

LEAD CONTAMINATION OF ENVIRONMENT IN MEZA VALLEY
A Preliminary Report

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Recently great attention is being paid to the problems of lead contamination in the urban atmosphere due to emission from motor vehicles exhaust. Numerous studies are in progress on this subject, especially in the USA. The aim of these studies is to establish the lowest level of lead in the urban atmosphere that will produce a measurable change in the body due to exposure to respirable and absorbable lead particles.

On the other hand, in the world literature a great number of papers have been published in the last decades on occupational exposure in lead and lead intoxication.

In Yugoslavia there are two areas in which the population is exposed to higher levels of lead than urban populations are but lower than occupational exposures. These areas are around two big lead mines, and possessing and smelting plants.

The first mine is located in Slovenian Alps and the second one at Trepca on Kosovo, toward Albanian border. We started our ecological study on lead contamination in the biosphere and population exposure around lead mine "Mežica" in Slovenija. Later we intend to develop a similar study around the Trepca mine. In such a way we hope to fill the gap between studies on low lead exposure of urban populations and high occupational exposures of workers and lead miners.

Location of "Mežica" lead mine and smelting plant

The lead mine "Mežica" is located in the valley of river Meža, in Slovenian Alps on the Austrian border. The valley is situated on about 600 m. over sea level, but the surrounding mountains reach 1624 m. This results in a closed long space in the center of which the lead smelting plant is built.

The lead mine is about 300 years old, possessing ore with an average lead content of 6-6.5% in the form of lead sulfides (80%) and lead oxides (20%). The ore contains also 2-3% of Zinc, 0.01% of Arsenic, 0.3% Cadmium and 0.0003% of Bismuth.

In 1746 the smelting plant in Žerjav was founded. In the second half of 19th century it was producing about 2,500 tons of lead yearly. After 1900 production was increased until today the production is about 22,000 tons of lead and 11,000 tons of zinc a year.

The chimney of the smelting plant emits lead aerosols (lead oxides) which contaminate the valley. The lead aerosols from the air contaminate the soil, waters, plants and food. The flotation of smelting plant heavily contaminates the river Meža. Therefore, animals and population of this valley are exposed to lead due to inhalation and ingestion of contaminated air and food.

In the valley of river Meža near lead mine and smelting plant four main and many small settlements are located.

In the center of the valley Žerjav, where the smelting plant is located, in 1961 there were 1,053 inhabitants.

About 2 km. south from Žerjav the new settlement Rudarjevo was recently built with some hundreds of inhabitants. About 5 km. south-west the old settlement Crna with 2,198 inhabitants in 1961 is situated. About 10 km. north west from the smelting plant village Mezica is situated with 2,515 inhabitants in 1961.

In 1967 we started a broad study of lead contamination in plants, especially vegetables, and food.

We planned to perform a complete ecological study of lead contamination in the biosphere and man. That means we planned to establish lead contamination levels in all links of the ecological chain: air-water-soil-plants-animals-food-man. Now we wish to report some preliminary results obtained in 1967 and 1968. We are preparing some detailed papers to be published in the near future (1, 2, 3, 4, 5).

Lead in air

A group of experts in the area sampled the air daily at nine spots in the valley from summer 1967 through 1968 to determine lead and sulphur dioxide levels.

A team from our Institute performed grab sampling on microsorban filters determining lead by dithizone method in May 1967 and 1968. They also sampled using a thermoprecipitator to determine the particle size distribution at the various sites.

Geographic and topographic situation together with meteorological factors, especially north-south winds, produce contamination along the valley. For years the smoke from smelting plants emitted daily 15 m^3 per second without filters, dispersing lead aerosols. In the middle of 1969 the first filter (Lurgi) was installed which reduced the contamination a great deal.

In Table 1 some results of lead determination in the air on various days at the same sites are presented. It clearly shows the influence of meteorologic and topographic factors on daily distribution of lead. These results are obtained from J. Perman, Ch. E., chief of the group of experts following the level of lead in air.

Lj. Jablanov from our Institute performed determination of particle size taken by a thermoprecipitator. The results from the thermoprecipitator measurements are presented on Table 2 and show that with distance the percentage of particles sized under 1 micron is increased which is a very important fact from the toxicologic point of view (Table 2).

Lead in water, snow and soil

We established that the lead in drinking water of the local piping system is under MPC values $\text{MPC}: 0.05 \text{ mg/l}$. Also water samples from wells in various parts of the valley were analyzed showing values under 0.035 mg/l of lead. All these results suggest that drinking water does not represent any dangerous contamination for man (2).

Creeks coming into the Meza River, and the Meza River before flotation, contain similar quantities of lead. Flotation at the smelting plant, however, represents an immense source of contamination of the Meza River. The level of lead in this river is continually decreasing until at the mouth of the big river Drava, a very low lead content is found (2). These results are presented on Table 3.

