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ORIGINAL PAPER

Environmental Behaviour of Synthesized and Commercial Agricultural Zinc Products: Leaching, Migration, and Availability in Soils

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Abstract

The aim of this paper is to examine the environmental effect of different chemical characteristics of Zinc (Zn) sources, assessing the transport, leaching and accumulation in the environment in sand, acidic (AS) and calcareous (CS) soils. Comparative short- and long-term studies applying ZnO sources [bulk, laboratory-synthesized and commercial nanoparticles (NP)], $ZnSO_4$, complexed Zn (Zn-lignosulfonate) and chelated Zn (Zn-diethylenetriamine-pentaacetate, Zn-hydroxyethylenediamine-tetraacetate and Zn-ethylenediamine-tetraacetate) were carried out. For all treatments and media, the medium- and long-term dissolution kinetic model was fitted to a logistic function. The applied Zn in the form of ZnO was mainly retained at the upper half (0–7.5 cm) of the columns and in very available form (ranging 40–61% of added Zn in AS and 29–31% in CS). Leached Zn reached values below 6% in AS and 3% in CS. The use of chelated Zn in both soils and complexed Zn, and $ZnSO_4$ in AS resulted in excessive leaching of Zn (around 70%). The amount of Zn available at the upper half of the column was less than 5%. In the CS, these fertilizers showed a higher aging than ZnO sources, negatively affecting its availability as a nutrient for crops. ZnO NP showed short- and medium-term dissolution kinetics that allow gradual nutrient release and high availability at the medium-term. These products provide an effective solution for plant nutrition while mitigating the environmental problems observed with more traditional sources related to leaching.

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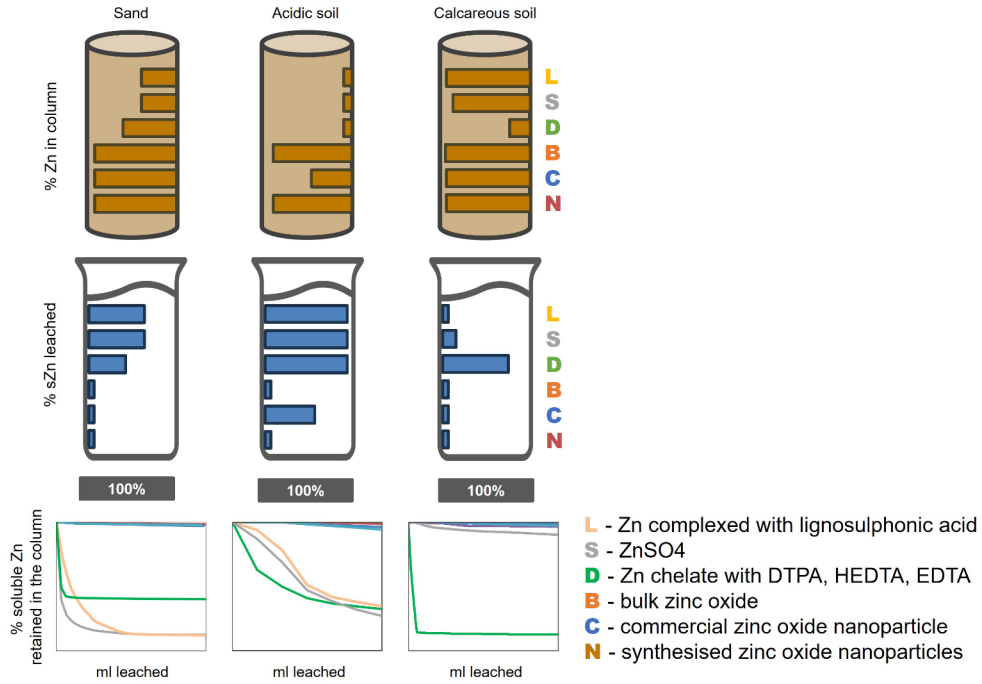
Graphical Abstract



Keywords ZnO nanoparticles · Dissolution kinetics · Sequential extractions · Zn bioavailability

1 Introduction

Zinc (Zn) is unevenly distributed in soils, with a very wide range of concentrations ranging from 10 to 300 mg kg^{-1} and an average concentration in soil of 64 mg kg^{-1} (Kabata-pendias and Mukherjee 2007). The appropriate fertilisation rates in soils depend on both the needs of each crop and the availability of Zn in the soil (Broadley et al. 2007). On the one hand, there are crops sensitive to Zn deficiency, which greatly reduce their yield and quality when Zn concentrations are deficient. Khan et al. (Khan et al. 2022) reported that a suitable range of Zn concentrations in the plant is between 20 and 100 mg Zn kg^{-1} dry matter. Although according to Marschner (2012) the minimum leaf Zn concentration required for adequate growth is close to 15–20 mg Zn kg^{-1} dry matter. On the other hand, the soluble fraction of Zn is critical for plant availability. In addition, available Zn concentrations above the recommended levels may pose an environmental risk due to the polluting effect of Zn as a heavy metal (Luo et al. 2001). Therefore, the application rate of a fertiliser to cover the Zn needs of the plant depends on the effectiveness of the fertiliser and the crop requirements. For example, Almendros et al. (2019) reported that a dose of 0.5 kg ha^{-1} was sufficient to achieve the maximum yield of a barley crop in a Mediterranean calcareous soil. However, when $ZnSO_4$ was used as fertiliser in the same soil and crop, the recommended dose to achieve the highest yield was 5 kg ha^{-1} (Gonzalez et al. 2019).

The availability of Zn in soil is influenced by various factors, including the total Zn content, organic matter content (Sun et al. 2023b), clay and calcium carbonate content (Alloway 2009), electrical conductivity (Zou et al. 2023), redox conditions, soil moisture status (Ferraro et al. 2023), microbial activity in the rhizosphere (Luo et al. 2023), concentrations of other trace elements (Liu et al. 2023), concentrations of macronutrients (especially phosphorus) (Sun et al. 2023b) and climate (Sun et al. 2023a).

Soil pH is also a significant factor affecting Zn availability (Zou et al. 2023). It is widely reported the higher Zn availability in acidic soil compared to calcareous soil (Almendros et al. 2015). In acidic soils, Zn availability increases due to the predominant form of Zn^{2+} in soil solution, whereas in alkaline soils it precipitates in the form of carbonates or hydroxides and creates strong bonds with soil oxyhydroxides (Alloway 2013). In alkaline soils Zn availability decreases due to the reaction of Zn^{2+} with organic ligands present in the soil such as OH-, CO_3^{2-}, HPO_4^{2-} and PO_4^{3-} and the formation of insoluble compounds. It has been estimated that for every unit increase in pH, Zn availability decreases by approximately a factor of 100 (Alloway 2013).

Zinc is found in the soil associated with different soil fractions, varying in terms of loss through leaching or availability of Zn to plants. Chemical extractions on soil samples with different extractants have been used to estimate the Zn concentration in plants (Alloway 2013, 2009). This availability can be validated if there is a correlation between soil concentrations and amounts of metal in plants (Almendros et al. 2020). Techniques such as sequential extractions are used to determine and quantify the distribution of this Zn associated with soil fractions and to understand the availability and mobility of metals and the associated environmental risks (Araújo et al. 2022; Kraus and Wiegand 2006; Meite et al. 2022). The soluble Zn fraction is the most labile and therefore the most bioavailable and easily leachable. The concentrations of Zn adsorbed on clay minerals, iron and aluminium oxides, i.e. the colloids present in the soil, as well as the fraction bound to organic matter play a very important role in the medium-term availability of the trace element (Barrow 1993).

In order to ensure an adequate amount of Zn for crop production, the use of Zn sources is becoming increasingly important. Chelates, complexes, salts and oxides are commonly used as Zn sources in soils. These products differ in their solubility and in the form of the released Zn, which influences the reactivity. According to Chahal et al. (2023) the efficacy of a source is related to the ability to reduce sorption reactions that limit the availability of Zn. While salts and oxides provide free zinc (Zn^{2+}), coordinated compounds (complexes and chelates) also provide dissolved cations in coordinated forms, which protect Zn from the formation of insoluble compounds. Chelates and complexes are designed to keep Zn in soluble form, facilitating its assimilation by plant roots (Norvell 1991). Zn sulphate, known for its high-water solubility, is advantageous for short-term enrichment of Zn-deficient soils. In contrast, ZnO fertilizers are slow dissolving, which benefits the controlled release of this trace metal (Mikula et al. 2020). However, the nano-sized particles of these compounds, as ZnO, are adapted to increase the solubility of their poorly soluble non-nanoscale counterparts and are being used in agriculture as nanofertilizers (Yadav et al. 2023).

