

## IMMOBILIZATION OF HEAVY METALS AND ARSENIC IN TOPSOIL DUE TO APPLICATION OF DIFFERENT REMEDIATION METHODS

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**ABSTRACT.** The article presents some results about the immobilization of heavy metals (lead, copper, zinc) and arsenic in the topsoil of grey forest soil due to application of several remediation methods. These methods were as follow: neutralization of soil pH to neutral point by means of carbonate addition; neutralization of soil pH by means of cow manure addition; immobilization of the soil pollutants by means of apatite addition, and partial neutralization of soil pH followed by the apatite addition. The study was realized by means of laboratory-scale zero suction type lysimeters. The efficiency of each variant was assessed on the base of the changes in the concentration of the soil pollutants, their distribution amongst the main mobility fractions and bioavailability to soil organisms, before and after treatment.

Keywords: heavy metals, uranium, immobilization, soil

### ИМОБИЛИЗИРАНЕ НА ТЕЖКИ МЕТАЛИ И АРСЕН В ПОВЪРХНОСТЕН ПОЧВЕН СЛОЙ ВСЛЕДСТВИЕ ПРИЛАГАНЕТО НА РАЗЛИЧНИ МЕТОДИ ЗА ПРЕЧИСТВАНЕ

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**РЕЗЮМЕ.** Статията представя някои резултати относно имобилизирането на тежки метали (олово, мед, цинк) и арсен в повърхностния почвен слой на сива горска почва вследствие прилагането на различни методи за пречистване. Тези методи са както следва: неутрализиране на почвената киселинност до рН 7.0 посредством внасяне на варовик; неутрализиране на почвената киселинност посредством внасяне на кравешка тор; имобилизиране на почвените замърсители посредством внасяне на апатит, и частична неутрализация на почвената киселинност, последвано от добавянето на апатит. Това изследване беше проведено в лабораторни лизиметри без поддържане на понижено налягане по време на опробването. Ефективността на всеки метод беше оценена на базата на промени в концентрацията на почвените замърсители, тяхното разпределение по основни мобилни фракции и биоусвояемостта им към почвените организми преди и след третиране.

### Introduction

The soil pollution with heavy metals is a concomitant negative effect of the activity of several main industrial sectors – mining, smelting, chemical industry, and transport. As a result, the concentration of heavy metals in topsoil is higher than the acceptable permissible levels for the relevant soil types in around 200 000 decares in Bulgaria, and about of 5 % of EU land, respectively (The implementation of the Soil Thematic Strategy and ongoing activities, 2012).

The remediation of soil contaminated with heavy metals is a research task studied very intensively in the last years. There are several approaches for soil decontamination and *in situ* methods are the most promising not only because of the satisfying results but also of their low capital and investment costs. *In situ* methods could be divided into two groups having in mind the fate of the pollutants during the soil treatment. The first group of methods is based on the pollutants leaching from the upper soil horizons towards the deeply lying clay horizons. The efficient soil remediation in this case is a result of precisely manipulation of the indigenous soil microflora activity and formation of stable dissolved complexes between heavy metals and organic and some inorganic ligands (Georgiev and Groudev, 2010). The indigenous soil microflora

takes an active role in the processes of heavy metals solubilization by means of the processes of protonation, redoxolysis as well as complexolysis. The mobility of the presented complexes through the soil profile is strongly depended on their net surface charges which have a defining effect on their sorption on the soil constituents' surfaces.

The second group of methods is based on the processes of accumulation and immobilization of the heavy metals in the soil horizon due to specific sorption of heavy metals ions on the surface of some sorbents (Georgiev and Groudev, 2009). As a result of this, the contaminants are blocked steadily and permanently in the topsoil which determined their extremely low rate of leaching, lower bioavailability and exposition of the soil organisms.

