**Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy**

Volume 13 Article 20

January 2010

# Effect Of Phosphorous, Organic And Sapropel Amendments On Lead, Zinc And Cadmium Uptake By Triticale From Industrially Polluted Soils

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# Chapter 19

# EFFECT OF PHOSPHOROUS, ORGANIC AND SAPROPEL AMENDMENTS ON LEAD, ZINC AND CADMIUM UPTAKE BY TRITICALE FROM INDUSTRIALLY POLLUTED SOILS

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## ABSTRACT

A comparative study has been carried out on the effect of some soil amendments (phosphorus compounds, organic fertilizers and sapropel) on the quantity of the phytoaccessible forms of Pb, Zn and Cd and the accumulation of these elements by the Triticale. The effect of the used soil amendments on the mobile forms of the Pb, Zn and Cd is specific without clearly expressed tendencies. Only with the natural fertilizer there is a clear tendency for their reduction in all of the three studied elements. No direct relation between the quantity of the mobile forms and the absorption of Pb, Zn and Cd by the Triticale was established.

The superphosphate and $KH_2PO_4$ are effective phytostabilizing amendments for soils contaminated with lead. In combined contamination, however, adding superphosphate is not appropriate, as it increases the content of zinc and cadmium in the overground parts of the plants, while $KH_2PO_4$ can be used successfully.

Keywords: phytostabilization, heavy metals, soil amendments

## 1. INTRODUCTION

Chemical immobilization is a promising technique for decreasing the mobility of the contaminants in the ecosystems, in which chemical and mineralogical materials are added to the contaminated soils in order to decrease the solubility and phytoaccessibility of the metals, through absorption and/ or sedimentation.

The additives, used in phytostabilization, should quickly deactivate the metals; they have long-lasting effects, should not be expensive, and are easily added to the soil. Most often, for decreasing the phytoaccessibility of the metals, phosphorus and organic fertilizers such as ferrous and manganese hydroxides and natural or synthetic clay minerals are used. The

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mechanisms, through which the additives affect the polluters, differ depending on the [§]type of the additives and the degree and the nature of the pollution. The suggested mechanisms include sedimentation, complex formation, sorption and change in the degree of oxidation (Berti and Cunninggham, 1997; Hettiarachi et al., 2001; Yang et al., 2001; Hettiarachchi and Pierzynski, 2002; Geebelen et al., 2002; Cao et al., 2003; Seaman et al., 2003; Walker et al., 2003).

One of the most progressive directions in phytostabilization of toxic metals in the soils is the use of phosphorus fertilizers and phosphorus containing compounds, such as hydroxyapatit and phosphorus minerals (Chloplecka and Adriano, 1997; Boisson et al., 1999; Basta et al., 2001; Knox et al., 2001, 2003; Scheckel and Ryan, 2003). This method has gotten much more attention in recent years. The immobilization of lead with phosphorus containing compounds is a result of the formation of lead phosphate (pyromorphite), which is very stable even at low pH. The formation of pyromorphite significantly reduces the mobility of Pb in the soil (McGowen et al., 2001; Cao et al., 2003; Zhu et al., 2004), and, as a final result, its phytoaccessibility for the plants and the human digestion systems (Cheng and Hseu, 2002). Chemical immobilization with phosphorus compounds is preferable because of their relevantly low price and also because of the fact that adding phosphates in the soil is normal practice in the agriculture. Achieving a significant effect, however, requires the quantity of the additives to be much higher than the normal fertilization (5 g P/kg soil for deactivation of the lead, compared to 15-30 mg P/kg in most crops) (Hettiarachchi and Pierzynski, 2002). While the positive effect of the phosphorus additives on the reduction of the phytoaccessibility of the lead is indisputable, the evaluation of their complex effect on the absorption of the important nutrients for plants' microelements and the rest of the toxic metals requires further study.

There have been attempts for immobilization of heavy metals in the soil through the use of different organic additives (Berti and Cunninggham, 1997; Geebelen et al., 2002; Cao et al., 2003; Seaman et al., 2003, Jamode et al., 2003, Walker et al., 2003, 2004). It has been established that more of the organic materials, such as composites, fertilizers, and waste, can inactivate more toxic metals (lead, cadmium, copper, zinc, etc) as a result of sorption or complex formation. For some of the organic additives, it has been established that they reduce their solubility and obstruct their transition into the soil solution (Ciecko et al., 2001). The tests on soils polluted with lead, however, prove that its decreased solubility after the organic additives does not always lead to its decreased absorption by the plants.

