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Geoscience research and applications are of crucial interest in science and many areas of modern life. For this reason, exchanging knowledge in various relevant areas is essential for development in scientific, engineering and programming activities. The conference aims to highlight the importance of joint research of experts in these fields and provide a platform for knowledge exchange.

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CONTENTS

Invited Lectures

Invited Progress Reports

Progress Reports

Posters

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Contributed paper

CHANGES IN CONCENTRATION OF DTPA-EXTRACTABLE FORMS OF METALS IN RESPONSE TO SOIL TREATMENT WITH VARIABLE SEASHELL DOSES

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Abstract: Seashells piled in coastal areas worldwide, particularly near commercial mollusk farms, may pose a substantial environmental and health risk. Utilizing seashell waste (SW) as a natural liming material represents a meaningful contribution to the sustainable development of the aquaculture industry through resource recovery. This study assessed the effects of adding various doses of finely ground SW to acidic agricultural soil with elevated total concentration of Cu (219.2 mg/kg) on the bioavailability of selected metals (Cu, Zn, Fe, Mn, Co, Pb, Ni, and Cd). The concentration of DTPA-extracted forms of Cu and other elements decreased significantly with the increase in SW dose from 0.15% to 2%, whereas differences between 2% and 5% treatments were not significant. The association of metals' bioavailability with the agrochemical properties of control and treated soil samples revealed the leading influence of soil pH. Furthermore, the DTPA-extracted amounts of Cu and Zn were negatively correlated with carbonate and organic carbon content, and bioavailable Zn forms were negatively correlated with the content of accessible phosphorus. As a cost-effective, sustainable, and renewable source of calcium carbonate, organic carbon, and available phosphorus, SW is a candidate material for acidic soil amelioration, including the immobilization of a range of toxic and potentially toxic metals. However, the study's results underline that SW dose optimization through preliminary tests is a necessary research component that requires observing soil fertility parameters, particularly the status of essential metals.

Keywords: Soil remediation; seashell waste; metal immobilization; bioavailability; DTPA-extraction

1. Introduction

Increasing land degradation and decreasing productive land due to metal contamination and acidification incited a growing interest in readily available, economical, and highly effective technologies for soil remediation. Among these technologies, soil amendments as immobilizing agents and pH improvers have been developed extensively for large-scale applications because of their easy application and commercial viability. A variety of soil amendments have been widely employed to reduce the mobility and bioavailability of metals in contaminated soils by immobilizing them into stable forms via adsorption, precipitation, and complexation, including organic (e.g., animal wastes, biochar, biosolids, and compost) and inorganic (e.g., clay minerals, coal fly ash, liming materials, metal oxides, and phosphates) materials (Palansooriya et al., 2020).

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The research on high-performance soil amendments that fulfill sustainable remediation principles has intensified in the last two decades. Naturally occurring waste materials and residues have received particular attention because of their availability, low cost, and relatively high efficiency in achieving remediation goals. Seashells have proven an emerging alternative to conventional liming materials for the remediation of acidic and metal-contaminated soils due to their high calcium-carbonate content (Barros et al., 2009). This approach also benefits the coastal ecosystems, by using the waste material from the growing seafood industry and enabling sustainable seashell aquaculture. Seashells act as soil conditioner, as they provoke changes in the fractionation of metals (e.g., Cd, Cu, Pb, Zn, Cr, and Ni) by increasing their sorption and precipitation, and improve soil nutrient contents and bacterial community structure (Jović et al., 2019). Nevertheless, adding seashells to agricultural soils demands caution and additional research to ensure the immobilization of toxic and potentially toxic metals while safeguarding the sufficient availability of essential ones (Santás-Miguel et al., 2022). In that sense, the behavior and bioavailability of Cu is of a particular significance, as this metal is a micronutrient essential for plant development and crop yield in certain low amounts while exhibiting high toxic potential at elevated concentrations.

