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ORIGINAL PAPER

The Development of a Model for Recommending the Application of Zinc Fertilizer in the Mediterranean Region of Central Chile

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Abstract

The main aim of this study is to develop a mechanistic model of fertilization for recommending the application of zinc (Zn) fertiliser for maize based on the mass balance of Zn. The model would consider the critical Zn level for maize (Zn_{CL}), Zn availability in the soil (Zn_A) and Zn buffering capacity (Zn_b). Soil samples were collected from 78 maize fields for chemical and physical characterization including measuring Zn_A and Zn_b. Additionally, a crop management survey was carried out in each field. The classification and regression trees method (CART) was used and relationships between Zn_b and some soil properties were established, clay content being the most relevant to the model, besides soil reaction (pH) and silt content. The application of Zn fertilizer can be adequately calculated by a mechanistic model that considers Zn_A, Zn_b and Zn_{CL} above that which maize crop yields do not increase. This work highlights the importance of Zn_b evaluation by the incubation procedure and the extraction of available Zn by DTPA solution. As hypothesised and then demonstrated in this work, Zn_b is closely related to soil pH and texture (clay and silt). Our results suggest that, in between 51 and 97% of fields examined, it would be necessary to apply Zn fertilisers to produce the maximum maize yield.

Keywords Soil fertility · Zinc · Soil buffering capacity · Maize, Modelling

1 Introduction

Maize (*Zea mays* L.) is the third most important crop worldwide after rice (*Oryza sativa* L.) and wheat (*Triticum aestivum* L.). In Chile, maize covered approximately 80,000 ha during the 2018–2019 season, producing 1 million tons of grain, representing 13% of the total annual crop surface with a mean yield of 12 t ha^{-1}, one of the highest in the world. This is largely due to the favourable temperature and solar radiation conditions of the Mediterranean climate. In Chile, maize is cultivated using conventional irrigation systems during the growing season. To maintain these high yields, farmers need to apply high levels of nitrogen (N), phosphorus (P), potassium (K) and other nutrients. Nájera et al. (2015) carried out a survey of 31 soils cultivated with maize in central Chile under Mediterranean conditions and found that there was a dominance of neutral-alkaline soils with low soil organic matter content (SOM < 2.5%). In addition, the authors reported that when available forms of N, P and K showed high concentrations in the soil, soil pH and Zn content were identified as the most important variables controlling maize yield. The results of Nájera et al. (2015) suggest that in neutral-alkaline soils cultivated with maize and high inputs of N, P and K, there may be an increase in maize yield in response to Zn application. Low plant availability of Zn in crops may be expected in most countries with a Mediterranean-type climate, where alkaline-calcareous soils represent an important type of agricultural soil (Rengel

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2015; Noulas et al. 2018). Soil Zn availability is a critical problem for cereal production, causing a severe reduction in both the yield and nutritional quality of grains which can affect human health especially in regions with cereal-based diets (Cakmak 2008; Sadeghzadeh 2013; Ryan et al. 2013). On the other hand, in several industrial areas high soil Zn levels might cause environmental problems if it is dispersed into the trophic chain or into water (Muthusaravanan et al. 2020). Soil analysis enables possible deficiencies to be determined in advance of growing the crop so that appropriate fertilisation or other treatments can be made to prevent the yield and/or quality of the future crop being impaired by Zn deficiency (Alloway 2008). However, maize small farmers in central Chile do not extensively use soil analyses to determine the required fertiliser dosage.

Plants take up Zn from the soil solution as Zn^{2+} (Dang et al. 1994), so the amount of the element in the liquid phase and its replenishment by exchange processes determines its availability for plants (Barber 1995). Available Zn can be determined by ammonium acetate at pH 7.0, $MgCl_2$ or other chemical and isotopic analysis procedures (Sinaj et al. 2004). A correlation between crop yield and Zn extracted by different solutions has been reported by several authors (Lindsay and Norvell 1978; Bansal et al. 1980; Lins and Cox 1988). The pioneering work of Lindsay and Norvell (1978) showed a high correlation between Zn soil concentration extracted by diethylenetriaminepentaacetic acid (DTPA) method and crop yield. Although DTPA solution removes Zn from labile pools, it also could remove some non-exchangeable Zn which is not plant available (Sinaj et al. 1999).

