

**EFFECT OF SOME MINERALS AND DISSOLVED
ORGANIC CARBON ON THE BEHAVIOUR OF
SOME HEAVY METALS IN SOILS**

By

ASHRAF LATIF ISKANDER BOTROUS

B.Sc. (Microbiology and Chemistry), Ain Shams University, 2002

A thesis submitted in partial fulfillment

of

the requirements for the degree of

MASTER OF SCIENCE

in

**Agricultural Science
(Soil)**

**Department of Soil
Faculty of Agriculture
Ain Shams University**

2010

Approval Sheet

EFFECT OF SOME MINERALS AND DISSOLVED ORGANIC CARBON ON THE BEHAVIOUR OF SOME HEAVY METALS IN SOILS

By

ASHRAF LATIF ISKANDER BOTROUS

B.Sc. (Microbiology and Chemistry), Ain Shams University, 2002

This thesis for M. Sc. degree has been approved by:

Dr. Khaled Hassan Mahmoud El-Hamdi.....

Prof. of Soil Pedology, Faculty of Agriculture, El- Mansoura
University

Dr. Mohamed Ahmed Mostafa

Prof. Emeritus of Soil Chemistry, Faculty of Agriculture,
Ain Shams University

Dr. Abd El-Aziz Saad Nasr Sheta

Prof. of Soil Pedology, Faculty of Agriculture, Ain Shams
University

Dr. Eid Morsy Khaled

Prof. of Soil Chemistry, Faculty of Agriculture, Ain Shams
University

Date of Examination: 16/ 12 / 2010

EFFECT OF SOME MINERALS AND DISSOLVED ORGANIC CARBON ON THE BEHAVIOUR OF SOME HEAVY METALS IN SOILS

By

ASHRAF LATIF ISKANDER BOTROUS

B.Sc. (Microbiology and Chemistry), Ain Shams University, 2002

Under the supervision of:

Dr. Eid Morsy Khaled

Prof. of Soil Chemistry, Department of Soil, Faculty of
Agriculture, Ain Shams University (Principal Supervisor)

Dr. Abd El-Aziz Saad Nasr Sheta

Prof. of Soil Pedology, Department of Soil, Faculty of
Agriculture, Ain Shams University

ABSTRACT

Ashraf Latif Iskander Botrous: Effect of Some Minerals and Dissolved Organic Carbon on the Behaviour of Some Heavy Metals in Soils. Unpublished M.Sc. Thesis, Department of Soil, Faculty of Agriculture, Ain Shams University, 2010.

In this study the effect of natural minerals such as zeolite and bentonite and the dissolved organic carbon on the behavior of heavy metals (Zn, Mn and Ni) in two different soil samples (sand and clay soils) were carried out. The main results can be summarized as follows:

1- Adsorption and desorption experiment:

The studied minerals zeolite and bentonite showed considerable variations in Zn, Mn and Ni sorption properties and DTPA extractability. Bentonite has the highest ability for Mn and Ni sorption, while zeolite has the highest ability for Zn sorption. Zeolite retains a relatively high percentage of the sorbed Zn against the extraction by DTPA. Zinc, manganese and nickel sorption data were described by a Freundlich and Langmuir adsorption model. The results showed that Langmuir constants for Zn, Mn and Ni sorption [maximum adsorption ($b \text{ mmol kg}^{-1}$)] have been in the following decreasing order: Bentonite Mn > Bentonite Ni > Zeolite Mn > Bentonite Zn > Zeolite Ni > Zeolite Zn. While the [binding strength values ($k \text{ in mmol l}^{-1}$)] was in the order: Zeolite Mn > Zeolite Zn > Zeolite Ni > Bentonite Mn > Bentonite Zn > Bentonite Ni. The results suggest that natural zeolite and bentonite minerals have a high potential for Zn, Mn and Ni retention. The availability of the retained Zn, Mn and Ni was higher for Zn compared with Mn and Ni, and zeolite seems to have the highest ability for Zn sorption and extractability by DTPA. Bentonite has intermediate characteristics for Zn, Mn and Ni sorption.

