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Influence of pH and Industrial Activity on Total Zinc Concentrations in Agricultural Soils, Sewage Sludges, and Beach Sands: Relationship with Plant (*Saccharum officinarum*) Availability

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Zinc is an essential micronutrient for the human organism, because it activates a long number of enzymes (King and Keen 1994). Recently, in different epidemiological studies, it has been pointed out that this mineral plays an important function in the genesis and progressin of several diseases related with the oxidative stress (Martin-Lagos et al. 1997; Ames 1998).

The existence of zinc in soils is related to several factors, including geographic location, type of rock, oxidation-reduction potential, pH, nature of drainage waters, cation exchange capacity, clay content, and type of plant grown (Fageria and Zimmermann 1998; Herawati et al. 1998; Amrani et al. 1999; Ramos et al. 1999; Blasser et al. 2000). This element is absorbed by plants and, in certain circumstances, it could become a risk for the environment and health. The bioavailability of this element depends mainly of the factors mentioned above which are related to the mobility and extractibility of zinc. Due to the complexity of the soil plant system and despite the enormous amount of existing information, the search for better methods to determine the uptake and bioavailability of zinc to plants continues to be very important (Herawati et al. 1998). It is necessary to point out the pH of these soils. In relation to soil pH, some authors observed that acid pH values (pH $<$ 5.5; Romkens and Salomons 1998) facilitated an enhancement in zinc solution concentrations. This fact would allow a higher uptake of this element by different species of plants (upland rice, wheat, corn, common bean and cowpea; Fageria and Zimmermann 1998).

This investigation was initiated to assess the total zinc content in agricultural soils, sludges and beach sands from the Mediterranean coastal area of Motril (SE Spain). pH values of samples were also measured in order to evaluate their influence on zinc content. This way we could have better knowledge of some factors such as total zinc content in agricultural soils and corresponding pH values, and their influence both in plant uptake and bioavailability and, as a consequence, zinc levels in plants grown on in this zone, whose concentrations were formerly determined (Terres et al. 2001). Besides we also considered it interesting to study the influence of human and industrial activities on total zinc levels and pH values in agricultural soils located in the surrounding area, as our research group previously done for other metals in the referred area (Navarro et al. 1993). Therefore, the way as they could affect the

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bioavailability and total concentrations of this element in sugar cane plans (the most important crop of the zone) grown on in these soils, were also considered.

MATERIALS AND METHODS

Agricultural soil, sewage sludge and sand samples considered in the present study (n= 48) were directly obtained of Motril (a Mediterranean coastal city of SE Spain). Agricultural soils were taken according to the random model suggested by Bridges and Davidson (1982) from the arable layer at 10-15 cm depth in 32 different sampling sites. Sewage sludges were collected in four different places in a gully (gully of Brujas) that crosses the study zone at which sewages of the zone were collected. Beach sand samples were directly sampled in 12 locations from beaches existing in the zone. All samples were laid out to dry in thin layers at room temperature in the laboratory for 14 days. Then they were passed through a 340 μm sieve, homogenized and finally stored in polyethylene containers until the analysis was carried out. The homogenized sample (agricultural soil, sediment or sand) (300 mg) was placed in a 100-ml volumetric flask, and digested by addition of 5.0 ml of concentrated HNO_3 and heating at 115°C for 45 minutes in a sand beaker. Another 5.0 ml of 4:1 mixture of HNO_3 and $HClO_4$ was added and heating continued at 115°C for an additional 75 minutes. Then, the temperature was rised to 150°C and sample was left there for 30 additional min until the sample was mineralized. The digest was then cooled and the resulting solution diluted to 25 ml with double-distilled water. A second dilution was prepared by taking different aliquots of the previous dissolution and diluting with double-distilled water. Zinc determination was carried out by direct aspiration into the flame atomic absorption spectrophotometer (Perkin-Elmer model 1110-B) fitted with a zinc hollow cathode lamp.

