

DTPA and NH_4HCO_3 -DTPA extractable Fe, Mn and Zn levels in the Ebro Valley

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ABSTRACT

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DTPA and NH_4HCO_3 -DTPA extractable Fe, Mn and Zn levels in main soil groups from the Ebro Valley were studied.

Mn content seems to be adequate, while Fe levels are in the medium-low range and Zn content is generally low, specially in the Serozem group.

Several highly significant correlations between Fe, Mn and Zn levels and pH, O.M. and CaCO_3 contents were found.

Although in most cases the NH_4HCO_3 -DTPA test give sistematically higher values, both methods are well correlated. However the regression equation is different for each soil group.

INTRODUCTION

The DTPA test was proposed by LINDSAY and NORVELL (1967) to evaluate micronutrient available levels. LINDSAY and NORVELL (1978) extensively reviewed the works published during the first decade of the test's use. Afterwards many workers have kept on studying the effects of several variations in the analytical procedure (SOLTANPOUR and SCHWAB, 1977; KHAN, 1979-a, 1979-b; SEVERSON, MCNEAL and DICKSON, 1979; GRASSI, DÍEZ and ACEBAL, 1980).

This micronutrient test has been specially developed for calcareous soils. Most soils in the Ebro Valley have high carbonate contents (MONTAÑÉS, HERAS and SANZ, 1980). Any study about Mn and Zn available levels has not been carried out yet. The Fe available content in some typical soils has been published (MILLÁN *et al.*, 1979).

The objectives of the present work are: i) to evaluate available Fe, Mn and Zn levels in several soil groups of the area, ii) to study the correlations between these available levels and some soil properties, iii) to determine if the micronutrient levels obtained by two methods (LINDSAY and NORVELL, 1978 and SOLTANPOUR and SCHWAB, 1977) are different.

MATERIAL AND METHODS

Seventy six surface (0-30 cm) soil samples were taken in the Ebro Valley (figure 1). These soils were air-dried and ground to pass through a 2 mm stainless steel sieve.

The soils have been divided into three groups (terrace, alluvial, xero-rendzine and calcareous brown soils —SC; Serozems —S; and soils with a calcium carbonate content of less than 5% —SNC).

Table 1 summarizes the characteristics which will be correlated with the micronutrient levels. CaCO₃ equivalent was determined by a gasometric method and O.M. by the Walkley-Black method. pH was measured in water with a (1:2,5) soil: solution ratio.

TABLE 1. — *Characteristics of soils.*

	<i>Organic matter</i>		<i>CaCO₃</i>		<i>pH</i>	
	<i>range</i>	<i>mean</i>	<i>range</i>	<i>mean</i>	<i>range</i>	<i>mean</i>
All samples	0,21-9,50	1,57	0-53,9	26,42	4,5-10,14	8,06
S	0,21-2,07	1,10	23,14-49,3	33,64	7,8-10,14	8,40
SNC	0,24-9,50	2,48	0- 4,3	0,74	4,5- 8,3	7,06
SC	0,48-2,86	1,48	13,88-53,9	32,27	7,8- 8,5	8,26

Fe, Mn and Zn were extracted with DTPA (LINDSAY and NORVELL, 1969) and NH₄HCO₃-DTPA (AB-DTPA) solutions (SOLTANPOUR and SCHWAB, 1977). The shaking procedure has been modified, since a vibratory shaker and 75 ml polyethylene flasks have been used. The soil-extracting solution ratio was 1:2 (10 g: 20 ml). The extracts

