RESPONSE TO REVIEWER COMMENTS ON MANUSCRIPT: Comparative efficacy of individually and combined application of compost, biochar, and bentonite on Ni dynamics in a calcareous soil Egusphere-2025-2147

The authors would like to thank anonymous reviewer for time, invaluable comments and suggestions for substantially improving this manuscript. Please find detailed responses to each comment below.

ALL CHANGES ARE INDICATED IN GREEN HIGHLIGHT IN THE REVISED MANUSCRIPT

ANONYMOUS REFEREE #1

General comments

The study titled "Com*arative efficacy of individually and combined application of compost, biochar, and bentonite on Ni dynamics in a calcareous soil"* evaluates the effectiveness of various soil amendments in reducing nickel (Ni) availability in a calcareous soil from Iran. Overall, the study is well-designed, and the results are clearly presented and thoughtfully discussed. While the topic is not entirely novel, it remains relevant, particularly in exploring the effectiveness of these specific amendments across different soil types and characteristics.

That said, the manuscript requires further revision before it can be considered for publication.

1.One of my main concerns is the selection of a calcareous soil, which is inherently high in pH. It is well established that pH is a major factor influencing metal availability in soils, and under alkaline conditions, metal solubility is generally very low. Therefore, the rationale behind selecting a soil type where Ni availability would not typically pose a significant problem should be clarified. Why was this specific soil chosen for the study?

Authors' response: We sincerely thank the reviewer for their insightful and valuable feedback regarding the selection of a calcareous soil for our study. The choice of a calcareous soil was driven by the specific objectives of our study, which aimed to investigate Ni dynamics in a context representative of agricultural soils of Iran where calcareous soils predominate. Calcareous soils, characterized by high calcium carbonate content and alkaline pH, are widespread in many arid and semi-arid climates, covering approximately 30% of global agricultural lands. Anthropogenic activities (e.g., industrial discharge, application of contaminated biosolids or fertilizers, mining) can lead to significant Ni accumulation in these soils. Although the immediate risk may be low, the long-term environmental fate and "latent" risk are critical assessment endpoints. Furthermore, Calcareous soils provide a rigorous testbed for an immobilizing amendment. If an amendment can further reduce the already low extractable pools of Ni or transform it into more stable phases (e.g., promoting formation of distinct Ni precipitates rather than just relying on adsorption at high pH), it demonstrates a robust and potentially superior remediation mechanism. This is a more challenging scenario than immobilizing metals in an acidic soil where simple pH elevation often has a dramatic effect. Success here suggests the amendment could be effective across a wider range of pH conditions. To address the reviewer's concern, we propose to enhance the clarity of our rationale in the revised manuscript by adding the following text to the Materials and Methods section (2.1.):

"The selection of a calcareous soil for this study was motivated by its prevalence in agricultural soils of Iran and the need to address a knowledge gap regarding Ni dynamics in high-pH environments. Contrary to the well-established principle that high pH reduces metal solubility, recent studies suggest that specific pedogenic factors and anthropogenic contamination may facilitate increased Ni mobilization in calcareous soils (Shahbazi et al., 2022)″

2.Additionally, to better contextualize the work, it would be helpful to include the threshold values for Ni contamination in Iranian soils. This information would provide a clearer understanding of the extent to which the applied treatments are potentially effective or relevant.

Authors' response: We thank the referee for this insightful and constructive comment. We have added the threshold value for Ni contamination in Iranian soils within the introduction section. Please see the revised manuscript.

The threshold value for Ni contamination in Iranian soils is 110 mg kg^{-1} soil (Shahbazi et al., 2020).

3.Regarding the non-contaminated soil used in the study, I believe it is not appropriate to assess the effectiveness of the amendments in such a context. When Ni concentrations are already very low, the changes induced by treatments may be below quantifiable limits, and the results could be unreliable. I recommend removing these results from the text. Please include the quantification and detection limits for Ni used in the analytical methods section.

Authors' response: The detection limit for Ni quantification using a PG990 AAS in flame mode (Air/Acetylene) is 3.0 μg L^{-1} (ppb) under optimized analytical conditions. In the non-contaminated soil sample, the total Ni concentration was measured at 38 mg kg^{-1}, while the WsEx fraction contained 6.75 mg kg^{-1}. Consequently, the concentrations of Ni across all measured chemical fractions were found to be orders of magnitude above the instrumental detection limit, thereby confirming the suitability of the PG990 AAS for reliable quantification in this study. We have added the detection limits for Ni used in the analytical methods section.

2.8.4 *Detection limits and precision*

The detection limit for Ni with the PG990 in flame mode was ~3 μg L^{-1} under optimized conditions. Analytical precision was verified by duplicate sample runs, with relative standard deviations (RSDs) consistently below 5%.

Specific comments:

4.In the Materials and Methods section (2.5), please provide detailed steps and reagents used for the sequential extraction procedure**.** Given that the residual fraction is frequently discussed in the manuscript as a potential sink for metal removal, it would be valuable to elaborate on its potential composition and significance. In particular, please address the plausibility of metals being incorporated into mineral phases (which are the typically implied when referring to the residual phase) within a two-month period.

