THE INFLUENCE OF DIFFERENT SOIL CONDITIONS TO THE LEAD BIOAVAILABILITY TO PLANTS

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ABSTRACT

This work is aimed to present the forms of lead in soil taking in the account its' acid and basic conditions. Different forms of heavy metals in soil could have a negative impact on plants and human beings, particularly if they present in higher concentrations than maximum allowed. Various soil conditions cause the different bioavailability of some forms of heavy metals to plants. This paper considers the bioavailability of lead to some plants in acid and basic soil conditions using computer software and comparing results to those obtained by experiment in the laboratory. Obtained results in this work could be used to predict the behavior of heavy metals in different soil conditions, particularly those that are present in very small concentrations, such as lead, cadmium, etc.
Key words: heavy metals, soil, plants, lead

1. INTRODUCTION

The lead has the long-term period of half-life, from 740 to 5900 years. Research performed in Europe, showed three sources of lead in the soil. The first layer of soil contented the lead form seventieths, when the lead gasoline was used. The second layer contented the lead from the period industrial of industrial revolution, from 19th century and the presence of lead in the third layer originated from Roma period, when the lead processing started. Detection of lead after many years showed, it is really dangerous pollutant. The research of other many scientists performed until today, has showed, the soil close to roads, industrial areas is very polluted[6]. Reactions acting on phase soil solution and solid are presumably determined and constrained by soil properties: soil texture, content of organic, matter, content and type of clay minerals and Al, Fe and Mn oxides; and prevailing physicochemical conditions in the soil: soil saturation, soil aeration, pH, and redox potential.

Plants accumulate the lead in non-soluble forms with organic matter, via root, from soil solution, but also from air via leaves. Big concentration s of lead in soil has less influence on its content in edible parts of plants, with exception of roots[5]. A key factor in the solubility of lead is the pH of the soil. The soil acidity is used as indicator of lead intake by plants, but usual level of acidity for agricultural soils, show that there is not significant influence on lead intake by plants[2].

Lead is molecularly sticky in that is forms Pb complexes with organic matter, sorbs on clay and oxide particles, and precipitates as carbonates, hydroxides, and phosphates Since lead bonds strongly with soil minerals and organic matter, it is difficult for plants to extract it from the soil and into its roots. Once lead is absorbed by the plant, it complexes with plants nutrients limiting its ability to be translocated to the harvestable shoots. Soil pH is a significant parameter in the uptake of metal contaminants. This is a result of the fact that the soil pH value is one of the principal soil factors controlling metal availability[3]. By maintaining a moderately acidic pH in the soil through the use of

ammonium containing fertilizer or soil acidifiers, lead metal bioavailability and plant uptake has been shown to increase. At lower pHs the lead in soil has a greater potential to translocate from a plants roots into its shoots. However, it is essential to keep in mind that the ideal pH range for the growth of most plants and grasses is from 5.0-8.0. Thus, a pH around 5.0 seems to an optimum pH level, since lower values may inhibit plant growth. Increasing Pb solubility increases the chance for it to enter the groundwater. In addition, the increased bioavailability to plants also makes it easier for Pb to enter the food chain by being ingested by animals eating the plants. Organic matter in soil which consist humic and fulvic acids also influence on Pb availability. In order to define influence of organic matter in soil, synthetic chelats, such as EDTA (ethylenediaminetetraacetic acid) are used. Synthetic chelates, such as EDTA (ethylenediaminetetraacetic acid), have been shown to aid in the accumulation of Pb2+ in the plant tissue. EDTA and other chelates have been used in soils and nutrient solutions to increase the solubility of metal cations and the translocation of Pb into shoots. Despite an overall increase of Pb in the shoots, there are differences, however, in the extent of accumulation at equivalent chelate levels among various plant species[4]

