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Effect of Soil Texture, Nanoparticle Size, and Incubation Period on the Dissolution of ZnO Nanoparticles

Wajid Umar [1],* , **Imre Czinkota [1]**, **Miklós Gulyás [1],***, **Muhammad Ashar Ayub [2]** , **András Sebők [1]**, **Muhammad Yousaf Nadeem [3]** and **Muhammad Arslan Zulfiqar [4]**

[1] Institute of Environmental Science, Hungarian University of Agriculture and Life Sciences, 2100 Gödöllő, Hungary

[2] Institute of Agro-Industry and Environment, Faculty of Agriculture and Environment, The Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan

[3] College of Agronomy, Nanjing Agricultural University, Nanjing 210095, China

[4] Faculty of Agriculture, Hungarian University of Agriculture and Life Sciences, 2100 Gödöllő, Hungary

* Correspondence: wajidumar30@gmail.com (W.U.); gulyas.miklos@uni-mate.hu (M.G.);
   Tel.: +36-70-5536937 (W.U.)

Abstract: Zinc is an essential plant and human nutrient and its primary source is Zn-rich food consumption. The only way to enrich plants with Zn is through the application of Zn fertilizers including various chemical and organic sources of ZnO nanoparticles (NPs). The Zn bioavailability from ZnO NPs must be considered for their recommendation as a fertilizer, and very little is known about the efficacy of such fertilizers in the Hungarian soil environment. In the present investigation, we prepared ZnO NPs of different sizes and applied them in two distinct textures of soils (sandy loam (SL) and silty clay (SC)) in an incubation experiment. The prepared ZnO NPs were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). ZnO NPs were applied in both soil types at 500 mg L^{-1} in the form of a suspension, and $ZnSO_4$ was applied in the form of a solution. The soils were incubated for 7 and 14 days. Column leaching was performed to analyze the dissolved Zn. Retained Zn in the soil matrix was extracted using 0.05 M EDTA. The results showed that approximately 21–23% and 10–13% higher Zn was observed in the pore water of SL and SC soils, respectively, when spiked with small-sized NPs compared to large-sized NPs, while 14–26% higher dissolved Zn was observed in SL soil compared to SC soil. It is concluded that the size of NPs and the soil texture are the main factors that play important roles in deciding the fate of NPs under an alkaline soil environment.

Keywords: ZnO nanoparticles; dissolution; fate; soil texture; leaching; metal pollution

1. Introduction

Engineered nanoparticles (ENPs) have recently risen to favor for use in agriculture and other fields because of their novel properties [1–3]. The World Bank and Food and Agriculture Organization (FAO) are taking steps to promote their use in the agriculture sector [4]. Such activities may lead to an upsurge in the use of NPs in the agriculture sector, which will ultimately increase the concentration of engineered NPs in agricultural soils [5]. Currently, the usage of NPs as nano-fertilizers, nano-pesticides, and nano-herbicides is on the rise [6]. However, along with the rapid advancement in the utilization of NPs in agriculture, there is increasing concern about their mobility, transportation, and fate in the soil system.

Zinc is considered one of the most important micronutrients for crop plants because it is part of their structural components and also acts as a co-factor for several proteins and enzymes [1,7]. The use efficiency of Zn is very low under alkaline calcareous soils due to its low solubility and higher fixation and precipitation with calcium carbonate [7–9]. The use of ZnO NPs as a micronutrient nano-fertilizer has been increasing in recent times

because of their unmatched properties such as high reactivity, high specific surface area, high charge density, and solubility [7,10]. The solubility and bioavailability of ZnO NPs also depend on the size of NPs. It was reported that smaller-sized ZnO NPs have higher reactivity, solubility, and bioavailability compared to bulky materials [11,12]. Along with their beneficial aspects, several studies have reported the toxic behavior of ZnO NPs in living organisms [2,13–15]. In a recent study, Shah et al. [16] evaluated the effect of ZnO NPs and iron NPs on soil bacterial and fungal communities. They observed that the application of iron NPs and ZnO NPs along with poultry manure significantly decreased the CFU of bacteria and fungi. They also stated that application of NPs along with organic manure significantly reduced the nitrogen mineralization, which ultimately had a negative impact on the plant growth. Based on the potential of ZnO NPs as a soil contaminant, there is a dire need to determine the mobility, transport, fate, and dissolution behavior of ZnO NPs in different soils.

