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APPLICATION OF AMENDMENTS OBTAINED THROUGH PROCESSING LIMESTONES FOR THE IMMOBILIZATION OF HEAVY METALS IN CONTAMINATED SOILS

Mihaela COSTEA[1, 2], Dumitru-Marian MOTELICĂ[1], Nicoleta-Olimpia VRÎNCEANU[1], Mirela-Alina SANDU[2], Costică CIONTU[2]

[1]National Research and Development Institute for Soil Science, Agrochemistry and Environment - ICPA Bucharest, 61 Marasti Blvd, District 1, Bucharest, Romania
[2]University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Marasti Blvd, District 1, Bucharest, Romania

Corresponding author email: cosmihaela96@gmail.com

Abstract

This study presents the results of testing various amendments for use in the immobilisation of metals in contaminated soils. The incubation tests were carried out for five indigenous amendments from different sources, and the results showed significant changes in the pH value of the contaminated soil following their application. At the same time, the effects of the application of these limestone amendments on the mobility of metals in the soil were estimated by specific extractions of different forms of metals existing in the soil. The results obtained allowed the ranking of the tested amendments according to their immobilization ability. Thus, for cadmium, lead and zinc, the calcium carbonate from Murfatlar and the calcium carbonate from Fieni showed the highest immobilization efficiency. The ground limestone from Baita had the lowest efficiency compared to the other amendments studied. The results obtained showed that the use of indigenous limestone amendments had significant effects on the decrease in the mobility of heavy metals in contaminated soil, providing promising prospects for their use in the restoration of these soils.

Key words: *amendments, contamination, immobilization, metals, soil.*

INTRODUCTION

The contamination of soil with heavy metals is a growing problem worldwide. Metal accumulation in soil can pose a risk to the ecosystem and to human health in the long term (Lyang et al., 2014; Sur et al., 2017).

Heavy metals become toxic when they reach concentrations close to the maximum permissible limit. The overall effect of heavy metal pollution is to reduce soil fertility and worsen nutrition conditions for plants, thus affecting their growth and development processes. The behaviour of potentially toxic metals in the biogeochemical cycles of terrestrial ecosystems produces long-term implications mainly affecting the productivity of agricultural and forestry soils, the nutrition cycles of plants and animals, and dynamics of life in soil. Various technologies have been used to remediate metal-contaminated sites, including soil washing, stabilisation/immobilisation, excavation, and phytoremediation (Hamid et al., 2020). One of the most used methods for soil remediation is the *in situ* immobilisation of heavy metals.

Efficiency and low cost are the main advantages of this method (Pérez-de-Mora et al., 2006; Lee et al., 2009). By applying additives to the soil, this method reduces the mobility and bioavailability of heavy metals in the soil. A number of soil amendments including gypsum, lime and limestone have been tested in recent years (Houben et al., 2012; Karalić et al., 2013; Zhou et al., 2014; Hamid et al., 2020), red mud (Pavel et al., 2015), biochar (Embren, 2016), natural zeolites (Ulmanu et al., 2011; Radziemska et al., 2013) or combination of these amendments (Zhou et al., 2014), rock phosphate (Zhao et al., 2014) and different type of clay (Xu et al., 2010; Liang et al., 2014). He and colleagues (2013) state that these immobilizers minimize metal mobility through precipitation, reduction of solubility, provision of adsorption sites, and via metal-agent surface complexes.

Nejad et al. (2018) consider that even if liming was primarily intended to improve soil acidity, it is increasingly being used as an important management tool to reduce the toxicity of heavy metals in soils.

Various soil extraction tests are used to assess the bioavailability of metals.

For predicting plant availability of metals, extractions such as the NH_4NO_3 (1M) method have proven to be more reliable (Bolan et al., 2014; Guarino et al., 2022).

The primary objective of the present study was to evaluate the effectiveness of various lime amendments in reducing metal mobility in a contaminated soil in order to limit the adverse effects of soil metal contamination.

MATERIALS AND METHODS

The immobilization of heavy metals in the soil was achieved by applying amendments containing calcium carbonates from different sources located in Romania. Their characteristics and sources are presented in Figure 1.

The soil material used to carry out for the incubation experiment in the laboratory was collected from a heavy metal contaminated area, located about 1500 m from the exhaust chimney of the industrial enterprise S.C. SOMETRA Copşa Mică - the main source of heavy metal pollution in the area (Figure 2).

