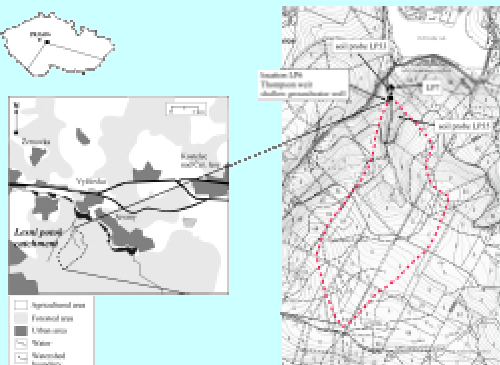


The biogeochemical cycle of lead in an acidified forested catchment in central Czech Republic

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Fig. 1: Position of the Lesní Potok Catchment in Czech Republic



Introduction

The site, Lesní Potok Catchment (LPC) is located 30 km SSE from Prague. The catchment is completely forested by European beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*). The catchment is underlain with granite bedrock.

The observed descending trend of lead (Pb) deposition is explained by the gradual decline in the consumption of the leaded gasoline. Reported annual Pb-deposition flux F_{Pb} at TR in the year 1994 was $3.41 \text{ kg.km}^{-2}.\text{yr}^{-1}$. It gradually decreased to $0.49 \text{ kg.km}^{-2}.\text{yr}^{-1}$ in 2001. The decrease is comparable with those observed in Germany and in the USA in 1970s and 1980s. The total ban of leaded gasoline sales in the Czech Republic since the 1st January 2001 was accompanied by a pronounced decrease of the F_{Pb} in a single year. The lead deposition at LPC site decreased by 63%, when compared to year 2000. The residual Pb-deposition flux is assigned to both: (1) the long-range transport of the finegrained vehicular lead aerosol (with long residence time in the atmosphere) and to (2) the emissions from power plant boilers burning the lignite mined in the Czech northwest coal basin. The F_{Pb} of lead correlates strongly with those of As, Cd, Cu, Zn and Be, the typical elements of the coal fly ash.

Comparison of the individual biogeochemical fluxes of lead at LPC revealed that the atmospheric input is still the most important flux of this element. Difference between the lead inputs and outputs in the catchment proved the ongoing accumulation of lead in the soils of central European landscape. The uptake of Pb by vegetation was detected but with regard to extent of soil contamination is less important.

Fig. 2: The Lesní Potok brook and surrounding European beech forest

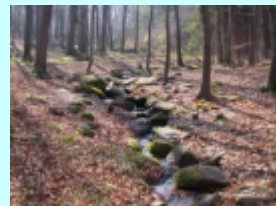


Fig. 3: The Thompson weir and beech throughfall samplers



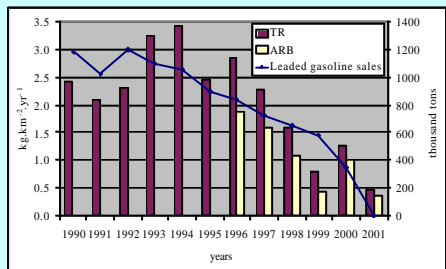
The lead deposition

The figure 4 shows decreasing trend of Pb deposition (bulk precipitation) during the last 11 years at the central Czech Republic. The decrease of Pb emissions correlates positively with the descending trend of leaded gasoline sales. However the decrease in year 2001 after the total ban of the leaded gasoline sales shows influence of other sources.

The other sources of Pb emissions include the coal burning power plants and the long-range transport of the Pb aerosols.

The higher deposition rates at site TR are due to its position. The sampling site is located 30m from the small road. The site ARB is located over 1km away from this road.

Fig. 4: Bulk Pb deposition and the relation to the sales of leaded gasoline in CR



Electron microprobe study of the solid aerosol samples collected at the locality TR in 1994 revealed numerous small aggregates (<3 μm diameter), containing Pb and C as major chemical constituents (Fig. 5.6). No such material was found neither directly in glass funnels of the bulk precipitation collectors, nor in the solid residues caught on the membrane filters after the sample elaboration. It can be therefore supposed that the aggregates (easily soluble at low pH of acidified samples) are generally formed by lead (oxy)-carbonates formed directly from the Pb-halides escaping from the exhaust gasses of leaded-gasoline powered vehicles.

