Lead in New-Fallen Snow Near a Lead Smelter

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In a mountainous area of Yugoslavia, where a lead mine and smelter have been in operation for some 300 years, samples of new-fallen snow were obtained within three zones situated at increasing distances in different directions from the two centrally located stacks of the smelter, and were analyzed for their lead content. The lead content of new snow would be a factor of the quantities of lead in the air through which precipitation of moisture has occurred. The results confirmed the expectation that, with increasing distance from the source of lead emission, the snow contained consistently decreasing quantities of lead. Moreover, samples of new-fallen snow collected at altitudes that differed from that of the stacks yielded results that deviated from each other to such an extent as to alter significantly the negative correlation of the results with an increasing distance of the sampling sites from the stacks.

At Žerjav, Yugoslavia, in the upper valley of the Meža River, 542 meters above sea level, in an Alpine area not far from the Austrian border, a lead mine and smelter have processed a rich lead-zinc ore for some 300 years. Until January 1969, when a Lurgi filter was installed, 200 to 300 tons of metallic lead and lead oxide per year were discharged into the air from two stacks in the plant area at a level of 623 meters above sea level.

Determinations of the lead content of new-fallen snow (during or shortly after its fall) were made to establish the removal from the air of particulate metallic lead and its compounds, as well as the extent and the variability of these phenomena, at upland and lowland points located at various distances and in various directions along the courses of the rivers and streams that drain this mountainous region.

Methods

Sampling Sites.—Sites in three areas fanning out along three different axes from the central position of the stacks (actually along the courses of the Meža River and two of its tributaries) were selected to examine any quantitative differences in lead content of snow as variables in distance from the stacks and comparative altitude with respect to the stacks. The three areas were that nearest the stacks, extending outward for about 700 meters, designated as the stack zone; that extending outward from the stacks from 700 to 7,000 meters, designated as zone A; that expected to be a transition area from slight to negligible contamination by effluents from the stacks, extending from 7,000 to 17,000 meters, zone B. An addi-

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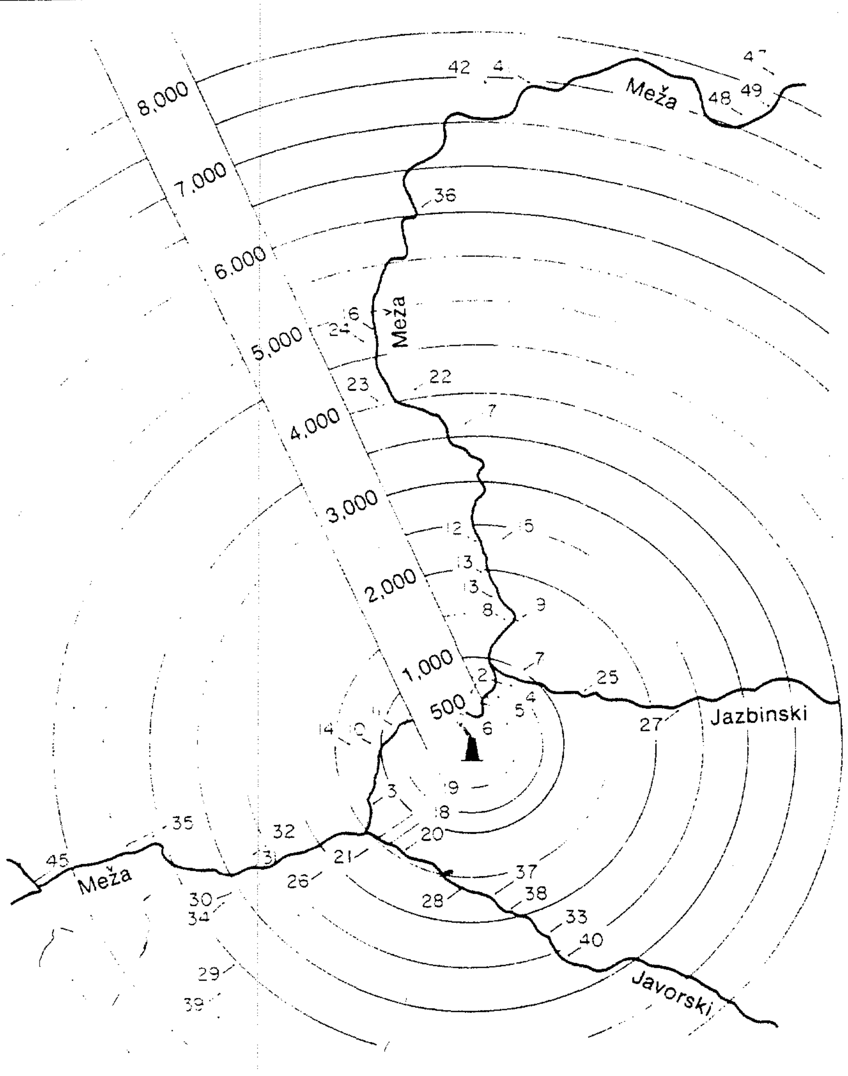