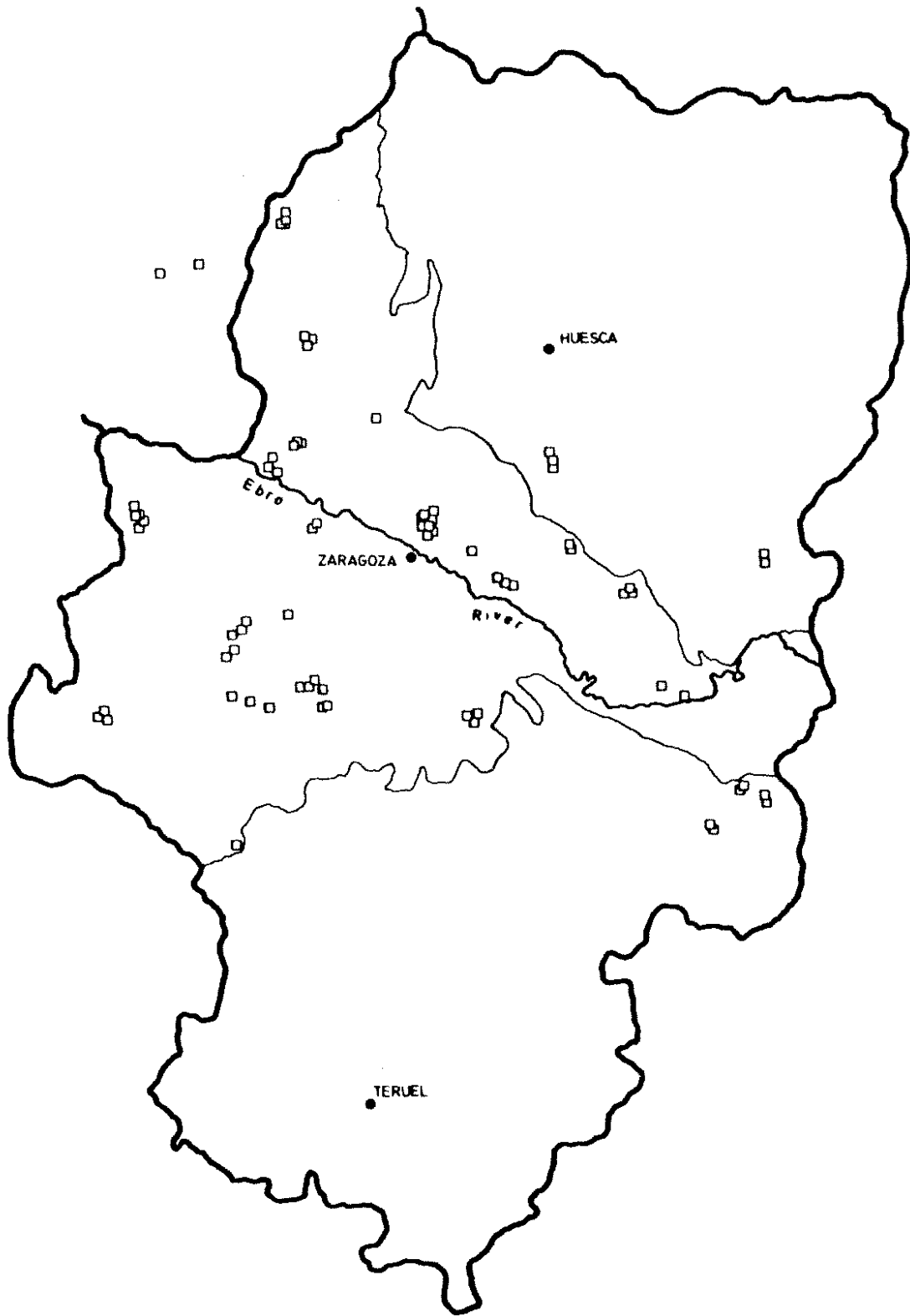


FIGURE 1. Location of sampling sites.

were analyzed using a 303 Perkin-Elmer atomic absorption spectrophotometer and appropriate standards.

Micronutrient extractable levels are affected by shaking procedure (SOLTANPOUR, KHAN and LINDSAY, 1976). As the shaker speed employed here is higher than in the two original methods we expect this test will give larger levels in all the samples.

In the comparisons of the Fe, Mn and Zn values from both modified methods with those obtained from original ones this feature must be kept in mind.

RESULTS AND DISCUSSION

Microelement levels

Table 2 and figure 2 show the micronutrient available levels obtained by both methods.