The lead content of the snow in the valley was also determined (3). Many factors influence the quantity of lead. In the first place, meteorologic and topographic factors are important, as in the case of lead in air and soil. But, duration of the snow cover in days is also extremely important. The snow sample was taken by a metal model with standard surface. In non-contaminated areas the lead content in snow is $0.002\text{--}0.02 \text{ mg/kg}$. In contaminated areas the results are between $0.13\text{--}262 \text{ mg/kg}$, depending on mentioned factors. Determination of lead in snow could represent a good control of determination of lead in air. Namely, this quantity represents integral measurements of the lead in the air that has settled out for duration of the snow cover. We are evaluating now these results.

Determination of lead in soil represents a very important point in our study: (a) lead content represents results of integral contamination with lead aerosols, (b) these results are important for the study of lead absorption by plants to establish absorption coefficients.

Therefore, we performed soil sampling on 33 sampling spots together with sampling of plants and vegetables. First determination of total lead content in soil was performed. Using results of lead determination in underground parts of vegetables to calculate absorption (discrimination) coefficient, we obtained very dispersed and unrealistic results. It was obvious that total lead does not represent a real factor of absorption into the plants. Therefore, we applied determination of so called AL-dissolved, the absorbable, physiologically active lead. Soil samples were extracted with mixture of 0.1 N ammonium lactate and 0.4 N acetic acid and lead determined in the extract. In Table 4 the results of total lead and AL-soluble lead determinations are presented.

It is obvious that only a certain percentage of total lead is absorbable into the plants (Table 4). Great differences exist ranging from 1.3% to 50% of AL-soluble Pb due to various factors. We assume that physico-chemical properties of the soil, mechanical properties, quality, humidity, pH and other factors influence percentage of AL-soluble lead. It is evident that soil in Meža valley is highly contaminated with lead, from a "normal level" to 25 grams per kg and that high levels of lead contamination of plants could be expected.

In January 1969 a filter was fixed and contamination through the chimneys dropped almost 50%. We are continuing lead determination in soil to see the consequences of this reduced input into the atmosphere.

Lead in plants and food

We mentioned that plant samples were taken on the same spots with the soil samples. We took above ground and under ground parts of the plants washed them well with tap and distilled water and dried, cut and used them for lead determination. Sampling was performed regularly at the end of July and at the end of October each year. Thousands of results are now tabulated but here we wish to give only first impressions.

Evaluation of these results on lead content in plants must be divided in two groups: above ground and under ground parts. Content of

lead in above ground parts represents adsorption and absorption of deposited lead on the surface. In underground parts only absorption from the soil exists.

We determined lead in above ground parts of various vegetables and plants as endive, parsley, cabbage, common leek, onion, garlic, carrot, red carrot, turnip cabbage, garden rutabaga, bush beans, celery and grass. We found the greatest lead content in hay and grass. Therefore, these results could be used for evaluation of contamination by lead aerosols.

Under ground parts are of greater interest from the physiological point of view. In Table 5 some results are presented divided in 3 groups by level of lead content: high, medium, low. It is obvious that parsley, rutabaga and garden beet are not suitable for soil with high lead content because they will absorb higher lead quantity and represent a danger as human food. Common leek, red carrot, celery, onion, garlic and potato are more suitable due to lower absorption.

We also calculated absorption coefficients using Pb value of vegetables and total lead content of soil (C_T) and AL-soluble lead of the soil (C_{AL}). In Table 6 such coefficients are presented for parsley, red carrot and potato as representatives of mentioned three groups (Table 5).

It is evident that calculated C_{AL} coefficients are less dispersed than C_T (Table 6). 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, than with total Pb. Statistical evaluation will be performed for other vegetables.

It is evident that AL-soluble Pb represent more authoritative data for the determination of absorption coefficient of Pb into the plants than total lead content. We are continuing this study to find out if some other kind of lead determination (ionized lead) will give better results.

Also we are evaluating results of some other food and cooked food lead content. In this way we hope to obtain data for evaluation of population exposure in the case of lead absorption due to (1) inhalation and (2) inhalation and ingestion, which is the case for the population in Meza valley.

Exposure of population to lead

To evaluate lead exposure we performed a broad epidemiologic study on persons who are not professionally exposed to lead, mostly women

and children. In 1968 we performed a screening test using ALA determination in urine of 912 persons. Results of these determinations are presented in Table 7, together with results obtained on control group. For comparison we are giving also some results of miners and workers professionally exposed to lead.

All persons included in this study completed a long questionnaire about personal anamnesis, status, all complaints, nutritional habits and source of used food (from contaminated area or not) and many other relevant data.

