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Journal of Agricultural Science (2011), **149**, 461–472. © *Cambridge University Press* 2010
doi:10.1017/S0021859610001085

Organic and inorganic fertilization effects on DTPA-extractable Fe, Cu, Mn and Zn, and their concentration in the edible portion of crops

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(*Revised MS received 30 July 2010; Accepted 13 September 2010; First published online 17 December 2010*)

SUMMARY

The application of organic composts to soil may affect the availability of micronutrients and their concentration in plants. The present field research study compared soil micronutrient extractability after 5 years of organic fertilization *v.* conventional inorganic fertilization. Iron (Fe), copper (Cu), manganese (Mn) and zinc (Zn) were extracted from soil using diethylene triamine pentaacetic acid (DTPA) and the data obtained were compared with the concentration of these micronutrients in the edible portion of the crop. The study was carried out on a loam soil classified as a Xerofluvent. The soil was fertilized with composted plant residues or with conventional inorganic fertilizer and all treatments were replicated four times in a randomized complete block design. In all cases a crop rotational system was applied. The use of organic fertilization resulted in a higher extractability for all the elements studied; however, the micronutrient content in the edible part of the crops was variable depending on the plant species and element. Crop yields depended on the type of crop rather than the type of soil fertilization. The present study showed that the use of plant compost and the elimination of synthetic fertilizers result in an increase of Fe, Cu, Mn and Zn extractability compared to soil treated with inorganic fertilization, which should provide long-term fertility benefits.

INTRODUCTION

Organic farming is growing rapidly due to its potential to produce foods perceived as healthy. Conventional agriculture can result in loss of organic matter (OM), causing a degradation of cultivated soils (Fliessbach *et al.* 2007). In addition, farmers have been applying increasing amounts of fertilizers in intensive cropping that mainly contain major nutrients (nitrogen: N, phosphorus: P and potassium: K), and this practice might well have contributed to an increased prevalence of micronutrient deficiencies in soil and consequently, in crops (Biswas & Benbi 1997; Dar 2004; Nube & Voortman 2006).

The transition from conventional to organic farming is accompanied by changes in an array of soil chemical properties and processes that affect soil fertility (Clark *et al.* 1998). These changes affect nutrient availability to crops, either directly by contributing to nutrient pools, or indirectly by influencing the soil chemical and physical environment (Bulluck *et al.* 2002).

It is widely accepted that the behaviour of micronutrients in soils cannot be assessed by measuring only the total metal concentration. There is no universal extracting solution that can be used to estimate the micronutrients and metal bioavailability to plant because of the complexity of metal ion dynamics in the soil system and the interactive role of plant and environmental factors on the whole process. Several authors, such as Rupa & Shukla (1999), Adiloğlu & Kurşun (2003) and Alvarez & Gonzalez (2006), have indicated that chelating extractants may give results that are well correlated with the plant uptake of metals.

The uptake of plant micronutrients is a very complex process governed by several factors, including both natural and anthropogenic factors. Soil parameters and plant absorption ability are the main

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factors influencing metal uptake by plants (Kabata-Pendias 2004). Thus, it would be interesting to know the micronutrient contents in the edible portions of vegetables managed with organic and inorganic fertilization.

Pomares *et al.* (1994) found no significant differences in the contents of micronutrients in citrus from conventional and organic farming; however, Beltrán-González *et al.* (2008) found that organic farming of mandarin oranges resulted in juice with a higher content of zinc (Zn) and manganese (Mn) compared to conventional juice. Warman & Havard (1997, 1998) indicated in a study with carrots, potatoes and corn that the content of Mn and copper (Cu) after 3 years of organic farming were higher in conventional farming, but in general the differences were small, suggesting that the results depended on the type of nutrient as well as on the crop. Warman (2005) indicated that the improvement in soil parameters after compost addition did not yield increased nutrients in the edible portions of several plants. Most of the studies about the effect of fertilization on nutrient uptake by plants were mainly related to macronutrient concentration, a few studies have been related to the application of vegetable compost, which supplies a small amount of micronutrients (Herencia *et al.* 2007; Hargreaves *et al.* 2008). The aim of the present work was to determine the effect of organic fertilization over a period of 5 years under an irrigated system on the following factors: (i) the bioavailability of micronutrients in soils, (ii) the content of these elements in the edible part of different vegetables and (iii) their crop yield. Results were compared with those obtained using conventional chemical fertilization.

MATERIALS AND METHODS

Field study

The field study was performed on a loamy soil classified as a Xerofluvent (Soil Survey Staff 1999), located in the Guadalquivir River Valley of southwest Spain. The study site was located at the CIFA 'Las Torres-Tomejil' farm in Alcalá del Rio (Sevilla) (37°8′ N; 5°16′W, 11 m asl). The area has an annual rainfall of 650 mm, an average temperature of 18 °C and 4 mm of average daily evotranspiration. The textural and chemical characteristics of the soil at the beginning of the experiment are shown in Table 1. The field trial was established as a completely randomized design with two treatments (organic and inorganic) and four replicates per treatment. Three plots (P1, P2 and P3), measuring 10 × 20 m, with different rotation systems were established (Fig. 1). The organic treatment utilized plant compost (crop residues and pruning waste) and the inorganic treatment was managed with chemical fertilizer. The organic plant