Egerić et al. (2019) demonstrated that seashell waste (SW) could be employed to improve essential properties of the acidic agricultural soil with elevated Cu-concentration in terms of the increase in pH, carbonate, organic carbon, and available phosphate content and decrease in environmental mobility of Cu and other metals. This study aimed to evaluate the impact of different seashell doses on the availability of essential micronutrients (Cu, Fe, Mn, and Zn) and other selected metals (Cd, Co, Ni, and Pb) to plants, using the extraction with diethylenetriaminepentaacetic acid (DTPA). The relationship between the bioavailability of these elements and the agrochemical properties of the soil altered by various doses of the additive was assessed.

2. Materials and methods

The topsoil (0–20 cm) was sampled from an agricultural parcel in Slatina village, near the town of Bor (Serbia), in which a copper mining and smelting complex (Serbia Zijin Bor Copper, formerly known as RTB Bor) has been operating for more than a century. Dried soil was homogenized and sieved to <2 mm fraction. The composite SW, collected from the North Greek Aegean Sea coast, was washed from impurities, ground into a fine powder, and characterized as described previously (Egerić et al., 2017). The SW was mixed with soil at 0.15%, 0.3%, 2%, and 5% w/w bases (samples SW0.15, SW0.3, SW2, and SW5; Egerić et al., 2019). The treatments have been carried out in pots (triplicates), maintaining ~60% of soil water capacity for two months.

Ten grams of control soil (S) and treated samples were extracted with 20 ml of DTPA- solution (International Organization for Standardization, 2001). The extracting solution was prepared by dissolving 0.005 mol/L DTPA, 0.1 mol/L triethanolamine (TEA), and 0.01 mol/L $CaCl_2$ in deionized water and adjusting the final pH to 7.3 with 6 M HCl. Extractions were conducted at room temperature, for two hours, on a rotary shaker (15 rpm). Liquid phases were separated by membrane filtration (0.45 μm), and the concentrations of metals (Cu, Fe, Mn, Zn, Cd, Ni, Co, and Pb) were measured within 24 h by Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific iCAP 6500 Duo), with matrix-matched calibration standards. The concentrations of elements are presented on a dry matter basis.

3. Results and discussion

The results obtained from the DTPA test of the control and treated soil samples are graphically shown in Figure 1. The difference in metal availability between the samples was identified by Fisher's least significant difference (LSD) test.