There is a good relationship for Mn between the two methods. The Serozem soils present the lowest values and the non-calcareous soils the highest. The Calcareous soil average (8,1-9,6 ppm) is similar to the value cited by KHAN and RYAN (1978) (8,2 ppm). Mn levels are always higher than the critical level estimated by LINDSAY and NORVELL (1978) (1,2 ppm) using DTPA, and SOLTANPOUR and WORKMAN (1979) (0,5 ppm) with AB-DTPA.

High salinity levels occur in the Serozem soils (MONTAÑES, HERAS and SANZ, 1980). This feature could explain their Mn levels (DAHIYA and MAHENDRA SINGH, 1978).

The AB-DTPA method gives larger Fe values than the DTPA test. In the Serozem and Calcareous groups the average values are close to the critical levels proposed by BOER and REISENAUER (1973) (6 ppm) and LINDSAY and NORVELL (1978) (4,5 ppm for sorghum) using DTPA test; and slightly higher than the values estimated by SOLTANPOUR and WORKMAN (1979) (from 3 to 5 ppm) with AB-DTPA test.

For the Serozem soils the average Zn values (0,59-0,53 ppm) are lower than the critical level for sorghum (0,6 ppm) and corn (0,8 ppm) suggested by LINDSAY and NORVELL (1978) and BROWN, QUICK and EDDING (1971) (0,5 ppm) using DTPA test. However the Zn value reported here is within the range of 0,5 ppm-1,0 ppm proposed as marginal by SOLTANPOUR and WORKMAN (1979) using the AB-DTPA test.

In all the cases the coefficient of variation was <20% (for Fe and Mn <5%). The Zn coefficients of variation could be caused by the very low values of this element in the soils studied.

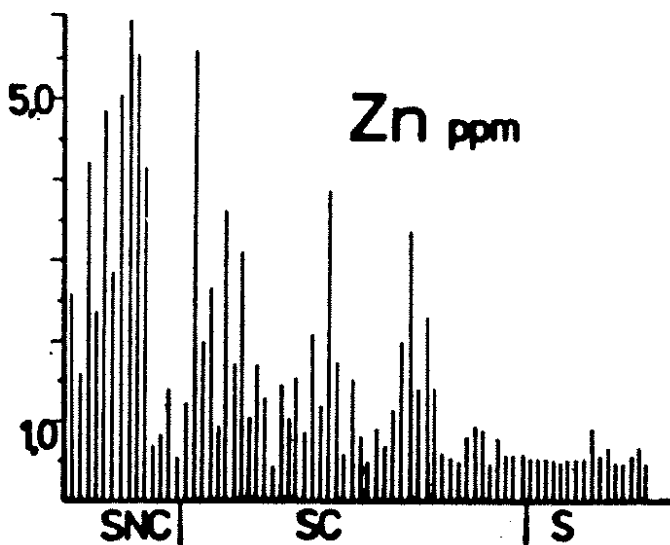
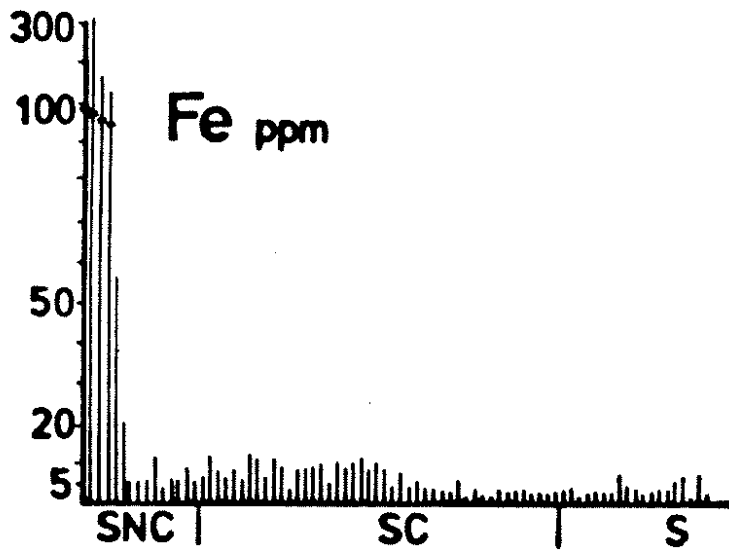
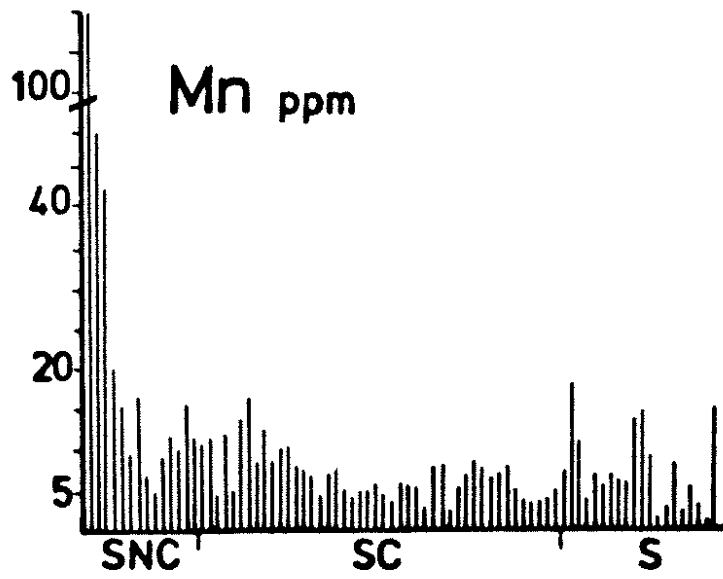