2- Incubation experiment:

Data of the incubation showed that there are gradual increasing in the concentration of studied heavy metal in all fractions by increasing the rates of metals loading on zeolite and bentonite and as a results of incubation times. This increasing for the concentration of heavy metals (Zn, Mn and Ni) under study not only in the means of rates of doses of zeolite and bentonite but also in the means of incubating times. In the control clay soil, the background Zn, Mn and Ni in each fraction were generally in the order carbonate > Fe–Mn oxides > organic matter > exchangeable > water soluble fraction. While in the untreated sand soil, the background Zn, Mn and Ni in each fraction were generally in the order Fe–Mn oxides > exchangeable > carbonate > organic matter > water soluble. It was observed that after the period of incubation, metals in exchangeable fraction were predominant in all treatments of both soils with some exception. Moreover the increases in the other fractions were also observed. It may indicated that a fast process of metal distribution among the fractions occurred during the first 2-days incubation. The redistribution process from 2-weeks to 4-weeks is much slower comparing with that in 2-days. At the end of 4-weeks incubation, the percentages of Zn, Mn and Ni in exchangeable fraction were still very high. This observation was possibly due to the slow transformation of metals from loosely bound fractions such as exchangeable fraction to strongly bound.

3- Column experiment:

Addition of the natural mineral loaded by Zn, Mn and Ni to surface of the soil resulted in a marked increase in the amount of total Zn, Mn and Ni in both soil. The increases corresponding, in general, to the concentrations of metals loaded in the clay mineral. For the rate of natural clay mineral (0.4%) were chosen for application, total amounts

were presented (mg/kg soil) as a function of soil depth. Maximum total concentrations of metals were found in the surface layer of soil (0-5 cm) for all metal ions. Data revealed that the amounts of Zn and Mn extracted by DTPA solution were generally decreased with increasing soil depth this in case of Zn and Mn. While Ni has a different pattern where it decreases by depth then increased in the last segment of column especially in case of sandy soil. Mobility of heavy metals were followed the order $Mn > Zn > Ni$.

Key words:

Heavy metal, Zeolite, Bentonite, and Dissolved Organic Carbon (D.O.C).

ACKNOWLEDGEMENTS

First of all, great thanks and praises be to Allah, who guided me to accomplish this work and assist me in all my life. All words are not be enough to thank Allah. I would like to express my deepest gratitude to my advisers, **Prof. Dr. Eid Morsy Khaled** and **Prof. Dr. Abd El-Aziz Sheta**, Soils Department, Faculty of Agriculture, Ain Shams University, for suggesting the problem, supervision, continuous helping and introducing all facilities needed throughout the whole investigation and during writing the manuscript. Thanks are also extend to all staff members at Soil Department, Faculty of Agriculture, Ain Shams University, for their help and encouragement and supporting the equipment to this research works. Special thanks are also extended to my friends who are always nice and friendly. Finally, I would like to express my deepest love to my father, mother, brother and my sister for their encouragement and support that have enable me to succeed in my life.

CONTENTS

	Page
LIST OF TABLES	IV
LIST OF FIGURES	VII
I. INTRODUCTION.....	1
II. REVIEW OF LITERATURE	3
1. Heavy metals.....	3
1.1. Behavior of heavy metals in soils.....	4
1.2. Solubility and Mobility.....	5
1.3. Bioavailability.....	7
2. The processes that control heavy metal mobility in soil.....	8
2.1. Cation exchange.....	8
2.2. Specific adsorption.....	8
2.3. Precipitation.....	9
2.4. Complexation.....	10
3. Factors affect the bioavailability and immobilization of heavy metals in soils.....	11
3.1. Effect of the soil pH	12
3.2. Effect of redox reactions	14
3.3. Effect of organic matter.....	15
3.4. Effect of iron oxides.....	18
3.5. Effect of complex formation.....	20
3.5.1. Complexation by inorganic ligands.....	20
3.5.2. Complexation by organic ligands.....	20
4. Adsorption process and heavy metal adsorption on natural minerals.....	22
4.1. Adsorption Process.....	22
4.2. Adsorption Isotherms.....	22
4.2.1. Langmuir Isotherm.....	23
4.2.2. Freundlich Isotherm.....	23

