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Zinc Speciation in Soils and Relation with Its Concentration in Fruits

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An attempt was made to identify the zinc species in the soil that is most responsible for the plant-available Zn. The Zn concentrations of the fruit and soil samples were determined by using flame atomic absorption spectrometry (FAAS). The soil samples related to these fruits were digested and extracted by using different digestion and extraction reagents. The relation between the fruit-Zn and soil-extractable-Zn concentrations was examined in order to explain the Zn uptake of fruit from soil. Probable chemical forms of Zn in soil were evaluated.

Key Words: Speciation, Zinc, Soil, Fruit, Flame atomic absorption spectrometry.

INTRODUCTION

The levels of trace elements in food and agricultural samples have been shown to influence human and plant metabolism[1]. Therefore, accurate measurements of total metal contents in soils are required to assess their potential risks. However, only soluble, exchangeable and chelated metal species in the soil are the mobile and mobilizable fractions and hence more available for plants[2]. Chemical forms and the different shapes of binding of heavy metals in soil are very important for evaluation of their mobility, bioavailability and ecotoxicity.

In one broad definition of speciation[3], (i) the species are defined by their function, as, for example, 'plant available forms', 'exchangeable cations' or 'labile species'; (ii) operationally defined speciation, the use of oxalic acid to extract elements associated with the "moderately reducible" components of soil; and (iii) the specific chemical compounds or oxidation states of an element. Although their precise chemical forms may be indeterminate, the function is quite precise.

The general approach for the soil speciation studies has been to separate the soil into different chemical reagents or solvent fractions and by analyzing each fraction, to determine the amount of element combined or associated with each soil fraction or phase[4]. A number of extractants, including ethylenediaminetetraacetic acid (EDTA), diethylenetriamine pentaacetic acid (DTPA), acetic acid, ammonium acetate, calcium chloride and NH_2OH, HCl have been tested to identify metal species as exchangeable, carbonate-bound, Fe and Mn oxide-bound, organically bound and to estimate the plant available trace metals[4–9].

Many surveys of nutrient intake in industrialized countries have found that low dietary Zn poses a potential nutritional problem[10, 11]. Therefore, the accurate Zn determination in food and soil is very important. In this study, Zn concentrations in the fruit and soil samples were determined by flame atomic absorption spectrometry (FAAS). The soil samples were dissolved by using the chemical reagents such as the mixture of HNO_3/H_2O_2, oxalic acid, Na_2EDTA, acetic acid and citric acid. So, the relation between the fruit zinc contents and the Zn contents of soil extracts was investigated. In addition, the possible chemical forms of Zn in soil were also evaluated.

EXPERIMENTAL

An ATI UNICAM 929 Model flame atomic absorption spectrophotometer (AAS) equipped with ATI UNICAM hollow cathode lamp was used for the Zn determination. The optimum conditions for FAAS are given in Table-1.

TABLE-1
OPERATING PARAMETERS FOR Zn DETERMINATION BY FAAS

Parameter	
Wavelength (nm)	213.9
HCl current (mA)	9.5
Acetylene flow rate (L/min)	0.5
Air flow rate (L/min)	4.0
Slit width (nm)	0.5

Unless stated otherwise, all chemicals used were of analytical-reagent grade. Throughout all experimental work, doubly distilled water was used. All glass apparatus have been kept permanently full of 1 M nitric acid when not in use. In the digestion and extraction procedures, concentrated nitric acid (65%, Merck), hydrogen peroxide (35%, Merck), oxalic acid (Merck), citric acid (Merck), ethylenediaminetetraacetic acid disodium salt (Na_2EDTA, Merck) and acetic acid (96%, Merck) were used. Stock solution of Zn (1000 mg L^{-1}) was prepared by dissolving $Zn(NO_3)_2$ in 1.0 mol L^{-1} nitric acid.

Preparation of Samples

Seven sites were selected from the major agricultural areas in Elazig, Turkey. The soil samples were taken from these different locations, with the sampling at a depth of about 10 cm below the surface. The fruit samples were also gathered at each of these locations, at distances not more than 100 cm from the location of the soil sample. Morello cherry, cherry, mulberry, strawberry, apple, grape and pear were chosen for the present study as they are commonly consumed in Turkey. The fruits chosen were washed separately and thoroughly with running tap water and further rinsed twice with distilled water and then allowed to drain on a filter paper. Then, both fruit and soil samples were dried at the temperature of 85°C.