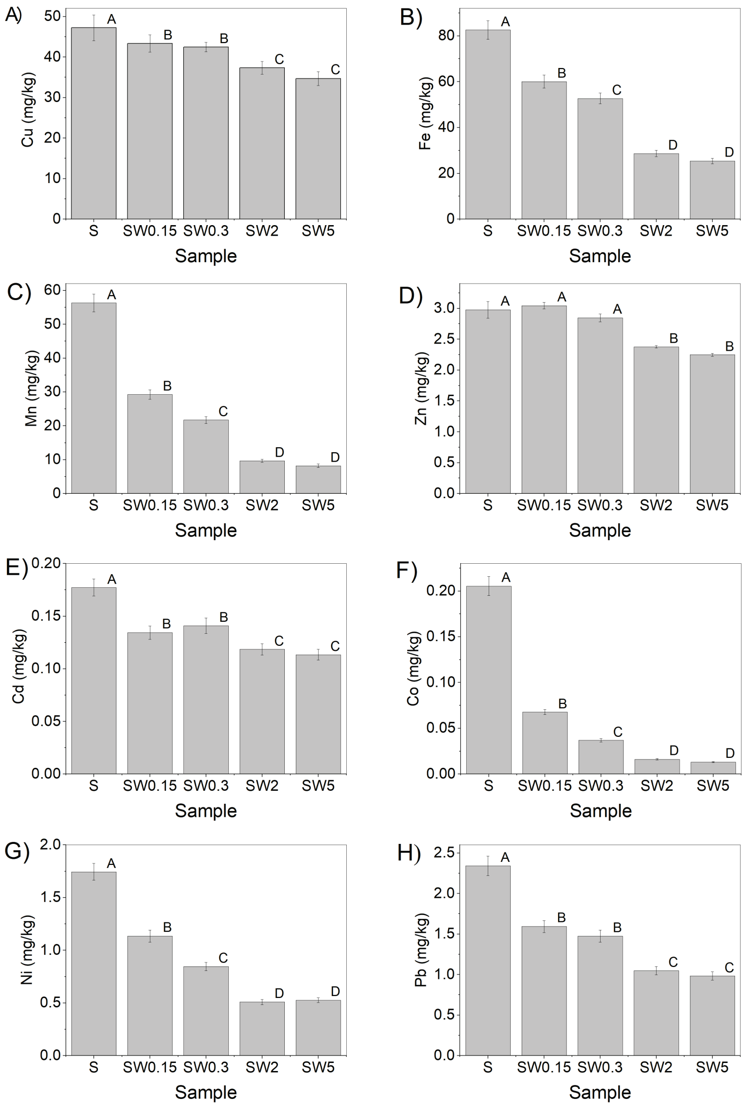

Figure 1. The DTPA-extracted concentrations of Cu (A), Fe (B), Mn (C), Zn (D), Cd (E), Co (F), Ni (G), and Pb (H) in the soil before and after treatment with different doses of SW, including one-way analysis of variance (ANOVA) and the Fisher's least significant difference (LSD) test at the level of significance α = 95% (p < .05).

Some of the metals are essential nutrient elements for the proper growth and development of plants (e.g., Cu, Zn, Fe, and Mn). Consequently, it is important to monitor their availability to plants. Determination of critical concentrations of bioavailable micronutrients in soil has been the focus of numerous studies, which pointed out variations across different extraction methods, soil types, properties, and specificities associated with plant species (Fageria et al., 2002). Recommended soil micronutrient values based on the results of the DTPA test (Barrett et al., 2017), are presented in Table 1.

Table 1. Recommended micronutrient concentration values in soil (mg/kg) based on the DTPA test (Barrett et al., 2017)

Metal	Very low	Low	Medium	High	Very high
Cu	0–0.3	0.3–0.8	0.9–1.2	1.3–2.5	>2.5
Fe	0–5	6–10	11–16	17–25	>25
Mn	0–4	5–8	9–12	13–30	>30
Zn	0–0.5	0.5–1.0	1.1–3.0	3.1–6.0	>6.0

The concentrations of available Fe (82.6 mg/g), Mn (56.3 mg/g), and Cu (47.2 mg/g) can be classified as very high in the control soil, and the bioavailability of Zn (2.9 mg/g) can be labeled as medium level. The bioavailability of Fe and Mn is commonly increased in acidic soils, while a very high level of bioavailable Cu signifies its anthropogenic input through mining and industrial activities in the vicinity of the sampling site. The DTPA extracted concentration of potentially toxic and toxic metals was generally low, highest for Pb (2.34 mg/kg), followed by Ni (1.74 mg/kg), Co (0.205 mg/kg), and Cd (0.177 mg/kg). These results agree with analyses of pseudo-total concentrations of trace elements in the soil (Egerić et al., 2019), showing that only Cu concentration was elevated (219.2 mg/kg) and above the remediation value (190 mg/kg) prescribed by Serbian legislation.

Statistically significant differences in the bioavailability of the investigated metals were detected between the control and treated soils, and the applied doses of SW had different effects on the availability of individual metals (Figure 1). Even after applying 0.15% SW, a significant reduction in the bioavailability of all elements, except for Zn, was observed. Generally, no significant differences in the bioavailability of essential micronutrients and other tested metals were found between the SW2 and SW5 samples.

Applying SW in all treatment variants did not decrease the bioavailability of microelements below the levels critical for plant growth and development. The SW dose had the greatest impact on the concentration of available Mn. According to Table 1, after the application of 0.15% and 0.3% SW, the concentration of available Mn was high and reached medium and low levels with a further SW dose increase (2% and 5%). Considering all treatments, Fe and Cu bioavailable concentrations remained very high. It is crucial to consider that these values are recommendations, which may not be in accordance with the actual requirements of specific crops, because the need for micronutrients depends on the type of crop, expected yield, pH value, and other soil properties (Barrett et al., 2017). For instance, bioavailable concentrations (DTPA test) over 50 mg/kg were found to reduce the dry matter yield of several vegetables (Yang et al., 2022). Finally, in all samples, the DTPA-extracted concentrations of Zn remained within the range of medium availability.