FIGURE 2. DTPA extractable Fe, Mn and Zn levels.

TABLE 2.—Ranges and means () of Mn, Fe and Zn levels; variation coefficients and correlation with some soil characteristics.

	No. of samples	ppm															
		C.V.						r									
		DTPA		AB-DTPA		DTPA		AB-DTPA		pH/ DTPA		pH/ AB-DTPA		Ca CO ₃ / DTPA		Ca CO ₃ / AB-DTPA	
Mn	All soils	1.8 - 115.5 (11.2)	2.0 - 121.0 (11.9)	0-10.4 (3.1)	0-18.7 (3.5)	0.384**	0.386**	-0.554**	-0.540**	-0.306**	-0.421**						
	S	1.8 - 19.4 (7.5)	2.0 - 17.0 (6.0)	0- 8.3 (3.0)	0- 8.7 (2.9)	NS	0.480*	NS	-0.455*	NS	NS						
	SNC	5.4 - 115.5 (24.3)	5.5 - 121.0 (25.6)	0- 8.3 (3.6)	0-18.7 (4.3)	NS	NS	-0.520*	NS	NS	NS						
	SC	2.8 - 16.0 (8.1)	3.0 - 23.5 (9.6)	0-10.9 (2.5)	0-16.9 (3.6)	0.501**	0.612**	NS	NS	-0.482**	-0.306*						
Fe	All soils	1.8 - 304.0 (14.7)	1.8 - 300.2 (21.4)	0-14.6 (3.0)	0-27.4 (4.2)	0.740**	0.746**	-0.777**	-0.812**	-0.365**	-0.399**						
	S	1.8 - 3.6 (6.1)	1.8 - 58.9 (9.5)	0- 6.7 (3.1)	0-27.4 (4.5)	NS	NS	NS	NS	NS	NS						
	SNC	2.5 - 304.0 (48.1)	4.9 - 300.2 (59.8)	0- 6.0 (3.0)	0-27.0 (4.9)	0.790**	0.789**	-0.865**	-0.915**	NS	NS						
	SC	2.2 - 12.4 (6.7)	3.4 - 27.0 (13.3)	0-14.9 (3.1)	0-17.0 (3.8)	0.366*	0.373*	-0.469**	-0.376*	NS	-0.308*						
Zn	All soils	0.45- 7.7 (1.6)	0.2 - 8.45 (1.9)	0-37.9 (5.7)	0-61.4 (8.1)	0.598**	0.586**	-0.589**	-0.501**	-0.480**	-0.367**						
	S	0.48- 0.93 (0.59)	0.20- 0.95 (0.53)	0-23.9 (5.8)	0-28.3 (9.6)	NS	0.686**	NS	NS	NS	NS						
	SNC	0.54- 7.7 (3.19)	0.6 - 8.45 (3.2)	0-14.0 (4.3)	0-61.4 (8.8)	0.581*	0.679**	-0.526*	NS	NS	NS						
	SC	0.45- 5.6 (1.51)	0.40- 8.9 (2.10)	0-37.9 (5.7)	0-30.7 (6.7)	0.466**	0.594**	-0.371*	-0.443**	NS	NS						

* ** Significant at 0.01 and 0.05 level respectively.

