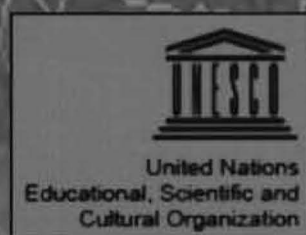


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**ANTHROPOGENIC EFFECTS ON THE
HUMAN ENVIRONMENT IN THE
NEOGENE BASINS IN THE SE EUROPE**

PROCEEDINGS

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CADMIUM CONCENTRATION IN THE SOILS OF THE VILLAGE GUJNOVCI

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Abstract

This paper is an overview of the soil contamination of heavy metals in the village Gujnovci particularly of Cd. The region is known for use intense agricultural and other anthropological activities, mining activities that also have an impact on the distribution of some microelements in the soils. The highest value for cadmium in soil is $8.38\text{mg}\cdot\text{kg}^{-1}$, and the minimum value is $6.01\text{mg}\cdot\text{kg}^{-1}$, the mean value is $7.20\text{mg}\cdot\text{kg}^{-1}$. The content of Cd in wheat crops in the soils of the village Gujnovci is $>0.01\text{ mg/kg}$. The examinations were carried out in the laboratory of the Faculty of Mining and Geology in Štip.

Key words: cadmium, soil, heavy metal, wheat

Introduction:

Cadmium is regarded as one of the most toxic trace elements in the environment.

Two trace elements of great risk for the environmental health are lead and the cadmium, Kabata 1992. Cadmium in soils is derived from both natural and anthropogenic sources. Natural sources include underlying bedrock or transported parent material such as glacial till and alluvium. Anthropogenic input of cadmium to soils occurs by aerial deposition and sewage sludge, manure and phosphate fertiliser application. Cadmium is much less mobile in soils than in air and water. The major factors, governing cadmium speciation, adsorption and distribution in soils are pH, soluble organic matter content, hydrous metal oxide content, the composition of the soil, particularly clay content and type, presence of organic and inorganic ligands and competition from other metal ions (OECD 1994, 1996)

The use of cadmium-containing fertilisers and sewage sludge is most often quoted as the primary reason for the increase in the cadmium content of soils over the last 20-30 years in Europe (Jensen and Bro-Rasmussen 1992).

Cadmium in soils must be distinctly classified in three separate areas with regard to their relative effects on human health and the environment. These three areas are agricultural soils, non-agricultural soils and controlled landfill.

Cadmium in agricultural soils is likewise relatively immobile under normal conditions, but could become more mobile under certain conditions such as increased soil acidity and its cadmium level may be enhanced by the usage of phosphate fertilisers, manure or sewage sludge. The average natural abundance of cadmium in the earth's crust has most often been reported from 0.1 to 0.5 ppm, but much higher and much lower values have also been cited depending on a large number of factors.

The content of Cd depends on the mineral and texture of the soil (Pospilova and Lastinkova 1988) as well as on the primary material that formed the soil (Mengel and Kirkby 1979)

Changes of heavy metal presence in the soil are the result of various interaction processes that can be grouped as follows:

- anthropogenic; changes resulting from agricultural amangement (e.g. fertilizers) and atmospheric deposition
- soil dynamic: change resulting from soil cultivation (e.g. tillage) biological activity (e.g. earth worms), dissolved or as particles that are transported by water flow, erosion or other processes.
- Procedure errors: changes resulting from all kinds of possible errors associated with soil sampling, physical soil preparation and analytical procedure.

As heavy metal Cd is dangerous to the environment The danger ensuing from this metal derives from its tendency to accumulate in the vital organs of humans, animals and plants.

Among all the heavy metals, cadmium plays an important part in soil pollution. Owing to serious cadmium pollution, much attention has been paid to its effect. Cadmium can damage kidney, liver, skeleton and other organs; what is more, cadmium is a definite carcinogen, it can cause cancer in many organs.

