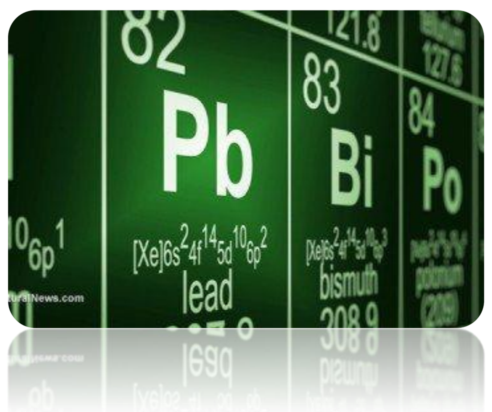

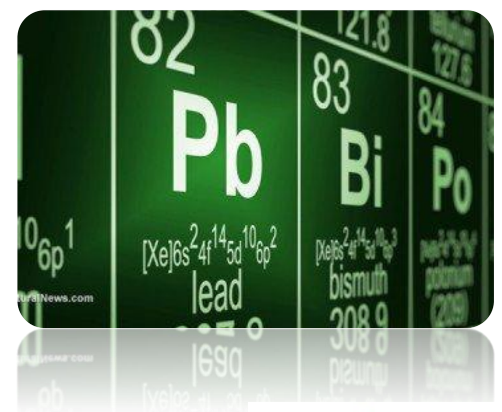

BIOAVAILABILITY OF METALS OCCURRING IN POLLUTED SOIL AND ITS ACCUMULATION IN PLANT FOOD

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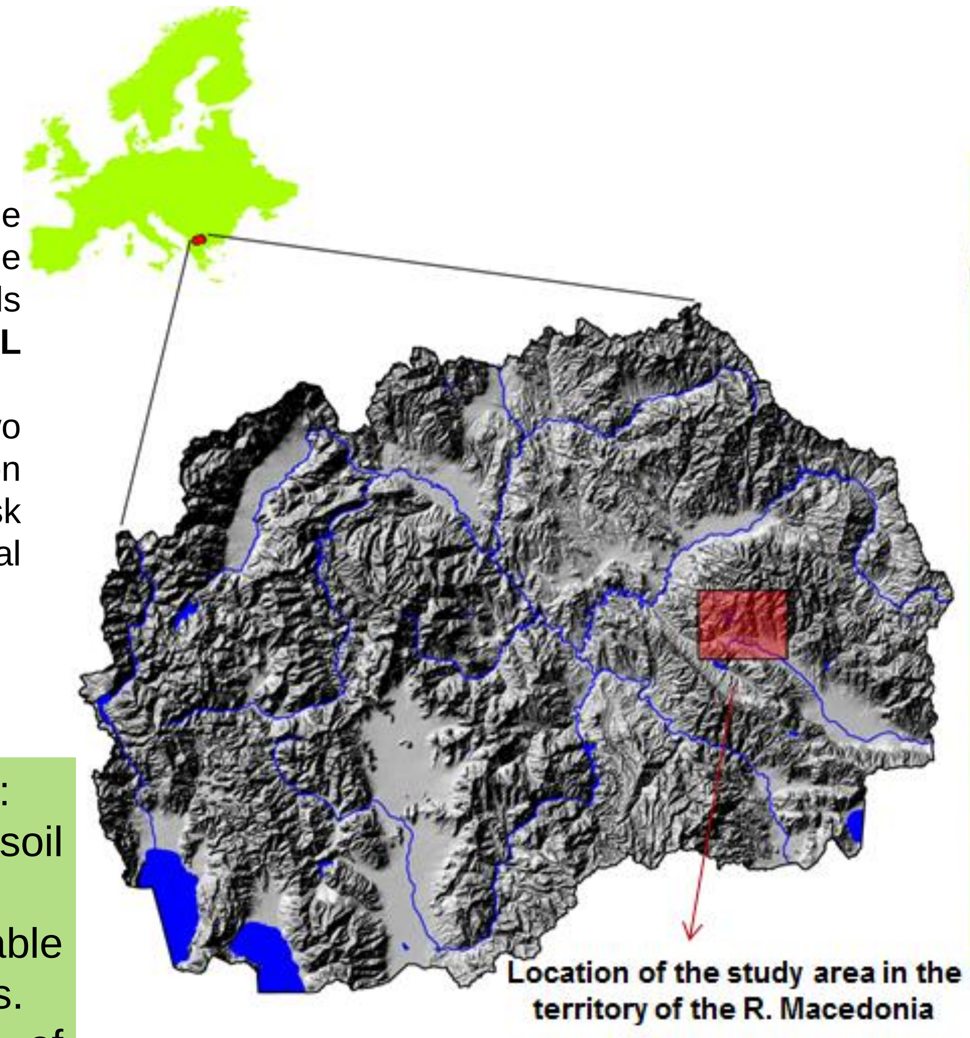
INTRODUCTION