Different soil types possess different soil properties based on their mineral composition and other factors. Transformation of ZnO NPs in soil decides the outcome: aggregation, fixation/stabilization, or dissolution [17,18]. That transformation mainly depends on soil properties and ZnO NPs' physico-chemical characteristics. One of the most important parameters determining the destination of ZnO NPs in the soil is pH. A higher pH of the soil reduces the Zn bioavailability. Different soil parts such as Al/Fe oxyhydroxide, clay aluminosilicates, and organic ligands contain hydroxyl groups, and the deprotonation of those hydroxyl groups leads to an increase in the pH of the soil and increase in the retention of Zn [19,20]. Higher soil pH also leads to the precipitation of Zn ions into less soluble minerals such as Zn phosphates, carbonates, and hydroxides. Similarly, soil pH also significantly affects the behavior of ZnO NPs [20]. Aggregation of NPs increases when the pH reaches the point of zero charges (PZC). After that, a pH higher than the PZC leads to increased stability of NP colloids in soil solution due to a higher negative charge on the surfaces of NPs [21]. Few studies are reporting the behavior of NPs in the soil environment [2,22], but it is imperative to evaluate the behavior of ZnO NPs, their destination, and the dissolution potential in different soil types. Recently, Wu et al. [12] evaluated the solubility and destination of ZnO NPs in two different minerals (geothite and γ-Al$_2$O$_3$). They reported that the solubility of ZnO NPs was higher in γ-Al$_2$O$_3$ compared to goethite. They also observed that the NPs were highly soluble at a lower pH compared to a higher pH. Similarly, Wang et al. [17] also evaluated the fate of ZnO NPs in the soil and reported that ZnO NPs disappear even after a short period of application. They concluded that after application, the majority of the ZnO NPs converted to the Zn^{+2} form. Most of the dissolution studies of ZnO NPs were conducted in different liquid media, or generally, in soil, considering the factors such as soil pH, long-term incubation, dissolved organic matter, etc. In this study, we focused on the soil texture and collected soil of two extremes, one with low clay contents and the other with very high clay contents, taken from two different regions of Hungary. We also evaluated the interactive effect of soil texture with the size of ZnO NPs on the soil water solubility of NPs. This is a first-of-its-kind study in Hungarian soil and provides a foundation for future advanced research in Hungary by characterizing the basic behavior of ZnO NPs in Hungarian soils.

This study particularly aimed to:

- Evaluate the effect of different textures (high clay and low clay) on the pore water solubility of ZnO NPs.
- Evaluate the role of the size of NPs on the soluble fraction of Zn.
- Evaluate the effect of the incubation period on the leached amount of Zn.

2. Material and Methods

2.1. Chemicals

All the chemicals utilized were of the highest analytical quality. Potassium hydroxide (KOH), zinc sulfate (ZnSO$_4$), and ethylene diamine tetra acetic acid (EDTA 99.9%) were

purchased for RENAL laboratories, Budapest, Hungary. Nitric acid (HNO_3 65%) and hydrochloric acid (HCl 37%) were obtained from Molar Chemicals, Budapest, Hungary.

2.2. Synthesis of ZnO NPs and Characterization

2.2.1. Small-Sized NPs

ZnO NPs of different sizes were prepared using the precipitation method. The methodology proposed by He et al. [23] was used to prepare smaller-sized NPs with slight modifications. According to the given method, 0.2 M solutions of $ZnSO_4$ and KOH were prepared. The solution of KOH was mixed drop-by-drop into the $ZnSO_4$ solution under stirring using a magnetic shaker (BIG SQUID, IKA-WERKE, GmbH and Co., Staufen, Germany). After that, the mixed solution was stirred for another 3 h and left standing for 24 h, followed by filtration using Whatman No. 42 filter paper. Then, d.H_2O and ethanol were used to wash the precipitates to remove the impurities. The washed precipitates were dried at 80 °C in an oven (LABOR-MIX, LP-321, Budapest, Hungary) and ground into powder form. Calcination of the ground powder was carried out in a furnace at 250 °C (LABOR-MIX, LR-202, Budapest, Hungary), and after that, the calcined precipitates were ground again into fine powder.

2.2.2. Large-Sized NPs

Larger-sized NPs were obtained from a 0.5 M concentration of $ZnSO_4$ and 0.4 M concentration of KOH. Similar to the above-mentioned method, the solutions of $ZnSO_4$ and KOH were shaken together for 3 h, followed by filtration, drying, calcination, and grinding.

The synthesized ZnO NPs were then characterized with the help of an X-ray diffraction (XRD) technique (Rigaku Ultima IV X-Ray Diffractometer) for crystal size analysis. The instrument was equipped with Cuα as the source of radiation, Bragg–Brentano geometry, and a monochromator of graphite. The analyses of samples were carried out at 50 kV/40 mA from 3 to 80° 2θ. A HITACHI S-4700 Field Emission-Scanning Electron Microscope was used to analyze the morphology of ZnO NPs.

2.2.3. Crystal Size Calculation of NPs

The crystal size of the NPs was calculated using software that worked based on the Scherrer equation:

$$L = \frac{K\lambda}{\beta cos\theta}$$

In this equation, L represents the main dimension of the crystallite (in nanometers or Angstrom) along a line to the reflecting plane. λ is the wavelength applied, K is the Scherrer constant (0.89–0.94), and β is the peak width calculated from the middle of the peak, normally expressed in radians of *2θ*, which is also known as the Bragg angle. The peak widths of the samples were corrected by calculating the peak width of the standard sample as the instrumental broadening at half the maximum correction curve.