Dry Ashing of Fruits

Approximately 0.25–0.5 g samples of oven dried materials were placed into evaporating dishes and ashed at 480°C in an ashing furnace for 4 h. This process was repeated if necessary until a white ash was obtained. The mixtures of nitric acid-hydrogen peroxide (2 + 1) (for 0.5 g of dried matter, 1.0 mL of mixture was used) were added to the ashed samples and dried with occasional stirring on a hot plate with low heat. Then, the residue was dissolved with 2.0 mL of 1.5 mol L^{-1} nitric acid and if necessary, diluted to suitable volume. The clear digests were analysed for Zn by FAAS. A blank digest was carried out in the same way.

Digestion and Extraction of Soil

Soil pH was measured on soil suspension using soil : distilled water at 1 : 5 (w/v). The mixture of nitric acid-hydrogen peroxide (2 + 1) of 1.5 mL was added to the soil samples of 0.25 g and dried with occasional shaking on a hot plate. After cooling, 2 mL of 1.5 mol L^{-1} nitric acid was added to the remainder and centrifuged. After necessary dilution, the clear digests were analyzed by using FAAS. A blank digest was carried out in the same way.

The soil extracts were obtained by shaking separately, 0.25 g of soil samples with 1.0 mL of 0.05 mol L^{-1} Na_2EDTA, 1.0 mol L^{-1} oxalic acid and concentrated acetic acid. The mixture was evaporated with occasional shaking on a hot plate. Then, 2 mL of 1.5 mol L^{-1} nitric acid was added and centrifuged (hot extraction). In addition, 1.0 mL of 0.05 mol L^{-1} Na_2EDTA, 1.0 mol L^{-1} oxalic acid, concentrated acetic acid and 1.0 mol L^{-1} citric acid were also, one by one, added to 0.25 g of soil samples at room temperature and centrifuged after stirring by vortex for 5 min (cold extraction). The clear digests were analyzed for Zn by using FAAS. The blank digests were carried out in the same way.

RESULTS AND DISCUSSION

The amounts of Zn added to the fruit and soil samples were recovered to check accuracy of the analyses performed (Table-2). It was found that at least 90% of the Zn added to the fruit and soil samples was recovered. The effect of contamination was eliminated by subtracting values obtained for blanks. Adsorption loss can be excluded as the procedure was followed in exactly the same way, using the same glassware and the same reagents that were used throughout. Therefore, the effect of contamination or adsorption may be reliably overlooked.

TABLE-2
RECOVERIES OF Zn FROM FRUIT AND SOIL BY USING HNO_3/H_2O_2 MIXTURE
(DRIED WEIGHT BASIS)

The Results Are Mean Values ± Standard deviation; n = 3

Sample	Zn levels in fruit ($mg\ kg^{-1}$)			Zn levels in soil ($mg\ kg^{-1}$)		
	Added	Found	Recovery (%)	Added	Found	Recovery (%)
Mulberry 1	0.0	6.0 ± 0.4		0.0	32 ± 2.3	
Mulberry 1	2.0	7.9 ± 0.5	95	10.0	41 ± 2.5	90
Morello cherry 4	0.0	2.1 ± 0.1		0.0	49 ± 2.0	
Morello cherry 4	1.0	3.0 ± 0.2	90	10.0	59 ± 2.4	100
Strawberry 1	0.0	7.0 ± 0.5		0.0	50 ± 2.3	
Strawberry 1	2.0	8.9 ± 0.6	95	10.0	59 ± 2.6	90

Calibration curve was obtained by using the Zn solutions of 0.2, 0.4, 0.6, 0.8, 1.0, 1,5 and 1.5 $mg\ L^{-1}$. The graph obtained was rectilinear in the concentration range described above and the equation of the curve was as follows:

$$Y = 178.2X + 0.75, \quad R^2 = 0.$$

Zinc Contents of Fruits and Soils

Table-3 gives the Zn concentrations of fruit by using dry ashing and the soil samples by using different extraction reagents. The mean total zinc concentrations for all studied fruits were in the range of 1.5–11.0 $mg\ kg^{-1}$ which is the lowest level for morello cherry and the highest level for mulberry. Soil EDTA-extractable Zn concentrations are commonly used to indicate the likely availability of metals in plant uptake[12]. Our results also show that these evaluations for Zn are valid for all studied fruits except strawberry and apple. Other observations concerning Table-3 are as follows:

From Fig. 1, it is seen that the Zn concentrations in morello cherry were dependent on only Zn concentrations in the hot EDTA extracts of soil ($R^2 = 0.83$). In addition, there is a linear tendency between Zn concentrations of the morello cherry and soil-hot concentrated acetic acid extracts ($R^2 = 0.66$).