Authors' response: thanks for your excellent suggestion. We have added a Table in the Materials and Methods section (2.5) for providing detailed steps and reagents used for the sequential extraction procedure. We have also expanded the Discussion to include a more detailed examination of the composition and environmental significance of the Residual fraction, as now detailed in the revised manuscript.

Table 2. Sequential extraction procedure (Salbu and Krekling, 1998).

Fractions	Reagent	Agitation time
Soluble+exchangeable (WsEx)	20 mL of 1 M NH_4OAc (pH=7)	2 h
Carbonate-bound (Car)	20 mL of 1 M NH_4OAc (pH=5)	2 h

FeMnOxide-bound (FeMnOx)	20 mL of 0.04 M NH_2OH. HCl in 25 % (v/v) CH_3COOH	6 h at 60˚C
Organic-bound (OM)	15 mL of 30 % (v/v) H_2O_2 (pH=2, HNO_3)	5.5 h at 80˚C (on water bath)
	and after cooling, 5 mL of 3.2 M NH_4OAc in 20 % (v/v) HNO_3	30 min
Residual-bound (Res)	Calculated by subtracting the sum of four fractions from total Pb	

The Res fraction, which incorporates metals within the crystal lattice of primary and secondary minerals (e.g., feldspars, micas, phosphates) and resistant minerals (zircon and rutile) (Shen et al., 2022), represents the most stable and geochemically inert pool. Its increase signifies a transition from bioavailable forms to a long-term sink, drastically reducing ecological risk through immobilization within a three-month incubation period (Boostani et al., 2024b).

5.Lines 385–387: The metal-phosphate fraction should not be classified as part of the residual fraction. Please revise this categorization.

Authors' response: We thank the reviewer for this valuable comment. In many schemes, Ni–phosphate precipitates are classified as a specific fraction (e.g., metal-phosphate) or included in the residual fraction if tightly bound in mineral lattices. In the present study, there was a positive and significant correlation between residual fraction and Olsen-P. Due to this, we prefer to classify it as residual fraction.

6.Lines 351–352 and 358–359: Biochar contributes carbon, but not organic matter per se. This distinction should be corrected.

Authors' response: We thank the reviewer for this insightful comment. The referee is correct to highlight the important technical distinction between carbon and organic matter. We have corrected the manuscript to clarify. Please see the revised manuscript.

7.To avoid confusion, consider changing the abbreviation "B" used for either biochar or bentonite in the treatment labels. Using the same letter for both may lead to misinterpretation.

Authors' response: We thank the referee for this helpful suggestion. We have revised the manuscript to use 'R' for biochar and 'B' for bentonite in all treatment labels and text to avoid any potential confusion. Please see the revised manuscript.

8.In all tables, there appears to be an extra row and an extra column without titles. Please clarify their meaning or remove them if they are not necessary. In addition, it is unclear what the comparisons indicated by capital letters and lowercase letters represent.

Authors' response: We sincerely thank the referee for their careful review and for identifying this lack of clarifications. We have now revised all tables in the manuscript to address both points. Please see the revised manuscript.

10.Include standard deviation in tables and graphs

Authors' response: We thank the referee for this important comment. We have now included the standard deviation values for all data in Tables (3, 4, 5, 6, 7). Furthermore, error bars representing the standard deviation have been added to all relevant figures (Figures 4). These changes provide a clear indication of data variability throughout the manuscript. Please see the revised manuscript.

11.Figure 5 requires revision to enhance clarity and interpretability. I recommend applying a consistent color palette or uniform symbols across treatments or Ni doses to facilitate direct comparison. Additionally, it would be beneficial to present, within the same figure, a series of smaller panels depicting the kinetics by treatment group (or by Ni level group)

Authors' response: We thank the referee for this excellent suggestion. To enhance interpretability, Figure 5 was reconfigured into a series of panels grouped by treatment, each showing the kinetic data for all Ni doses. Uniform axis scales were maintained across all panels to ensure comparability. Please see the revised manuscript.

12.Finally, please include some discussion about the fact that these results are obtained from an artificially contaminated soil, and those could change with a field contaminated soil.

Authors' response: We thank the reviewer for this important comment. We fully agree that results from artificially contaminated soil can differ from those in field-contaminated soils, and we have now included a concise discussion on this point within the revised manuscript (and conclusion sections).

The End of discussion….

//The use of an artificially contaminated soil was a necessary step to establish clear cause-effect relationships under controlled conditions, isolating the variables of interest (e.g., contaminant concentration and type of treatments) from the complex confounding factors present in the field. However, we acknowledge that historically contaminated field soils often exhibit reduced bioavailability and different sequestration patterns, which can influence remediation efficacy//.

The End of conclusion…

// It is also suggested that Ni immobilization efficacy by these amendments must be evaluated via using a broader range of historically contaminated soil types under plant cultivation //