The idea, for the use of Black-sea deepwater organogene-mineral sediments (DOMS) in agriculture and the environment is based on the experience of the use of lake and swamp sapropels in the agricultural practice (Dimitrov and Velev, 1988). They were formed 8000 ago as result of an ecological catastrophe cause by the inflow, through the Bosporus, of oceanic waters, which were mixed with the Black sea waters. Then occurred the mass development and dying of plankton organisms and the bottom of the sea were precipitated sediments with thickness of 1-3 m, know as DOMS. The source substances of DOMS is the dying flora and fauna of Black sea, which, as a result of the activity of anoxia bacteria, undergo the process of turning into animal and plant planktons and bentos and form biolite mineral substances with special physical-mechanic and biogeochemical characteristics.

It is known that adding sapropel in the soil leads to neutralization of the soil acidity, increases the moisture capacity of the soils and the content of microelements, and stimulates the growth of the plants by accelerating their maturity and increases the yields in some crops (Lopotko et al, 1992). Our preliminary study shows that DOMS stimulate the vegetation and the growth of the root system of the cereal crops – wheat, corn and barley, and lead to increase of the chlorophyll content and soluble protein in the leaves. It is also known that the sapropel has the ability to inactivate and restrict the entrance of heavy metals in the plants (Vashkov, 1996). Its quality evaluation as a heavy metals and radionuclides absorbent is at initial stage. There are no systematic and profound studies in this direction in science literature. Despite this, it is suggested (Maskalchuk and Klimava, 2003; Shnyukov and Ziborov, 2004; Maskalchuk and Pozilova, 2005) that DOMS could be successfully used as absorbents for recultivation of tailing dumps from uranium production and lead-zinc and copper mines.

Taking into consideration the positive effect of the sapropels on the growth of the plants, we believe that it is useful to clarify the issues, regarding their use as phytostabilizers of toxic elements in the soil.

The present study has the following three objectives: (i) to broaden and increase the knowledge of effect of the different soil additives (phosphorus compounds, organic fertilizers and sapropel) on the quantity of the phytoaccessible forms of Pb, Zn and Cd (ii) to compare the effect of the selected additives on the accumulation of heavy metals by the Triticale and (iii) to estimate the effect of the introduction of additives on the phytostabilization of contaminated with heavy metals soils.

## 2. MATERIALS AND METHODS

### 2.1 Soils

Soil used in this experiment was sampled from the vicinity of the area contaminated by the NFMW (Non-Ferrous-Metal Works) near Plovdiv, Bulgaria. The soil needed for the pot experiments was collected from the surface (0-20 cm depth) of fields located at 0.5 km from the NFMW. It characterizes by alkaline reaction, moderate calcium carbonate content, loamy texture and moderate content of organic matter (Table 1).

*Table 1.* Soil properties

| Classification | Depth, cm | pH, ($H_2O$) | Humus, % | $CaCO_3$, % | Clay, % |
|---|---|---|---|---|---|
| Calcaric Fluvisol | 0 - 20 | 7.72 | 2.19 | 7.30 | 29.35 |

The soil characteristics are favourable to low metal availability to plants, and DTPA-extractable Pb, Zn and Cd concentrations are low for Zn, and moderate for Pb and Cd. The total content of Pb, Zn and Cd is high and considerably exceeding the maximum permissible concentrations (Table 2).

*Table 2.* DTPA - extractable and total content of Pb, Zn and Cd in the soil.

| Element | DTPA extractable | Total content | DTPA - extractable/ total content, % | MPC* |
|---|---|---|---|---|
| Pb | 106.8 | 217.7 | 39.3 | 80 |
| Zn | 145.0 | 621.8 | 23.3 | 340 |
| Cd | 3.4 | 7.6 | 44.7 | 2,5 |

*MPC - maximum permissible concentration (approved for Bulgaria)

## 2.2 Soil amendments

Several amendments belonging to different categories were tested. The main reason for their selection was the requirement not to contaminate additionally the soil and to contribute for the soil fertility.

### 2.2.1 Phosphorus additives

$KH_2PO_4$ and superphosphate were chosen as phosphor soil amendments. The analysis of superphosphate showed that it does not contain lead, while the zinc and cadmium content reached 163.5 and 9.55 mg/kg, respectively. $KH_2PO_4$ did not contain detectebale Pb, Zn and Cd.

### 2.2.2 Organic additives

Rotten natural fertilizer and biomanure were chosen as organic soil amendments, obtained in the process of natural fertilizer and other organic waste by the Californian worm. In Table 3 are shown the agrochemical characteristics of the used organic fertilizers.