Table 1. *Selected physico-chemical characteristics of the soil before start the experiment. Data are means of all plots*

	Mean	S.D.*
Sand (g/kg)	440	44·8
Silt (g/kg)	296	23·1
Clay (g/kg)	264	21·6
pH	8	0·06
Electrical conductivity (dS/m)	0·2	0·04
CEC (mmol/kg)	151	2·6
$CaCO_3$ (g/kg)	249	20·9
Total organic carbon (g/kg)	7·6	0·42
Kjeldahl N (g/kg)	0·9	0·07
Olsen-P (mg/kg)	20	2·1
K (mg/kg)	382	32·3
Fe (mg/kg)†	5·5	0·82
Cu (mg/kg)†	1·6	0·18
Mn (mg/kg)†	12	1·9
Zn (mg/kg)†	2	0·1

* S.D., standard deviation.
† Extractable Fe, Cu, Mn, Zn content (DTPA).

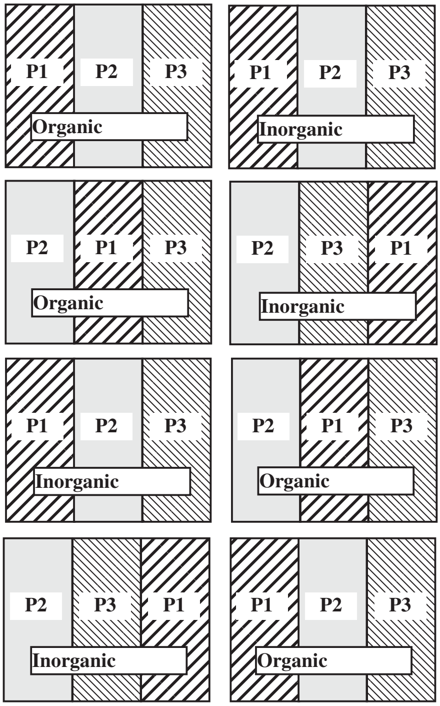

Fig. 1. Sketch of layout of plots in the study. Three plots (P1, P2 and P3) with different rotation systems, two treatments (organic and inorganic) and four replicates per treatment were established.

compost was chosen because it constituted a low-cost material that came from the experimental farm and did not depend on external input. The compost was made by the wind-row method. The raw materials, previously crushed to a size more or less homogeneous in long narrow piles, were agitated or turned on a regular basis. Typically, the wind-rows were 1 m high. During the process the compost piles were turned frequently to regulate their temperature and moisture content and to ensure an equal decomposition level throughout the pile. Due to the climatic characteristics of the area, the humidity was controlled with a mobile sprinkler system installed over the pile. The usual length of time for composting was 10–12 weeks.

Chemical fertilizers used were those recommended by the literature for each crop in the region (Maroto 1995). The commercial fertilizers were ammonium nitrate (335 g N/kg), polyfeed (200-50-320 g N, P_2O_5, K_2O/kg), potassium nitrate (130-0-460 g N, P_2O_5, K_2O/kg) and ammonium phosphate (120-606-0 g N, P_2O_5, K_2O/kg). Commercial pesticides were not used during the present study on any experimental plots, but authorized products for organic agriculture were used for pest and disease control.

From 12 March 2001, a crop rotational system (Regulation (EEC) No. 2092/91) was carried out in all plots (organic and inorganic fertilized). The data reported here are the results obtained after 5 years of organic and inorganic fertilization. In the fifth year of the experiment, the crops planted were an association of broccoli (*Brassica oleracea* cvar Italica Plenk), cauliflower (*B. oleracea* cvar Botrytis L.) and lettuce (*Lactuca sativa* (L.) cvar Oreja de mulo) in plots P1 (eight plots), potato (*Solanun tuberose* (L.) cvar Spunta) in plots P2 (eight plots) and carrot (*Dancus Carota* (L.) cvar Nantesa) in plots P3 (eight plots). All crops were irrigated by surface irrigation and water was supplied weekly through furrow irrigation according to evaporation data given by the class A evaporation plan. The organic treatment applied 30 t/ha of the compost by superficial tillage in each crop. This superficial tillage meant that soil was only disturbed to a depth of 200 mm.

The doses of the inorganic fertilizer were based on agronomic recommendations for each crop (Maroto 1995). The most relevant characteristics of the compost are shown in Table 2 (these data are the mean of eight samples used in the experiment). The compost was analysed using methods of MAPA (1994) and the inorganic fertilizer by the methods of AOAC (1990). The average content of micronutrients in the inorganic fertilizer was Cu (22 mg/kg), iron (Fe; 1811 mg/kg), Mn (30 mg/kg) and Zn (126 mg/kg).

Data of crop management and fertilization applied for organic and inorganic plots are shown in Table 3. For yield assessment, the entire area of the plots was harvested.