Mining and processing metal ore can be a significant source of **HEAVY METAL CONTAMINATION** of the environment. The environmental concern in mining areas is primarily related to physical disturbance of the surrounding landscape, spilled mine tailings, emitted dust and acid mine drainage transported into rivers. Excessive accumulation of heavy metals in agricultural soils around mining areas, resulting in elevated heavy metal uptake by plant food, is of great concern because of **POTENTIAL HEALTH RISK** to the local population.
The consumption of plants produced in contaminated areas, as well as ingestion or inhalation of contaminated particles is two principal factors contributing to **HUMAN EXPOSURE TO METALS**. Cultivation of crops for human or livestock consumption on contaminated soil can potentially lead to the uptake and accumulation of trace metals in the edible plant parts with a resulting risk to human health. Increasing evidence shows that heavy metal pollution of mined areas caused health damage to the local inhabitants.



Methodology

SOIL PRETREATMENT - Three methods were applied for the study of the plant-availability of the elements:
(1) Extraction with deionized H_2O, that provides information on the actual availability of eleme nts fromthe soil solution;
(2) Extraction with 0.1 M HCl for 1 h and filtered with an acid-resistant filter, displacing potentially available forms that are not easily extracted. Total digestion was applied for determining of total elements contents.
(3) Extraction of the soluble species of trace elements in a mixed buffered solution (pH = 7.3) of triethanolamine (0.1 mol l^{-1} TEA) with $CaCl_2$ (0.01 mol L^{-1}) and diethylenetriaminepentaacetic acid (DTPA, 0.005 mol L^{-1}), that is often recommended for the extraction of toxic or biogenic metals. DTPA extracting solution was preparing in this way: 0.005 M DTPA (diethylenetriaminepentaacetic acid), 0.01 M $CaCl_2$ and 0.1 M TEA (triethanolamine) was adjusted to pH to 7.30±0.05 with 1:1 HCl.

PLANTS PRETREATMENT – Plants samples were totally digested with application of closed wet digestion method using HNO_3 and H_2O_2 for total tissue digestion.

RESULTS

Table 1. Basic statistics for elements contents in soil extracts and plant species (contents given in mg/kg on dried mass) [1]

	H_2O	0.1 mol/L HCl	DTPA–$CaCl_2$–TEA	TOTAL CONTENTS			
				Cu mine (site 1)	Fe-mine (site 2)	Reference area (site 3)	Urban area (site 4)
Ag	<0.01	0.02±0.01	<0.01	0.47	0.76	0.46	1.09
Al	23.9±16.5	**62.9±46.2**	0.78 ±0.88	58992	61061	59467	59643
As	<0.25	**<0.25**	<0.25	**26.9**	23.4	18.9	**48.7**
Ba	0.18±0.05	**10.9±5.81**	0.71±0.40	311	403	343	437
Ca	104±47.7	**3421±430**	1222±197	22677	20447	21954	35394
Cd	0.01±0.001	0.05±0.03	0.05±0.03	**1.06**	0.96	0.86	0.59
Cr	0.04±0.02	0.06±0.03	0.01±0.003	**63.6**	41.9	55.8	54.2
Cu	0.30±0.06	1.57±1.97	**8.60±6.65**	**100**	63.7	34.3	79.0
Fe	27.9±18.1	4.43±4.84	28.0±33.4	**43025**	32629	32646	31242
K	56.2±15.6	**155±47.2**	81.6±26.6	23716	19805	16173	20290
Li	0.01±0.004	0.04±0.006	0.006±0.005	7.79	5.70	7.74	9.81
Mg	21.7±6.15	**305±79.6**	103±28.7	10676	6583	8956	8629
Mn	0.47±0.31	**44.4±28.5**	10.6±2.82	521	577	575	567
Mo	0.04±0.04	0.04±0.02	0.03±0.03	4.0	3.2	2.8	2.5
Na	6.91±4.67	9.73±5.94	6.06±5.35	8582	**9248**	8506	7956
Ni	0.18±0.05	**0.84±0.54**	0.55±0.22	19.6	**39.0**	23.9	34.0
P	16.6±3.75	**177±24.8**	5.19±1.41	1385	931	995	**2184**
Pb	0.25±0.07	0.38±0.26	**1.71±1.15**	24.4	44.8	36.8	**83.9**
V	0.08±0.03	0.10±0.08	0.06±0.04	**93.8**	72.2	82.7	67.9
Zn	0.28±0.11	**6.02±5.34**	5.02±5.10	78.8	72.9	73.2	**181**

