

Decreasing immissions of vehicular lead in central Bohemia?

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Abstract: Total atmospheric deposition of Pb and several trace elements was sampled to study their cycling in the experimental catchment "Lesní potok" in central Bohemia, Czechoslovakia. The study area was situated in a forested landscape about 30 km SE from the center of Prague, i.e. in the direction of prevailing winds from this significant source of atmospheric emissions. The chemical composition of 28 cumulative precipitation samples collected monthly shows the significant decrease of their Pb content between May 1989 and August 1991. This finding is suggested to reflect mainly the decrease of vehicular Pb emissions in western Europe.

Key words: Lead, atmosphere, transport, deposition, sources, wash-out effect

INTRODUCTION

About 96 % of lead present in the atmosphere is of anthropogenic origin, main portion of it (60 to 70 %) being emissions from cars with internal combustion engines (Craig, 1980, Nriagu, 1990). Tetra-alkyl compounds of Pb (TAL) represent the main additives to gasoline since 1923 (Vuorinen, 1983). These compounds are transformed during the combustion into alkylated oxides of lead. At high temperatures (above 900°C) conditions are favourable for depositing of metallic lead on the walls of cylinders and pistons. Another additives, usually ethylene dibromide and ethylene dichloride, are therefore applied to promote scavenging Pb compounds out of the exhaust pipes, by forming

volatile halogenides and oxyhalogenides of lead. These compounds are condensing mostly into submicron solid particles and they cause the contamination of atmosphere with relatively highly water soluble compounds of lead.

The size distribution of emitted particles causes typical characteristics in the distribution pattern of vehicular lead : most of it settles in the closest vicinity of the roads and the background levels of it are found even in the remotest regions of Earth, such as in the surface layers of Antarctica and Greenland ice (Kingston *et al.*, 1988).

Lead is a significant toxic trace element and its compounds represent hazard for the environment and for human population. Owing to their migration characteristics, the reaction products of the Pb immissions concentrate in the uppermost layers of soil and are expected to cause serious problems in the future. For all these reasons there are efforts to minimize or completely exclude the use of lead additives and replace them by ecologically less harmful compounds.

In an effort to curb the landscape burden caused by vehicular lead deposition the average amount of TAL compounds added to gasoline in the Czechoslovakia has been reduced gradually from 1.0 to 0.15 g.l⁻¹ during the last 10 years (Sucharová *et al.*, 1990, Tlustý, 1992). This fact might be reflected by the gradual reduction of Pb deposition.

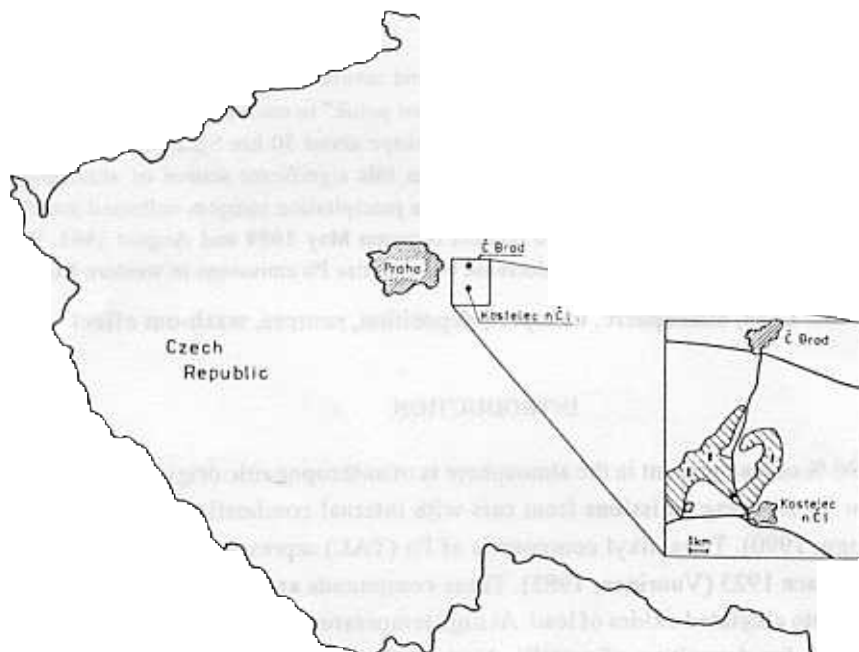


Fig. 1 Location map of the sampling site in central Bohemia.