2.3. Sampling and Characterization of Soil

Two types of soils, sandy loam (SL) (Gödöllő Szárítópuszta, Hungary 47°34′41.8″ N 19°24′11.6″ E) and silty clay (SC) (Atkár, Hungary 47°42′24.5″ N 19°54′35.6″ E), were used in this study. The samples were taken from a depth of 0–15 cm during 2019–20 for SL and during 2021 for SC. The soil samples were stored at room temperature followed by homogenization, drying, and then grinding. Before use, soil samples were sieved through a 2 mm sieve. The physico-chemical properties of both of the soils are listed in Table 1. Briefly, the SL soil possessed following characteristics: EC 0.0634 dS m^{-1}, pH 8.80, $CaCO_3$ 7.76%, CEC 14.6 cmol$^+$ kg^{-1}, organic matter 0.61%, P 170 mg kg^{-1}, and Zn 1.26 mg kg^{-1}. The physico-chemical characteristics of SC soil were as follows: EC 0.095 dS m^{-1}, pH 7.91, exchangeable Ca 26.75 cmol$^+$ kg^{-1}, CEC 40.1 cmol$^+$ kg^{-1}, organic matter 4.90%, P 23.75 mg kg^{-1}, and Zn 2.31 mg kg^{-1}.

Table 1. Physico-chemical characteristics of sandy loam (SL) and silty clay (SC) soils.

Elements	Units	SL	SC
pH		7.10	8.80
EC	dS/m	0.0634	0.095
CEC	cmol$^+$/kg	14.6	40.1
Exch. Ca	cmol$^+$/kg		26.75
CaCO$_3$	%	7.76	
OM	%	0.61	4.90
Sand	%	65	3
Silt	%	25	45.05
Clay	%	10	51.95
Textural class		Sandy loam	Silty Clay
P	mg kg^{-1}	170	23.75
Zn	mg kg^{-1}	1.26	2.31

2.4. Spiking of Soil with ZnO NPs

Briefly, 200 g of dried and sieved soil was weighed in plastic pots, and each replication contained a separate pot with 200 g of soil. The ZnO NPs (smaller-sized and larger-sized) and conventional ZnSO$_4$ were added in the form of suspension with a Zn concentration of 500 mg L^{-1}, where 30 mL of suspension volume was added to each pot. To prepare the suspensions, the required quantity of powdered NPs and the ZnSO$_4$ salt were weighed and sonicated in d.H$_2$O for 10 min using a sonication bath (Elma TRANSSONIC T460, Singen, Germany). The NP suspension was completely mixed with soil using a spatula. The water level in the soil was kept at 80% of the field capacity. The weights of the samples were noted and distilled water was added according to the requirement. All the containers were covered with aluminum foil and several holes were made in the aluminum foil for air exchange. The spiked soil was incubated for 7 or 14 days. The soil samples without NP spiking were used as control treatments. At the end of the incubation period, soil samples were crushed, ground, and homogenized for leaching. The experiment was repeated thrice.

2.5. Leaching of Spiked Soil

Leaching of dissolved Zn and ZnO NPs was carried out using a steel column attached with an isocratic pump (ECOM, KAPPA 10, Prague, Czech Republic), with the following specifications: length of column 24 cm, width of column 2.2 cm, and volume 91 mL. The setup of the leaching system is given in Figure 1. The eluent volume required to leach the NPs was pre-optimized. Around 130 g of NP spiked soil was placed in the column and the bottom and upper caps were tightened. The bottom and upper caps included a spacer and there was an inbuilt filter in the upper cap of the column. The water was pumped from the bottom of the column to achieve full saturation of the soil with a flow rate of 1 mL per minute. The elute was collected from the upper outlet (5 mL each), for analysis of the Zn concentration, using an atomic absorption spectrophotometer (AAS) (Perkin Elmer 300, USA). For each sample, a total of 40 mL of elute was collected. Leaching was carried out in triplicate.
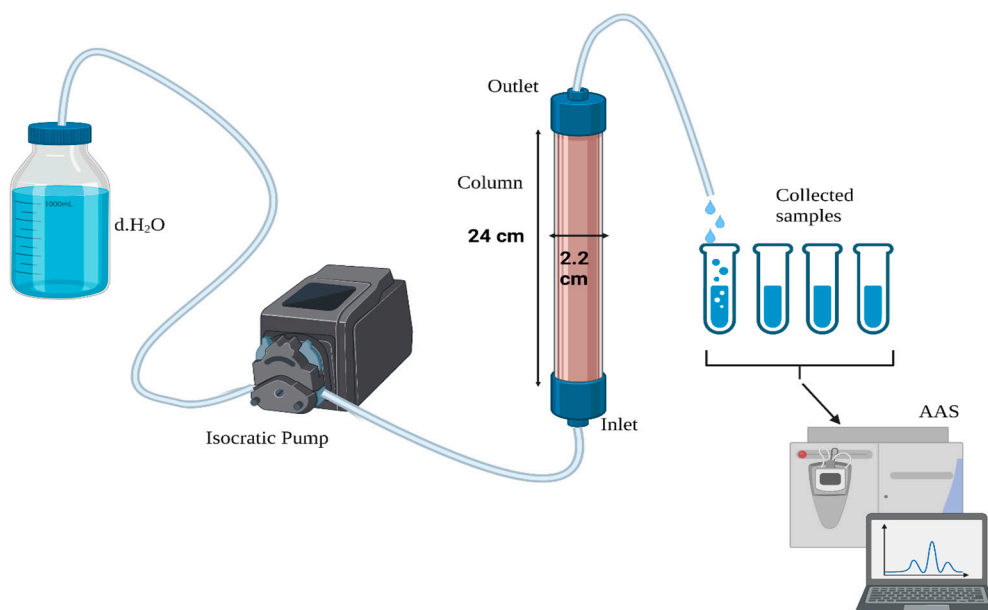
Figure 1. Schematic illustration of the leaching process.