### 2.2.3 Sapropel

The deep-water organogen mineral slimes from the Black sea are at peat stage in their development. Because of the anaerobic environment in which they precipitate, they do not pass the stage of complete decomposition and in semi-decomposed state are preserved in suppurated hydrogen zone. Considering the fact that the cocolitophoryde, diatom, and sapropel slimes stratify each other and are a relatively homogeneous mixture, they could be treated as a complex organogen-mineral fertilizer, of which the sapropels represent 80 % of the general volume of the raw material.

*Table 3.* Agrochemical characteristics of the used organic fertilizers

| Fertilizer | pH ($H_2O$) | Organic content % | N % | $P_2O_5$ % | $K_2O$ % | CaO % | MgO % | Pb mg/kg | Zn mg/kg | Cd mg/kg |
|---|---|---|---|---|---|---|---|---|---|---|
| Natural fertilizer | 7.46 | 17.65 | 0.850 | 0.42 | 0.77 | 1.10 | 0.37 | 23.1 | 162.4 | 0.80 |
| Biomanure | 7.80 | 34.94 | 1.963 | 0.74 | 1.37 | 1.25 | 0.68 | 38.8 | 111.0 | 0.38 |

The organogen mineral slimes are valuable not only for their organic substance, but also for their carbon ingredient and the amorphous silicates. In their mineral part, which is homogeneous with the organic, there are nutrients macroelements such as calcium, magnesium, potassium, the microelements ferrous, chrome, manganese, etc. In the sediments, there are quartz, plagioclase and volcanic glass, opal and chalcedony (rare grains), marcasite, calcite and aragonite, there also particles of shell detrite.

For the experiments with Triticale were use samples from DOMS, taken from the bottom of the Black sea at a depth of 1500-1800 m. The sapropel, used by us, has the following chemical content: Organic content - 3%, $SiO_2$ – 3.15%, CaO – 14.5%, MgO - 2.73%, $Fe_2O_3$ - 4.57%, $Al_2O_3$ -11.5, $P_2O_5$ -1.32%, Cu - 0.03%, Cr - 0.0125%, Mn - 0.0365%, Zn - 0.0085%, Mo - 0.0175%, Co - 0.0155%, Ni - 0.0073.

## 2.3 Pot experiment

### 2.3.1 Experimental design

The pot experiment was conducted on investigated soils with phosphorus additives, organic additives, and sapropel at 5% addition rates (calculated on soil dry weight basis). Soils were passed through a 1-cm sieve. Amendments were added and thoroughly mixed by hand. The pots were filled with 9 kg soil. All treatments were performed in triplicates. Three control pots were also set up without amendment. Pots were watered and stored in a greenhouse, where they were left to settle a minimum of 6 weeks at room temperature before planting the Triticale.

### 2.3.2 Plants

Triticale was chosen as a test-plant for greenhouse pot experiment. Ten seeds of Triticale were sown in pots and, after germination, thinned to three plants per pot. The plants were harvested 78 days after germination separated into aboveground parts (stems, leaves and seeds) and roots. The latter were washed free of all adhering soil in distilled water.

## 2.4 Sample preparation and analysis

Soils: (i) *Total content* of heavy metals in soils was determined in accordance with ISO 11466. The soil sample was decomposed on a sand bath heater for 3 h with 21 ml of concentrated HCI + 7 ml of concentrated $HNO_3$. After cooling the sample, the residue was transferred into a 50-ml flask, and water was added to the mark. (ii) *The mobile heavy metals* contents have been determined in 0.005 M diethylentriaminepentaacetic acid (DTPA) and 0.1 M triethanolamine (TEA) buffered at pH 7.3 (ISO 14870). Soil samples were shaken for 2 hours at 20$^o$C. After shaking, the soil- solution system was centrifuged and filtered. The ratio soil to liquid was 1:2 by weight to volume.

Plants: The samples were treated by the method of dry ashing. A 1 g sample was weighed into a quartz crucible and put into a furnace (400$^o$C) until ashing occurred. After cooling to a room temperature 1 ml $HNO_3$ (1:1) was added, evaporated in a sand bath and put again into the furnace (400$^o$C). The procedures were repeated until the ash was white. It was finally dissolved in 2 ml 20 % HCl (v/v), transferred in a graduated 25 ml flask and brought to volume with doubly distilled water.

Soil amendments: Total heavy metal analysis was performed on finely ground samples of soil amendments (phosphorus additives, organic additives and sapropel) by using the same procedure, described for the soil samples.