MATERIALS, METHODS

The site in which the atmospheric deposition was sampled is located within a forestry research area of the Prague University of Agriculture near the small town Kostelec n. Č. lesy (Fig.1.). The nearest road, with very limited traffic, is running about 200 m E from the sampling site being protected by a strip of spruce forest. The level of atmospheric deposition was expected to be low on this sampling site so that it was considered as a background one.

Sampling was carried out using the device described in Fig. 2. The sampling procedure was adopted with respect to the main task – study of trace element cycling in the environment. Between April 27, 1989 and September 2, 1991 the cumulative samples of total atmospheric deposition (both wet and dry) were collected monthly (see Table 1 for precise timing). At the beginning of each sampling 5 ml of diluted (22 %) nitric acid (Fluka, p. p.) were inserted into the sampling bottle in order to avoid adsorption of cations and their complexes on the walls of the sampling bottle.

At the end of sampling period the bottle was removed and its content was filtered in the laboratory using the nitrocellulose membrane filter (Sartorius, type 11306-47-N, pore size -0.45 μ m) of a known weight. Volume of the filtrate was measured and amount of separated solid particles was determined by weighing the dried membrane filter. The content of studied trace metals was determined using graphite furnace or flame AA spectrophotometry.

Concentrations of studied metals determined in this way represent the sum of their dissolved forms in wet deposition together with their forms weakly bound to solid particles of the dry deposition, dissolved in the acidified solution.

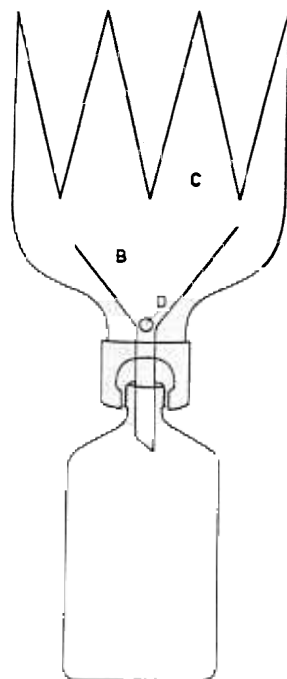


Fig. 2. Device used for the cumulative total deposition sampling.

The polyethylene bottle A, of 1 litre volume, is equipped with glass funnel B (12 cm in diameter) inserted into the cap of the bottle. A device made from the other (5 litre) bottle C serves to protect the funnel from birds. Its bottom is cut off and the walls are formed in the zigzag pattern. It is attached upside down to the cap of the sampling bottle. Small glass ball D placed in the mouth of the funnel avoids pollution of the sampling bottle with organic particles (seeds etc.) and insects.

Table 1. Results of lead (and zinc) deposition monitoring.

P	S	N	V	M	C ₁	D _{Pb}	D _{Zn}
1	30.05.89	33	1203	14.30	12.0	14.5	96.5
2	30.06.89	31	1910	12.00	13.0	24.8	
3	28.07.89	28	3316	13.10	15.0	49.7	132.6
4	01.09.89	35	1141	8.50	13.0	14.8	
5	29.09.89	28	2997	5.80	10.0	30.0	
6	01.11.89	33	1096	3.70	8.0	8.8	
7	01.12.89	30	1123	4.10	13.0	14.6	
8	02.01.90	31	796	2.60	5.0	4.0	143.7
9	01.02.90	30	354	2.90	10.0	3.5	
10	28.02.90	27	2290	5.60	5.0	11.5	
11	30.03.90	30	884	6.90	5.0	4.4	
12	27.04.90	28	2246	4.80	6.0	13.4	336.3
13	07.06.90	40	928	18.70	6.0	5.6	
14	02.07.90	24	1618	3.10	5.0	8.1	
15	27.07.90	25	177	3.20	6.0	1.1	
16	31.08.90	35	1061	10.20	4.0	4.2	191.0
17	01.10.90	31	1538	5.60	4.0	6.2	
18	02.11.90	32	1052	4.00	5.0	5.3	
19	05.12.90	33	1786	2.57	8.0	14.3	
20	03.01.91	29	1035	3.43	4.0	4.2	
21	04.02.91	32	212	.45	6.0	1.3	29.3
22	28.02.91	24	460	4.24	8.0	3.7	
23	02.04.91	33	1114	4.45	4.0	4.5	89.5
24	02.05.91	30	1079	6.37	10.0	10.8	
25	31.05.91	29	1424	5.12	3.0	3.6	
26	01.07.91	31	2440	18.02	1.0	2.4	
27	31.07.91	30	3289	5.38	2.0	6.6	
28	02.09.91	33	2307	8.03	3.0	6.9	

