



1984

Soil Department  
Faculty of Agriculture  
Ain Shams University

18458-



THESES  
Submitted in Partial Fulfillment of  
The Requirements for the Degree of  
MASTER OF SCIENCE  
in  
SOIL SCIENCE

B. Sc. Agric., (Soil Science) Ain Shams University 1980

MOHAMED ABDEL-FATTAH MOHAMED EID

By

631.869  
M.A.

9720419

STUDIES ON SOME HEAVY METALS  
IN SOILS AND WATERS.

1984

Date : 28 / 10 / 1984.

(Committee in Charge)

Prof. Dr. M.K. S. ....

Prof. Dr. A. M. H. ....

Prof. Dr. A. S. ....

This thesis has been approved by:

SOILS AND WATERS.

Title : STUDIES ON SOME HEAVY METALS IN

Name : Mohamed Abdel Fattah Mohamed Ebd.

APPROVAL SHEET  
=====



The author is deeply indebted and grateful to Prof. Dr. Abdel Alim Metwally, Prof. of Soil Chemistry, Soil Dept. Ain Shams Univ., and Prof. Dr. Talat El-Kobbie, Prof. of Plant Nutrition, Soil Dept., Ain Shams Univ., for planning this work, valuable guidance, faithful help and precious advice during the preparation of this thesis.

I am particularly grateful to all members of Soil Science Department, Faculty of Agriculture, Ain Shams University, for affording all the facilities needed throughout this work.

---

ACKNOWLEDGEMENT.

|                                                                         |    |
|-------------------------------------------------------------------------|----|
| 1. INTRODUCTION.....                                                    | 1  |
| 2. REVIEW OF LITERATURE.....                                            | 4  |
| 2.1. Cadmium content in soils.....                                      | 4  |
| 2.2. Cadmium behaviour in soils.....                                    | 5  |
| 2.3. Cadmium uptake by plants.....                                      | 8  |
| 2.3.1. Effect of pH.....                                                | 8  |
| 2.3.2. Accumulation of cadmium in plants.....                           | 9  |
| 2.3.3. Effect of cadmium addition.....                                  | 10 |
| 2.4. Toxicity of cadmium.....                                           | 12 |
| 2.5. Mercury content in soils.....                                      | 15 |
| 2.6. Mercury uptake by plants.....                                      | 18 |
| 2.7. Toxicity of mercury.....                                           | 20 |
| 3. MATERIALS AND METHODS.....                                           | 23 |
| 3.1. Sampling of soils, plants, sewage sludge and sewage effluent.....  | 23 |
| 3.1.1. Soil samples.....                                                | 23 |
| 3.1.2. Plant samples.....                                               | 23 |
| 3.1.3. RI-Gabal RI-Asfar wastewater treatment plant.....                | 24 |
| 3.1.4. Sewage sludge and sewage effluent sampling.....                  | 25 |
| 3.2. Pot experiment.....                                                | 27 |
| 3.3. Methods of analysis.....                                           | 28 |
| 3.3.1. Physical and chemical analysis.....                              | 28 |
| 3.3.2. Extraction of total heavy metals in soil and sludge samples..... | 28 |
| 3.3.3. Extraction of total Hg in soil and sludge samples.....           | 30 |
| 3.3.4. Extraction of available heavy metals in soils and sludges.....   | 30 |

# CONTENTS.

|    |                                                                                                             |
|----|-------------------------------------------------------------------------------------------------------------|
| 30 | 3.3.5. Extraction of Cd and Hg in plant tissues.....                                                        |
| 31 | 3.3.6. Colorimetric determination of cadmium....                                                            |
| 32 | 3.3.7. Determination of mercury with cold vapour technique.....                                             |
| 32 | 3.3.8. Determination of Fe, Zn, Cu, Pb, Ni and Co.....                                                      |
| 33 | 4. RESULTS AND DISCUSSION.....                                                                              |
| 33 | 4.1. Total Cd in soils under irrigation with sewage effluent.....                                           |
| 33 | 4.2. Available Cd in soils under irrigation with sewage effluent.....                                       |
| 36 | 4.3. Total Hg in soils under irrigation with sewage effluent.....                                           |
| 37 | 4.4. Available Hg in soils under irrigation with sewage effluent.....                                       |
| 39 | 4.5. Cadmium and mercury in sewage sludge.....                                                              |
| 41 | 4.6. Cadmium and mercury in sewage effluent.....                                                            |
| 45 | 4.7. Heavy metal content in soils under irrigation with sewage effluent.....                                |
| 47 | 4.8. Cadmium content in plant under irrigation with sewage effluent.....                                    |
| 51 | 4.9. Mercury content in plant under irrigation with sewage effluent.....                                    |
| 55 | 4.10. Effect of sewage sludge application on plant growth and Cd & Hg content and uptake by bean plant..... |
| 59 | 5. SUMMARY.....                                                                                             |
| 65 | 6. REFERENCES.....                                                                                          |
| 70 | == ARABIC SUMMARY.                                                                                          |