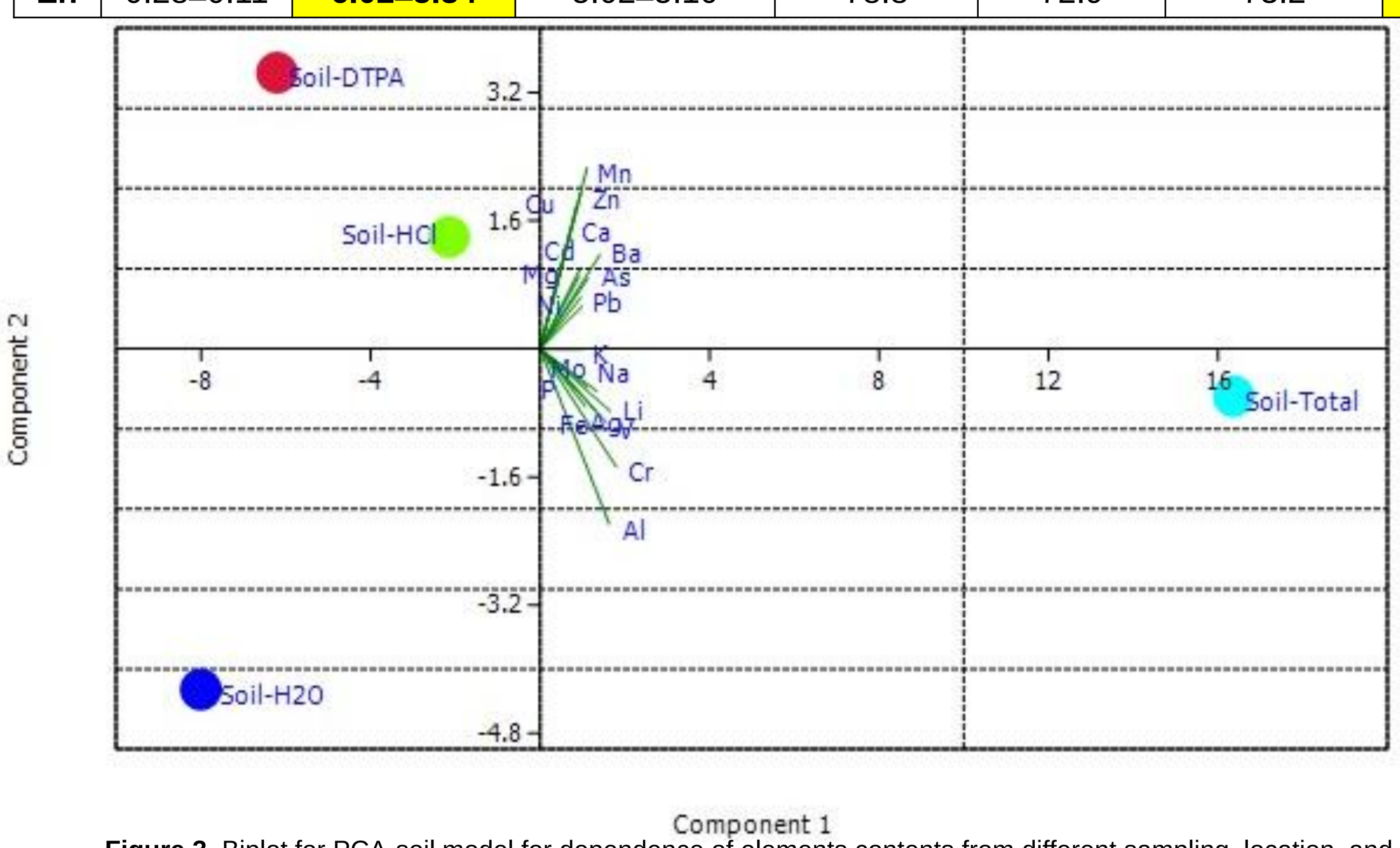


Figure 3. Biplot for PCA-soil model for dependence of elements contents from different sampling location, and different soil extraction solution