Equipment: To determine the heavy metal content in the samples, inductively coupled emission spectrometer (Jobin Yvon Horiba "ULTIMA 2", France) was used. The working wave lengths were as follows: Zn - 213.9 nm; Pb - 220.4 nm; Cd - 214.4 nm. Detection limit for Pb was 1.5 µg/l, for Cd - 0.09 µg /l, for Zn - 0.15 µg /l. A commercial multielement standard solution (Merck) with concentration 100 mg/L was used as a stock solution. The calibration standard solutions have the following concentrations: 0; 0.2; 0.5; 2.0 and 5.0 mg/L. The acidity of the standard and sample solutions was the same.

Data were evaluated using analyses of variance (ANOVA) procedures.

# 3. RESULTS AND DISCUSSION

## 3.1 Effect of soil amendments on the mobile forms of Pb, Zn and Cd

In most of the plants, there is a direct connection between the content of microelements in the soil solution and their assimilation by the plants. This relation is most evident with the cadmium and less evident with zinc and lead (Kabata Pendias, 2001).

In many plants there is a direct relation between the content of microelements in the soil solution and their absorption by the plants. This relation is most evident with the cadmium and less evident with the zinc and the lead. (Kabata Pendias, 2001). The soil amendments used for the phytostabilization may have a significant effect in the mobile forms of Pb, Zn and Cd as a result of sedimentation, absorption and change in the degree of oxidation. This effect, however, is not unidirectional, which makes necessary the testing of every single case.

Table 3 shows the quantities of the mobile forms of Pb, Zn and Cd in the control sample from naturally contaminated soil, used in the experiment and their change 6 weeks after the soil amendments were added.

*Table 3*. Influence of the soil amendments on the quantity of the mobile forms of Pb, Zn and Cd

| Element mg/kg | Control | Soil amendments | | | | |
|---|---|---|---|---|---|---|
| | | $KH_2PO_4$ | Superphosphate | Natural fertilizer | Biomanure | Sapropel |
| Pb | 106.8 | 84.6 | 84.8 | 77.2 | 113.2 | 123.2 |
| Zn | 145.0 | 108.4 | 196.2 | 79.6 | 112.8 | 79.6 |
| Cd | 3.36 | 3.54 | 3.7 | 2.44 | 3.66 | 4.92 |

The results in Table 3 show, that the effect of the soil amendments on mobile forms of lead is in various directions and relatively weak, as the deviations from the control are up to 28 %. The phosphorus additives and the natural fertilizer decrease the quantity of the mobile lead with about 21% and 28 %, respectively. This is explainable, considering the high pH in the soil solution and the fact that the lead easily forms the hard to dissolve pyromorfite with degree of solubility at 25$^{o}$C 4.10$^{-12}$ (Ma et al., 1995; Zhang et al., 1997; Laperche et al., 1997). Adding biomanure practically does not affect the quantity of the mobile lead, and the sapropel increases it with about 15 %.

The tendency of decreasing the mobile forms under the influence of the additives is more evident in the case of zinc, as in the natural fertilizer it is almost double. Only the superphosphate is an exception in which the content of the mobile zinc increases with 35%.

In the change of the mobile forms of the cadmium the tendency is reverse. In most of the cases their quantity increases, as this is most evident with the biomanure (46 %). Only with the natural fertilizer the quantity of the mobile cadmium decreases with 27 %.

The results in Table 3 show that the effect of the used soil amendments on the mobile forms of the Pb, Zn and Cd is in various directions and hard to explain. Only with the natural fertilizer there is a clearly expressed tendency for decreasing the quantity of the mobile forms of the three studied elements.

## 3.2 Effect of phosphorous amendments on the Pb, Zn and Cd accumulation in Triticale

The results for the influence of the phosphorous additives on the accumulation and distribution of Pb, Zn и Cd in the test-plant investigated are presented in Table 4. The change of the heavy metals content in comparison with the control (in %) is presented too.