The soil material was collected from 0-20 cm layer of an Aluvisol located in the Lunca Târnavei Mari.

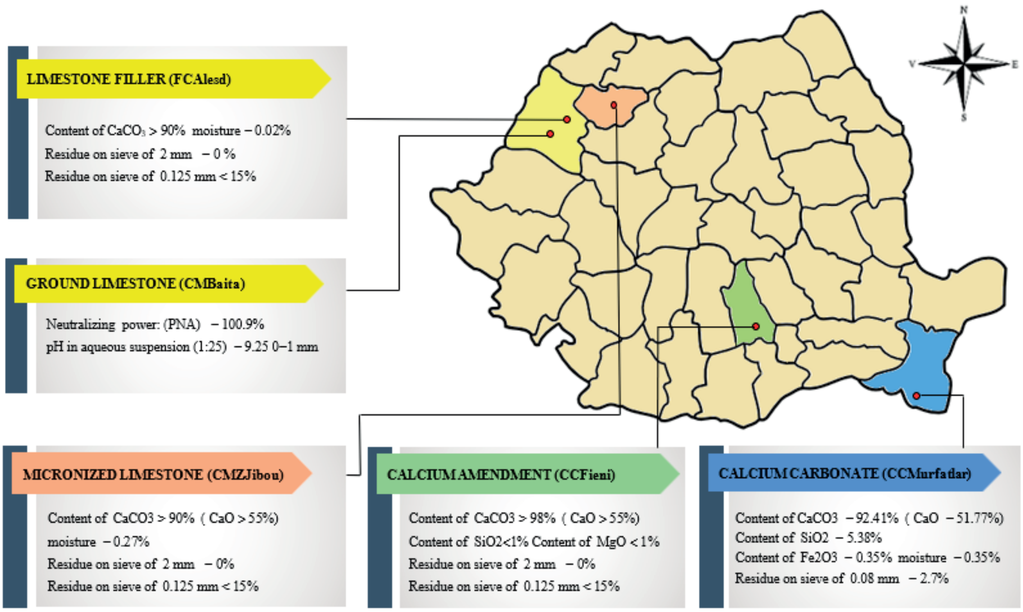


Figure 1. Characterization of amendments used to immobilise heavy metals in soil

The purpose of the incubation experiment was to assess the effects of the application of different lime materials on the mobility of heavy metals in soil. For this purpose, 100 g of air-dried and sieved (2 mm) contaminated soil was filled into 200 mL plastic beakers and lidded to avoid contamination. Five treatments including the control (CK) were applied at 4 concentrations (0.5%, 1%, 1.5% and 2% w/w):

- a_1 - Limestone from Aleşd, Bihor County ($FC_{Aleșd}$);
- a_2 - Ground limestone 0-1 mm from Băiţa-Plai, Bihor County ($CM_{Băița}$);
- a_3 - Lime amendment from Fieni, Dâmboviţa County (CC_{Fieni});
- a_4 - Micronized limestone from Jibou, Salaj County (CMZ_{Jibou});
- a_5 - Calcium carbonate from Murfatlar, Constanţa County ($CC_{Murfatlar}$).

All experimental trial was tested in 3 replicates. After the incorporation of the amendment, the homogenization of the soil-amendment mixture

and the addition of 15 ml of distilled water to each glass, the mixtures were put into the oven for 72 hours, at a temperature of 60°C. After this period, the soil samples were air dried, ground and passed through a 2 mm sieve before chemical analysis. A potentiometric method (1:2.5 w/v, soil: water) was used to measure soil pH.
NH_4NO_3-extractable heavy metals were obtained from 10 g of soil using 20 ml of extraction solution (NH_4NO_3, 1M). A GBC Avanta 932AA flame AAS spectrometer was used to analyze the extracted samples for heavy metal content. Triplicate analyses were performed for all laboratory analyses and the averages of these three replicates are reported. To compare the means of the different treatments, statistical analyses were performed using analysis of variance (ANOVA). For paired comparisons between treatments and control, Tukey's honestly significant difference (HSD) test was used.