NS Not significant.

Relationships between AB-DTPA and DTPA tests and some soil properties

Correlation coefficients between micronutrient levels and some soil characteristics are presented in table 2.

In the Calcareous group (SC) the extractable Mn is correlated with O.M. This relation has not been found by KHAN and RYAN (1978) in Calcareous soils of Lebanon. SIMS *et al.* (1978) considered that O.M. fraction has a slight influence, in soils with high pH, on the DTPA extractable Mn. Mn levels in the soils studied are negatively correlated with Calcium Carbonate in good agreement with KHAN and RYAN (1978) and DAHIYA and SINGH (1977).

For the Serozem group (S), with a Calcium Carbonate content similar to SC group, the extractable Mn is also correlated with CaCO_3 content, but the correlation coefficients are lower than in the Calcareous group. A wide heterogeneity is present in this group, that pools saline, alkali-saline soils, etc.

In the non-calcareous soils (SNC), the Mn values are negatively and slightly correlated with pH.

If all the soils are considered together significant correlations with pH, O.M. and CaCO_3 contents have been found. This results differ from the obtained by RANDALL, SCHULTE and COREY (1976) in soils with a low O.M. content (<6%). The available Manganese-pH dependence has often been described (FOLLET and LINDSAY, 1971; SIMS *et al.*, 1977).

Extractable Fe in calcareous soils is correlated with O.M. (positively), Ph and CaCO_3 (negatively). Similar relationships between available Fe and both pH and O.M. contents have been cited in other calcareous soils (SINHA *et al.*, 1978).

For the Serozem group there is no correlation between available Fe and soil characteristics. This lack of correlation may be originated by the previously cited group heterogeneity.

In the case of non-calcareous soils (SNC) the Fe levels are highly correlated with O.M. and pH.

If all the soils are considered Fe correlates with pH, O.M. and CaCO_3 contents.

The Zn extractable levels, in the calcareous group (SC), are correlated with O.M. ($r > 0$) and pH ($r < 0$). This feature has been already indicated by SINHA *et al.* (1978) in similar soils.

There is only correlation, for Serozem group (S), with O.M. using SOLTANPOUR-SCHWAB test.

In non-calcareous soils (SNC), the available Zn is correlated with M.O. ($r > 0$) and pH ($r < 0$); r values are lower than for Fe.

