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Registry No. Tryptophan, 73-22-3.

Investigation of Contents of Some Elements in Soil and Apricots by Atomic Absorption Spectrometry

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In this work, the relationship between the concentrations of six metals (Cd, Zn, Mn, Pd, Cu, Fe) in acetic acid extracts (2.5%) of soil and their respective concentrations in apricots grown in the same soil has been investigated. Soil extracts and apricots have been analyzed by atomic absorption spectrometry with injection or loop sample introduction. Metals were preconcentrated with activated carbon by using ammonium pyrrolidinedithiocarbamate (APDC) as a complexing agent at pH 6.

It is well-known that sodium, potassium, calcium, magnesium, and iron are essential for human life and are supplied by feeding. Improvements in analytical techniques show that copper, chromium, cobalt, manganese, selenium, molybdenum, and zinc are also essential for human life and take part in enzyme structure. It is also well-known that mercury, cadmium, lead, and talium, which are toxic to human life, are also taken through feeding. Many countries accept threshold levels for such elements.

For the analysis of food samples, the main problem is preparation of samples for measurement. Food samples can be decomposed either by wet digestion or by dry-ashing methods, depending on the elements being analyzed. For volatile elements like Cd, Zn, Tl, etc., the wet digestion method is preferred (Stoeppler and Brandt, 1979; Verloo, 1982; Hoenig and Borger, 1983; Demir et al., 1985).

A wide range of extractants have been used in soil analysis to suit many purposes. For agriculture, the total trace-element content of a soil has become less important than the extractable contents. The selective chemical extraction of soil components with various extractants has been outlined (Pickering, 1981).

In soil testing, it is important to select a solvent that can extract many elements simultaneously. Some trace elements in the extractants may be in lower concentrations; thus, many elements cannot be directly determined. In these cases, preconcentration steps and/or different sampling techniques have been applied (Pederson et al., 1980; Roberts et al., 1976; Berndt and Messerschmidt, 1982).

When soil is polluted with toxic elements, there is no possibility of elimination but such a situation may be improved by controlling the soil pH by liming, thus leading to irreversible fixation.

EXPERIMENTAL SECTION

Reagents. All chemicals were analytical reagent grade unless otherwise stated. Deionized water was used throughout. Stock solutions (1000 mg/L) were used to prepare standard solutions of metals by diluting with 2 M HNO_3. Ammonium pyrrolidinedithiocarbamate solution and activated carbon suspension were prepared as stated elsewhere (Gücer and Demir, 1987). Buffer (pH 6) was prepared by mixing 5 mL of glacial acetic acid with 117 g of ammonium acetate and diluting the resultant mixture to exactly 1 L.

Apparatus. A Perkin-Elmer Model 400 atomic absorption spectrometer (without background corrector) assembled with a 5-cm air/acetylene burner head was used for atomic absorption measurements. Single-element hollow cathode lamps (S/C Juniper) were used as a radiation source. Wavelengths were selected from the instrumentation manual, and a 2.0-nm slit width was used. Acetylene and air flow rates of 2.6 and 9.6 L/min, respectively, were used throughout the measurements. Analyses of Fe, Cu, and Mn have been done by a conventional flame atomic absorption spectrophotometric method in which 100-μL sample solutions are aspirated directly into the flame. A loop device (Berndt and Messerschmidt, 1979, 1982) was used as a sample introducer (10 μL) for measurements of Zn, Cd, and Pb. When the loop device was used, a silica tube (6-mm i.d. and 47-mm length) was used as a collector and positioned ca. 5 cm above the burner head. A 10-μL sample solution was injected on the platinum loop and dried by passing 3-A ac current through the loop (ca. 20 s). Then, the loop was transported under the window of collection tube through which the light was passing, and shock heating was applied for 0.2 s elec-