Figure 2. Location of the area from which the contaminated soil material was harvested
(satellite image source – Google Earth Pro, map source – Wikipedia)

RESULTS AND DISCUSSIONS

The study included detailed soil analyses before (Table 1) and after the amendments were applied, assessing parameters such as heavy metal content, soil pH and other relevant indicators.
The acidic reaction of the soil favors the high solubility of heavy metals leading to their high mobility in the soil-plant system.
Liming materials were selected because of their properties to interact with heavy metals, forming less soluble compounds and thus reducing their mobility in the soil.

Influence of amendments on soil pH value
At the end of the incubation, an increase in the pH of the incubated soil was observed when the amendments were applied. There was a statistically significant effect on the pH of the soil in which they were incorporated for all 5 carbonate materials tested. Lime amendment from Fieni produced the highest increase in pH value, reaching 7.23 after applying dose of 2% w/w.

Table 1. The average values of the main chemical and physical properties of the soils

Characteristic	U.M.	Mean value (n = 10)
pH	-	4.90
Kjeldahl nitrogen content	%	0.090
Organic carbon content	%	1.32
Available phosphorus content (P_{AL})	mg/kg	22
Available potassium content (K_{AL})	mg/kg	120
Copper content (aqua regia)	mg/kg	183
Zinc content (aqua regia)	mg/kg	2628
Cadmium content (aqua regia)	mg/kg	34.4
Lead content (aqua regia)	mg/kg	2871
Copper content (NH_4NO_3)	mg/kg	5.95
Zinc content (NH_4NO_3)	mg/kg	535
Cadmium content (NH_4NO_3)	mg/kg	29.7
Lead content (NH_4NO_3)	mg/kg	401
Textural class	SM - medium texture – sandy loam	

The ground limestone (0-1 mm) from Baița had the lowest influence on pH value of treated soil.

Comparing the pH values after the application of the $FC_{Aleșd}$, $CC_{Murfatlar}$ and CC_{Fieni} there are no significant changes in soil pH (Figure 3).

Analysing the influence of the amendment's doses applied, in general, the increase in the amount of product led to an increase in soil pH values, and this increase was statistically ensured (Figure 3).

The hydrolysis of $CaCO_3$ in lime to hydroxyl ions may be related to soil elevation, according to Hamid et al. (2020).

Miura et al. (2016) noticed liming are mainly effective in improving the soil pH and controlling metals precipitation or by increasing adsorption sites by causing deprotonation at soil surface.

Changes in pH values influence the mobility of heavy metals in the soil, reduce their absorption by plants and thus helping to reduce the phytotoxic effects of heavy metal pollution in soil.

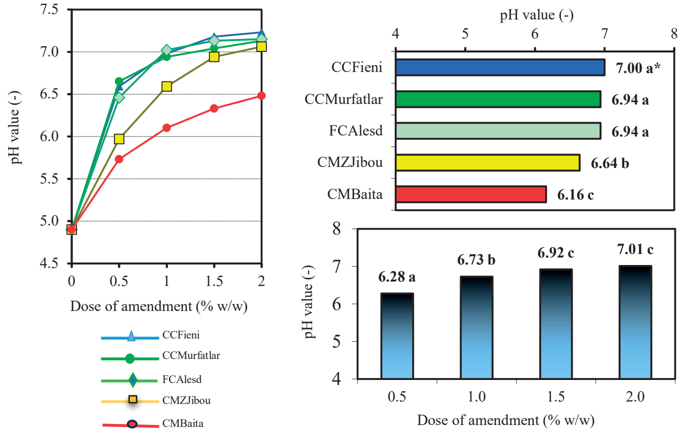
Among the most effective amendments to increase the pH value of soil were lime amendments from Fieni, calcium carbonate from Murfatlar and limestone from Aleșd.

Amendments influence on heavy metal mobility (assessed by specific extraction methods)

The bioavailability of metals is related to soil pH. Therefore, the effects of treatments on pH are reflected on metal bioavailability. This is assessed by NH_4NO_3 extractable metal fractions. Therefore, the effects of treatments on pH are reflected on metals bioavailability assessed by NH_4NO_3-extractable metal fractions. This extraction method can be considered suitable for measuring the actual available content of metals in pore waters since it reproduces pH values commensurate to the ones of the soil solutions This extraction method can be considered as a suitable method for the measurement of the actual available content of metals in pore waters since it reproduces pH values corresponding to those of soil solutions (Guarino et al., 2022).

All treatments caused a significant decrease of the values content of NH_4NO_3-extractable Cu in soil. After the application of the first treatment (0.5% w/w), an approximately 10-fold decrease in the mobile copper content in the soil was observed (Figure 4).