P – serial number of sampling period (month), beginning from May 1989

S – sampling date

N – time span of the individual sampling period (days)

V – Precipitation rate ($\text{ml} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$)

M – amount of the dry deposition over the time span N (mg)

C₁ – analytical concentration of Pb in the filtered sample (ppb Pb)

D_{Pb} – evaluated average daily deposition rate of Pb ($\text{mg Pb} \cdot \text{day}^{-1} \cdot \text{m}^{-2}$)

D_{Zn} – evaluated average daily deposition rate of Zn ($\text{mg Zn} \cdot \text{day}^{-1} \cdot \text{m}^{-2}$)

mg

RESULTS AND DISCUSSION

For lead and zinc, the data are shown in Table 1. Regression analysis of the Pb deposition rate on selected variables (P, V, and M) revealed fair correlation with the serial number of sampling period (P), and especially with the precipitation rate (V). Multiplicative model of the regression analysis proved to give best fit to the data (Table 2). The correlations actually show gradual decrease of the Pb deposition rate with time during the whole sampling period and its increase with the intensity of precipitation.

dependent variable: D_{Pb}					
independent variable	model	prob. level	corr. coeff.	R^2 (%)	standard error of est.
P	$Y=aX^b$.00048	-0.6163	37.98	0.70371
V	$Y=aX^b$.00002	0.7095	50.33	0.62975
M/N	$Y=aX^b$.02089	0.4344	18.87	0.80486

Data on average daily deposition of zinc, (Table 1) allow to distinguish the character of our sampling locality. The evaluated amounts of annual Zn deposition correspond almost precisely to the mean value for rural sites in central Europe ($550 \text{ g Zn}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$), presented by Nriagu (1990). Main global source of Zn in the atmosphere is the burning of fossil fuel. Deposition of Zn on the locality Truba is influenced from this point of view mainly by the emissions of Prague and possibly to a lesser extent by large coal-burning power plants scattered in the NW part of Bohemia in a distance of approx. 100 km.

On the other hand, the annual deposition rate of Pb in 1989, evaluated from the values for P 1 to 8 (Table 1, columns D_{Pb} and N) corresponds to the minimum value for rural sites in central Europe (Nriagu 1990, $63 \text{ g Pb}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) and the values for years 1990 and 1991 are even much lower. It must be noted, that the values presented by Nriagu (1990) were evaluated from data presented before the year 1981.

If the sampling site is considered as a background locality for the lead deposition, then the correlation between variables M/N and D_{Pb} cannot be expected. Coarse particles representing dry atmospheric deposition are not the main carriers of vehicular lead. Correspondingly, no significant correlation between the amount of dry deposition and the deposition rate of Pb over the same time period was indicated (Table 2).

Majority of vehicular lead present in atmosphere is in the form of submicron carbonaceous particles with relatively high residence time in the gaseous phase. Estimated mean diameter of its particles reaching the rural and remote areas is 0.56 μ m (Nriagu, 1990). This is a value typical of optically active smog aerosol which is not subject to rapid gravitational sedimentation. Majority of such particles is washed-out from the atmosphere by liquid or solid precipitation (rain and snow). The intensity of the washing-out effect is dependent on the character of an individual precipitation event: A long-time fine drizzle should be more efficient than an intensive short cloud-burst of the same precipitation volume. This is one of the reasons for correlation between the precipitation rate and the amount of deposited lead being not completely unambiguous.