Table 2. *Characteristics of the plant compost (oven dry basis)**

	Mean	S.D.†
Moisture (g/kg)	265	21·1
pH	7·7	0·24
Electrical conductivity (dS/m)	2·2	0·85
Total organic carbon (g/kg)	157	37·3
Kjeldahl N (g/kg)	9	1·8
C:N ratio	17	
P total (g/kg)	4·3	0·82
K total (g/kg)	4·7	1·44
Ca total (g/kg)	121	11·8
Mg total (g/kg)	5·5	2·22
Na total (g/kg)	1·1	0·31
Fe total (g/kg)	7·5	1·18
Mn total (mg/kg)	305	78·8
Cu total (mg/kg)	20	2·1
Zn total (mg/kg)	54	4·8

* Data are the means of eight samples.
† S.D., standard deviation.

Sampling and soil analysis

Following the harvest, soil samples from the upper layer (0–150 mm) were randomly taken from each plot and air dried and sieved (< 2 mm mesh size) before further determinations. Soil pH was determined in the 1:5 soil/water extract. Kjeldahl-N was determined by the method of Hesse (1971); available-P was determined using the Olsen *et al.* (1954) method as well as available K (MAPA 1994) and OM, using the method of Jackson (1958). Cation exchange capacity (CEC) was determined using the method of Tucker (1954). Particle size distribution was determined by the Boyoucos densimeter (Gee & Bauder 1979) and carbonate content was determined by the manometric method (Demolon & Leroux 1952). The total metal content of the soils was determined using a three-acid method (Perez-Rodríguez *et al.* 1990). The extractable elements were determined both in inorganic and organic fertilized soil samples using DTPA (Lindsay & Norvell 1978). The concentration of the elements was performed using inductively coupled plasma (ICP).

Plant analysis

At harvest, representative plant samples were taken randomly. The edible part of the plants were carefully removed, washed with tap water to remove any attached particles, rinsed twice with distilled water and dried at 60 °C to constant weight. Afterwards, dried samples were ground to pass through a 40-μm mesh screen. For Fe, Cu, Mn and Zn determination, the samples were dry ashed, the ash was treated with hot concentrated hydrochloric acid (HCl) and the

Table 3. *Crop rotation and management, fertilizer treatment, rate and methods of application used during the fifth year of the study*

	Crop Management				Fertilization			
					OF	IF (kg/ha)		
							Time of application	
Plot	Crop	Date planting/harvest	Plant spacing (m × m)	Irrigation	t/ha	N-P-K (kg/ha)	Pre-planting	Growing crop
P1	Broccoli	25 Oct 2005/28 Mar 2006	0·75 × 0·50	Surface	30	120-150-150	120-150-150	0-0-0
	Cauliflower	20 Oct 2005/22 Mar 2006	0·75 × 0·25					
	Lettuce	17 Oct 2005/23 Jan 2006	0·75 × 0·25					
P2	Potato	20 Mar 2006/26 Jun 2006	0·9 × 0·2	Surface	30	125-75-250	75-75-250	50-0-0
P3	Carrot	10 Oct 2005/15 Mar 2006	0·75 × 0·4	Sprinkler/surface	30	120-100-250	20-100-75	100-0-175

OF, organic fertilization; IF, inorganic fertilization.

Table 4. *Total micronutrients content of pre-experiment soil and after 5 years of different fertilization treatments (mg/kg)*

Element	Treatment*	Plot 1	Plot 2	Plot 3
Fe†	Init.	22	23	24
	Org.	24	23	22
	In.	23	24	24
S.E.D. (D.F. = 11·0)		2·4	2·0	2·1
Cu	Init.	22	25	22
	Org.	25	26	21
	In.	20	22	22
S.E.D. (D.F. = 11·0)		2·5	2·1	2·9
Mn	Init.	420	419	432
	Org.	413	422	438
	In.	408	420	429
S.E.D. (D.F. = 11·0)		11·9	7·5	9·6
Zn	Init.	64	65	62
	Org.	66	69	63
	In.	65	65	59
S.E.D. (D.F. = 11·0)		4·3	5·0	7·2

* Init., original soil; Org., plant compost; In., inorganic fertilizer.
† Values for Fe are in g/kg.
S.E.D., standard error difference.

concentration of the elements was determined by inductively coupled plasma (ICP).

Statistical analysis

Statistical analysis was carried out using SPSS 11.0 for Windows and the results were expressed as mean values. Differences between treatments were examined by the Students *t* test at $P < 0{\cdot}05$. The three plots were independently analysed because plots were managed differently (i.e. different crop rotation) throughout the 5 years of the study. The results in Table 4 were analysed by an analysis of variance (ANOVA) by comparing the means of three variables. The statistical significance of differences between the treatments and the original values were established using Tukey's test at a significance level of $P < 0{\cdot}05$. A correlation matrix of the different metals in soil and plant was carried out based on Pearson correlation coefficients ($P < 0{\cdot}01$ and $P < 0{\cdot}05$). To investigate complex relationships, a multivariate statistical analysis technique (Varimax-rotated principal component analysis (PCA)) was used, and the first three components were retained.

RESULTS

Pre-experiment soil samples from both fertilization treatments and samples taken after 5 years of

Table 5. *Total nutrients applied via compost or inorganic fertilizer after 5 years of experiment*

Element	Plant compost	Inorganic fertilizer
N (g/kg)	0·45	0·38
P (g/kg)	0·22	0·14
K (g/kg)	0·24	0·37
Fe (g/kg)	0·38	0·05
Mn (mg/kg)	15·5	0·08
Cu (mg/kg)	1·01	0·06
Zn (mg/kg)	2·7	0·30

fertilization were analysed for their total Fe, Cu, Mn and Zn content (Table 4).