The effects of lime amendments application on contaminated soil are presented in Figure 5. The obtained results indicated a significant reducing of cadmium mobility after applications of 0.5% (w/w) for each amendment. The lowest value of NH_4NO_3 extractable cadmium content was obtained in the case of soil treated with CC_{Fieni}, but there are no significant differences from the values obtained in the case of treatments with $FC_{Aleșd}$ and $CC_{Murfaltar}$.

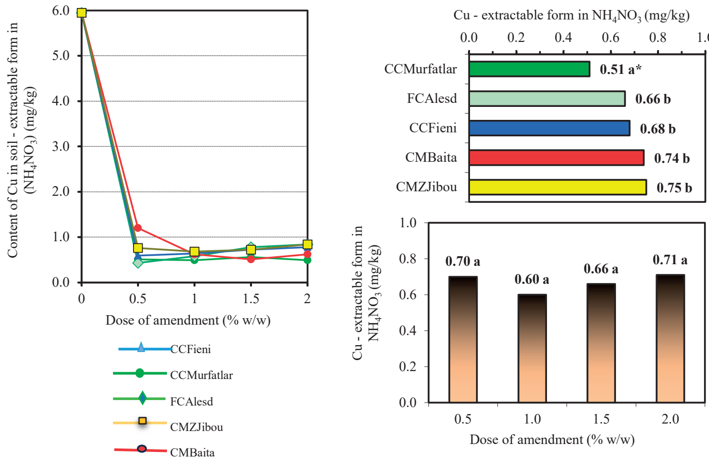


* Values followed by the same letter (a, b, ...) do not differ significantly between them (Tukey multiple comparison method - significance threshold α=0.05).

Figure 3. Effects of applying different amendments at different rates on the pH of soil material

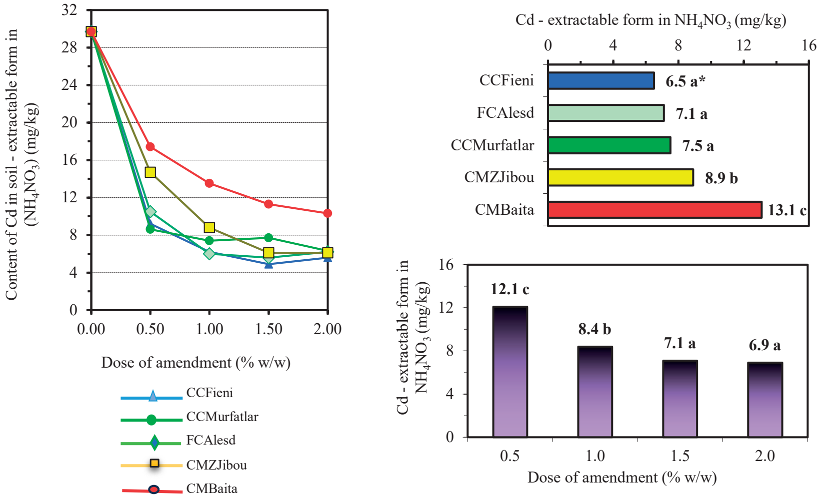
Cadmium contents significantly reduced to 6.5, 7.1 and 7.5 mg kg^{-1} respectively with CC_{Fieni}, $FC_{Aleșd}$ and $CC_{Murfatlar}$ application as compared to CMZ_{Jibou} and $CM_{Băița}$ (8.9 and 13.1 mg kg^{-1}). Similar results were obtained by Liang et al., (2014) which demonstrated in a study conducted in paddy soil that precipitation was the dominant process in Cd immobilization in soils treated with $CaCO_3$. The application of calcium carbonate treatments produced significant changes in lead mobility compared to control (Figure 6). There are significant decreases of NH_4NO_3 extractable Pb content in contaminated soil treated with different doses of amendments. The lowest values of mobile Pb content in soil were reported after application rates equivalent to 1.5% respectively 2.0% (w/w) amendments.

Along the same lines, Lim et al. (2013) noted that the application of $CaCO_3$ immobilized Cd and Pb considerably, as indicated by the decreased metal extractability. They concluded that increasing soil pH in response to applying $CaCO_3$ to contaminated soils was the primary cause of the significant decreases in cadmium and lead extractables observed.