Nevertheless, the main Pb flux from the atmosphere should result primarily from wet deposition as it is shown by Remoudaki and Bergametti (1991). This is also confirmed by the strong correlation between the daily precipitation rate and the average deposition rate of Pb within our data set.

The contribution of Pb from natural sources such as soil and rock in the deposition sample can be evaluated by comparison of Pb content in the deposition and in the corresponding soil or rock with concentrations of some of the typical terrigenous elements determined in the same materials (Boutron *et al.*, 1991). For this purpose we used the content of Sr. The enrichment factor (E_f) is thus defined as mean $^{Pb}/_{Sr}$ ratio in sample divided by $^{Pb}/_{Sr}$ mean concentration ratio in the bedrock of the sampling site.

Table 3. Mean concentrations of Pb and Sr in deposition and rock for the evaluation of E_f .

material	element	content
total deposition	Pb	6.9 ppb
	Sr	5.6 ppb
rock (permian sediments)	Pb	18.3 ppm
	Sr	102.3 ppm

Data necessary for the evaluation of E_f are presented in the Tab.3. From the above definition the E_f equals to 6.88. It means that the natural contribution to Pb content in deposition from rock and soil dust is not significant – it amounts only to 14.5 %.

The dependence of the Pb deposition rate on both the precipitation rate and on the serial sampling number was graphically processed using the program SURFER. This relationship was approximated through interpolation and regression using various poly-

Table 4. Functions used for the polynomic regression			
No.	function	std. error	corr. coeff.
1	$D_{Pb} = 14.49 - 0.71 P + 2.09 \times 10^{-6} V^2$	5.58	0.930
2	$D_{Pb} = -0.72 + 0.013 V - 4.23 \times 10^{-4} PV$	4.03	0.964
3	$D_{Pb} = 2.66 - 0.70P + 0.04 P^2 + 0.012 V + 8.68 \times 10^{-7} V^2 - 6.03 \times 10^{-4} PV$	3.41	0.977

nomes with differing degree of correlation. Table 4 presents some examined forms of polynomic regressions together with the values of the corresponding statistical criteria – the standard error and correlation coefficient.

Fig. 3 represents the spline interpolation. The diagram featured in the form of distorted netted area mirrors distinctly the irregularities of the experimental values.

