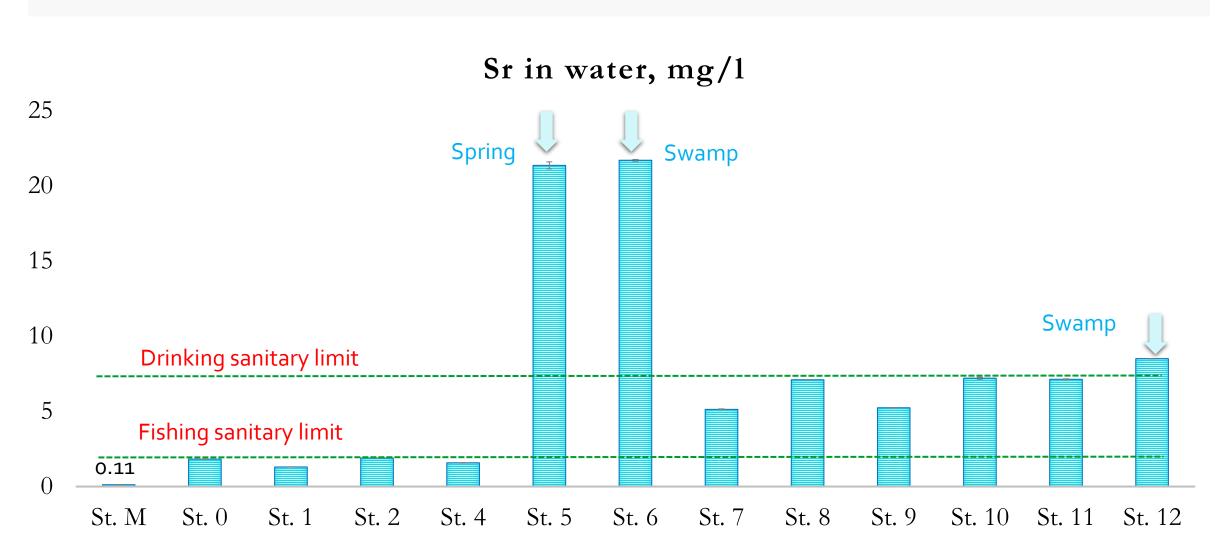
- » Water fixation with nitric acid
- » Drying in an oven at 40°C for 3 days
- » Homogenization by the planetary mono mill
- » Drying again at 105°C for 1 day
- » Determination of levels of 15 elements by the ICP-OES
- » The following certified reference materials were used for quality control assurance: INCT-OBTL-5 (Oriental Basma Tobacco Leaves) and NIST 2709a (San Joaquin Soil Baseline Trace Element Concentrations).
- » The standard deviation for any element was less than 4 % for each measured sample

RESULTS

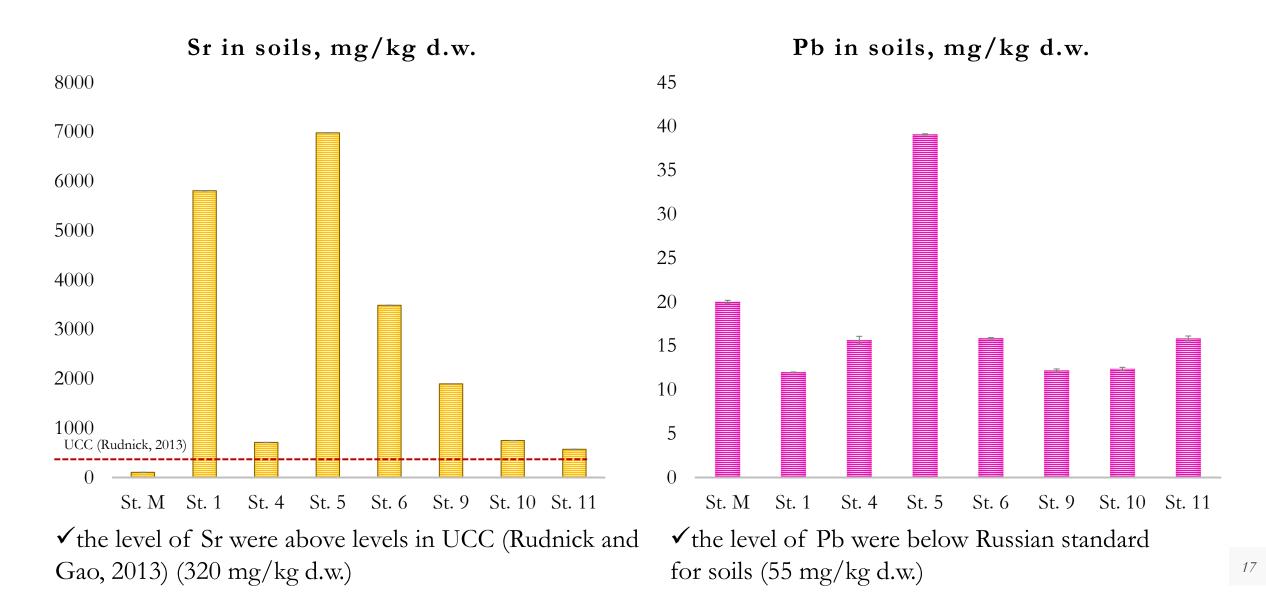
Studied elements (soils, mg/kg d.w.)

