THE INFLUENCE OF ANTHROPOGENIC LEAD ON CONTAMINATION OF SOIL

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Abstract: In this study was investigated the state forest soils around Lenora (district Prachatice) of risk of elements lead. The aim of your experiment was to assess the influence of glassworks in Lenora (1834–1995) on the pollution of forest soils. From the neighborhood of Lenora were collected 42 samples from 5 locations, further sorted out into 8 sampling points up to 3 km in area of Velké Nivy, Radvanovické saddle, the hill Chlustov, the hill Ptáčník, Zátoňská mountain. EDTA-extractable (bioavailable) lead in the collected soil is the most accumulated in humus (H) organic horizons due to its high sorption capacity. The found average content of EDTA-extractable lead in the evaluated forest soils are in the range 8.5 to 28.6 mg/kg DM with a mean value of 17.6 mg/kg DM. Only three of the eight sampling points (Velká niva, Hill Chlustov east and Radvanovické saddle-spruce forest) exceeds the determined content of 30 mg/kg DM.

Key Words: EDTA, lead, soil, glassworks

INTRODUCTION

In nature, the lead is pervasive as most of the trace elements, the average concentration is about 36th place of elements in the Earth's crust. In the last 50 years it was extracted and concentrated a large amount of lead from ore and it was re-released into the environment in the form of e.g. tetraethyl in leaded gasoline. Thus, animals are exposed to the health risks and their body tissues and fluids can contain more lead than would correspond to the natural background. Infants and children may be at risk if they inhale the dust-bound pollutants. The lead content in the blood is generally accepted as the indicator organism load (Komárek et al. 2008).

The main source of error in the determination of lead in environmental and biological samples could be the secondary contamination that may occur during sampling and during their own analysis. Lead enters the environment during production, use and recycling of the lead compounds, the combustion of fossil fuels (coal, gas), the use of mineral fertilizer, sewage etc. The estimation of emissions from individual lead sources shows that anthropogenic sources in the atmosphere are more important in contrary with the natural sources (Chen et al. 2009).

The lead contamination of the atmosphere is estimated to be 5,000 years old (younger Stone Age-Neolithic). It began when the first imperfect smelting was done in Southwest Asia (Mesopotamia). The former world lead production was approximately 200 tons per year. Isotopic studies of lead can provide information on the pollution of the various parts of the environment. Lead is a toxic element, which has no known function in biological systems (Hansmann and Köppel 2000).

The aim is to obtain information about the properties of lead and its geochemical position especially in forest soils, which are characterized formed soil horizon.
MATERIAL AND METHODS

Description of locations

The examined locations are located in the area former glassworks of Lenora. In the nearby of Lenora village on Prachatice region, is located eight sampling sites (Figure 1) at a height of 786 m AMSL. The samples were collected mainly on forest soils according to the developed horizons. From the area of the top of the hill Chlustov located on the west side of Lenora at a height of 1094 m AMSL, the samples were collected from the beech stand on the western side of the hill and on the east side of beech-fir forest. From the area of the hill Ptáčník which lies eastward from the village at a height of 868 m AMSL were collected samples of spruce forest as well as from the experimental area around ZF JCU directly above the Lenora and from the area of forest Velká Niva. Additional sampling site is located at Zátoňské mountains (1028 m AMSL), where is the vegetation change on spruce-beech. Next samples were collected from the site of Radvanovické saddle lies from the south side of the village. Examined samples were collected from the two places characterized by different vegetation of spruce and beech stands. Mentioned sampling areas were located about 100 m apart. Considering the fact, the location belongs to Šumava National Park, there is necessary to have an entry permit from the competent forester from Zátoň.

Figure 1 Map of locations

Table 1 GPS locations around Lenora

<table>
<thead>
<tr>
<th>Location</th>
<th>GPS coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>The hill Chlustov – west (VCH-Z)</td>
<td>N 48° 55.612’; EO 13° 45.167’</td>
</tr>
<tr>
<td>The hill Chlustov – east (VCH – V)</td>
<td>N 48° 55.734’; EO 13° 45.649’</td>
</tr>
<tr>
<td>Zátoňská mountain (ZH)</td>
<td>N 48° 56.664’; EO 13° 50.108’</td>
</tr>
<tr>
<td>The hill Ptáčník (VP)</td>
<td>N 48° 55.572; EO 13° 48.481’</td>
</tr>
<tr>
<td>Experiment area ZF JCU</td>
<td>N 48° 55.535’; EO 13° 48.418’</td>
</tr>
<tr>
<td>Velká niva (VN)</td>
<td>N 48° 55.505’; EO 13° 48.709’</td>
</tr>
<tr>
<td>Radvanovické saddle (RS)</td>
<td>N 48° 53.706’; EO 13° 47.460’</td>
</tr>
</tbody>
</table>

MATERIAL AND METHODS

Soil samples of forest sites were sort out by soil horizons, which are created in the soil. Samples were divided to the the litter (L), fermentation horizon (F), humification horizon (H), the first mineral
horizon (A1) and the second mineral horizon (A2). The strength of horizons were different, and it was depended on the type of vegetation, the rate of decomposition of substances in these horizons and stand age. Other forest soils samples were divided by the depth of sampling to 15 cm, 30 cm and 40 cm. Horizons L, F, H of forest soils were collected using a garden shovels, mineral horizons and other soil samples were collected using a soil sampling probe. All the samples were stored in plastic bags with a precise description of the location and the date of collection. Subsequently, they were allowed to air dry, to be prepared for further processing Kudravá and Rúriková (2005).