Other key factors on which lead bioavailability are dependent are the presence of phosphate, oxide, silicate etc. Research performed on 38 soil samples and 5 mine-waste samples from Butte, Montana, demonstrated that the samples contain predominantly sulphide/sulphate and oxide/phosphates of lead (Pb)-bearing phases associated with mine waste. The oxide/phosphate assemblage consists of pH-neutral soils in which a plausible paragenetic sequence of PbO to Pb phosphates, PbMnO, or PbFeO is proposed, dependent on the activity of P, Mn, Fe, and Cl in the soil. The low solubility of the Pb-bearing minerals resulting from encapsulation in non-Pb-bearing reaction rinds may provide an explanation for the limited Pb bioavailability observed when Butte soils were fed to rats. Further evidence of the lack of absorption of lead from these soils is provided by the results of a blood-Pb study indicating very low blood-Pb levels in Butte children. The lower bioavailability of Pb from mining sites, compared to smelting and urban environments, is also due to kinetic limitations that control dissolution rates of Pb-bearing solids relative to the residence time of soil in the gastrointestinal (Gl) tract. When the test soil was fed to New Zealand White rabbits, only 9% of the total Pb was solubilised in the stomach, and therefore available for absorption. An *in vitro* assay, developed to estimate maximum available Pb from soil, demonstrates that ingestion of mine-waste-bearing soil results in limited Pb dissolution, and produces results similar to the *in vivo* testing.[1]

2. MATERIALS AND METHODS

Preparation of samples, including soil and fresh vegetables was performed by conventional methods of digestion; dry burning and wet mineralization.

Lead was determined by simultaneous and individual analyses.

Standard solutions for heavy metals determinations used in experiment are suprapure chemicals produced by Merck.

Analyses of lead were performed in various supporting electrolytes, including, KNO_3, KCl with the following instrumental parameters:

- Working Electrode (WRK): HMDE; Referent Electrode (REF): Ag/AgCl (1 M KCl), E = 0.22 V, Potentials:

Metal	Initial	Final
Lead	-0.65 V; -0,6 V	-0.4 V; 0,3 V

- Deposition Time 300 s in samples, Speed of Scanning 2 mV/s, Deaeration Time 120 s
- Amplitude 0.05 V

Equipment:
- Electrochemical Cell, Princeton Applied Research (EG & G) model 303A with Working (HMDE), Referent (Ag/AgCl) and Supporting (Pt-wire) Electrode, Potenciostat/Galvanostat, PAR, model 263 A, Computer P II with software Model 270/250 Research Electrochemistry Software, version 4.3.

3. RESULTS AND DISCUSSION

In order to use the soil for the laboratory observation of heavy metals intake, some analyses are performed such as organic matter, alumosilica, ox-redox potential, conductivity, capacity of cation exchange, capacity of anion exchange,

Results of mentioned analyses: - Capacity of cation exchange, 25,7 cmol/kg, - Capacity of anion exchange, 1,62 cmol/kg, - Conductivity, 1120 µS/cm, - Soil texture, 50 % sand, 27 % clay i 23 % dust, - Soil pH 7,45

In the following tables, results of some analyses are given:

Table 1.Results of determination of oxides in soil

Ingredient	Percentage (%)
SiO_2	67,59
Fe_2O_3	5,43
Al_2O_3	14,97
CaO	1,04
MgO	1,77
SO_3	0,56
Lost by drying	8,40

Table 2. The content of exchangeable ions in soil

Ingredient	Concentration (mmol/l)
Al^{3+}	0,68
Ca^{2+}	0,013
Cl^-	1,6
CO_3^{2-}	0,385
Fe^{3+}	0,152
K^+	0,00225
Mg^{2+}	0,011
Na^+	0,003
NH_4^+	0,00631
NO_3^-	0,0231
PO_4^{3-}	0,0014
SO_4^{2-}	0,01521