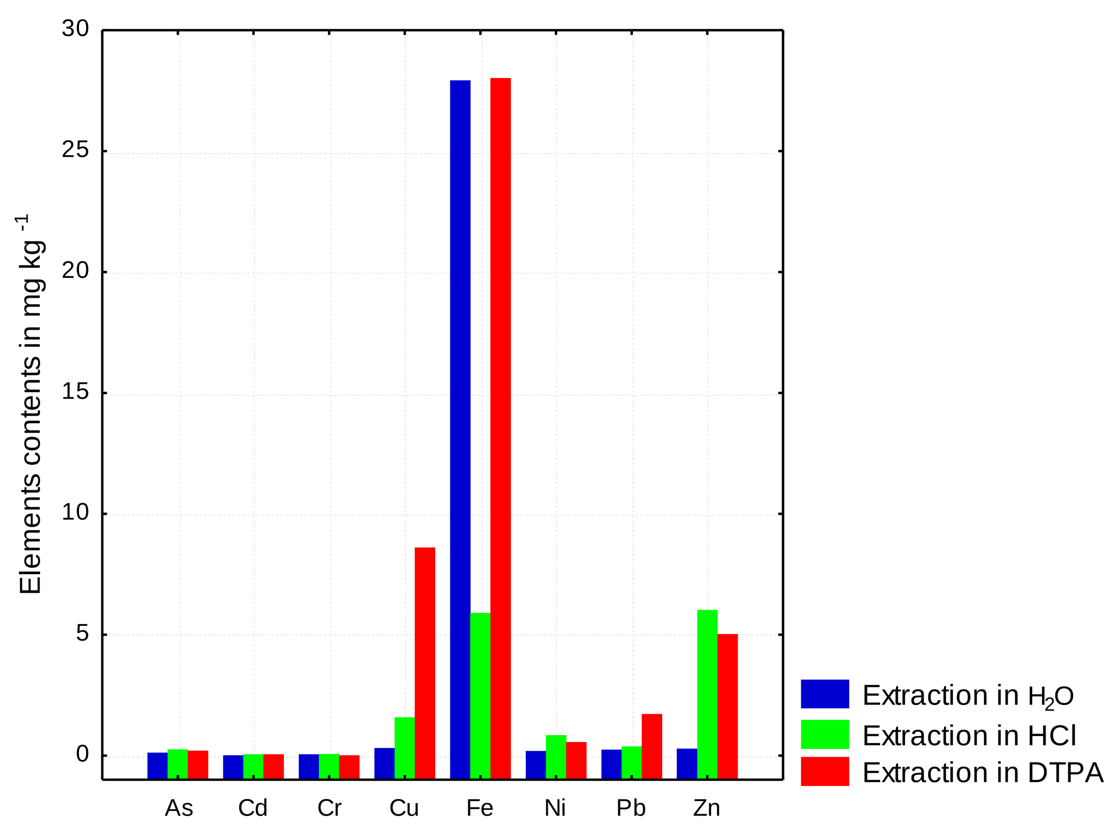


Figure 2. Bar plots for available forms - extracted elements contents in three different extracts solutions [2]
(H_2O, 0.1 M HCl and DTPA–$CaCl_2$–TEA)

Table 2. Basic statistics for elements contents in shoots and roots of plant species (contents are given in mg/kg of dried matter)

	Rumex acetosa		*Urtica dioica*		*Spinacia oleracea*	
	Shoot	**Root**	**Shoot**	**Root**	**Shoot**	**Root**
Ag	**0.15**	0.037	0.091	0.058	0.08	0.04
Al	55.8	328	223	**494**	172	308
As	<0.25	0.76	<0.25	0.89	0.44	<0.25
Ba	3.49	10.7	13.2	10.6	4.40	9.90
Ca	3777	5526	21763	4773	4049	2819
Cd	0.039	0.053	0.01	0.08	0.13	**0.17**
Cr	0.22	0.66	0.40	1.01	0.49	0.83
Cu	8.07	12.9	**15.3**	10.0	7.74	6.45
Fe	79.2	238	154	**459**	133	272
K	21751	8493	14800	10181	30809	21854
Li	0.081	0.18	0.17	0.31	0.13	0.20
Mg	1521	1192	1237	809	1396	1237
Mn	17.7	11.5	23.8	**31.4**	23.3	19.9
Mo	0.76	0.57	1.26	0.09	0.51	0.15
Na	77.8	214	53.7	125	82.1	314
Ni	0.77	1.55	1.51	**3.32**	1.45	1.84
P	1927	1418	2506	2225	2810	3198
Pb	0.70	0.65	0.65	**1.24**	0.68	0.76
Sr	4.16	30.9	51.3	25.0	14.2	21.3
V	0.091	**2.91**	0.32	1.93	0.32	0.95
Zn	23.3	23.7	15.4	20.9	**56.8**	28.6