Fig 2. – The same area as in Fig 1 shows location of stacks of the smelter, and sweep of the valley of the Meža River and tributaries, where samples of new-fallen snow were obtained. Distances (in meters) of sampling sites from stacks is shown by concentric circles. Sites of individual samples are indicated by numbers along the course of rivers.

izontally over its base. The enclosed snow was transferred with a vinyl spatula into a wide plastic dish fitted with a lid of the same material. Two samples were collected, side by side, and both were emptied into the same dish. The volume of the two samples of snow from each site, when melted in the dish (which comprised the sample for further handling), was measured and found to be usually 160 ml. To it were added 0.5 ml of 0.01N H_2SO_4 and 1 to 2 ml of concentrated HNO_3, after which the liquid was evaporated to dryness.

The quantity of lead in the prepared sample was determined by a micromethod described elsewhere.[1] The results of the analyses are expressed in terms of the concentration of lead in milligrams per liter of liquid, and are presented in the Table, according to the designated zones of sampling. The identification of each sample, except the two samples taken in the control zone, is indicated by its number on the map (Fig 2), and by a local place name, together with the difference between its altitude and that of the top of the stacks, and the horizontal distance of its position from that of the stacks, as well as the lead content of each sample.

Results and Comment

The outstanding feature of the data in the Table is the sharp decrease in the quantities of lead found in the freshly fallen snow, as the distance between the sampling sites and the stacks increased. The quantities of lead found in the samples did not fall in sequence in strict accordance with their distances from the stack, but as the Table indicates clearly, the magnitude of the values decreases so nearly regularly from above downward (with increasing distances) as to yield striking evidence of the trend. In view of the topography of the terrain in the entire area, and the likelihood of air currents of varied direction and velocity, the slight incongruities in the results are not remarkable. The degrees of the correlation between the concentration of lead in the samples of snow (z) and their distances (x) from the source of the emissions is shown by the correlation coefficient (r_{zx}) which turns out to be -0.50 for the total number of 24 samples and $P = .05$. When, however, the differences in the altitude at which the samples were obtained from the altitude of the top of the stacks are eliminated, the partial correlation coefficient $r_{zx \cdot y}$ becomes -0.62 and $P = .01$.

Thus, the sampling of freshly fallen snow presents a consistent pattern which derives from the fact that the snow, in falling through an atmosphere that contains considerable quantities of lead at its lower levels, removes lead from the air as it falls, but is not subject to important subsequent fallout of lead upon its surface, if it is sampled promptly after falling. Whether it cleanses the air completely and reveals the total lead content of the air, under a variety of conditions associated with variations in the density and the duration of the snowfall, and more particularly, of the degree of dispersion of the lead compounds is another matter. Certainly, some very small particles of lead escape snow showers, as they do rain showers, and remain airborne.[2] As a means of sampling the air for lead in a given locality, involving comparable effluents, falling or new-fallen snow, in considerable volume, in relatively quiet air, can be a useful means of measuring change in the lead content of the air, as, for example, before and after a counteracting or remedial procedure. Such a conclusion is justified by the data in the Table.