The bioavailability of other investigated metals, Pb, Cd, Co, and Ni, was simultaneously reduced by SW treatments (Figure 1), maximally by 33 % for Cd, 58 % for Pb, 70 % for Ni, and even 93 % for Co, at the highest SW dose of 5 %. The SW treatments induced changes in soil agrochemical attributes (Egerić et al., 2019). The descriptive statistics of selected essential properties are shown in Table 2. According to coefficients of variation, the addition of various amounts of SW most affected (i.e., increased) the content of carbonate, electrical conductivity (EC), the content of available phosphorus, organic carbon, and soil pH, while the total nitrogen content and cation exchange capacity (CEC) were least affected.

Table 2. Descriptive statistics of agrochemical properties of control and amended soil samples (Egerić et al., 2019)

Variable	Mean	Standard Deviation	Coefficient of variation	Minimum	Maximum
CaCO3 (%)	1.89	2.55	134.72	0.00	6.09
CEC (meq/100g)	11.58	0.172	1.48	11.40	11.85
Ntotal (%)	0.172	0.003	2.22	0.168	0.177
Corganic (%)	1.768	0.310	17.55	1.479	2.279
Available P (mgP2O5/100g)	4.210	1.102	26.17	2.880	5.400
pH	6.482	1.110	17.13	4.930	7.650
EC (dS/m)	0.684	0.314	45.94	0.378	1.122

The association between extracted metal concentrations and soil properties was analyzed using Pearson's correlation test (Table 3). A significant ($p < .05$) negative correlation has been observed between soil pH and metal bioavailability, which is in agreement with previous findings in the literature (Fageria et al., 2002). The EC exhibited a statistically significant ($p < .05$) negative correlation with the concentrations of Cu, Zn, and Fe in the DTPA extract. This can be attributed to the influence of the SW dose, which leads to an increase in soil pH and EC. Also, the bioavailability of Cu and Zn demonstrated a significant ($p < .05$) negative correlation with carbonate and organic carbon content.

Table 3. The Pearson's correlation coefficient between the agrochemical properties of soil samples and bioavailable concentrations of the investigated metals determined by DTPA extraction

Metal	$CaCO_3$	CEC	N_{total}	$C_{organic}$	Available P	pH	EC
Cu	–0.909*	–0.055	0.338	–0.928*	–0.858	–0.985*	–0.888*
Zn	–0.907*	0.170	0.550	–0.887*	–0.980**	–0.897*	–0.915*
Fe	–0.820	–0.044	0.183	–0.852	–0.830	–1.000*	–0.914*
Mn	–0.708	–0.082	–0.034	–0.770	–0.697	–0.974*	–0.830
Ni	–0.704	–0.008	–0.016	–0.762	–0.740	–0.977*	–0.858
Pb	–0.747	–0.126	0.027	–0.800	–0.719	–0.986*	–0.852
Co	–0.586	–0.127	–0.215	–0.670	–0.548	–0.911*	–0.720
Cd	–0.735	–0.297	0.012	–0.787	–0.632	–0.958*	–0.806

Note. $*p < .05$, $** p < .01$

Soils with high $CaCO_3$ content generally exhibit lower bioavailability of micronutrients (Chatzistathis, 2014). On the other hand, depending on the total content and composition, organic matter can have different effects on the mobility and bioavailability of micronutrients. The high affinity of Cu to the organic phase of the soil often leads to reduced bioavailability of this essential element, attributed to either the formation of insoluble organometallic complexes or soluble complexes, but difficult to uptake by plants (Fageria et al., 2002). A significant negative correlation ($p < .01$) was also found between bioavailable Zn and accessible phosphorus content. This indicates that in case of fertilizing the soil with phosphate fertilizers, the amount of bioavailable Zn potentially can be reduced below the concentrations critical for plants growth and development.

