INNSPUB

International Journal of Agronomy and Agricultural Research (IJAAR)
ISSN: 2223-7054 (Print) 2225-3610 (Online)
http://www.innspub.net
Vol. 7, No. 5, p. 59-71, 2015

RESEARCH PAPER OPEN ACCESS

Available zinc levels in soils of Argentina

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Article published on November 21, 2015

Key words: Soils, Fertility, Micronutrients

Abstract

Adequate grain zinc (Zn) concentration is important because of its influence on human health. The Argentina Pampas region (APR) provides between 86% and 90% of total grain exports by the country. Soils of the Argentina Pampas region had high fertility under pristine condition but intensification of agriculture, increasing grain yields, and poor or no Zn fertilization could reduce soil available Zn. The objectives of this work were to determine the distribution of available Zn in agricultural and pristine soils of the Argentina Pampas region and its relationship with some chemical characteristics. Soil samples (0-20 cm depth) were collected and georeferenced (approximately 550 for each condition), and soil organic matter, pH, extractable phosphorus, cation exchange capacity, and available Zn by extraction with diethylenetriaminepentaacetic acid (DTPA-Zn) were measured. For geostatistical analysis, indicator kriging (non-parametric method) was utilized as interpolation method. Agriculture decreased soil organic matter, pH, extractable phosphorus and DTPA-Zn (26.9, 4.6, 57.8 and 69.5%, respectively). Relative decrease of DTPA-Zn was only significantly associated with the relative decrease of soil organic matter, although this association was low (r=0.41). Regionally, the DTPA-Zn distribution was very heterogeneous and soil organic matter, pH, extractable phosphorus and cation exchange capacity did not adequately predicted soil DTPA-Zn concentrations (r^2=0.16 to 0.26). Agricultural soils of northern, northwestern and southwestern APR (approximately 12,150,000 ha) showed DTPA-Zn values below 1 mg kg^{-1}, and therefore would present some degree of Zn deficiency for sensitive crops.

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Introduction

Low available Zinc in soils reduces crop growth, grain yield and the quality of crop products. Obtaining grains with adequate Zn concentrations is one of the next challenges in agriculture because of its influence on human health (Cakmak, 2008). Hotz and Brown (2004) reported that Zn deficiency affects, on average, one-third of world's population.

In the quinquennium 2007-2011, Argentina has been the leading exporter of soybean (*Glicine Max* Merr.) oil and meal, the third largest exporter of soybeans, and the second and seventh of corn (*Zea mays L.*) and wheat (*Triticum aestivum L.*), respectively (FAOSTAT, 2015). Of the total exported, 86% to 90% is produced in the APR, geographical area that is located in the center-east of the country (from 31° to 39° S and from 58° to 64° W, Fig. 1). The climate of this region is temperate subhumid to temperate humid (14 to 18°C mean annual temperature; 750-1100 mm mean annual rainfall), with decreasing temperatures and rainfall from north to south and from east to west, respectively (Panigatti, 2010). The soils belong mostly to the order Mollisol (Panigatti, 2010), and in its original state have high fertility conditions because they derived from the sedimentary material known as "Pampa loess" (Sayago, 1995; Gallet *et al.*, 1998; Zárate, 2003). Total Zn values of this material ranges from 52 to 72 mg kg^{-1} (Gallet *et al.,* 1998), which could be considered from medium to high concentration according to Alloway (2009). In addition, most agricultural soils have pH values less than 7.1 (Sainz Rozas *et al.*, 2011), conditions that favor a high Zn availability.

Fig.1. World regions with Zn deficient soils (taken from Alloway, 2009). The box indicates the area covered by the Argentina Pampas region.