ANOVAs showed that the content of all elements studied were not significantly different between treatments and original values.

From the metal contents of the inorganic fertilizer and compost (Table 2), as well as the doses applied to each plot during the 5 years of the experiment (18 and 0·7 kg/m^2 for organic and inorganic fertilized), and assuming that the compost was uniformly incorporated in the upper 200 mm layer, a theoretical increase in the total content for each micronutrient could be calculated (Table 5). It was found that the plant compost addition caused little effect on any, which was in agreement with the similar values of the total content of these elements in the soil after both fertilization techniques (Table 4).

At the end of the experiment, the amount of Fe extracted with diethylene triamine pentaacetic acid (DTPA) was significantly higher in all plots managed organically (Fig. 2), ranging from 3·87 to 5·91 and 5·18 to 8.0.2 mg/kg for inorganic and organic plots, respectively. The amount of Cu extracted by DTPA (Fig. 2) ranged from 1·51 to 2·48 and 1·62 to 2·69 mg/kg for inorganic and organic plots, respectively. The content of extracted Cu in the plots fertilized organically was significantly higher than for inorganic fertilized soils for plots 2 and 3. The Mn extracted by DTPA ranged from 11·36 to 15·77 and 18·16 to 21·78 mg/kg for inorganic and organic plots, respectively (Fig. 2). The content of extracted Mn in the plots fertilized organically was higher than in inorganic plots, and the differences were always significant. The available Zn extracted by DTPA ranged from 1·44 to 2·41 and from 2·78 to 4·16 mg/kg for inorganic and organic plots, respectively. The content of extracted Zn in the plots organically fertilized was higher than in the inorganic plots and, as for Fe and Mn, the differences were always significant.

The micronutrient contents in the edible part of the different crops for both types of fertilization are shown in Fig. 3. The amounts of Fe ranged from 46·4 to 245 mg/kg, with carrot in the upper range and cauliflower in the lower range (Fig. 3). The concentration of this element was higher for the organic broccoli and cauliflower, but the differences were significant for Fe, Cu and Zn in broccoli and for Mn and Zn in cauliflower. The amounts of Cu ranged from 4·4 to 14·8 mg/kg, with lettuce in the upper range and cauliflower in the lower range. For Cu, the results depending on the plant type were inconclusive. The differences for Cu content in broccoli and potato from organic and inorganic plots were significant but showed different trends: broccoli was higher for organic plots, whereas potato was higher for inorganic plots. The values of Mn varied somewhat between the different crops and concentrations ranged from 7·04 to 52·3 mg/kg, with the lowest value for potato and the highest for lettuce. Cauliflower and potato had higher values on organic plots. The content of Zn ranged from 8·82 to 50·38 mg/kg, with the lowest value for potato and the highest for broccoli. Broccoli displayed higher Zn values for the plants obtained from organically fertilized plots and potato displayed higher Zn values for the plants obtained for plots fertilized conventionally. A similar content of Zn was found for lettuce from both soil fertilizations methods.

In summary, the concentration of Fe, Cu and Zn of broccoli and Mn and Zn of cauliflower were higher for organic plots than for inorganic plots; however, the opposite was true for Fe in lettuce and potato, and Cu in potato.

The association among variables was checked by PCA. The Varimax-rotated component matrix is shown in Table 6. Those components with eigenvalues greater than 1 were selected as principal components.

The first factor, with 0·32 of the total variance, comprised only the data of soil extractable metals and represents soil extractability. All soil metal data had positive loadings in this factor. The second factor, with 0·25 of the total variance, comprised the Fe and Cu crop contents, and the third factor (0·22 of the total variance) comprised the Mn and Zn crop contents, respectively. Table 6 shows that little association existed between soil and plant metal contents. A further PCA was done with the soil metal data alone, and the results are shown in Table 7. Three principal components explained 0·99 of the soil data variance (Table 7), indicating that Cu (0·99) and Zn (0·76) were strongly associated within the first component, and Fe and Mn in the second and third component, respectively. Figure 4 shows the scatter for the soil data of every pot projected on the plane of the first two components. Two different clusters are observed for organic and inorganic fertilization, respectively.

The Varimax-rotated component matrix of the PCA of metal plant content is also shown in Table 7. The results indicated that Mn (0·93) accounted for most of the first component. The largest coefficients of