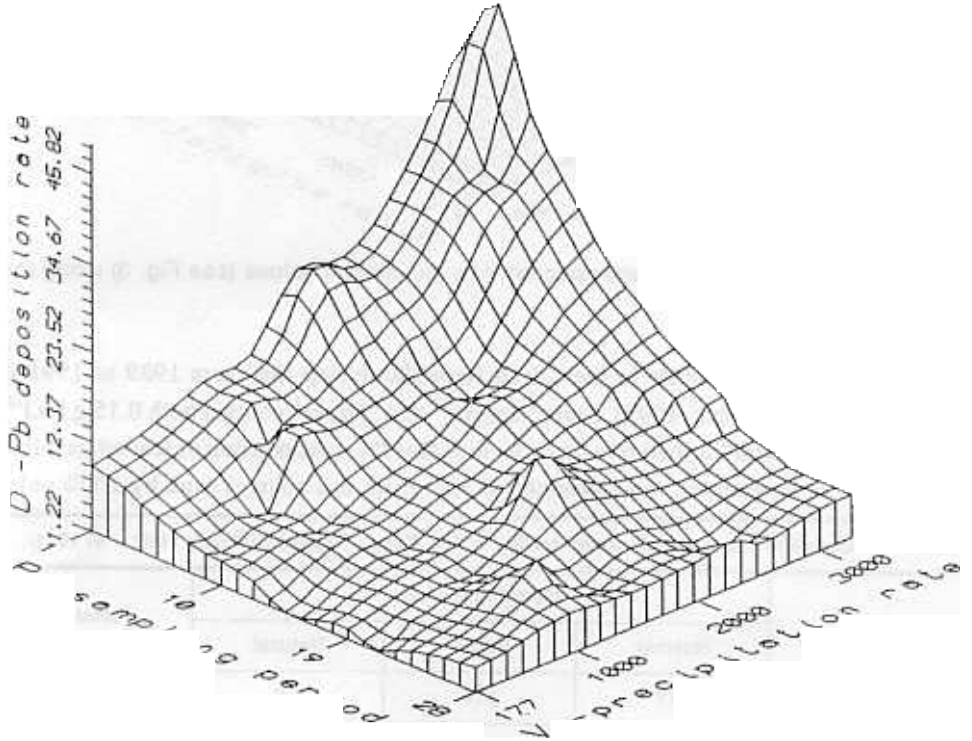


Fig. 3. Spline interpolation diagram – dependence of Pb deposition rate on precipitation volume and period of sampling.

Fig. 4 presents the graphical form of the polynomial regression presented in Tab. 4 under No. 2, which gives perhaps the best optical notion of the relationship.

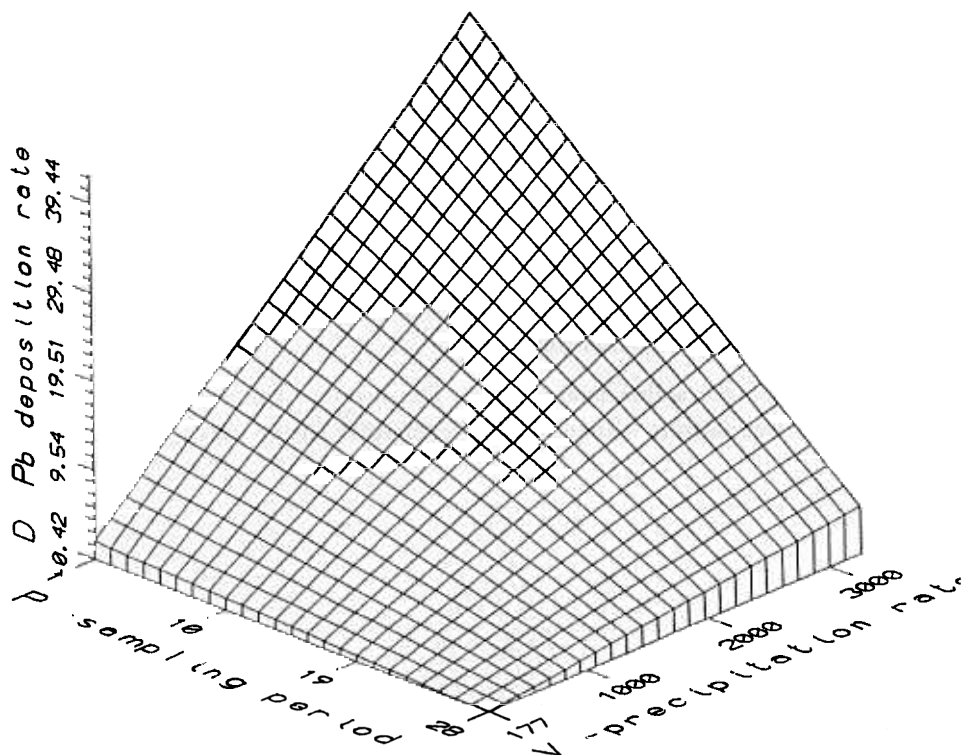


Fig. 4. Polynomial regression diagram of experimental values (see Fig. 3) using the function No. 2, Tab. 4.

Consumption of gasoline in the Czech Republic during the years 1989 to 1991 is shown in Table 5 (Roček, 1992). Sorts “Special” and “Super” contain both 0.15 g Pb.l⁻¹ whereas the “Natural” is lead free. It is obvious that the consumption of leaded gasoline (and, in the same manner, the emissions of lead from this source) sank by 14 % only

Table 5. Gasoline consumption (road traffic) in the Czech Republic (Roček 1992 – in 10³ t):

year	type of gasoline			total
	Normal	Super	Natural	
1989	877	314	3.6	1194.6
1990	827	338	9.5	1174.5
1991	725	294	27.5	1046.5

The observed decrease of Pb immissions in the sampling site Truba cannot be thus explained by this fact.