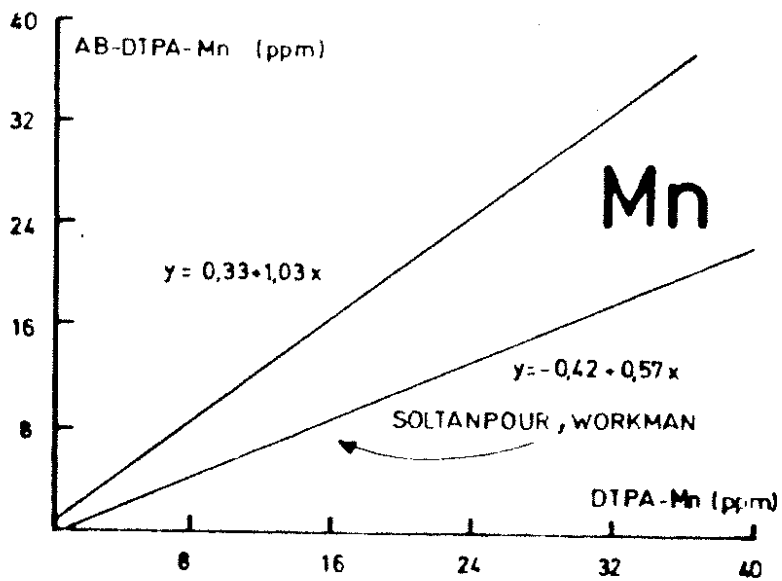
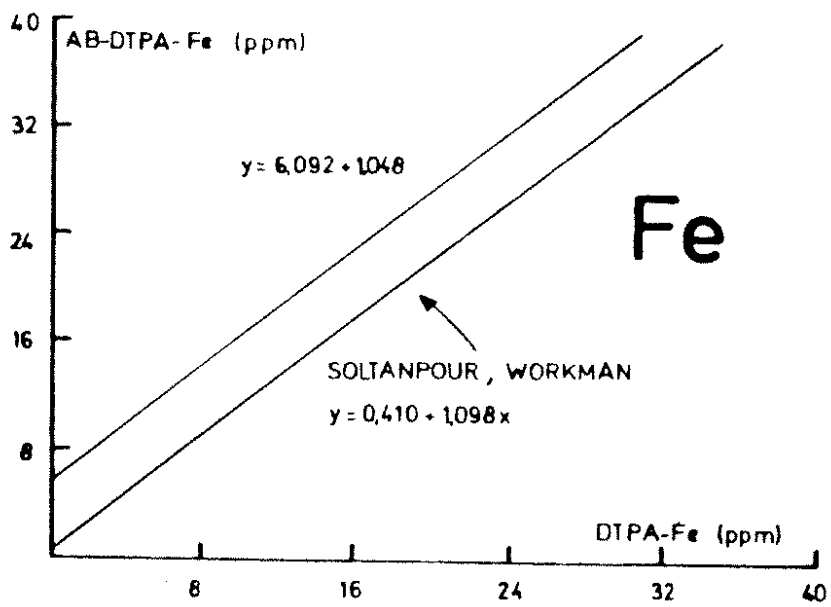
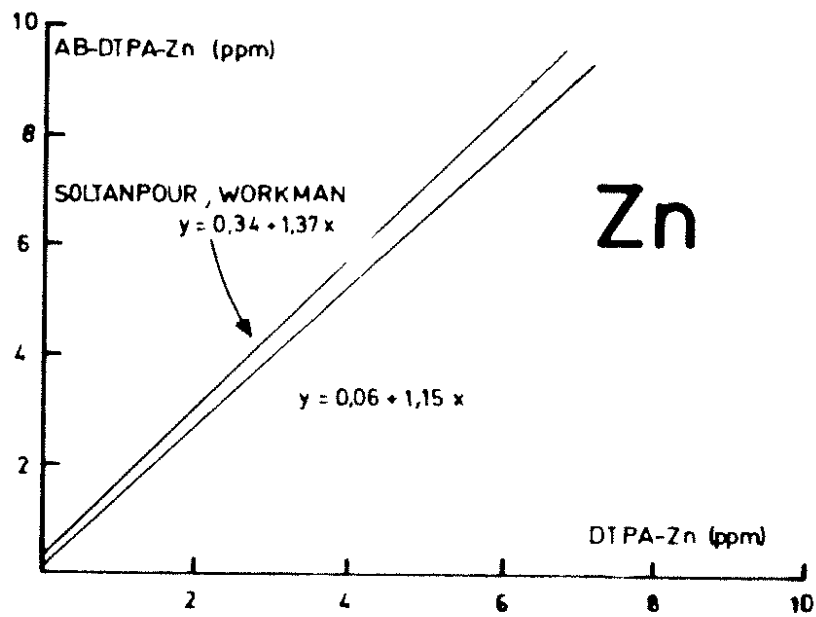


FIG. 3. Correlations between DTPA and AB-DTPA tests.

If the seventy-six soils are considered as a whole, there are correlations with O.M. pH ($r < 0$) and CaCO_3 ($r < 0$). These correlations are similar to the found by KOVANCI, HAKERLERLER and HOFNER (1979).

Relationships between methods

The high correlation coefficients obtained between the two tests (in all the cases significant at 0,01 level) are shown in table 3. The results of application of the null hypothesis test (SNEDECOR and COCHRAN, 1972) are also presented in table 3. The two methods give systematically different values except for Mn and Zn in non-calcareous soils and Zn in Serozem group. The SOLTANPOUR-SCHWAB test provide higher values than LINDSAY-NORVELL'S except for Mn in Serozem soils.