**Preparation of the sample for analysis**

Firstly, well-dried samples were processed using a mortar and pestle or a laboratory mixer (for horizons L and F). They were pulverized to a fine part and then sieved through a sieve of mesh size 2 Mesh screen (Bollhöfer and Rosmann 2001). In this process, the samples were rid of coarse impurities. The treated samples were re-sieved in a mortar and then they were passed through sieve 0.5 Mesh screen.

**Analytical methods**

The 0.05 M EDTA solution was prepared. 18.6 g of Chelatone-3 was dissolved and transferred into a 1 l volumetric flask. pH of the solution was determined on pH meter (Mettler DL25, Switzerland) and adjusted by adding approximately 6 ml of ammonia solution (p. a. Penta manufacturer) until stabilization of pH = 7. The 0.5 g of soil was transferred to vials for extraction (Falcon tubes) then the 25 ml of extraction solution EDTA was added. Samples were mixed on a shaker for 60 minutes (Bermond et al. 1998). After that, the samples were centrifuged on ultracentrifuge (type 2–5, Sigma, Germany) for 10 minutes on 3900 rpm. The supernatant was filtered through a filter paper with a blue stripe type (Watmann, GB). Overall lead content in the extract were determined by ICP - OES (ICAP 6000, Thermo Scientific Cambridge UK). Prior the analysis, the samples were diluted according to the lead concentration approximately of 20 µg/l (Chrastný et al. 2008).

**RESULTS AND DISCUSSION**

EDTA-extractable content (Organic accessible) of lead in soils is shown in the following graph (Figure 2). The graph shows the most of the lead is accumulated in humus (H) organic horizons. This trend could be explained by the high sorption capacity of this kind of soil.

*Figure 2 The content of EDTA-extractable lead in forest soils near Lenora*

The total content of lead in the most soils of the Czech Republic regardless of type (forestry, agriculture), its diameter does not exceed 20 mg/kg DM (Sanka and Materna 2004). The found average content of EDTA-extractable lead in the evaluated forest soils are in the range 8.5 to 28.6 mg/kg DM with a mean value of 17.6 mg/kg DM. Only three of the eight sampling sites (Velká
niva, the hill Chlustov east and Radvanovické saddle - pine grove) exceed the determined content of 30 mg/kg DM (Figure 2). Velká niva, Radvanovické saddle are comparable stands (spruce) and also the order of the contents of lead large floodplain corresponds to 21.1 ± 14.7 mg/kg DM, Radvanovické saddle - spruce corresponds to 22.6 ± 14.6 mg/kg DM. Velká niva is closer to the source of the order of about 2 km from the glassworks in the direction of the prevailing winds than Radvanovické saddle pine grove. Radvanovické saddle spruce forest is about 4 km north of the source from which it follows that it should not be equally affected by glassworks. In terms of soil horizon (Figure 3) is the most contaminated horizon H which reaches 39.7 ± 15 mg/kg DM, which is twice higher the lead content in soils according to Weiss et al. (1999). However, H-term horizon forest soil is very thin (a few centimeters). The minimum value of lead concentration at the site of the Velký Ptáčnik experimental area was estimated to 14.4 mg/kg DM and the maximum value of the lead concentration on the area of hill Chlustov east was estimated to 82.4 mg/kg DM. Other horizons, except F horizon, is varied in the range 6.5 ± 2.6 mg/kg DM, 13.4 ± 1.4 mg/kg DM, which is lower than results by Maříková (2008). The average value of the content of Pb²⁺ in all horizons at all locations is approximately a half lower in the comparison with H horizon 18.5 ± 7.1 mg/kg DM. This result is in good agreement with the results by Papanikolaou et al. (2005).

Figure 3 Average content of EDTA-extractable lead in the soils at all locations

Legend: VN - Velká niva, VCh-V hill Chlustov east, VP - 2 hill Ptáčnik, VP-1 hill Ptáčnik over the experimental area, ZH - Zátoňská mountain, RS-b Radvanovické saddle - beech forests, VCh-Z The hill Chlustov west, RS-S Radvanovické saddle - spruce forest

Figure 4 Average content of EDTA-extractable lead in soil horizons

Legend: litter (L), fermentation horizon (F), humification horizon (H), the first mineral horizon (A1) and the second mineral horizon (A2)
Determined levels of lead in selective locations Radvanovické saddle in the most contaminated H-horizons (spruce 45 mg/kg DM, beech 23 mg/kg DM) could be explained by the higher adsorptive capacity of greater leaf area spruce stand.

CONCLUSION
All samples were collected from soil horizons L, F, H, A1 and A2. It was found that EDTA-extractable (bioavailable) lead in the collected soil is the most accumulated in humus (H) organic horizons due to its high sorption capacity. The obtained average content of EDTA-extractable lead in the evaluated forest soils was in the range from 8.5 to 28.6 mg/kg with a mean value of 17.6 mg/kg DM. The EDTA-extractable Pb\(^{2+}\) usually represents only about one tenth of the total content. Only three of the total eight sampling sites (Velká niva, the hill Chlustov east and Radvanovické saddle - pine grove) exceed the limit 30 mg/kg DM of lead.

ACKNOWLEDGEMENT
The authors would like to thank the IGA IP 3/2015 FA MENDELU project for financial support.

REFERENCES