In the last 20 years, the average yields of soybean, corn, barley, and wheat have increased at a rate of 26, 129, 69 and 42 kg ha^{-1} yr^{-1}, respectively (SIIA, 2015). The lack of Zn application as fertilizer and the greater Zn removal due to higher yields could decrease soil Zn available fractions. The yield increase was due in part to increased application of nitrogen and phosphate fertilizers. However, phosphorus replacement of that extracted in grains varies from 50 to 55%, which has led to decreased levels of EP in soils of the APR (Sainz Rozas *et al.*, 2012). In sub-acid and acid soils, negative variations of EP levels could increase the Zn availability by decreasing its adsorption onto hydrous Fe oxides (Wang and Harrell, 2005). In addition, long-term application of ammoniacal and phosphate fertilizers acidifies soil, thus increasing Zn availability (El-Kherbawy and Sanders, 1984; Shuman, 1986; Moraghan and Mascagni, 1991; Fabrizzi *et al.*, 1998; Wei *et al.*, 2006). Soil acidification increases Zn availability by diminishing adsorption and chemisorption processes and the precipitation of poorly soluble compounds (Lindsay, 1991; Alloway, 2009). Furthermore, long-term application of some phospate fertilizers could increase Zn availability providing this nutrient as an impurity (Li *et al.*, 2007; Richards *et al*, 2011). On the other hand, SOM levels in soils of the APR have decreased significantly compared to original levels by a less frequent inclusion of pastures in the rotation, the use of conventional tillage and the high frequency of low aboveground biomass-producing crops, such as soybean (Studdert and Echeverría, 2000; Sainz Rozas *et al.*, 2011). This could accentuate Zn deficiencies because low molecular weight organic acids form soluble complexes with Zn and contribute to the total soluble concentration (Catlett *et al.*, 2002).

This background suggests that long-term cropping may have opposite effects on soil Zn availability although the net effect on soil of the APR is unknown. Average critical levels of soil DTPA-Zn concentration reported for different crops (maize, soybean, and rice) range from 0.7 a 1.0 mg kg^{-1} (Lindsay and Norvell, 1978; Havlin and Soltanpour, 1981; Sing and Takkar, 1981; Anthony *et al.*, 2012). In an earlier study conducted in north APR, it was determined that 20% of samples showed DTPA-Zn values below the critical threshold (Ratto de Míguez and Fatta, 1990). Others studies have shown that DTPA-Zn concentration ranged from 0.8 to 1.2 mg kg^{-1} for soils of northwestern and southwestern APR (Volmer and Ratto, 2005). However, there is a lack of information on the DTPA-Zn status of major soils of the APR.

Soil properties are highly variable and the information usually comes from punctual samples, providing an incomplete picture of reality (Heuvelink and Webster, 2001). Therefore, maps illustrating the geographic distribution of soil variables require the application of interpolation techniques which allow estimating values at unsampled locations. Interpolated values are subject to uncertainty due to the presence of sampling and model errors which affects the practical application of the estimated values (Heuvelink, 1996; Goovaerts, 2001). Geostatistics provides the means to characterize and quantify spatial variability, use this information for rational interpolation, and estimate the variance of the interpolated values (White *et al.*, 1997; Oliver and Webster, 2014). Frequently, soil properties have extreme values, which affect both the characterization of the spatial patterns and subsequent predictions (Goovaerts, 2009). Commonly in these cases it is necessary to transform the data to achieve normality, although this is not always possible. Also, the reverse transformation procedure can introduce additional errors (Saito and Goovaerts, 2000). Another way to reduce the impact of outlier values is through the use of non-parametric statistical methods as the indicator kriging (Goovaerts, 2009; Lloyd and Atkinson, 2001). This approach involves defining thresholds in the cumulative frequency distribution curve of the soil variables (Goovaerts, 1997).

The importance of the APR as a global food producer and Zn as an essential nutrient determines the need to quantify Zn availability in soils of this region. The objectives of this study were to develop maps illustrating the geographic distribution of DTPA-Zn in surface horizons of pristine and agricultural soils, and to relate the DTPA-Zn concentrations with some soil chemical characteristics.

Materials and methods

Soil sampling

In 2010 and 2011, georeferenced soil samples (1100) were taken at 0-20 cm depth in major soil great groups of the APR. Samples were taken from geographically even-distributed sites at a target interval varying from 25 to 30 km (Fig. 2). In each site, one composite sample (30 subsamples) was randomly taken of soils belonging to the same series under long-term cropping (more than 20 years) and under pristine condition (parks and confined areas without animals). Pristine soils were away not more than 480 m from agricultural soils.