3. Conclusion

The application of waste seashells for improving soil pH and agrochemical properties affected the bioavailability of investigated elements. After the treatment with SW, and with SW dose increase, a decrease in the concentrations of all investigated elements in the DTPA extract was observed, indicating the suitability of using this additive to treat multiple metal contamination. The increase in soil pH value is the most significant factor affecting the immobilization of metals. The results indicate that selecting the amount of SW for treating a certain acidic soil must consider the bioavailability tests of essential elements. Adding 2% of SW was best for investigated soil, as a further increase in SW amount did not significantly reduce the bioavailable Cu fraction while affecting the excessive reduction of bioavailable Mn. Applying seashells with other amendments could improve Cu-immobilization capacity, thus, such an approach deserves further attention.

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References

Barrett, W., Jones, N., Chu, P., Pohlman, K., Coleman, G., Poole, H., Goff, D., Spiva, C., Griffith, L., Zwiep, J., & Hohla, J. (2017). *Agronomy Handbook. Soil and Plant Analysis Resource Handbook*. Midwest Laboratories, INC.

Barros, M. C., Bello, P. M., Bao, M., & Torrado, J. J. (2009). From waste to commodity: transforming shells into high purity calcium carbonate. *Journal of Cleaner Production*, 17, 400–407. https://doi.org/10.1016/j.jclepro.2008.08.013

Chatzistathis, T. (2014). *Micronutrient Deficiency in Soils and Plants*. Bentham Science Publishers. https://benthamscience.com/ebook_volume/1540

Egerić, M., Smičiklas, I., Dojčinović, B., Sikirić, B., Jović, M., Šljivić-Ivanović, M., & Čakmak, D. (2019). Interactions of acidic soil near copper mining and smelting complex and waste-derived alkaline additives. *Geoderma, 352*, 241–250. https://doi.org/10.1016/j.geoderma.2019.06.015

Egerić, M., Smičiklas, I., Mraković, A., Jović, M., Šljivić-Ivanović, M., Antanasijević, D., & Ristić, M. (2017). Experimental and theoretical consideration of the factors influencing cationic pollutants retention by seashell waste. *Journal of Chemical Technology and Biotechnology, 93*(5), 1477–1487. https://doi.org/10.1002/jctb.5516

Fageria, N. K., Baligar, C., & Clark, R. B. (2002). Micronutrients in Crop Production. *Advances in Agronomy, 77*, 185–268. https://doi.org/10.1016/s0065-2113(02)77015-6

International Organization for Standardization (2001). S*oil quality — Extraction of trace elements by buffered DTPA solution* (ISO Standard No. 14870:2001). https://www.iso.org/standard/25232.html

Jović, M., Mandić, M., Šljivić-Ivanović, M., & Smičiklas, I. (2019). Recent trends in application of shell waste from mariculture. *Studia Marina, 32*(1), 47–62. http://www.studiamarina.ac.me/pdf/32/Recent%20trends%20in%20application%20of%20shell%20waste%20from%20mariculture.pdf

Palansooriya, K. N., Shaheen, S. M., Chen, S. S., Tsang, D. C. W., Hashimoto, Y., Hou, D., Bolan, N. S., Rinklebe, J., & Ok, Y. S. (2020). Soil amendments for immobilization of potentially toxic elements in contaminated soils: A critical review. *Environment International*, *134*, Article 105046. https://doi.org/10.1016/j.envint.2019.105046

Santás-Miguel, V., Campillo-Cora, C., Núñez-Delgado, A., Fernández-Calviño, D., & Arias-Estévez, M. (2022). Utilization of mussel shell to remediate soils polluted with heavy metals. In I. Anastopoulos, E. C. Lima, L. Meili, & D. A. Giannakoudakis (Eds.), *Biomass-Derived Materials for Environmental Applications* (pp. 221–242). Elsevier. https://www.sciencedirect.com/book/9780323919142/biomass-derived-materials-for-environmental-applications

Yang, X.-E., Long, X.-X., Ni, W.-Z., Ye, Z.-Q., He, Z.-L., Stoffella, P.-J., & Calvert, D.-V. (2002). Assessing copper thresholds for phytotoxicity and potential dietary toxicity in selected vegetable crops. *Journal of Environmental Science and Health B*, *37*(6), 625–635. https://www.tandfonline.com/doi/abs/10.1081/PFC-120015443

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