The supply of plant available Zn depends on soil pH, organic substances, clay minerals, carbonates and rhizospheric interactions with microorganisms (Rengel 2015; Moreno-Lora and Delgado 2020). Among these, soil pH is likely the most important soil parameter controlling soil Zn availability, especially due to its effect on the amount of Zn adsorbed onto soil particles (Bradl 2004; Rengel 2015). The classic work by Bar-Yosef (1979) showed that by increasing soil pH, the Zn concentration in soil solution decreased, while the amount of Zn adsorbed onto soil particles increased. Furthermore, in alkaline soils, Zn concentration in soil solution is observed to decrease as calcium carbonate concentration increases and the opposite is observed with increasing soil organic matter content (Reyhanitabar and Gilkes 2010).

The complexity of the exchange and desorption process can be summarized in the 'buffering power (*b*)' concept. The buffering power controls the release of Zn^{2+} from the soil solid phase that replenishes the soil solution (Dang et al. 1994). By determining the soil solution Zn concentration and the amount of adsorbed Zn through the DTPA method, Dang et al. (1994) noted that Zn buffering power (Zn_b) regulates the Zn supply to crops. They found that Zn_b accounted for as much 62% of the difference in yield of wheat in an Australian Vertisol (soil pH ranging from 7.5 to 9.0). An extension of the buffering power concept can be applied for the addition of fertilizer to the soil and the change that it produces in the amount of available nutrients extracted. This approach has already been used for the addition of phosphorus to soils (Vásconez and Pinochet 2018).

The favourable soil properties in Mediterranean central Chile, e.g. deep, neutral pH, low salt and sodium content (Casanova et al. 2013) suggest that the yield of maize could be increased if an adequate soil fertility program is implemented, for example through Zn fertiliser application. There are general recommendations on Zn fertiliser doses for maize production in different countries with optimal doses ranging from 15 to 36 kg $ZnSO_4 \bullet 7H_2O$ ha^{-1} (Meena et al. 2013; Liu et al. 2016). On the other side, critical levels for Zn-DTPA on soil have been defined for maize in different countries such as Bangladesh with 0.84 mg Zn kg^{-1} (Akter et al. 2020) and Zimbabwe with 0.80 mg Zn kg^{-1} (Manzeke et al. 2019) which are within the critical deficiency concentration range for Zn-DTPA in soil of 0.5 to 1.5 mg kg^{-1} reported by Alloway (2008). In China, Liu et al. (2017) found that the optimal soil Zn-DTPA concentration required to attain high maize grain yields (> 10 t grain ha^{-1}) was 4.7 mg kg^{-1}. The evaluation of soil Zn levels is critical to determine a fertilization strategy (Lins and Cox 1988) and to prevent the loss of Zn to drinking water which can cause adverse effects in human beings (Muthusaravanan et al. 2020).

Based on the processes mentioned above, we hypothesised that Zn availability in the soils under study is mainly determined by clay content and soil pH and that these relationships can be integrated using a mechanistic model to calculate Zn fertiliser application dosage for maize. Thus, the main aim of this study was to develop a mechanistic model for recommending Zn fertiliser application dosage for maize based on the Zn concentration in the soil (Zn-DTPA) and soil Zn_b. These measurements were combined with critical soil Zn levels determined by the Zn-DTPA extraction procedure previously reported in the literature. Some specific objectives of this study were (i) to identify correlations between the Zn_b with other soil properties and (ii) to analyse whether it is necessary to apply Zn fertiliser to maize fields in the study area.

2 Materials and Methods

2.1 Site Description

The study was carried out on 78 maize fields located in the Central Valley of the O'Higgins Region (between 33° 90′ S and 34° 80′ S) (Figure S1). Maize was sown in spring (September–October 2015) and harvested in autumn (March–April 2016). A commercial hybrid maize adapted to this area was drilled with 10-13 cm intervals with a spacing between rows of 75 cm, for an anticipated stand of approximately 95,000 plants ha^{-1}. In the study area, the maize grain yield ranged from 11 to 19 t ha^{-1}.

