THE EFFECT OF SOIL pH ON HEAVY METAL TRANSPORT IN THE VADOSE ZONE

by

MALAK ELZAHABI

Department of Civil Engineering and Applied Mechanics
McGill University
Montreal, Quebec, Canada

A Thesis submitted to the Faculty of Graduate Studies and
Research in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

0-612-69874-2

Canada

ABSTRACT

Although sorption and transport of heavy metals in fully saturated soil systems have received considerable attention in many reported studies, the problem of vadose transport and the influence of the soil system pH regime have 1-2 not had much attention. Given that most containment situations show transport from source contamination through the vadose zone prior to saturated zone transport, and since contaminant plume arrival at the saturated layer is not a desirable goal, it becomes necessary to seek management control of a contaminant plume in the vadose zone. Another significant reason for the need to study vadose zone transport is the fact that the "initial conditions" established at the saturated zone interface will be considerably affected by vadose zone results, thereby impacting directly on the success of models designed to predict transport in the saturated zone.

This research study provides the experimental information necessary for numerical analyses, structured to account for vadose zone transport of heavy metals. Particular attention is payed to the effect of degree of saturation, the presence of carbonate, soil pH and heavy metals concentrations. In addition, attention is directed to an evaluation of the coupled solute-water transport mechanisms. A method that fully describes the coupling effects on the transport coefficient based on experimental evidence provides successful predictions of the rate of transport of the heavy metals through the unsaturated soil in a pH-controlled environment.

In the experimental part of this research, one dimensional solute and moisture flow (leaching) tests, using different heavy metal permeants, were conducted on an unsaturated illitic soil at varying pH values. Variations of moisture content with distance were measured for different time durations, and

2-2

concentrations of heavy metals in the liquid and solid phases were analyzed. The migration and retention profiles of contaminants along the soil column were determined for each individual layer in the soil. Experimental results showed that the retention and migration of heavy metals are highly dependent on the soil pH, the presence of carbonates, the degree of saturation, the influent concentration and the time duration. At high soil pH and carbonate content, heavy metals were retained in the soils if the buffering capacity was high enough to resist the acidic input solution, and sorption processes will prevail in the carbonate phase. As the soil pH decreases, the dissolution of carbonates increases and cation exchange capacity becomes the more dominant process in heavy metals retention.

The numerical study developed a model to analyse and predict the transport of the contaminant in unsaturated clayey soils in which some of the species were adsorbed on clay particles surfaces. The proposed mathematical model was based on the postulates of irreversible thermodynamics and is also applicable in a one-dimensional case. In this model, various solute transport mechanisms such as diffusion and sorption were considered. The numerical solution of the governing coupled solute and moisture flow equations were obtained using the implicit finite difference method. The diffusion coefficient was expressed as a function of the volumetric water content and the solute concentration. Diffusion parameters were determined using the Powell method for nonlinear optimization and were based on the experimental results obtained from laboratory leaching column tests. These experimental results were compared to predicted ones. Results indicated that the diffusion coefficient is necessary to provide a good agreement between the experimentally measured and the theoretically predicted values of contaminant transport through the soil. The numerical results of the coupled solute and moisture equations showed that the transport coefficients strongly and accurately depend on

solute and volumetric water content.

RÉSUMÉ

Bien que la sorption et le transport des métaux lourds dans un système du sol totalement saturé ont reçu une attention considérable de la plupart des chercheurs scientifiques, le problème de zone de transition ou bien le transport non saturé et l'influence du système du sol de pH régime n'a pas reçu beaucoup d'attention. Étant donné que la plupart des situations de mouvement du contaminant du point de source à travers la zone sèche antérieurement vers la zone saturée, et que l'arrivée du contaminant plume à la zone saturée n'est pas un but désirable, il devient donc nécessaire de chercher une bonne conduite pour contrôler le mouvement du contaminant dans la zone de transition. Une autre raison significative pour Le besoin ou bien la nécessité d'étudier le transport dans la zone sèche, est le fait que les conditions initiales établies à l'interface de la zone saturée sont considérablement affectées par les résultats de la zone sèche. Par conséquent, ils influencent directement le succès du modèle dessiné pour prédire le transport dans la zone saturée. Cette étude fournit l'information expérimentale nécessaire pour les analyses numériques structurées afin de calculer et prédire le movement des métaux lourds dans les sols non-saturés ou bien dans la zone sèche, avec une attention particulière aux: effets du degré de la saturation, à la présence du carbonate, au pH du sol et les concentrations des métaux lourds.

Des tests de percolation mono-dimensionnelles, combinés de mouvement d'humidité et de soluté avec différent perméants des métaux lourds, ont été effectués dans un sol illitic non saturé et avec du ph de sol varié. Les variations du contenant d'humidité avec distance ont été mesurés pour différente durée de temps, ainsi que les concentrations des métaux lourds solubles dans l'eau et retenues par la phase solide du sol ont été encore analysées. Finalement, les profils des migrations à travers la colonne du sol ont été déterminés pour chaque

couche individuelle du sol. Les résultats expérimentaux ont démontré que la rétention et la migration des métaux lourds sont fortement dépendante du pH du sol, de la présence du carbonate, du degré de la saturation, de la concentration du perméat et de la duré du test. Avec un pH de sol et un contenu de carbonate élevé, les métaux lourds ont été retenus par le sol si la capacité cationique échangeable est assez élevée pour resister à l'introduction du perméat acide sinon la rétention est dominée par la présence du contenu de carbonate dans le sol. Pendant que le ph du sol dimimue, la dissolution du carbonate augmente donc, la capacité cationique prend place et sera plus en plus dominante pour la rétention.

L'étude numérique développe un modèle pour analyser et prédire le transport du contaminant à travers les sols argileux non saturés dans lesquels ces composés sont adsorbés à la surface des particules d'argile. Le modèle mathématique proposé est basé sur les postulats de la thermodynamique irréversible et est aussi applicable dans les cas mono-dimensionnelles. Dans ce modèle, les mécanismes du transport de concentration d'ion (diffusion et adsorption) sont considérés. La solution numérique des équations gouvernant combinés de concentration et de masse d'eau a été obtenue par l'utilisation de la méthode implicite de différence finie. Le coéfficient de diffusion est utilisé comme une fonction de la concentration du soluté et du contenant volumétrique d'eau. Les paramètres de diffusion ont été déterminés par la méthode de Powell dans le cas d'optimisation non linéaire. Celui-ci a été appliquée aux résultats expérimentaux obtenus au laboratoire à partir des tests dans des cellules de percolation.

Ensuite, les résultats expérimentaux obtenues au laboratoire sont comparés avec les prédictions théoriques. Ceux-ci indiquent que la présence d'un coefficient de diffusion est nécessaire pour obtenir un bon accord entre les prédictions théoriques et les mesures expérimentales selon le temps du contaminant à travers

le sol étudié. Les résultats numériques supportent fortement la dépendance des coéfficients de transport, dans les équations gouvernant le débit combiné de concentration et d'humidité sur la concentration et le contenu volumétrique d'eau et montrent l'exactitude des coéfficients de diffusion choisis.

ACKNOWLEDGEMENTS

The author would like to express her sincere appreciation and gratitude to her research supervisor, Professor Raymond N. Yong, William Scott Professor of Engineering and Applied Mechanics and Director of the Geotechnical Research Center at McGill University, for his invaluable guidance, continued encouragement and useful comments and advise throughout this study.

The author also wishes to express her sincere appreciation to:

- Dr. A.M.O. Mohamed, Associate Director of the Geotechnical Research Centre and Faculty Lecturer, for his scientific advice and discussions.
- Professor Japp, Chairman of the Department of Civil Engineering and Applied Mechanics at McGill University for his cooperation and help throughout this research study.
- The Geotechnical Research Center technicians, Dr. Rosa Galvez-Cloutier, Ms. Sangeetta Khanna and Mr. Frank Caporuscio, and their laboratory staff for their technical assistance during the laboratory work.
- Dr. Issa Shooshpasha, research colleague, for his helpful comments which are duly appreciated, Dr. Catherine Mulligan for providing the author with her helpful suggestions and Mr. David Coles for reading this manuscript.

Much appreciation is expressed for the technical support and assistance given by the Civil Engineering Department technicians: Mr. Merik Prykorski for his guidance, Mr. Damon Kipperchuck for preparing the cells, Mr. John Bartczak and Mr. Ron Shepparo for their support and help as well as, Ms. Daina Brumelis, technician of the environmental laboratory, for lending me the hot plates and the glassware all throughout the experiments. Also, Mr. Raymond Langlois, technician of the Mining and Metalurgical department for his help in grinding the soils despite the acidic dust as well as use of laboratory facilities throughout the laboratory work.

Special appreciation and gratitude is extended to the author's parents for their continuous inspiration and great moral support, as well as other family members and friends for their encouragement and assistance. Finally, the author greatly appreciates the continuous help and support received by Mr. M. Berjaoui in various ways throughout the course of this study.

to my Lovely children Sarah, Ranya

and Karim for their love and patience.

TABLE OF CONTENTS

ABSTRACT i

RÉSUMÉ iv

ACKNOWLEDGEMENTS vii

TABLE OF CONTENTS x

LIST OF FIGURES xvi

LIST OF TABLES xxv

LIST OF PUBLICATIONS xxvi

CHAPTER 1 1

INTRODUCTION 1

- 1.1 General 1
- 1.2 Statement of the Problem 6
- 1.3 Objectives of the Present Study 16
- 1.4 Tasks 16
- 1.5 Organization of the Thesis 18

CHAPTER 2 20

LITERATURE REVIEW 20

- 2.0 Introduction 20
- 2.1 Physical Transport Mechanisms Through Clayey Soils . . 20
- 2.2 Contaminant Transport Processes and Models 22
  - 2.2.1 Darcy's law and fluid flow in unsaturated soil 22
  - 2.2.2 Ficks law and solute transport 27
  - 2.2.3 Fluid and solute transport in unsaturated soil 30

2.2.4 Adsorption-desorption model 30
2.3 Irreversible Thermodynamic Approach in Coupled Flow 32
2.4 Sorption Characteristics of Heavy Metals in the Vadose Zone . . 34

CHAPTER 3 39

Materials and Methods 39
3.1 Materials 39
3.1.1 Soil material 39
3.1.2 Leachate solution 40
3.2 Sample Preparation 41
3.2.1 Soil mixing 41
3.2.2 Soil compaction 41
3.2.3 Sample extrusion 42
3.3 Laboratory Tests 43
3.3.1 Test apparatus 43
3.3.2 Leaching column Test 44
3.4 Soil Characterization Study 47
3.4.1 Geotechnical Characterization 48
3.4.2 Geochemical analysis 49
3.4.2.1 Cation exchange capacity 49
3.4.2.2 Specific surface area determination 50
3.4.2.3 Soil carbonate content determination 50
3.4.2.4 Soil pH , organic and amourphous content measurement 51
3.5 Metal Partitioning Analysis 52
3.5.1 Soluble phase 52

3.5.2 Solid phase 53
3.6 Partitioning Coefficient Determination 54

CHAPTER 4 57

SOIL CHARACTERIZATION RESULTS AND DISCUSSION 57
4.0 General 57
4.1 Geotechnical Aspects 57
4.1.1 Particle size distribution 62
4.1.2 Atterberg limits 64
4.1.3 Hydraulic conductivity test 66
4.2 Geochemical Aspects 69
4.2.1 Cation exchange capacity 69
4.2.2 Specific surface area 75
4.3 Summary 77

CHAPTER 5 79

SORPTION CHARACTERISTICS RESULTS AND ANALYSIS 79
5.1 General 79
5.2 Moisture Distribution 80
5.2.1 Analytical volumetric water content 82
5.2.2 Volumetric water content results at high soil pH . . 83
5.2.3 Volumetric water content distribution in soil C 84
5.2.4 Volumetric water content distribution in soil D 87
5.3 Sorption Characteristics Results 93
5.3.1 Metal partitioning analysis 93