Results and discussion

Determination of macro elements, trace elements was done on 15 soil samples taken from wheat fields. Samples were taken 20 cm in depth.

Samples were dried for 48 hours at 40°C. Dry samples were prepared according to ISO 11464. They were crushed and sieved through 45 µm sieve.

One gram of sample was wetted in 2.0 mL redistilled water and with slow and constant stirring 12 ml HCL and 6 mL HNO₃ were added. The glass was covered with a glass watch and kept at room temperature for 16 hours and heated until wet salts were obtained. Wet salts were closed in 5 mL concentrated HNO₃ and the content was filtered through paper with white track. The material was put in a 100 mL measure flask. Determination of macro elements and trace elements was done by AES-ICP. Values of macroelements (in %) and micro elements (in mg/kg) in the soils of Gujnovci are shown in table 1 and 2

Table 1. Values of macroelements (in %) and micro elements (in mg/kg) in the soils of Gujnovci.

	1	2	3	4	5	6	7	8
Al	4,39	4,13	4,20	3,21	4,79	5,16	4,50	5,68
Fe	3,92	3,94	3,78	3,52	3,68	3,88	3,72	4,19
Ca	0,88	0,93	0,91	1,79	3,59	1,35	2,67	1,21
Mg	0,96	0,93	0,97	1,08	1,49	1,33	1,46	1,38
Na	2,31	2,60	1,61	0,51	1,29	0,76	0,99	1,05
K	0,91	0,92	1,01	0,60	0,87	0,62	0,82	0,62
Mn	0,10	0,10	0,10	0,26	0,11	0,08	0,13	0,08
Ti	0,05	0,05	0,06	0,04	0,06	0,09	0,08	0,11
P	0,04	0,05	0,05	0,07	0,07	0,03	0,08	0,03
Sr	143,49	161,44	142,87	143,93	216,60	135,64	189,18	137,96
Ba	565,34	708,93	627,80	519,66	370,10	508,16	386,31	582,01
Ni	17,90	17,23	20,52	41,71	58,26	29,75	51,59	24,43
Cr	23,22	22,19	27,81	33,71	56,62	39,30	50,34	35,34
Zn	87,39	89,46	88,60	414,05	99,85	80,43	136,35	91,05
Cu	21,54	22,52	23,29	58,28	33,33	20,43	38,35	22,82
Pb	46,74	51,26	43,73	466,95	47,18	31,85	71,75	40,82
Co	15,55	15,33	15,51	18,23	19,37	16,78	19,71	17,17
Cd	6,54	6,60	6,39	7,43	6,58	6,60	6,20	7,21
V	289,94	255,75	333,99	507,47	420,51	670,59	507,77	729,18
Mo	3,12	3,06	2,70	2,41	1,79	2,92	1,98	2,99

Table 2. Values of macro elements (in %) and micro elements (in mg/kg) in the soils of Gujnovci

	9	10	11	12	13	14	15
Al	5,44	3,70	3,27	3,15	4,27	3,47	2,89
Fe	4,11	3,43	4,19	4,00	3,98	3,67	3,52
Ca	1,04	2,03	1,66	1,40	1,79	1,93	1,62
Mg	1,37	1,24	1,12	1,09	1,39	1,29	1,12
Na	2,42	1,60	1,45	1,21	2,08	1,22	1,13
K	0,70	0,65	0,58	0,55	0,82	0,64	0,50
Mn	0,08	0,09	0,16	0,19	0,12	0,09	0,11
Ti	0,08	0,07	0,08	0,10	0,05	0,11	0,10
P	0,03	0,09	0,09	0,10	0,09	0,09	0,11
Sr	160,18	200,47	198,02	179,01	211,65	188,92	177,20
Ba	524,68	402,69	470,83	483,67	531,83	481,86	444,59
Ni	25,28	32,56	33,30	35,37	36,88	32,54	30,01
Cr	36,71	31,08	32,03	31,44	39,53	32,56	27,78
Zn	93,88	124,68	403,03	337,34	101,15	138,94	107,02
Cu	21,13	29,93	40,37	51,69	32,17	37,01	33,48
Pb	42,21	64,38	268,83	245,14	53,36	54,40	51,59
Co	16,29	16,03	20,85	20,41	18,12	17,63	16,10
Cd	6,76	6,10	8,38	7,58	6,54	6,21	6,01
V	553,29	488,67	583,31	816,15	359,56	17,72	784,81
Mo	2,28	2,52	3,13	2,85	2,78	2,78	2,63