In the study area, farmers applied two fertilisers with different formulas: a mixed fertiliser containing 25% N; 10% P_2O_5; and 10% K_2O at planting using subsurface band, and urea (46% N) by side dressing after planting during vegetative stages V5–V6, with overall levels of nutrients supplied of between 350 to 560 kg N ha^{-1}, 75 to 90 kg P_2O_5 ha^{-1} and 75 to 90 kg K_2O ha^{-1} (Corradini et al. 2015; Salazar et al. 2017). The fields did not receive additional Zn fertilization. During the growing season, the maize was irrigated using a furrow system with low water use efficiency (< 45%), where between 10,000 and 18,000 m^3 ha^{-1} of water was applied during the crop cycle.

According to the Soil Taxonomy the soils belong to the Soil Orders: mollisols (57% of the total), alfisols (19% of the total), vertisols (18% of the total) and inceptisols (6% of the total) (Soil Survey Staff 2014), occupying alluvial plains (CIREN 2006; Casanova et al. 2013). The climate in the study area is classified as temperate, with dry and hot summers and relatively cold winters, corresponding to Csa (hot-summer Mediterranean climate) according to the Köppen-Geiger System (Beck et al. 2018).

2.2 Soil Sampling and Analyses

In each field, soil samples were collected at 0-20 cm depth intervals between July and September 2015 before sowing and a composite soil sample of 10 to 20 constituent samples was collected. The soil samples were dried at room temperature and sieved at 2 mm. Chilean standard methods for chemical soil analysis according to Sadzawka et al. (2006) were used for measuring soil fertility parameters that may have a direct impact on the Zn concentration of soils in the study area, such as Zn by the DTPA method, soil pH was determined in a 1:2.5 soil:water ratio, and soil organic matter (SOM) by calcination (360 °C). The Zn concentrations by the DTPA method were classified as very low (< 0.25 mg kg^{-1}), low (0.25–0.5 mg kg^{-1}), medium (0.51–1 mg kg^{-1}) and high (> 1 mg kg^{-1}); whereas, SOM contents were classified as very low (< 1.5%), low (1.6–3.0%), medium (3.1–4.5%), high (4.6–6%) and very high (> 6%). In addition, soil texture was determined by the hydrometer method and soil bulk density with cylinder (Sandoval et al. 2012). All Zn concentration measurements were carried out in a Microwave Plasma Atomic Emission Spectrometer (MP-AES 4200).

2.3 Zinc Soil Buffering Capacity Measurement

It has been shown that the reactions of ions in soil continue over time, even so the largest amount of Zn applied to a soil reacts after a couple of days in an incubation experiment at 60 °C (Barrow 1986). Therefore, we believe that the Zn buffer capacity can be assessed after a discrete incubation time. We adapted the method proposed for soil P buffer capacity used in Chile to assess the buffer capacity of Zn (Sadzawka et al. 2006), which is similar than that used by Barrow (1986) (Fig. 1). An initial Zn_b test using three soil samples with different textural classes was carried out to determine the number of Zn concentrations needed for the soil incubations. It was necessary to add four Zn concentrations: 0, 25, 50 and 100 mg Zn L^{-1} to fit a linear equation associated with Zn_b.

The procedure to measure Zn_b consisted of six steps: (i) soil samples were air-dried (30 to 35 °C) until mass-loss ceased and then sieved at 2 mm; (ii) a 3-mL volume of a 2-mm sieved soil was weighted, four replications of this were prepared and put into a plastic flask (250 mL); (iii) four Zn concentrations: 0, 25, 50 and 100 mg Zn L^{-1} were added to each of the soil samples; (iv) the samples were incubated at 60 °C for 24 h; (v) 20 mL DTPA $CaCl_2$-TEA was added to the plastic flask with shaking for 2 h and (vi) the DTPA-extractable Zn concentration was measured using the procedure described by Katyal and Sharma (1991).