The total content of organic matter was 7,9 %. In this content, the presence of fulvic and humic acid was 39,3 % and 60,7 %, respectivly. The total content of lead in soil for laboratory observation was 7,764 mg/kg dry matter or $1,507 \cdot 10^{-7}$ mol/l. For laboratory purposes, the soil of the same charactersitcs is used, but observation of lead intake by plants was performed with its' normal and ten times higher soil content. Experiments were performed for acid and alaklo soil conditions. Natural, basic pH was 7,5, and it was adjusted by $Al_2(SO_4)_3$ p.a acid conditions, 5,8 to 6,2. Software for prediction of lead forms in which it is avalibale to plants need concentrations in mol/l or mmol/l. Model NICA-Donnan describes the bonding of cations to organic anions, and it is involved in Software WinhumicV. In the next tables fraction distribution of lead has been given in its natural and increased content in the soil, in acid and alakali conditions.

Table 3.Fraction distribution of natural (%) lead in soil

pH	Solution	Clay	Humic acid	Fulvic acid	Rest
6	2,852	1,328	88,287	7,333	0,2
7,5	3,354	0,025	92,109	4,500	0,012

Table 4.Fraction distribution of lead in soil with higher concentration (%)

pH	Solution	Clay	Humic acid	Fulvic acid	Rest
6	3,297	1,258	89,175	6,087	0,182
7,5	13,703	0,077	77,452	8,729	0,039

The following tables give complex forms of lead in acid and alkali soil conditions in its' natural and increased content.
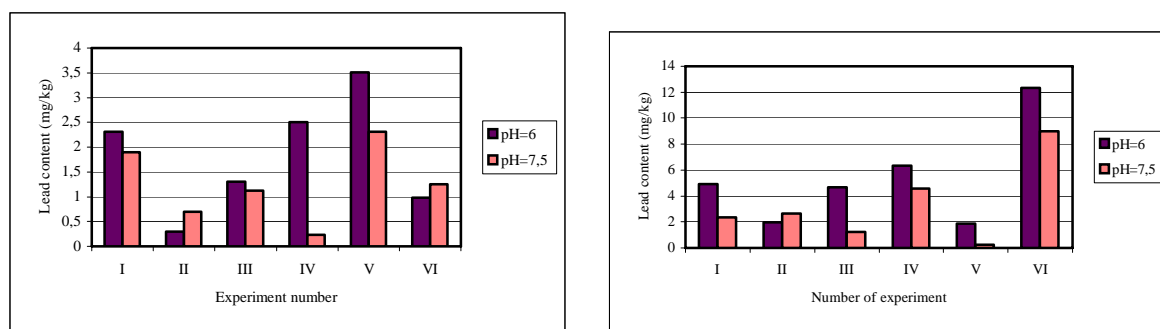
Table 5.Ionic forms and complexes of lead in solution with its natural content

pH =6		pH=7,5	
Complex	Conc. (M)	Complex	Conc. (M)
$Pb(CO_3)_2^{-2}$	$6,17 \cdot 10^{-11}$	$Pb(CO_3)_2^{-2}$	$3,15 \cdot 10^{-9}$
$Pb(OH)_2$	$5,43 \cdot 10^{-17}$	$Pb(OH)_2$	$3,08 \cdot 10^{-16}$
$Pb(OH)_3^-$	$2,44 \cdot 10^{-22}$	$Pb(OH)_3^-$	$4,81 \cdot 10^{-20}$
Pb^{+2}	$1,85 \cdot 10^{-10}$	Pb^{+2}	$1,34 \cdot 10^{-12}$
$PbCl^+$	$3,34 \cdot 10^{-12}$	$PbCl^+$	$1,88 \cdot 10^{-14}$
$PbCl_2$	$7,72 \cdot 10^{-15}$	$PbCl_2$	$3,56 \cdot 10^{-17}$
$PbCO_3$	$4,06 \cdot 10^{-9}$	$PbCO_3$	$1,93 \cdot 10^{-9}$
$PbOH^+$	$6,02 \cdot 10^{-13}$	$PbOH^+$	$1,19 \cdot 10^{-13}$
$PbSO_4$	$2,77 \cdot 10^{-11}$	$PbSO_4$	$1,27 \cdot 10^{-13}$