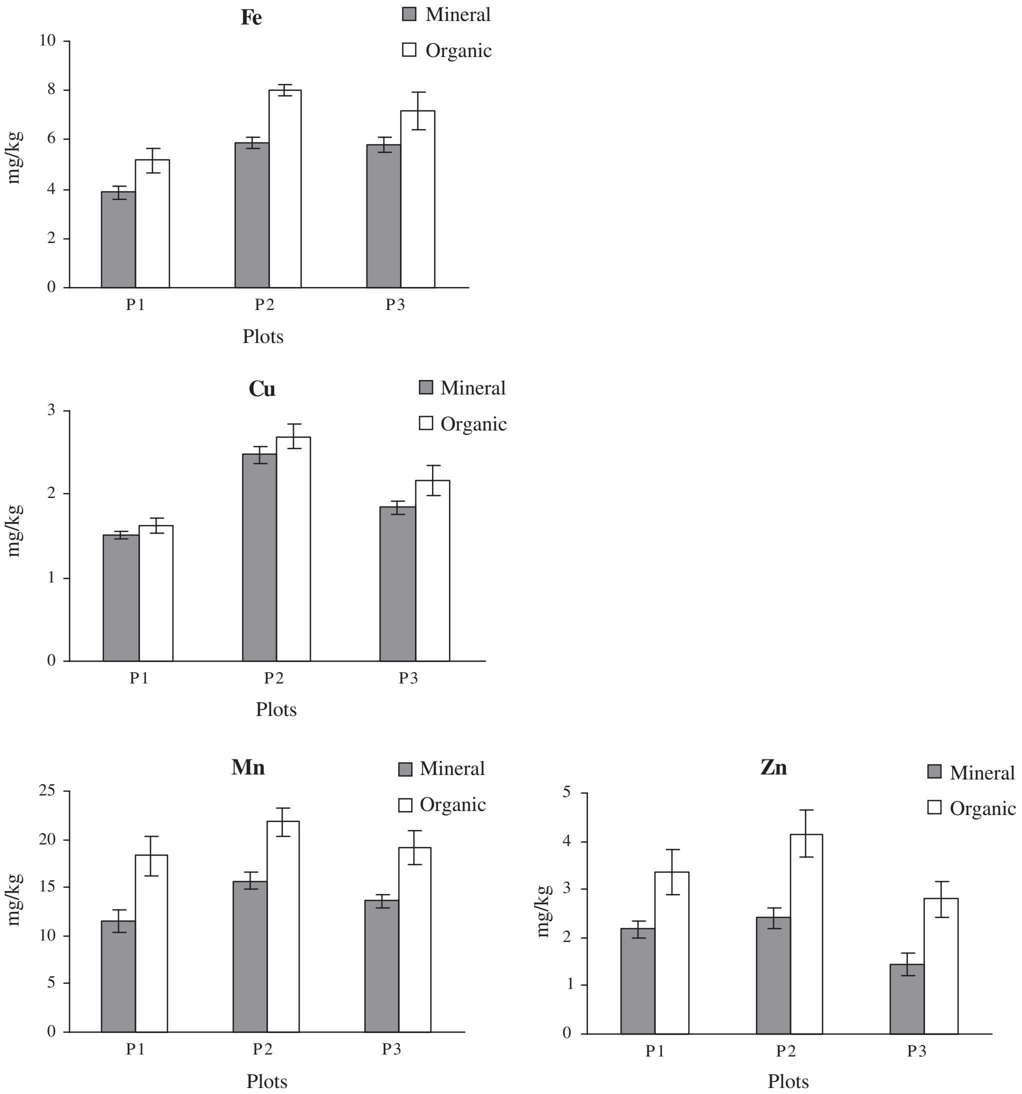

Fig. 2. DTPA-extractable micronutrients after 5 years of organic and mineral fertilization (mg/kg). Data are presented as means ± S.E.M. of four replicates.

the second component were Fe (0·98), and Cu (0·78), while the largest coefficient of the third factor was for Zn (0·96). Figure 5 showed the scatter for the plant data of every pot projected on the plane of the first two components.

The crop yields obtained in conventional and organic plots in the fifth year of treatment are shown in Table 8. Broccoli and cauliflower had higher yields in the inorganic plots as compared to the organically fertilized plots; however, the lettuce yield was higher in the organic system. The crop yields of potato and carrot were not significantly different between treatments.

DISCUSSION

Effect of fertilization on soil micronutrients

It is noticeable that there were no significant differences between the mean total micronutrient contents of the plots before the start of the experiment and after 5 years of organic or inorganic fertilization (Table 4), which is in agreement with the small amount of micronutrients applied via compost or inorganic fertilizer after the 5 years of organic and inorganic fertilization (Table 5). The effects on the availability of the micronutrients studied correlate to soil fertilization but not to differences in the total micronutrients of the plots under treatment; however, in other papers (i.e. Singh & Agrawal 2007) the increase in metal availability was found to be due to the application of metal-contaminated amendments, like sewage sludge.