For each soil sample, a lineal regression function was fitted to the relationship between Zn extraction (mg Zn kg soil^{-1}) after the addition of increasing Zn concentration (0, 25, 50 and

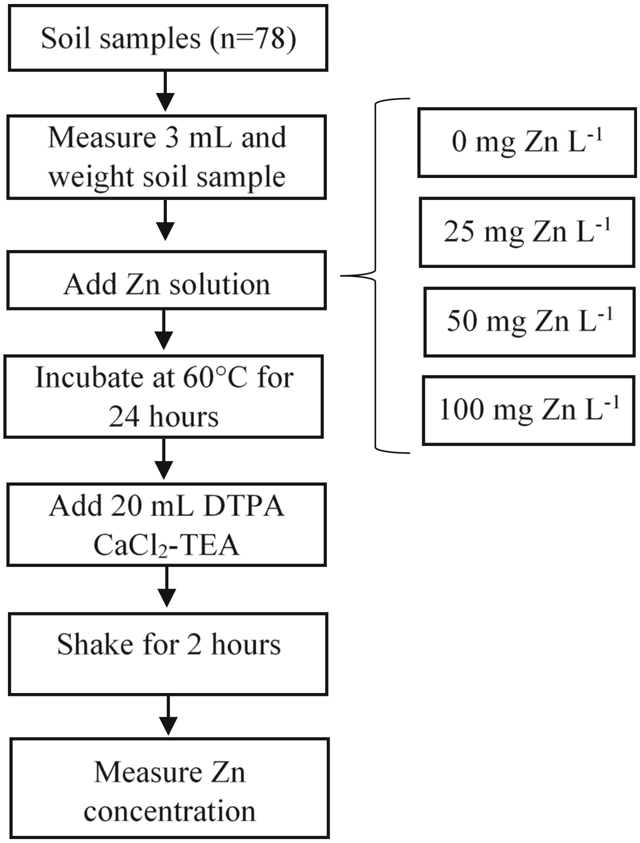

Fig. 1 Procedure for measuring zinc soil buffering (Zn_b)

100 mg Zn L^{-1}) and the application of different concentrations of Zn per soil mass (mg Zn kg^{-1}). The Zn_b (kg Zn ha^{-1}/mg Zn kg^{-1}) was the reciprocal of the slope of the lineal regression function that was calculated.

2.4 Model for Zn Fertiliser Recommendation

The Zn rate per hectare was calculated as follows:

$$\text{Zn rate}\left(\text{kg Zn ha}^{-1}\right) = \left[\text{Zn}_{\text{CL}}\left(\text{mg Zn kg}^{-1}\right) - \text{Zn}_A \ \left(\text{mg Zn kg}^{-1}\right)\right] \times \text{Zn}_b\left(\text{kg Zn ha}^{-1}/\text{mg Zn kg}^{-1}\right) \quad (1)$$

where available Zn on soil (Zn_A) is the measured soil analysis value for Zn-DPTA in the soil (mg Zn kg^{-1}); Zn_b is the Zn soil buffering capacity (kg Zn ha^{-1}/mg Zn kg^{-1}); and the critical Zn level for maize was obtained from the literature (Zn_{CL}) ranging from 1.0 to 4.7 (Alloway 2008; Liu et al. 2017; Manzeke et al. 2019; Akter et al. 2020). To determine the amount of Zn to be applied per hectare, during the incubation procedure the volume and mass of each soil sample was registered.

2.5 Statistical Analyses

To identify and predict the relationship between Zn_b and relevant variables with soil properties such as texture (sand, silt and clay), pH and SOM, which are non-independent variables between each other, the decision tree algorithm (CART), a non-parametric procedure was used to detect the most relevant variables, which allows the percentage of Zn_b variation related to the selected categories to be explained. Yang et al. (2013) noted that CART divides the data in homogenous subsets using binary recursive partitions according to the following steps: (i) the most discriminative property is first selected as the root node to partition the data set into branch nodes; (ii) the partitioning is repeated until the nodes are homogenous enough to be terminal which are called leaves; (iii) in a tree structure, leaves represent class labels (i.e. Zn_b categories) and branches represent conjunctions of features (i.e. soil properties) that lead to those class labels; and (iv) a CART can grow larger than it needs to be and then be pruned back to find the best tree.

In addition, descriptive statistics (mean, maximum, minimum, variance, standard deviation and coefficient of variation) were used to characterize soil properties and Zn_b values. Statistical analyses were performed using Infostat® Software version 2018 (Di Rienzo et al. 2018) and the violin plot with GrapPad Prism® v8.