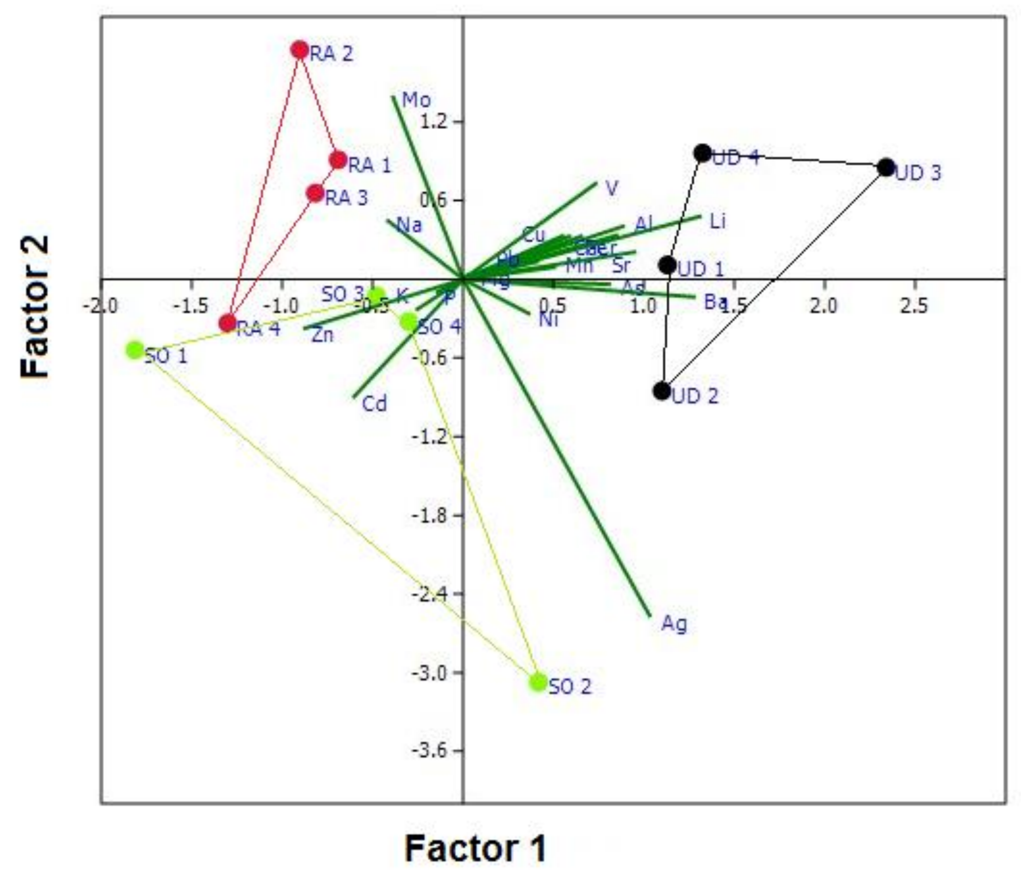


Figure 1. Principle components for type's vegetable species and its elements contents; Site 1 and 2 – polluted area; Site 4 – urban area; Site 3 – control area

CONCLUSIONS

- Even in lower contents in partially contaminated soil As, Cd, Cu, Ni and Pb are very extractible and available from cultivated plants.

- Present investigation suggested that common nettle (*U. dioica*), spinach (*S. oleracea*) and sorrel (*R. acetosa*) are mostly efficient for bio-accumulation of Cd and Pb in potentially polluted areas.

- None of the species was specified as a hyper accumulator; nevertheless all three species show potential for phytoextraction and phytostabilization of Cd, Cu, Pb and Zn.

- In addition, further studies are required to determine the growth performance, biomass production and metal accumulation of these species in metal contaminated soils for their better management, conservation and assurance of better food quality when growing on urban, industrial and agricultural land near mines.

References
[1] B. Balabanova, T. Stafilov, K. Bačeva, (2015) Bioavailability and bioaccumulation characterization of essential and heavy metals contents in R. acetosa, S. olearacea, and U. diuoica form copper polluted and referent areas. Journal of Environmental Health Science and Engineering 13(2):1-13.
[2] B. Balabanova, T. Stafilov, K. Bačeva (2015) Application of principal component analysis in the assessment of essential and toxic metals in vegetable and soil from polluted and referent areas. Bulgarian Journal of Agriculture Science, 21(3):536-544.

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