5.3.2 Heavy metals profiles in the pore fluid 94

5.3.2.1 Heavy metals concentrations in the pore fluid in soil C 94

5.3.2.1a Case of high input concentration . . 94

5.3.2.1.b Case of low input concentration . . 95

5.3.2.2 Heavy metals concentrations in the pore fluid in soil D 96

5.3.2.2a Case of high input concentration . . 96

5.3.2.2b Case of low input concentration . 97

5.3.3 Heavy metals sorbed profiles 103

5.3.3.1 Heavy metals sorbed profiles in soil C 106

5.3.3.1a Case of high input concentration . 106

5.3.3.1.b Case of low input concentration . 107

5.3.3.1 Heavy metals sorbed profiles in soil D 109

5.3.3.2a Case of high input concentration . 109

5.3.3.2b Case of low input concentration 110

5.4 Partitioning Coefficient Profiles (K_d) 119

5.5 Cations Migration and Redistribution 126

5.6 pH Distribution 146

5.7 Summary and General Discussion of Sorption Results 149

CHAPTER 6 156

COUPLED MOISTURE AND SOLUTE EQUATIONS FOR ONE DIMENSIONAL FLOW THROUGH UNSATURATED SOIL 156

6.1 Introduction 156

6.2 Assumptions 157

6.3 Coupled Moisture and Solute Diffusion Equations Development 157
6.4 Finite Difference Formulations 161
6.5 Determination of Diffusion Parameters and Unkown Materials Coefficients 165
6.6 Model Calibration 167
6.7 Initial and Boundary Conditions 174
6.8 Diffusion Coefficient 176
  6.8.1 Moisture diffusivity 176
  6.8.2 Solute diffusivity 176
  6.8.3 Solute moisture diffusivity 177
  6.8.4 Moisture solute diffusivity 177
6.9 Model Validation and Prediction 190
6.10 Summary 190

CHAPTER 7 197
SUMMARY AND CONCLUSIONS 197
7.1 Summary 197
7.2 Conclusions 203
7.3 Statement of Originality 204
7.4 Suggestions for Further Studies 205

CHAPTER 8 207
References 207

APPENDIX I 218

A Sample of Input and Output Data 218

APPENDIX II 228

Coupled Moisture and Solute Diffusion Parameters Determination Program . 228

LIST OF FIGURES

Figure 1.1 Soil Hydrologic Process 5

Figure 1.2 Schematic Representation of Clay Particles and Bounds 8

Figure 1.3 Sensitivity of Canadian Land to the Atmospheric Deposition of Acids. (Env. Canada 1988) 9

Figure 1.4 Schematic Representation of the Vadose Zone. 11

Figure 3.1 Schematic Diagram Showing Laboratory Leaching Cell 45

Figure 3.2 Schematic Diagram Showing Leaching Column Test Procedures 46

Figure 4a Dry Density-Water Content Relationship for Soil A (pH 9.5) . . . 61

Figure 4b Dry Density-Water Content Relationship for Soil B (pH 6.9) . . . 61

Figure 4.1 Particle Size Distribution for Soils A, B, C and D. 63

Figure 4.2 Results of Some Modified Atterberg Limits Tests 65

Figure 4.3 Liquid Limits Obtained with DW and 5000 mg/l Pb Solution 65

Figure 4.4 Cation Exchange Capacity 72

Figure 4.5 Exchangeable Cations 73

Figure 4.6 Solubles Cations 74

Figure 4.7 Specific Surface Area 76

Figure 5.1 Volumetric Water Content Distributions with Time and Distance in Soil B. 89

Figure 5.2 Volumetric Water Content Distributions with Time and Distance in Soil C:

(a) Lead 89

(b) Copper 90

(c) Zinc. 90

Figure 5.3 Volumetric Water Content Distributions with Time and Distance in Soil D for:
(a) Lead 91
(b) Copper 91
(c) Zinc 92
Figure 5.4 Migration of Pb, Cu, and Zn, (2500 mg/l input concentration)
(a) Soil C, Time: 52 hrs. 99
(b) Soil C, Time: 17.8 days 99
(c) Soil D, Time: 52 hrs. 100
(d) Soil D, Time: 17.8 days. 100
Figure 5.5 Migration of Pb, Cu, and Zn, (5000 mg/l input concentration)
(a) Soil C, Time: 52 hrs. 101
(b) Soil C, Time: 17.8 days 101
(c) Soil D, Time: 52 hrs. 102
(d) Soil D, Time:17.8 days. 102
Figure 5.6 Amount of Lead Retained as a Function of Time, Soil pH and Distance, (5000 mg/l input). 112
Figure 5.7 Amount of Copper Retained as a Function of Time, Soil pH and Distance, (5000 mg/l input). 112
Figure 5.8 Amount of Zinc Retained as a Function of Time, Soil pH and and Distance, (5000 mg/l input). 113
Figure 5.9 Amount of Lead Retained as a Function of Time, Soil pH and Distance, (2500 mg/l input) 113
Figure 5.10 Amount of Copper Retained as a Function of Time, Soil pH and Distance, (2500 mg/l input). 114
Figure 5.11 Amount of Zinc Retained as a Function of Time, Soil pH and and

Distance, (2500 mg/l input). 114

Figure 5.12 Amount of Heavy Metals Retained as a Function of Distance in Soil C, (5000 mg/l input):

(a) Soil C: Time 52 hrs. 115

(b) Soil C: Time 17.8 days 115

Figure 5.13 Amount of Heavy Metals Retained as a Function of Distance in Soil D, (5000 mg/l input):

(a) Soil D: Time 52 hrs. 116

(b) Soil D: Time 17.8 days. 116

Figure 5.14 Amount of Heavy Metals Retained as a Function of Distance in Soil C, (2500 mg/l input):

(a) Soil C: Time 52 hrs. 117

(b) Soil C: Time 17.8 days. 117

Figure 5.15 Amount of Heavy Metals Retained as a Function of Distance in Soil D, (2500 mg/l input):

(a) Soil D: Time 52 hrs. 118

(b) Soil D: Time 17.8 days. 118

Figure 5.16 K_d Profiles of Pb, Cu and Zn for Soil D, (2500 mg/l):

(a) Soil D: 52 hrs, input Concentration: 2500 mg/l 122

(b) Soil D: 17.8 days, input Concentration : 2500 mg/l 122

Figure 5.17 K_d Profiles of Pb, Cu and Zn for Soil D, (5000 mg/l):

(a) Soil D: 52 hrs, input Concentration: 5000 mg/l 123

(b) Soil D: 17.8 days, input Concentration : 5000 mg/l. 123

Figure 5.18 K_d Profiles of Pb, Cu and Zn for Soil C, (2500 mg/l):

(a) Soil C: 52 hrs, input Concentration: 2500 mg/l 124

(b) Soil C: 17.8 days, input Concentration : 2500 mg/l. 124

Figure 5.19 K_d Profiles of Pb, Cu and Zn for Soil C, (5000 mg/l):
(a) Soil C: 52 hrs, input Concentration: 5000 mg/l 125
(b) Soil C: 17.8 days, input Concentration : 5000 mg/l. 125
Figure 5.20 Migration of Calcium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Pb:
(a) Time: 52 hrs. 130
(b) Time:17.8 days. 130
Figure 5.21 Migration of Calcium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Pb:
(a) Time: 52 hrs. 131
(b) Time: 17.8 days. 131
Figure 5.22 Migration of Calcium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Cu .... .132
Figure 5.23 Migration of Calcium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Copper. 132
Figure 5.24 Migration of Calcium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Zinc .... .133
Figure 5.25 Migration of Calcium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Zinc. 133
Figure 5.26 Migration of Magnesium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Lead:
(a) Time 52 hrs. 134
(b) Time 17.8 days .... .134
Figure 5.27 Migration of Magnesium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Lead:
(a) Time: 52 hrs. 135

(b) Time: 17.8 days. 135
Figure 5.28 Migration of Magnesium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Copper 136
Figure 5.29 Migration of Magnesium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Copper 136
Figure 5.30 Migration of Magnesium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Zinc. 137
Figure 5.31 Migration of Magnesium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Zinc 137
Figure 5.32 Migration of Potasium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Lead:
(a) Time: 52 hrs. 138
(b) Time: 17.8 days 138
Figure 5.33 Migration of Potasium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Lead:
(a) Time: 52 hrs. 139
(b) Time: 17.8 days. 139
Figure 5.34 Migration of Potasium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Copper. 140
Figure 5.35 Migration of Potasium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Copper. 140
Figure 5.36 Migration of Potasium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Zinc. 141
Figure 5.37 Migration of Potasium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Zinc. 141

Figure 5.38 Migration of Sodium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Lead:
(a) Time: 52 hrs 142
(b) Time: 17.8 days. 142
Figure 5.39 Migration of Sodium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Lead:
(a) Time: 52 hrs. 143
(b) Time: 17.8 days 143
Figure 5.40 Migration of Sodium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Copper 144
Figure 5.41 Migration of Sodium as a Function of Soil pH and Distance for 2500 mg/l input of Copper. 144
Figure 5.42 Migration of Sodium as a Function of Soil pH and Distance for 5000 mg/l input Concentration of Zinc. 145
Figure 5.43 Migration of Sodium as a Function of Soil pH and Distance for 2500 mg/l input Concentration of Zinc 145
Figure 5.44 pH Distributions with Time and Distance in Soil B 147
Figure 5.45 pH Distributions with Time and Distance in Soil C 147
Figure 5.46 pH Distributions with Time and Distance in Soil D 148
Figure 6.1 Grid Points for the Implicit Finite Difference Formulation 162
Figure 6.2 Calibration Program Flow Chart 170
Figure 6.3 Volumetric Water Content Model Calibration for Soil D (5000 mg/l input concentration of Zn) 171
Figure 6.4 Volumetric Water Content Model Calibration for Soil D (5000 mg/l input concentration of Pb) 171
Figure 6.5 Volumetric Water Content Model Calibration for Soil D

(5000 mg/l input concentration of Cu) 172
Figure 6.6 Model Calibration for Retained Zinc Concentration (5000 mg/l input) 172
Figure 6.7 Model Calibration for Retained Lead Concentration (5000 mg/l input) 173
Figure 6.8 Model Calibration for Retained Copper Concentration (5000 mg/l input) 173
Figure 6.9 Moisture Diffusivity and Volumetric Water Content Variations with Distance (Zinc) 178
Figure 6.10 Moisture Diffusivity and Volumetric Water Content Variations with Distance (Lead) 178
Figure 6.11 Moisture Diffusivity and Volumetric Water Content Variations with Distance (Copper) 179
Figure 6.12 Moisture Diffusivity and Zinc Concentration Variations with Distance 179
Figure 6.13 Moisture Diffusivity and Lead Concentration Variations with Distance 180
Figure 6.14 Moisture Diffusivity and Copper Concentration Variations with Distance 180
Figure 6.15 Solute Diffusivity and Volumetric Water Content Variations with Distance (Zinc) 181
Figure 6.16 Solute Diffusivity and Volumetric Water Content Variations with Distance (Lead) 181
Figure 6.17 Solute Diffusivity and Volumetric Water Content Variations with Distance (Copper) 182

Figure 6.18 Solute Diffusivity and Zinc Concentration Variations with Distance 182

Figure 6.19 Solute Diffusivity and Lead Concentration Variations with Distance 183

Figure 6.20 Solute Diffusivity and Copper Concentration Variations with Distance 183

Figure 6.21 Solute Moisture Diffusivity and Volumetric Water Content Variations with Distance (Zinc) 184

Figure 6.22 Solute Moisture Diffusivity and Volumetric Water Content Variations with Distance (Lead) 184

Figure 6.23 Solute Moisture Diffusivity and Volumetric Water Content Variations with Distance (Copper) 185

Figure 6.24 Solute Moisture Diffusivity and Zinc Concentration Variations with Distance 185

Figure 6.25 Solute Moisture Diffusivity and Lead Concentration Variations with Distance 186

Figure 6.26 Solute Moisture Diffusivity and Copper Concentration Variations with Distance 186

Figure 6.27 Moisture Solute Diffusivity and Volumetric Water Content Variations with Distance (Zinc) 187

Figure 6.28 Moisture Solute Diffusivity and Volumetric Water Content Variations with Distance (Lead) 187