* Values followed by the same letter (a, b, ...) do not differ significantly between them (Tukey multiple comparison method - significance threshold α=0.05).

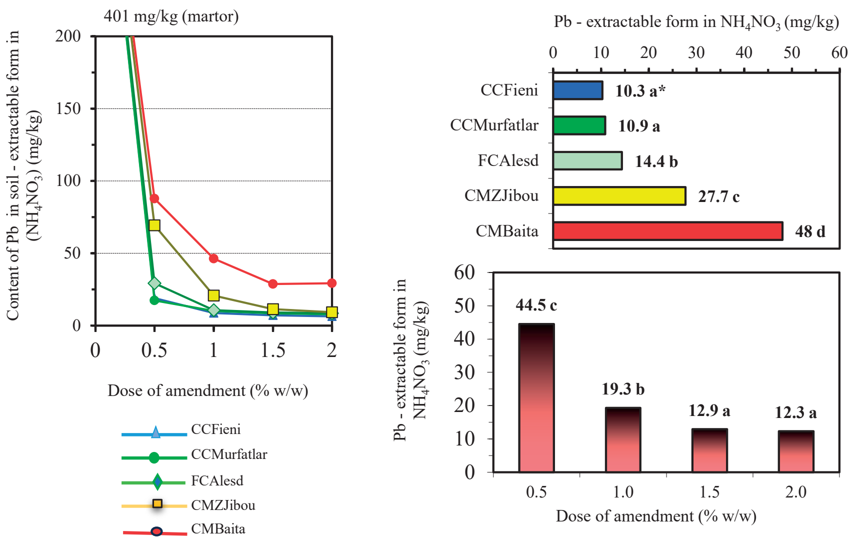
Figure 4. Effects of application amendments on soil copper content (extractable form in NH_4NO_3)



* Values followed by the same letter (a, b, ...) do not differ significantly between them (Tukey multiple comparison method - significance threshold α=0.05).

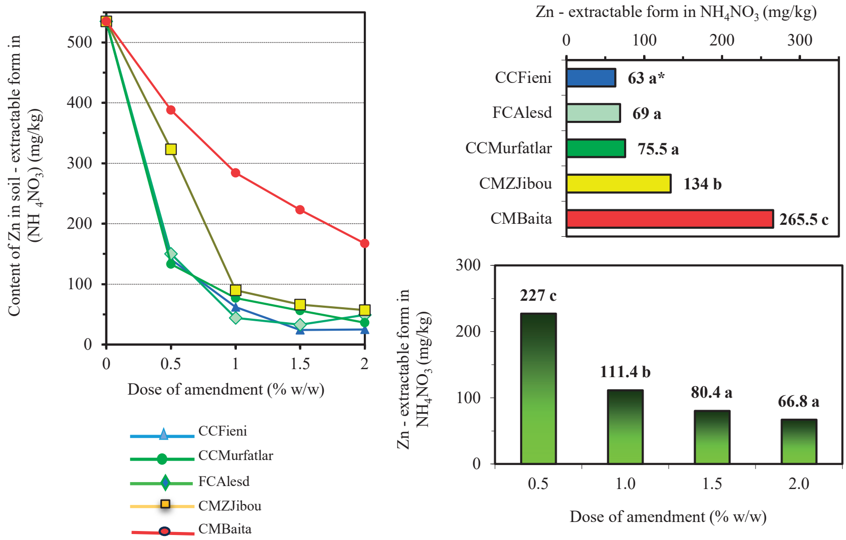
Figure 5. Effects of application amendments on soil cadmium content (extractable form in NH_4NO_3)

All treatments with different application rates of amendments reduce the mobility of zinc in contaminated soil (Figure 7). As soil pH increases, the solubility of Zn decreases. Alloway (2009) considered that the increased adsorption capacity of soil solids surfaces due to increased negative charge as a function of pH, the formation of hydrolytic forms of Zn, chemisorption to calcite, and co-precipitation in ferric oxide are responsible for the increase in Zn concentrations.



* Values followed by the same letter (a, b, ...) do not differ significantly between them (Tukey multiple comparison method - significance threshold α=0.05).

Figure 6. Effects of application amendments on soil lead content (extractable form in NH4NO3)



* Values followed by the same letter (a, b, ...) do not differ significantly between them (Tukey multiple comparison method - significance threshold α=0.05).