The correlations obtained by SOLTANPOUR and WORKMAN (1979) with the ones estimated in the present work have been represented in figure 3.

For Zn the relations between both variables are similar in the two works while for Fe there is a change in their intercept and for Mn the slope is different.

This fact can be originated by methods variability due to different work conditions as much as soil characteristics. The latter may be seen, for instance, among several soil groups for Zn (figure 4).

These findings emphasize the importance of carrying out new experiments to standarize and correlate the different procedures.

TABLE 3. — Relationships between the two methods.

		No. of samples	Correlation DTPA/AB-DTPA/(x/y)		Difference between methods	
			y =	r	(null hypothesis test)	Highest values method
Mn	All soils	76	$0,339 + 1,033x$	0,983**	+	AB/DTPA
	S	20	$-0,254 + 0,840x$	0,969**	+	DTPA
	SNC	15	$0,681 + 1,028x$	0,992**	—	—
	SC	41	$-0,072 + 1,197x$	0,861**	+	AB/DTPA
Fe	All soils	76	$6,092 + 1,048x$	0,980**	+	AB/DTPA
	S	20	$-0,070 + 1,643x$	0,986**	+	AB/DTPA
	SNC	15	$10,677 + 1,020x$	0,982**	+	AB/DTPA
	SC	41	$3,410 + 1,467x$	0,698**	+	AB/DTPA
Zn	All soils	76	$0,058 + 1,152x$	0,918**	+	AB/DTPA
	S	20	$-0,182 + 1,221x$	0,639**	•—	—
	SNC	15	$0,208 + 0,937x$	0,937**	—	—
	SC	41	$-0,383 + 1,637x$	0,960**	+	AB/DTPA