Figure 6.29 Moisture Solute Diffusivity and Volumetric Water Content Variations with Distance (Copper) 188

Figure 6.30 Moisture Solute Diffusivity and Zinc Concentration Variations with Distance 188

Figure 6.31 Moisture Solute Diffusivity and Lead Concentration Variations with Distance 189
Figure 6.32 Moisture Solute Diffusivity and Copper Concentration Variations with Distance 189
Figure 6.33 Predicted Volumetric Water Content for Soil D (5000 mg/l input concentration of Zn) 192
Figure 6.34 Predicted Volumetric Water Content for Soil D (5000 mg/l input concentration of Pb) 192
Figure 6.35 Predicted Volumetric Water Content for Soil D (5000 mg/l input concentration of Cu) 193
Figure 6.36 Predicted Zinc Concentration 193
Figure 6.37 Predicted Lead Concentration 194
Figure 6.38 Predicted Copper Concentration 194
Figure 6.39 Comparison between Predicted and Measured Volumetric Water Content (case of Zinc after 17.8 days) 195
Figure 6.40 Comparison between Predicted and Measured Volumetric Water Content (case of Zinc after 50 days) 195
Figure 6.41 Comparison between Predicted and Measured Heavy Metal Concentration Profiles (Case of Zinc after 17.8 days) 196
Figure 6.42 Comparison between Predicted and Measured Heavy Metal Concentration Profiles (Case of Zinc after 50 days) 196

LIST OF TABLES

Table 4.1 Geotechnical Properties of illitic Soil A 58

Table 4.2 Soil Physico-Chemical Characteristics of Soil A 59

Table 4.3 Soil Physico-Chemical Characteristics of Soil B, C and D 60

Table 4.4 Hydraulic Conductivity Test Results on Compacted Illitic Soils B. 67

Table 4.5 Hydraulic Conductivity Test Results on Compacted Soils C 68

Table 4.6 Hydraulic Conductivity Test Results on Compacted Soils D. . . . 68

Table 5.1 Analytical Saturated Volumetric Water Content. 83

Table 5.2 Summary of Volumetric Water Content Results for Illitic Soil at pH 4, (5000 mg/l input concentration). 85

Table 5.3 Summary of Volumetric Water Content Results for Illitic Soil at pH 4, (2500 mg/l input concentration). 86

Table 5.4 Summary of Volumetric Water Content Results for Illitic Soil at pH 3.5, (5000 mg/l input concentration). 87

Table 5.5 Summary of Volumetric Water Content Results for Illitic Soil at pH 3.5, (2500 mg/l input concentration). 88

Table 5.6 Percentage of Heavy Metal Sorption by Soil Region and Phase. Illitic Soil at pH 4, (5000 mg/l input concentration). 107

Table 5.7 Percentage of Heavy Metal Sorption by Soil Region and Phase. Illitic Soil at pH 4, (2500 mg/l input concentration). 109

Table 5.8 Percentage of Heavy Metal Sorption by Soil Region and Phase. Illitic Soil at pH 3.5, (5000 mg/l input concentration). 110

Table 5.9 Percentage of Heavy Metal Sorption by Soil Region and Phase. Illitic Soil at pH 3.5, (2500 mg/l input concentration). 111

LIST OF PUBLICATIONS

The following papers have been presented at scientific conferences during the course of this study:

1. M. Elzahabi and R.N. Yong and A.M.O. Mohamed, (1996), "The Effect of Soil pH on Heavy Metal Transport in the Vadose Zone". Presented at the Third Annual Civil Engineering Graduate Student Society Conference (CEGSS) at McGill University, Montreal, Quebec, Canada, February 29, 1996, pp.10-11.

2. M. Elzahabi and R.N. Yong, (1997), " Vadose Zone Transport of Heavy Metals", Proceedings of the First Geoenvironmental Engineering Conference organized by the British Geotechnical Society and the Cardiff School of Engineering, University of Wales, Cardiff, September 1997, pp. 173-180.

3. M. Elzahabi, (1999), " pH Influence on Sorption Characteristics of Heavy Metal in the Vadose Zone", Proceedings of the 2nd Geoenvironmental Engineering Conference on Ground Contamination organized by the British Geotechnical Society and the Cardiff School of Engineering, and held in London at the Institution of Civil Engineers, September 1999, pp. 255-263.

4. M. Elzahabi and R.N.Yong, (1999), "pH Influence on Sorption Characteristics of Heavy Metal in the Vadose Zone ". Engineering Geology (accepted).

5. M. Elzahabi and R.N. Yong, (2001), " A Numerical Determination of Coupled Moisture and Heavy Metal Transport Parameters in Partially Saturated Soil". Proceeding of the International Symposium on Suction, Swelling, Permeability and Structure of Clays in relation to Soil Contamination and Waste Disposal organized by the Japanese Geotechnical Society and held in Shizuoka, Japan, January 2001 (in revision).

6. M. Elzahabi and R.N. Yong, "Soil Acidification Effect on some Physico-Chemical Soil Properties in the Vadose Zone". Engineering Geology (in preparation).

CHAPTER 1

INTRODUCTION

1.1 General

Since the second world war, there has been an increasing threat of subsurface contamination. The growth of population, industrial and agricultural production increased the energy development requirements and began for the first time in man's history to produce quantities of wastes that are greater than that which the environment can easily adsorb (Freeze and Cherry, 1979). Problems also arise from our history of dumping wastes without regard for the serious environmental consequences that followed. In 1976, the problem of Love Canal, and others that arose from contaminant migration through soil, increased public awareness of environmental problems and became the major focus of investigation and research. In fact, concerns about the quality of air and surface water pollution, the safe disposal of waste materials and the pressure to reduce surface pollution has caused another threat to the groundwater. Deep well injection of liquid wastes and sanitary landfills for solid wastes disposal are two disposal techniques that are now being used to minimize the risk of soil and groundwater contamination. These two techniques can also cause subsurface pollution.

Heavy metals migration through the vadose zone is one of the most serious environmental problems and is a major topic of investigation and research worldwide. The heavy metals largely originate with the combustion of fossil fuels or from spills or uncontrolled dumping of solvents and wastes. The occurence of acid rain can influence the transport of these heavy metals through the vadose zone.

Chlopecka et al. (1996) supported the view of previous studies that metals derived from anthropogenic sources are more mobile than those from soil parent materials. For the last decade, acid deposition has occurred in many places in the north of United States and adjacent Canadian provinces and has become a major source of concern for many researchers as it continues to defile major areas of the planet. This deposition may indirectly affect human health by two main pathways, by a possible effect on drinking water quality and by the intake of trace elements in fish or crops. The impact on drinking water involves the potential of acidified waters to leach toxic metals such as lead, mercury, cadmium, aluminum and copper from the soil and water distribution system. CO_2 and other compounds in the atmosphere determine the initial pH value of raindrops. Acid rain occurs in areas of major industrial emissions of sulfur dioxide (SO_2) and the nitrogen oxides (NOx). These emissions are transformed into sulfate and nitrate particles and to sulfuric and nitric acids by combining with vapor after they are emitted to the atmosphere. They then return to the earth in the form of dew, drizzle, fog, snow and rain. Today, where heavy rainfalls predominate over wide areas of eastern North America and northern Europe, rain falls have a pH value close to 4, and occasionally to 3. The concern is related largely to the effects of acidity on the aquatic system, the potential damage to forests, and to the accelerated deterioration and the corrosion in most materials used in the construction of buildings, bridges, dams, industrial equipment, water supply networks, underground storage tanks, hydroelectric turbines and power and telecommunications cables. After entering the groundwater, acid rain increases the solubility of toxic metals such as lead and copper from water pipes (Hare et al., 1989; Elliot et al., 1986), and zinc, cadmium, mercury, iron and manganese, speeding their spread through the environment and polluting the groundwater system.

As rain percolates through the soil, its CO_2 content increases, increasing the amount of $CaCO_3$ the water can dissolve.

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2\ HCO_3^- \qquad (1.1)$$

The acidity can be neutralized by the presence of calcite and the by alkalinity in the ground water. If the acidity is greater than the alkalinity of the initial water, all the alkalinity will be consumed and acid water will result. Soil internal acidification processes have to be distinguished from external acid input to soils. Impact on soils can be divided into two complexes: loss of acid neutralizing capacity connected with the loss of nutrients like calcium (Ca), magnesium (Mg), and potassium (K), and the build up of a base neutralizing capacity connected with the protonation of exchange sites and the accumulation of cation acids such as aluminum (Al), manganese (Mn), and iron (Fe), together with sulfate.

After chemicals are introduced into the terrestrial environment, they can move by different paths and mechanisms: by runoff, errosion to the aquatic environment, by volatilization to the air environment, and by leaching to the ground, (Figure 1.1). The basic problem of hazardous waste arises from the movement of the leachate, caused by the infiltration and precipitation of rain water and surface runoff into the buried waste. The latter will migrate slowly from its storage facilities through the unsaturated or vadose zone and create environmental contamination

In September 1993, new regulations were proposed in the U.S. under the Resource Conservation and Recovery Act (RCRA) under subtitle D for solid waste landfills. New guidelines generally require the adoption of a composite geomembrane/compacted clay soil liner, a leachate collection system and a landfill cover that is no more permeable than the bottom liner (Rowe, 1993). The USEPA guidance document specifies that all liner systems should be constructed in unsaturated soil. Compacted barriers of local clayey soil can be composed of kaolinite, illite, chlorite, vermiculite or smectite clay, either locally weathered or deposited (Quigley, 1993). A coefficient of permeability no greater than 10^{-7} cm/sec is specified for natural or recompacted soil liners and a permeability of not less than 10^{-2} cm /sec for leachate collection layers.The low hydraulic conductivity and the high adsorption have led to the use of clay materials as a barrier to prevent the migration of contaminants from waste disposal. In addition to hydraulic conductivity, which is the major concern in choosing the barrier material, diffusion is one of the most important factors that may significantly affect the migration rate of leachate through barriers. Waste can migrate through clay barriers via molecular diffusion, even with the absence of a hydraulic gradient (Shackelford,1988).

Traditionally, the design and construction of an earth liner relied on soil properties such as density, moisture content and permeability. Recently, development has shown that other factors should be considered to guarantee a satisfactory design. These include macro structure features, soil fabric, mineralogical composition, compaction effort, weathering conditions, fluid removal, and collection efficiency. Design should concentrate on how to prevent the waste liquid migration, and should consider mineralogical, chemical and physical properties of the constructed materials of the barrier, the chemical and physical nature of the contained wastes, the hydraulic conditions and the performance criteria required to meet standard regulations (Oakley, 1987). Viscosity, pressure, density, soil properties (such as tortuosity, void ratio, soil-water potential, pore size distribution, fabric, composition mineralogy and soil structure) and soil-water

