Available micronutrients in agricultural soils of Tenerife (Canary Islands). I: copper and zinc.

M. FERNANDEZ-FALCON, A. BORGES-PEREZ, J.F. PEREZ-FRANCES*, A.A. BORGES**, I. LOPEZ-CARRENO*
Instituto de Productos Naturales y Agrobiologia de Canarias.
C.S.I.C., La Laguna, Tenerife, España.
*: Dpto. Biologia Vegetal, Univ. de La Laguna, Tenerife.
**: Dpto. Bioquimica y Biologia Molecular, Univ. de La Laguna, Tenerife

INTRODUCTION. — Total micronutrient content is generally high in cultivated soils. Deficiency of the forms available to the plant is nevertheless observed due to soil factors such as texture (RYAN, 1967), organic matter (ADRIANO, 1986), pH (HAYNES & SWIFT, 1985), and micronutrient interactions (REDDY *et al.*, 1987).

There is various evidence to show that the organically bound Cu in the soil is found in an available form (MALAREN & CRAWFORD, 1973), and these Cu fractions can also be expected to dominate in ordinary soils (MCBRIDE & BOULDIN, 1984). Moreover, the amount of organically bound Cu will be small in calcareous soils, even in the presence of high O.M. levels. This is caused by the high pH encountered in the calcareous soils, which enhances the Cu precipitation like carbonate and does not favour the complex formation with humic and fulvic acids (MITCHELL, 1964). Because of the importance of organically bound Cu in regulating Cu supply to plant roots, chelating agents have been widely accepted as extractants to measure available Cu in the soil (SELVARAJAH *et al.*, 1982). Thus, the complexing agent EDTA, being capable of extracting the organically bound Cu (MCLAREN & CRAWFORD, 1973), shows significant correlations with plant uptake (SILLANPÄÄ, 1982). Often, extractable or available Cu is used as a diagnostic criterion to identify Cu deficiency conditions for plants (JOKINEN & TÄHTINEN, 1987).

Zn is known as one of the most soluble and mobile micronutrients under acidic conditions. Although Zn may exist as an organic complex in soil solution, it may also exist as a divalent cation (KNEZEK & ELLIS, 1980). It is generally agreed that the plant-available Zn in soil can best be predicted by extractants that remove only a fraction of the total amount of this micronutrient.

In this sense, Lindsay & Norvell (1978) pointed out that the most suitable index of Zn deficiency in soils is the DPTA test.

Symptoms of micronutrient deficiency have been observed during the last fifteen years in crops in most agricultural areas of Tenerife (Garcia *et al.*, 1984; Barroso *et al.*, 1985). This is probably due to several factors such as organic matter shortage in the soils, the increasing purity of chemical fertilizers in use today, and the alkalinization of soils. As a result, the lack of one of these micronutrients is a limiting factor to obtain high yields. This study was undertaken to verify the soil availability of Cu, Fe, Mn and Zn for crops in agricultural soils of Tenerife by using two extraction methods with AAAc-EDTA (for Cu and Fe) and DTPA (for Mn and Zn) as extractants. Correlations have also been calculated with some soil properties. In this first paper we present the results concerning available Cu and Zn.

Material and methods. — Three hundred and fifty seven different topsoil samples were used in this study; they were taken from most of the agricultural zones of Tenerife. No samples were taken from tropical crops (banana and avocado) because they receive a heavy fertilization which includes micronutrients.

The parent materials of the soils are mainly basaltic although an important area correponds to phonolithic pumices. Different types of soils exist due to a great variety of microclimate and age of the parent materials. On the northern side of the island the following soil types were recognised: Xererts, Tropepts (with andic properties), Ustands, and Ustults; on the southern side: Vitrands, Orthents (pumices), Tropepts, and Orthids; the latter present salinization features.

Analytical techniques. — The extraction methods employed in this work are those used by FAO/Unesco in a micronutrient study undertaken in soils of many countries growing wheat and maize plants (Sillanpää, 1982). AAAc-EDTA was used as extractant of copper and DTPA as extractant of zinc.