In order to determine pH , a previously optimized method by our research group was employed (Diaz et al. 1996). The measurement was performed with a pH meter. A Beckman buffer (Beckman instruments Inc.), with a pH interval from 4.00 to 9.18 was used.

Sugar cane (*Saccharum officinarum*) samples were obtained directly in the field, from the agricultural soils located in the study zone. This plant specie was selected from all crops grown on there because it is the predominant one, and a considerable number of samples were available (n= 16). These samples were transported to the laboratory, where they were dried in an oven at 60°C for 48 h. Finally, samples were homogenized and kept at -18°C until analyzed. For evaluating zinc concentration in sugar cane the procedure employed was indicated elsewere (Terrés et al. 2001).

Mean recovery for the several added samples considered was 100.30 ± 4.39%. The mean zinc concentration determined in the standard reference materials (National Institute of Standards and Technology, NIST SRM 2704 Buffalo river sediment, Gaithersburg, MD: 427.7 ± 5.8 μg/g and NIST SRM citrus leaves: 27.4 ± 3.1 μg/g) were not significantlly different than certified levels (438.0 ± 12.0 μg/g and 29.0 ± 2.0 μg/g, respectively). Relative standard deviations (RSD) for zinc in the samples analyzed in this study were better than 3.30%.

RESULTS AND DISCUSSION

Zinc concentrations in the different types of samples analysed are shown in Table 1. Mean total zinc concentrations determined in the three groups of samples considered (agricultural soils, sewage sludges and beach sands) were significantly different among them ($P < 0.001$); particularly, zinc levels measured in sewage sludges and agricultural soils were statistically higher than those found in sands. This finding could be related with the different type of sample considered as previously was underlined by other researchers (Giordano et al. 1999). In this sense, agricultural soils belong to the group of calcareous fluvisols, a group (fluvisols) with an elevated content in organic matter, which is mainly related with its high capacity for retaining several minerals and specifically zinc. This finding indicates the influence of the geological characteristics of soil in the total content in this element. On the contrary beach sands, included in the group of miscellany beach have a low content of organic matter with no significant clay fraction; therefore, polluting compounds such as zinc are not strongly bound within the structure of clay mineral, where complex adsorption/absorption phenomena may occur, but instead adhere to the surface of beach sands (Giordano et al. 1999).

Table 1. Zinc concentrations in agricultural soils, sediments and beach sands

Sample	Mean[a] ± SD (µg/g)	Range (µg/g)	CV[b] (%)
Soils	121.3 ± 40.1	70.5-242.5	33.1
Sewage sludges	145.8 ± 32.2	110.1-187.5	22.1
Beach sands	81.0 ± 22.7	51.9-136.2	28.0

[a]$P < 0.001$
[b]Coefficient of variation

In general, zinc levels measured by us in agricultural soils from SE Spain are sligthly higher than those pointed by others arround the world (Meneses et al. 1999; Blasser et al. 2000). The posssible origin of the anthropogenic heavy metal input in the study area would be either the industrially produced fly ash deposited upon agricultural soils in the surroundings and the sedimentation processes during the flood periods of the Guadalfeo river in recent years, similary to that indicated by Schulze et al. (1997) in an industrial area of Germany.

Zinc content in soils could be influenced by factors such as soil pH (Romkens and Salomons 1998; Fageria and Zimmermann 1998; Amrani et al. 1999) or the nature of waters which drain through them. Shallari et al. (1998) determined pH values (7.56 ± 0.68) in soils from industrial sites in Albania, very similar to those measured in the present study (7.55 ± 0.27; Table 2). These authors similarly observed a sligthly alkaline character of the soils studied. Additionally we checked that pH values in the beach sands were significantly higher than those found in agricultural soils and sewage sludges (Table 2). A regression analysis between the total zinc contents and corresponding pH values in agricultural soils was also performed, establishing that the zinc concentrations are inversively related to pH values [$P < 0.001$, (pH = 8.610 – 0.007 [Zn, ppm], r = -0.473)]. This finding reinforces the fact that the industrial contamination is a significant a source of acidification in agricultural soils and of elevated zinc concentrations.