Table 6. Ionic forms and complexes of lead in solution with its increased content

pH =6		pH=7,5	
Complex	Conc. (M)	Complex	Conc. (M)
$Pb(CO3)_2^{-2}$	$7,13 \cdot 10^{-10}$	$Pb(CO_3)_2^{-2}$	$1,29 \cdot 10^{-17}$
$Pb(OH)_2$	$6,3 \cdot 10^{-16}$	$Pb(OH)_2$	$1,26 \cdot 10^{-14}$
$Pb(OH)_3^-$	$2,83 \cdot 10^{-21}$	$Pb(OH)_3^-$	$1,98 \cdot 10^{-18}$
Pb^{+2}	$2,15 \cdot 10^{-9}$	Pb^2	$5,48 \cdot 10^{-11}$
$PbCl^+$	$3,87 \cdot 10^{-11}$	$PbCl^+$	$7,73 \cdot 10^{-13}$
$PbCl_2$	$8,92 \cdot 10^{-14}$	$PbCl_2$	$1,46 \cdot 10^{-15}$
$PbCO_3$	$4,7 \cdot 10^{-8}$	$PbCO_3$	$7,91 \cdot 10^{-8}$
$PbOH^+$	$6,99 \cdot 10^{-12}$	$PbOH^+$	$4,88 \cdot 10^{-12}$
$PbSO_4$	$3,17 \cdot 10^{-10}$	$PbSO_4$	$5,19 \cdot 10^{-12}$

The most present lead complex with its' increased content in soil, slightly acid conditions, pH=6, is $PbCO_3$, $4,06 \cdot 10^{-9}$ M. However, in slightly alkali conditions pH = 7,5, the most present ionic form of lead is $Pb(CO_3)_2^{-2}$, $3,15 \cdot 10^{-9}$ M. Ionic lead form is the second present with its natural content, pH = 6, the concentration was $1,85 \cdot 10^{-10}$ M and $1,34 \cdot 10^{-12}$ M, with pH =7,5, respectively. Free ionic lead is the second present in solution with its increased content in slightly acid conditions, $2,15 \cdot 10^{-9}$ M, and the third in slightly alkali conditions $5,48 \cdot 10^{-11}$ M. The most present lead form with pH = 6 and its' increased content is $PbCO_3$, where concentration was $4,7 \cdot 10^{-8}$ M, but with pH = 7,5, it was $Pb(CO_3)_2^{-2}$, $1,29 \cdot 10^{-7}$ M. Next figures show the lead content in carrot samples grown in different soil conditions.

a) natural content   b) increased content
Figure 1. The lead content in six carrot samples grown in different soil conditions

In the Figure 1, the content of lead in carrot is shown, in slightly acid and alkali conditions. An average lead content in carrot was below 3,5 mg/kg dry matter, with exception of sample from experiment V, slightly conditions, where concentration was 3,504 mg/kg dry matter. The lowest value of lead in carrot was in carrot sample from experiment IV, where concentration was 0,234 mg/kg dry matter. An average content of lead with its' increased level in soil was the highest in sample from experiment VI, slightly acid conditions, but the lowest in V, slightly alkali conditions. The content of lead was 12,3451 mg/kg dry matter, and 0,2367 mg/kg dry matter, sample VI and V, respectively.

4. CONCLUSIONS

1. Commercial software, by the determination of the presence of lead in soil and soil characteristics, could be used for prediction of lead bioavailability;
2. Lead is bond in different forms in soil, and soil conditions must be changed for its bioavailability;
3. Most present lead form within pH range, from 5 to 8, is carbonate;
4. Generally lead was more available to plants when the content in soil was increased.

5. REFERENCES

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