Table 3. Normal intervals of contents and maximum allowable limits of heavy metals in soils (Kloke, 1980).

Element	Intervals of normal contents mg/kg	Maximum allowable limits
Cd	0.1-1.0	3
Co	1-10	50
Cr	2-50	100
Cu	1-20	100
Ni	2-5	50
Pb	0.1-20	100
Zn	3-50	300

Fig1 shows that the concentration of Cd is high in all samples

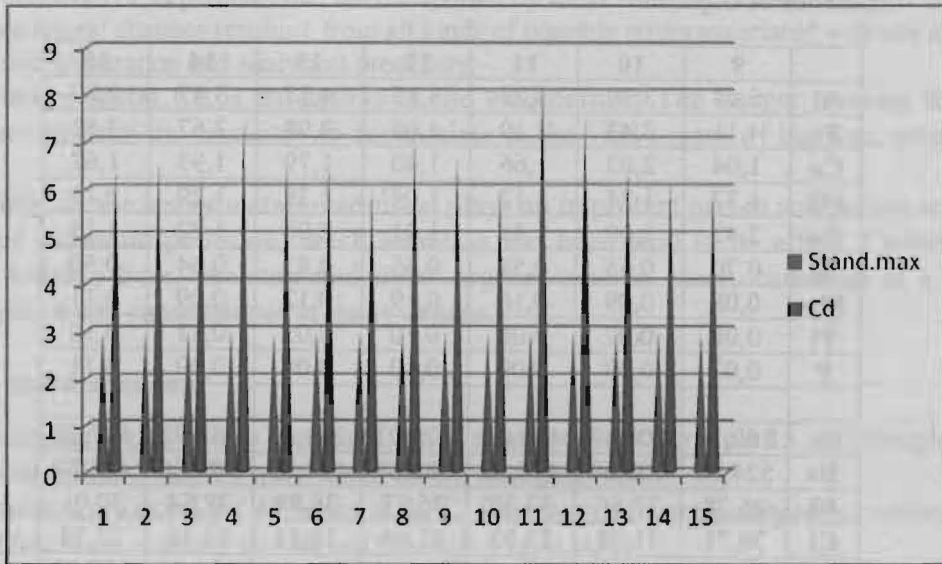


Fig. 1. Concentration of Cd in soils of village of Gujnovci

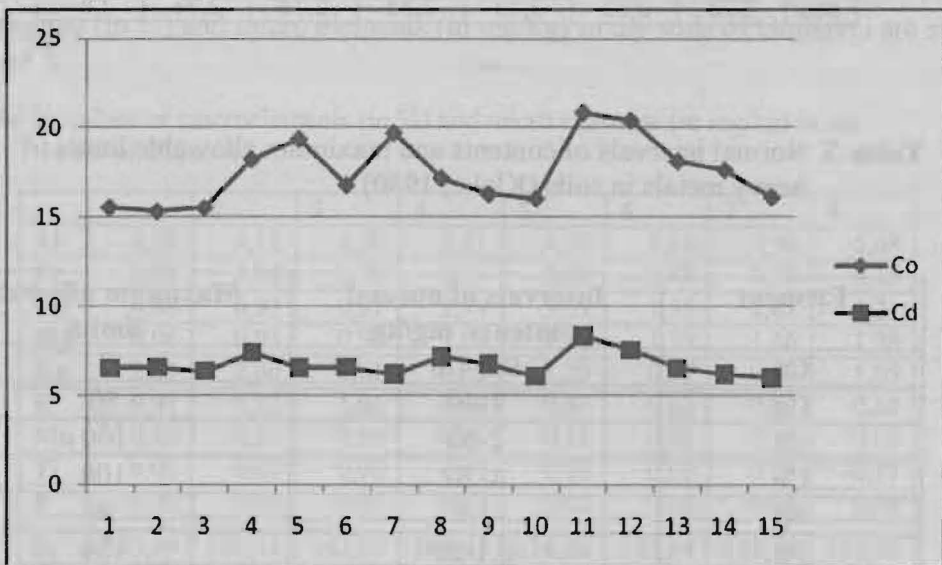


Fig. 2. Proporcional dependence between Co and Cd

Fig 2 shows the proporcional dependence between Co and Cd

In table 4 is shown comparison between coconcentration of heavy metals in soils of Gujnovci, some soil in Japan and some soils in World.

Table 4 Average concentration of heavy metals in Gujnovci-Macedonia, Japan by Yamasaki (2001), and World by Kabata-Pendias (2001).

	Gujnovci	Japan	World
Cd	6.01-8.38	0.02-3	0.01-4
Cr	22.19-56.62	1.4-233	1-1500
Co	15.33-20.86	0.2-61.3	0.1-275
Ni	17.19-58.26	0.2-107.4	0.2-3240
Cu	21.13-38.28	0.9-234.9	1-323
Zn	80.43-403.03	2.5-331	3-770
Pb	43.73-466.95	1-1098	1.5-286
Mo	1.98-3.13	0.1-8	0.2-17.8

International standard value of Cd concentration in crops adopted by Codex 0.2(mg/kg)

International standard value (Codex) of Cd in wheat crops is 0.2 mg/kg)

Value of Cd concentration in wheat crops of the village Gujnovci is >0.01 mg/kg. The concentration of other elements is as follows: *Ca-350*, *Mg-1530*; *Na-100*; *P-2250*; *k-4320*; *Fe-34*; *Mn-25*; *Al-5*; *Zn-22*; *Cu-6.3*; *Ba-3.7*; *Sr-3.5*; *Ni>0.12*; *Ti- 0.9*; *Cr->0.05*; *As->1.0*; *Mo-0.7*; *Pb->3.8*; *Co->0.01*; *V-0.2*; *Ag->0.55*