The growth of urban areas has increased the problem of depositing human wastes at a time when a growing public awareness of environmental problems has stopped the emptying of crude sewage into rivers or the sea in many places. Meanwhile, in many arable areas, there are problems of decline in soil fertility and a deterioration in soil structure because of falling soil humus levels. It is apparent that soil is one of the nature's best decontaminating agents. Sewage materials have proved to be a valuable source of plant nutrients. Also, the effect of such materials in improving soil structure, aeration, water retention of soil and other soil physical properties is well-documented. Consequently, if sewage material can be used satisfactorily as a soil amendment, just as stable manure has been used over the ages, the land application of sludge will beneficially return waste material to land and make use of its nutritive value to crops. Crop yields will, very likely, be increased with a consequent saving in fertilizers. An increase in food production would be invaluable in a world which demands more food.

However, this practice offers a challenge in crop production, since sludge, depending on its source, contains certain heavy metal ions which may find their way in toxic

# 1. INTRODUCTION.

needed in terms of crop production, soil and water of municipal wastes on agricultural land is urgently Therefore, a proper evaluation of the disposal problems.

minimized in food plants to avoid hazardous health and animal, particularly Cd, Hg and Pb, etc. should be tain heavy metals which are potentially toxic to human It is generally accepted that the levels of cer-

soil pH and genetic factors. accumulation in plant tissues are largely affected by heavy metals to plants, and therefore, their absorption and dustrial units. In addition, the availability of these tion density and the byproducts impurities of the in- ever, vary with the dietary habits of the locality, popula- Chemical characteristics of sewage wastes, how-

countries. sewage materials is now recognized in all industrial were reported by many investigators. The danger in using Cd in plants growing in soils treated with sewage sludge live and toxic concentrations of Cu, Zn, Ni, Co, Pb and levels into the edible plants and their products. Exces-

The present research is, therefore, directed to:-

1. Evaluation of heavy metal accumulation in soils under irrigation with sewage effluent for many years in El-Gabal El-Astar area with a special reference to Cd and Hg.
2. Evaluation of heavy metal content in sewage sludge and sewage effluent with special reference to Cd and Hg.
3. Evaluation of Cd and Hg contents in field crops and citrus trees grown on soils under irrigation with sewage effluent.
4. Studying the effect of high rates of sludge application to soils on plant uptake of Cd and Hg.

2.1. Cadmium content in soils.

Cadmium content in agricultural soils drew the attention of many investigators as a potentially toxic heavy metal. Mills et al. (1975) found that cadmium content of agricultural soils in Manitoba ranges from 0.4 to 1.7 ppm with an average of 1.0 ppm. Alchberger et al. (1982) found that cadmium content was 0.07-2.4 ppm at different geological regions of upper Austria. Aoyama et al. (1982) reported that in sediments of Kajiya Bay, Japan and its associated rivers concentration of Cd was Trace-1.44 ppm.

Dudas et al. (1975) found that the total content of Cd in chernozemic soils from Alberta was approximately 0.5 ppm, whereas the total content of Cd was as much as 16-48 times higher in the sewage samples. Gaynor et al. (1976) pointed out that the addition of sludge to sandy loam and clay soils increased DTPA-extractable Cd 2 to 5 times. Baerug et al. (1977) found that the sludge increased the content of total Cd and the content of readily soluble Cd in soils. Hinesly et al. (1977) and (1978) pointed out that sludge application resulted in significant increases of total and 0.1N HCl-extractable Zn and Cd in

## 2. REVIEW OF LITERATURE.

Bingham *et al.* (1976) found that greatly reduced cadmium concentration in soil solutions under flood management may account for the greater tolerance of rice to soil Cd under flood culture. This reduced availability of Cd in flooded soils is attributed to precipitation of CdS. Bingham *et al.* (1983) reported that the distribution of estimated Cd species in the saturation extract changed with Cl treatment. The treatment caused the percentage of estimated  $Cd^{2+}$  to decrease and that of estimated  $CdCl^+$  to increase. Herms *et al.* (1979) showed that in soil rich in organic matter increases in the Cu, Zn, Cd and Pb content of the soil solution occurred as a result of the presence

## 2.2. Cadmium behaviour in soil.

normal inorganic fertilization. Input of Cd to land will approximate the input from ppm Cd) are utilized as phosphorous fertilizers, the (1983) pointed out that if normal Danish sludges (3-5 of Cd, Zn, Pb and Cu largely increased. Hansen *et al.* soil in sewage sludge as measured by DTPA extraction (1982) showed that the availability of metals added to the soil. Williams *et al.* (1980) and RI-Nemah *et al.*

of microbially formed soluble organic complexes. Khan (1983) reported that a very high proportion of Cd and Pb added to the soil in water soluble form became insoluble with one hr. of contact with the soil.