		Al	Р	S	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Sr	Cd	Ba	Pb
St. M	Background station	7169	4126	1889	54	42	2674	27896	13	24	19	103	106	0.76	329	20
St. 1	Zone 1 Celestine outcrops	6322	961	1376	45	36	641	18965	13	20	10	39	5808	0.39	245	12
St. 4		6764	1367	1137	54	43	1179	20970	16	22	14	52	711	0.46	141	16
St. 5	Zone 2. Spring in swamp	25039	4839	14040	138	124	881	63375	29	66	55	214	6980	1.84	864	39
St. 6		12653	1888	1889	59	50	538	38670	16	25	21	71	3488	0.61	358	16
St. 9		4500	708	1201	48	38	909	20150	12	20	11	40	1899	0.37	199	12
St. 10	Zone 3.	12915	397	419	37	30	389	14349	10	14	9	34	752	0.36	261	12
St. 11	River and swamp	13345	728	724	46	39	801	18984	13	17	12	49	573	0.49	305	16
Chen 2018	Russian standard for heavy metals	-	-		-		-	-	-	2.6	3.5	16	-	0.76	-	55
Dyache nko, 2014	Average Soil of the North Caucasus	81505			126	109	930			47		106	216		720	

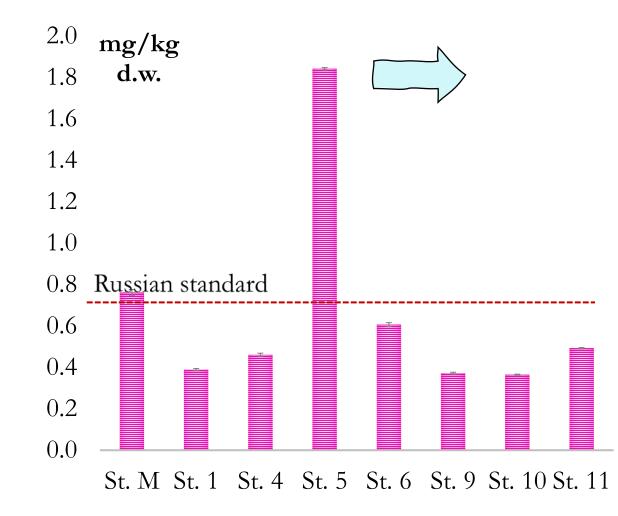
Initial levels in water



Sr and anthropogenic elements (Pb) in soils



Anthropogenic elements (Cd) in soils



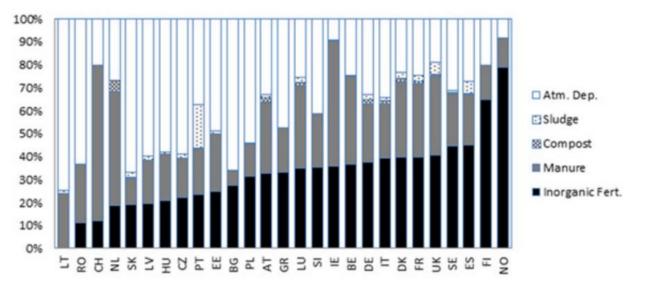
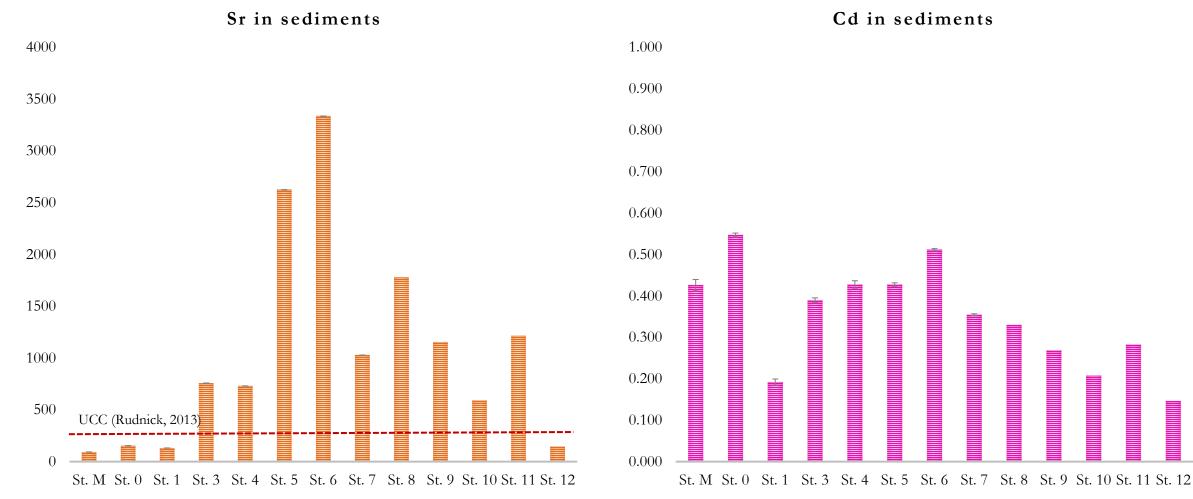