Fine particles of vehicular lead can be transported over a very long distance (Hamelin *et al.*, 1989). To evaluate the average residence time (RT) of lead in the atmosphere represents rather complicated task because of the diversity of its sources and resulting heterogeneity of its particles.

With respect to the average diameter of Pb-aerosol particles and to the significance of the wash-out effect for the removal of lead from atmosphere its RT has to be at least 9 days, which is the average RT of water in the global atmosphere (Moldan, 1983). RT determined from the behavior of ^{210}Pb isotope in the environment was estimated to be four weeks (Hill, 1960). This value compared with the average velocities of air masses allows to anticipate the idea that the transport of vehicular lead is a matter of very large regions, perhaps whole the Northern Hemisphere.

Indeed, study of the lead isotopes in aerosols at Barbados has shown that majority of Pb in the atmosphere of this region can be attributed to the European vehicular emissions. The air masses are supposed to be transported over north Africa to its west coast and by the trade winds to sampling site at Barbados, in the distance 8 000 km from the emission sources. The transit time of the air mass in this case is 1 to 2 weeks (Hamelin *et al.*, 1989). This distribution pattern of atmospheric lead indicates that its deposition on our background locality probably reflects more the average emissions of it over at least the whole central Europe than those produced in central Bohemia. This idea is also supported by the fact that the wash-out effect of the atmospheric water is much more efficient in the cloud-forming phase, than during the precipitation (Moldan, 1983).

The Pb deposition rate should consequently reflect the amounts of consumed gasoline and the average concentrations of Pb additives of whole the European region. It should also reflect the increasing consumption of the unleaded gasoline in the western Europe.

CONCLUSIONS

Study of the total atmospheric lead deposition carried out on the sampling site in central Bohemia suggests the following conclusions:

- (1) Average deposition of Pb (and Zn) corresponds to the mean values reported for the rural sites of central Europe.
- (2) Pb deposition rate is positively correlated with corresponding precipitation volume and negatively with the serial number of sampling period (i. e. time).

- (3) Deposition rate of Pb decreased gradually by 70 % during the whole sampling period (May 1989 to August 1991).
- (4) Contribution of Pb from natural sources in deposition amounts by less than 20 %.
- (5) Massive decrease in the Pb deposition rate cannot be attributed to the local vehicular emissions, as the consumption of leaded gasoline in Czech Republic sank by 14 % only during the same period of time.
- (6) The migration character of vehicular lead aerosol allows to explain the decrease of Pb deposition rate as a result of the increasing consumption of unleaded gasoline and following decrease in emissions of vehicular lead in western Europe.

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Klesající imise vehikulárního olova ve středních Čechách ?

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V práci jsou popsány výsledky sledování atmosférické depozice olova na lokalitě v oblasti středních Čech, svým charakterem odpovídající odlehlým oblastem, nezatíženým lokálními zdroji atmosférických emisí. Studium chemického složení 28 kumulovaných vzorků celkové depozice, odebíraných v měsíčních intervalech, ukázalo výrazný pokles obsahu Pb v období mezi květnem 1989 a srpnem 1991. Bylo zjištěno, že obsah Pb v depozici koreluje s jejím objemem (velikostí srážek) a že nekoreluje s množstvím tuhých částic depozice. Znamená to, že hlavním mechanismem transportu atmosférického Pb na zemský povrch je vymývání jemných částic jeho aerosolu, vznikajícího při spalování aditivovaného benzínu v zážehových motorech. Doba setrvání vody a tím i aerosolu Pb v atmosféře předurčuje jeho transport na značné vzdálenosti. S ohledem na převládající směr proudění vzduchu nad sledovanou lokalitou a zvláště frontálního proudění je možno předpokládat, že snížení depozice Pb v této oblasti je příznivě ovlivněno omezováním emisí vehikulárního Pb v západní Evropě.