The solubility of nanoparticles is influenced by factors such as size, shape, surface chemistry, and the surrounding environment. The influence of the particle size on the solubility is indeed considered in the Ostwald-Freundlich equation (Ely et al. 2014). Therefore, nanoscale particles of poorly soluble fertilizers are designed to be more soluble than their bulk counterparts, but dissolve more slowly to meet the different needs of plants at different phenological stages (Carmona et al. 2022). Nanofertilizers improve the efficiency of fertilizers in plant nutrition by increasing dissolution kinetics and reducing losses and potential contamination (Timilsina et al. 2023). Additionally, the use of nanofertilizers can reduce the amount of fertilizer required, leading to cost savings and reduced environmental contamination (García-Gómez et al. 2020). Ensuring soil quality and food security is crucial for sustainable soil management, aligning with the United Nations Sustainable Development Goals (UN SDGs). In this context, it is crucial to study the behaviour of different Zn sources used as agricultural fertilizers and to monitor the dynamics of this essential micronutrient in different environments.

In last decades numerous studies have emerged evaluating the effectiveness of different soil-applied Zn sources as fertilisers for specific crops (Almendros et al. 2013, 2015, 2019, 2020; Chahal et al. 2023; Feng et al. 2005; Gonzalez et al. 2019; Knijnenburg et al. 2019; Obrador et al. 2003; Ponce-García et al. 2023; Zou et al. 2023). These studies report differences in the performance of soil-applied Zn sources on the availability of the nutrient in the soil and its uptake by the plant. These studies focus on the analysis of plant parameters (e.g. yield, Zn concentration in the crop) and soil parameters (mainly Zn availability) at the end of the crop. However, the evolution of these forms of Zn in the soil over the whole period is not explored. On the other hand, other studies have evaluated the partitioning and stability of soil-applied zinc in different fertilisers. According to Šebesta et al. (2020) column experiments may provide a better understanding of Zn fixation (applied in different chemical forms) to soil components and how these mechanisms differ between species or chemical forms. However, these studies have been conducted on a very short-term basis (Šebesta et al. 2020), with few Zn sources (Knijnenburg et al. 2021; Milani et al. 2012; Reyhanitabar and Gilkes 2010; Sun et al. 2023b), used in macronutrient fertiliser coatings (Milani et al. 2012, 2015), only under ideal experimental conditions (sand columns) (Knijnenburg et al. 2021) or in very specific soil (Knijnenburg et al. 2019; Obrador et al. 2003).

Previous studies (Alvarez 2007; Alvarez et al. 2001; Obrador et al. 2003) with Zn chelates or complex fertilisers have reported that the different physico-chemical properties of soils and the source of the micronutrient are influential factors in the leaching, the distribution of Zn between soil fractions and the availability of the nutrient to the plant. According to Milani et al. (2012) it is necessary to study the dissolution behaviour of ZnO nanoparticles in porous media without the presence of plants in order to understand the dissolution process of these particles in soils.

To our knowledge, there are no studies comparing the dynamics of this nutrient (Zn) in soil when supplied in the form of different traditional and emerging sources and their comparative implications along the soil profile, availability, and leaching potential with respect to traditional Zn sources.

The hypothesis of this study is that ZnO nanoparticles can exhibit beneficial behaviour with respect to dissolution kinetics, leaching potential and distribution in the soil profile for use as a source of Zn in the agro-environment. Therefore, the main goal of the research reported here was to evaluate the behaviour of emerging (commercial and laboratory-synthesised NPs) and traditional (chelates, complexes, sulphates, and oxides) Zn products used in agriculture. The specific objectives of the work were: (i) to determine the dissolution kinetics of different Zn sources, (ii) to study the leaching potential of these sources, and (iii) to assess the distribution of Zn in different soil fractions and its behaviour in different soil types. To achieve these objectives, various short or medium-term Zn dissolution experiments were conducted in sand and both acidic and calcareous soils.

2 Materials and Methods

2.1 Zinc Sources

The Zn sources used in this study were as follows: Zn sulphate heptahydrate (22.7% p/p Zn, Merck) [$ZnSO_4$], Zn complexed with lignosulphonic acid (Zn concentration:12% p/p; Rayplex, powdered) [LIG], Zn chelated with DTPA, HEDTA, EDTA (90.0 g water-Soluble Zn L^{-1}, $\rho = 1.29$ g cm^{-3}; BMS Micro-Nutrients) [CHE], bulk Zn oxide (80.4% p/p Zn, Sigma-Aldrich) [BULK], Zn oxide nanoparticles synthesised in the laboratory (80.4% p/p Zn) [NP-SINT] and commercial Zn oxide nanoparticle (80.4% p/p Zn, Aldrich Chemistry) [NP],

NP-SINT synthesis followed a co-precipitation method (Huy et al. 2019). $Zn(NO_3)_2$ and NaOH were purchased from Sigma Aldrich. 180 mL of 0.3 M NaOH solution was slowly added dropwise into a glass beaker containing 180 mL of 0.15 M $Zn(NO_3)_2$ solution. The solution was vigorously stirred for 180 min at room temperature. The colourless solution turned milky-white, indicating the formation of Zn compound particles. The precipitate was collected by filtration, washed with distilled water thrice, and dried at 80 °C for 24 h.

2.2 Characterisation of ZnO Particles

Hydrodynamic size and Zeta potential were recorded using dynamic light scattering (DLS) technique in a Zetasizer Nano ZS equipment. The particle size distribution was accomplished by transmission electron microscopy (TEM), scanning electron microscope (SEM) images were taken using a JEOL JSM 6335 F. The specific surface area and pore size distribution were obtained using Micromeritics ASAP 2010 equipment. The amount of carbon, hydrogen, nitrogen, and sulphur was analysed using the LECO CHNS-932 elemental microanalyzer. The XRD patterns of the three ZnO nanoparticles have been collected in a D8 Venture diffractometer (Bruker AXS). XRD classic analyses were carried out from 5 to 100º (2θ), with a 0.105º (2Theta) step of measurement and 1.0 s $step^{-1}$. In this case, the used anode was Cu K α1 + 2 (λ = 1.54184 Å).

2.3 Soil Characterization

The two original soil surface horizons used in this study were obtained from two different regions of Spain: acidic soil from an agricultural land in Valladolid (latitude 42°13'01.4"N longitude 5°17'22.5"W) and calcareous soil from National Center of Irrigation Technology "CENTER", Madrid (latitude 40°24'59.2"N, longitude 3°29'46.9"W). Both were soils commonly used to cultivate cereals.

Soil samples from the Ap horizon (0–28 cm) were air-dried, sieved (< 2 mm), and then analysed according to the Spanish official methodology (MAPA 1994). The acidic soil (pH 5.9) was classified as Luvisol (IUSS. Working Group WRB 2022) and its main characteristics were as follows: sand, 803 g kg^{-1}; silt, 116 g kg^{-1}; clay, 81 g kg^{-1}; electrical conductivity, 67.2 µS cm^{-1}; extractable P, 18.3 mg kg^{-1}; oxidizable OM, 4.1 g kg^{-1}; total N, 0.64 g kg^{-1}; C: N ratio, 3.7; exchangeable Na, 58 mg kg^{-1}; exchangeable P, 115 mg kg-1; exchangeable Ca, 805 mg kg-1; exchangeable Mg, 263 mg kg^{-1}. The calcareous soil (pH 8.2) was classified as Fluvisol and its main characteristics were as follows: sand, 304 g kg^{-1}; silt, 641 g kg^{-1}; clay, 55 g kg^{-1}; electrical conductivity, 159 µS cm^{-1}; extractable P, 8.3 mg kg^{-1}; oxidizable OM, 14.5 g kg^{-1}; total N, 1.3 g kg^{-1}; C: N ratio, 6.5; exchangeable Na, 71 mg kg^{-1}; exchangeable P, 713 mg kg^{-1}; exchangeable Ca, 3499 mg kg-1; exchangeable Mg, 287 mg kg^{-1}. The DTPA–triethanolamine (TEA)-extractable Zn was lower in the acidic soil (0.38 mg kg^{-1}) than in the calcareous soil (0.93 mg kg^{-1}). Zn concentrations in both soils are deficient, with DTPA-Zn < 0.5 mg kg^{-1} in the acidic soil, and < 1.2 mg kg^{-1} in the calcareous soil (Lindsay and Norvell 1978).