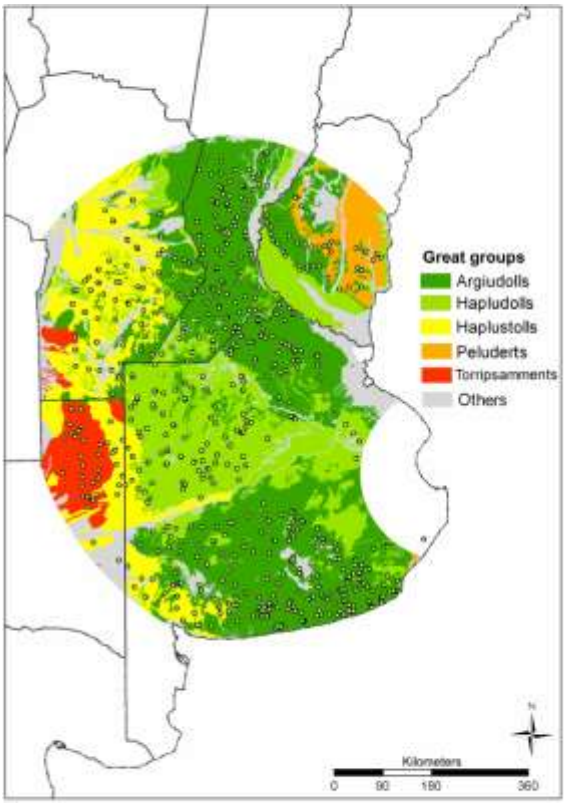

Fig. 2. Soil map of the Argentine Pampas region scale 1: 500,000 (INTA, 1990). Each point represents a sampling site.

Soil analysis

Soil samples were dried at 30°C, crushed with a wood mallet, and sieved through a 2 and 0.5-mm nylon screen. Precautions were taken to avoid contamination during sampling, drying, crushing, and storage. Soil organic matter (SOM-Walkley and Black, 1934), extractable phosphorus (EP-Bray and Kurtz, 1945) and pH (soil/water ratio of 1:2.5 v:v) were determined in samples sieved by 0.5 mm. Cation exchange capacity (CEC-Chapman, 1965) and DTPA-Zn (Lindsay and Norvell, 1978) were determined in samples sieved by 2 mm. Briefly, for the determination of DTPA-Zn, 10g of soil was placed in a 125-ml conical flask, and 20 ml of the DTPA extracting solution (pH 7.30) was added. After two hours shaking, the suspensions were filtered by gravity through Whatman no. 42 filter paper. The filtrates were analyzed for Zn using atomic absorption spectrophotometry and appropriate standards.

Statistic analysis

For each soil parameter, descriptive statistics as mean, median, standard deviation, minimum, maximum, percentiles, skewness and kurtosis were performed for each soil condition (agriculture and pristine). The normality of data was tested using the Shapiro and Wilk (1965) test at the 0.05 level. Average values of agricultural and pristine soils were compared using the t test at the 0.05 level (SAS Institute, 1998). When was necessary, all data were logarithmically transformed (using $\log_{10}$) before performing test for means comparison or regression analysis.

Exploratory data analysis using graphs and maps were performed to analyze spatial variability and the existence of trend was analyzed by using multiple regression procedures. To check for anisotropy, empirical variograms in two orthogonal directions (with a tolerance of 22.5°) were made, by considering the predominant wind direction during the genesis of soil parent materials reported by Krohling (1999) and Zárate (2003).

Geostatistical analysis was performed transforming the sample values into indicators values depending if these exceeded or not a zk threshold value (Isaaks and Srivastava, 1989). Thus, for each sample location u, there was an indicator I (u, zk) for each k threshold of zk values (Equation 1). Less information is lost when greater is the number of thresholds used (Goovaerts, 1997).

$$I(k, z_k) = f(x) = \begin{cases} 1, & z_u \leq 0 \\ 0, & z_u > 0 \end{cases} \quad (1)$$

Indicator semivariograms were calculated for each k threshold using the transformed data. Indicator semivariogram values indicate how far apart two points to each other belong to different categories, as they are above or below a zk threshold (Goovaerts, 1997). Finally, a unique frequency distribution was obtained from which the values of soil DTPA-Zn concentrations were calculated by inverse transformation of the indicator values, in order to make comparable the results with other interpolation methods. Data were processed using the GIS program ESRI ArcMap (2009) program. For both soil conditions, maps were performed by using the following ranges: 0.2-0.5, 0.5-1.0, 1.0-1.5, 1.5-2.0 and 2.0-5.0 and 5.0-10.0mg DTPA-Zn kg^{-1}. The goodness of fit was evaluated by cross-validation. Similarly, it was done by removing one point to the data set and then applying the predefined geostatistical model to the remaining n-1 data (Isaaks and Srivastava, 1989). Then, the new estimated value for each analyzed point was compared with the original value. This procedure was repeated for each n value of dataset. Finally, the criteria for evaluation of these results were based on the mean value and the sum of squared errors obtained for n interpolations.