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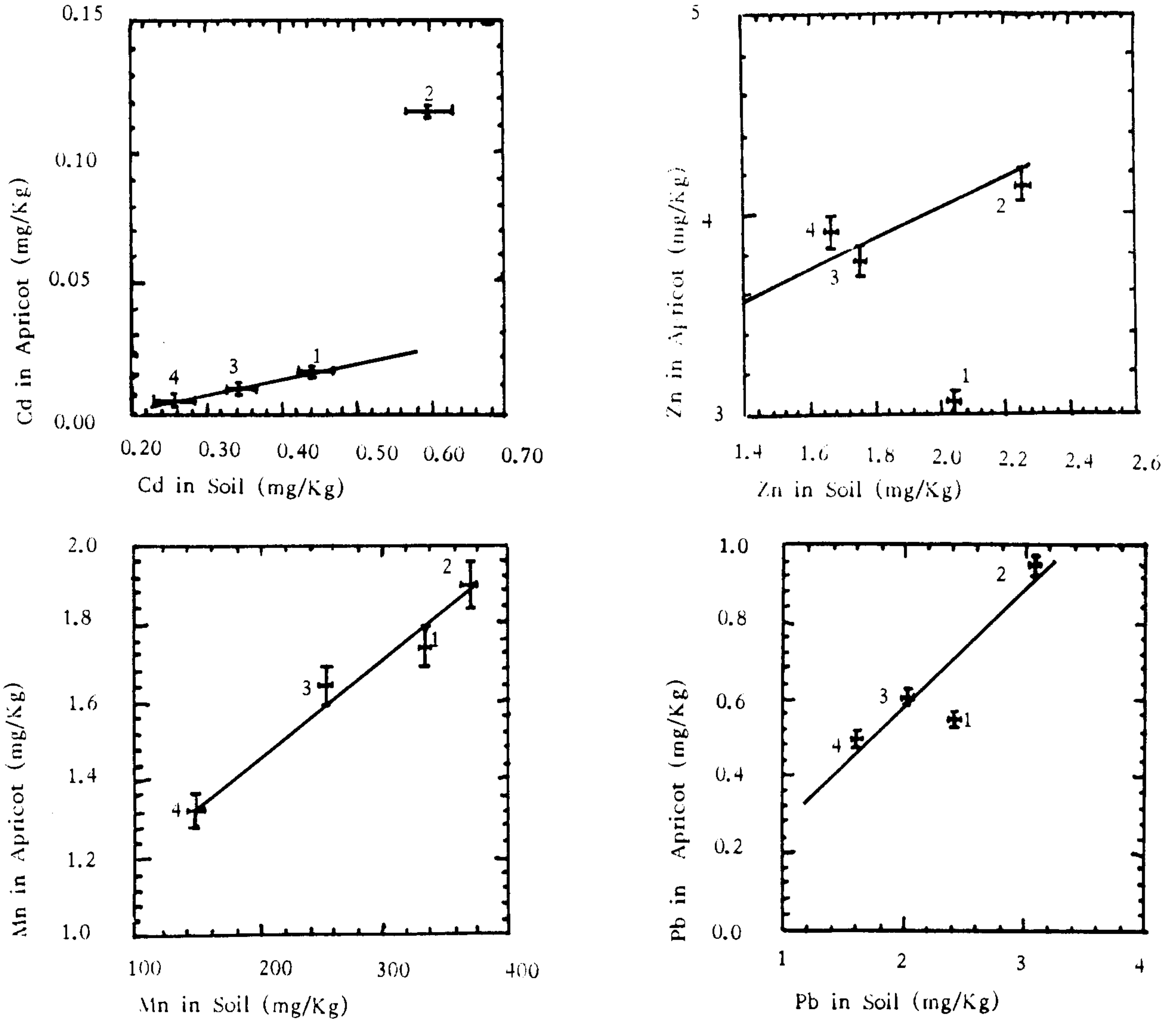

Figure 1. Soil-apricot relations of Cd, Zn, Mn, and Pb (numbers indicate regions of soil and apricot samples taken).

trically. Peak height measurements were used to calculate absorbance values.