Soil extraction with DTPA was used to assess the availability of these micronutrients in both fertilization systems because the OM can interact with trace elements, increasing the solubility of the former or contributing to their immobilization (Diaz-Barrientos *et al.* 2003; Rodriguez-Rubio *et al.* 2003). The Fe extracted with DTPA was higher in all cases for the plots managed organically (Fig. 2) and this difference was statistically significant. The higher values of extracted Fe obtained in plots fertilized organically is in agreement with other authors. Sharma *et al.* (2000) indicated that DTPA-extractable Fe was positively correlated with OM content in soil. After 5 years of fertilization, the organic plots in the present study showed OM content values of 14·5 *v.* 8·0 g/kg for inorganic plots. In addition, the organic amendments may increase the solubility of Fe through the effects on the soil redox potential, as indicated by Rengel *et al.* (1999). In general, the content of extracted Cu in the plots fertilized organically was higher than for soils fertilized with inorganic products. Katyal & Sharma (1991) found that DTPA-extractable Cu was significantly correlated with soil OM content, as it was in the present study. The higher levels of Cu extracted in the plots fertilized organically may be due to the formation of organo–Cu complexes (Bolan & Duraisamy 2003). In high pH soils, such as the soil used in this study, complexation will promote the maintenance of Cu in dissolved forms, increasing the availability of this element in soils. The effect of OM addition in the behaviour of Mn is important because the OM has the effect of creating reducing conditions in soil with fine texture (such as the soil used in the present study, Table 1), which will favour Mn solubilization (Mandal & Mitra 1982). Microbial decomposition of OM leads to reducing conditions by utilizing oxygen from the soil atmosphere, and produces CO_2 and organic acids. Microbial soil activity is known to be largely responsible for the oxidation and reduction of manganese compounds (Gadd 2004). In these organic plots, microbial biomass and enzymatic activities were greater than in the inorganic plots (Melero *et al.* 2008). The content of extracted Zn in the plots fertilized organically was higher than in inorganic plots, and the differences were always significant (Fig. 2). The addition of exogenous OM with functional groups having the ability to form stable complexes promotes Zn availability in soils (Almas *et al.* 2000). Katyal & Sharma (1991) also found a significant correlation coefficient between DTPA-Zn and OM content of soil. In a longer experiment carried out over 6 years, with compost addition at higher rates (40 t/ha), the OM

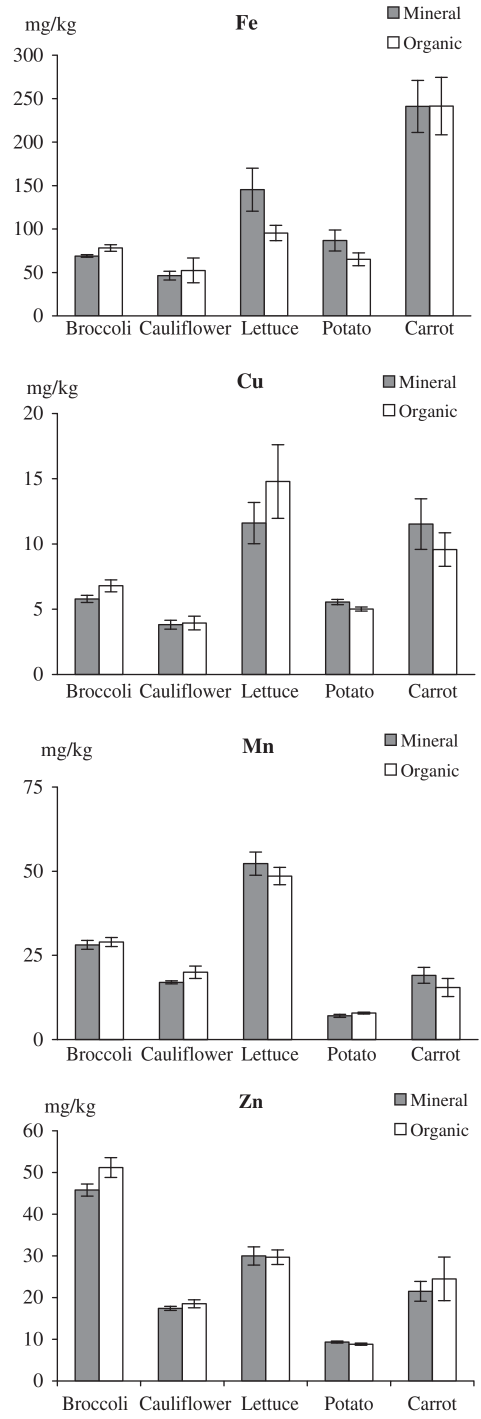

Fig. 3. Fe, Cu, Mn and Zn content in the edible part of crops after 5 years of organic and mineral fertilization. Data are presented as means ± S.E.M. of four replicates.

Table 6. *Correlation coefficients between extractable soil and crop metal contents, and the Varimax-rotated principal components (PC) and communalities (proportions of variance of each variable accounted for) (all data). Values >0·6 are in bold (40 observations)*

	Element	PC1	PC2	PC3	Commonalities
Soil	Fe	0·506	**0·658**	−0·231	**0·742**
	Cu	**0·755**	0·013	−0·072	0·575
	Mn	**0·717**	−0·284	0·361	**0·725**
	Zn	**0·982**	0·109	0·016	**0·976**
Crop	Fe	−0·080	**0·957**	−0·022	**0·923**
	Cu	0·049	**0·799**	0·496	**0·887**
	Mn	−0·035	0·105	**0·923**	**0·864**
	Zn	0·145	−0·005	**0·796**	**0·655**
Eigenvalue		2·581	2·001	1·766	
Cumulative proportion of total variance		0·323	0·573	**0·794**	

Table 7. *Correlation coefficients between extractable soil and crop metal contents, and the Varimax-rotated principal components (PC) (proportions of variance of each variable account for) (soil and crop data separately considered). Values >0·6 are in bold (40 observations)*

	Element	PC1	PC2	PC3
Soil	Fe	0·095	**0·988**	0·113
	Cu	**0·994**	0·013	0·063
	Mn	0·142	0·102	**0·983**
	Zn	**0·757**	0·381	0·514
Eigenvalue		2·321	0·902	0·745
Cumulative proportion of variation		0·58	0·81	0·99
Crop	Fe	−0·045	**0·983**	0·006
	Cu	0·571	**0·781**	0·097
	Mn	**0·933**	0·062	0·316
	Zn	0·262	0·037	**0·964**
Eigenvalue		2·146	1·251	0·504
Cumulative proportion of total variance		0·54	**0·85**	**0·97**

caused Zn and Fe to move from less soluble forms to more plant-available forms (Herencia *et al.* 2008*a*).