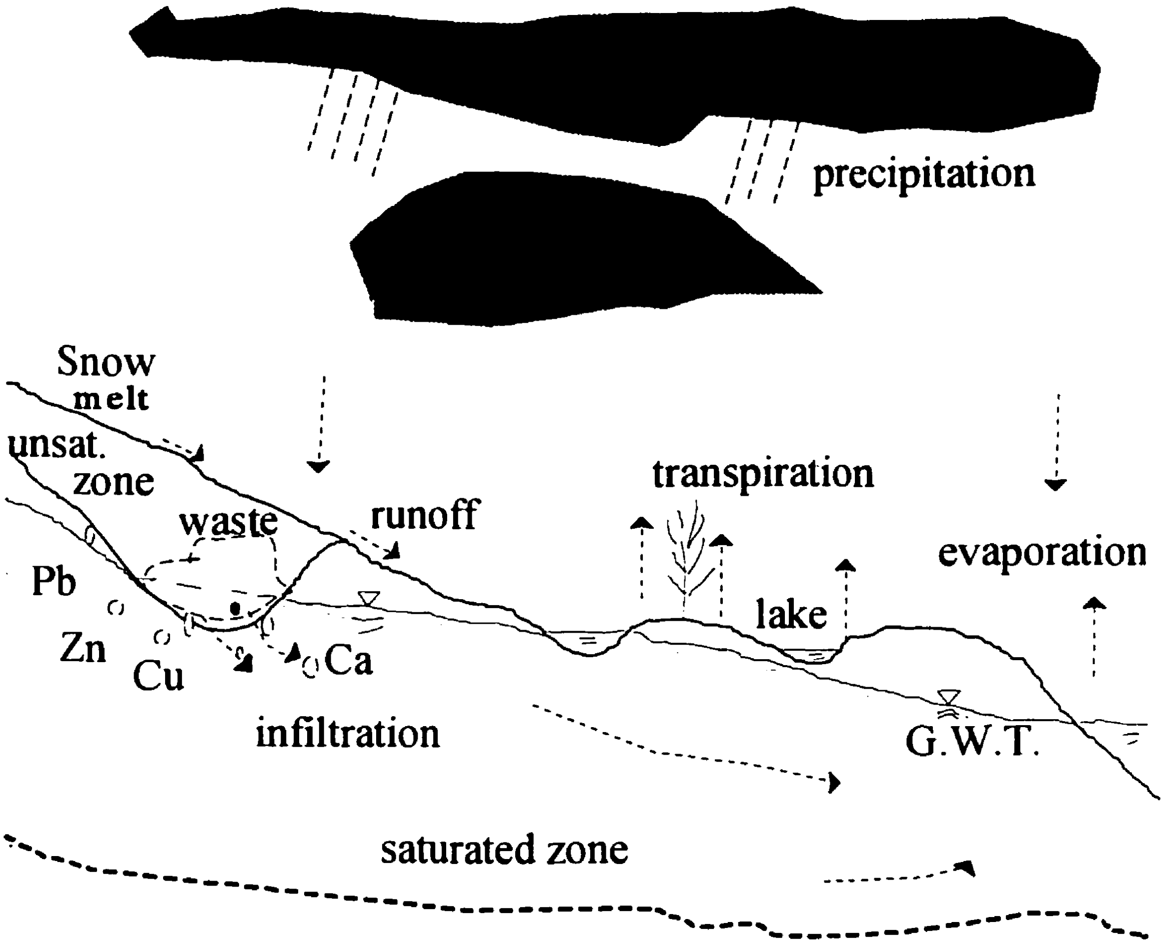


Figure 1.1 Soil Hydrologic Process

interactions (heat of wetting, ionic concentration, thickness of layers of water held to soil particles) are all factors associated with the forces holding water to soil and clay-water interaction (Yong et al., 1992a).

1.2 Statement of the Problem

The problem that this research addresses is that the transport of heavy metals through the vadose zone can not be accurately quantified. Consequently, the hazard associated with the deposition of heavy metals, through acid rain or through landfill leaching or surface spills of contaminants, is not fully understood. In particular, the transport of heavy metals through the vadose zone at an acidic pH, is at present only poorly understood. It is possible that heavy metals may accumulate in the vadose zone, only to be released in great quantity to the saturated zone once a sufficiently acidic soil pH is reached. This would result in delayed and unexpected water contamination. This thesis experimentally investigates heavy metal transport through the vadose zone at varying pH and at two contaminant concentrations, and derives a theoretical model of the process.

Cheremisinoff et al. (1979), estimated that 90% by weight of hazardous wastes are liquid products with the ratio of 60% organic and 40% inorganic. Usually, heavy metals found in sludge and landfill leachates are highly toxic to humans, animals and aquatic life. The most common heavy metals found in leachate solution are lead (Pb), copper (Cu), zinc (Zn), cadmium (Cd), chromium (Cr) and nickel (Ni). The concentration of these heavy metals varies from 0-100 ppm in municipal solid waste leachate to 100-10,000 ppm in sewage sludge, mining wastes and various industrial wastes (Yong and Di perno, 1991). Their solubility is highly pH dependent and increases with the decrease in the soil pH. The same is true for sorption of heavy metals in soil minerals. Since both translocation of heavy metals as well as the uptake by most soil organisms require that the metal be in the solution phase, the influence of acidification on the cycling of metals, and their transfer to aquatic systems is of primary importance. Moreover, several studies have shown that soil pH is an important factor in the fate of heavy metal retention and transport in soil. The migration of low pH leachate through the soil will affect the soil pH and the sorption of heavy metals in the soil (Yong et al., 1990e; Mohamed and Yong, 1993; Elzahabi and Yong, 1997). Mannings et al. (1996) examined the effect of acid deposition regimes on soil acidification and metals mobilization.

Movement of chemicals in the ground is primarily a liquid phase process involving the movement of water and dissolved solutes. Chemicals that are not sorbed will exist primarily in the dissolved phase and their movement in the ground water will be controlled by the relative amount of water, and by soil processes. Soil is an excellent adsorbent for both organic and inorganic chemical compounds. The major adsorbing surfaces in soil are clay particles and organic matter. The interactions between contaminants and soil fractions can be expected to influence the physical and physico-chemical behaviour of the material.

Natural soil consists of clay particles, sand and silt particles. These are bonded together by many bonds such as amorphous, organic and carbonate bonds, (Figure 1.2). Carbonates are one of the most important inorganic bonding materials holding particles together at field water content. The presence of calcium carbonate in natural soil increases the soil buffering capacity and its ability to retain heavy metals (Yong et al., 1992a).

Records by Jeffries (1991) show that 43% of Canada's land and 82% of Quebec's land are classified as highly sensitive to the atmospheric deposition of acids, having noncarbonated bedrock and low potential for neutralizing precipitation acidity. The permeation with acid in clay soils decreases their pH and increases their hydraulic conductivity and may be explained by three mechanisms: flocculation