2.4 Dissolution Kinetics of Zn Fertilizers

Dissolution kinetics experiments were conducted using sand columns to isolate the effect of soil on the Zn source dissolution. Columns measuring 15 cm in height and 1.5 cm in diameter were filled with 20 g of washed sand. The fertilizers (15 mg Zn per column) were added and topped by 10 g of sand. In order to simulate environmental conditions of water supply, irrigation or rainfall, leachate collections were performed twice a week, collecting a 25 mL sample each time. To collect these volumes, a flow of 10 mL h^{-1} of

0.01 M $CaCl_2$ solution was added from the top of the columns. Leachates were collected for 40 days to a total of 300 mL. Each treatment had three replicates, and a control treatment with only sand was included (total column number: 21). The leachates were filtered through 0.22 µm pore size membrane filters to determine the soluble Zn concentrations.

2.5 Experiments in Soil Columns

Dissolution kinetics were determined using the method described by Milani et al. (2012) with modifications. Columns with a height of 15 cm and a diameter of 1.5 cm were filled with 20 g of soil (acidic or calcareous soil). Each product was added to provide 15 mg of Zn, followed by the addition of 5 g of soil on top. Sand and a grate were placed at the bottom of all columns for better drainage. There were six replicates for each treatment, a control treatment with only soil was also included (total column number: 42 for each soil).

In order to simulate environmental conditions of water supply, irrigation or rainfall, leachate collections were carried out twice a week. In the acid soil, a 10 mL sample (1.16 pore volume) was collected in each leachate. Due to the high retention of Zn in the calcareous soil columns, 25 mL of leachate (1.78 pore volume) was accumulated in each collection. To collect these volumes, a flow of 10 mL h^{-1} of 0.01 M $CaCl_2$ solution was added from the top of the columns at the time of leachate collection. The leachates were collected until the leaching losses in at least one of the treatments exceeded 60%. In the acid soil leachates were collected for 20 days up to a total of 60 mL (6.98 pore volume) and in the calcareous soil leachates were collected for 100 days up to a total of 750 mL (53.57 pore volume) (medium term). In this soil, half of the columns (3 replicates) were dismantled when the total volume collected reached 225 mL (32 days) to assess the short-term Zn status of the soil. Leachates were filtered using 0.22 µm pore size membrane filters (Milani et al. 2012), and soluble Zn concentrations were determined by flame atomic absorption spectrophotometry (FAAS) (Perkin-Elmer model AAnalyst 800).

2.6 Soil Analysis

The soil columns were divided into two portions for further analysis: the upper half corresponded to the soil between the top 0 and 7.5 cm of the column and the lower half corresponded to the soil between the 7.5 and 15 cm depth of the column. Figure 1 of Supplementary Material shows a schematic figure of the procedure used in the soil analyses of the columns. Zinc fractions were determined following a sequential extraction using 2 g of soil sample with the following extractants:

- Deionized water (1:30, g: mL): shake 16 h, centrifugate 15 min at 3000 rpm and filter. **Water soluble Zn** (Beesley et al. 2010).
- NH_4NO_3 1 M (1:30): shake 24 h, centrifugate 15 min at 3000 rpm and filter. **Exchangeable Zn** (Kraus and Wiegand 2006).
- NH_4Ac 1 M, pH 6 (1:30): shake 24 h, centrifugate 15 min at 3000 rpm and filter. **Adsorbed Zn** (Kraus and Wiegand 2006).
- The **residual fraction** was calculated as the difference between the total Zn extracted by wet acidic digestion (acid mixture of HNO_3:HF: double deionized water (1:1:1) followed by digestion in Teflon bombs) and the sum of the other fractions.

All extracts were analysed for Zn by FAAS.

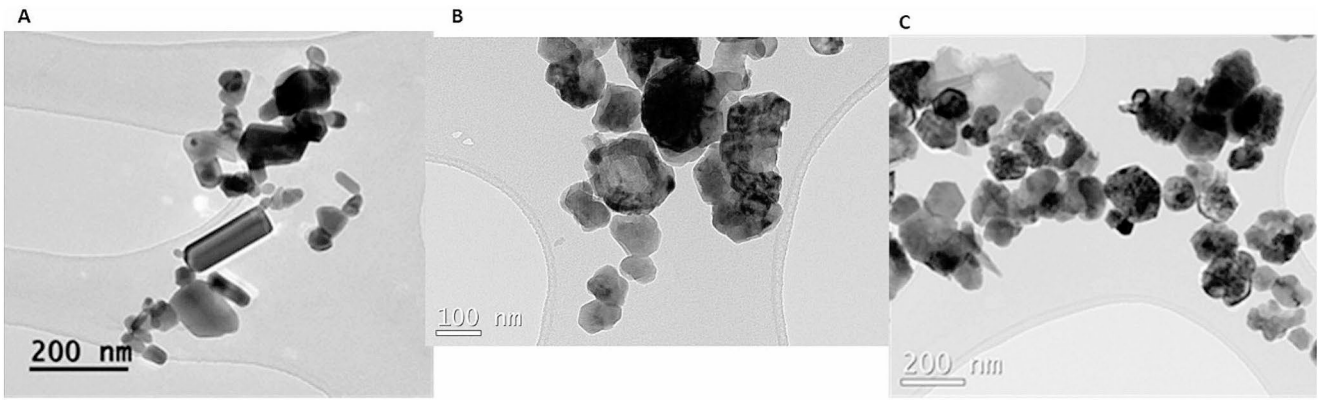


Fig. 1 TEM (Transmission Electron Microscopy) micrographs of commercial ZnO (**A**); bulk ZnO (**B**); NP-SINT (synthesised ZnO) nanoparticles (**C**)

2.7 Determination of Extractable Zn Concentration by LMWOAs in Soil

This method is based on the simulation of the rhizosphere-soil condition, estimating the available Zn (Feng et al. 2005). A mixture of low molecular weight organic acids (LMWOAs) (10 mM combination of organic acids solution containing acetic, lactic, citric, malic, and formic acids in a molar ratio of 4:2:1:1:1, respectively), end-over-end agitation for 16 h, centrifugate 10 min at 5200 rpm. The extracts were filtered, and Zn concentrations were determined by flame atomic absorption spectrophotometry (FAAS) (Perkin-Elmer model AAnalyst 800).

2.8 Statistical Analysis

Statistical analysis was performed using Statgraphics Centurion XVII 17.2 software (Manugistic, Rockville, MD). Box-Cox transformations were applied to ensure homogeneity of variances and normality of the data obtained from soil experiments. Analysis of variance was applied with a general linear model for a one-factor design. P-value < 0.05 was used to evaluate the differences between the Zn sources treatment average values.

To propose a common model for each medium, describing the changes in applied Zn leaching with the different sources over the total volume collected, different models proposed in the literature were tested (Boostani et al. 2019; Burnham 2015; Kawano et al. 2020). The R package *drc* (Ritz et al. 2015) was used to determine the dissolution curves of the different products. The dissolution kinetics of the Zn sources were successfully fitted to a sigmoidal or logistic curve, of the form:

$$leached\ Zn\ concentration = \frac{d}{1 + e^{b\cdot(\log(volume)-\log(e))}} \quad (1)$$

Where, **d** is the maximum value that the curve reaches when the volume tends to infinity; **e** corresponds to the point volume where the curve reaches half its maximum value; and **b** (< 0) is the curve gradient.

3 Results

3.1 Characterizations of ZnO NP

Zeta potential measurements of the bulk, synthesized and commercial ZnO nanoparticles in water at natural pH (pH = 7) have been accomplished. Zeta potential values of -14.7, 12.3 and -13.5 ± 1.0 mV have been obtained for bulk, synthesized and commercial ZnO nanoparticles, respectively. Zeta potential indicates the degree of repulsion or attraction between particles. A potential between -30 mV and 30 mV indicates instability, so the solution in water will tend to not form stable suspensions and form aggregates.

The average particle size measured by TEM were of 83 ± 17.45, 76 ± 22.89 and 62 ± 21.28 for bulk ZnO, NP-SINT and commercial ZnO nanoparticles, respectively (Fig. 2 of Supplementary Material). The TEM images of the commercial ZnO nanoparticles revealed particles with an elongated shape, as can be observed in Fig. 1A. On the other hand, bulk ZnO nanoparticles showed a slightly higher particle size, if it is compared to the commercial ZnO particles, but showing a similar shape (Fig. 1B). Finally, the synthesized ZnO nanoparticles (NP-SINT) showed a more regular and spherical shape, as can be seen in the TEM micrograph (Fig. 1C).

Similar specific surface area (S_{BET}) values were determined for the ZnO particles. Specifically, a S_{BET} of 21.4 $m^2\ g^{-1}$ was obtained for the bulk ZnO particles, 21.2 $m^2\ g^{-1}$ was determined for NP-SINT and 19.7 $m^2\ g^{-1}$ was obtained for the commercial nanoparticles. Additionally, an average pore sizes of 15.2, 17.9 and 17.0 nm have been measured for the and bulk, synthesised and commercial ZnO nanoparticles respectively. These values are in the same range as those reported by García-Gómez et al. (2020) for similar commercial ZnO nanoparticles and by Sharma and Ghose (2015) and Huy et al. (2019) for NP-SINT.