In 1969 a detailed medical examination of these groups was performed together with many laboratory analyses as blood picture, determination of lead, coproporphyrine and porphobilinogen in urine. In some cases also determination of ALA-dehydrogenase in blood was performed. Naturally, in 1969 also determination of ALA in urine was performed.

We mentioned that in January 1969 a filter was fixed in the smelting plant and that contamination dropped on almost 50%. It is interesting to note a drop in ALA values in summer of 1969 in comparison with results from the summer of 1968. In Žerjav the drop was 48%, in Mežica 38% and Črna only 19%. Results are presented on Table 8 for same individuals in two successive years.

It is necessary to point this example as a possibility to evaluate technical measures by means of exposure tests performed on biological samples of exposed persons. Now evaluation of the data from populations is in progress. We intend to use analysis by computer technique to compare subjective complaints and objective findings.

Beside all these tests for exposure we would like to get some data about body burden of lead of exposed populations. Therefore, in the summer of 1970 we studied mobilization of lead by injection of Ca-EDTA in 160 exposed persons. We also determined excretion of lead before injection and in 24 hours sample of urine after injection, determination of ALA, and zinc in urine, determination of blood picture, etc. We obtained highly interesting results showing impressive body burden in women, children and men nonprofessionally exposed to lead.

In such a way we hope to elucidate exposure and body burden of exposed population and to find out possible consequences of chronic exposure to lead. It is necessary to keep in mind that the population of the valley is constantly exposed to lead from the beginning of this century, now for the third generation.

We hope also to calculate particular exposure only due to inhalation and to combination of ingestion and inhalation using results obtained by analysis of food.

Results and evaluation of results in two - three years will give some interesting conclusions on contamination of biosphere and population around this lead-zinc mine.

We hope to extend this study on environment around the lead mine "Trepca" in Kosovo region (near Albanian border). This environmental study will be more complicated due to the presence of other heavy metals: Zn, Cd, Bi and other trace metals.

Table 1
Lead in Air in Micrograms/m³

Date	Mežica	Žerjav Center	Žerjav East	Črna Center	Črna East
10/4/67	1.3	13	30	7.6	4.2
10/11/67	15	84	68	36	25
10/18/67	9.6	18	66	3.2	4.2
10/25/67	24	-	68	60	29

Table 2

Particle Size Distribution of Lead Aerosols

Size in Microns	Percentage of the Whole Sample				
	At smelting plant-Žerjav		Črna Center	Črna East	Mežica
	5/25/68	5/30/68	5/29/68	5/29/68	5/29/68
0.3	35.48	44.08	43.88	55.00	43.25
0.8	23.26	22.06	26.33	25.00	26.14
1.0	12.85	14.40	12.28	7.50	12.61
1.5	5.50	4.23	5.26	5.00	4.50
2.0	2.75	3.38	3.50	2.50	3.60
2.5	3.66	1.70	1.75	2.50	1.80
3.0	2.75	0.84	-	-	0.90
4.2	2.75	1.70	3.50	2.50	2.70
5.6	5.50	3.38	1.75	-	1.80
6.9	5.50	4.23	1.75	-	2.70

Table 3

Lead Content of Meza and Drava Rivers
30-31 October 1968

Sampling Spot	Pb in mg/l
Various creeks coming to Meža River	0.0013-0.02
Meža 150 m. before flotation (Zerjav)	0.0068
Meža just after flotation (Zerjav)	685.12
Meža 300 m. after flotation	226.36
Meža in center of Zerjav	158.45
Meža in Polena	136.37
Meža in Poljana-10 km. from flotation	92.28
Meža at mouth to Drava-22 km. from flotation	2.89
Drava River from mouth of Meza to Maribor	0.0114-0.0055

Table 4

Pb in Soil in mg/kg

Location No.	Height in Meters (over sea level)	Distance in Meters from Chimneys	July 1968				October 1968				
			Total	Pb	Active Pb	%	Total	Pb	Active Pb	%	
1	540	200	24	880	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				

Table 4 Continued

Location No.	Height in Meters (over sea level)	Distance in Meters from Chimneys	July 1968				October 1968			
			Total Pb	Active Pb	%		Total Pb	Active Pb	%	
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					

Table 5

Lead Content of Underground Parts of Vegetables

Plant-Underground Part (peeled or scraped)	mg Pb/kg		
	Maximum Value	Minimum Value	Non-contaminated Area (Maximum)
Parsley (<i>Petroselinum Hortense Hoffm.</i>) (October 1968)	51.12	0.80	0.22
Rutabaga (<i>Beta Vulgaris L.</i>)-nonpeeled	39.72	0.80	0.22
Gardenbest (<i>Beta Vulgaris L.</i> , SSP <i>Esculenta</i>)	33.45	0.22	0.14
Common Leek (<i>Allium Ampeloprasum L.</i>)	17.60	1.41	0.21
Red Carrot (<i>Daucus Carrota L.</i>)	17.39	0.61	0.29
Parsley (July 1968)	16.18	0.52	0.45
Celergy (<i>Apium Graveolus L.</i>)	13.20	2.25	0.53
Onion (<i>Allium Cepa L.</i>)	4.53	0.22	0.30
Common Garlic (<i>Allium Sativum L.</i>)	1.52	0.11	0.30
Potato (<i>Solanum Tuberosum L.</i>)	1.01	0.14	0.12