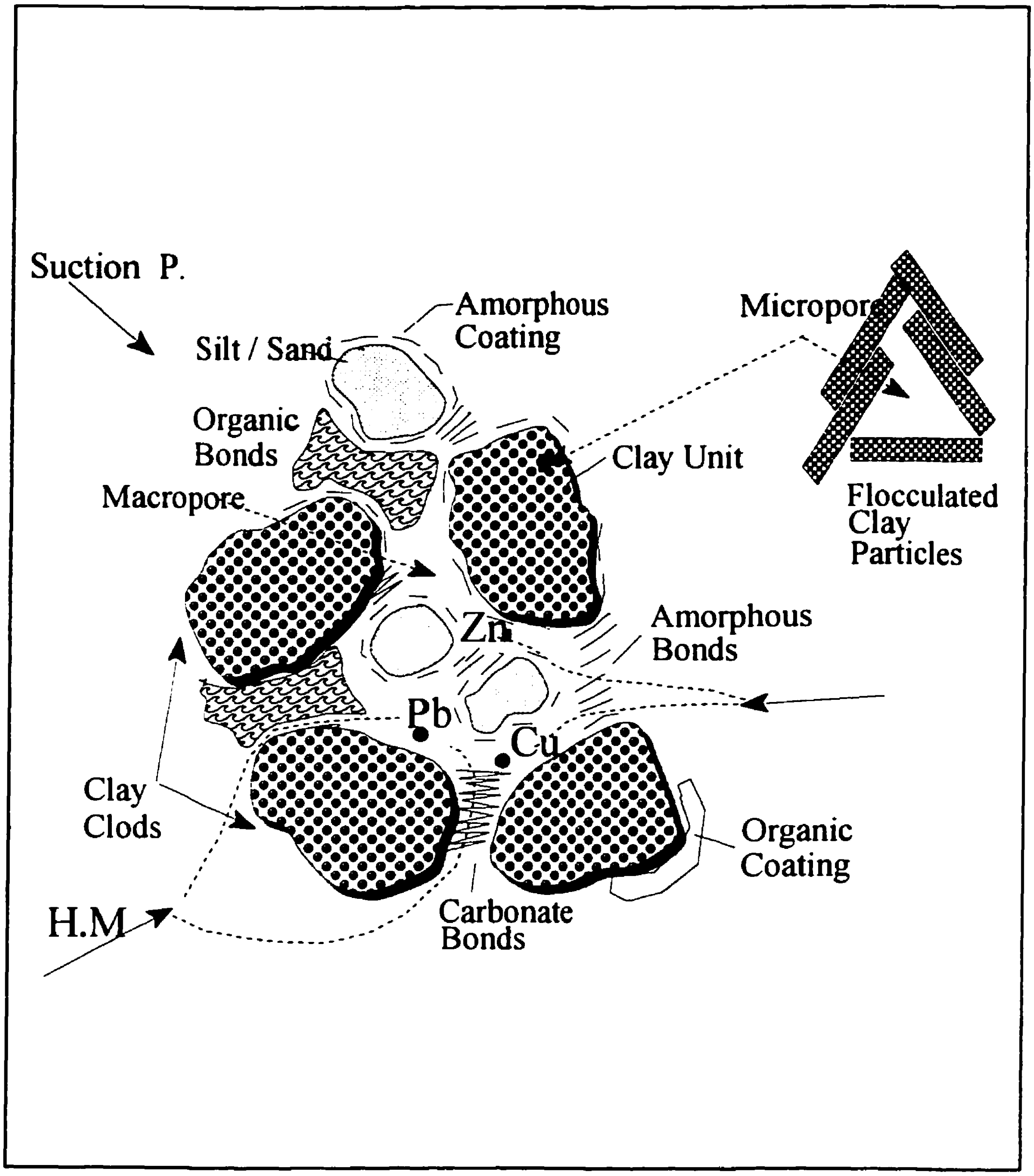


Figure 1.2 Schematic Representation of Clay Particles and Bonds

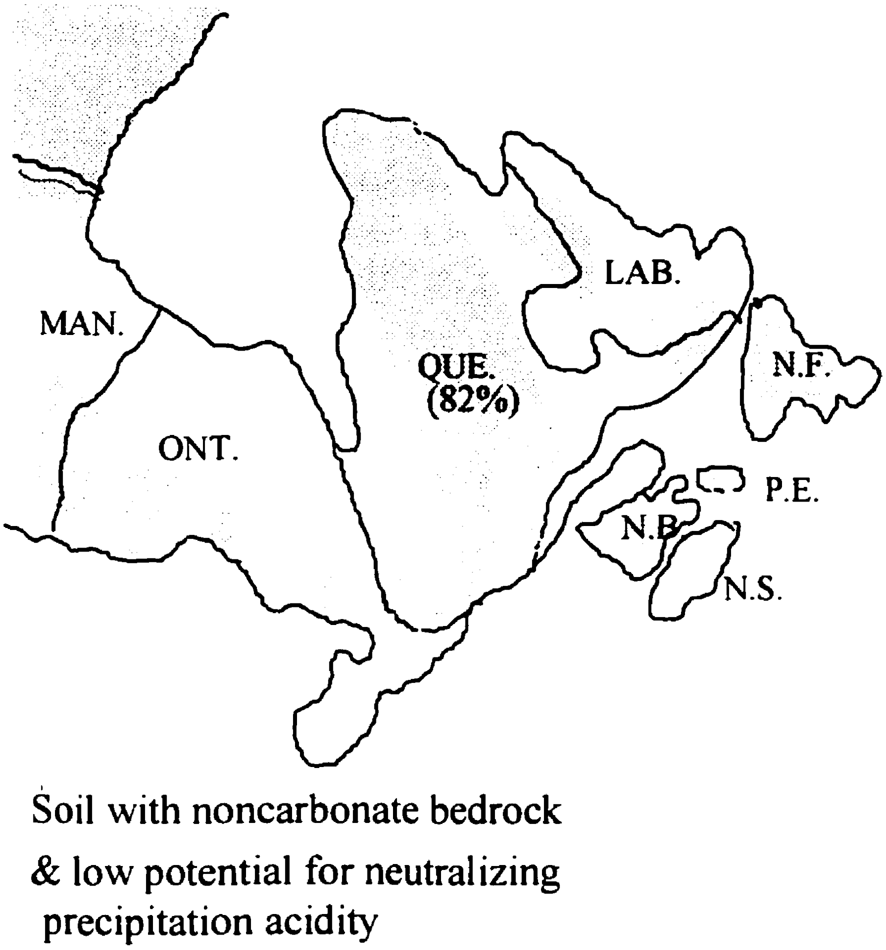
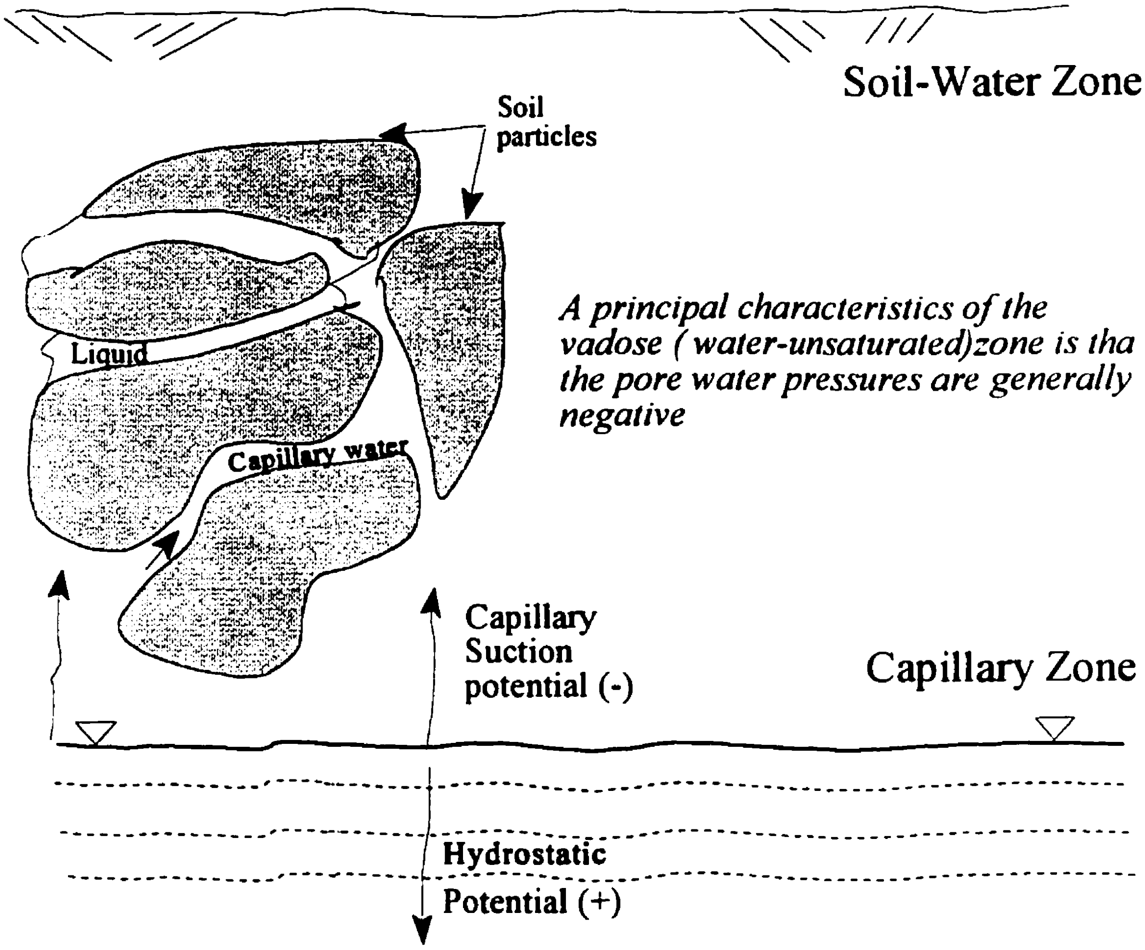


Figure 1.3 Sensitivity of Canadian land to the Atmospheric Deposition of Acids. (Env. Canada, 988).

of clay, dissolution of clay minerals (aluminosilicates) and dissolution of other minerals such as carbonates ($CaCO_3$, $CaMg(CO_3)_2$) and nitrates ($Ca(NO_3)_2.4H_2O$. Dissolution of minerals may increase the hydraulic conductivity. Buffering, re-precipitation, pore clogging and a decrease in hydraulic conductivity are initially due to the dissolution of carbonates. Depletion of the buffering capacity decreases the soil pH, dissolves the soil constituents and may increase the hydraulic conductivity, Shackelford (1994). Clay minerals are negatively charged and surrounded by hydrated cations called a double-layer of water. Any chemical changes that will contact the double layer and open this reference pore will increase the hydraulic conductivity of the barrier unless it physically consolidates in the presence of insitu-field stress. The higher the specific surface area and cation exchange capacity, the greater the amount of bound water and the lower the hydraulic conductivity (Quigley, 1993).

Sorption and diffusion can be considered as the principal mechanisms in predicting migration rates and contaminant fluxes through fine-grained soils used as barriers to the migration of contaminants. Sorption characteristics and diffusion parameters of saturated soils have been extensively studied, while little is known about unsaturated soils (vadose zone). The vadose zone cannot be ignored in the study of contaminant movement because it may be a significant reservoir for capture, storage and release of contaminants to the ground. Where soil is present, the movement of water is largely controlled and may be prevented from continued movement by factors of attraction, the so-called internal gradients (such as capillary and osmotic or adsorption) developed by forces within the soil. Theoretically, water infiltration to the underground is due to gravity effects when all the pores in the soil are filled with water. Thus, the transport of contaminants will be tied more closely to water movement and the diffusion of contaminants will be seen to be dependent on the water content of the soil and various characteristics and properties that control the internal gradients. Part of this zone may be saturated and may contain several important subdivisions although the term unsaturated soil is often used to refer to the vadose zone. There are three major subdivisions, soil water or root zone which lies between the ground surface and the maximum depth



A principal characteristics of the vadose (water-unsaturated)zone is tha the pore water pressures are generally negative

Figure 1.4 Schematic Representation of the Vadose Zone to which roots penetrates, intermediate zone contains a residual moisture determined by the capillary and osmotic potential and capillary fringe where this zone marks the final transition between the vadose and the saturated zone. A principal characteristic of the vadose zone (water-unsaturated) zone is that the water is held by capillary and adsorption forces and the pore water pressures are generally negative while the water present below the phereatic surface creates a positive hydrostatic pressure. So, the mechanisms and processes governing the transport of inorganic chemicals through saturated soils are also relevant for unsaturated soils. The key difference between them lies in the definition of the transport parameters (Lim et al., 1995).

Various theoretical models describing contaminant movement in the soil based on a saturated system have been reviewed by many researchers such as Anderson (1979), Gillham and Cherry (1982), Rowe (1987), Yong and Warith (1990), Yong and Samani (1987), Yong et al. (1990b). The majority of these models are either advective (neglecting dispersion) or advective-dispersive. Various test methods of one dimensional diffusive transport in saturated clayey soil have been reviewed and studied theoretically and experimentally by many researchers such as Barry (1993), Cooke (1993), Rowe (1988), Airey (1993), Yong et al. (since 1985), Best et al. (1993), Barone (1993), and Shackelford (1988).

The migration of heavy metals through unsaturated clay barriers has received little attention, and models describing the movements of contaminants in unsaturated soil are very few. Yong et al. (1994) studied the affect of soil composition on the migration of heavy metals and showed that the addition of Champlain sea clay to the clay liner material improved its performance. Lim et al. (1995), studied the effect of degree of saturation on the sorption characteristics of potassium chloride in sandy and silty soils, in controlled diffusion tests, and related the factor causing the decrease of adsorption to a discontinuity in the liquid phase. The effect of degree of saturation on the diffusion coefficient has also been studied by Porter et al. (1960). Van Genuchten and Wierenga (1976) developed a theoretical model for unsaturated soil by using the concept of mobile and immobile water and assumed that all sites were available without considering the possibility of the discontinuity of the liquid phase. Silvestri et al. (1994) modeled the variation of water content in clay deposits. Yong et al. (1990a, 1990c, 1990d, and 1994) developed a transport model to predict coupled heat and moisture flow in unsaturated clay-based materials. Badv and Rowe (1996) examined the migration of chloride and sodium through an unsaturated stone collection layer underlying a compacted clay liner and reported low Darcy velocities and due to the very low volumetric content, this layer could serve as an effective barrier.

Sorption is an important process in the modelling and prediction of movement of heavy metals in unsaturated clay barriers. Although liner systems are constructed in unsaturated (vadose) soil, most researchers have studied the sorption and transport of leachate under saturated conditions while ignoring the effect of the initial insitu soil saturation under acidic conditions. The existance of naturally acidic soils and pollutant laden acid rain makes the transport of heavy metals in the vadose zone an important field of investigation. The degree of water connectivity between the various soil pore classes strongly impacts the hydrologic flux and the mass transfer of contaminants in the system. Contaminant migration from shallow land barrier sites is confined to micropores (matric) regions and most frequently involves unsaturated transport processes unless perched water tables or downslope convergent processes are prevelant, Jardine et al., 1993. During unsaturated conditions, coupled processes of solute and hydrologic factors control the subsurface transport of contaminants. The extent to which these coupled processes control the movement of contaminants in the vadose zone is largely unkown and questionable in many situations.

Sorption data are needed to determine the transport properties of the soil with respect to the contaminants under consideration. Test data permits one to calculate the partition coefficient K_d required in the contaminant transport equations. Most transport models use K_d obtained from 'linear' adsorption isotherms – i.e. as a constant parameter (Freeze and Cherry, 1979; Rowe, 1988). Simplification of (K_d) as a constant and linear function may lead to an improper evaluation of the adsorption/desorption phenomena. " Although it is well recognized that the partitioning coefficient can play a crucial role in controlling the rate mass transfer through saturated soils and has been extensively investigated, there is an unfortunate dearth of information on the effect of partial saturation on the partitioning coefficient," (Fityus et al., 1999). Davidson et al. (1976) concluded that at high concentrations, the assumption of a linear isotherm can lead to serious errors in predicting contaminant migration. "Although the convenience of the approach is beyond dispute, its validity as a means of developing reliable predictions of the behaviour of inorganic contaminants in actual ground water systems is questionable in many situations," (Cherry et al., 1984).

The partition coefficient reflects the degree of retardation by reversible ion exchange, and may also include the effects of solute adsorption. Batch equilibrium tests used for determination of adsorption isotherms utilize small portions of soil and representative contaminants. The problems arising therefrom relate to the question of whether or not a small quantity of totally disturbed soil is appropriate to simulate the field conditions or situations, and the variability of K_d from one soil to another. The batch technique does not necessarily reflect actual leachate soil interaction. The ratio of solution to soil and the time required to attain equilibrium does not always give a good estimate of the migration and adsorption of heavy metals through the clay barrier, (Darban, 1997). Sorption characteristics obtained from leaching column tests provide a better means for evaluation of soil sorption performance. The results obtained include the effects of partial soil saturation, and effective exposed surface area of the soil system.

Besides the partitioning coefficient, the diffusion of heavy metals in unsaturated soil is also highly dependent on the moisture content or the degree of saturation. However, most existing transport models use an average diffusion coefficient without considering the degree of saturation in order to predict the movement of heavy metals along the soil column. Simplification of the diffusion coefficient as a constant and of the degree of saturation as a linear function cannot be considered a good assumption and may lead to an improper evaluation of the sorption phenomenan in the vadose zone and also to serious errors in predicting contaminant migration. Therefore, "an adequate characterization of moisture content dependence of the diffusion coefficient is essential for realistic modelling of diffusive mass transport through the unsaturated zone," (Fityus et al., 1999).

Given that most containment situations show transport from source contamination through the vadose zone prior to saturated zone transport, and since contaminant plume arrival at the saturated layer is not a desirable goal, it becomes necessary to seek management control of a contaminant plume in the vadose zone. Another significant reason for the need to study vadose zone transport is the fact that the "initial conditions" established at the saturated zone interface will be considerably affected by vadose zone results, thereby impacting directly on the success of models designed to predict transport in the saturated zone. Analysis and prediction of coupled solute and moisture flow through unsaturated clay barriers, needs to be based on the dependence of diffusion and sorption characteristics on the degree of saturation or moisture content along the soil depth. Also, there are other factors which should be considered in heavy metals (H.M.) transport in the vadose zone, such as the presence of carbonate, the soil pH and the influent H.M. concentration. Then, a new method that describes the full coupling effects of solute and moisture on transport coefficients based on experimental evidence and applied to the unsaturated transport theory is needed to predict the rate of transport of heavy metals through the unsaturated soil in a pH-controlled environment.