### Materials and methods

The soil samples were taken from the main horizons of the grey forest soil which for decades have been flooded periodically by waters polluted by acid mine drainage. The samples were dried initially to air-dry weight and ground in a clean, dust-free room. The total content of heavy metals and arsenic before and after the soil remediation was determined

by preliminary alkaline melting followed by AAS and ICP analysis. The mobility of pollutants was determined by well-known sequential extraction method (Tessier et al., 1978). The acid-base soil properties were determined by standard methods (Page et al., 1982; Sobek et al., 1978). The type and concentrations of exchangeable cations was used to determine the liming requirement of the studied topsoil (Soil pH and Plant Analysis Council, 2000). The bioavailability of the heavy metals and arsenic in soil was determined by DTPA and EDTA leaching tests (Lindsay and Norvell, 1978). These results were used to calculate the orthophosphates requirement for effectively heavy metals immobilization into the soil horizon (Ma and Rao, 1997).

The liming experiments of the acidic topsoil were carried out with air-drought natural carbonate with size particles between 0.8-0.5 mm and carbonate content of 58.4 % (expressed as  $\text{CO}_3^{2-}$ ). The air-drought cow manure was characterized with (in %) 3.06 CaO, 1.14  $\text{P}_2\text{O}_5$  and 1.8 total N, respectively. The content of  $\text{P}_2\text{O}_5$  in apatite was 14.1 %.

The experiments for heavy metals into topsoil were carried out in PVC laboratory lysimeters. Each of them was filled with 2.5 kg of topsoil. A permeable layer consisting of gravel and sand was formed below the soil sample in each lysimeter. By this way, the soil solutions moving downwards through the soil macro-pores due to gravity force, drained effectively into a collecting vessel. The following variants were studied: variant 1 – sample from topsoil irrigated once a week with tap water; variant 2 – as variant 1 plus carbonate addition for soil pH neutralization from acidic to neutral point; variant 3 – as variant 1 plus cow manure addition for acidic soil pH neutralisation; variant 4 – as variant 1 plus apatite addition; variant 5 – as variant 1 plus carbonate addition for partial acidic soil pH neutralisation followed by apatite addition. The applied irrigation rate for all variants during the experiment was 200 l / t soil / week.

The quality of the gravity-moving-soil-solutions in all variants was measured regularly. The water samples were characterized by means of pH, Eh, acidity/ alkalinity. The heavy metals concentration was determined by means of AAS and ICP, respectively (APHA, 1995; Lurie, 1973).

## Results and discussion

The soil sample was taken nearby to Curilo mine where *in situ* leaching of uranium have been applied for decades. The generation of Acid Mine Drainage (AMD) is still going in spite of the fact that the production activity was ceased in 1992. AMD is a product of the activity of the indigenous chemolithotrophic bacteria, which had been accelerated due to the fragmentation of ore body with aim to intensify the *in situ* leaching process. For that reason, the main source of soil pollution in the area was infiltration of waters with low pH and higher concentration of iron, heavy metals and uranium through the soil profile. Due to the higher solubility of the non-ferrous metals in acidic pH and their ability to exist as free ions as well as stable complexes with sulphates, these elements were leached from the soil. As a result, the concentration of copper, zinc, and nickel in the upper soil horizon was below the relevant maximum permissible levels (Table 1). Regardless of

this fact, the higher portion of the pollutants were presented as easily mobile forms (such as non-specifically sorbed ions as well as some voluminous precipitates) due to very low soil pH (Table 2). In addition to the soil characteristic, the concentrations of lead and arsenic due to their specific geochemical properties were higher than the relevant permissible levels for soil with similar properties.

Table 1.

*Data about the chemical content of a sample from grey forest soil polluted by acid mine drainage*

Index	Depth, cm		Permissible concentration for soil with pH < 6.0
	0 – 15	16 – 40	
$\text{SiO}_2$ , %	63.4	62.5	-
$\text{Al}_2\text{O}_3$ , %	18.7	22.4	-
CaO, %	0.6	0.08	-
MgO, %	0.17	0.05	-
$\text{Fe}_2\text{O}_3$ , %	12.0	11.0	-
Humus, %	1.63	0.61	-
Pb, mg/kg	102	28	90
Zn, mg/kg	84	49	220
Cu, mg/kg	68	44	80
Ni, mg/kg	23	12	70
As, mg/kg	43	21	30

Table 2.