2.6. Extraction of Zn Retained in Soil Matrix

To extract the Zn contents retained in the soil matrix, 0.05 M EDTA was used. The soil was extracted following a weight-to-volume ratio of 1:10 [24].

In 50 mL tubes, 3 g of soil was weighed and 30 mL of 0.05 M EDTA solution was added. The tubes were capped and shaken for 2 h on a rotating shaker at room temperature. After shaking, the samples were centrifuged at 5000 rpm followed by filtration using Whatman No. 42 filter paper. The extraction of each sample was carried out in three replications. The extractant samples were then analyzed on AAS.

2.7. Analysis of Leachate

The collected samples of leachates were centrifuged at 5000 rpm for 35 min at room temperature for the separation of leached ZnO NPs. After centrifugation, the samples were filtered using 0.20 μm PTFE syringe filters (DURAN, Germany). A few drops of concentrated HNO_3 were added to each filtered sample and analyzed on AAS.

2.8. Statistical Analysis

We used Microsoft Excel for storing and handling the data. Statistical analysis and data visualization were performed using R software. The packages used in R software were as follows: "Tidyverse/dplyr/tidyR" for data wrangling and transformation, "aov" and "tukeyHSD" base functions for ANOVA and mean comparison, and "ggplot2" for data visualization.

3. Results and Discussion

3.1. Characterization of ZnO NPs

The mobility, fate, and dissolution of NPs are of the major concerns nowadays due to their increased use in different sectors, e.g., as nano-fertilizers, nano-pesticides, and nano-herbicides in agriculture.

SEM and XRD were used for morphological and crystal size characterization of ZnO NPs (Figures 2 and 3). The results revealed that the small-sized NPs were variable in shape and mostly appeared rectangular. On the other hand, large-sized NPs appeared round to rectangular. The mean crystal sizes of the small- and large-sized NPs were around 31 ± 7 nm and 140 ± 39 nm respectively. The XRD peaks at planes (101), (102), (110), (002), (100), (103), (201), and (112) testified to ZnO's presence in the form of NPs. It was also noted

that smaller-sized ZnO NPs appeared in aggregated form. Aggregation is quicker for them than for larger-sized NPs because the Brownian motion of smaller-sized NPs is greater than that of large-sized particles due to excessive collision between the particles [22,25]. Similar findings were also stated by Tso et al. [26], who observed that smaller-sized ZnO NPs aggregated quickly into micrometer-scale aggregates. In the present study, we prepared large-sized NPs by increasing the molar concentration of Zn salt while keeping the molar concentration of precipitating agent constant. The synthesis of ZnO NPs of larger size might occur due to the increased ratio of Zn^{+2}/OH^-. Since there were reduced OH^- ions, the attraction of Zn^{+2} was reduced toward negative charges, resulting in the development of larger-sized aggregates [27]. Similar results were also presented by Smolkova et al. [28], who reported that an increase in the size of ZnO NPs in the last stage of the reaction was caused by incomplete consumption of Zn salt. Such incomplete consumption of Zn salt might be due to the low molar ratio of precipitating agent.
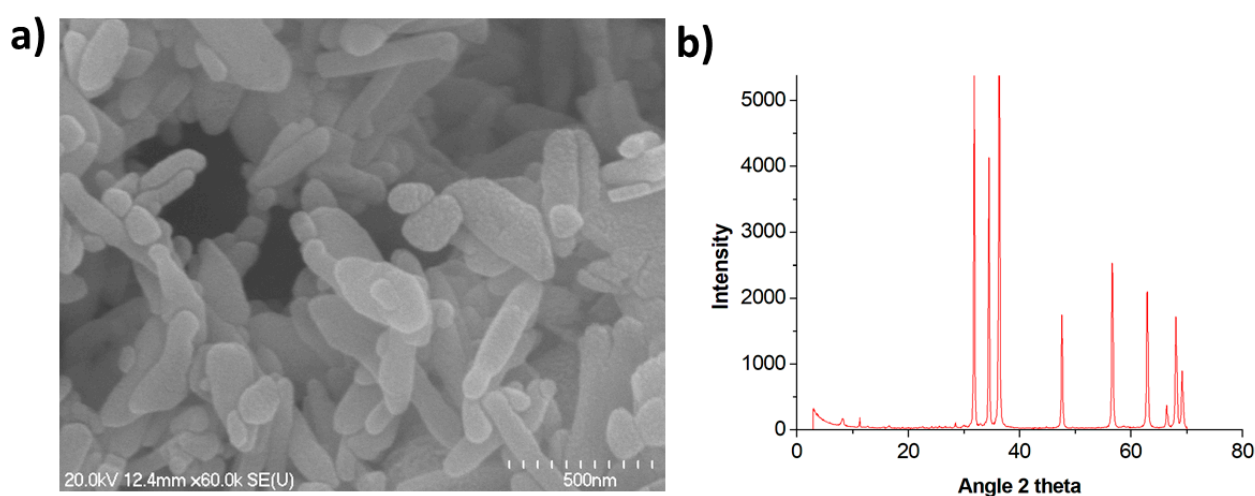