Figure 2.5 Contribution of different sources of Cd to arable land in EU Member States and associated countries (de Vries et al., 2016).

✓ St. 5: the level of Cd increase in arable land due to fertilizers

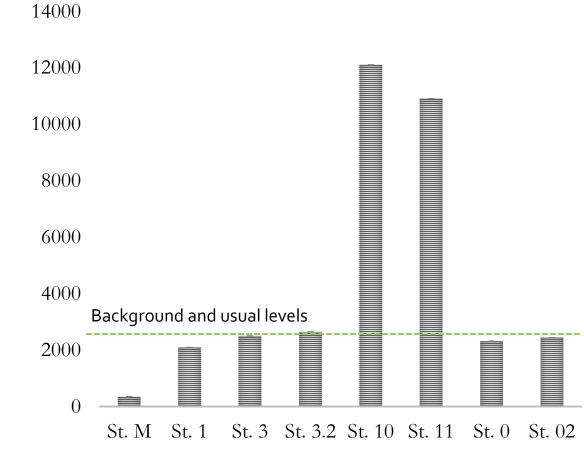
Sediments: Sr and Cd



 ✓ Cd and other volatile anthropogenic elements washed out from sediments and remaining in the soils

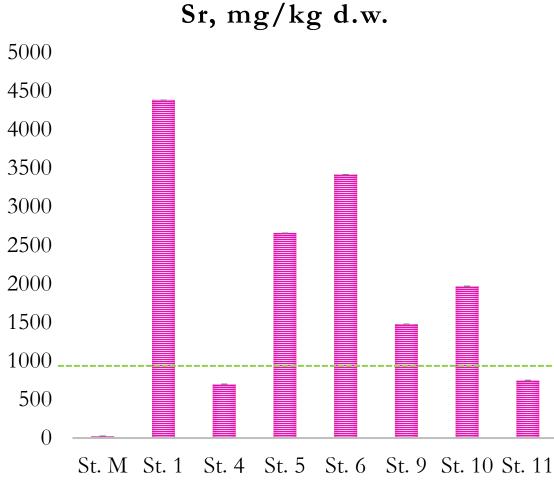
Shells of Bivalvia molluscs (Unio sp.)

Sr in shells, mg/kg d.w.





Buttercup (Ranunculus repens)