Regarding to the Dynamic Light Scattering (DLS) studies, an average particle size of around ~350 nm has been obtained for NP-SINT nanoparticles. Additionally, low polydispersity index (PDI) values (< 0.342) were measured, indicating that the nanoparticles in the sample showed similar size. In the case of commercial ZnO nanoparticles, an average particle size of 511.1 nm was obtained; as well as bulk ZnO nanoparticles showed an average particle size of 541.0 nm. In both cases, the particle size obtained was higher than that of the synthesized nanoparticles. In the same way, low polydispersity index values, e.g., < 0.405 and < 0.574, were obtained for commercial and bulk ZnO nanoparticles, respectively. Hydrodynamic diameter is the size of the hypothetical sphere that has the same diffusion coefficient as that of the particle being measured, assuming a hydration layer around the particle or molecule. Therefore, the hydrodynamic diameter size values provide an idea of the expected particle sizes.

The X-ray diffraction patterns of the commercial ZnO nanoparticles, bulk ZnO nanoparticles and the synthesized nanoparticles (NP-SINT) can be found in Fig. 2 of Supplementary Material. As can be seen in Fig. 3A, the three samples showed very similar XRD patterns, with slight differences in the intensity of the peaks. This is indicative of

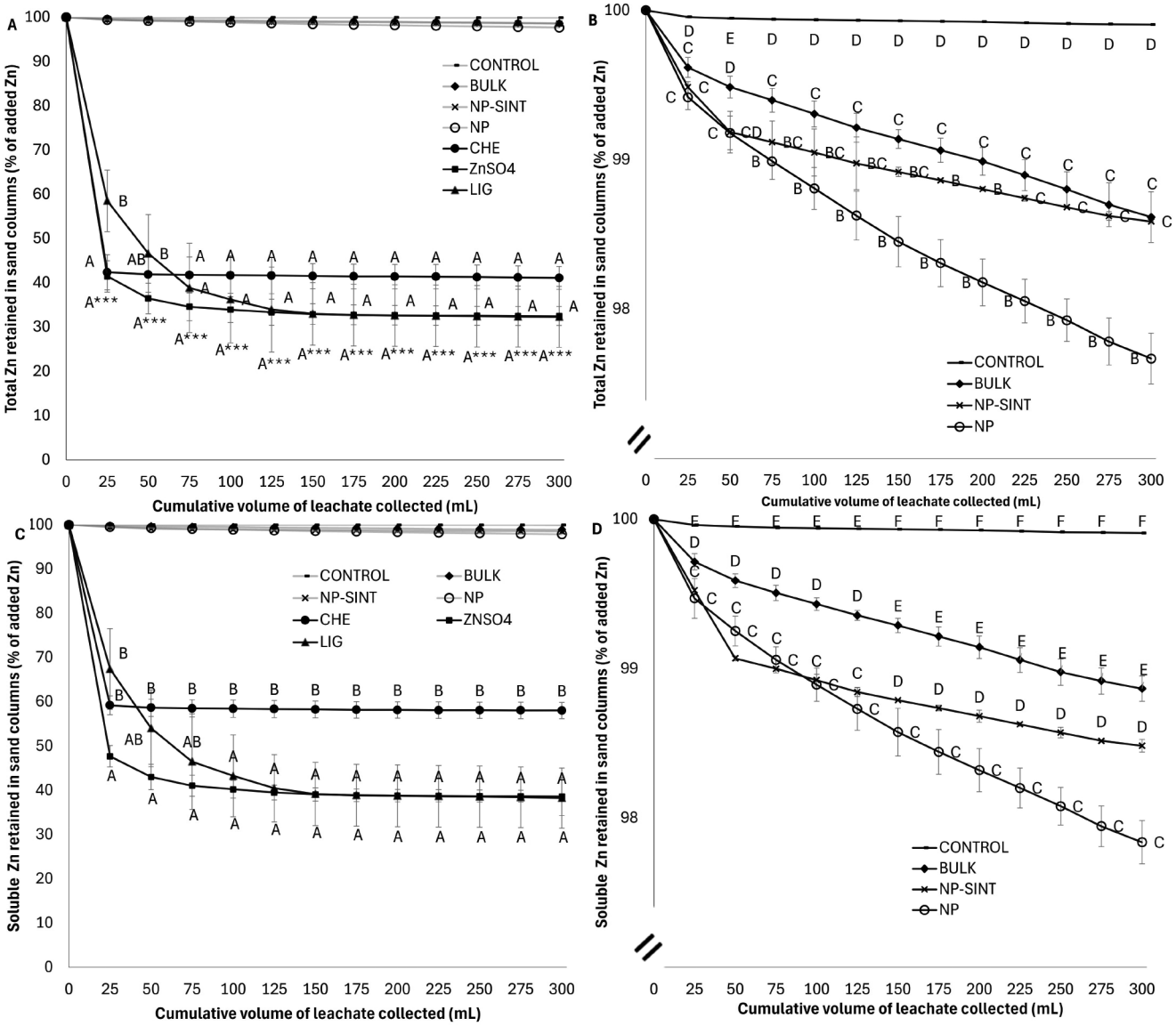


Fig. 2 Percentage of total Zn (**A, B**) and soluble Zn (**C, D**) retained in the sand columns after each leaching, with respect to the Zn input. **B** and **D** show respectively the detail of the percentage of total Zn and soluble Zn retained in the sand columns for the ZnO sources and control. Vertical bar at each of the data points represents the standard error. Statistical differences at $p \leq 5\%$ (LSD test) between sources for the same volume leached are indicated by capital letters. ***, **, and * significant at 0.01%, 0.1%, and 5% levels. BULK: bulk ZnO; NP-SINT: synthesised ZnO NP; NP: commercial ZnO NP; CHE: Zn chelate with DTPA, HEDTA, EDTA; ZnSO4: Zn sulphate ($ZnSO_4$-$7H_2O$); LIG: Zn complexed with lignosulphonic acid

that the synthesis of the ZnO nanoparticles was successfully carried out. Separate XRD patterns are shown in Fig. 3B in order to observe more clearly each individual XRD profile. The high intensity and sharp peaks are indicative of a high crystalline degree of the three samples, synthesized nanoparticles included. Thus, the obtained XRD patterns are in high agreement to some others reported in the literature (Huy et al. 2019; Pholnak et al. 2011).

The elemental analyses of the bulk, synthesized and commercial ZnO nanoparticles have been carried out. Nitrogen (N), carbon (C), hydrogen (H) and sulphur (S) composition in the commercial ZnO particles were: % N, 0.38 ± 0.01; % C, 0.14 ± 0.01; % H, 0.24 ± 0.01; % S, 0.01; for synthesised NP-SINT samples (metal precursor, $Zn(NO_3)_2$; hydroxide source, NaOH) were % N, 0.47 ± 0.01; % C, 0.17 ± 0.01; % H, 0.27 ± 0.01, and % S ≤ 0.01 and the analysis of bulk ZnO nanoparticles were: % N, 0.40 ± 0.01; %C, 0.15 ± 0.01; %H, 0.29 ± 0.01; %S, 0.03.