The results presented in Table 4 show that the lead content in the roots of the Triticale decreases by 24% after adding $KH_2PO4$, while when superphosphate is added the decrease is much less. The obtained results are in accordance with the results of other authors who investigated the influence of the phosphorous compounds as a soil amendments. According to Laperche et al. (1997) adding apatite in the soil has a significant effect on the Pb content in plants roots. The authors have established the presence of Ca-substituted pyromorphites in the plants, grown in soils treated with apatite. Such particles were not found on the surface of the roots of the plants, grown in untreated soil. Apparently, adding apatite to the contaminated soils leads to sedimentation of pyromorphite particles on the root surface (on the outer layer). The local acidity in the risosphere may increase the local solubility of the apatite granules or other phosphorous compounds, which makes easier the sedimentation of the pyromorphite. Cotter-Howells and Capron (1996) also establish sedimentation of the Ca-substituted pyromorphites on the plants roots (*Agrostis capillaris),* grown in soils contaminated with Pb. In this case, their sedimentation is a result of root-exudate phosphates, which increases the phosphorus quantity in the risosphere. In any case, however, the formation of pyromorphite decreases the phytoaccessibility of the Pb. The tendency to decrease the lead content in the formation of phosphorous amendments is more evident with the aboveground parts of the plants - stem, leaves and seeds. Adding more superphosphate decreases the quantity in the stems (79% decreasing compared to the control), while $KH_2PO_4$ – in the stems (78%). Similar results were obtained by Laperche et al. (1997). Adding apatite to lead contaminated soil decreases the Pb content in the stems of sudax grass (*Sorghum bicolor* L. Moench) a hybrid of sorgum (Sor*ghum vulgare* L. Moench) and sudan grass (*Sorghum vulgare* var. *sudanese*) from 87% to 96%.

It is different with the zinc and the cadmium. Adding $KH_2PO_4$ decreases both their mobile forms and their content in all the parts of the plant, while when adding supephosphate we see the opposite tendency. The possible reason for this is the additional introduction of these elements in the soil with the superphosphate. As it was mentioned above, the superphosphate does not contain lead, while its content of zinc and cadmium is 163.5 и 9.55 mg/kg. The obtained results show the in the cases of soils contaminated with lead, $KH_2PO_4$ and superphosphate are effective soil amendments for the purpose of phytostabilization. The main reason for this is the formation of insoluble phosphates in the plant tissues and the soil. In combined contamination of the soil, however, adding superphosphate is not appropriate, as it increases the content of zinc and cadmium in the overground parts of the plants, $KH_2PO_4$ can be used successfully.

## 3.3 Effect of organic amendments on the Pb, Zn and Cd accumulation in Triticale

The results for the influence of the organic additives on the accumulation and distribution of Pb, Zn и Cd in the test-plant investigated are presented in Table 5.

Table 4. *Influence of the phosphorous amendments on the quantity (mg/kg) and distribution of Pb, Zn and Cd in the Triticale*

| Element | Plant material | Control | $KH_2PO_4$ | | Superphosphate | |
|---|---|---|---|---|---|---|
| | | | Result | Change, % | Result | Change, % |
| Pb, mg/kg | Roots | 32.1 | 24.4 | - 24 | 31.0 | - 3 |
| | Stems | 1.9 | 0.82 | - 57 | 0.40 | - 79 |
| | Leaves | 7.8 | 1.75 | - 78 | 4.5 | - 42 |
| | Seeds | 0.9 | 0.9 | - | n.d | - |
| Zn, mg/kg | Roots | 192.4 | 120.2 | - 38 | 132.9 | - 31 |
| | Stems | 69.5 | 61.4 | - 12 | 99.3 | + 43 |
| | Leaves | 131.8 | 93.7 | - 29 | 280.0 | + 112 |
| | Seeds | 46.7 | 30.0 | - 36 | 72.6 | + 55 |
| Cd, mg/kg | Roots | 2.4 | 2.0 | - 17 | 1.7 | - 29 |
| | Stems | 0.45 | 0.32 | - 29 | 0.6 | + 33 |
| | Leaves | 3.2 | 0.28 | - 91 | 3.4 | + 6 |
| | Seeds | 0.44 | 0.06 | - 86 | 0.5 | +14 |

*Not detectable.

The content of organic substance in the soil has a significant effect on the absorption and the carrying of heavy metals in the soil and their assimilation by the plants. The zinc, the lead and the cadmium are absorbed in the organic substance and form stable forms, which leads to their accumulation in the organic horizons of the soil and the peat (Kabata Pendias, 2001). The stability of the metal-organic compounds and their participation in the carrying and the absorption of heavy metals, however, strongly depends on pH environment. Gambus and Gorlach (1996) prove that organic fertilizers have a favorable effect on oats as they reduce the content of the cadmium in the overground parts of the crop with 24%. Gambus and Gorlach (1996) and Ciecko et al. (2001), also establish decrease of the absorption of the cadmium by he plants when peat amendments are used.