There is little doubt that in any situation involving high temperatures of the combustion of materials containing lead, as ores or painted surfaces, particles of minute dimensions are emitted and remain in the atmosphere for long periods of time, to be depleted by conglomeration, precipitation, and by removal through entrainment in rainfall or snowfall even at great distance from the point or origin. That wide dispersal occurs is indicated by the accumulations of lead in polar ice as reported by Murozumi et al,[3] by Jaworowski,[4] and by Picciotto et al.[5] A more local dispersal is shown by the data presented here, in that the quantities of lead found in snow in the control area, while minute, never go down to the very low levels found in snow or rainfall in areas remote from human habitation.[6] The evidence indicates that the control area was not entirely free from local contamination with lead.

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Lead Content of New-Fallen Snow

Sample No., Fig 2	Place	Altitude Above (+) or Below (−) Top of Stack, Meters	Distance (Laterally) From Stack, Meters	Concentration of Lead (Pb^{++}) in Melted Snow, mg/Liter
		Stack Zone		
6	Žerjav	−82	400	15.76
1	Žerjav	−80	650	23.50
2	Žerjav	−82	680	17.40
		Zone A		
7	Žerjav 26	−82	1,050	4.20
10	Mušenik	−32	1,100	3.65
3	Rudarjevo	− 8	1,260	2.67
14	Mušenik	+78	1,350	4.01
18	Črna	−22	1,400	1.29
19	Črna	−22	1,450	1.79
8	Žerjav 13	−82	1,450	1.49
28	Sp. Javorje	+28	1,670	0.74
38	Sp. Javorje	+ 8	1,900	0.75
13	Plat 5	−92	2,000	1.08
31	Pristava	−42	2,700	0.90
34	Pristava 14	+78	3,180	0.32
35a	Škrnbej	+78	3,620	0.48
35	Podpeca 75	+78	3,900	0.61
23	Polena	−122	4,020	0.23
16	Mežica	−142	4,850	0.22
45	Topla	−35	4,920	0.27
		Zone B		
41	Poljana	−172	7,450	0.08
48	Prevalje	−172	7,600	0.13
49a	Prevalje-Ravne	−172	7,800	0.09
(Not in Fig 2)	Ravne	−222	9,750	0.04
		Control Zone		
				0.02
(Not in Fig 2)	Maribor		62,500	0.04

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[illegible]MAN BODY BURDEN OF LEAD: PRELIMINARY [illegible]SERVATIONS ON THE RELATIONSHIP WITH AGE

[illegible] of lead and other trace metals in the [illegible] humans exposed to the "normal" environment of [illegible] been conducted in order to validate methods [illegible] burden analyses and to interrelate the consequen- [illegible] exposure with variables such as age, sex, [illegible] and state of health. This report pre- [illegible] observations related to the age variable.

[illegible] were obtained at autopsy with the cooperation [illegible] coroner's office. Standard sections representing [illegible] tissues were obtained from each individual. Any unusual features of the standard section or organ were noted at the time of autopsy and at the time of subsequent dissection for metal analysis. The tissues were ashed with the aid of nitric acid and analyzed for lead by the dithizone method and for copper, zinc, and cadmium by atomic absorption spectrophotometry. The results of the lead analyses of 42 white men, 20-84 years of age, are presented here.

Regression lines for age and the concentrations of lead in several tissues are shown in Figure 1. These lines represent the least squares fit for data points which have considerable scatter. This scatter increases as age increases for the bones and aorta (not the other tissues) as is shown in Figure 2 for skull bone. Thus, on an overall basis the bones and aortas tended to increase with age while most of the soft tissues remained at relatively constant levels of 1 ppm or less. The kidney and liver shown in Figure 1 are two of several tissues which decreased with age. These decreases were generally correlated with pathological changes in these organs which will not be discussed here.