Multiple regression models between relative decline of DTPA-Zn concentration (dependent variable) and relative changes of pH, SOM, CEC and EP (independent variables) were fitted. The relative change of each soil variable (ΔSV) was calculated by the following equation (2):

$$\Delta SV\ (\%) = (PSV - ASV)/PSV * 100 \quad (2)$$

where PSV and ASV represents soil variable for agriculture and pristine condition, respectively. Each value was the average of the points included within a

25-km-radius circle (3-4 points per circle). Also, for each soil use condition, multiple regression analysis was performed to evaluate the relationship between DTPA-Zn and SOM, pH, CEC and EP using PROC REG procedure (SAS Institute, 1998) at the 0.05 level. The stepwise selection method was used to determine the best variable combination to explain DTPA-Zn.

Results

Table 1 presents the descriptive statistics of the soil properties in the study area. Under both soil use conditions the results showed that, except pH, the spatial variability of soil properties was high, particularly for EP and DTPA-Zn. Data were not normally distributed ($P<0.05$) and exhibited positive skewness and kurtosis, because both parametres deviated from from zero, characteristic value of normal population. In soils under agriculture, the EP and DTPA-Zn showed the highest values of skewness and kurtosis (Table 1). Under agriculture, the DTPA-Zn values with higher occurrence frequencies ranged from 0.3 to 2mg kg^{-1} (Fig. 3).

Table 1. Descriptive statistics of pH, soil organic matter (SOM), cation exchange capacity (CEC), extractable phosphorus (EP) and extractable Zn with diethylenetriaminepentaacetic acid (DTPA-Zn) at the surface horizon (0-20 cm depth) of pristine and agricultural soils of the Argentine Pampas Region.

Statistics	Soil condition									
	Pristine					Agricultural				
	pH	SOM	CEC	EP	DTPA-Zn	pH	OM	CEC	EP	DTPA-
		g kg^{-1}	cmol kg^{-1}	------mg kg^{-1}------			g kg^{-1}	cmol kg^{-1}	-------mg kg^{-1}-----	
Average	6.82 (6.80a†)	43.1 (40.2a)	18.36 (17.48a)	68.50 (44.90a)	4.29 (3.21a)	6.51 (6.49b)	31.7 (29.4b)	17.91 (17.1a)	23.70 (18.95b)	1.25 (0.98b)
Standard deviation	0.62	16.1	5.77	63.60	3.11	0.48	12.6	5.49	20.62	1.19
Minimum value	5.10	12.0	6.40	3.5	0.30	5.4	10.0	6.60	2.80	0.20
Maximum value	8.80	98.0	39.00	376.30	18.10	8.70	69.0	41.20	166.90	10.70
percentile (0.25)	6.40	31.3	14.40	22.80	1.80	6.20	22.3	14.00	12.50	0.60
percentile (0.50)	6.70	40.5	17.80	45.60	3.40	6.40	29.0	17.20	17.90	0.90
percentile (0.75)	7.18	52.0	21.40	93.30	6.20	6.70	38.0	21.15	27.28	1.40
percentile (1.00)	8.80	98.0	39.00	376.30	18.10	8.70	69.0	41.20	166.90	10.70
Skewness	0.57	0.71	0.74	1.64	1.01	1.42	0.81	0.73	3.45	3.52
Kurtosis	0.30	0.25	0.78	2.94	0.50	3.37	0.17	0.91	15.83	16.44
Variation coefficient (%)	9.10	37.40	31.40	92.80	72.50	7.49	39.75	30.65	87.00	95.20