Effect of fertilization on micronutrient content in plants

It is widely accepted that micronutrient uptake by crops can be correlated with some extractable fraction of the element in soil. The available Fe content was higher in the plots fertilized organically; however, the content in the plants followed a different trend (i.e. the concentration of this element was higher for broccoli from organic plots and lower for lettuce and potato) (Fig. 3). This behaviour could be related to the plant type and soil characteristics. In calcareous soils, pH is regulated by the bicarbonate ion (HCO_3^-). According to Mengel & Kirkby (1982), this ion is very important for Fe, indicating that Fe content in solution with bicarbonate decreases the absorption of Fe by plants. Mengel *et al.* (1979) indicated that this is due to the plant physiology and not due to the availability of the soil; the plant exerts control during uptake or rejection of some elements by appropriate physiological reactions (Kabata-Pendias & Pendias 2001). In addition, the microbial activity increased in the organic plots (Melero *et al.* 2008) and CO_2 was produced (Lindsay & Thorne 1954; Ruiz *et al.* 2000), and, consequently, the bicarbonate content increased.

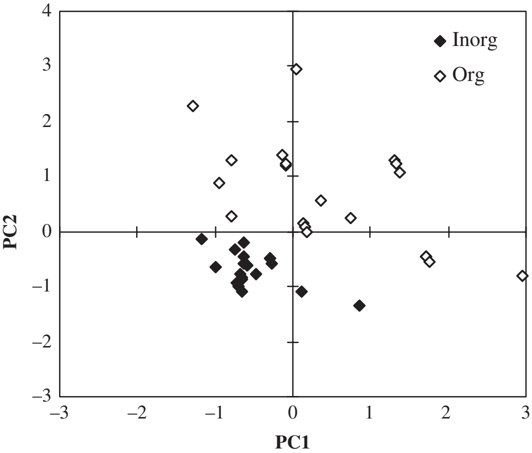

Fig. 4. Scatter of the data of the soil extractable metals, projected on the plane of the first two principal components (PC1 and PC2). Inorg, inorganic fertilization; Org, organic fertilization.

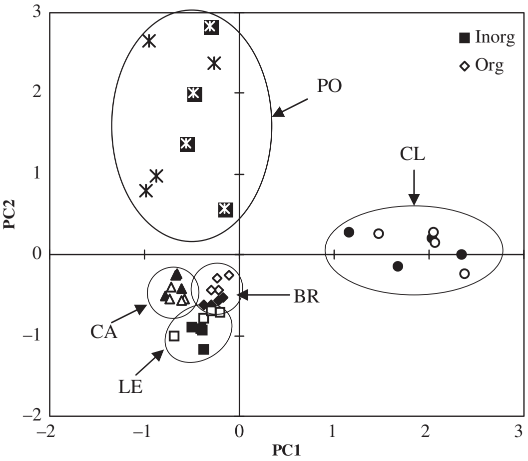

Fig. 5. Scatter of the data of the crop metal content, projected on the plane of the first two principal components (PC1 and PC2). Inorg, inorganic fertilization; Org, organic fertilization. Crop: BR, broccoli; CA, carrot; CL, cauliflower; LE, lettuce; PO, potato.

Table 8. *The effect of fertilization on crop yields (t/ha)*

	Inorganic		Organic		
Crop	Mean	S.D.*	Mean	S.D.*	*P*
Broccoli	11	1·7	7	0·9	< 0·001
Cauliflower	19	3·2	11	2·3	0·010
Lettuce	60	3·8	67	5·5	0·048
Potato	33	7·3	33	6·3	0·891
Carrot	18	4·9	14	4·0	0·181

* S.D., standard deviation.

