Y / Nro , /

# A STUDY OF THE INTERACTIONS AMONG CERTAIN HEAVY ELEMENTS USING TRACER TECHNIQUE

55

Ву

160/1/

#### MAMDOUH FATHY ABDEL-SABOUR

B.Sc. El-Azhar University 1972

M.Sc. El-Azhar University 1982

#### THESIS

Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy

in

Soil Science

631.41 M. F

Soils Department

Faculty of Agriculture

Ain Shams University

24991



1987

## APPROVAL SHEET

Name : Mamdouh Fathi Abd El-Sabour.

Title: A study of the interactions among certain

heavy elements using tracer technique.

This thesis has been approved by:

Prof. Dr.: popekend

Prof. Dr.: Daleat E Mallew

(Committee in charge)

Date: 23 / 4/1987.



#### **ACKNOWLEDGEMENTS**

I especially wish to record my whole hearted and sincers gratitude to Prof. Dr. T.M. El-Kobbia, Head of soil Department, Faculty of Agriculture, Ain Shams University, for his active supervision, constant guidance, readiness to give advise, many valuable suggestions, constructive criticism during the preparation of the manuscript and deep interest in the study.

Many thanks go to Prof. Dr. M.A. Massoud Head of soil and water research Department, Nuclear research center, for his continuous encouragement, suggestions and friendship throughout the course of this work. Special thanks go to Prof. Dr. J.J. Mortvedt soil chemist, at the National fertilizer Development Center, Tennessee Valley Authority (TVA), USA for his permission to use the facilities of the agricultural research branch (TVA) during part of the research, also for his help advise, valuable guidance and suggestions.

Thanks go to Dr. M.S. Dahdoh, Lecturer of soil, soil Department, desert institute, for his hospitality and his sincer help in accomplishing this work.

I wish to thank my parents and my wife for their continued support and encouragement.

## CONTENTS

	Page
1. INTRODUCTION	1
2. REVIEW OF LITERATURE	4
2.1 Cadmium and Environmental Contamination	4
2.2 Cadmium sources and concentrations in soils	5
2.3 Chemical forms of Cd in soil and soil solution	6
2.4 Some soil factors affecting Cadmium availabi-	
lity in soil	9
2.4.1 Soil PH	10
2.4.2 Organic Matter	11
2.4.3 CaCO <sub>3</sub> content	13
2.5 Cadmium uptake and content in plants	14
2.6 Zinc-Cadmium relationships	16
3. MATERIALS AND METHODS	21
3.1 Soil samples	21
3.2.Laboratory experiment	23
3.3 Greenhouse experiment	24
3.3.1 Experiment 1:	25
3.3.2 Experiment 2:	26
4. RESULTS AND DISCUSSION	28
4.1. Effect of Zn and Cd application on 115Cd	
retention and the extracted Cd forms in the	
investigated soils of Egypt	28

1	1
-	

		Page
	4.2 Greenhouse experiments:	44
	4.2.1 Effects of applied Zn and Cd on Corn grown	
	on a Zn-deficient soil	44
	4.2.2 The residual effects of Cd and Zn applica-	
	tion on Swiss chard:	47
	4.2.3 Sequential extraction of Cd and Zn in	
	Crowely soil	53
	4.2.4 Effect of applied Zn and Cd on the growth	
	and contents of both elements in Squash	
	plants	59
	4.2.5 The residual effect of applied Zn and Cd	
	on Sorghum content of Cd and Zn	63
5.	SUMMARY	72
6.	REFERENCES	<b>7</b> 5
	ARABIC SHWMARY.	

#### 1. INTRODUCTION

The world-wide industrial use of Cadmium (Cd) is increasing, and production rose from 6,000 tons in 1950 to 18,000 tons in 1980. Because of its high toxicity, the presence of Cd as a contaminant in the environment has been viewed with increasing concern in recent years.

The major source of Cd intake in man is food.

Airborne Cd has been shown to contribute significantly
(20-60%) to the total Cd in crops grown in rural areas.