*Data about the acid-base properties of a sample from grey forest soil polluted by acid mine drainage*

Index	Depth, cm	
	0 – 15	16 – 40
$\text{CO}_3$ , %	0,72	-
S as sulfide, g/t	90,1	28,2
Acid generating potential, kg $\text{CaCO}_3$ / t	281,6	88,1
Neutralization potential, kg $\text{CaCO}_3$ / t	5,7	-2,2
Net neutralization potential, kg $\text{CaCO}_3$ / t	- 275,9	-90,4
pH ( $\text{H}_2\text{O}$ )	3,95	3,80
pH (KCl)	3,55	3,41

The acid-base properties of the studied soil were characterized with very acidic soil pH, measured for both main upper soil horizons – 0-15 and 16-40 cm, respectively (Table 2). It was determined by the very low carbonates content as well as the presence of diluted sulfuric acid in soil solutions. As a result of this, the net neutralization potential of the upper two soil horizons were markedly negative.

Remediation of the polluted soil was studied by means of different research approaches. By means of variant 1 the decrease of the pollutants concentration due to infiltration of tap water through the topsoil was studied. The main remediation mechanism in that case was the exchangeable reaction between base cations (calcium and magnesium) from soil solution with hydrogen ions and cations of non-ferrous metals sorbed on the soil surface. However, the concentration of suitable ligands (chlorides, nitrates, organic monomers) in soil as well as in the irrigating solutions was negligible which didn't allowed dissolution and migration of lead, for example. So, if such ligands would be introduced into the topsoil the

higher part of the heavy metals would be dissolved and leached out of the topsoil – 5.4 mg/kg and 20.9 mg/kg for lead and copper, respectively (Table 4). In addition to this, a number of soil parameters as soil pH, activity of soil microflora, etc., weren't changed dramatically which revealed the restricted capacity of this mechanism (Table 4).

By means of variants 2 and 3 the effect of soil liming on soil pH and the mobility of heavy metals was studied. In variant 2 these processes were achieved by means of carbonates addition into the topsoil which initiated the reaction of chemical neutralization between carbonates and hydrogen ions from soil solution. As a result of this, soil pH was steadily increased and the soil solution was enriched with calcium ions. The ferric iron and the cations of non-ferrous metals were displaced by the calcium ions from the soil's surface which led to ferric hydroxides formation as well as precipitation and co-precipitation of the heavy metals as hydroxides and sulfates. So, at the end of soil treatment soil pH was increased to 6.86 (Table 3) and the heavy metals mobility was restricted significantly (Table 4). So, the concentration of the heavy metals dissolved in the pregnant soil solutions was decreased between two times (for lead and zinc) to more than fifty times (for copper), respectively (Table 4). The main shortcoming of this approach was that the newly-formed-heavy metals minerals were leached easily if the soil pH dropped back below 4.5.

In variant 3 the neutralization of soil pH was a result of whole range of chemical and biological reactions which led to slightly acidic soil pH (5.12) and lower mobility of the heavy metals at the end of experiment. The rate of acidic soil pH neutralization was lower in comparison to the rate measured in variant 2 because of negative effect of strongly acidic pH on the microbial processes connected directly with H<sup>+</sup> ions consumption – such as ammonification, bacterial reduction of ferric iron hydroxides, and microbial oxidation of organic acids (Marschner and Noble, 2000). For example, the dividing line of 5.00 for soil pH was reached at the 2<sup>nd</sup> month after the start of experiment for variant 2. In comparison, more than 8.0 months were needed to reach the same pH for soil in variant 3. Regardless of the lower rate of neutralization, manure is widely used as a main or supporting liming agent lately due to its complex chemical and mineral content and the positive effect that it have on other main soil parameters such as the content of bioavailable forms of nitrogen and phosphorous, number and activity of soil microflora, etc., (Brookes, 1995; Kolesnikov et al., 2000).