The acid ammonium acetate-EDTA extraction solution (0.5 M CH_3COONH_4, 0.5 M CH_3COOH, 0.02 M Na_2EDTA) was made by dilution 571 ml 100% CH_3COOH, 373 ml 25% NH_4OH and 74.4 g Na_2EDTA (EDTA = ethylenediaminetetraacetic acid) to 10 litres with water. The pH was adjusted to 4.65 with acetic acid or ammonium hydroxide. Soil (25 ml) and extracting solution (250 ml) were shaken for 1 h (end over end, 27 r.p.m.). The suspension was filtered using Whatman No. 42 filter paper. The concentrations of Cu were determined with an atomic absorption spectrophotometer (Perkin Elmer 2380, air-acetylene flame).

The DPTA extracting solution was prepared with 0.005 M DPTA (diethylene-triamine pentacetic acid), 0.01 M $CaCl_2$, 0.1 M TEA (triethanolamine) and was adjusted to pH 7.3 with HCl (LINDSAY & NORVELL, 1978). Soil (25 ml) and extracting solution (50 ml) were shaken for 2 h (end over end, 27 r.p.m.). The suspension was filtered using SCHLEICHER & SCHÜLL Selecta 589/3 filter paper. The concentration of Zn were determined with an atomic absorption spectrophotometer (Perkin Elmer 2380, air-acetylene flame).

To obtain background information on factors affecting the micronutrient contents, a number of additional analytical data of the soils (from the same sampling) were used (BORGES PEREZ & GUTIERREZ JEREZ, unpublished data). These data include sand, silt and clay contents, cation exchange capacity (CEC), pH, electrical conductivity (EC), $CaCO_3$ and organic matter content (O.M.). We shall discuss only those parameters which are relevant.

RESULTS AND DISCUSSION. — Data study has been performed considering, on the one hand, the totality of sampled soils on the island, and on the other, two well differentiated zones (northern and southern zones) as we mentioned above.

The results of the micronutrient analyses of soil have been expressed on a volume basis (mg L^{-1}), because it can be assumed that the density of root and nutrient absorption by plants are much better related to soil volume than to the weight of the soils.

Table 1 shows the mean contents and extreme values of available Cu and Zn in the soils of Tenerife taken as a whole as well as those corresponding to the northern and southern zones.

Copper. — The mean Cu content over the whole island was 4.75 mg L^{-1} (Table 1), presenting a great variability with values ranging from 0.5 to 58 mg L^{-1}. This mean value is slightly lower than that found by FAO/Unesco (6.00 mg L^{-1}) (SILLANPÄÄ, 1982).

TABLE 1. — Mean values of available Cu and Zn (mg L^{-1}) in the soils of the Tenerife island.

	Mean	S.D.	Minimum	Maximum	n
			COPPER		
Tenerife	4.75	± 6.09	0.5	58.0	357
North	6.69	± 8.06	0.8	58.0	171
South	2.97	± 2.25	0.5	13.3	186
			ZINC		
Tenerife	4.80	± 7.28	0.18	70.4	357
North	7.08	± 9.34	0.32	70.4	171
South	2.71	± 3.56	0.18	28.6	186

Fig. 1a shows frequency distributions (in percentage) for the Cu content in Tenerife soils. Most samples (86.52%) ranged from 1-10 mg L^{-1} Cu, values that are considered as normal in agricultural soils when the same extractant is used (KISHK *et al.*, 1973; MITCHELL, 1964; SILLANPÄÄ, 1982). Values between 1 and 2 mg L^{-1} (22.13% of samples) could be considered as marginals for some crop types (marginal or transitional zones are defined as a non definitive range of soil test values where a response to fertilization cannot be accurately predicted). Thus, JOKINEN & TÄHTINENE (1987) reported 1.5-2 mg L^{-1} of Cu as the critical level for Avena crops. Almost 6% of the soils present contents below 1 mg L^{-1}, value that is considered critical for this micronutrient by different authors in many crops (MITCHELL, 1964; LINDSAY & NORVELL, 1978; SILLANPÄÄ, 1982). These soils with deficient Cu levels contain significantly lower O.M. contents and significantly higher sand percentages (at 5% level both) than those observed in the remainder of the Tenerife soils. Only 3.64% of analyzed soils present equal or higher values than 17 mg L^{-1}, levels considered as high (SILLANPÄÄ, 1982).