Table 2. Values of pH determined in samples analysed in the present study

Sample	Mean pH ± SD	Range	CV (%)
Agricultural soils	7.55 ± 0.27	7.03-7.98	3.58
Sewage sludges	7.70 ± 0.33	7.38-8.14	4.29
Beach sands	8.68 ± 0.41[a]	8.22-9.63	4.72

[a]$P < 0.001$

The agricultural soils were divided into two groups depending of their sampling zone: industialized zone (n= 12) including soil samples obtained from sampling stations located around industries existing in the area (power station, paper mill, petrol tanks, industrial complex) and the port of Motril and Motril city; and the non-industrialized zone (n= 20). We found that zinc levels measured in agricultural soil samples form the industrialized zone were statistically higher ($P < 0.01$) than those found in samples from the non-industrialized zone (Table 3). This finding showed the direct influence of the industrial activity on zinc concentrations in agricultural soils of the surrounding area. Similary, Shallari et al. (1998) observed that zinc concentrations in soils from Albania were less than 111 μg/g except for the site of Rubik (an industrial zone) where it reached 2,495 μg/g.

Table 3. Influence of the industrial activity on pH and total zinc concentrations of agricultural soils

Location	Mean pH value ± SD	Mean Zn ± SD
Non-industrialized zone	7.63 ± 0.26[a]	99.7 ± 15.4[b]
Industrialized zone	7.42± 0.23[a]	157.3 ± 46.1[b]

[a]$P < 0.05$
[b]$P < 0.01$

In addition to the total zinc concentrations, pH was also mesured in these agricultural soils from the industrial zone. In was found that the pH values of agricultural soils located in the non-industrialized area were significantly higher (Table 3). This finding shows a slow and progressive acidification of soils included in the industrialized area.

In general, zinc concentrations measured in sugar cane samples varied considerably (mean zinc concentration= 5.48 ± 5.24 μg/g, fresh weight). This variation could be related to the different agricultural practices followed by farmers in relation to the amount and type of fertilizers used or application of seawage sludges to the soils, these are known to influence total zinc content and availability by plants grown up there (Otabbong et al. 1997; Fageria and Zimmermann 1998). Additionally, overliming and excessive application of superphosphate to agricultural soils caused a zinc deficiency and so reduced zinc uptake by fodder plants (Ray et al. 1997). Therefore, although the industrial activity enhances statistically total zinc concentrations in agricultural soils located in the surroundings, no similar effect was observed for the main crop (sugar cane) grown there possibly due to the short grant period of this plant. Additionally, the total zinc present in these soils, taking into consideration its industrial origin may not have been in an available form for sugar cane plants as others have previously pointed out (Knight et al. 1997; Shallari et al. 1998).

In the present study no significant ($P < 0.265$) correlation was found between total zinc content in the agricultural soils and metal levels in sugar cane samples grown on them. Therefore the zinc uptake by plant was independent of total zinc concentrations present in agricultural soils such as others pointed out for other crops (Knight et al. 1997; Shallari et al. 1998). Similarly, Peijnenburg el al. (2000) pointed ont for lettuce that plant tissue concentration of zinc appeared to be regulated at more or less fixed levels independiently of soils.

Amrani et al. (1999) observed that mobility and plant availability of zinc increased significantly when the soil pH decreased. Nevertheless, in our study no significant correlation betwen the soil pH and zinc concentrations in sugar cane was found ($P > 0.05$), despite that a negative correlation coefficient was also obtained between these variables ($r = -0.145$). Additionally, the pH of soils is an important factor which influences different fractions into which the zinc present in soils can be distributed (speciation), finally influencing the solubility and bioavailability (Hooda et al. 1997). In this sense, future research is needed in this area to exactly know how the soil pH influences the distribution of this element in the different physico-chemical forms at which it appears, and therefore their bioavailability by sugar cane plants.

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