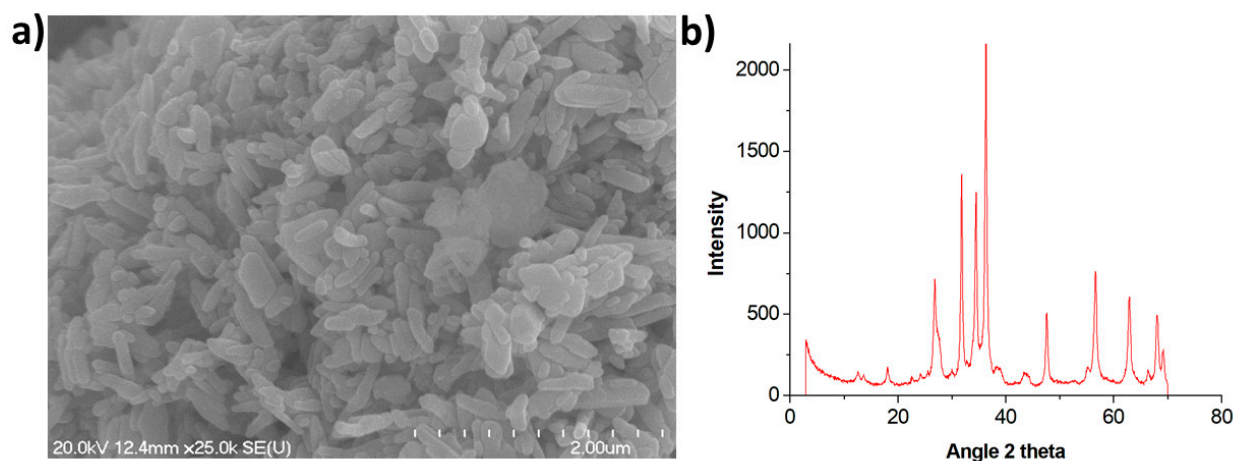**Figure 2.** Characterization of small-sized (31 ± 7 nm) NPs: (**a**) SEM, (**b**) XRD.

Figure 3. Characterization of large-sized NPs (140 ± 39 nm): (**a**) SEM, (**b**) XRD.

3.2. Zn Concentration in ZnO NP Spiked Soil Leachates

Based on the analysis of soil leachates, elution curves were prepared (Figures 4 and 5) for both soil types. The concentration of Zn in elution curves was presented after subtracting the Zn concentration obtained in control treatments (without Zn spiking). It was noted that the amount of soluble Zn in pore water was reduced significantly ($p < 0.05$) over time. Maximum pore water Zn was analyzed in the first 5 mL of the elute followed by continuous