When a study is made by zones, it is observed that the highest contents of available Cu appear in the northern zone (mean value: 6.69 mg L^{-1}, max: 58 mg L^{-1}, min.: 0.8 mg L^{-1}), while the soils from the southern part show significant lower values at the 1% level (mean value: 2.97 mg L^{-1}, max.: 13.3 mg L^{-1}, min.: 0.5 mg L^{-1}). In the north (Fig. 1b), the diagram of frequency distributions indicates that 74.5% of samples present levels ranging between 1 and 7 mg L^{-1} of Cu, while in the south (Fig. 1c) a similar percentage of data (70.41%) range into a shorter interval with a lower value on the high side (1-4 mg L^{-1}) is observed. Values considered as marginals (1-2 mg L^{-1}) appear in a higher proportion in the south (27.4% of soils) than in the north (16.3%). Further more, only a 1.17% of sampled soils in the north shows deficient values of Cu lower than 1 mg L^{-1}, while the south soils have a percentage of 10.21%.

Table 2 presents some correlations and regression models between available Cu and different soil parameters taken into account in this study. A negative influence of sand percentage on Cu contents in Tenerife soils is observed, also confirmed by several authors (SHUMAN, 1979; ADRIANO, 1986). On the other hand, Cu levels are positively correlated with organic matter and clay con-