The Zn concentrations in mulberry were dependent on Zn concentrations of the HNO_3/H_2O_2 digests ($R^2 = 0.98$), cold oxalic acid extracts ($R^2 = 0.84$) and cold ($R^2 = 0.86$) and hot ($R^2 = 0.98$) EDTA extracts of soil (Fig. 2). In addition, there a linear tendency between Zn concentrations of the mulberry and hot oxalic acid and hot concentrated acetic acid extracts of soil.

TABLE-3

RESULTS OF Zn CONTENTS OF FRUITS AND SOILS (DRIED WEIGHT BASIS)

The results are mean values ± standard deviation n = 3, pH ± 0.2

Sample of fruit and soil on grown**	Zn in fruit (mg/kg)	Zn in soil, mg/kg							
		HNO_3/H_2O_2	Oxal.* 1 M	Oxal.* 1 M	EDTA* 0.05 M	EDTA 0.05 M	Acetic* conc.	Citric* 1 M	Soil pH
Morello cherry 1	1.6 ± 0.1	31 ± 3	15 ± 1	8.6 ± 0.7	14 ± 0.7	4 ± 0.2	4 ± 0.3	4 ± 0.2	6.4
Morello cherry 2	2.2 ± 0.2	49 ± 3	34 ± 3	9.0 ± 0.7	16 ± 0.9	4.5 ± 0.3	10 ± 0.7	7 ± 0.4	6.3
Morello cherry 3	1.5 ± 0.1	55 ± 3	25 ± 2	12.0 ± 0.9	14 ± 0.8	7.5 ± 0.5	7.5 ± 0.5	8 ± 0.4	6.4
Morello cherry 4	2.1 ± 0.1	49 ± 2	38 ± 3	10.0 ± 0.7	15 ± 0.9	8 ± 0.6	9 ± 0.6	4 ± 0.2	6.2
Morello cherry 5	2.6 ± 0.2	52 ± 2	30 ± 2	15 ± 1.0	20 ± 1.2	9 ± 0.6	10.5 ± 0.7	9 ± 0.4	6.1
Cherry 6	6 ± 0.4	63 ± 3	30 ± 2	8.0 ± 0.6	15 ± 1.0	5 ± 0.4	6 ± 0.4	3 ± 0.2	6.6
Cherry 4	5 ± 0.3	45 ± 2	36 ± 3	9 ± 0.7	12 ± 0.8	4 ± 0.3	5 ± 0.3	4 ± 0.2	6.3
Mulberry 1	6 ± 0.4	32 ± 2	17 ± 1	9 ± 0.6	16 ± 0.9	4.3 ± 0.3	4.4 ± 0.3	4 ± 0.2	6.4
Mulberry 3	8.8 ± 0.5	43 ± 2	20 ± 2	10.5 ± 0.7	22 ± 1.5	5.5 ± 0.4	8 ± 0.5	9 ± 0.5	6.4
Mulberry 4	10 ± 0.5	45 ± 2	36 ± 3	11 ± 0.9	27 ± 1.8	8 ± 0.5	10 ± 0.6	6 ± 0.3	6.4
Mulberry 5	11 ± 0.5	48 ± 2	26 ± 1	13 ± 0.8	30 ± 1.9	10 ± 0.7	7 ± 0.5	6 ± 0.3	6.5
Strawberry 1	7 ± 0.5	50 ± 2	35 ± 3	14 ± 0.9	36 ± 2.5	3.5 ± 0.2	8 ± 0.5	5 ± 0.2	6.5
Strawberry 6	4 ± 0.2	70 ± 3	46 ± 3	10 ± 0.7	39 ± 2.7	11 ± 0.9	6 ± 0.4	2 ± 0.1	6.6
Apple 4	3.0 ± 0.2	40 ± 2	30 ± 2	11 ± 0.8	30 ± 1.9	12 ± 0.9	13 ± 0.8	5 ± 0.2	6.3
Apple 7	2.5 ± 0.1	100 ± 4	87 ± 5	50 ± 3.7	58 ± 3.1	11 ± 0.8	4.0 ± 0.5	29 ± 3	6.4
Grape 5	2.5 ± 0.1	47 ± 3	27 ± 2	13 ± 0.9	25 ± 1.4	4.5 ± 0.3	7 ± 0.5	7 ± 0.3	6.4
Grape 7	3.0 ± 0.2	45 ± 2	38 ± 3	20 ± 1.2	23 ± 1.6	4 ± 0.3	4.5 ± 2.3	3 ± 0.2	6.7
Pear 7	6.0 ± 0.4	39 ± 2	30 ± 2	18 ± 1.1	21 ± 1.1	4.5 ± 0.3	8 ± 0.5	3 ± 0.2	6.5