Agriculture significantly decreased soil pH and most of the samples from agricultural soils showed pH values between 6.20 and 6.70 (Table 1). Farming also caused a decrease of SOM and the difference between the initial SOM level (pristine soils) and current SOM level (agricultural soils), on average, was 26.8% (Table 1). Nevertheless, agriculture did not change the CEC despite its effect on the reduction of SOM (Table 1). Agricultural activity decreased the EP concentration compared to pristine soils by almost 58% (Table 1). Soils under agriculture management also showed DTPA-Zn concentration values lower than pristine soils (on average 69.6%). The 75 and 50% of samples from agricultural soils showed values equal or lower than 1.4 and 0.9 mg kg $^{-1}$, respectively (Table 1). The relative decrease in DTPA-Zn concentrations was associated only with the relative decrease of SOM, although r^2 value was low (Fig. 4).

Previous mapping and regression analysis showed high DTPA-Zn spatial variability in both datasets (agricultural and pristine soils), without the presence of a trend in the spatial distribution (P>0.05). Data with significant trend are frequently nonstationary, i.e., the spatial variance varies with location (White *et al.*, 1997). Due to the high variability observed in previous mapping, a total of 10 z_k thresholds were set *a priori* to characterize the cumulative distribution frequencies curves of DTPA-Zn. No evidence of anisotropy was found by analyzing the experimental variograms indicators in the azimuthal directions orthogonal N45 and N 135.

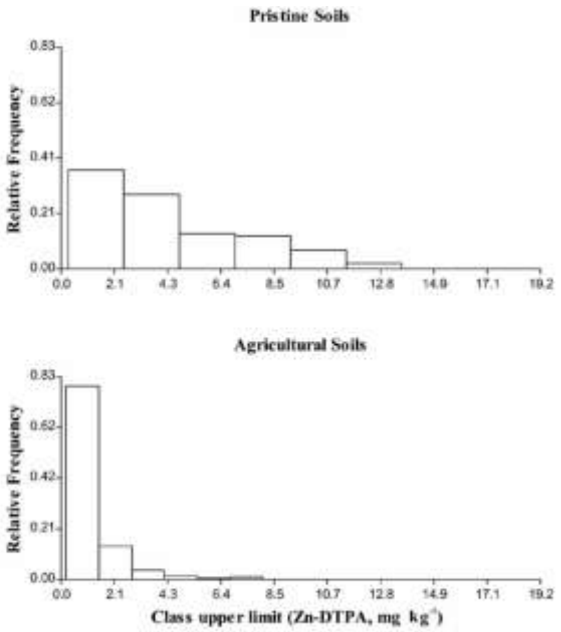

Fig. 3. Frequency distributions of DTPA-Zn in soils of Argentine pampas region.

The variograms were fitted to theoretical models, whose parameters are: nugget variance, sill and range Adjusted models were exponential and spherical. Variograms adjusted for different z_k thresholds in pristine and agricultural soils showed a similar behavior with respect to sill and nugget variance (Fig. 5). Variograms adjusted for z_k thresholds ranging from 0.6 to 1.3 mg kg^{-1} and from 2.3 and 5.5 mg kg^{-1} for agricultural and pristine soils, respectively (which represent most data, Table 1), showed that the nugget effect had a great contribution to sill. The maximum range across which the data showed spatial correlation was 20 and 30 km for pristine and agriculture soils, respectively. Instead, z_k thresholds near to the extreme values, i.e., 0.4 and 2.7 mg kg^{-1} for agricultural soils and 0.7 and 8.6 mg kg^{-1} for pristine soils, showed a lower nugget variance (Fig. 5).

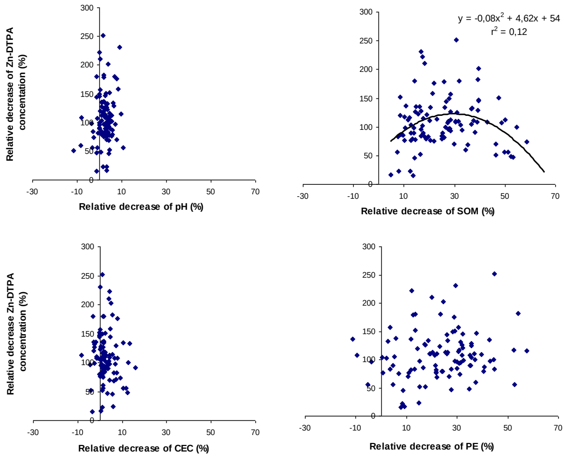

Fig. 4. Relationship between relative decrease of DTPA-Zn and relative decrease of soil pH, soil organic matter (SOM), cation exchange capacity (CEC) and extractable phosphorus (PE) induced by agriculture for soils belonging to the great groups of Argiudolls, Hapludolls and Haplustolls. Negative values in x axis indicate greater value in the agricultural than in the pristine soil. Transformed data were used.