Procedure. Apricots were collected from four different regions of Malatya, Turkey, and seven samples were taken from each region. In order to prevent microbiological activity, samples were sulfured by holding them in SO_2 vapor and they were dried in air. After being dehydrated at 110 °C in an oven for 48 h (15-20% with respect to air-drying), 5 g of pulverized sample was decomposed with mixtures of concentrated nitric acid, concentrated sulfuric acid, and 30% hydrogen peroxide (10/5/1 ratio) (Demir et al., 1985), evaporated to dryness, heated 30 min with 150 mL of deionized water, and filtered through blue-band filter paper. Ammonia was added to the filtrate to pH 6, then 20 mL of buffer solution (pH 6), 20 mL of APDC solution, and 4 mL of activated carbon suspension were added, and the resultant mixture was shaken for 1 h with a shaker (Hitofrig, 160 rpm). The mixture was filtered through blue-band filter paper, and the residue was dried in an oven for 1 h at 110 °C. After addition of 2 mL of concentrated nitric acid to the residue and evaporation to dryness, the residue was shaken with 5 mL of 2 M nitric acid. The solution was separated by centrifugation (5000 rpm) and used for AAS measurements with either direct injection into the flame (100 μL) or loop introduction into the heated silica tube (10 μL).

Soil acetic acid extracts were prepared and analyzed as stated elsewhere (Gücer and Demir, 1987). Calibration graphs used in soil analysis and apricot analysis were drawn from the data in which the same analytical procedures had been applied as with the samples analyzed.

RESULTS AND DISCUSSION

For the analysis of soil extracts by AAS, different sample introduction techniques have been applied depending on the amounts in extracts. For example, for copper, iron, and manganese, the extraction solution is directly aspirated to the flame whereas loop sampling with a collection tube has been applied for zinc. On the other hand, loop with collection tube, following a preconcentration step with activated carbon, has been applied for cadmium and lead systems. In this way, the detection limit has been increased about 20 times by applying a preconcentration step with activated carbon. An additional, about 10 times, increase in detection limit has been reached by using a collection tube followed by preconcentration and loop sampling. Relative standard deviations of absorption measurements are given in Table I.

It is well-known that plants take up not only essential elements necessary for their normal development but also other ones if these are present in growth medium in a sufficiently mobile form. Accumulation of nonessential elements influences plant production quantitatively as well as qualitatively.

The relationship between the content of elements in soil, their concentrations in plant tissues, and growth is a complex phenomena. In most cases, mineral contaminants accumulate in the upper layer of the soil where