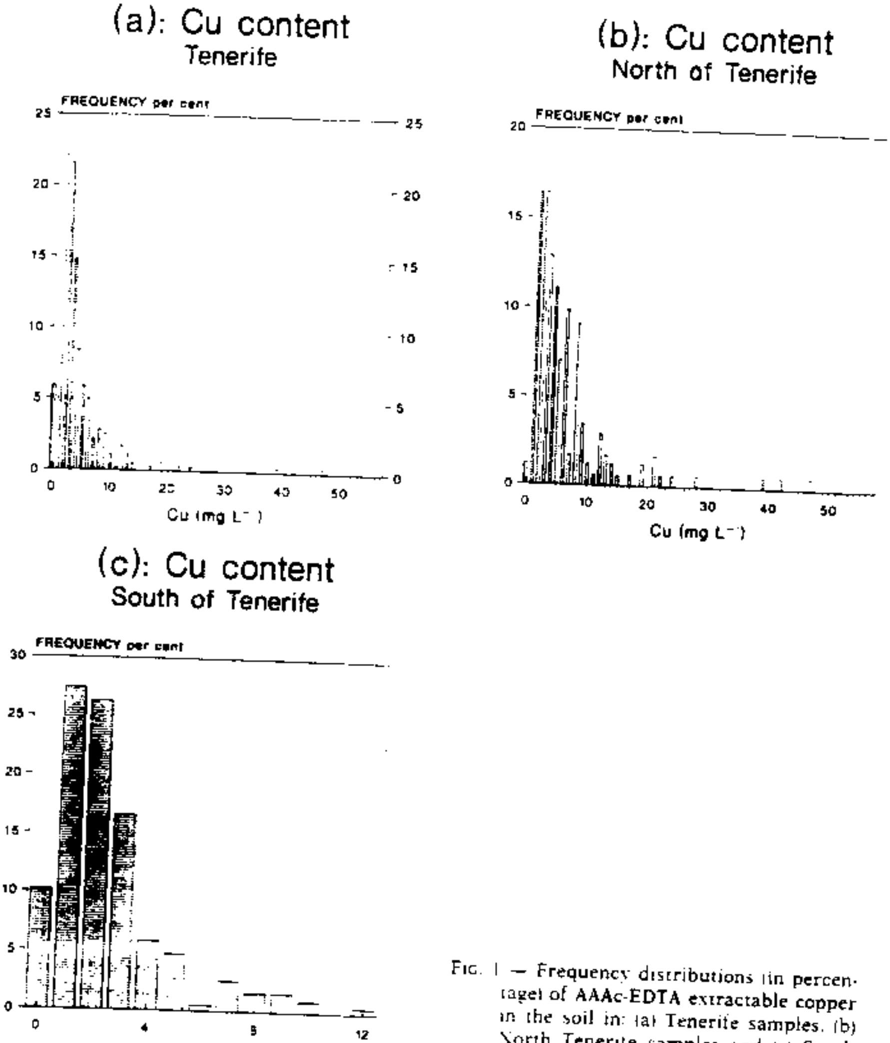

FIG. 1 — Frequency distributions (in percentage) of AAAc-EDTA extractable copper in the soil in: (a) Tenerife samples, (b) North Tenerife samples and (c) South Tenerife samples.

tents (at 0.1% significance level). Similar behaviour has been observed by SHUMAN (1979) and SAKAL *et al.* (1988) for organic matter, and by DRAGUN & BAKER (1982) and ADRIANO (1986) for clay content.

Zinc. — The mean content of available Zn in Tenerife soils (Table 1) is 4.80 mg L^{-1}, a value sensibly higher than those reported by FAO-Unesco (mean value: 1.97 mg L^{-1}). Although our

TABLE 2. — Equations and correlation coefficients (r) for regressions of AAAc-EDTA extractable soil Cu on various soil factors.

Location	Y	x	n	Regression	r
Tenerife	Cu	O.M.	357	$\log y = 0.30 + 0.81 \log x - 0.52 (\log x)^2$	0.356***
Tenerife	Cu	Sand	357	$y = 19.65 - 9.06 \log x$	-0.256***
Tenerife	Cu	Clay	357	$y = 1.89 - 0.12 x$	0.239***

(***): Highly significant at P = 0.001

data are within the range considered as normal by some authors (DAVIES & ROBERTS, 1975; SILLANPÄÄ, 1982) or high by others (ADRIANO, 1986), they show a great variability (s.d.: ±7.28), with a variation interval of 0.18-70.4 mg L^{-1}.

The diagram of frequency distributions for available Zn levels when all sampled soils of the island are considered (Fig. 2a), indicates that 6.44% of the soils present Zn deficiency conditions (<0.5 mg L^{-1}) for most crop plants (SINGH *et al.*, 1987; KULDEEP & GUPTA, 1986), while 16.80% of the soils are potentially deficient or are found in a marginal zone (0.5-1.0 mg L^{-1}) according to other authors (LINDSAY & NORVELL, 1978; SAKAL *et al.*, 1984; KULDEEP *et al.*, 1987). This 6.44% of soils presenting Zn deficiency conditions contain considerably lower percentages of O.M. and sand (at 5% and 1% level) than the remainder of the soils of the island. Values higher than 10 or 20 mg L^{-1} (according to crops) considered as excessive in available Zn (SILLANPÄÄ, 1982) appear, respectively, in 12.35% and 7.59% of our soils.

Marked differences in Zn contents (at 1% level) between both the studied zones were noted: The northern zone presents mean levels (7.08 mg L^{-1}, max: 70.4 mg L^{-1}, min.: 0.32 mg L^{-1}) sensibly higher than those of the southern zone (2.71 mg L^{-1}, max.: 28.6 mg L^{-1}, min.: 0.18 mg L^{-1}). 4.09% of northern soils show deficiencies and 5.26% of them are within the interval considered as marginal, while these percentages reach 8.60% and 27.41%, respectively, in the south (figs. 2b and 2c). On the other hand, values considered as excessive (>10 mg L^{-1}) are present in 20.46% of northern soils, while these are only detected in 4.83% of the samples from the southern zone.

