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LEAD CONTAMINATION OF ENVIRONMENT IN MEŽA VALLEY-YUGOSLAVIA

Some considerations on lead content in soil and plants. +/

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In Yugoslavia two areas exist in which population is exposed to higher level of lead in relation to urban population exposed to lead from automobile fumes. These areas are located around lead and zinc mines, possessing smelting plants: Mežica (Slovenia) and Trepča (Kosovo).

The Mežica lead and zinc mine us located in Slovenian Alps toward Austrian border. The valley is situated on about 600 m.over sea level with sourounding mountains reaching 1624 m. Meža river is flowing along the valley sampling waters from creeks. In the middle of this long valley the source of lead contamination is located: the smelting plant built in 1896, producing now about 22 000 t. of lead and 11 000 t. of zinc. The plant is emitting more than 200 t. of lead aerosols yearly, contaminating whole valley. Flotation installations are heavily polluting Meža river with lead.

In 1967 we started a broad ecologic study on lead contamination of air, snow, water, soil, various plants and food and evaluation of exposure of population to lead. All these results will be published elsewhere. Here we like to present some experience in establishing lead absorption of various plants from the soil.

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Material and methods.

The soil samples were taken in same areas (gardens, fields) where the plant samples were taken. We took soil samples on 4 corners of a square 10 m.long. The surface layer of soil (about 0,5 cm. thick) was removed with plastic spade and next layer, 3-4 cm. deep, was sampled. All 4 samples are mixed and put in plastic vessel every sample is dried on air at room temperature and sieved through a sieve with 2 mm. holes. For Pb analysis 0,5-2 gr. of dried sample was taken. Lead determination is performed by modified dithizone method similar to plant samples (1).

Physiologically active Pb (absornable), AL-Dissolved (was determined by AL-method described by Riehm for Potassium) 2/.5 gr. of soil sample is put in polyethylene flask of 250 ccm and following mixture /100 ccm/ is added: 0,1 N ammonium lactate and 0,4 N acetic acid. Extraction is performed by shaking in machine for 2 hours. Mixture is filtered through wrinkled paper filter /white band/ and 1-5 ccm of filtate is analyzed for dissolved lead by dithizone method.

The plant samples /overground and underground part of vegetables, hay, fruits/ were taken at end of July and end of October each year. The plant is washed well with watter and dimeniralized water to clean it from soil. The sample is cut as used for preparation of food. We prepared peeled and non-peeled samples of potato /Solanum,Tuberosum/, garden beet /Beta Vulgaris L./, /SSP Esculenta/, turnip cabbage/ Brassica Oloracea.Var.Gongylodes L./, gardon rutabaga/Brassica Napus Var., Napobrasica Peterm./, rutabaga /Beta Vulgaris L./, pear /pirus Communis/ apple /Malus Domestica Borkh./. The samples were scraped on surface in the case of parsley /Petrolinum Hortense Hoffm./, red carrot /Daucus Carota L./, celery /Apium Graveolens L./, radish. The outside layer is removed in onion /Allim Cepa L./, [illegible] common garlic /Allium Sativum L./, common leek /Allium Ampeloprasum L, f. Porrum RGL/. Products of bush bean /Phaseolus vulgrais L., var. intermedius/was washed and cut whole. Climbing bean /Phaseolus

Vulgaris, var. altus/ was dried and crushed in mortal. The leaves of salads /lettuce, endivie/, parsley, cabbage /Letuca Sativa Var. Capitata/, celery, hay, after grass were dried and cut.

All prepared samples were dried in drying cabinet at 80-90°C. Therefore, all results cited here are expressed in relation to weight of dry substance. For Pb analysis performed by dithizone method /1/ 0,5-2 gr. of samples was used.

Figure 1 represent a sketch of geographic position of Meža valley with marked spots on which samples of soil and plants were taken.

Results and discussion.

Here we like to present results of Pb determination in soil and underground parts of some vegetables.

As we mentioned underground parts were washed, peeled or scraped, cutted, dried and analyzed. Rutabaga was prepared unpeeled as used for feeding of animals.

The results of Pb analysis are presented on Table 1. Obtained results could be divided in 3 groups/using maximal values/:

1/ vegetables with relatively high content of Pb, reaching over 30 mg/kg

2/ vegetables with medium content reaching over 10 mg/kg

3/ vegetables with low Pb content under 5 mg/kg.

The differences in the Pb content of the same kind of vegetable on various sampling spots represent consequence of variations in the Pb content of the soil and adequate absorption.

The other differences are due differences and variations of plants. To mention the most important factors:

1/ differences in physiology and capacity of absorption

2/ shape and size of rooth

3/ deepnes of rooth into the soil

4/ surface properties of rooth: smoothness, roughness.

It is interesting to note that same kind of vegetable showed always much higher Pb content when raised in summer and fall (October) than in the spring (July sample).

In Table 1 the results of parsley for July 1968 and October 1968 are quoted. October results are 3 times higher for samples on the same sampling spot. This fact can be explained by greater duration of exposure (growing time) and difference in climatic factors.