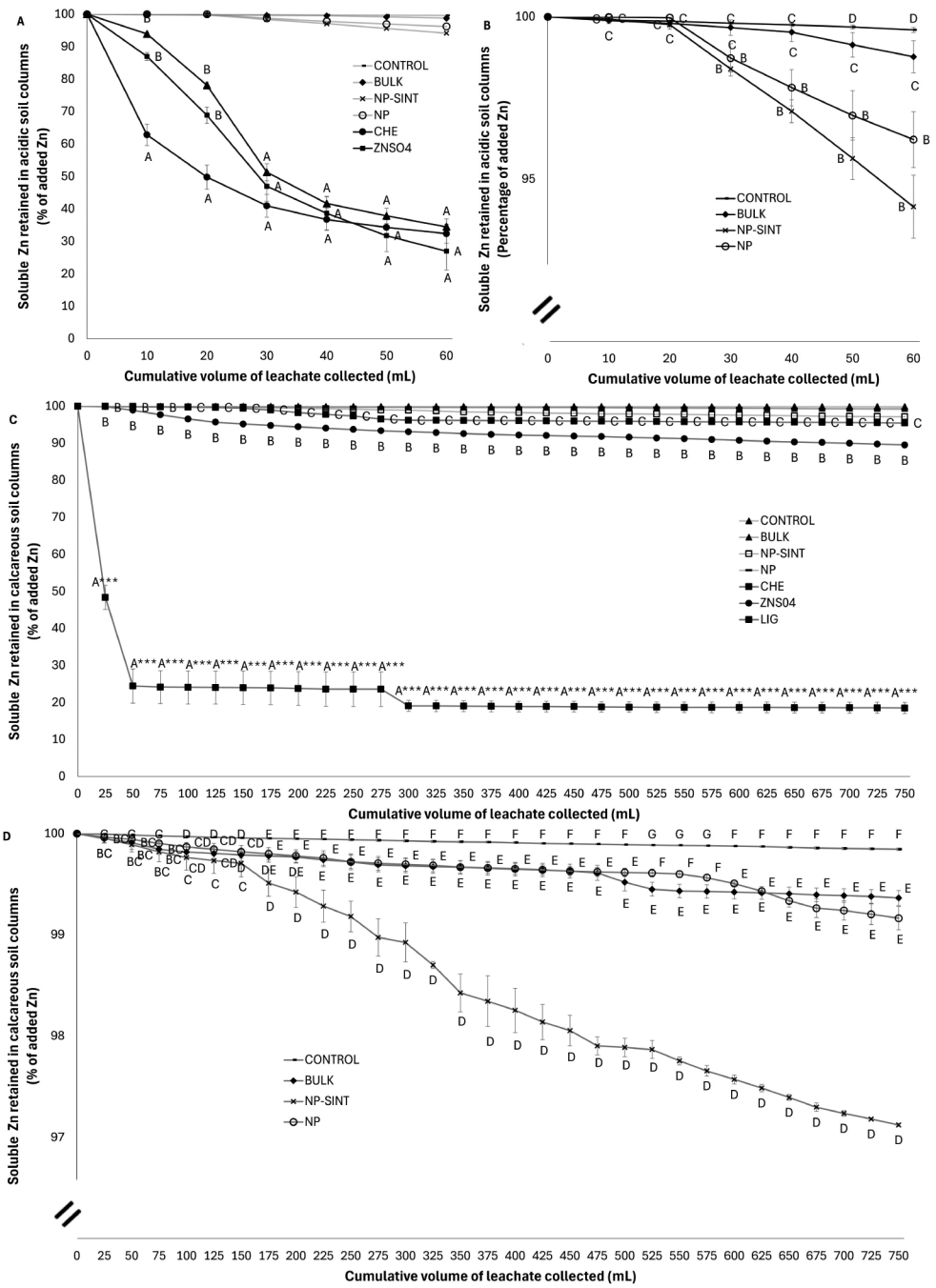


Fig. 3 Percentage of soluble Zn retained in the acidic (**A, B**) and calcareous (**C, D**) soil columns after each leaching, with respect to the Zn input. B and D show the detail, for the ZnO sources and control, of the percentage Zn soluble retained in the acidic and calcareous columns, respectively. Vertical bar at each of the data points represents the standard error. Statistical differences at $p \leq 5\%$ (LSD test) between sources for the same volume leached are indicated by capital letters. ***, **, and * significant at 0.01%, 0.1%, and 5% levels. BULK: bulk ZnO; NP-SINT: synthesised ZnO NP; NP: commercial ZnO NP; CHE: Zn chelate with DTPA, HEDTA, EDTA; ZnSO4: Zn sulphate ($ZnSO_4$-$7H_2O$); LIG: Zn complexed with lignosulphonic acid

3.2 Behaviour of Zn Sources in Inert Media. Dissolution Kinetics of Zn Fertilizers

Table 1 presents the amount of accumulated leached Zn and soluble Zn in sand columns. The evolution of retained Zn in these sand columns is shown in Fig. 2 (total Zn Fig. 2A and B and soluble Zn Fig. 2C and D). The percentages of total Zn retained in the column revealed two distinct trends. The more soluble sources (CHE, $ZnSO_4$, and LIG) released a substantial amount of total Zn (58.09%, 63.52%, and 53.39%, respectively) within the first 50 mL of leachate from the sand columns. Above 50 mL, the more soluble sources no longer leach. On the contrary, the less soluble sources (BULK, NP, and NP-SINT) experienced a lower but more constant release. These ZnO sources leaching similar values for the first 50 mL. However, a trend difference in Zn leaching was observed at higher leaching volumes.

The leaching trends for soluble Zn (Fig. 2C and D) were similar to those observed for total Zn. Soluble Zn leached by the more soluble fertilizers (CHE, $ZnSO_4$, and LIG) increased rapidly during the first 50 mL (41.35%, 52.32% and 45.98% of added Zn, respectively), then decreased to

Table 1 Amount of accumulated leached Zn and soluble zn in sand columns. Mean ± SD. Different letters indicate significant differences between treatments for each column (P-value < 0.05). Box-cox transformations. Powers: [1]0.047; [2]0.083. BULK: bulk size ZnO; $ZnSO_4$: Zn sulphate ($ZnSO_4$-$7H_2O$); LIG: Zn complexed with lignosulphonic acid; NP: commercial ZnO NP; NP-SINT: synthesised ZnO NP

	Sand[1] (total Zn)		Sand filter[2] (soluble Zn)	
Treatment	Mean (mg)		Mean (mg)	
CONTROL	0.013 ± 1.6E-04	a	0.013 ± 0.001	a
BULK	0.213 ± 0.049	b	0.167 ± 0.026	b
NP-SINT	0.244 ± 0.008	bc	0.234 ± 0.009	c
NP	0.350 ± 0.050	c	0.319 ± 0.043	d
CHE	8.835 ± 0.681	d	6.286 ± 0.481	e
$ZnSO_4$	10.155 ± 0.647	d	9.205 ± 0.398	f
LIG	11.306 ± 1.788	d	9.159 ± 1.769	f
P-value	0.00001		0.00001	

a nearly constant value up to leaching added Zn percentage between 41.99% and 61.74% (CHE and LIG, respectively). BULK, NP-SINT and NP leached small amounts of total soluble Zn (below 0.5 mg, 3.3% of added Zn). The results obtained in the logistic model (Eq. 1) indicated significant differences in the value of the *d parameter* between the less mobile sources (BULK, NP-SINT, and NP) and the rest of the sources (Table 1 Supplementary Material). This parameter estimated the maximum amount of leached soluble Zn that will be reached when the leached volume tends to infinity. It is remarkable that in the case of the less mobile sources the model estimated a maximum leached soluble Zn percentage that reached 3.7% of the added, however with the more mobile sources these values reached 42% (CHE), 70.4% ($ZnSO_4$) and 65% (LIG) of the added Zn. The model also showed significant differences for *e* and *b parameters* between the sources with higher leaching. The values of *e parameter* indicated that CHE have a higher initial leaching of soluble Zn, followed by the source $ZnSO_4$ and then LIG. The *b parameter* indicated the gradient of the model curve, which in all cases is less than zero, implying a decrease in the amount of soluble Zn leached in successive collections. The *b-values* close to -1 indicated a constant slope in the behaviour of the ZnO sources. This parameter was more negative for CHE, which showed a higher slope, i.e. a higher leaching rate. The value of *b parameter* showed no significant differences between $ZnSO_4$ and LIG.

3.3 Zinc Leaching in Agricultural Soils. Dissolution Kinetic Models in Soil Columns

In general, Zn leaching from the applied sources decreased in both soils compared to the amounts leached into the sand. As shown at Fig. 3A and B two clear trends were observed in the acidic soil. On the one hand, the more soluble sources leached in total more than 60% of Zn, such as $ZnSO_4$ (73.02%), CHE (67.63%), and LIG (65.51%). On the other hand, the less soluble sources leached less than 10% of Zn, including NP-SINT (5.85%), NP (3.78%) and BULK (1.23%). The most soluble sources ($ZnSO_4$, CHE, and LIG) exhibited similar patterns, soluble Zn leached gradually and stabilized around 30 ml. However, different trends were observed for the less soluble sources, where an increase in Zn leaching was observed at 20 ml of leachate for the two NPs (NP and NP-SINT). The ZnO bulk treatment leached small amounts more gradually showing significant differences with respect to the nano-sized sources (Fig. 3B).

The values of the three parameters estimated in the logistic model (Eq. 1) (Table 2 Supplementary Material) indicated significant differences between the most soluble sources (CHE, $ZnSO_4$ and LIG) and ZnO in the *d-parameter* (LIG vs. ZnO, P<0.01; CHE vs. ZnO, P<0.01; $ZnSO_4$ vs. ZnO, P<0.0001). As indicated above, this *d-parameter* estimates the maximum amount of leached Zn that will be reached in this acid soil when the leached volume tends to infinity. The model estimated Zn leaching losses reaching 92% (CHE), 71% (LIG) and 99.4% ($ZnSO_4$) of the added Zn. In addition, significant differences in the *e-parameter* were also observed between the more soluble sources (LIG vs. CHE, P<0.05; $ZnSO_4$ vs. CHE, P<0.05). The *e-parameter* values indicate that CHE showed higher initial Zn leaching, followed by the LIG source and then $ZnSO_4$. It is noteworthy that no significant differences were observed between treatments in *b-parameter*, indicating a similar gradient of the model curve in all cases. The negative value of this parameter indicated a decrease in the amount of Zn leached from this acid soil in successive collections.