The heavy metals mobility in soil was decreased quicker in variant 3 in comparison to variant 2. The reason was the higher content of phosphorous in the manure which was presented as inorganic compounds mainly. Due to the acidic pH, these compounds were protonated and dissolved in a chemical way which determined a peak in orthophosphate concentration in the soil solutions (up to 12 mg/l) very soon after the experiment's beginning. Orthophosphates reacted with heavy metals cations which led to their precipitation as phosphates. At later stage of experiment, the orthophosphates dropped to 5.5 – 7.0 mg/l due to the exhaustion of inorganic fraction and its replacement by means of enzymatic hydrolysis of phosphorous-containing organic compounds as a source of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup>, respectively. By this way, the

concentration of heavy metals in soil solution was maintained below the relevant permissible levels till the end of experiment. As a result, all soil pollutants with the exception of arsenic were immobilized in the topsoil of the studied soil.

Table 3.  
Data about the content of heavy metals in the topsoil at the end of the relevant experiments

Index	After treatment				
	Variant 1	Variant 2	Variant 3	Variant 4	Variant 5
Content of heavy metals, mg/kg					
Pb	100	97	90	100	98
Cu	56	66	62	66	66
Zn	75	81	77	78	80
As	38	40	31	28	40
pH (H <sub>2</sub> O)					
	4.12	6.86	5.12	4.35	6.62

Table 4.  
Data about the bioavailability of heavy metals in the topsoil at the end of the relevant experiments

Index	After treatment				
	Variant 1	Variant 2	Variant 3	Variant 4	Variant 5
Bioavailability of Pb					
1	5.4	3.8	3.1	1.1	1.3
2	0.08	0.04	0.06	< 0.03	< 0.03
Bioavailability of Cu					
1	20.9	17.1	19.5	7.3	7.6
2	1.12	0.02	0.006	< 0.004	< 0.004
Bioavailability of Zn					
1	24.6	13.3	16.8	11.5	12.2
2	0.65	0.2	0.33	0.14	0.2
Bioavailability of As					
1	12.9	5.7	11.2	10.6	5.9
2	0.07	< 0.01	0.10	0.18	< 0.01

1 – bioavailability measured by EDTA leaching, mg/kg;  
2 – concentration in the pregnant soil solution at the end of experiment, mg/l

By means of variant 4 the effect of apatite addition on the heavy metals mobility in soil was studied. Apatite and its secondary products are studied widely to assess their capacity to immobilize heavy metals as well as radionuclides in environment. The core reactions of this remediation strategy are protonation of apatite crystal lattice, followed by liberation of orthophosphates as well as an exchange reaction between calcium ion from mineral structure and ion of heavy metal with similar radius from pore solution. This method is suitable for soils with acidic pH due to the fact that hydrogen ions are needed to trigger off the initial reactions. The final product of both processes is formation of the relevant phosphate minerals of the heavy metals presented as an ion in the environment before that. So, at the end of soil treatment experiment, lead concentration in topsoil wasn't change practically (Table 3) and the mobility of almost all presented in the topsoil heavy metals was decreased significantly (Table 4). For example, the bioavailability of lead and copper compared with the results from variant 1 were decreased with 79.6 and 65.1 %, respectively. It was determined by pyrrmorphite (Pb<sub>10</sub>(PO)<sub>4</sub>(OH)<sub>2</sub>) formation which is the mineral of lead with one of the lowest solubility amongst the minerals of this