reduction in the Zn concentration. The maximum concentration of Zn in pore water was measured in ZnSO$_4$ spiked soil followed by NP spiked soil. It was observed that the size of NPs significantly ($p < 0.05$) affects the pore water Zn concentration. That concentration was significantly higher in both soil types when spiked with small-sized ZnO NPs. The results showed that, cumulatively, a 10–13% higher concentration of soluble Zn was observed in the pore water of SC soil when spiked with small-sized NPs, followed by 21–23% in SL soil, compared to large-sized NPs (Figure 6).
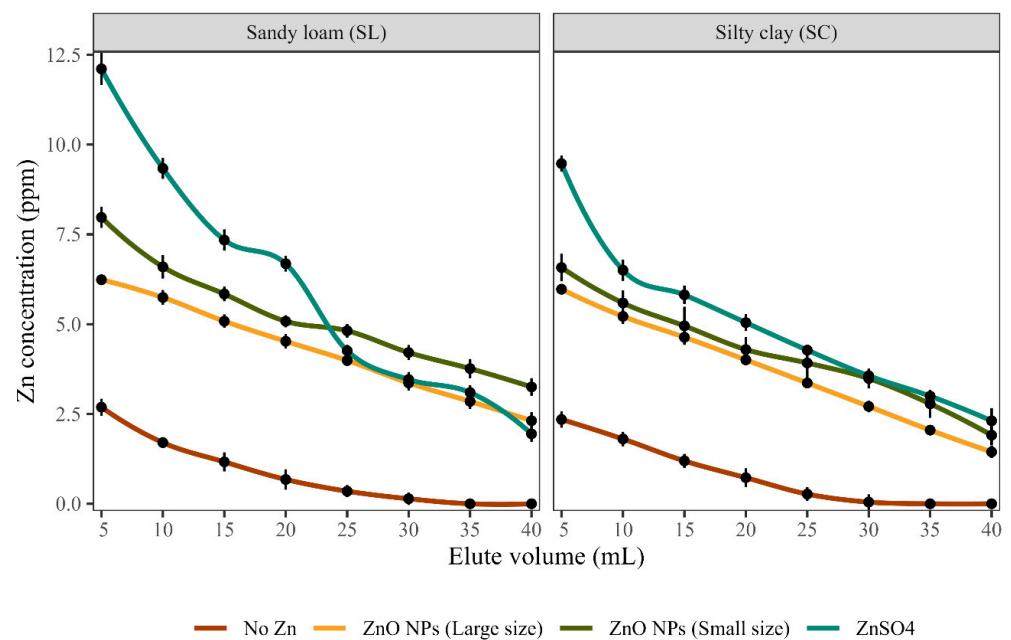

Figure 4. Zn concentrations in leachate obtained from SL and SC soil spiked with ZnSO$_4$, small-sized NPs, and large-sized NPs after 7 days of incubation.
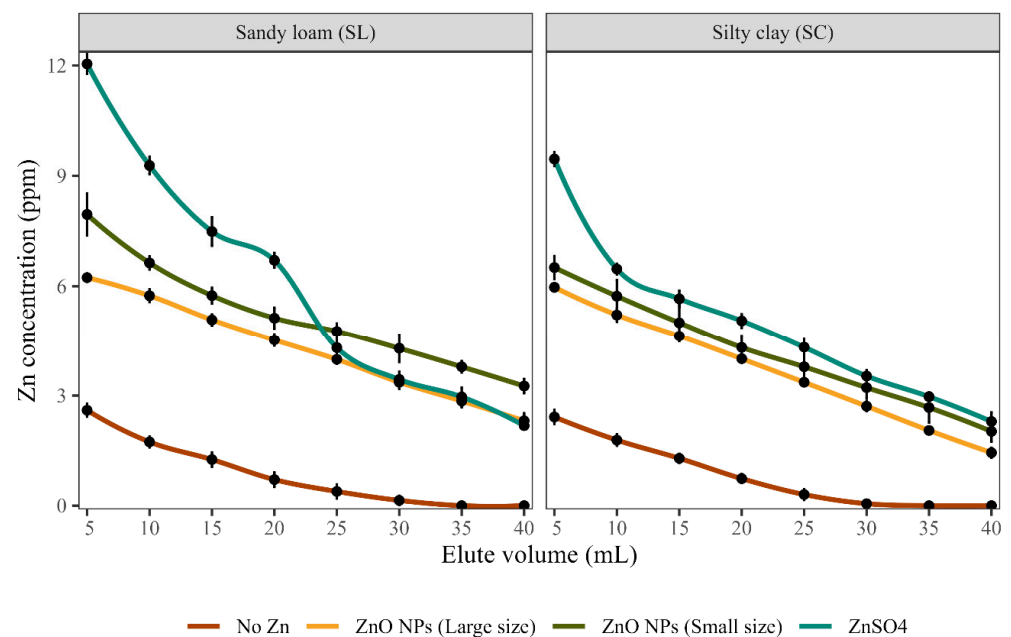