In the calcareous soil (Fig. 3C, D), CHE showed the highest percentage of leached Zn, reaching 75.55% within the first 50 ml collected. The remaining sources leached a total of less than 15% of added Zn, with $ZnSO_4$ (10.49%) and LIG (4.58%) leaching the most Zn among them. In this soil, the short-term Zn leaching model fitted the model proposed in Eq. 1, however, in the medium term the model obtained was slightly different (Eq. 2). This variation was probably due to the lower Zn leaching rate in the calcareous soil, for the same volume of extract added, with respect to the acid soil or the calcareous soil in the short term:

$$leached\ Zn\ concentration = \frac{d}{1 + e^{b\cdot(\mathrm{volume}-\mathrm{e})}} \quad (2)$$

Where, **d** is the maximum value that the curve reaches when the volume tends to infinity; **e** corresponds to the point volume where the curve reaches half its maximum value; and **b** (< 0) is the curve gradient.

The values of the three parameters estimated in the logistic models (Table 2 Supplementary Material) for Zn leached in calcareous soil indicated significant differences between treatments in *d-parameter* (CHE versus other sources and $ZnSO_4$ versus control, P<0.0001 in all cases) and in *e-parameter* ($ZnSO_4$ versus CHE P<0.0001 and LIG versus CHE P<0.05), for short- and medium-term. Statistical analysis of the long-term results also showed significant differences (P<0.0001) in *d-parameter* between CHE versus LIG and CHE versus NP-SINT. According to the values of *d-parameter* obtained in these models, the maximum amount of leached Zn that will be reached in this calcareous soil when the leached volume tends to infinity will be higher with the CHE source, and will reach a value between 56% and 73%, depending on the model. It is also remarkable the low amount of leached Zn that will be reached with the $ZnSO_4$ treatment (0.9% and 5.3%, depending on the model used), reaching values similar to those of the ZnO sources.

3.4 Migration, Extractability, and Bioavailability in Soil

When a Zn source was applied to the soil, a part of the Zn was lost by leaching. The magnitude of leaching varied depending on the source applied, as indicated in the previous section. The Zn remaining in the soil was distributed along the profile in different ways. Figure 4 shows the distribution of Zn in different soil fractions and at different depths (upper and lower halves) of the soil profile, for each applied source and for each of the soils studied.

In the acidic soil when analysing the combined data on leached Zn and the soil Zn status within the columns, two distinct trends in Zn behaviour were identified, depending on the applied source. The first trend encompassed the CHE, LIG, and $ZnSO_4$ sources, which resulted in leaching of over 90% of the added Zn. Consequently, the Zn retained within the column reached extremely low values. It is noteworthy that the largest proportion of Zn retained in the soil when applying these sources remained in the lower half of the column (especially with $ZnSO_4$ and LIG) and that the Zn concentrations in the more labile fractions were very low (Fig. 4A; Table 3 Supplementary Material).

The second trend in the acidic soil involved the ZnO sources. The application of BULK, NP-SINT and NP resulted in the leaching of less than 10% of the applied Zn content. However, the Zn retained in the column was predominantly concentrated in the upper part, half of which was found in WS and EXC (labile forms accessible to plants). In the nanoparticle size sources (NP-SINT and NP) a higher percentage of mobile (leachable) Zn was observed compared to its bulk size counterpart. It is remarkable the percentages of Zn associated to the available fractions (WS, EXC and ADS) in the upper part of the column, which exceeded 62 and 69% for NP-SINT and NP, respectively. The BULK source showed not only the lowest leaching losses but also the highest proportion of Zn retained at the top of the column (80% of added Zn).

In the calcareous soil, the behaviour of Zn was studied at two time points: short term and medium term (Fig. 4B and C), in relation to the applied source. Different trends were observed at short-term in calcareous soil as a function of the applied source, in the behaviour of Zn (leached Zn and Zn status in the soil column) (Fig. 4B). The first trend was observed in the CHE treatment, which was the fertilizer with the highest percentage of leached Zn (76.40%). In the short term, the Zn concentration retained in the upper part of the column represented 18.04% of the total Zn, compared to 5.57% accumulated in the lower part of the column.

The second trend was observed in the LIG and $ZnSO_4$ treatments, where approximately 40% of the Zn retained in the column was concentrated in the upper part. However, the most plant-available Zn concentration (WS and EXC) was approximately 10%. At the top of the column, plant-available Zn associated with the WS, EXC and ADS fractions was found in proportions of 22.57 and 23.45% for $ZnSO_4$ and LIG, respectively (Table 4 Supplementary Material). The third trend was observed in treatments with ZnO (BULK, NP-SINT, and NP), where the highest amount of Zn remained in the upper part of the column. Also, plant-available Zn associated with the WS, EXC and ADS fractions was found in proportions of 75.43%, 76.99% and 86.49%, for NP-SINT, NP, and BULK, respectively (Table 4 Supplementary Material). In this part of the column, the most available Zn in the form of WS and EXC was found in similar percentages (approximately 30%).

In the medium term, the trends observed in the short term persist (Fig. 4C; Table 4 Supplementary Material). The evolution of the percentage of Zn associated with the WS + EXC + ADS forms in the short and medium term is noteworthy. It is observed that the percentage of Zn associated with these fractions, with respect to the total Zn retained in the soil, decreased in the medium term, compared to the short term. These reductions between the short and medium term reached percentages ranging between 0.13 and 0.34% of the total Zn retained in the soil, for the ZnO and CHE sources. However, the decrease in the amount of Zn associated with these fractions reached 2.23% for the LIG source and 2.29% for the $ZnSO_4$ source.

The concentration of bioavailable Zn estimated by the low molecular weight organic acid mixture (LMWOAs) (Table 2) showed that the ZnO treatments had the highest concentration of available Zn in the upper half (0–7.5 cm) of the column in both soils (with values up to 26.79% and 23.35% of the added Zn, for BULK in the acid soil and