Several workers have found a significant correlation
between traffic density and Cd levels in soil and vegetation in zones adjacent to roads. The application of
sewage sludge, municipal and industrial wastes, to
cropland is receiving increasing attention as this
practice introduces not only the essential plant nutrients but also some nonessential, potentially toxic metals
(e.g., Cd) to the soil.

There is insufficient data available to make broad generalizations about how most non-essential heavy metals behave in plants and soils under varying environmental

conditions. Cadmium uptake by plants from soil is influenced by various practices such as liming, soil
dressing, water management, and application of organic
materials with concomitant application of other metals.

Physiological studies conducted with animals and human indicate that 2n chelates may help to alleviate. Cd toxicity. In view of the importance of preventing or impeding introduction of Cd to man through food crops, many studies have been performed to determine the possibility of a similar interaction in the soil plant system.

Previous studies of Cd uptake by plants have shown conflicting results which may be related to plant species, source of Zn and Cd (organic and inorganic forms) and Zn: Cd ratio in the soil solution or growth media. More studies of Cd and Zn interactions and the chemical partitioning of Zn and Cd in soil after cropping may help to elucidat reasons for interaction effects.

The objectives of this study were to further investigate Zn-Cd interrelationships by (1) determining the effect of varying Cd and Zn ratios in soils (deficient soils or those enriched in heavy metals) on Cd and Zn uptake by some plant species and (2) studying the effect of both Cd and Zn forms in solid and liquid phases in the soil system on plant uptake of these elements.

#### 2. LITERATURE REVIEW

### 2.1 Cadmium and Environmental Contamination:

Cadmium is of concern because it may be highly toxic to some plants or readily accumulated by others with possible effects on human health. The toxic effects of Cd on man, stem from the metal's tendency to be accumulated and retained in mammals; Cd is estimated to have a biological half life of 20-30 years in the human body (Gunnarsson, 1983). Therefore, high concentrations of Cd in the body arise with chronic exposure to the element. Cadmium is particularly concentrated in the liver and kidney; it may replace In in certain enzymes causing disease (Lagerwerff 1972). The extensive literature on Cd toxicology, such as that referring to erythrocyte destruction, testicular damage, and renal degradation, is based on observation of injury incurred by acute exposure to Cd in animals or man. Chronic, low levels of Cd in man may result in respiratory disorders and intestinal dysfunction, anemia, osteomalacia, and hypertensive heart disease (Lewis et al., 1969 and Schroeder, 1965).

### 2.2 Cadmium Sources and Concentrations in Soils:

Because Cd is a normal contituent of phosphate ores, it reaches the rooting zone of plants as an impurity in P fertilizers; furthermore, Cd is a constituent of some fungicides used on crops. Cadmium is found in many soils by well travelled highways because of its occurrence in car tires and motor oils (Lagerwerff and Specht, 1970). Fallout from atmospheric pollution and wind-blown dusts are important sources of Cd and are concentrated in urban and industrial areas. Incidental dispersion of refuse, litter and deliberate addition of waste products to the soil, such as, soot, cinders, pulverized fuel ash, sewage sludge, municipal compost, or even untreated domestic rubbish, also result in Cd contamination of soil (Purves. 1977).

The background level of Cd in uncontaminated soil is normally very low. Vinogradov (1959) quoted an average level of 0.5 mg/kg for the total content of Cd in soil with probably 25% of this amount available to plants. Gunnarsson (1983) reported that the natural Cd content of agricultural soils ranges from < 0.1 mg/kg to > 1 mg/kg.

Fleischer et al., (1974) reported that normal back ground levels of Cd in soil are < 1 mg/kg (average 0.4

mg/kg), but contaminated soils may contain considerably higher amounts.