Data in tables 1 and 2 show that concentration of cadmium is up 6.01 mg/kg to 8.38 mg/kg .

The results have proved that Cd content in all samples is significantly higher than the standard values.

Conclusion:

The investigations carried out on the presence of trace elements in soils in the vicinity of Gujnovci are characterized by increased anthropogenic impacts. Investigations revealed increased concentrations of Cd. The high Cd concentrations is due to the intense anthropogenic influence, notably the disasters that occurred in the lead and zinc flotation dams. The region is built up of volcanic tuffs of Tertiary age so that pedogenesis of the soils consists mainly tuffs.

The increased cadmium concentrations come from the flotation plants of the Zletovo Mines. The mines is situated 20 Km far away from Gujnovci.

The highest value found for cadmium in soil is $8.38\text{mg}\cdot\text{kg}^{-1}$, and the minimum value is $6.01\text{mg}\cdot\text{kg}^{-1}$, the mean value is $7.20\text{mg}\cdot\text{kg}^{-1}$, The concentrations of other rare elements are within the allowed limits and the values reported for such types of soils.

Wheat crops from investigation soils not contained increase concentration of cadmium.

These cadmium contaminated soils can be cleaned by using plants for phytoremediation. Phytoremediation is a method of remedying environmental contaminates with hazardous substances utilizing the innate capabilities of plants.

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