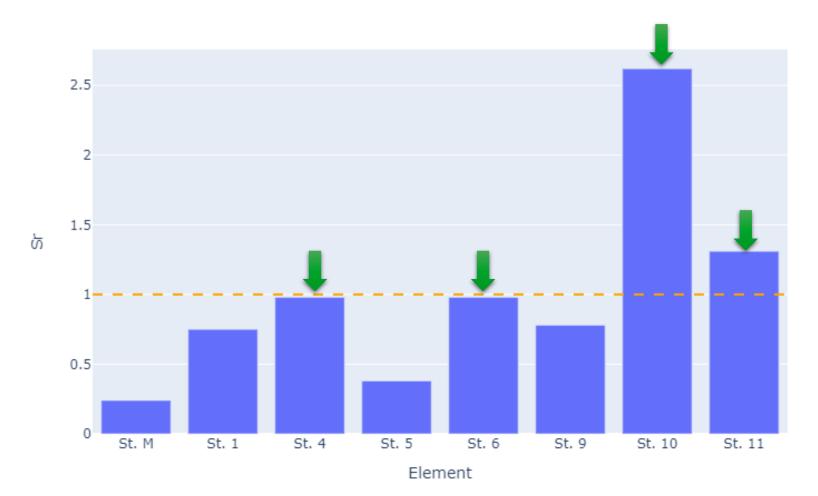


Usuall levels in leaves 100-1000 mg/kg



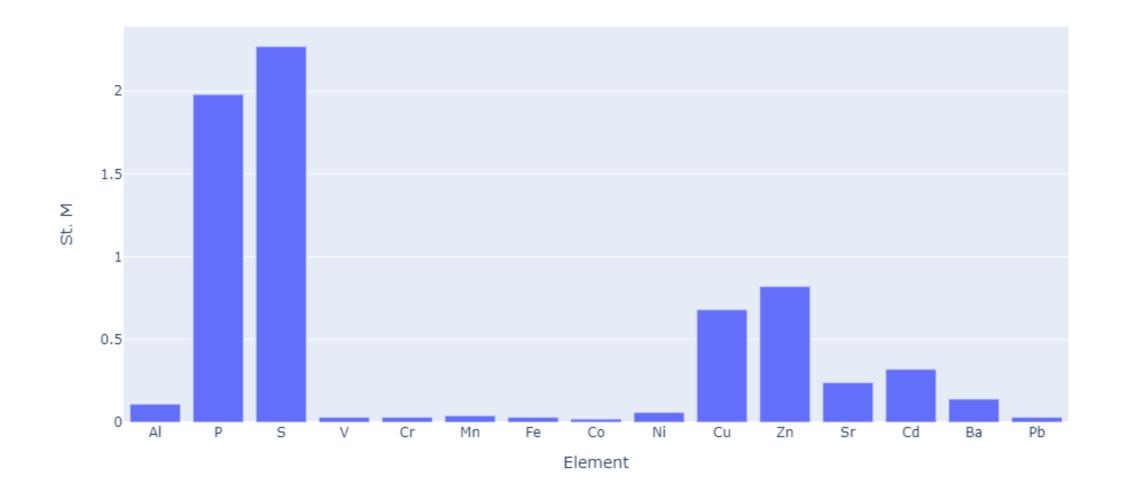
Bioaccumulation of Sr in buttercup/soil

Levels of Bioaccumulation factor



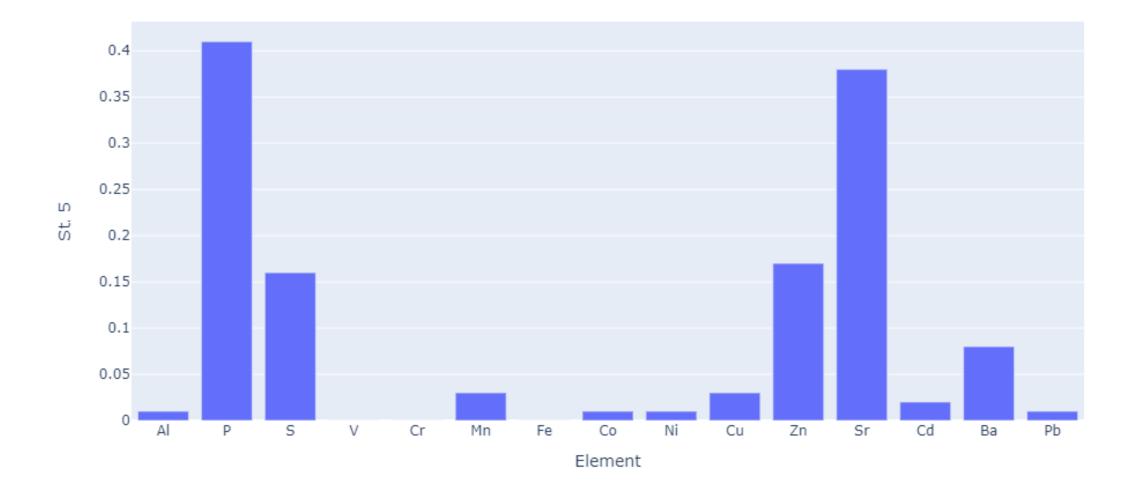
St. M (background): low levels of accumulation

Levels of Bioaccumulation factor



St. 5: the specificity of bioaccumulation

Levels of Bioaccumulation factor



Conclusions and Suggestions

- » Using local aquatic vegetation with the soil in biomonitoring
- » The key problem is to find a proper background, with typical local geological features, relief and direction of rivers
- » The anthropogenic influence could be separated by the typical elements such as Cd and Pb
- » The levels of anthropogenic Pb were below Russian standard limits in soils, however, such elements as Ni, Cu, Zn were higher in all studied zones that indicated typical excess of all elements in Tula region in comparison with the average Russian soil standard. This agreed with the soils of the North Caucasus.
- » Lithogenic group could be associated with the elements of the appropriate origin, for example Al
- » The small natural protected area should be studied in detail to provide the real background levels of such elements as V, Cr, Ni, Zn, Cd, Ba
- » The buttercup samples demonstrated the high levels of Sr at st. 1, 5,6, 9, 10. However, the bioaccumulation coefficients (compared to soils) were lower than unit. Sr are not bioaccumulated in this plant.
- » The shells of Bivalvia molluscs indicated the high accumulation levels in comparison with the water. The levels of Sr were higher in Ista river (st. 10 and 11) in comparison with the other zones, background and typical levels for such molluscs



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