Figure 5. Zn concentrations in leachate obtained from SL and SC soil spiked with ZnSO$_4$, small-sized NPs, and large-sized NPs after 14 days of incubation.
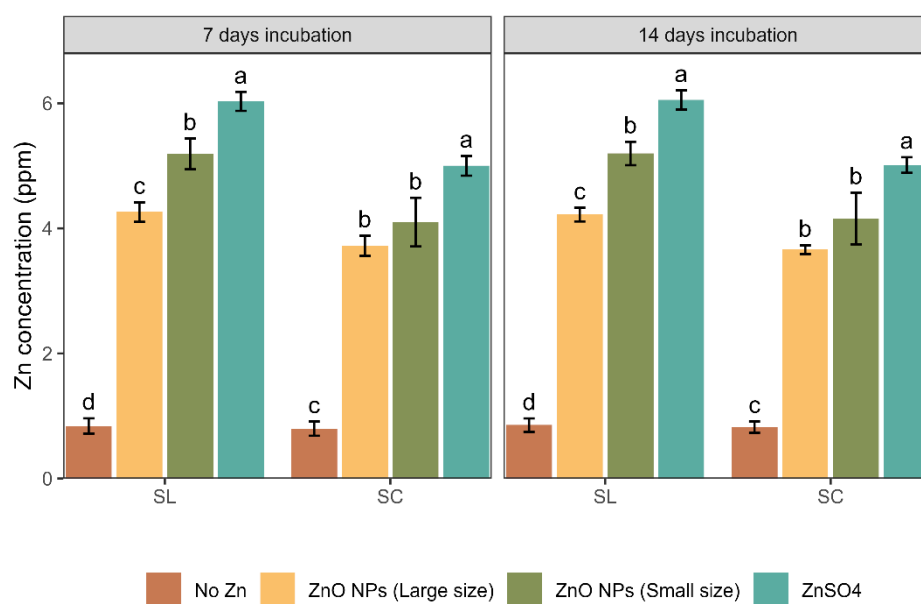
Figure 6. Cumulative Zn released from SL and SC soil spiked with $ZnSO_4$, small-sized NPs, and large-sized NPs after 7 and 14 days of incubation.

The higher concentration of Zn as small-sized NPs might be due to their larger specific surface area [29] because NPs that possess a higher surface area also have higher surface energy, which forces ions to break away from the lattice structure [12]. This fact was supported by Mudunkotuwa et al. [30], who noted a higher dissolution rate for 4-nm-sized ZnO NPs compared to larger-sized ZnO NPs. According to Bian et al. [31], the fractions of atoms at the corners and edges of small-sized ZnO NPs are much higher compared to those for larger-sized ZnO NPs, and they make it easy for clusters and ions to break away from the lattice structure and enhance the solubility of ZnO NPs. The size of NPs also affects the aggregate size. It was reported that larger-sizes NPs lead to larger-sized aggregate formation compared to smaller-sized NPs [32]. The researchers reported that ZnO NPs of 30 nm size formed aggregates of 199 nm, smaller than the 769.2 nm aggregates formed by the NPs of >200 nm size. This was proposed to be because larger-sized NPs have a very low collision rate due to their low kinetic energy compared to small-sized NPs. It was reported that NPs with a low collision rate produce larger-sized and more dendritic aggregates compared to the NPs with a higher collision rate [33].

The results of our experiment also showed that the soil type significantly affects the pore water Zn concentration. It was noted that the pore water Zn concentration was significantly higher in SL soil compared to SC soil. In SL soil, the pore water Zn concentration was noted to be 20.6%, 26.5%, and 14.5% higher in soil spiked with $ZnSO_4$, small-sized NPs, and large-sized NPs, respectively, compared to SC soil. This might be due to a difference in soil properties such as the cation exchange capacity, organic matter, exchangeable calcium and $CaCO_3$, EC, etc., between SL and SC soils. Soil pH is one of the main factors that affects the dissolution of ZnO NPs [20]. In our study, the pH of SL soil was lower (7.10) compared to that of SC soil (8.80). Under alkaline soil conditions, complexation with organic ligands, chemisorption, and precipitation to elements such as Ca and P were the main mechanisms that reduced the solubility and availability of Zn and other cations [11]. Meanwhile, the high pH buffering capacity of alkaline calcareous soils limit the solubility and diffusion of NPs. This notion was supported by Han et al. [34] and Bian et al. [31], who reported that Zn ions precipitate in the form of $Zn(OH)_2$ under alkaline conditions. Similarly, a higher ionic strength also leads to the aggregation of NPs [35]. Stewart et al. [36] reported the higher aggregation of ZnO NPs at 50 mM $CaCl_2$ compared to 5 mM $CaCl_2$. These results support our findings, as SC soil possesses higher EC compared to SL soil. The higher organic matter content and higher CEC could also be

responsible for the reduced dissolution of ZnO NPs in SC soil. It was reported that organic matter fractions such as humic acid and oxalic acid increased the aggregation of NPs, which ultimately reduced their solubility [18,37]. Apart from that, the dissolved organic matter fractions make a coating on NPs and increase their sedimentation through changes in the zeta potential and reduced surface reactivity [38]. Similarly, Josko and Oleszczuk [37] and Moghaddasi et al. [39] reported that higher organic matter content of the soil reduced the dissolution and bioavailability of ZnO NPs.

In this study, SC soil consisted of a higher amount of clay (51.95%) and higher CEC (40.1 cmol$^+$ kg^{-1}) compared to SL soil, which could have been one of the reasons for the low solubility of ZnO NPs or higher fixation of Zn^{+2} on the exchange sites of clay. It was reported in the literature that a higher clay content reduced the availability of Zn [40,41] via greater numbers of exchange sites and higher surface charges. According to Josko and Oleszczuk [37], soil with higher CEC possesses higher sorption affinity for NPs, which leads to their immobilization. Meanwhile, the incubation period has no significant effect ($p > 0.05$) on the soluble Zn in the pore water.