Table 3 presents some regression equations and correlation coefficients found between available Zn and several factors studied

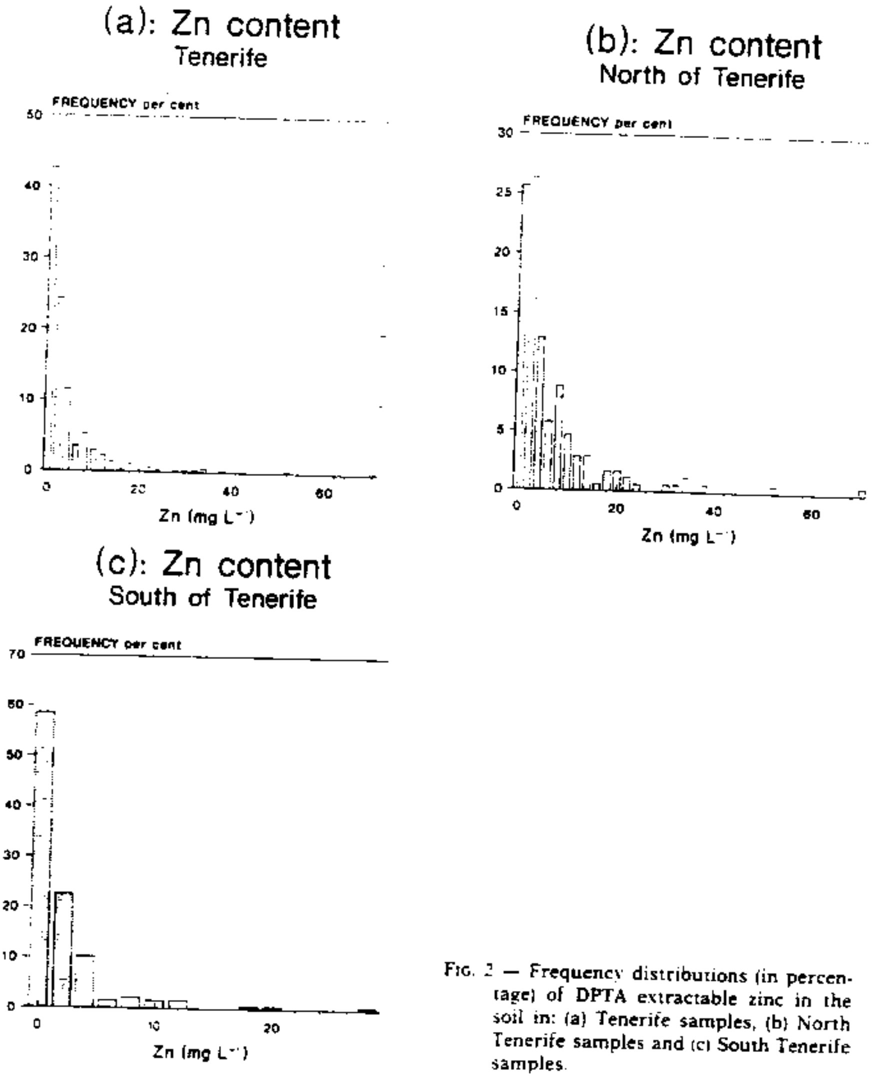

FIG. 2 — Frequency distributions (in percentage) of DPTA extractable zinc in the soil in: (a) Tenerife samples, (b) North Tenerife samples and (c) South Tenerife samples.

in the soils of the island. Soil pH affects the Zn availability, indicating a negative correlation between both parameters, such as researchers have already reported (PATEL & DANGARWALA, 1984; KULDEEP & GUPTA, 1986). This correlation results positive when the northern zone only is considered, since the soils of this zone present pH values appreciably lower (mean value: 5.57) than southern soils (mena value: 7.01), producing an increase in the Zn extraction capacity by EDTA when the pH increases under

TABLE 3. — Equations and correlation coefficients (r) for regressions of DTPA extractable soil Zn on various soil factors.