3 Results

3.1 Soil Properties Related to Zinc Buffering Capacity

Table 1 shows the results of the measurement of some soil properties that are related to Zn buffering capacity (Zn_b) in soils. Soil pH analyses showed that soils were classified as: slightly acidic (15% of the total), neutral (58% of the total), slightly alkaline (26% of the total) and moderately alkaline (1% of the total). Clearly, there was a dominance of neutral-alkaline soils that is mainly due to the low rainfall and high reference level of evapotranspiration in the Mediterranean zone, so there is little leaching of base-forming cations to the lower soil horizons (Casanova et al. 2013). Soil samples showed SOM content ranging from very low (5% of the total), low (71% of the total), medium (14% of the total), high (3% of the total) and very high (8% of the total). It is important to note that in these soils the highest SOM levels were found in lacustrine landforms (Casanova et al. 2013). In contrast, the soils with very low SOM content were found where farmers usually burn crop residues after grain harvest (Nájera et al. 2015). A variability of soil texture classes were found in the studied soils ranging from sandy loam (6% of the total), loam (14% of the total), sandy clay loam (9% of the total), silty loam (1% of the total), clay loam (32% of the total), silty clay loam (3% of the total), silty clay (1% of the total) to clay (33% of the total). The soils had Zn-DTPA concentrations with a mean value of 1.27 mg Zn-DTPA kg^{-1} which was close to the mean value reported by Nájera et al. (2015) in soils cultivated with maize in the same study area (1.58 mg Zn-DTPA kg^{-1}). The Zn_b values ranged between 0.47 and 1.5 kg Zn ha^{-1}/mg Zn kg^{-1}. Most of the Zn-DTPA soil concentrations reported in this work are lower than the most common Zn critical levels (Zn_{CL}) reported in the literature for maize, which consider values around 1 mg Zn-DTPA kg^{-1} (Alloway 2008; Manzeke et al. 2019; Akter et al. 2020), 2 mg Zn-DTPA kg^{-1} (Zare et al. 2009) or the highest value of 4.7 mg Zn-DTPA kg^{-1} recently reported by (Liu et al. 2017).

After the addition of increasing Zn concentration (0 to 100 mg Zn kg soil^{-1}) during soil incubation, a high variation in soil measured Zn-DTPA was found. This was highest when 100 mg Zn kg soil^{-1} was added (Fig. 2). Because of this high variation, the classification of Zn_b including more soil properties was carried out. The CART method showed that Zn_b was related to clay and silt contents and soil reaction (pH) (Fig. 3). Seven nodes were found, where node 0 included all the soil samples analysed ($n = 78$), nodes 1 and 2 demonstrated that clay content was the most important soil property related to Zn_b, whereas silt (nodes 3 and 4) and soil pH (nodes 5 and 6) were identified as having an intermediate relation to Zn_b.

Table 1 Descriptive statistics of some soil properties and Zn buffering capacity (Zn_b) in the study area ($n = 78$)

Soil properties	Descriptive statistics[1]						
	Units	μ	min	Max	σ	σ^2	CV (%)
pH	-	7.03	6.00	7.90	0.44	0.19	6.30
Soil organic matter	(%)	2.84	0.68	14.20	2.02	4.09	71.10
$\text{Clay}_{(<0.002\ \text{mm})}$	(%)	36.27	14.90	69.70	13.11	171.79	36.10
$\text{Silt}_{(0.05\text{–}0.002\ \text{mm})}$	(%)	30.78	13.80	52.30	8.61	74.15	27.90
$\text{Sand}_{(2\text{–}0.05\ \text{mm})}$	(%)	32.95	9.20	69.50	14.56	211.97	44.20
Zn-DTPA	(mg kg^{-1})	1.27	0.12	8.72	1.19	1.41	93.60
Zn_b	(kg Zn ha^{-1}/mg Zn kg^{-1})	0.84	0.47	1.50	0.23	0.05	27.38

[1] *μ*, arithmetic mean; *min*, minimum value; *max*, maximum value; *σ*, standard deviation; σ^2, variance; *CV*, coefficient of variation

Based on the CART after tree pruning, it was possible to group the soils into four categories according its Zn_b and textural classes as shown in Table 2.