elements. In similar way, copper was immobilized due to copper phosphate  $\text{Cu}_3(\text{PO}_4)_2$  formation. In comparison to lead, arsenic was presented as oxyanions in soil solutions which determined completely different behavior in comparison to the behavior of the other heavy metals cations. At acidic soil pH, the most soil surface was positively charged due to the adsorption of cations (mainly  $\text{H}^+$ ) from soil solution. This surface positive charge was neutralized partially by means of an outer layer formation with net negative charge due to the presence of anions in it. By this way, the oxyanions of arsenic ( $\text{HASO}_4^{2-}$ ,  $\text{H}_2\text{AsO}_4^-$ ) were concentrated in this outer layer situated near to the surface of the soil particles. Any changes in the content of soil solutions had an immediate effect on the content of this outer layer. For that reason, the higher concentration of orthophosphates into the soil solutions due to the apatite as well as manure (as in variant 3) addition, led to the strong competition and exchange reactions with arsenic oxyanions from an outer layer. It determined higher arsenic concentration in soil solution and its higher leaching potential from the topsoil in comparison to variant 1. So, at the end of experiment arsenic concentration in topsoil was decreased significantly – with 27.9 % and 34.8 % for variants 3 and 4, respectively (Table 4). As a result of this, the bioavailability of pollutant was also decreased – with 13.2 and 17.8 % for variants 3 and 4, respectively.

By means of variant 5 a combination of soil liming and apatite addition to the topsoil was studied as an experimental approach for remediation of soil polluted with heavy metals having completely different geochemical properties. The method was realized in two stages. In the first stage a liming agent was added (in that case – calcium carbonate) and soil pH was changed from strongly to slightly acidic (5.5 - 5.8) within next 3.5 – 4 months. It was connected with iron hydroxides precipitation due to the ferric iron ions hydrolysis. The mineral surface of the newly formed voluminous hydroxides was characterized with net positive charge which was compensated by means of anions attraction, including arsenic ones, from soil solutions and their specific adsorption on it as a final step. As a result, arsenic was steadily entrapped and finally capsulated in the ferric hydroxides lattice due to the deposition of a new layer of iron hydroxides (Belzile and Tessier, 1990). As a result, arsenic leaching potential from topsoil was reduced greatly due to the liming of the polluted soil. For example, the arsenic concentration in the pregnant soil solution was decreased below 0.01 mg/l (Table 4).

The second stage of soil remediation was realized by means of apatite addition. The hydrolysis and precipitation of ferric iron and aluminum ions, which had been triggered off by soil liming, produced enough amounts of hydrogen ions in soil solutions. These ions were able to initiate the process of apatite degradation and the heavy metals immobilization in topsoil (Chen et al., 1997). The higher concentration of orthophosphates into the soil solution enhanced the hydroxides of the heavy metals, already formed as secondary products at liming stage, to be transformed to significantly more stable and resistant phosphate minerals. So, within 5.5 – 6.0 months since the apatite addition the heavy metals mobility in topsoil has been reduced dramatically (Table 4). For example, the bioavailability of lead, copper, and zinc determined at the end of experiment was similar to that measured in the variant with apatite addition.

The best remedial option for soils polluted with heavy metals, relying on immobilization of the pollutants into the topsoil, was liming and apatite addition, realized in two consecutive stages. As a result of this, soil pH was increased almost to the neutral point and pollutants (lead and arsenic) were steadily immobilized in topsoil. The period needed for the method realization was almost a year.

## Conclusions

1. Apatite and its secondary products have excellent sorption properties allowing heavy metals such as lead and copper to be immobilized effectively into the topsoil, at slightly acidic soil pH and aerobic conditions. The end products of the process are characterized with very low solubility and bioavailability to the soil organisms;
2. Soil liming is the best approach for neutralization of soil acidity. As a result, heavy metals and ferric iron ions precipitate which led to formation of some hydroxides with prevalent net positive surface charge. Arsenic oxyanions from soil solution take part in electrical neutralization of this charge as a result of their specific adsorption followed by the pollutant's capsulation into the ferric hydroxides. As a result of this mechanism, mobility and bioavailability of arsenic to soil organism was reduced significantly.
3. The combination of soil liming and apatite addition organized as two consecutive stages is a suitable approach for remediation of soils polluted with heavy metals having completely different geochemical properties.

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