From the first glance on Table 1 it is possible to conclude that plants from the first group are not suitable for growing on soil with great Pb content. For such soil is better to develop plants from the second, especially third group, showing small lead absorption. That means, in such areas it is better to grow potato, onion and garlic, less suitable are common leek, red carrot and celery. Rutabaga, parsley and garden beet are very dangerous, especially when growed during summer and fall, showing great absorption and Pb content.

We paid a special attention to the problems of lead absorption from soim by these vegetables.

The presence of lead in underground parts of plants represent result of absorption of lead from the soil. Therefore it would be of interest to calculate absorption coefficient from Pb content of soil and plant. That means it could be possible to find out discrimination factors for lead absorption from soil into underground parts of these plants. In such way it would be possible to follow transfer of lead through various members of the ecological chain: fall-out-soil-plants-food-man.

For this purpose, we performed analysis of Pb in samples of soil taken on same areas (gardens) where plant samples were taken. Obtained results showing total Pb content in the soil are presented on Table 2. For every sampling spot we are quoting high over sea level in meters and distance (air distance) from the source of lead contamination, that means chimneys of the smelting plant.

Using these data about total quantity of lead in the soil, we tried to calculate absorption coefficient (C_T) for analyzed underground parts of vegetables by relation:

$$\frac{\text{Pb content of the plant}}{\text{Pb /total/ in the soil}} = C_T$$

Calculated values are very dispersed showing great variations between two similar sampling spots. We concluded that total Pb content could not represent an authoritative data for lead absorption into the underground part of plants. Our opinion was supported by data in agriculture literature quoting so called "physiologically active" part of elements present in the soil ("aborbable", "available", "AL-soluble").

Namely, Riehm /2/ developed a method for determination of this part for Potassium using extraction of the soil by ammonium-lactate: acetic acid mixture /so called AL-method/. By analogy, we concluded that only a part of the total Pb present in the soil, is ready to be absorbed by plants /physiologically active Pb, absorbable, available, AL-soluble Pb/. We assumed that this part could be determined by AL-extraction method. We performed this extraction on the same soil samples and determined Pb in the extract. We marked these results as AL-Pb in soil and calculated absorption coefficient C_{AL} using relation:

$$\frac{\text{Pb conten of the plant}}{\text{AL-Pb in the soil}} = C_{AL}$$

The results of AL-Pb are also presented in Table 2. It is obvious that great difference exist in relation between total and AL-Pb expressed in percentage of the second to first one/from 50 % to 1,3 %/. We assume that physico-chemical properties of the soil, mechanica properties, quality, pH-humidity and other factors are influencing this relation. The quantity of total lead is also playing a role. When total Pb content is high /over 4 gr/kg/, generally higher percentage of Al-Pb could be expected. In soils under 4 gr of total lead no correlation exist showing great differences in C_T and C_{AL}.

We calculated C_T and C_{AL} for all vegetables mentioned in Table 1 and they are presented in Table 3 for one representative of every group: parsley, red carrot and potato.

It is evident that calculated C_{AL} coefficients are less dispersed than C_T. In the case of red carrot we performed statistical evaluation and established much higher correlation between Pb content of this vegetable with AL-soluble Pb /r-0,74/ than with total Pb.

It is for sure that AL-soluble Pb/physiologically active represent more authoritative data for determination of absorption coefficient that total Pb content of the soil.

Studying results for C_{AL} it is evident that absorption is very low in very contaminated soil, that means discrimination is very high. Naturally, absolute Pb valu in these plants is higher.

On the other hand, in the case of low contaminated soil absorption is much better reaching $60 \cdot 10^{-2}$ for red carrot. Absolute Pb value is lower.

We hope that these consideration would be of interest for hygienitss as for botanists showing absorption of one important ubiquitar element from the soil into the plants. We like to evaluate statistically C_T and C_{AL} for other vegetables.

R E F E R E N C E S:

1/ Ž.Kerin: Bestimmung von Mikromengen Blei in pflanzlichen Material Mikrochimica Acta 5/1968/927

2/ A.Riehm: Die Ammoniumlaktate essigsaure-Methode zur Bestimmung des Kaliumversorgungsgrad von Boden, Agrochimica /1958/1

T A B L E 1

Lead content of underground parts of vegetables

Plant-underground part (peeled or scraped)	mg Pb/kg Maximum value	Minimum value	Non-contaminated (maximum)
Parsley (Petroselinum Hortense Hoffm.) (October 1968)	51,12	0,80	0,22
Rutabaya (Beta vulgaris L.)-nonpeeled	39,72	0,80	0,22
Gardenbeet (Beta vulgaris L., SSP Esculenta)	33,45	0,22	0,14
po Common leek (Allium Amloprasum L.)	17,60	1,41	0,21
Red carrot(Daucus carrota L.)	17,39	0,61	0,29
Parsley (July 1968)	16,18	0,52	0,45
Celery(Apium graveolus L.)	13,20	2,25	0,53
Onion(Allium Cepa L)	4,53	0,22	0,30
Common garlic (Allium sativum L.)	1,52	0,11	0,30
Potato(Solanum Tuberosum L.)	1,01	0,14	0,12