** Significant at 0,01 level.

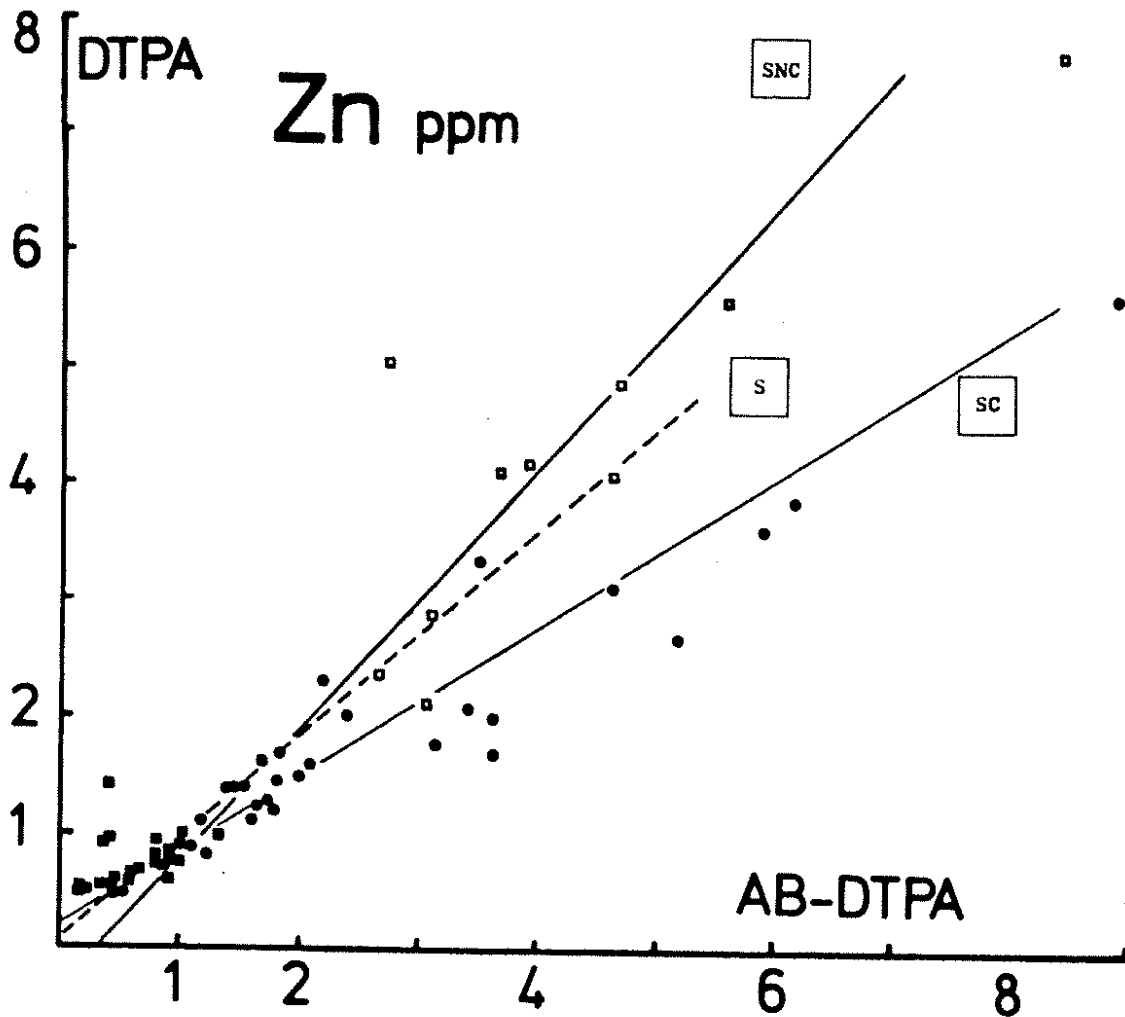


FIGURE 4. Correlations between methods in soil groups for Zn.

CONCLUSIONS

In most cases the two methods give systematically different, but well correlated values. So both methods can be indistinctly used. The C.V. are also similar.

The Fe levels in Serozem and Calcareous soils seem to be low. It looks like some deficiencies could appear in short cycle crops, besides the known deficiencies in fruit trees (HERAS *et al.*, 1976). These Fe levels except for Serozem soils, are correlated with O.M., pH and CaCO_3 content.

Zn levels found in Serozem and also in some Calcareous soils, are low. It is suggested the probability of some Zn deficiencies specially in Saline areas which have been just irrigated. There is a clear correlation with O.M., mainly when the SOLTANPOUR-SCHWAB test has been used.

Mn levels seem to be adequated for normal crop growth. These values are related with O.M., pH and CaCO₃ except for non-calcareous soils.

However there are several reasons that do not allow to exclude the risk of some deficiency in the area. A wide range of crop requirements makes general critical levels unsuitable and so specific levels have to be fixed. The whole standarization of analytical procedures (SOLTANPOUR *et al.*, 1979) has also a great importance, since little modifications could origin big differences in micronutrient extractable levels.

For instance, available Fe levels are higher than the critical ones proposed by LINDSAY and NORVELL (1978) and other workers (≈ 5 ppm), but the existence of Fe deficiency symptoms in fruit trees occurs in these soils as a constant characteristic.

Therefore to exclude any micronutrient deficiency in the area it is necessary to relate soil and plant analysis, fertilization responses, deficiency symptoms and others.

RESUMEN

Se han estudiado los niveles de Fe, Mn y Zn extractados por DTPA y NH₄HCO₃-DTPA en 76 muestras pertenecientes a los principales grupos de suelos de la zona del valle del Ebro.

Los niveles de Mn parecen ser adecuados, mientras que los de Fe son medios-bajos. Los valores de Zn son generalmente bajos, especialmente en los suelos Serosenes.

Se han correlacionado los niveles de Fe, Mn y Zn extractables por ambos métodos con los valores de pH, M.Q. y % de CaCO₃, para los diferentes grupos de suelos, encontrándose relaciones significativas.

Los niveles de microelementos extractables por ambos métodos se correlacionan entre sí, aunque en la mayor parte de los casos, el DTPA proporciona valores sistemáticamente superiores. Las ecuaciones de regresión entre métodos varían para cada tipo de suelos.

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