The first category were soils with less than or equal to 37% clay and less than or equal to 51% silt. Their prediction in terms of Zn_b was on average 0.714 kg Zn ha^{-1}/mg Zn kg^{-1} (Fig. 3, node 3). The second category were soils with less than or equal to 37% clay and more than 51% silt. Their prediction was on average 1.190 kg Zn ha^{-1}/mg Zn kg^{-1} (Fig. 3, node 4). The third category were soils with more than 37% clay and a pH less than or equal to 7.45. Their prediction was on average 0.961 kg Zn ha^{-1}/mg Zn kg^{-1} (Fig. 3, node 5). And finally, the fourth category were soils with more than 37% clay and a pH more than 7.45 with a prediction of 1.290 kg Zn ha^{-1}/mg Zn kg^{-1} (Fig. 3, node 6). To summarize, clay, silt and pH were the most important variables used when estimating Zn_b in these soils.

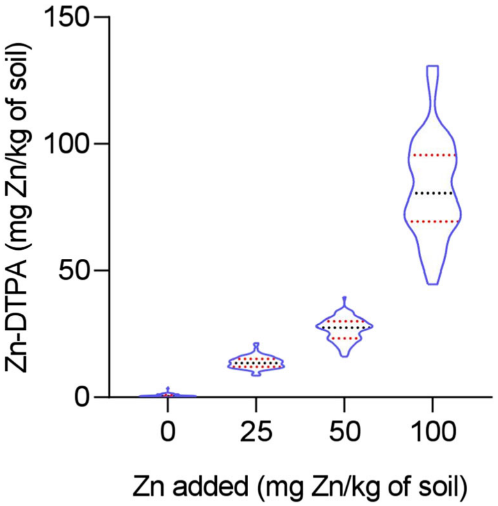

Fig. 2 Relationship between Zn added to soil incubation samples and soil measured Zn-DTPA after incubation. Data distribution was presented by violin plots with median (black-dashed line), interquartile range (red-dashed line) and frequency distribution (blue outline line)

3.2 Dose of Zn Fertiliser Based on the Proposed Model

Across the study area, the mean maize grain yield was 15.3 t ha^{-1}, with grain yield ranging from 11.0 to 19.3 t ha^{-1}. It was found that in most soils the available Zn was lower than the most common Zn_{CL} reported in the literature, i.e. in the range of 1 to 4.7 mg Zn kg^{-1} (Alloway 2008; Liu et al. 2017). Therefore, in 51%, 86% and 97% of the total fields, it should be necessary to apply Zn fertilisers for future maize production if the Zn_{CL} is 1, 2 and 4.7, respectively. Regarding the highest reported Zn_{CL} value of 4.7 mg kg^{-1} that was proposed by Liu et al. (2017) in a field experiment in China, it is important to note that this value is associated with a high maize yield of 12.6 t ha^{-1} when cultivated in a moderately alkaline silty loam alluvial soil in China similar to the most commonly reported maize yield and soil type from this study. The proposed doses of Zn fertilizer ranged from 0 kg of Zn for those soil samples with high Zn level that are above the Zn critical value to a maximum dose of 5.36 kg Zn ha^{-1} (Zn_{CL} = 4.7 mg Zn kg^{-1}) for those soil samples with very low Zn concentration. In the Table 3, the recommended rate of Zn fertilizer dosing for future maize production was also expressed as the more common Zn salts: $ZnSO_4{\bullet}H_2O$ and $ZnSO_4{\bullet}7H_2O$.

4 Discussion

The CART analysis explained up to 58% of Zn_b variation and allowed four categories of Zn_b to be established based on textural class and soil reaction (pH) for the soils in Mediterranean Central Chile. It was found that Zn_b was positively correlated with clay content, soil reaction (pH) and silt content. Similarly, Dang et al. (1994) found that soil pH accounted for most of the variation in Zn_b in a group of Australian Vertisol ($n = 14$) that had clay content ranging from 38 to 76%.