Fig. 5: The analysis of the solid Pb aerosol

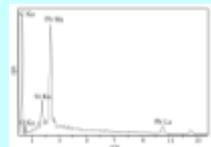
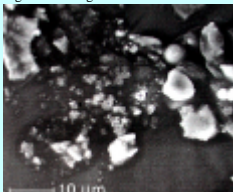


Fig. 6: The image of the solid Pb aerosol



The lead in soils

The highest concentrations of Pb were found in the top layers with the highest content of organic matter. The concentrations of Pb in deeper layers usually correlate with content of the clay minerals in the particular layer.

The uppermost layers of the studied profiles LP33 and LP35 contained 67 mg.kg^{-1} and 53 mg.kg^{-1} , respectively. However the lower layers G1 and G2 in profile LP33 located in the riparian zone of the LPC brook contained 76 and 93 mg.kg^{-1} of the lead. The content of the finest particles <0.01mm in layers G1 and G2 was the highest (43% and 44%). Lower layers of the profile LP35 contain lower concentrations of Pb compared to LP33 profile. The Pb concentration in the profiles LP35 is decreasing with depth.

Portion of 45-50% of the lead in the top layers of all the soil horizons is acid leachable. The acid leachable part represents the lead adsorbed on the Fe, Al, Mn hydroxides, on an organic matter and on clay particles. The portion of lead leachable by the NH_4NO_3 attributed to the cation exchangeable (CEC) sites correlates with the content of the finest particles.

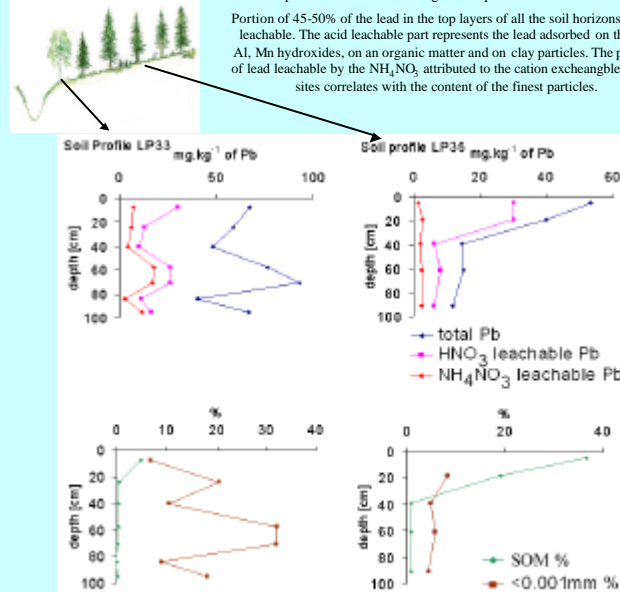


Fig. 7: The lead concentrations in soil profiles of the catchment

The lead in the surface water and shallow groundwater

The concentrations of DOC in the LPC surface water are low ($\sim 5 \text{ mg.L}^{-1}$) and thus the concentrations of lead are low. The highest concentration found in the LPC surface water was 1.8 μg.L^{-1} . It is necessary to take into account that some 20% of the total Pb concentration is associated with the particulate matter and is filtered off by 0.45 μm cellulose filter. The most of Pb measurements during the 7 years of surface water monitoring were below the detection limit of the AAS (0.5 μg.L^{-1}). Nevertheless, the Pb concentration may increase during the episodic events. In this case the stream water becomes a mixture of the shallow groundwater (low in DOC, low in Pb) and water (higher in DOC, higher in Pb) running and penetrating the topsoil layers. The spring snowmelt waters can also contain increased Pb concentrations because of the Pb deposited on the melting snow.

During the dry periods a ferric precipitate appears at the streambed of the LPC brook. This precipitate was sampled and analyzed for the Pb content. The concentration found on this $\text{Fe}(\text{OH})_3$ precipitate reached $60 \text{ mg.kg}^{-1} \text{ d.m.}$. Voluminous precipitate of ferric hydroxide, together with adsorbed organic ligands, represent suitable environment for the entrapment of the dissolved Pb ions.

In the summer 2001, an acidification experiment of the LPC surface stream was performed during a baseflow period (discharge $\sim 1.7 \text{ L.s}^{-1}$). The experiment was designed to reveal and evaluate the buffering capacity of the streambed. Amount of 22 moles of HCl was added to the stream during 4 hours, lowering the pH value of water from 4.9 to 3.7. The Pb concentration increased from initial 0.7 μg.L^{-1} to 1.8 μg.L^{-1} during the experiment. This proved the presence of mobile lead on the stream substrate. The lead can be released by the increased H^+ input. Main reasons for the mobilization of Pb may be either the charge changes of the stream substrate surface and the consequent release of the adsorbed molecules, and/or the concurrent dissolution of the Al and Fe precipitates.