Figure 7. Effects of application amendments on soil zinc content (extractable form in NH_4NO_3)

The mobile zinc contents significantly reduced to 63, 69 and 75.5 mg kg^{-1} respectively with CC_{Fieni}, $FC_{Aleșd}$ and $CC_{Murfatlar}$ application as compared to CMZ_{Jibou} (134 mg kg^{-1}) and $CM_{Băița}$ (266 mg kg^{-1}). Compared to the effects of these treatments on cadmium and lead mobility, the reduction in zinc mobility is less obvious.

Ranking of the tested amendments according to their ability to immobilize metals in polluted soil was made using experimental data obtained from incubation and laboratory tests.

This analysis underlines that the effectiveness of the amendments in raising the pH value and immobilization of metals is influenced by the type of metal, and the various amendments have different effects on the degree of immobilization depending on the studied metal.

It is noted that for cadmium (Cd), lead (Pb) and zinc (Zn) metals, the ranking of amendments according to the immobilization capacity set at the minimum rate application (0.5% w/w) remains consistent and at higher doses, respectively 1%, 1.5%, and 2% (w/w) This suggests that the relative effectiveness of each amendment in the immobilisation of these metals is generally maintained as the amendment rate application increases.

CONCLUSIONS

The research carried out has highlighted several important aspects regarding the use of calcium amendments of indigenous origin for the purpose of immobilizing metals from contaminated soil.

The amendment application on contaminated soil, by the modification of the most important soil property, pH, leads to the reduction of the mobility of heavy metals.

Incubation experiments conducted to improve the properties of contaminated soil have provided significant results.

The amendments tested brought significant statistical changes to the pH value of the soil. At a dose of 2%, there was a significant increase in pH from 4.90 to 7.01. Among the most effective amendments to increase the pH value were calcium carbonate from Fieni, calcium carbonate from Murfatlar and limestone from Aleşd.

In terms of copper immobilisation, the calcium carbonate from Murfatlar and the limestone from Aleşd have achieved significant results, with a degree of immobilisation of 92.7% and, respectively, of, 91.5% at a dose of 0.5% (w/w).

For cadmium, the calcium carbonate from Murfatlar and the calcium carbonate from Fieni were effective, with a significant decrease of mobility observed at a dose of 2%. The amendments calcium carbonate from Murfatlar and calcium carbonate from Fieni proved effective in immobilizing lead, with a degree of immobilization of over 95% at the dose of 0.5%. For zinc, calcium carbonate from Murfatlar and calcium carbonate from Fieni showed significant immobilisation rates, increasing to 95.4% and 93.3% at a dose of 2%. These amendments had a positive impact on contaminated soil, improving pH values and immobilising heavy metals. Doses of 0.5% were generally sufficient to achieve the desired results, except for zinc, where the 2% dose was required for significant changes.

According with their ability to immobilize the heavy metals, the lime amendments applied in rate of 0.5% (w/w) were ranked as follows:

- Cu: $FC_{Aleşd} = CC_{Murfatlar} = CC_{Fieni} = CMZ_{Jibou} > CM_{Băiţa}$
- Cd: $CC_{Murfatlar} = CC_{Fieni} = FC_{Aleşd} > CMZ_{Jibou} > CM_{Băiţa}$
- Pb: $CC_{Murfatlar} \geq CC_{Fieni} \geq FC_{Aleşd} > CMZ_{Jibou} > CM_{Băiţa}$
- Zn: $CC_{Murfatlar} = CC_{Fieni} = FC_{Aleşd} > CMZ_{Jibou} = CM_{Băiţa}$

The amendment with ground limestone from Băiţa presented the lowest degree of immobilization for all metals tested.

Calcium carbonate, added to the soil as an amendment, acted as a binding agent, turning heavy metals into stable compounds.

The results obtained from this study not only highlighted the effectiveness of the immobilization process, but also revealed the potential to improve soil fertility. By neutralising heavy metals and stabilising them in a less toxic form, the path to revitalising the affected soil has been opened, providing opportunities for its further use for agricultural or recreational purposes.

Prospects for this approach could include expanding research on other soils and heavy metals, as well as adapting the method to local soil and ecosystem specificities. By integrating calcium carbonate into contaminated soil management strategies, this study proposes a sustainable and potentially effective approach to reducing the risks associated with the presence of heavy metals in the environment.

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