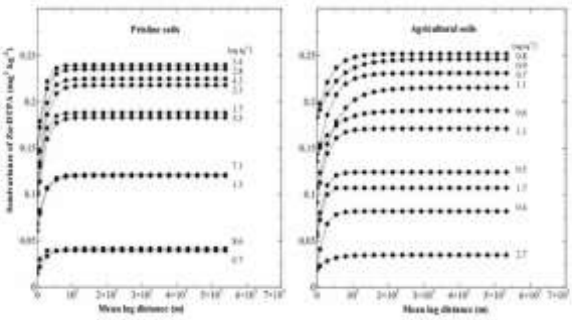

Fig. 5. Semivariograms indicators of soil DTPA-Zn concentration for pristine and agricultural soils.

The goodness of fit of the interpolation is showed in *Fig*. 6. In general, the average errors were close to zero (-0.006 and -0.052 mg kg^{-1} in pristine and agricultural soils, respectively) with low skewness. However, the fit was better in agricultural than in pristine soils because in the first cross-validation errors were concentrated in a lower range and mean square error was lower (0.452 and 6.124 in agricultural and pristine soils, respectively).

Soils under agricultural activity of most Córdoba province, southwestern Santa Fe province, and northern and southwestern Buenos Aires province showed values of DTPA-Zn concentrations lower than 1 mg kg^{-1} and in some cases, values lower than 0.5mg kg^{-1} (Fig. 7). The rest of the APR showed DTPA-Zn values ranging from 1 to 2mg kg^{-1} (Fig. 7).

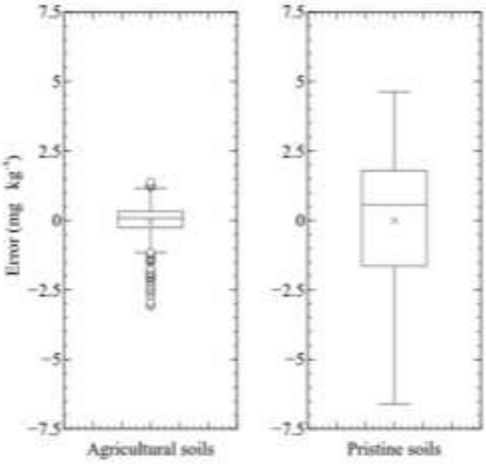

Fig. 6. Distribution of error estimation of DTPA-Zn with indicator kriging methodology.

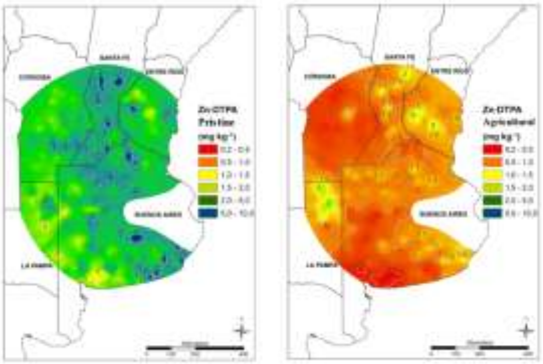

Fig. 7. Concentration ranges of DTPA extractable zinc (DTPA-Zn) in pristine and agricultural soils (0-20 cm depth) of the Argentinean Pampas region.

Multiple regression models to predict the DTPA-Zn in agricultural and pristine soils showed low correlation coeficentes (Table 2). The EP and MO were positively related to the DTPA-Zn, whereas the pH did negatively (Table 2).

Table 2. Multiple regression models to predict soil DTPA-Zn (0-20cm depth) in agricultural and pristine soils of the Argentine Pampas Region.