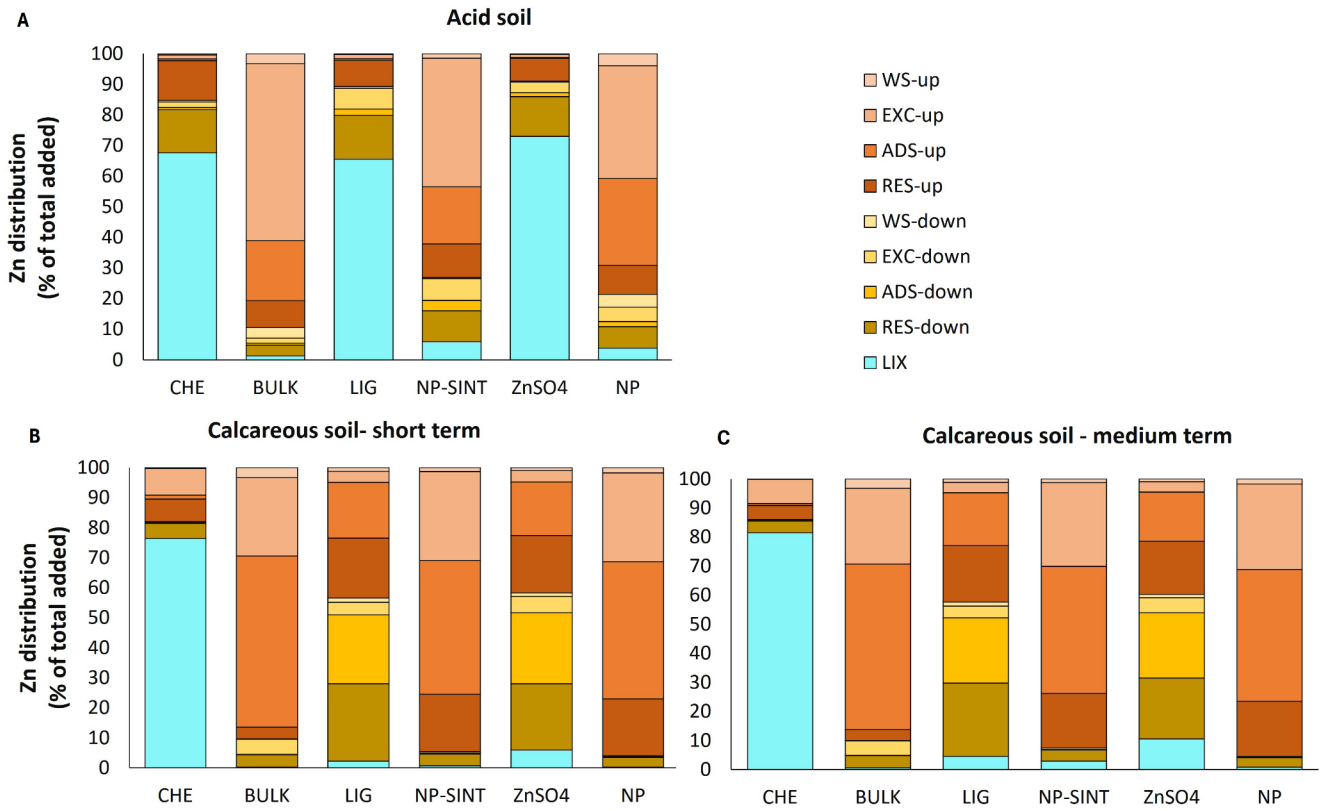


Fig. 4 Distribution of Zn in soil and leachate, as a percentage of the total amount of Zn in each of the sources [BULK: bulk ZnO; NP-SINT: synthesised ZnO NP; NP: commercial ZnO NP; CHE: Zn chelate with DTPA, HEDTA, EDTA; ZnSO4: Zn sulphate ($ZnSO_4$-$7H_2O$); LIG: Zn complexed with lignosulphonic acid]: LIX: leached Zn; WS: Zn associated with the water-soluble fraction in soil; EXC: Zn associated with the exchangeable fraction in soil; ADS: Zn associated with the adsorbed fraction in soil; RES: Zn associated with the residual fraction in soil. UP: upper half (corresponded to the soil between the top 0 and 7.5 cm of the column), DOWN: lower half (corresponded to the soil between the 7.5 and 15 cm depth of the column)

Table 2 Amount of available zn extracted by low Molecular Weight Organic acids (LMWOAs) in soils. Different letters indicate significant differences between treatments for each column (P-value < 0.05). Box-cox transformations. Powers: [1]0.021; [2]0.194; [3]0.025; [4]0.059

	Acidic soil				Calcareous soil			
Treatment	Upper half (0–7.5 cm)[1]		Lower half (7.5–15 cm)[2]		Upper half (0–7.5 cm)[3]		Lower half (7.5–15 cm)[4]	
CONTROL	0.011 ± 0.004	a	0.041 ± 0.05	a	0.002 ± 0.001	a	0.003 ± 0.001	a
BULK	4.019 ± 0.856	d	0.199 ± 0.095	c	3.402 ± 1.056	d	1.085 ± 0.051	c
NP-SINT	3.668 ± 0.788	d	0.803 ± 0.209	e	3.3 ± 0.775	d	0.024 ± 0.024	b
NP	3.334 ± 0.522	d	0.552 ± 0.286	d	3.503 ± 0.851	d	0.023 ± 0.013	b
CHE	0.022 ± 0.006	b	0.037 ± 0.007	a	0.114 ± 0.066	b	0.027 ± 0.015	b
$ZnSO_4$	0.013 ± 0.002	a	0.099 ± 0.025	b	0.734 ± 0.098	c	3.185 ± 0.501	d
LIG	0.045 ± 0.008	c	0.202 ± 0.058	c	0.697 ± 0.387	c	3.095 ± 0.375	d
P-value	0.00001		0.00001		0.00001		0.00001	

NP in the calcareous soil, respectively). While in the acid soil the Zn concentration estimated as bioavailable by this extraction for the $ZnSO_4$ and LIG sources were relatively low (up to 0.3% and 1.3% of the added Zn, for LIG, top and bottom of the column respectively), in the calcareous soil higher available Zn concentrations were obtained, especially in the lower part of the column (up to 4.9% and 21.2% of the added Zn for $ZnSO_4$, top and bottom of the column respectively).

4 Discussion

The dissolution kinetics study was carried out in columns filled with a porous medium of washed sand to eliminate the influence of the soil. In recent years, different studies have evaluated the environmental performance of different products using their dissolution in sand columns as a model (Knijnenburg et al. 2019; Milani et al. 2012; Xu et al. 2020). In this inert media, the more soluble sources ($ZnSO_4$, CHE, and LIG) released a substantial and rapid amount of total and soluble Zn in a first stage, corresponding to the first leachates. Subsequently, the release was extremely low. However, the ZnO sources (BULK, NP, and NP-SINT) showed a continuous and constant release of Zn throughout all leachates. These results are not in agreement with traditional models of nanoparticle dissolution that propose very high dissolution rates at the beginning of dissolution and a further suppression of the release rate with time (Knijnenburg et al. 2019, 2021; Milani et al. 2012). The conditions of our experiment, with large water inputs to simulate environmental conditions of irrigation or rainfall, and the comparison with traditional Zn sources that involved excessive initial leaching have influenced the models obtained.

In soils, leaching of Zn can be influenced by various factors, including soil pH, texture, and the presence of other minerals (Liu et al. 2023; Sun et al. 2023a, b). Since Zn concentration is crucial for availability of Zn to plants (Carmona et al. 2022; Zou et al. 2023), it is essential to know the amount of Zn leached in each soil depending on the Zn source used. In our study, the soil characteristics had a significant impact on the Zn leaching. In general, Zn leaching from the applied sources decreased in both soils compared to the amounts leached into the sand. However, the trend of Zn leaching from the sources showed differences between the two soils.

In the acidic soil, the use of traditional sources (CHE, LIG, and $ZnSO_4$) resulted in excessive and rapid Zn leaching, adversely affecting its availability as a nutrient for crops. Mikula et al. (2020) reported that a basic problem with traditional fertilizers is the high initial release rate of inorganic nutrients. On the other hand, BULK, NP-SINT and NP sources enhanced Zn availability for plants, as a substantial amount of Zn was present in fractions accessible to plants in the upper half of the column. In the calcareous soil the CHE showed the highest percentage of leached Zn. This treatment is more efficient in Zn mobilization but if this nutrient is not utilized by the plant it will tend to be wasted. The ZnO treatments exhibited the highest available Zn concentration at the upper half (0–7.5 cm) in this soil. Alloway (2009) reported that the Zn added to the soil associates with soil components and is retained by them. Our results are in agreement with those obtained by Karak et al. (2004) how reported that in alkaline soils the adsorption of applied Zn from Zn chelates (as Zn-EDTA) by soil colloids was much lower than that of the Zn applied through $ZnSO_4$. However, our results are not in agreement with those obtained by Šebesta et al. (2020) who evaluated the retention by soil solids of Zn applied as ZnO in nanoparticle and bulk size and of ionic Zn ($ZnSO_4$) by studying different partitioning coefficients after 24 h of agitation. These authors concluded a lower retention of Zn from ZnO (both nanoparticle and bulk size) in calcareous soil compared to acid soil. However, the retention of ionic Zn (applied as $ZnSO_4$) was higher in the calcareous soil. These differences with respect to our results were probably due to the conditions of our experiment, which simulated real conditions of permanence of Zn sources in soils.

Chelated sources reduced nutrient losses and enhanced crop uptake. These molecules enclose the nutrient ion with a larger organic molecule (ligand/chelator), protecting against soil reactions. They improve nutrient safeguarding from pH, moisture, and other soil conditions that can cause nutrient immobilization, oxidation, precipitation, or leaching. We observed significant leaching losses of the chelated compound (CHE) in both soils. The amount of Zn retained in the column was halved at 20 mL of leaching (2.32 pore volume) in the acid soil and at 25 mL of leaching (1.78 pore volume) in the calcareous soil. These results are not in line with those reported by Alvarez (2007), who obtained a Zn leaching in an acid soil (pH 6.28) amended with a Zn chelate (mixture of three synthetic chelating agents, DTPA, HEDTA, and EDTA, 90 g water-soluble Zn L^{-1}) similar to that of the control soil, reaching in 60 days of experiment the 1.11% of the applied Zn. However, our results confirm the findings reported by Obrador et al. (2003), who when applying a chelate (with a mixture of three synthetic chelating agents, DTPA, HEDTA, and EDTA, 70 g water-soluble-Zn L^{-1}) of Zn to a calcareous soil obtained in 60 days of experiment (1.88 pore volume) a cumulative leaching of 49.4% of the Zn applied. Several authors (Chandrika et al. 2021) have reported that the use of synthetic chelating agents can lead to environmental risks such as contamination of aquifers or human risks along the food chain. This behaviour of the Zn-chelate (CHE) in both soils can be attributed to the high stability constant (K) of the chelates (log K Zn-DTPA = 19.5, log K Zn-EDTA = 17.5, and log K Zn-HEDTA = 15.3 at an ionic strength of 0.01 mol L^{-1}) (Lindsay and Norvell 1978). This allows higher amounts of Zn to be maintained in the soil solution. According to Sinha et al. (1977) the kinetics reaction of Zn (from chelated compounds as Zn-EDTA) in alkaline soils follows a first order reaction kinetics for reaction periods of up to 5 days. Subsequently, a slow rate of displacement of Zn^{2+} from the chelate is observed. Reyhanitabar and Gilkes (2010) reported that the kinetics of the

Zn-DTPA in alkaline soils follows an exponential rate equation for reaction periods of up to 192 h. The experimental conditions of our study, in the longer term and with higher water inputs, showed a model that fits a logistic curve.