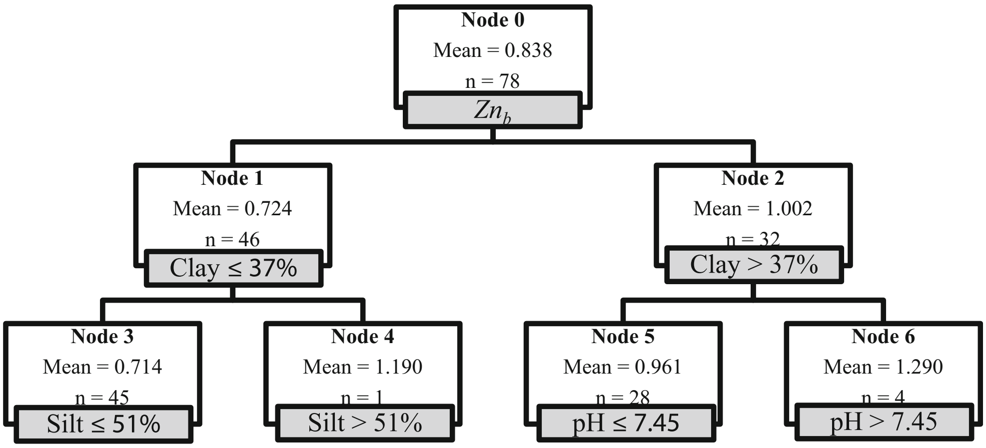

Fig. 3 Nodes of the decision tree algorithm (CART) for predicting Zn buffering capacity (Zn_b) based on clay, silt and pH after tree pruning

Rashid and Ryan (2004) noted that in Mediterranean soils Zn deficiency is the most widespread problem among micronutrient deficiencies due to alkaline soil pH. In a study carried out by Sims (1986), the amount of exchangeable Zn, Cu and Mn decreased drastically with pH rise. Similar results were reported by Iyengar et al. (1981) for the relationship between Zn and soil pH. Furthermore, available Zn-DTPA concentration declined with a rise in pH and a fall in clay content (Katyal and Sharma 1991). This behaviour is likely due to an increase in the negative charge of clay surfaces as soil pH rises which ultimately increases the amount of adsorbed Zn (Saeed and Fox 1979; Gupta et al. 1987). Clay minerals seem to play a central role in retaining Zn on soil minerals either with variable charge or with permanent charge (McKenzie 1980; González-Costa et al. 2017). In some extent, the adsorption process can be irreversible at high pH values since specific bonds are formed (Zhao and Selim 2010). Therefore, two soil parameters, clay content and soil pH, are related to controlling Zn availability (McKenzie 1980; Bradl 2004). The combined effect of pH and clay content in the present study explained the observed soil Zn_b. In those soils with more than 37% clay content and a pH value higher than 7.45, the Zn_b was the highest among the soils evaluated. These results suggest that Zn availability in the soils studied here is likely controlled by clay content and soil pH. The effect of pH does not only affect the surface charge of clay minerals but also the charge of soil organic matter. An increase in soil pH will increase the amount of negative charge of the SOM (Bradl 2004) which adsorbs metal cations forming metallic complexes (Van Dijk 1971). However, depending on the nature of the ligands and functional groups present in humic acids (HA), some Zn-HA complexes can be available for plants (Boguta and Sokołowska 2016). Despite the variation of SOM in the soils under study, this parameter had no influence on the dose of Zn predicted by the tree decision–based algorithm.

Soil Zn_b was also related to soil silt content. An important proportion of the soils under study presented a Zn_b associated with clay and silt fractions (Fig. 3, nodes 1, 3 and 4). Although it has been shown that silt has a secondary role in controlling Zn availability, due to the few clay minerals that can adsorb Zn (Nielsen 1990), Lair et al. (2007) showed that the silt fraction could also be responsible for Zn adsorption. The contribution of the silt fraction to Zn adsorption could be related to the building of microaggregates with clay minerals and SOM (Stemmer et al. 1998).