[illegible] 2 shows the plot of individual lead concen- [illegible] the skull versus age. The concentrations in [illegible] are very similar to those obtained for the tibia and correlate well with other bones as to relative lead concentrations. These correlations are shown by desig- [illegible] in Figure 2, and are based on the [illegible] average levels of four bones (rib, skull, tibia, [illegible] vertebrae), compared to the bones of other in- [illegible] the same age group. The skull sections did [illegible] change as seen in the rib and ver- [illegible] the lead concentrations of the skull [illegible] present concentrations of lead in the [illegible]

[illegible] the body burden of lead [illegible] "plateau" after the third decade of life [illegible] continuous increase in body burden [illegible] life (2); and others suggest a decrease in body burden of lead after the sixth decade of life (3). In these studies it was assumed that the skeleton contains most [illegible] of the body's lead.

[illegible] that the lead in skullbone is a good repre- [illegible] long-term environmental exposure to lead and [illegible] environmental levels of lead did not change ap- [illegible] the last sixty years (there is some evi- [illegible] that Cincinnati airborne lead actually [illegible], the data in Figure 2 could indicate that 2/3 [illegible] the skull section at 15 ppm or less, dotted line) of the population was in a reasonably steady-state relationship with lead in their environment, from age 20. (Seventy-seven percent of the tibia sections were at 15 ppm or less.) The other 1/3 showed varying degrees of continuous increase of body burden of lead with increasing age.

There were suggestive relationships between body burden and occupation listed at the time of death. It would be desirable, if possible, to investigate the exposure histories of these individuals in order to attempt to relate their exposure with body burdens. In any event, these studies provide reliable baseline information which may be compared with future studies to look for changing patterns in man's body burden of lead with age and environmental exposure.

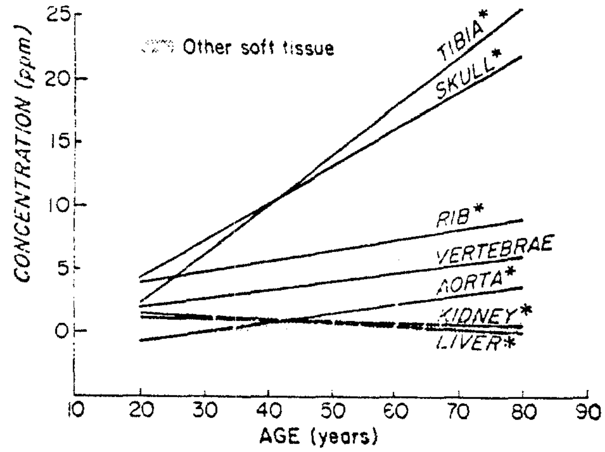

Figure 1. Regression lines for tissue lead concentration (wet weight basis) with age. The asterisks represent statistical significance at the 95% confidence level.

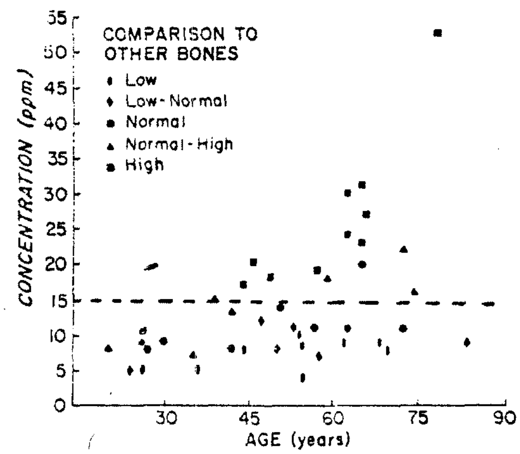

Figure 2. Skull lead concentrations (wet weight basis).

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