Dependent variable	Variable	Parameter value	p value	Parcial R^2	R^2
	Agricultural soils				
DTPA-Zn	Intercept	0.14	0.0572		0.16
	EP†	0.30	0.0001	0.09	
	SOM‡	0.49	0.0001	0.04	
	pH	-1.05	0.0076	0.02	
	CEC§	-0.31	0.0224	0.01	
	Pristine soils				
DTPA-Zn	Intercept	0.94	0.0003		0.26
	EP	0.24	0.0001	0.11	
	SOM	1.23	0.0001	0.08	
	CEC	-1.03	0.0001	0.07	

Variables selected according to the stepwise approach at the 0.05 probability level. Transformed data were used.

† Extractable phosphorus (mg kg^{-1}).

‡Soil organic matter (g kg^{-1}).

§ Cation exchange capacity (cmol kg^{-1}).

Discussion

The spatial variability of soil properties was high, particularly for EP and DTPA-Zn. In soils under agriculture, the EP and DTPA-Zn showed the highest values of skewness and kurtosis because more than half of samples from agricultural soils showed low DTPA-Zn concentration. This could be due to low or no replenishment of nutrient in soils under agriculture. For agricultural soils of southeastern China, Shi *et al.* (2008) also reported high DTPA-Zn variation coefficients, which were similar to this work.

The pH change caused by agriculture can be attributed in part to increased use of fertilizers in the last twenty years. Similar pH results were reported by Sainz Rozas *et al.* (2011) on a previous sampling. Previous studies have reported that at low soil pH the Zn availability is increased by a greater solubilization of poorly soluble compounds, desorption from oxide and $CaCO_3$. This can increase the amount of Zn in the water-soluble, exchangeable and organic fractions, which are positively related with the DTPA extractable fraction, and with Zn absorption by crops (Iyengar *et al.*, 1981; Sims, 1986; Shuman, 1986; Moraghan and Mascagni, 1991; Alloway, 2009).

Agricultural activity caused a decrease in the SOM and and the measured values were similar to those reported by Sainz Rozas *et al.* (2011) for a previous sampling in the same region. Particulate or active SOM is the first pool to be affected by changes in soil management (Galantini and Rosell, 2006), accounting for most of the early losses when cultivation of virgin soil begins. Decreased SOM content could be associated with declines in the amount of available Zn fractions (solution, labile organic and exchangeable). Mandal *et al.* (1988) reported that increasing SOM increased exchangeable Zn. Also, organic acids, polysaccharides, and fulvic acids can attract this cation from the edges of mineral structures and chelate or bind it in stable organomineral complexes and, if these complexes are soluble, the Zn availability for crops would be increased. Accordingly, Alma *et al.* (2000) and Catlett *et al.* (2002) reported that Zn^{+2} concentration (DTPA extractable) was positively correlated with SOM. It has also been reported that increasing SOM organic increased organic and exchangeable fractions, and decreased the oxide fractions—due to reducing conditions which make Zn more bioavailable (Mandal and Mandal, 1987a, b).

Agricultural activity did not change the CEC despite its effect on the reduction of SOM. This would be because the passive organic matter is most closely associated with CEC and, as already mentioned, this pool decreases slowly when pristine soils are brought into agriculture (Brady and Weil, 2008).

Agricultural activity decreased the EP concentration compared to pristine soils. This is because P budgets are negative, with P removal exceeding P inputs through fertilization or others by 45-50%, particularly in production systems of the northwest and west of the APR (Sainz Rozas *et al.*, 2012). Reduced P availability could increase Zn availability decreasing adsorption on the oxide fraction by reducing its negative charges (Wang and Harrel, 2005).

As discussed above, the lower levels of pH, SOM, and EP for agricultural soils relative to pristine soils could affect the Zn availability. However, the relative decrease in DTPA-Zn concentrations was associated only with the relative decrease of SOM, although, as mentioned, the r^2 value was low. This suggests that the negative soil Zn budgets would be the main factor in defining the decrease of DTPA-Zn concentrations.