Table 6

Pb Content of Vegetables and Absorption Coefficients

Location #	Parsley (October 1968)			Red Carrot (July 1968)			Potato (October 1968)		
	Pb mg/kg	C _T	C _{AL} ⁻²	Pb mg/kg	C _T	C _{AL} ⁻²	Pb mg/kg	C _T	C _{AL} ⁻²
1	51.12	0.21x10 ⁻²	0.42x10 ⁻²	17.39	0.7x10 ⁻²	0.14x10 ⁻²			
2	40.12	0.47	1.68						
3	22.14	0.44	1.16						
4	17.14	0.55	4.58	6.55	0.24	1.21	0.01	0.02x10 ⁻²	0.05x10 ⁻²
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	12.66	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	1.98	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				0.89	2.28	49.44			
33	1.03	2.93	35.66	1.27	4.53	60.47			

Table 7

Determination of ALA in Urine of Exposed
Population in mg/l in Summer 1968

Settlement	No. of Samples	Minimal Value	Maximal Value	Average Value
Lampreč [✓]	55	2.5	21.2	9.82
Črna [✓]	273	3.0	27.0	11.10
Glančnik [✓]	12	3.7	18.0	11.16
Rudarjevo	138	2.1	35.9	11.70
Polena	165	0.7	44.0	11.94
Žerjav	269	1.4	42	12.97
Total	912			
Control Group	50	0.35	8.55	5.20
Lead Miners	7	24.5	50.4	31.80
Lead Smelters	70	7.5	117.0	54.40

Table 8

ALA Values in the Urine of Inhabitants
of the Meza Valley

Settlement	No. of Inhabitants Examined	<u>Average ALA Values in mg/l</u>	
		Summer 1968	Summer 1969
Zerjav	99	19.6	10.16
Crna	130	16.0	13.0
Mezica	60	16.7	10.66
<u>Control Group</u>			
Mislinja	51	5.20	

Decrease of average ALA values in 1969 in relation to 1968

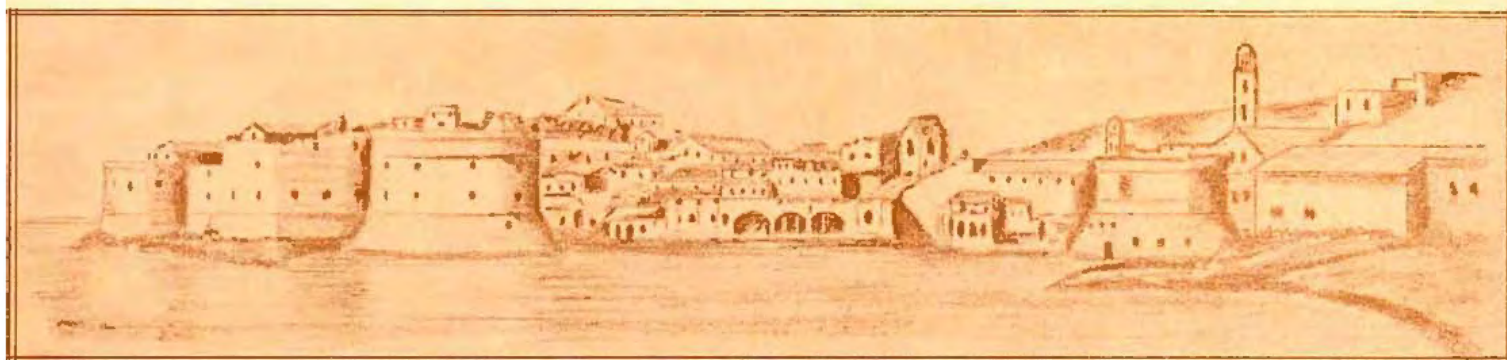
Žerjav for 48%
Crna for 19%
Mežica for 38%

References

Following papers are prepared for publications:
"Lead Contamination of Environment in Meza Valley"

1. Djuknić, V., Lj. Jablanov, and D. Djurić: Determination of Lead in Air.
2. Kerin Ž., and D. Djurić: Determination of Lead in Waters.
3. Kerin, Ž.: Determination of Lead in Snow.
4. Kerin, Ž., and D. Djurić: Lead Content of Overground Parts of Plants.
5. Djurić, D., and Ž. Kerin: Some Considerations on Lead Content of Soil and Plants.

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