Very low concentrations of Pb were detected in the shallow groundwater of the LPC. During year 2000, shallow groundwater was collected from the well situated close to the LP6 Thompson weir. Mean concentration of lead in samples originating approx. 2m below the groundwater level was 0.037 μg.L^{-1} . In order to evaluate the precise concentration of Pb in the groundwater, the samples were preconcentrated by the sub-boiling evaporation.

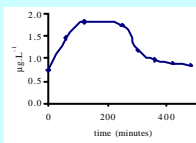


Fig. 9: Release of Pb from the stream substrate during an acidification experiment

The lead in soilwater

At profile LP33, soilwater from top 5cm (\sim in the middle of A hor.) exhibited concentrations up to 12.4 μg.L^{-1} . In depth of 15cm (below the A hor.) the Pb concentration in the soilwater decreased to values $\sim 1.5 \text{ μg.L}^{-1}$. Even deeper soilwater from the depth of 45cm (below the first 15cm of G hor.) exhibited almost the same concentration $\sim 1.6 \text{ μg.L}^{-1}$ as the soilwater from 15cm. The content of DOC decreases with depth.

The concentrations of lead in soilwaters at profile LP35 were $\sim 4.3 \text{ μg.L}^{-1}$ (below the O hor.) and $\sim 3.7 \text{ μg.L}^{-1}$ (in the middle of A hor.). The soilwaters from the top LP35 layers are rich in DOC.

The topsoil layers contain the anthropogenic lead. The lead is bound to organic matter and maybe mobilized by the acid leaching. However in the riparian zones the lower soil layers can contain high Pb concentrations due to the high content of the finest particles (layers G1 and G2). High concentrations of the Pb in the soil and soilwaters of the profile LP33 in riparian zone are a result of the Pb transport from the hillslope areas to the riparian zones. When the organic complexes are broken down by the bacterial activity in the riparian zone, the lead adsorbs to the clay particles. The adsorption to clay particles was confirmed by the high NH_4NO_3 leachable concentrations in the lower layers of the profile LP33. The lowest Pb concentrations in the bottom horizons of the LP35 profile infer the transport of the Pb to the riparian zone.

The lead in vegetation

The vegetation uptake of lead is low compared to the availability of the labile Pb forms in the soil. The concentration of Pb was studied in the stem wood, bark and assimilatory organs of the European Beech and Norway spruce. The highest concentrations of Pb were found in the stemwood of spruce trees (2.49 mg.kg^{-1}). The beech stemwood contained 0.42 mg.kg^{-1} of lead, only. Equal concentrations of Pb were detected in the bark of both the spruce and beech (2.23 mg.kg^{-1}). The higher concentrations of Pb detected in the wood of spruce trees, as a result of the typical spruce shallow rooting. On the other hand, the rooting system of beech reaches deeper and intakes water with lower Pb concentration (see soilwater chapter).

The Pb content in beech leaves is increasing during the individual growing season from values around the detection limit $< 0.18 \text{ mg.kg}^{-1} \text{ d.m.}$ in April to $0.53 \text{ mg.kg}^{-1} \text{ d.m.}$ in November. This increase may be caused by scavenging of Pb rich solid atmospheric aerosols and/or the tree may transport the Pb to the leaves and then releases them. This mechanism, however, was not detected for the spruce, where even the oldest needles (5-7 years) did not contain detectable Pb concentration.

Conclusions

- Deposition of Pb in central CR decreased during the past 10 years by 75% and it corresponds to the rural sites of central Europe.
- Results of monitoring revealed that deposition of vehicular lead diminished, but burning of brown coal in power plants represents still a significant part of the deposited anthropogenic lead.
- The deposited, mostly anthropogenic, lead remains in the uppermost soil layers. Soil waters near the surface contain high concentrations of Pb (up to 11 μg.L^{-1}). Increased Pb concentration were found in riparian zone soils and soilwaters.
- Concentration of dissolved forms of lead in surface water is low. However the lead is present in the streambed and may be mobilized as was proved during the experimental acidification. The amount of dissolved Pb is controlled by the adsorption/coprecipitation with ferric hydroxide and organic matter.
- The root uptake of Pb by forest trees is too low to influence significantly the Pb biogeochemical cycling. Higher uptake occurs at shallow rooting spruce growing on places with higher water table.