In addition, there are a number of interactions between elements; an increase in P yielded a decrease of Fe absorption by plants (Jones *et al.* 1991). It is known that with the organic addition, the supply and availability of P is high (Table 5). The concentration of available phosphorous in the plots managed organically was significantly higher than in inorganic plots. At the end of the experiment, the amount of available P was 40 and 20 mg/kg for organic and inorganic plots, respectively (Herencia *et al.* 2008*b*). Antagonistic interaction between Fe and other metals has also been observed in several crops (Kabata-Pendias & Pendias 2001). Excess amounts of other metals, especially Zn and Mn, decrease Fe uptake by plants greatly. In general, there was no correlation between Cu content of the edible part of the plants and the micronutrient extracted by DTPA. It seems that for Cu, the results are not conclusive and depend on the plant type. The data from plants indicated that differences were significant in only two cases: one is higher for organic (broccoli) and other for inorganic fertilized plots (potato). Possibly, the interaction between nutrients could be the reason for this behaviour. According to the literature, the extractability of trace metals with DTPA in calcareous soils is the best procedure for determining the real availability of this element for several crops. Many authors, such as Van Der Watt *et al.* (1994), have found that the concentration of metals (Cu, Mn and Zn) in DTPA extracts were significantly correlated with plant uptake of the metals; the correlation may be increased including the pH. However, the uptake of Cu by plant roots in our organic plots could be decreased by the antagonistic effect of other elements, which reduce Cu absorption, such as Ca, P and K. These elements affect uptake of Cu via differential complexing and other surface effects, which determine soil solution activities of the metal and membrane permeability (Loneragan 1981). In the present work, the values of available K in the plots fertilized organically were higher than in the corresponding inorganically fertilized plots (Herencia *et al.* 2007, 2008*b*). In addition, the absorption of Zn and Cu have an antagonistic behaviour, because both are absorbed in the same way, and the amount of available Zn in the organic plots is higher than in the inorganic ones (Fig. 2). On the other hand, plants such as lettuce, broccoli and cauliflower are those with a higher content of copper in their edible parts in plots fertilized organically, which indicates that the type of plant, possibly its physiology, plays an important role in uptake of nutrients and inter-elements effects. Mn content in the edible part of the different crops is shown in Fig. 3. The value of this element somewhat varied between the different crops, with the lowest value for potato and the highest for lettuce. Available Mn content was higher in plots fertilized organically; however, the content in the crops followed this trend only for cauliflower, broccoli and potato.

Mn uptake by plants depends on both biological and geochemical interactions. Mn–Fe antagonism is widely known, and both elements are interrelated in their metabolic functions. There are also interrelations with P depending on soil conditions and on the plants, and these interactions can increase or decrease Mn uptake by plants. There is antagonism also with K, N and Mn (Kabata-Pendias & Pendias 2001). These antagonisms among the various elements are the reason for the lower concentrations in plants grown in organic plots, where the availability of the interfering elements is higher, as indicated previously.

Kabata-Pendias & Pendias (2001) indicated that studies about interactions between major and trace elements showed clearly that Ca, P and Mg were the main antagonistic elements against the absorption and metabolism of several trace elements depending on the plant genotype or species.

For potatoes, Warman & Havard (1998) found that Mn in tuber as well as B and Fe in leaves were the micronutrients statistically influenced by treatments; however, leaf Mn and Cu content was always higher in the conventionally grown potatoes. Warman & Havard (1998) also indicated that conventionally grown carrot root were significantly higher in N, Mn and Cu, and organically grown carrot roots were higher in B, with the leaves higher in Na; therefore, the influence of soil fertilization on micronutrients behaviour depends greatly on plant type.

The content of Zn (Fig. 3) showed the lowest value for potatoes and the highest for broccoli. The available Zn content was higher in the plots fertilized organically; however, the content of Zn in the plants again followed an opposite trend in some cases. Broccoli displayed a higher value when grown from plots fertilized organically, and the values were statistically different from the corresponding plots fertilized inorganically, but opposite results were observed for potatoes. Slightly higher values were found in organic cauliflower and carrots, but a similar content of this element was found in lettuce from both soil fertilization methods. Zn–P antagonist interactions have been reported for several crops. This antagonism appears to be based on chemical reactions on the root media (Saeed & Fox 1977); however, some authors have indicated that this interaction is not only a process of immobilization but is also mainly a plant physiological characteristic (Smilde *et al.* 1974). This is in agreement with the present results because the metal content depended on the plant type, and the antagonism effects of other nutrients appeared to vary for a given plant or media.

Table 6 shows that little association existed between soil and metal contents. Figure 4 shows that the type of fertilization was the key factor clearly defining two different clusters in the results of extractable soil metals, clearly related to the greater content of extractable metals often found in the soils of the organic treatment.

The PCA of plant metal contents (Fig. 5) indicated that the metal concentration in each crop depended on their respective physiological characteristics rather than the type of fertilization method used.

Yield

The type of fertilization had little effect on plant production (Table 8). The application of compost had a positive effect on soil fertility; however, this fact did not correlate with crop yields. Given these results, it seemed that the effect of the treatment on the production depended, in some manner, on crop type because potatoes and carrots showed no significant differences between different soil fertilization systems. However, the lettuce yield was greater in the organic system, whereas other crops such as broccoli and cauliflower presented greater yields in the plots fertilized inorganically.

After 5 years of organic and inorganic fertilization, the main conclusion for the present work is that a higher extractability of Fe, Cu, Mn and Zn, determined by DTPA solution, is observed in the plots fertilized organically compared to the inorganic plots, particularly in the cases of Fe and Zn.

Based on the results of the present study, there were no significant differences between micronutrient content in the edible parts of plants and in the micronutrients extracted by DTPA, except for broccoli, and Mn and Zn for cauliflower. Possible interactions between major and minor elements that show an antagonistic effect could inhibit the micronutrient soil–plant transfer; however, it is noteworthy that this behaviour depends on the plant type. Broccoli and cauliflower had significant lower crop yields in organic *v.* inorganic fertilization. The decline in crop yield will also account for higher micronutrient concentration in crops. The use of DTPA extraction was not successful in assessing micronutrients soil–plant transfer in many cases.

PCA analysis showed a strong association between the type of fertilization and the extractable elements. On the other hand, a strong association between the type of crop and their micronutrients content was observed.

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