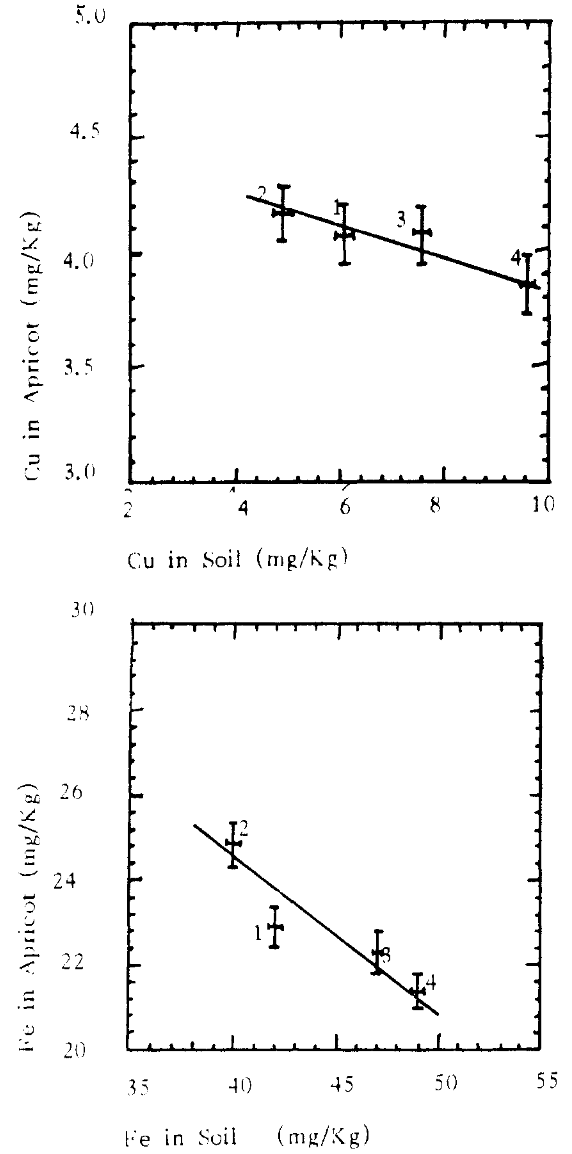

Figure 2. Soil–apricot relations of Cu and Fe (numbers indicate regions of soil and apricot samples taken).

they are integrated in the complex equilibrium system of precipitates, organomineral complexes, and adsorbed and exchangeable forms of free ions in solutions. Only free aquated metal ions are available to plants, and this fraction depends on pH, organic matter content, redox potential, etc.

It might be mentioned that soils containing very high total amounts of elements are harmless if they are fixed in an unavailable form.

Soil enrichment with toxic elements can result from different factors such as fall-out in industrial areas, dumping of industrial waste, use of sewage sludge in agriculture, intensive fertilization with some type of manure, and use of pesticides.

Increasing amounts of mineral elements in the growth medium result in different uptake patterns by plants. For example, increasing the mineral elements in growth media result in a highly pronounced concentration increase in tissue for zinc, lead, manganese, and cadmium while a limited increase or even a decrease for iron and copper was observed (Figures 1 and 2).

The uptake of trace elements is strongly influenced by external factors such as soil texture, pH, and redox potential, which influence the forms and the mobility of the elements. The uptake of manganese is more affected by these external factors than by its actual concentration in the growth medium (Dhaese, 1983).

Table I. Relative Standard Deviations of Absorption Measurements

element	concn of soln in 2 M HNO_3, ppm	rel std dev, %
Cu[a]	5	3.8
Fe[a]	5	10.2
Mn[a]	5	4.7
Zn[b]	0.1	6.3
Cd[b]	0.1	6.5
Pb[b]	2	4.2

[a] Direct aspiration of solution to flame. [b] Loop sample introduction to heated collection tube.

Table II. Some Characteristics of Soil Samples Being Analyzed

soil region no.	depth, cm	$CaCO_3$, %	org matter	pH
1	0–60	26.5	1.45	7.68
2	0–60	58.9	2.30	7.70
3	0–60	19.8	1.74	7.66
4	0–60	13.3	0.43	7.80

As can be seen from Figures 1 and 2 and Table II, concentrations of Cd, Zn, Mn, and Pb in soils and apricots can be related to the $CaCO_3$ content of soil texture. That is, the extractable metal concentration in soil and hence its concentration in apricot increase as the $CaCO_3$ content of the soil increases. Although the uptake of copper and iron by apricot was inversely related, its uptake was directly related to the $CaCO_3$ content of soil. It is suggested that $CaCO_3$ content in soil may be a more dominating factor controlling the amount uptake of copper and iron than their concentrations in the growth medium.

Several elements are much less absorbed by plants when soil pH is increased (Dhaese, 1983). This is especially the case for Cu and Fe.

The availability of trace elements in the soil environment for plants depends mainly on the interaction of these ions with the various soil constituents. Trace elements may be present in soil as free ions in the soil solution or as soluble organomineral complexes adsorbed on the colloidal phase and precipitated or bound in the soil phase.

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Registry No. Cd, 7440-43-9; Zn, 7440-66-6; Mn, 7439-96-5; Pb, 7439-92-1; Cu, 7440-50-8; Fe, 7439-89-6; $CaCO_3$, 471-34-1.