As it can be seen from the data, presented in Table 5, the tendency for reduction of the quantity of the lead and the cadmium in all parts of the studied crop is well evident in both soil amendments. The lead content in the roots decreases with 59% with manure and 61 % with biomanure, and the cadmium content decreases respectively with 50% and 49%. In the stems and the leaves the reduction is less, as for the lead it is 21 and 30%, and for the cadmium - 38 and

25%. The content in the seeds remains the same when natural fertilizers are used, and decreases with 62% when biofertilizer is used, while the content of the cadmium decreases drastically in both cases.

Table 5. *Influence of the organic amendments on the quantity (mg/kg) and distribution of Pb, Zn and Cd in the Triticale*

| Element | Plant material | Control | Natural fertilizer | | Biofertilizer | |
|---|---|---|---|---|---|---|
| | | | Result | Change, % | Result | Change, % |
| Pb, mg/kg | Roots | 32.1 | 13.3 | - 59 | 12.6 | - 61 |
| | Stems | 1.9 | 1.2 | - 38 | 1.5 | - 21 |
| | Leaves | 7.8 | 7.0 | - 10 | 5.5 | - 30 |
| | Seeds | 0.9 | 0.9 | - | 0.34 | - 62 |
| Zn, mg/kg | Roots | 192.4 | 81.4 | - 58 | 98.9 | - 49 |
| | Stems | 69.5 | 34.0 | - 51 | 67.8 | - 3 |
| | Leaves | 131.8 | 130.1 | -1 | 92.0 | - 30 |
| | Seeds | 46.7 | 45.5 | -3 | 32.9 | - 30 |
| Cd, mg/kg | Roots | 2.4 | 1.2 | -50 | 1.5 | - 49 |
| | Stems | 0.45 | 0.3 | - 33 | 0.28 | -38 |
| | Leaves | 3.2 | 2.4 | - 25 | 2.4 | - 25 |
| | Seeds | 0.44 | 0.10 | -77 | 0.11 | - 75 |

The obtained results regarding the absorption and the localization of the zinc are different. Although mobile forms in the soil decrease after manure is added, its content in the leaves and the seeds stays practically unchanged. The biofertilizer significantly decreases the zinc in the roots, the leaves, and the seeds, while its content in the stems stays unchanged. The obtained results show that the organic fertilizers are effective soil amendments for the soils, contaminated with Pb, Zn and Cd. Regarding the zinc, however, the results are unconvincing, especially when natural fertilizer is used.

## 3.4 Effect of sapropel on the Pb, Zn and Cd accumulation in Triticale

The deep-water marine slimes are in the pea stage of their development. Because of the anaerobic environment in which they precipitate, they do not pass the stage of complete decomposition and in semi-decomposed state are preserved in suppurated hydrogen zone.

In the sediments of the sapropel horizon the content of the organic carbon varies within a wide range - from 5 to 18% (Dimitrov and Velev, 1988). In their mineral part, which is homogeneous with the organic, there nutrient macroelements (K, Ca and Mg) and number of microelements (Cr, Mn, Fe etc.). The X-ray analyses show the presence of hydromica, caolite, vermiculite, and montmorillonite. From the carbonate minerals the most evident are calcite, dolomite, and aragonite; there are also amorphous oxides of the silicium.

*Table 6.* Influence of the sapropel on the quantity (mg/kg) and distribution of Pb, Zn and Cd in the Triticale

| Element | Plant material | Control | Sapropel | |
|---|---|---|---|---|
| | | | Result | Change, % |
| Pb, mg/kg | Roots | 32.1 | 24.0 | - 25 |
| | Stems | 1.9 | 1.3 | - 32 |
| | Leaves | 7.8 | 4.3 | - 45 |
| | Seeds | 0.9 | 0.7 | - 22 |
| Zn, mg/kg | Roots | 192.4 | 124.2 | - 35 |
| | Stems | 69.5 | 3.1 | - 67 |
| | Leaves | 131.8 | 24.9 | - 81 |
| | Seeds | 46.7 | 17.5 | - 63 |
| Cd, mg/kg | Roots | 2.40 | 1.50 | - 38 |
| | Stems | 0.45 | 0.06 | - 87 |
| | Leaves | 3.20 | 0.3 | - 91 |
| | Seeds | 0.44 | 0.13 | - 70 |

The possibilities to use the sapropel, independently or mixed with other substances, in agriculture as a mineral stimulator is a subject of an increasing interest. The studying of its potential for the purposes of phytostabilization is at initial phase. The results we obtained on the effect of the sapropel on the absorption and the localization of Pb, Zn and Cd in the Triticale are presented in Table 6.

As can be seen from the results presented in Table 6, the tendencies are the same for the three elements. The lead content decreases in all organs of the plant, as this is most evident in the stem (32%) and in the leaves (45%). With the zinc and cadmium, this process intensifies in all the parts of the plant, as in this case also, the reduction is less in the roots and the stems and more in the leaves (81% with Zn and 91% with Cd).