Location	y	x	n	Regression	r
Tenerife	Zn	pH	357	$\log y = -0.98 - 0.52\,x - 0.04\,x^2$	0.226**
Tenerife north	Zn	pH	171	$\log y = -0.19 - 0.14\,x$	-0.334***
Tenerife	Zn	O.M.	357	$\log y = 0.06 - 0.72 \log x$	0.510***

(**): Highly significant at P = 0.01; (***): Highly significant at P = 0.001.

acidity conditions (SILLANPÄÄ, 1982; ORTEGA *et al.*, 1988). A significant positive influence of O.M. on available Zn contents at 0.1% is observed. A similar behaviour has been reported by several authors (SILLANPÄÄ, 1982; PATEL & DANGARWALA, 1984; KULDEEP & GUPTA, 1986). Zn is absorbed by the O.M. of the soil presenting itself as an exchangeable ion and it can be detected in soil solution as a divalent cation and organic complex (KNEZEK & ELLIS, 1980). It is interesting to note that Zn and Cu did not show the known negative relationship with carbonate levels (UDO *et al.*, 1970; PATEL & DANGARWALA, 1984), probably due to its low concentrations detected in the soils (mean value: 0.2 g Kg⁻¹), that possibly do not markedly influence available Zn and Cu contents.

REFERENCES

ADRIANO D.C.: Trace elements in the terristrial environment. Springer-Verlag, New York Inc. 533 pp. (1986).

BARROSO A., DIAZ A., GARCIA V., ALTARES M.: Deficiencias de Zn y Mn en los cultivos de aguacates de Tenerife (Islas Canarias). *Fruits, 40*, 39 (1985).

DAVIES B.E., ROBERTS L.J.: Heavy metal in soils and radish in a mineralised limestone area of Wales, Great Britain. *Sci Total Environ. 4*, 249 (1975).

DRAGUN J., BAKER D.E.: Characterization of copper availability and corn seeding growth by a DPTA soil test. *Soil Sci. Soc. Am. J., 46*, 921 (1982).

GARCIA V., ALVAREZ C.E., FERNANDEZ M., DIAZ A.: Foliar analysis of the rose bush for cut flowers. *Agrochimica, 28*, 185 (1984).

HAYNES R.J., SWIFT R.S.: Effect of liming on the extractability of Fe, Mn, Zn and Cu from a peat medium and the growth and micronutrient uptake of highbush blueberry plants. *Plant Soil, 84*, 213 (1985).

JOKINEN R., TAHTINEN H.: Copper content of coarse mineral and peat soils and the growth in a pot experiment. *Ann. Agric. Fenniae, 26*, 227 (1987).

KISHK F.M., HASSAN M.N., GHANEM I., EL-SISSY L.: Status of copper in some calcareous and non-calcareous soils of Egypt. *Plant Soil, 39*, 487 (1973).

KNEZEK B.D., ELLIS B.G.: Essential micronutrient IV. Copper, iron, manganese and zinc. In: B.E. Davies (Ed.) *Applied Soil Trace Elements*, pp. 259-286 (1980).

KULDEEP S., GUPTA V.K.: Responses to chickpea (*Cicer arietinum*) to zinc fertilization and its critical level in soils of semiarid tropics. *Fertilizer Research, 8*, [illegible] (1986).