As DTPA solution extracts Zn from exchangeable positions (Sinaj et al. 1999) and as exchangeable Zn seems to be the main source for Zn plant uptake (Sims 1986), we postulate that the correction of the dose through Zn buffering capacity (Zn_b) will result in an increase in available Zn. The Zn_b can be a useful parameter to determine soil Zn availability. It should be complemented with a soil fertility test that determines the main soil parameters as defined in this study, e.g. Zn-DTPA level, pH and particle size distribution. With that information, we proposed a dose Zn fertilizer calculation by using the actual Zn level extracted by DTPA solution, the Zn_b and the soil Zn critical level. In this study, we did not determine the Zn critical level for maize by carrying out plant growth experiments. Nevertheless, several other authors determined critical levels by using classical experiments either with plants growing in greenhouses or under field conditions (Lins et al. 1988; Seth et al. 2018). These studies report soil Zn critical levels which are within the range of soil Zn concentration proposed

Table 2 Zn buffering capacity (Zn_b) categories according to textural class and soil reaction (pH)

Categories	Clay (%)	Silt (%)	pH	Zn_b (mean prediction) kg Zn ha^{-1}/mg Zn kg^{-1}
I	≤ 37	≤ 51	-	0.714
II	≤ 37	> 51	-	1.190
III	> 37	-	≤ 7.45	0.961
IV	> 37	-	> 7.45	1.290

Table 3 Zn fertiliser dosage recommendations according different Zn critical levels

Fertiliser Zn rate[1]	Zn_{CL}[2]		
	1	2	4.7
kg Zn ha^{-1}	0.28 ± 0.19	0.88 ± 0.38	2.97 ± 0.94
kg $ZnSO_4•H_2O$ ha^{-1}	0.77 ± 0.52	2.46 ± 1.06	8.05 ± 2.09
kg $ZnSO_4•7H_2O$ ha^{-1}	1.25 ± 0.86	4.02 ± 1.73	13.17 ± 4.74
% of total fields that need Zn fertilisation	51	86	97

[1] Fertilizer Zn rate shows arithmetic mean ± standard deviation

[2] Zn_{CL} is the Zn critical level in mg Zn kg^{-1}

in this study, even if the extractant solution was something other than DTPA. In the current study, the model for the recommendation of Zn fertiliser dosing for maize determined that for between 51 and 97% of all fields in the study, it would be necessary to apply Zn fertilisers depending on the Zn_{CL} used. Therefore, when a Zn_{CL} of 4.7 mg Zn kg^{-1} for maize with high yield is used (Liu et al. 2017), fertilization rates range from 2.4 to 15 kg $ZnSO_4•H_2O$ ha^{-1} depending on textural class and soil reaction (pH). Even considering the usual fertilization strategy, the results of the current study are within the values reported by Alloway (2008) for intensive maize production, which range between 2.2 and 34 kg $ZnSO_4•H_2O$ ha^{-1} broadcast and 1.1–4.5 kg $ZnSO_4•H_2O$ ha^{-1} banded. Montalvo et al. (2016) added that the large variation in the range of the Zn fertilizer dosage is related to the application method, soil type, deficiency level and the sensitivity of the crop. In this sense, banded fertilizer application increases soil solution concentration and favours plant influx (Barber 1995) which could explain some variations in the rate of Zn fertilizer reported in other studies. An alternative to soil fertilizer application is to use selected cultivars able to use Zn already present in the soil more efficiently or by using Zn foliar application (Singh et al. 2019; Haider et al. 2020). Promising developments in the area of nanoparticle fertilizers should also be taken into account, as they have been used to alleviate micronutrient deficiencies in crops (Bala et al. 2019). The Zn fertilizer dose calculation proposed here could also be adapted for other crops, especially those cultivated under saline conditions since Zn fertilization can alleviate salt stress (Nadeem et al. 2020).

5 Conclusions

The application dosage of Zn fertilizer can be adequately calculated using a mechanistic mass balance model that considers the current soil Zn level, the Zn_b, and the critical level above which maize crop yield does not increase. This works highlights the importance of Zn_b evaluation through an incubation procedure and the extraction of available Zn by DTPA solution. As hypothesised and demonstrated in this work, Zn_b is closely related to soil pH and texture, especially clay and silt content. Standard soil analyses commonly measured pH, particle size distribution and available micronutrient concentration, all of which can be used as complementary information for the proper determination of the amount of Zn to be applied as fertilizer for a crop of maize.

With this model, it is possible to calculate the amount of Zn fertilizer required to reach a Zn critical level in the soil in a straightforward way. In a practical sense, the model for Zn fertiliser dosing for maize determined that in between 51 and 97% of fields examined it would be necessary to apply Zn fertilisers to produce the maximum yield of maize.

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Compliance with Ethical Standards

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

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