Most likely, the reason for the observed processes is the strongly developed surface and the big absorption capacity of the sapropel. The obtained results give us reason to believe, that the sapropel is of great interest for the purposes of phytostabilization. The final answer to this question requires studying of its effect in wider range of agricultural crops both independently and mixed with other soil amendments.

## 4. CONCLUSIONS

A comparative study has been carried out on the effect of some soil amendments (phosphorus compounds, organic fertilizers and saprople) on the quantity of the phytoaccessible forms of Pb, Zn and Cd and the absorption of these elements by Triticale. It was established that:

1. The effect of the used soil amendments on the mobile forms of the Pb, Zn and Cd is specific without clearly expressed tendencies. Only with the natural fertilizer there is a clear tendency for their reduction in all of the three studied elements. No direct relation between the quantity of the mobile forms and the absorption of Pb, Zn and Cd by the Triticale was established.

2. The superphosphate and $KH_2PO_4$ are effective phytostabilizing amendments for soils contaminated with lead. In combined contamination, however, adding superphosphate is not appropriate, as it increases the content of zinc and cadmium in the overground parts of the plants, while $KH_2PO_4$ can be used successfully.

3. The organic fertilizers are effective soil amendments for the soils contaminated with Pb and Cd. Regarding the zinc, however, the results are not convincing enough, especially when natural fertilizer is used.

4. The sapropel presents a great interest for the purposes of phytostabilization. The evaluation of its potential, however, requires further studying of both the physical-mechanical and chemical characteristics, as well as its effect on wider range of agricultural crops.

## 5. REFERENCES

Basta, N. T., Gradwohl, R., Snethen, K. L., and Schroder, J. L. 2001. Chemical immobilization of lead, zinc, and cadmium in smelter-contaminated soils using biosolids and rock phosphate. J. Environ. Qual. 30, 1222 -1230.

Berti, W.R., and Cunninggham, S.D. 1997. In-place inactivation of Pb in Pb-contaminated soils. Environ Sci Technol. 31, 1359–1364.

Boisson, J., Ruttens, A., Mench, M., and Vangronsveld, J. 1999 Evaluation of hydroxyapatite as a metal immobilizing soil additive for the remediation of polluted soils. Part 1. Influence of hydroxyapatite on metal exchangeability in soil, plant growth and plant metal accumulation. Environ. Poll. 104, 225 - 233.

Cao, R.X., Ma, L.Q., Chen, M., Singh, S.P., and Harris, W.G. 2003. Phosphate-induced metal immobilization in a contaminated site. Environ Pollut. 122,19– 28.

Ciecko, Z., Wyszkowski, M., Krajewski, W., and Zabielska, J. 2001. Effect of organic matter and liming on the reduction of cadmium uptake from soil by Triticale and spring oilseed rape. The Science of the Total Environment 281, 37- 45

Cheng, S.F., and Hseu, Z.Y. 2002. In-situ immobilization of cadmium and lead by different amendments in two contaminated soils. Water Air Soil Pollut. 140, 73–84.

Chlopecka, A., and Adriano, D.C. 1997. Influence of zeolite, apatite and Fe-oxide on Cd and Pb uptake by crops. Sci. Tot. Environ. 207, 195-206.

Cotter-Howells, J., and Capron, S. 1996. Remediation of contaminated land by formation of heavy metal phosphates. Appl. Geochem. 11, 335-342.

Dimitrov, P., and Velev, V. 1988. Opportunities of using of deep-water sapropeloide slimes of Black Sea for agrobiological and industrial purposes. Ocealology 17, 92-95

Gambus, F., and Gorlach, E. 1996. Wplyw obornika, slomy i wegla ´brunatnego na fitoprzyswajalnosc metali ciezkich. Zesz.˙Ž . Ž Nauk AR Szczec Rol. 172, 131-137.

Geebelen, W., Vangronsveld, J., Adriano, D.C., Carleer, R., and Clijsters, H. 2002. Amendment-induced immobilization of lead in a lead-spiked soil: evidence from phytotoxicity studies. Water Air Soil Pollut.140, 261–277.

Hettiarachchi, G.M., and Pierzynski, G.M. 2002. In situ stabilization of soil lead using phosphorus and manganese oxide: influence of plant growth. J Environ Qual. 31, 564–572.

Hettiarachi, G.M., Pierzynski, G.M., and Ransom, M.D. 2001. In situ stabilization of soil lead using phosphorus. J Environ Qual. 30,1214– 1221.