5. Heavy metal adsorption by low-cost adsorbents (natural mineral)...	24
5.1. Zeolites.....	25
5.2. Bentonite clay	27
6. Dissolved organic carbon.....	28
7. Heavy Metal Movements down the Soil Profile.....	34
8. General features of the investigated heavy metals.....	40
8. 1. Zinc.....	40
8. 2. Manganese.....	42
8. 3. Nickel.....	44
III. MATERIALS AND METHODS.....	47
1. Adsorption and desorption experiment.....	48
1.1. Adsorption experiment.....	48
1.2. Desorption experiment.....	48
2. Loading of heavy element on clay mineral.....	48
3. Extraction of dissolved organic carbon from the one of its available sources (i.e., compost).....	52
4. Incubation experiment.....	52
5. Columns experiment.....	53
6. Methods of analysis.....	54
6.1. Soil analysis.....	54
6.1.1. Chemical and physical analysis.....	54
6.1.2. Fractionation of metals.....	55
6.2. Clay mineral analysis.....	57
6.2.1 XRD measurement.....	57
6.2.2. Surface area	58
6.2.3. Cation exchange capacity	58
6.3. Dissolved organic carbon determination	60
IV. RESULT AND DISSECTION.....	62
1- Sorption and desorption of Zn, Mn and Ni on clay minerals.....	62
2- Fractionation of heavy metals forms.....	73

2.1. Fractionation of Ni.....	89
2.2. Fractionation of Zn.....	92
2.3. Fractionation of Mn.....	95
3- Movement and distribution of heavy metals in soil column.....	100
V. SUMMARY.....	117
VI. REFERENCES.....	120
ARABIC SUMMARY	

LIST OF TABLES

Table No.	Page
1. Some physical and chemical properties of the studied soils.....	49
2. Some physical and chemical properties of the studied minerals.....	50
3. Selected chemical analyses of zeolite and bentonite minerals used in this study.....	51
4. Chemical analysis of the compost.....	51
5. Chemical analysis of the water dissolved organic carbon fraction...	51
6. Langmuir equations and constants (b and k) for Zn, Ni and Mn sorption by zeolite and bentonite.....	64
7. Freundlich equations and constants for Zn, Ni and Mn sorption by zeolite and bentonite.....	64
8. Amounts of sorbed Zn and DTPA extractable (three successive extractions) from Zn, treated and untreated zeolite and bentonite...	69
9. Amounts of sorbed Mn and DTPA extractable (three successive extractions) from Mn, treated and untreated zeolite and bentonite...	70
10. Amounts of sorbed Ni and DTPA extractable (three successive extractions) from Ni, treated and untreated zeolite and bentonite..	71
11. Effect of zeolite and bentonite and the watering solution on the water soluble form of Ni (mg.kg^{-1}) in the studied soils at different incubation periods.....	74
12. Effect of zeolite and bentonite and the watering solution on the exchangeable form of Ni (mg.kg^{-1}) in the studied soils at different incubation periods.....	75
13. Effect of zeolite and bentonite and the watering solution on the Carbonate form of Ni (mg.kg^{-1}) in the studied soils at different incubation periods.....	76
14. Effect of zeolite and bentonite and the watering solution on the Fe and Mn oxide form of Ni (mg.kg^{-1}) in the studied soils at different incubation periods.....	77

15. Effect of zeolite and bentonite and the watering solution on the organic matter form of Ni (mg.kg^{-1}) in the studied soils at different incubation periods.....	78
16. Effect of zeolite and bentonite and the watering solution on the water soluble form of Zn (mg.kg^{-1}) in the studied soils at different incubation periods.	79
17. Effect of zeolite and bentonite and the watering solution on the exchangeable form of Zn (mg.kg^{-1}) in the studied soils at different incubation periods.	80
18. Effect of zeolite and bentonite and the watering solution on the Carbonate form of Zn (mg.kg^{-1}) in the studied soils at different incubation periods.	81
19. Effect of zeolite and bentonite and the watering solution on the Fe and Mn oxide form of Zn (mg.kg^{-1}) in the studied soils at different incubation periods.....	82
20. Effect of zeolite and bentonite and the watering solution on the Organic matter form of Zn (mg.kg^{-1}) in the studied soils at different incubation periods.....	83
21. Effect of zeolite and bentonite and the watering solution on the water soluble form of Mn (mg.kg^{-1}) in the studied soils at different incubation periods.....	84
22. Effect of zeolite and bentonite and the watering solution on the exchangable form of Mn (mg.kg^{-1}) in the studied soils at different incubation periods.	85
23. Effect of zeolite and bentonite and the watering solution on the Carbonate form of Mn (mg.kg^{-1}) in the studied soils at different incubation periods.....	86
24. Effect of zeolite and bentonite and the watering solution on the Fe and Mn oxide form of Mn (mg.kg^{-1}) in the studied soils at different incubation periods.....	87
25. Effect of zeolite and bentonite and the watering solution on the	