1.3 Objectives of the Present Study

The objectives of this study on unsaturated soil-contaminant interaction is, therefore, to develop a method that describes the full coupling effects of solute and moisture on transport coefficients based on experimental evidence and applied to the unsaturated transport theory, with particular attention to the effect of degree of saturation, the presence of carbonate, soil pH and heavy metals concentrations. In addition, coupled solute and moisture transport parameters of heavy metals in unsaturated clay soil as a function of time and space will be evaluated and predicted based on the proposed method.

1.4 Tasks

The aforementioned objectives are accomplished through combined experimental and numerical studies. The information obtained from the experiments is used to provide a method that describes the full coupling effects of solute and water on transport coefficients based on experimental evidence and applied to the unsaturated transport theory.

To achieves the above objectives, the following tasks are performed :

1- A series of geotechnical and geochemical tests before and after soil acidification were used to investigate the effect of the soil pH and the presence of carbonate on soil properties and heavy metal transport in unsaturated illitic soil.

2- Laboratory evaluation of heavy metal migration using one dimensional solute and moisture flow (leaching column) tests using different heavy metal (such as lead, copper and zinc) permeants, were conducted on an unsaturated illitic soil at varying pH values in order to determine the migration and retention profiles of contaminants along the soil column for each layer in the soil column along with the partitioning coefficients. This provides the experimental information necessary for a numerical analyses structured to account for vadose zone transport of heavy metals, with particular attention to the effect of degree of saturation, the presence of carbonate, soil pH and heavy metals concentrations.

3- The migration profiles of cations (such as: calcium, magnesium, potassium and sodium) were determined through the soil column after leaching to investigate the role of the coupling effects of solute and moisture transport of heavy metals on the migration and the redistibution of the existing cations along the soil column.

4- Prediction of coupled solute and moisture transport of heavy metals in unsaturated clay soil as a function of time and space, involves the application of a computer code called Diffusion Parameter Determination Program (DPDP) in unsaturated soil developed by Yong et al. 1994, which was modified and developed by the author to accommodate this particular research and called Coupled Moisture and Solute Diffusion Parameter Technique (CMSDPT). The theory of irreversible thermodynamic, Fick's law, Darcy's law and equilibrium mass transfer principles are appllied according to Yong et al. (1992a). The diffusion parameter is calculated for each individual layer in the soil samples using Powell's optimization technique and the implicit finite difference method to solve the coupled diffusion equations. Volumetric water content and solute concentration as a function of space and time were predicted using the calculated diffusion parameters. Predicted and measured volumetric water content and contaminant concentration profiles were compared to validate the new method.

1.5 Organization of the Thesis

This thesis consists of seven chapters, two appendices and references arranged as follows:

Chapter 1	is an introductory chapter which explains the present problems, objectives and the methodology of the present study.
Chapter 2	provides a review of the physical and chemical mechanisms that affect the sorption and the transport of solutes through saturated soils and also presents a review of previous studies on coupled solute and moisture flow in unsaturated soils.
Chapter 3	describes the experimental methods, materials and testing procedures used in the coupled moisture and solute flow study.
Chapter 4	presents the soil geotechnical and geochemical test results and a discussion of all experiments described in chapter 3.
Chapter 5	investigates experimentally the effect of pH changes in the acidic range on the adsorption characteristics of heavy metals in unsaturated soil under isothermal conditions as a function of space and time.
Chapter 6	contains a new method that describes the full coupling effects on transport coefficients based on experimental work and applied to

the unsaturated transport theory and presents the diffusion parameter variations with coupled moisture and solute flow.

Chapter 7	includes summaries, conclusions, and contributions to knowledge with suggestions for further studies.

References

Appendix I	a sample of Input and Output Data.
Appendix II	provides a listing of the computer program used to determine the unknown coefficients of coupled moisture and solute flow equations.

CHAPTER 2

LITERATURE REVIEW

2. 0 Introduction

The following is a brief review of most contaminant transport processes and models in the vadose zone in order to determine the physical and chemical mechanisms and potentials that affect the sorption and the transport of solutes through unsaturated soil.

2.1 Physical Transport Mechanisms Through Clayey Soils:

Recently, considerable interest and attention have been directed to dispersion phenomena in flow through porous media. For one dimensional flow and constant average velocity through the length of the flow field, Banks and Ogata (1961) established a direct method to solve the differential equation governing the process of dispersion, assuming that the porous medium is homogeneous and isotropic and no mass transfer occurs between the solid and liquid phase. It was assumed that the solute transport, across any fixed plane, may be quantitatively expressed as the product of a dispersion coefficient and the concentration gradient. due to macroscopic velocity variations in the flow tubes.

The flow regime is governed by two processes: advection and dispersion.

The process by which the solutes are transported in response to a gradient in the total hydraulic head, is called advection. Due to advection, non reactive solutes or solutes which are not subjected to chemical or biological reactions, are transported at an average rate equal to the seepage velocity of the fluid, which is equal to Darcian velocity divided by the porosity .

Spreading and mixing of the solute resulting from molecular diffusion and pore velocity variations is called dispersion. The latter consists of two components: mechanical dispersion, which can be attributed to seepage velocity, and diffusion which is mixing due to spatial and temporal variations in concentration.

Diffusion is a transport process in which chemical species in solution (i.e.solute) flow in response to a hydraulic gradient in their concentration, Shackelford (1988), Yong et al. (1992a), Barone (1993). Diffusion refers to the movement of contaminants through the pore space in response to a gradient in the dissolved concentration (after Barone, 1993). It is always directed from high concentration to low concentration. The magnitude of the diffusion coefficient decreases with increasing hydrated radius, charge and concentration of the species themselves and the co-diffusion species (i.e., valence, concentration), as well as with increasing pore water viscosity.

Several studies performed by Desaulniers and Cherry (1989), Shackelford (1988), indicate and conclude that molecular diffusion tends to be the dominant mechanism of solute transport in fine grained soils.

Diffusion is only significant at relatively low seepage velocities and can be illustrated by break through curves (relations between concentration, C/C0 and time). Shackelford (1988) showed that at low velocities the effect of diffusion is not masked by the effects of advective and mechanical dispersion, and causes breakthrough of contaminants much earlier than would be predicted by assuming advective flow.

For most contaminant migration problems dispersion is a significant mechanism which should be considered, whether as diffusion through fine grained soils, or as predominantly mechanical mixing in coarse grained soils (Rowe,1987).

2.2 Contaminant Transport Processes and Models

2.2.1 Darcy's law and fluid flow in unsaturated soil

The movement of water in soils is a complicated phenomenon to describe due to the interaction of soil surfaces with water being transferred, and the changes of soil during the water movement process. Water movement in soils may be divided into two systems:

- The most common flow condition is the unsaturated flow or the partly saturated system where both air and water are present and the water is at negative potential. The mechanism for moisture transfer will depend upon whether the system is relatively dry or wet.
- The saturated system where all the voids are filled with water and the water is under zero or positive potential.

Factors associated with the forces holding water to soils, and clay-water interaction are: viscosity, pressure, density, soil properties such as turtuosity, void ratio, soil-water potential, pore size distribution, fabric and soil water interactions such as heat of wetting, ionic concentration, thickness of layers of water held to soil particles.

Unsaturated flow occurs when water and air are present in the voids. The biggest difference between saturated and unsaturated flow is the hydraulic conductivity. When the soil is saturated, all pores are filled and conducting, so conductivity is maximum. When the soil becomes dry or unsaturated, some of the pores become airfilled and the conductive portion of the soil cross section area decreases correspondingly. The value of the hydraulic conductivity is no longer constant and decreases rapidly with a decrease in the water content or the negative soil water potential. The rapid decrease of hydraulic conductivity with decreasing water content results from the large pores emptying first when the soil becomes unsaturated (Yong and Warkentin, 1975).

The equation most commonly used to describe steady soil-water movement is Darcy's law. Darcy (1856) presented a similar empirical relation to Fick's first law between the volume of fluid (water) passing through an area of porous media over time, the solute flux (specific discharge, or Darcy's velocity) and the total head gradient. His law is valid for two conditions:

- Flow rate is directly proportional to hydraulic gradient.
- Relationship between flow rate and hydraulic gradient is linear through the origin.

$$v = \frac{Q}{A\ t} = -k\frac{\delta h}{\delta x} = -k\ i \qquad (2.1)$$

Q is the volume of water [L^3], A is the cross sectional area through which the flow moves [L^2], t is the time of flow [T], v is the flow velocity of the solute flux or specific discharge [$L\ T^{-1}$], h is the hydraulic head [L], x is the coordinate, i (h/x) is the hydraulic head or hydraulic gradient and k is a constant, usually termed the coefficient of permeability by geotechnical engineers and the hydraulic conductivity by others concerned with flow through porous media [$L\ T^{-1}$]. The negative sign indicates that the water flows in the direction of a decreasing potential or hydraulic head.

In the case where the properties of water affecting are included, the equation of permeability can be written as follows:

$$v = - k' \frac{\gamma g}{\mu} i \qquad 2.2$$

where k' is the intrinstic permeability, g is the gravity, γ is the density of fluid and μ is the viscosity of fluid.

Hydraulic conductivity k, is a measure of the resistance of the soil to the flow of water. It was observed that the rate of water flow through a soil mass is proportional to the hydraulic head gradient. Darcy's law is based on the steady flow of pore fluid through soils and is determined by measuring the discharge from a column of soil. An underlying assumption of this average flow is that the fluid flow is steady and the velocity variations that exist within and on the scale of pore spaces make no significant contribution to the average flow rate. This is the basis of the equations principally used in groundwater investigations and predictions.

According to Buckingham (1907), Richards (1931), Childs and Collins-George (1950), Klute (1952) and Yong and Warkentin (1975), Darcy's law also applies for the flow of water through unsaturated soil. In order to confirm the application of Darcy's law in unsaturated soils, experimental results by Childs and Collins-Georges (1950) showed that the rate of water flow through an unsaturated soil is linearly proportional to the hydraulic head gradient, which is similar to the situation for a saturated soil with the coefficient of permeability being constant. Childs (1969), indicated that the derivation of the fluid-flow equation shows the validity of Darcy's law at low flow velocities of water in soil.

Unsaturated flow can be classified into three general types:

1- No change in soil fabric (pore geometry, porosity)

2- Change in soil fabric during flow but no change in porosity

  a) Non swelling soil

  b) Swelling soil

3- A complete change in fabric, change in pore geometry and porosity and volume change in soil.

Considering the case of unsaturated equations for no volume change, the unsaturated flow is generally described by an equation analogous to the heat-flow equation. By considering the validity of Darcy's law and replacing the hydraulic gradient, grad h, with the soil water potential gradient, (grad, div, δ/δx, or ∇)ψ, and for one dimensional unsaturated flow where the two parameters k and D are used, Darcy equation can be written as:

$$v = - k \nabla\psi \qquad (2.3)$$

Where v is the vector velocity.

$$\nabla\psi = (\frac{\delta}{\delta x} i)\psi \qquad (2.4)$$

By applying the continuity equation which states that the flow of water into or out of a unit of soil equals the rate of change in water content:

$$\frac{\delta v}{\delta x} = - \frac{\delta\theta}{\delta t} \qquad (2.5)$$

where θ is the volumetric water content and:

Substituting equation 2.5 into 2.3 yields a general one-dimentional diffusion equation.

$$\nabla \, v = \left(\frac{\delta}{\delta x} \, i\right) . \, v \tag{2.6}$$

Thus:

$$\frac{\delta}{\delta x} \, (k \, \nabla \psi) = \frac{\delta \theta}{\delta t} \tag{2.7}$$

$$v = - \, K(\theta) \, \frac{\delta \psi}{\delta x} \tag{2.8}$$

$$v = - \, K(\theta) \, \frac{\delta \psi}{\delta \theta} \, \frac{\delta \theta}{\delta x} \tag{2.9}$$

$$v = D(\theta) \, \frac{\delta \theta}{\delta x} \tag{2.10}$$

For horizontal water flow and where the gravity potential is zero, ψ_g, and by assuming only a matric potential which is a unique function of volumetric water content, θ, where x is the horizontal coordinate axis:

$$\frac{\delta \theta}{\delta t} = \frac{\delta}{\delta x} \left(k \, \frac{\delta \psi}{\delta \theta} \, \frac{\delta \theta}{\delta x}\right) \tag{2.11}$$

Then, the solution of the above equation is facilitated by introducing the diffusion coefficient of water D(θ), where, the diffusivity resulting from the definition described below:

$$D(\theta) = k(\theta) \frac{\delta\psi}{\delta\theta} \tag{2.12}$$

makes the equation analogous to those describing thermal diffusion.Yong and Warkentin (1975).