ISO 11466. 1995. Soil Quality- Extraction of trace elements soluble in aqua regia.

ISO 14870. 2001. Soil Quality- Exxtraction of trace elements by buffered DTPA solution.

Jamode, A. V., Rao, M., Chandak, B. S., Jamode, V. S., and Parwate, A.V. 2003. Applications of the inexpensive adsorbents for the removal of heavy metals from industrial wastewater: a brief review. J. Ind. Poll. Control. 19, 114 -134.

Johnston, A.E., and Jones, K.C. 1992. The cadmium issue long-term changes in the cadmium content of soils and the crops grown on them. Proc. Int. Workshop, Phosphate fertilizers and the environment, International Fertilizer Development Center, Tampa, 255 - 269.

Kabata-Pendias, A. 2001. Trace Elements in Soils and Plants, 3rd ed. CRC Press LLC, Boca Raton.

Knox, A S., Kaplan, D. I., Adriano, D. C., Hinton, T. G., and Wilson, M. D. 2003. Apatite and phillipsite as sequestering agents for metals and radionuclides. J. Environ. Qual. 32, 515 - 525.

Knox, A S., Seaman, J. C., Mench, M., and Vangronsveld, J. 2001. Remediation of Metal- and Radionuclides-Contaminated Soils. In: Environmental Restoration of Metals-Contaminated Soils, pp. 21 -60 (Iskandar, I.K., Ed.). CRC Press LLC, Boca Raton Florida.

Laperche, V., Logan, T.J., Gaddam, P., and Traina, S.J. 1997. Effect of apatite amendments on plant uptake of lead from contaminated soil. Environ Sci Technol. 31, 2745– 2753.

Lopotko, M.Z., Kuzmitski, P.L., and Evdokimova, G.A. 1992. Sapropels in agriculture. Minsk, Belarus.

Ma, Q.Y., Logan, T.J., and Traina, S.J. 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol., 29,1118-1126.

McGowen, S.L., Basta, N.T., Brown, G.O. 2001. Use of diammonium phosphate to reduce heavy metal solubility and transport in smelter-contaminated soil. J Environ Qual. 30, 493–500.

Moskalchuk, L.N., and Klimava, N.G. 2003. Recovery of Chernobyl-affected soils in the Republic of Belarus: Tendencies and trends, pp. 126-131 (IAEA-J9-CN-109 International Conference on the Protection of the Environment from the Effects of Ionizing Radiation: Stockholm, Sweden).

Maskalchuk, L.N., and Pozilova, N.M. 2005. Radioactive Contamination of Soils in Belarus: Experience and Trends of Rehabilitation, pp. 169-173 (IAEA-CN-135 International Conference on the Safety of Radioactive Waste Disposal: Tokyo, Japan).

Scheckel, K.G., and Ryan, J.A. 2003. In vitro formation of pyromorphite via reaction of Pb sources with soft-drink phosphoric acid. Sci Total Environ. 302, 253–65.

Seaman, J.C., Hutchison, J.M., Jackson, B.P., and Vulava, V.M. 2003. In situ treatment of metals in contaminated soils with phytate. J Environ Qual. 32, 153– 61.

Shnyukov, E.F., and Ziborov, A. P. 2004. Mineral resources of the Black Sea. Kiev, Naukova Dumka.

Yang, J., Mosby, D.E., Casteel, S.W., and Blanchar, R.W. 2001. Lead immobilization using phosphoric acid in a smelter-contaminated urban soil. Environ Sci Technol. 35, 3553– 3559.

Vashkov, H. 1996. Sapropel as an improver of soils contaminated by heavy metals. Himija v Selskom Hozyaistve 4, 5-7

Walker, D.J., Clemente, R., Roig, A., and Bernal, M.P. 2003. The effect of soil amendments on heavy metal bioavailability in two contaminated Mediterranean soils. Environ Pollut. 122, 303– 12.

Walker, D.J., Clemente, R., and Bernal, M.P. 2004 Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of Chenopodium album L. in a soil contaminated by pyritic mine waste. Chemosphere 57, 215 - 224.

Zhang, P., Ryan, J.A., and Yang J. 1997. In vitro soil Pb solubility in the presence of hydroxyapatite. Environ Sci Technol. 32, 2763– 2768.

Zhu, Y. G., Chen, S. B., Yang, J. C. 2004. Effects of soil amendments on lead uptake by two vegeTable crops from a lead-contaminated soil from Anhui, China. Environment International 30, 351– 356