The results show that, for both soil use conditions, the distribution of DTPA-Zn concentration is highly heterogeneous, with high differences between sampling points. This variability makes it difficult to predict a determined DTPA-Zn concentration value at distances greater than 20 or 30 km. A high nugget variance indicates a great influence of sampling and analytical error and/or soil spatial variation at distance shorter than the range interval (White *et al.*, 1997). In addition, the lower range value under pristine condition also indicates that there would be an associated effect of soil use on DTPA-Zn. Liu *et al.* (2006) reported that the extrinsic factors such as fertilization, cultivation, and other soil management practices change the spatial correlation after a long history of cultivation. In this regard, Rivero *et al.* (2007) reported that the northern and northwestern APR showed the highest levels of crop Zn extraction. This could be due to the high frequency of crops with high Zn harvest index such as corn and soybeans, which range from 0.62 to 0.70 (Gutiérrez Boem and Scheiner, 2006; Bender *et al.*, 2013). On the contrary, the highest values of DTPA-Zn in southeastern APR could be partially explained by a young cropping history and high frequency of crops with lower Zn harvest index such as wheat and barley, which are close to 0.40 (García and Berardo, 2006). Further, the spatial variability of DTPA-Zn would be initially generated by the interaction between the parent material and pedogenic processes associated with different types of landscape and climate. For the APR, parent material variability has already been described and discussed by numerous authors. Morrás (1999) and Zarate (2003) set out a summary of the different processes of genesis, deposition and re-deposition of soil parent materials. Differences in total P content of soil parent materials have also been reported by Morrás (1999). From an analysis of data published by Gallet *et al.* (1998), who determined the elemental composition of 21 loess samples from four countries (including Argentina), a significant correlation was found between apatite content and Zn content (r=0.59). Therefore, it is likely that the variation in total Zn content is also related with differences in the apatite content of soil parent materials.

In summary, the differences in soil parent materials, the intensity of predominant pedogenetic process, and crops and soil management practices induce a high complexity in describing DTPA-Zn spatial variability. This is reflected in the high levels of uncertainty in the interpolation and the low capacity of variables such as SOM, pH, EP and CEC to explain variations of DTPA-Zn~~.~~

Critical thresholds of DTPA-Zn for some crops (maize, soybean and rice) range from 0.7 to 1.0 mg kg^{-1} (Lindsay and Norvell 1978; Havlin and Soltanpour 1981, Sing and Takkar, 198; Anthony *et al.*, 2012), so 50% of the surveyed soils could be deficients in Zn~~.~~ In the earlier survey carried out by Ratto of Miguez and Fatta (1990) in northern APR, it was determined that 20% of the samples showed DTPA-Zn values below critical thresholds. Therefore, the results of this study show a progressive depletion of available Zn fractions. As mentioned, the lowest values of DTPA-Zn concentrations found in Córdoba province, southwestern Santa Fe province, and northern and southwestern Buenos Aires province PA-Zn concentration informed (maize, soybean and rice). For soil samplings carried out in 1995 and 2001 in the northern and northwestern APR, Rivero *et al.* (2007) reported DTPA-Zn values higher than those determined in our work (>1mg kg^{-1}). This difference could be attributed, as mentioned, to an aggravation of situation during the period elapsed between samplings (1995-2001 vs 2010-11) or that these authors worked with a fewer number of samples. For the Córdoba province, Volmer Buffa and Ratto (2005) reported DTPA-Zn values similar than those determined in our work.

The cultivated area in the RPA in 2012 was approximately 27,000,000 ha (SIIA, 2015). It could be estimated that 45% of evaluated area would have DTPA-Zn values lower than 1mg kg^{-1}. This result in an area of 12,150,000 ha with potential Zn limitation for normal crop growth and probably with grain Zn concentrations lower than those recommended for a high nutritional quality. This last point can become relevant because that average yields of cereals have almost doubled in the last decade (from 1.9 to 3.9 Mg ha^{-1} in wheat and from 4.4 to 7.9mg ha^{-1} in maize), an issue that deserves further research.

Conclusion

DTPA-Zn concentrations in the APR were described by high and complex spatial variability. The uncertainty associated with the estimation of their spatial distribution is large, even among points spatially near each to other. Therefore, on a regional scale, DTPA-Zn variability could not be adequately predicted by soil variables such as SOM, pH, CEC and

EP. Agricultural activity significantly decreased of DTPA-Zn concentrations relative to pristine soils and Zn availability may limit the growth of sensitive crops in a vast area of the APR. The decrease of DTPA-Zn caused by agricultural activity was partly explained by the decrease in SOM, and therefore, it would be mainly related to negative Zn budgets.

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