organic matter form of Mn (mg.kg ⁻¹) in the studied soils at different incubation periods.....	88
26. Total concentration of Ni (mg.Kg ⁻¹) for sandy column soil.....	102
27. Total concentration of Ni (mg.Kg ⁻¹) for clay column soil.....	102
28. Total concentration of Mn (mg.Kg ⁻¹) for sandy column soil.....	103
29. Total concentration of Mn (mg.Kg ⁻¹) for clay column soil.....	103
30. Total concentration of Zn (mg.Kg ⁻¹) for sandy column soil.....	104
31. Total concentration of Zn (mg.Kg ⁻¹) for clay column soil.....	104
32. Available concentration of Ni (mg.Kg ⁻¹) extracted by DTPA for sand column soil.....	109
33. Available concentration of Ni (mg.Kg ⁻¹) extracted by DTPA for clay column soil.....	109
34. Available concentration of Mn (mg.Kg ⁻¹) extracted by DTPA for sand column soil.....	110
35. Available concentration of Mn (mg.Kg ⁻¹) extracted by DTPA for clay column soil.....	110
36. Available concentration of Zn (mg.Kg ⁻¹) extracted by DTPA for sand column soil.....	111
37. Available concentration of Zn (mg.Kg ⁻¹) extracted by DTPA for clay column soil.....	111

LIST OF FIGURES

Fig. No.	Page
1. X- ray diffraction pattern of zeolite sample.....	59
2. X- ray diffraction pattern of bentonite sample.....	59
3. X- ray diffraction pattern of bentonite sample (Mg- saturated ethylene glycol treatments).....	59
4. Sorption isotherms of Zn, Mn and Ni by zeolite and bentonite.....	65
5. Langmuir and Freundlich plot of Zn adsorbed by zeolite and bentonite.....	66
6. Langmuir and Freundlich plot of Mn adsorbed by zeolite and bentonite.....	67
7. Langmuir and Freundlich plot of Ni adsorbed by zeolite and bentonite.....	68
8. Total concentration of Ni (mg.Kg^{-1}) for sandy and clay soils.....	105
9. Total concentration of Mn (mg.Kg^{-1}) for sandy and clay soils.....	106
10. Total concentration of Zn (mg.Kg^{-1}) for sandy and clay soils.....	107
11. Available concentration of Ni (mg.Kg^{-1}) extracted by DTPA for sandy and clay soils.....	113
12. Available concentration of Mn (mg.Kg^{-1}) extracted by DTPA for sandy and clay soils.....	114
13. Available concentration of Zn (mg.Kg^{-1}) extracted by DTPA for sandy and clay soils.....	115

I. INTRODUCTION

There is growing concern that the heavy metal contents of soil are increasing as the result of industrial, mining, agricultural and domestic activities. Although certain heavy metals, such as manganese and zinc, are essential for plant growth as micronutrients, they are toxic at higher levels, as are metals such as nickel.

Interactions of heavy metals (Zn, Mn and Ni) with phyllosilicate mineral such as bentonite or tectosilicate such as zeolite are important in the chemical speciation and fate of these metals in soils and other ecosystems. The processes that decrease the activity and extractability of these metals retained by above natural minerals are believed to be important in the availability of these metals added to soils and in the remediation of soils contaminated with these metals.

So understanding the sorption process by natural zeolite and bentonite are necessary for effective utilization of these minerals. It can be used in the soil as a trap for heavy metals and as nutrient adsorbents and consequently as slow releases to plant. The fate and transport of metal ions in the environment are generally controlled by sorption reactions. Adsorption and desorption are a major process responsible for accumulation of heavy metals. Therefore the study of adsorption processes is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase and vice versa.

Also the migration of heavy metals could be enhanced by their complexation with some fractions of the organic matter. In addition to humic-like substances, compost extract by water produces a water-soluble organic matter known as dissolved organic carbon (DOC), which can pass through a 0.45 μm filter. This DOC has a low molecular weight and is a mixture of polymeric materials containing a number of polar and non-polar sites.