Webber et al. (1975) reported that it is known

that when cadmium is added to a soil, it may be: (a)

precipitated as relatively insoluble compounds when the soil pH is greater than 6.5 to 7.0; (b) weakly chelated by soil organic matter as low solubility complexes and (c) adsorbed on the cation exchange sites of organic

matter. Singh et al. (1979) showed that soils exhibit

large capacities to adsorb Cd, however, a major por-

tion of adsorbed Cd was released by NaCl extraction.

The amount of Cd not released (fixed Cd) was correlated to the cation exchange capacity, pH and organic carbon

content of soils. Soon (1981) reported that cadmium

adsorption increased with increasing soil pH.

Dudas et al. (1975) stated that in poorly drained

soils cadmium content ranges from 0.13 to 0.92 ppm. The

high values obtained from many of the poorly drained

soils could additionally reflect the influence of ground

water flow. Biddappa (1982) mentioned that the Pb and Cu ions were less mobile than those of Zn and Cd and that Ni, Cd and Zn might pose a greater threat of ground water pollution than Cu and Pb. The specific migration properties of each metal ion varied depending on the nature of the ion and leaching solution. Tyler et al. (1982) reported that the least mobility of metals was observed in a mineral soil with a relatively high pH, C.E.C. and exchangeable base content. The timing of an acid mineral soil reduced metal mobility, but not to the extent expected from the very low mobility observed for a naturally non acid mineral soil. The order of mobility of the metals in the soils was:  $Cu \gg Zn \gg Ni \gg Cd$ . Alekseev et al. (1982) concluded that the mobility of Cd and its availability for plants are substantially greater in acid soils than in non-calcareous soils with neutral and alkaline pH's. On the other hand, Kuo et al. (1983) pointed out that the mobility of Cu, Zn and Cd in the soils was limited as evidenced by a sharp reduction in concentrations of the three elements with depth. Comparing subsoil concentrations of these elements with those from areas relatively

Bates et al. (1975) reported that soil pH did not affect the Cd concentration in ryegrass where the sludge was re-applied after each crop. Hyde et al. (1979) concluded that the concentration of Cd at the highest sludge application rate (160 metric tons/ha) was not substantially different from the concentrations of the same metal in grain from plants grown on the acid soil without sludge treatment. The results show that metal entry into plants can be minimized by growing plants on cal-

### 2.3.1. Effect of pH.

### 2.3. Cadmium uptake by plants.

zation of heavy metals takes place. complexes. After a mobilization phase, the immobilization of soluble, low molecular weight organic with soils, heavy metal solubility increased due to the decomposable organic matter (e.g. sewage sludge, manure) at pH 4-8 and the results indicate that after mixing heavy metal solubility in the order:  $Cu \gg Cd \gg Zn > Pb$  fresh and slightly decomposed organic material affected tions. Herms et al. (1983) reported that the addition of leachable than Cu or Zn under western Washington conditions. unpolluted by smelter fallout revealed that Cd was more

up was retained in the roots. The concentration in the  
tuce and water cress, more than 50 percent of Cd taken  
cluded that in all, except 3 species, i.e., kale, let-  
in a nutrient solution containing 0.01 ppm Cd. They con-  
shoots of 23 species was examined by Jarvis et al. (1976)  
straw. The distribution of Cd between the roots and

~~tions of Zn and Cd are lower in corn grain than in the~~  
Webber et al. (1975) reported that the concentra-

## 2.3.2. Accumulation of cadmium in plants.

presence of competing cations.  
pared to the governing parameters pH, soil type and  
portance in determining plant uptake of the metal, com-  
the source of Cd in the soil is probably of minor im-  
led inversely with soil pH. Hansen et al. (1983) mentioned that  
pH and/or elevated soil Cd. In leafy vegetables Cd var-  
nity gardens (soil in Washington D.C.) with low soil  
mium elevated in leafy vegetables from plots in commu-  
pH dependent. Freer et al. (1980) pointed out that cad-  
maximum permissible Cd addition was found to be strongly  
rates of Cd with sewage sludge and soil pH only. The  
content of rice grain to be dependent upon the addition  
careous soils. Bingham et al. (1980) found that the Cd