John et al., (1972) found 49 mg/kg of nitricacid-soluble Cd in the surface layer of a soil located

9 km from a battery smelter. Siddle and Sopper,
(1976) found that irrigation with waste water increased
soil Cd level in the 0-5 cm depth only. Hinesley et al.
(1978) showed that where large amounts of sewage sludge
had been applied annually for 7 years (374 metric tons/ha
of sludge solids), the soil surface (0-15 cm layer)
contained 21 mg Cd/kg compared with 0.3 mg Cd/kg in
control plots treated with commercial fertilizer.
El-Nannaa et al., (1982) indicated that using sewage
effluents annually for irrigation on a sandy soil increased total soil Cd by about 1.5, 3.0, and 1.9 mg Cd/kg
after 0, 25, and 47 years, respectively.

Many investigators reported that even a small addition of Cd to uncontaminated soil can produce striking increases in the Cd content of a number of widely different crops (Webber, 1973, Bingham et al., 1980). Cadmium is, therefore, an element which can adversely affect the mammalian food chain.

# 2.3 Chemical Forms of Cd in Soil and Soil Solution:

Knowledge of total concentration of an element in soil provides only limited information about the chemistry

Central Library - Ain Shams University

and consequent availability of that element to plants. Various methods have been proposed for extracting certain elements from soil. In order to better understand the chemistry and availability of certain elements in soil, Viets (1962) suggests the concept of various pools of micronutrients existing in the soil. In accordance with this concept, certain methods have been proposed for the fractionation of soil heavy metals into various forms (Stover et al., 1976; Cottenie et al., 1979; Sposito, et al., 1982).

the liquid and solid phase. The forms of Cd in soils have been investigated by Berrow and Wabber (1972), Pag (1974), Lagerwerff et al., (1976), Sommers et al., (1976) and McCalla et al., (1977). Webber et al. (1975) reported that when Cd is added to a soil it may be (a) precipitated as relatively insoluble compounds if the soil pH is 6.5 to 7.0; (b) weakly chelated by soil organic matter as slowly soluble complexes, and (c) adsorbed on the cation exchange sites of organic matter and soil clays. Numerous forms of Cd may occur in soils. Some of these are the exchangeable, sorbed, and organic-bound forms and also carbonates and sulfides (Stover et al., 1976).

The chemistry of Cd in the soil solution not only is related to the total concentration of Cd in the soil but also to the speciation between free ion and complexed forms. The study of the speciation of various forms of Cd in soil solution has been useful in studying the retention, release, and interaction of Cd in the soil and plant. Mahler et al. (1980) — used GEOCHEM to calculate the distribution of Cd species in saturation extracts of an acid soil amended with various levels of inorganic Cd. Free ionic Cd accounted for 67-73% of total Cd, the remainder being associated with sulfate, Chloride, and organic ligands.

Behel et al., (1983), using the computer program GEOCHEM, studied the effects of sewage sludge application on speciation of Cd in the soil solution of an acid soil. They concluded that Cd and Zn in the soil solution appeared to exist predominately as the free ion. Complexation of Cd by inorganic and organic ligands ranged from 9-37% of total soluble Cd and 3-22% of total soluble Zn respectively. The percentage of Cd complexed by organic matter depended on the model used to represent metal interaction with soluble organic C, phosphate, sulfate, and chloride formed inorganic complexes with Cd, but it constituted < 10% of the total Cd present.

Central Library - Ain Shams University

Cottenie et al. (1979) and Davis (1982) suggested that an extraction procedure is judged to be useful if it provides reproducible statistical correlations between extracted amounts of trace metals and plant uptake or growth response.

Numerous investigators showed that Cd uptake by crop plants grown in a sludge-amended soil can be correlated with some extractable fraction of Cd in the soil (Chaney and Giordano, 1976; Stover et al., 1976; Latterell et al., 1978; Mahler et al., 1980). However the effects of soil factors on soil chemical forms of Cd and Zn, also the variability in their extractability both with time and with the chemical extractants employed must be considered (Chaney and Giordano, 1976; Silviera and Sommers, 1977; Latterell et al., 1978).

# 2.4 Some Soil Factors Affecting Cadmium Availability in Soil:

The relationship between 'available' Cd and uptake by any species of plant will be modified by soil conditions. Varietal effects within species may also affect Cd uptake. Some soil Cd is exchangeable as Cd<sup>2+</sup> and may be considered immediately available to plants.