Thus, the general diffusion equation for one dimensional horizontal unsaturated flow can be simplified as:

$$\frac{\delta\theta}{\delta t} = \frac{\delta}{\delta x}(D(\theta) \frac{\delta\theta}{\delta x}) \tag{2.13}$$

2.2.2 Ficks law and solute transport

Fick (1855) is credited with the earlier mathematic description of diffusion theory which is an empirical relationship between the amount of solute mass passing through an area of a solution in a particular time interval and the solute concentration gradient. The proportionality coefficient defined is called the coefficient of molecular diffusion and the relationship or the fundamental equation for one dimensional diffusion transport which is Fick's first law of diffusion, is usually expressed as:

$$J_C = - D_0 \frac{\delta C}{\delta x} \quad [M_s L^{-2} T^{-1}] \tag{2.14}$$

where J_C is the chemical species transport rate per unit cross-sectional area, or diffusive mass flux $[M_s L^{-2} T^{-1}]$, D_0 is the coefficient of molecular diffusion $[L^{-2} T^{-1}]$, C is the chemical species concentration $[M_s L^{-3}]$, and x is the space coordinate [L].

Fick's first law describes steady state diffusion of a solute in a vessel of constant cross-section and for an invariant diffusion coefficient.

For a system with constant volume, Fick's second law can be derived from the first one by invoking the principle of mass conservation , and is written as:

$$\frac{\delta C}{\delta t} = D_0 \frac{\delta^2 C}{\delta x^2} \quad [M_s \, L^{-3} \, T^{-1}] \tag{2.15}$$

According to Fick's second law the diffusive transport equation :

$$\frac{\delta C}{\delta t} = D \left(\frac{\delta^2 C}{\delta x^2} + \frac{\delta^2 C}{\delta y^2} + \frac{\delta^2 C}{\delta z^2} \right) \tag{2.16}$$

Diffusive transport of contaminant in soil and how to find D:

D_0 = effective molecular diffusion coefficient which is considered constant.

In dilute solutions of a single ionic species, the infinite solution diffusion coefficient D_0 can be expressed in three different equations:

Nernst-Einstein :

$$D_0 = \frac{uRT}{N} = uk'T \tag{2.17}$$

Nersnt:

$$D_0 = \frac{RT\lambda_0}{\zeta^2 |z|} = 8.928x10^{-10} \frac{T\lambda^0}{|z|} \tag{2.18}$$

Einstein-Stokes:

$$D_0=\frac{RT}{6\pi N\eta r}=7.166x10^{-21}\frac{T}{\eta r} \tag{2.19}$$

u = absolute mobility of the solute

R = universal gas constant

T = absolute temperature

N = Avogadro's number

k' = Boltzmann's constant

λ^0 = conductivity of the ion or solute

r = radius of the hydrated ion or solute

η = absolute viscosity of the fluid

z = valence of the ion

ζ = Faraday's constant

The diffusion coefficient expressed as a function of solute concentration:

$$\frac{\delta C}{\delta t}=D_\pi(C)\frac{\delta c^2}{\delta x^2}+\frac{\delta D_\pi(c)}{\delta C}(\frac{\delta C}{\delta x})^2 \tag{2.20}$$

How to find D?

The D coefficient is generally taken to be:

$D = D_\pi + D_h$

$D_\pi = D_0\ \tau$ = effective molecular diffusion coefficient

$D_h = \alpha |v|$ = hydrodynamic mechanical dispersion coefficient

τ = Physical-chemical tortuosity factor

D_0 = infinite solution diffusion coefficient

α = dispersivity parameter

v = average advective velocity

$|v|$ = absolute value of v

2.2.3 Fluid and solute transport in unsaturated soil

Soil water movement in unsaturated soil is largely controlled by internal gradients developed by forces within the soil. Therefore, the transport of contaminants will be tied more closely to the water movement. The diffusion of the contaminants depends on the water content of the soil and the various soil characteristics and properties that control the internal gradients (Yong et al., 1992a).

Where contaminants are present in the pore water, the continuity equation which reflect mass conservation of both water and contaminants can be written as:

$$\frac{\delta}{\delta t}(\theta C) = -\frac{\delta J}{\delta x} \qquad (2.21)$$

$$J = -D_\pi \nabla(\theta C) \qquad (2.22)$$

$$\frac{\delta}{\delta t}(\theta C) = \frac{\delta}{\delta x}\left(D_\pi\,\theta\,\frac{\delta C}{\delta x} + D_\pi\,C\,\frac{\delta \theta}{\delta x}\right) \qquad (2.23)$$

2.2.4 Adsorption-desorption model

Most models currently used to predict the transport of nonreactive dissolved contaminants in the groundwater zone are based on the advection-dispersion equation. The development of this equation is described by Yong et al. (1992a). Advection refers to the transport as a result of differences in head. Dispersion refers to mixing and spreading of the contaminants resulting from molecular diffusion and pore velocity variations in the local regions within the soil system.

Advective-dispersive transport assumptions:

- Isothermal conditions
- Absence of significant density difference
- No volume change in the substrate (non deforming medium)
- Absence of internal sources.

The one-dimensional form for homogeneous saturated media of the advection-dispersion equation can be written as :

$$-U\frac{\delta C_l}{\delta X}+D\frac{\delta^2 C_l}{\delta x^2}-\frac{P}{\theta}\frac{\delta S_l}{\delta t}=\frac{\delta C_l}{\delta t} \qquad (2.24)$$

Advection + Dispersion - Sorption

The transport-sorption equation can be rewritten as the retardation equation:

$$-U\,\frac{\delta C_l}{\delta X} + D\,\frac{\delta^2 C_l}{\delta x^2} = \frac{\delta C_l}{\delta t}\,(1+\frac{\rho}{\theta}K_p) \qquad (2.25)$$

where the expression in parenthesis is the retardation factor, t_R

$$t_R = 1 + \frac{\rho}{\theta} k_d \qquad (2.26)$$

U = The average linear groundwater velocity, cm/s

D = Diffusion Dispersion coefficient in the direction of the flow, cm^2/s

Ci = concentration of species i in the solution phase, mol l^{-1}

X = distance in direction of flow, cm

Si = Species i sorbed in the solid phase, mol Kg^{-1}

θ = porosity [-] (volume of voids/volume total)

ρ = bulk density, Kg l^{-1}

K_d = the partitioning coefficient which is the slope between S and C , $Ms^{-1} L^3$

The diffusion dispersion coefficient accounts for various transport-controlled processes which includes dispersion (mixing) and diffusion transport of the contaminants in concert with the liquid movement in the pores of the soil (Yong et al., 1992a).

2.3 Irreversible Thermodynamic Approach in Coupled Flow

Thermodynamically, the energy potential can be regarded in terms of the difference in partial specific free energy between soil water and standard water. The total potential of soil water as the amount of work that must be done per unit quantity of pure water in order to transport reversibly and isothermally infinitesimal quantity of water from a pool of pure water at a specific elevation at atmospheric pressure to the soil water (at the point under conideration). This definition is based on the the specific differential Gibbs free energy function ($G= U + \rho V - TS$). The differential form provides a criteria of an equilibrium and the direction in which changes can be expected to occur in nonequilibrium systems. Equilibrium states occur only in nature and spontaneous processes tend to be irreversible.

- The first law of thermodynamics states that the energy can be converted from one form to another but can neither be destroyed or created:

$$dQ= dU +\rho\, dV + dW \tag{2.25}$$

where, dQ is the heat added to the system, dU is the change in internal energy, ρdV is the work of expansion done by the system (pressure or volume), and dW is all the other work done by the system on its surroundings.

- The second law of thermodynamics states that the direction of changes in an isolated system is always toward equilibrium:

$dQ = T\, dS$ (for reversible processes), and $dQ < T\, dS$ (for irreversible processes), where, T is the absolute temperature, S is the entropy, dQ is the head added to the system and dS is the change in entropy.

For irreversible processes where $dS > 0$, the entropy S tends to increase spontaneously, and the second law of irreversible thermodynamis can be stated as: $dU = T\, dS - \rho\, dV$, where dU is the change of internal energy .

The classical thermodynamics deals with reversible process and equilibrium states. It can predict whether and in what directions (but not what rate) a spontaneous process will occur in a system not at equilibrium.

To solve the problem at hand and by considering a non-equilibrium state condition, the theory of irreversible thermodynamics approach is used to formulate and to study the problem of coupled moisture and solute flow in unsaturated soils.

At equilibrium, the derivation of entropy with respect to time is equal to zero. The relationship between the rates of flow (fluxes J) and the thermodynamic forces, X, responsible for those fluxes, can be described by a power series. However, in a system which is not too far from equilibrium, fluxes and their forces are related linearly and the second postulate of irreversible thermodynamics stated by Lars Onsager (1931) can be expressed as:

$$J_i = \Sigma L_{ij} x_i \qquad (2.26)$$

where J_i is the flux component of type i, x_i is the potential gradient of type j and Lij is a scalar quantity called Onsager's coefficient (Onsager, 1931) and is the coupling or phenomenologiocal coefficient between flux type i and gradient type j.

Also, according to Onsager's reciprocity, the third postulate for coupling coefficients can be written as :

$$L_{ij} = L_{ji}. \qquad (2.27)$$

The validity of those relations may fail if the system is very far from equilibrium.

In the analysis of contaminant migration in soils, coupled pore fluid and solute mass fluxes driven by head and solute concentration gradients can be simplified in the following coupled equations:

$$J_H = L_{HH} X_H + L_{HC} X_C \qquad (2.28)$$

$$J_C = L_{CH} X_H + L_{CC} X_C \qquad (2.29)$$

where H and C refer respectively to hydraulic and chemical fluxes driven by head and concentration gradients. The direct flux components are fluid flow ($L_{HH} X_H$) which is described by Darcy's law, and diffusion flow ($L_{CC} X_C$) which is described by Fick's first law. Where the coupled components ($L_{CH} X_H$) are the streaming or the drag current, and ($L_{HC}X_C$) is the chemico-osmosis, (Yong and Warkentin, 1975).

2.4 Sorption Characteristics of Heavy Metals in the Vadose Zone

Movement of chemicals in the ground is primarily a liquid phase process involving the movement of water and dissolved solute. Chemicals that are not sorbed will exist primarily in the dissolved phase and their movement to the ground water will be controlled by the relative amount of water, and soil processes that govern the fate of contaminants. Soil is an excellent adsorbent for retaining both organic and inorganic chemical compounds. The major adsorbing surfaces in soil are clay particles and organic matter. These interactions between contaminants and soil fractions can be expected to influence the physical and physico-chemical behaviour of the material.

Sorption (adsorption and desorption) is an important process in the modelling and prediction of the movement of heavy metals in unsaturated clay barriers. Adsorption or the accumulation of matter at the solid-water interface is the basis of most surface-chemical processes. Adsorption of a chemical species (adsorbate) from the soil solution by the solid soil constituents (adsorbent) occurs due to the various interactions between the surface active particles and the adsorbate (chemical). Equilibrium adsorption of contaminants is attained when no further adsorbate is observed leaving the soil solution, (Yong and Samani, 1987). It was defined earlier as the concentrations of constituents at the colloidal surfaces. The curve relating the concentrations of materials adsorbed at a fixed temperature is called the adsorption isotherm. Adsorption isotherms describe solute adsorption by solids at constant temperature and pressure. They show the amount of solute sorbed as a function of its equilibrium concentration.