T A B L E 2

Pb in soil in mg/kg

Location No.	Height in meters (over sea level)	Distance in meters from chimneys	July 1968 Total Pb	July 1968 Active Pb	July 1968 %	October 1968 Total Pb	October 1968 Active Pb	October 1968 %
1	540	200	24 680	12 057	48,4	24 680	12	
2	540	500	3 960	1 251	31,6	8 508	2 395	28,2
3	540	230	4 624	924	20,0	5 084	1 905	37,5
4	540	520	2 696	542	20,1	3 147	374	11,9
5	540	1 100	3 584	-	-	2 576	909	35,3
6	540	2 200	2 478	712	28,7	4 916	542	11,0
7	700	1 850	1 320	232	17,6	1 455	78,9	5,5
8	550	3 500	1 228	397	30,8	955	184	18,5
9	500	3 980				582	186	32,0
10	620	1 620	1 183	243	20,5	1 140	252	22,1
11	600	1 950	696	275	39,5	1 023	89,9	8,8
12	630	2 570	384	155	40,4	938	112	12,0
13	580	5 800				408	39	9,6
14	480	4 520	387	25,1	6,5	365	43,4	11,9
15	640	2 000	784	30,0	4,0	658	45,4	6,9
16	650	2 030	975	31,8	3,3	1 000	50,0	5,0
17	580	3 010	1 430	241,0	16,9	1 077	317	29,4
18	650	3 520	1 974	26,8	1,4	745	26,4	3,5
19	550	4 420	661	27,6	4,2	371	38,8	10,5
20	700	4 100	643	32,9	5,1	397	29,9	7,5
21	730	3 500	360	13,6	3,8	204	17,2	8,4
22	710	4 750	3 538	224,0	6,3	3 718	93,2	2,5
23	600	970	1 052	183,0	17,4			
24	600	1 750	237	15,2	6,4	222	18,4	8,3
25	700	3 950	375	20,6	5,5			
26	750	1 500	531	45,7	8,6	595	39,7	6,7
27	930	2 250	295	14,4	4,9	191	12,8	6,7
28	970	7 170	213	9,6	4,5			
29	450	7 500	185	10,8	5,8			
30	450	7 250	563	13,9	2,5	363	40,4	11,1
31	450	9 600	66,5	0,9	1,3	35	2,1	6,0
32	400	9 350	39	1,8	4,7	24,6	1,5	6,1
33	364	17 100	28	2,1	7,5	36,5	3,0	8,2
Noncontaminated area - 12 samples			10,38 (2,6 - 20,8)	1,1 (0,4 - 2,2)	10,5			

T A B L E 3

Pb content of vegetables and absorption coeffcients

Location No	Parsley (October 1968)			Red carrot (July 1968)			Potato (October 1968		
	Pb mg/kg	C_T	C_{AL}	Pb mg/kg	C_T	C_{AL}	Pb mg/kg	C_T	C_{AL}
1	51,12	$0,21\times10^{-2}$	$0,42\times10^{-2}$	17,39	$0,7\times10^{-2}$	$0,14\times10^{-2}$			
2	40,12	0,47	1,68						
3	22,14	0,44	1,16				1,01	$0,02\times10^{-2}$	0,05x1[illegible]
4	17,14	0,55	4,58	6,55	0,24	1,21			
5	13,80	0,54	1,52	10,87			0,89	0,03	0,09
6				17,25	0,69	2,42	0,67	0,01	0,22
7	5,46	0,38	6,92	3,15	0,24	1,36	0,40	0,03	0,51
8	$12,6^{o}$	1,27	6,88	3,52	0,27	0,89			
9							0,63	0,11	0,34
10	4,80	0,42	1,90	14,04	1,19	5,78	0,35	0,03	0,14
11	1,73	0,17	1,92	13,45	1,93	4,89	0,37	0,04	0,41
12	2,60	0,28	2,32				0,21	0,02	0,19
13							0,63	0,15	1,61
14	2,94	0,81	6,77	1,34	0,35	5,34			
15	1,60	0,24	3,52				0,22	0,03	0,48
16	4,73	0,47	9,46	2,01	0,21	6,32			
17	10,33	0,96	3,26				0,23	0,02	0,70
18							0,65	0,09	2,46
19	2,73	0,74	7,04	1,69	0,26	6,12			
20	7,23	1,82	24,18				0,61	0,15	2,04
21				0,61	0,17	4,49	0,19	0,09	1,10
22	6,20	0,17	6,65						
23				2,67	0,25	1,46			
24	2,23	1,0	12,11	1,28	0,54	8,42	0,30	0,13	1,63
25				3,46	0,92	16,79	0,55		
26	7,14	1,20	17,98	1,93	0,37	4,33	0,30	0,05	0,76
27	1,27	0,66	9,92	1,05	0,36	7,29	0,21	0,11	1,64
28				1,01	0,47	10,50			
29				0,98	0,53	9,07			
30				2,45	0,44	17,62			
31	0,80	2,28	38,09				0,14	0,40	6,66
32				0,80	2,28	49,44			
33	1,03	2,93	35,66	1,27	4,53	60,47			