3.3. The Potential Availability of Zn Retained in the Soil Matrix

To evaluate the potential availability of Zn retained in the soil matrix, an extractant (EDTA 0.05 M) was used. EDTA is a strong chelating agent, which can extract a significant amount of metals from soil. EDTA can bind several heavy metals to make stable complexes [42]. According to Cheng et al. [42], 0.05 M EDTA extracted about 67% of Zn from the soil at pH 3, and a further increase in the concentration of EDTA did not increase the extraction efficiency significantly. In this study, we found that 0.05 M EDTA extracted a significant amount of bioavailable Zn from both SL and SC soils (Figure 7). The soil type, size of NPs, and incubation period did not affect the extracted concentration of Zn significantly. The extraction efficiency of 0.05 M EDTA ranged from 48% to 53.4% in SL soil and from 54.2% to 56.5% in SC soil. The extraction efficiency of EDTA varied from low to very high depending on conditions such as soil type, type of metal, concentration of metal, concentration of EDTA, and other soil properties [43].
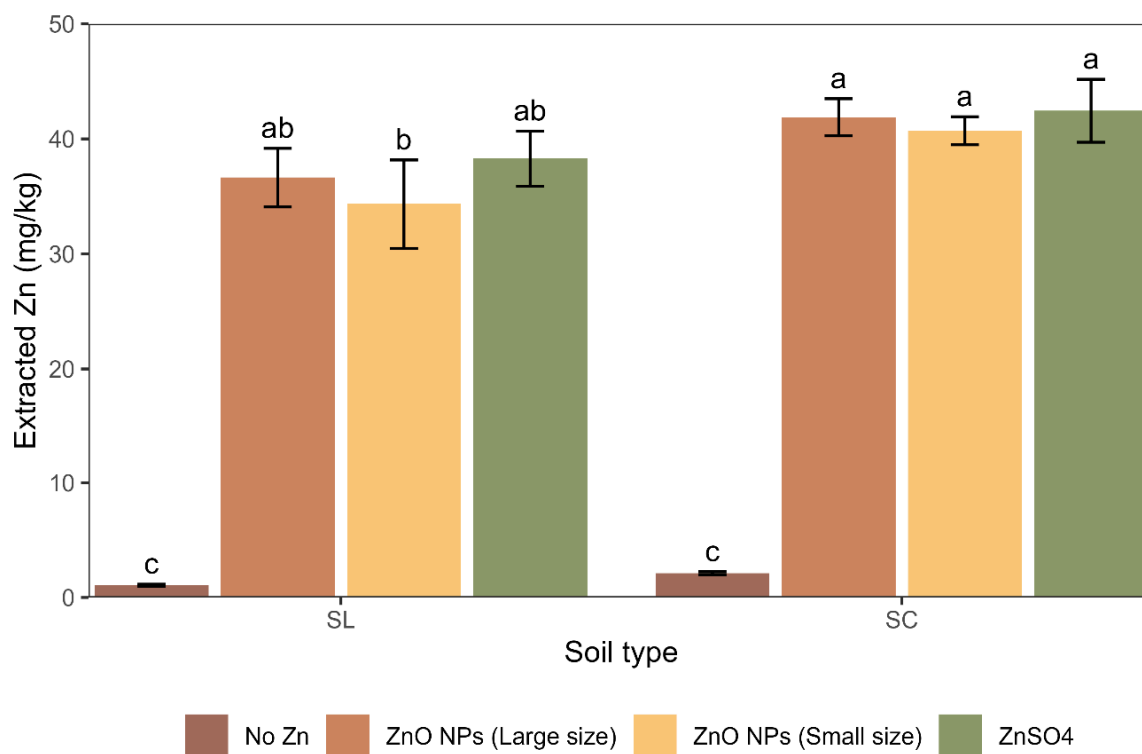

Figure 7. Extracted Zn from SL and SC soils spiked with ZnSO4, small-sized NPs, and large-sized NPs.

4. Conclusions

It is concluded that the overall behavior of NPs in the soil environment is a very complex phenomenon, which depends on the soil's physico-chemical characteristics and mineral composition. The present study showed that the size of the NPs and the soil pH are the main factors that play important roles in deciding the fate of NPs under an alkaline soil environment. The solubility of ZnO NPs in two different agricultural soils was investigated. It was confirmed that the solubility of small-sized ZnO NPs was higher in both soils compared to large-sized NPs.

In this study, the dissolved amount of Zn during the leaching process was very low in comparison with the added amount of Zn. This raised a question regarding the efficiency of ZnO NPs in alkaline calcareous soils as a Zn fertilizer. Long-term studies are required to further understand the behavior of ZnO NPs in alkaline calcareous soils. For future research in this field, we also suggest including other soil types to get a better understanding of the fate of the NPs.

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