It is remarkable the difference in leached Zn between the two soils when the sources LIG and $ZnSO_4$ were applied. The amounts of Zn leached in the calcareous soil were reduced 7-fold for $ZnSO_4$ and 14-fold for LIG, compared to Zn leached in the acid soil. Alvarez et al. (2001) obtained total Zn leaching in an acid soil (pH 6.28) amended with a Zn lignosulphonate complex (96 g water-soluble Zn L^{-1}) similar to that of the control soil (less than 1% of the applied Zn) at 1.04 pore volume. In our calcareous soil, the source complexed with lignosulfonate showed a lower Zn leached concentration than chelated-Zn and $ZnSO_4$, meaning a higher retention of Zn in this soil column. Natural organic binding agents have a tendency to form weak or very weak metal complexes, which are not effective in protecting the metal from retention by soil components (Almendros et al. 2015). On the other hand, the source $ZnSO_4$, a very soluble salt (solubility at 20 °C: 965 g L^{-1}), makes Zn available in the form of Zn^{2+}, which facilitates its retention in the soil. According to Alloway (2009) acidic conditions increasing the solubility of Zn. However, a high pH of soil causes the precipitation of Zn in the form of insoluble compounds and reduces its leaching potential.

Our results also suggest that over time, the retained Zn in soil from LIG and $ZnSO_4$ becomes less available for plant uptake. Almendros et al. (2013) reported that Zn aging processes in soil transfer part of the soil Zn from labile reserves to less soluble forms. These authors observed this behaviour in other complexed Zn sources such as Zn-aminelignosulfonate, Zn-polyhydroxyphenylcarboxylate, or Zn-ethylenediaminedisuccinate. However, our study observed relatively stable levels of bioavailable Zn (WS and EXC) at the upper half (0–7.5 cm) of the column in the BULK, NP-SINT, and NP treatments, indicating lower aging effects. These differences observed in the medium term underscore the significance of considering the long-term impact of various treatments on Zn availability in the soil.

The ZnO sources (NP, NP-SINT, and BULK) showed lower amounts of leached Zn, with the lowest Zn leaching value obtained with the BULK particles. In our study, the characteristics of the different ZnO particles played a role in the amounts of leached Zn, with different behaviour being observed in the inert medium and in the agricultural soils.

In the inert medium the highest leaching rate of total and soluble Zn was highest with commercial NPs (NP, Z potential − 13.5 mV, TEM particle size 62 nm, Hydrodynamic size DLS 511 nm), followed by synthesised particles (NP-SINT, Z potential 12. 3 mV, TEM particle size 76 nm, Hydrodynamic size DLS 350 nm) and BULK particles (Z potential − 14.7 mV, TEM particle size 83 nm, Hydrodynamic size DLS 541 nm). During initial leaching, the behaviour of commercial and synthesised NPs was comparable. However, at higher volumes, the commercial NPs showed higher leaching. Nano-sized materials are expected to disperse faster than macroscopic-sized particles of the same material (Borm et al. 2006). Our findings concurred with Singh et al. (2018), who found that, although the water solubility of Zn oxides is lower than that of other Zn sources such as $ZnSO_4$, nano-sized ZnO exhibits considerably higher dissolution/dispersion rates due to its reduced particle size.

However, in both agricultural soils a higher tendency of the synthesised particle (NP-SINT, Z potential 12.3 mV, TEM particle size 76 nm, Hydrodynamic size DLS 350 nm) to leach higher amounts of Zn was observed. The particle dispersion rate is influenced by the zeta potential, as an increase indicates the stability of the dispersion system (Alshora et al. 2019; Cho et al. 2012). In our study, the Zeta potential value of synthesised nanoparticles (12.3 mV), commercial NPs (-13.5 mV) and bulk size (-14.7 mV) indicates instability and aggregation tendency. Furthermore, different Zeta potential values, one positive and the other negative, could influence the leaching effect of the particles in the medium. In both agricultural soils (acidic soil pH 5.9; oxidizable OM, 4.1 g kg^{-1}; clay, 81 g kg^{-1} and basic soil pH 8.2; oxidizable OM, 14.5 g kg^{-1}; clay, 55 g kg^{-1}) the highest leaching is observed with the Z potential value positive and indicating instability of the dispersion system. Their dispersion in water might not form stable suspensions in these agricultural soils, forming agglomerates that affect the leaching of Zn from the column. However, the smaller hydrodynamic diameter values (NP, Hydrodynamic size DLS 511 nm; NP-SINT, Hydrodynamic size DLS 350 nm and BULK, Hydrodynamic size DLS 541 nm) indicate less aggregation which may have influenced a lower retention by the soil particles, leaching a higher amount of Zn.

The low Zn leaching rates obtained in our study indicate a low risk of toxicity from nanoparticles in the aquatic environment. However, the toxicity of ZnO NPs has been reported to be higher than the equivalent concentration of a zinc ion solution for different aquatic species (Xiong et al. 2011). In addition, particles can be classified as safe or hazardous depending on their specific properties (Yamini et al. 2023). De Francisco et al. (2024) reported that physical and chemical characteristics of the different nanoparticles had an impact on their toxic effect on seedling development. These authors found that ZnO particles with higher Zeta potential (ZP) or specific surface area (SBET), had a less harmful impact on tomato radicle length compared to other treatments studied. Other authors have reported various acute deleterious effects on soil microorganisms (Yamini et al. 2023) or on other soil bioindicator organisms

(De Santiago-Martin et al. 2015; García-Gómez et al. 2020; Kumah et al. 2023). However, Cornelis et al. (2014) reported that the actual risk of exposure to nanoparticles in natural soil depends on the bioavailability, i.e. the actual concentration of nanoparticles to which organisms are exposed and which can have effects on them. In our study the amounts of bioavailable Zn associated to the available fractions (WS, EXC and ADS) in the upper part of the column were high when ZnO particles were applied, however such high applications of Zn nanoparticles are not found naturally in the soil and do not correspond to the doses of Zn applied as fertiliser in the agricultural environment.

5 Conclusions

The dissolution kinetics in inert media show a fast and short time release of Zn from the most soluble and stable sources (added Zn complexed with lignosulphonic acid, Zn chelated with diethylenetriamine-pentaacetate, hydroxy-ethylenediamine-tetraacetate and ethylenediamine-tetraacetate and the ionic Zn source $ZnSO_4$) and a constant and prolonged time release from the most insoluble sources (ZnO in all sizes studied). The availability, distribution, ageing and leaching of Zn in the soil columns depend on the characteristics of the sources used and the type of soil. The solubility and stability of the traditional sources and the Zeta potential and Hydrodynamic size DLS (dynamic light scattering) values of the ZnO particles seem to be the key characteristics of their behaviour in soils. In acid soil, the application of Zn complexed with lignosulphonic acid, Zn chelated and $ZnSO_4$ resulted in high Zn losses by leaching and Zn accumulation in the lower zones of the column. The three ZnO sources (nanoparticle, synthesised nanoparticle, and bulk) could behave as a reservoir of micronutrients as they lead to a higher accumulation and availability at the top of the column, with very low amounts of Zn being leached. In the calcareous soil, the chelated Zn source increased its leaching risk, contrary to the other traditional fast dissolving sources (Zn complex and $ZnSO_4$) which kept higher amounts of Zn at the top of the column. ZnO sources again showed sustained nutrient release over time and improved nutrient retention in the upper soil layers. The slower dissolution kinetics of ZnO sources offer advantages compared to traditional fast-dissolving fertilisers, as they decrease the risk of leaching and environmental contamination and increase plant uptake, suggesting a promising strategy to improve the efficiency and sustainability of agricultural fertilisation. However, further research is needed to investigate the influence of nanoparticle characteristics on behaviour in crops and agricultural soils.

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Declarations

Conflict of Interest The authors declare that they have no conflict of interest.

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