KULDEEP S., SHUKLA U.C., KARWASRA S.P.S.: Chemical assessment of the zinc status of some soils of the semi-arid region of India. *Fertilizer Research*, 13, 191 (1987).
LINDSAY W.L., NORVELL W.A.: Development of a DPTA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. J.*, 42, 421 (1978).
MCBRIDE M.B., BOULDING D.R.: Long-term reaction of copper (II) in a contaminated calcareous soil. *Soil Sci. Soc. Am. J.*, 48, 56 (1984).
MCLAREN R.G., CRAWFORD D.V.: Studies on soil copper. I. The fractionation of copper in soils. *J. Soil Sci.*, 24, 172 (1973).
MITCHELL R.L.: Trace elements in soils. In: F.E. Bear (ed.) *Chemistry of the soil. Reinhold Publ. New York (1964).*
ORTEGA B.C., ORTEGA M.C., DE LAS HERAS J.G.: Influencia de diferentes factores del suelo sobre su contenido en microelementos asimilables: Mn, Fe, Cu y Zn. *Ann. Edaf. Agrobiol.*, 47, 659 (1988).
PATEL G.R., DARGAWALA R.T.: Availability of iron, manganese and zinc in paddy soils of South Gujarat. *Gujarat Agric. Univ. Res. J.*, 9, 29 (1984).
REDDY M.R., RAY TUCKER M., DUNN S.: Effect of manganese on concentrations of Zn, Fe, Cu and B in different soybean genotypes. *Plant Soil*, 97, 57 (1987).
RYAN P., LEE J., PEEBLES T.F.: Trace element problems in relation to soil units in Europa. *FAO*, Rome. World Soil Resources Report 31 (1967).
SAKAL R., SINGH A.P., SINGH B.P., SINHA R.B.: Assessment of some extractants for available zinc in relation to responses of rice applied zinc in Sub-Himalayan hills and forest soils. *Plant Soil*, 79, 417 (1984).
SAKAL R., SINGH A.P., SINGH S.P.: Distribution of available zinc, copper, iron and manganese in old alluvial soils as related to certain soil characteristics. *J. Ind. Soc. Soil. Sci*, 36, 59 (1988).
SELVARAJAH N., PAVANASASIVAM V., NANDASENA K.A.: Evaluation of extractants for Zn and Cu in paddy soils. *Plant Soil*, 68, 309 (1982).
SHUMAN L.M.: Zinc, manganese and copper in soil fractions. *Soil Sci.* 127, 10 (1979).
SILLANPÄÄ M.: Micronutrients and the nutrient status of soils: a global study. *FAO Soils Bull.*, 444 p. (1982).
SINGH J.P., KARAMANOS R.E., STEWART J.W.B.: The zinc fertility of Saskatchewan soils. *Can. J. Soil Sci.*, 67, 103 (1987).
UDO E.T., BOHN H.L., TUCKERT C.: Zinc adsorption by calcerous soils. *Soil Sci. Soc. Am. Proc.*, 34, 405 (1970).

SUMMARY. — A study about available Cu and Zn contents and the influence of some soil properties on the availability of these micronutrients for crops has been carried out in most of the agricultural zones of the Island of Tenerife (Canary Islands).

The mean Cu content was 4.75 mg L^{-1} (AAAc-EDTA extractable Cu). 22.13% of soils presented values considered as marginals (1-2 mg L^{-1} Cu), and 6% contained levels below the value estimated as critical (1 mg L^{-1} Cu). Only 3.64% of analyzed soils showed high Cu values (>17 mg L^{-1} Cu). With respect to available Zn, the mean content was 4.80 mg L^{-1} (DTPA extractable Zn), a value sensibly higher than that reported by an international study carried out by FAO Unesco. 6.4% of the soils were within the Zn deficient range (<0.5 mg L^{-1} Zn), while 16.80% were potentially deficient in this element (0.5-1.0 mg L^{-1} Zn). Levels considered as excessive (>10 mg L^{-1}) appeared in 12.35% of the soils. When the study was carried out by zones (north and south), the highest Cu and Zn contents were present in the northern zone (mean values: 6.69 mg L^{-1} Cu and 7.08 mg L^{-1} Zn). Various correlations between some soil parameters and the studied micronutrients were observed.

Pervenuto in redazione il 30 dicembre 1992