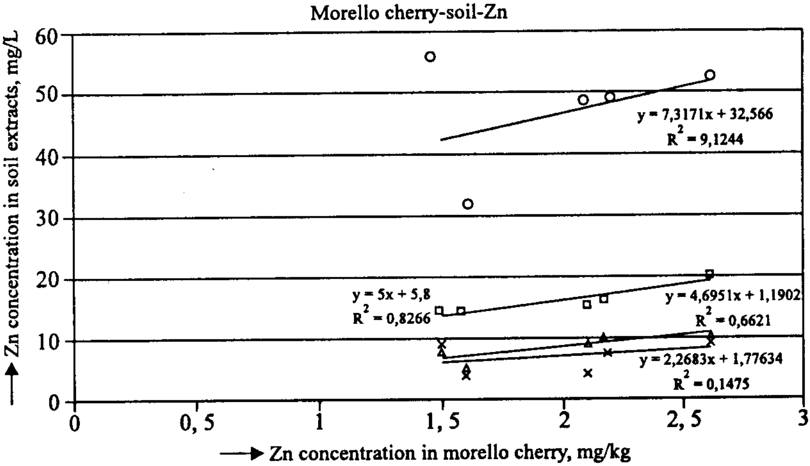

Fig. 1. The relationship between the Zn concentration of morello cherry and soil extracts. ♦: HNO_3/H_2O_2 digest, □ : hot EDTA extract, Δ : hot acetic acid, × : cold citric acid extract. It can be seen that the relationships between the morello cherry-Zn and the HNO_3/H_2O_2 digest of soil-Zn ($R^2 = 0.12$) and cold citric acid extract-Zn ($R^2 = 0.15$) were not good.

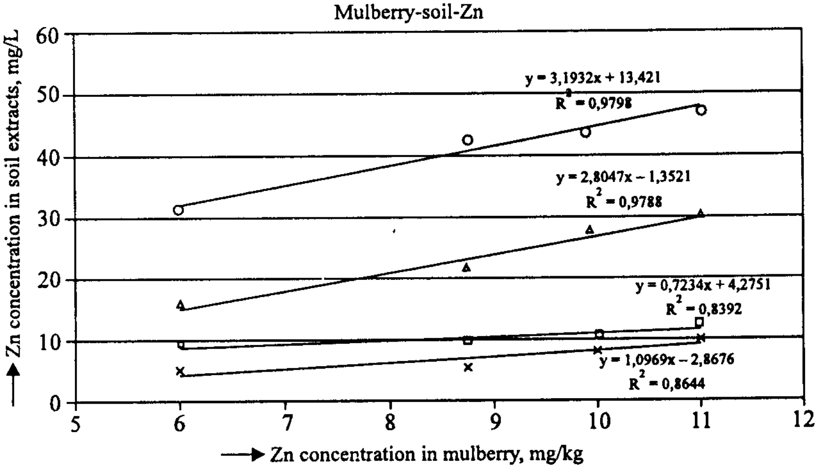

Fig. 2. The relationship between the Zn concentration of mulberry and soil extracts. ♦: HNO_3/H_2O_2 digest, Δ: hot EDTA extract, □ : cold oxalic acid extract, × :cold EDTA extract.

The Zn content of the cherry was dependent on the Zn concentrations of all soil extracts except hot and cold oxalic acid and cold citric acid.

The Zn content of the strawberry was dependent on the Zn concentrations of cold oxalic acid, hot concentrated acetic acid and cold citric acid extracts. The Zn content of the apple was dependent on only the Zn concentrations of cold EDTA extracts. The Zn content of the grape was dependent on the Zn concentrations of hot and cold oxalic acid and hot EDTA extracts.

Zn concentrations in the hot oxalic acid extracts of soil were close to the Zn concentrations in the HNO_3/H_2O_2 digestion of soil for all samples of the location

7. These results can be explained as Zn species in these samples are the reducible forms which adsorbed or occluded on minerals such as Mn and Fe oxide or hydroxides. So, oxalic acid plays the role of both acid and complexing agent, which form complexes with both Fe and Mn and thus, Zn releases from minerals (Overall complex formation constant of Fe^{3+}-oxalate = 6.3×10^{45}).

Because Zn concentrations of hot EDTA extracts of all soils taken from locations 1, 5 and 7 were found higher 50% than their HNO_3/H_2O_2 digests, it is said that Zn in these soil was organically bound or carbonate species.

More additional interpretation can be derived from the results in Table-3.

The comparative data by using various extraction reagents were found useful to identify zinc fractions in soil phases and to estimate Zn uptake of fruits from soils. The results obtained show that Zn contents of fruits are dependent on Zn concentrations of the different soil extracts as related to fruit types.

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