Sorption is usually incorporated into the contaminant transport equation in a manner based on the assumption that the concentration of the contaminant in the solution phase is a function of the concentration in the solid phase. This function is based on the assumption that equilibrium conditions exist between the solid (S) and the solution phase concentrations (C). This function is generally referred to as the distribution or the partitioning coefficient (K_d).The partitioning coefficient of a compound determines its concentration and residence time in soil water and hence the subsequent processes in that phase. It is a measure of the distribution of a given compound in two phases and is expressed as a concentration ratio.

Adsorption data are needed to determine the transport properties of the soil with respect to the contaminant under consideration. Test data permits one to calculate the partitioning coefficient required in the contaminant transport equations. Most transport models use K_d obtained from a 'linear' adsorption isotherm -i.e. as a constant parameter (Freeze and Cherry, 1979; Rowe, 1988). Simplification of K_d as a constant and linear function may lead to an improper evaluation of the adsorption/desorption phenomena. Davidson et al. (1976) concluded that at high concentrations, the assumption of a linear isotherm can lead to serious errors in predicting contaminant migration. 'Although the convenience of the approach is beyond dispute, its validity as a means of developing reliable predictions of the behaviour of inorganic contaminants in actual ground water systems is questionable in many situations,' (Cherry et al., 1984).

Batch equilibrium tests used for determination of adsorptions isotherms utilize small portions of soil and representative contaminants. The problems arising therefrom relate to the question of whether or not a small quantity of totally disturbed soil is appropriate to simulate the field conditions or situations, and the variability of K_d from one soil to another. The batch technique does not necessarily reflect actual leachate soil interaction. The ratio of solution to soil and the time required to attain equilibrium does not always give a good estimate of the migration and the adsorption of heavy metals through the clay barrier (Darban. 1997). Adsorption characteristics obtained from the leaching column tests provide a better means for evaluation of soil sorption performance. The results obtained include the effects of partial soil saturation, and effective exposed surface area of the soil system.

Therefore, this study on unsaturated soil-contaminant interaction investigates experimentally, the effect of pH changes in the acidic range on the sorption characteristics of heavy metals such as: Lead, Copper and Zinc. In order to determine the adsorption characteristics of the soils, one dimensional coupled solute and moisture flow tests, were conducted on an unsaturated illitic soil at varying pH values. Samples were tested in horizontal leaching column tests designed to simulate slow flow of leachate through unsaturated clay. Variations of volumetric water content with distance were measured for different time durations. Metal partitioning analysis of heavy metals in the pore fluid (soluble ions) and the solid phases (extractable ions) along the soil column were determined for each individual layer in the soil along with the partition coefficients (K_d). All results pertaining to the leaching column tests are presented in Chapter 5.

Furthermore, this research study provides the experimental information necessary for numerical analyses of transport of heavy metals in the vadose zone. Particular attention to the effect of degree of saturation, the presence of carbonate, soil pH and heavy metals concentrations are given. In addition, the significant reason for the need to study the vadose zone transport is the fact that the "initial conditions" established at the saturated zone interface will be considerably affected by vadose zone results, thereby impacting directly on the success of models designed to predict transport in the saturated zone. Therefore, a new method that describes the full coupling effects on transport coefficients based on experimental evidence is applied to the unsaturated transport theory, and to provide for successful predictions of the rate of transport of the heavy metals through the unsaturated soil in a pH-controlled environment. The numerical analysis of most of the data obtained from the leaching column tests is contained and discussed in Chapter 6.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Soil material

Compacted barriers of local clayey soil can be composed of kaolinite, illite, chlorite, vermiculite or smectite clay, either locally weathered or deposited (Quigley, 1993). To achieve the objectives of this study, a series of one dimensional horizontal leaching tests were performed on illitic soil (Domtar Sealbond). This soil is a commercial product obtained from Canada Brick Company, Ontario, which originates from pulverised Canadian old marine shale and is expected to have properties similar to the natural marine-deposited clays (Champlain clay deposit), (Wang 1990; and Mazus,1993). The choice of illitic soil was based on the premise of a low permeability and low hydraulic gradient (Quigley et al., 1983) and because Illites are probably the best barrier clays since they experience no interlayer compaction / expansion and yield a low hydraulic conductivity barrier if they constitute about 20% or more of well graded soils (Quigley ,1993). Therefore, waste disposal facilities located in a thick clayey Champlain Sea deposit area would have no significant potential for causing groundwater contamination. Furthermore, the contaminant is expected to migrate downward through the clay deposits only at very slow rates over long periods of time (Desaulniers and Cherry, 1989).

Soil pH was adjusted to the desired values by washing the soil several times with a 1:10 ratio of distilled water to a nitric acid over a long period of time (more than 10 months) to insure complete soil pH equilibrium. Approximatly. 195 ml of concentrated nitric acid were used to reduce the pH of 1 kg of the illitic soil from pH 9.0 to pH 3.5. During each time of wash, the solution was continuously stirred for more than one hour and the soil pH was then measured after at least 24 hrs. In case the soil pH did not reach the desired value, the soil suspension was left for a few days to settle. Then, the clear suspension was filtered and the procedure was repeated until a constant soil pH value was obtained for at least one week. The soil was then air-dried and ground to pass through a 2 mm sieve.

3.1.2 Leachate solution

Six different concentrations of heavy metal solutions of lead, copper and zinc in the form of nitrate salt ($Pb(NO_3)_2$, $Cu(NO_3)_2 - 2.5H_2O$ and $Zn(NO_3)_2 - 6H_2O$). were prepared and mixed with distilled water as follows:

1a - A 5000mg/l of Pb solution (given the molecular weight of Pb is 207.20) was prepared by adding 8.00 g of $Pb(NO_3)_2$ (molecular weight 331.20) to 1litre of distilled water.

1b - A 2500mg/l of Pb solution was prepared by adding 4.00 g of $Pb(NO_3)_2$ to 1litre of distilled water.

2a - A 5000mg/l of Cu solution (given the molecular weight of Cu is 63.55) was prepared by adding 18.32 g of $Cu(NO_3)_2 - 2.5H_2O$ (molecular weight 232.59) to 1litre of distilled water.

2b - A 2500mg/l of Cu solution was prepared by adding 9.16 g of $Cu(NO_3)_2 - 2.5H_2O$ to 1litre of distilled water.

3a - A 5000mg/l of Zn solution (given the molecular weight of Zn is 65.38) was prepared by adding 22.75 g of $Zn(NO_3)_2 - 6H_2O$ (molecular weight 297.49) to 1litre of distilled water.

3b - A 2500mg/l of Zn solution was prepared by adding 11.37 g of $Zn(NO_3)_2 \cdot 6H_2O$ to 1litre of distilled water.

The choice of these heavy metals is related to their mobility in soil and to the fact that these heavy metals are generally found in hazardous waste leachates (Phadungchewit, 1990; Darban, 1997). The concentration of each heavy metal was kept constant during the leaching.The pH of the solutions was adjusted to 2.8 by adding nitric acid (HNO_3) to the prepared solutions in order to keep an acidic environment and prevent metal precipitation in the solution (Cabral, 1992).

3.2 Sample Preparation

3.2.1 Soil mixing

Before testing, the dry soil was mixed with distilled water to reach optimum moisture content and then placed in the humid room for at least 24 hours to allow a uniform moisture distribution. The soil was then statically compacted directly into the leaching cell to its maximum dry density of 1.88 Mg/m^3 and 14.16 % optimum moisture content. After installation the specimens were left for 24 hours to reach equilibrium.

3.2.2 Soil compaction

The remoulding of soil clods and mixing of the soil before and during the compaction process approximates the compaction of a soil liner (Jonathan and Hermann, 1987). Compaction of soils may be done by several methods including impact, kneading, vibratory and static methods (Mitchell and Madsen, 1987). The optimum moisture content and the maximum dry density for soils were determined using the standard compaction test (impact method). Then, static compaction was chosen as a compaction method to meet the basic compaction criterion to simulate the pneumatic tired roller type used in the field. Rollers are used to compact to maximum dry density and low permeability (Jonathan and Hermann, 1987). Using the Instron testing machine, the material was statically compacted directly into the leaching cells to its maximum dry density in seven equal layers. 20 mm each, while the last layer was 25 mm to give a total soil column height of 165 mm. The weight of the soil needed for the individual compacted layers was calculated from the maximum dry density and the optimum moisture content. The compacted cells were left for a period of 24 hours to reach equilibrium. In order to check the uniformity of the soil dry density and the initial water content , a sample was sliced into eight sections before testing and just after being compacted. The distributions of the water content and the dry density were uniform within 1%.

3.2.3 Sample extrusion

After test completion, and for each time duration, the cell was removed, and completely dissassembled. Lucite caps, 0-rings and filter paper were removed with care. The sample and the cell were weighed. Then, the tested sample was extruded and sectioned into 16 slices 10 mm thick. Each slice was placed in a pre-weighed dish and dried at 105° C for moisture measurement tests which were performed according to ASTM D2216. The ratio of the weight of water present, which is the difference between the sample weight before and after oven driyng, to the weight of soil solids gave the moisture content. Then each slice was ground into powder form for chemical analysis and for measurement of the soluble and total extractable ion concentration profiles. Concentrations of heavy metals were determined using atomic absorption spectrophotometry (AAS). Leaching tests were repeated to obtain water content and heavy metal concentrations after 52 hours and after 17.8 days.

3.3 Laboratory Tests

3.3.1 Test apparatus

Samples were tested in horizontal leaching cells designed to simulate the slow flow of leachate through unsaturated clay. Each cell consisted of a hollow lucite plexiglass cylinder, 6 mm diameter thick, with an outside diameter of 870 mm and a total length of 165 mm. A porous stone, 3 mm thick, was made of coarse silica sand and epoxy glue following the procedures of filter design by Das (1983) and Karczewska (1987). Then, it was placed at the starting flow point and at the end of the soil core to ensure a uniform distribution of hydraulic pressure along the soil column. A rubber O-ring was placed between the cylinder and the base on both sides to prevent leaks. Filter papers were placed at both ends of the soil samples to prevent fines migration out of the cell.Two lucite plexiglass end caps were fixed at either end of the cell by four stainless steel rods and nuts. The left end cap was provided with two openings, one as a permeant inlet and the second as an air outlet, while the right side cap was provided with only one drainage outlet.

The permeant was introduced from a mariotte flask connected to the left side after placing the soil in the cell, and the effluent was drained from the right end side of the cell. Both ends were at atmospheric pressure and there was zero total head along the x-axis. Fluid diffused as a results of capillary-osmotic forces. Samples were tested at different drying stages and different initial water contents. Results were evaluated in terms of contaminant movement in relation to moisture content and contaminant concentration. A schematic representation of the laboratory leaching cell is shown in Figure 3.1.

3.3.2 Leaching column test

Laboratory evaluation of heavy metal migration was determined by using a leaching column test. This is an experimental technique commonly used in the laboratory to determine (a) the adsorption characteristics of the soil, and to describe (b) the migration profile of contaminants along the soil column (Yong et al.1992a). The results are used for the transport model to predict heavy metal migration. The model development and prediction is shown in Chapter 6.

Test procedures:

- Properties of clay soils were determined according to the ASTM test procedures.
- Soil A (pH 9.5) was subjected to 3 pre-treatments (Soil B (pH 6.9), Soil C (pH 4), and Soil D (pH 3.5)), only Soil C and Soil D will be studied for sorption (refer to Chapter 5 for sorption results)
- Dry density optimum moisture content relations were determined according to ASTM compaction method.
- The soils were compacted into a cylindrical plexiglass cell up to the maximum dry density and optimum moisture content (unsaturated soil), determined as mentioned above.
- The permeant solutions were leached into the soil after placing the clay soil in the leaching cells (duplicate leaching cells were performed). Each cell was leached with two different permeants: (a) 2500mg/l, and (b) 5000mg/l of lead, copper and zinc nitrate solutions (pH 2.8) at constant atmospheric pressure and under a negligible hydraulic gradient.
- The experiments were conducted at room temperature of 22±2°C.
- Water content and heavy metal concentrations were determined after 52 hours and 17.8 days. For each time duration, the test sample was removed and cross-sectioned horizontally into 16 layers 10mm thick for analysis and measurement of

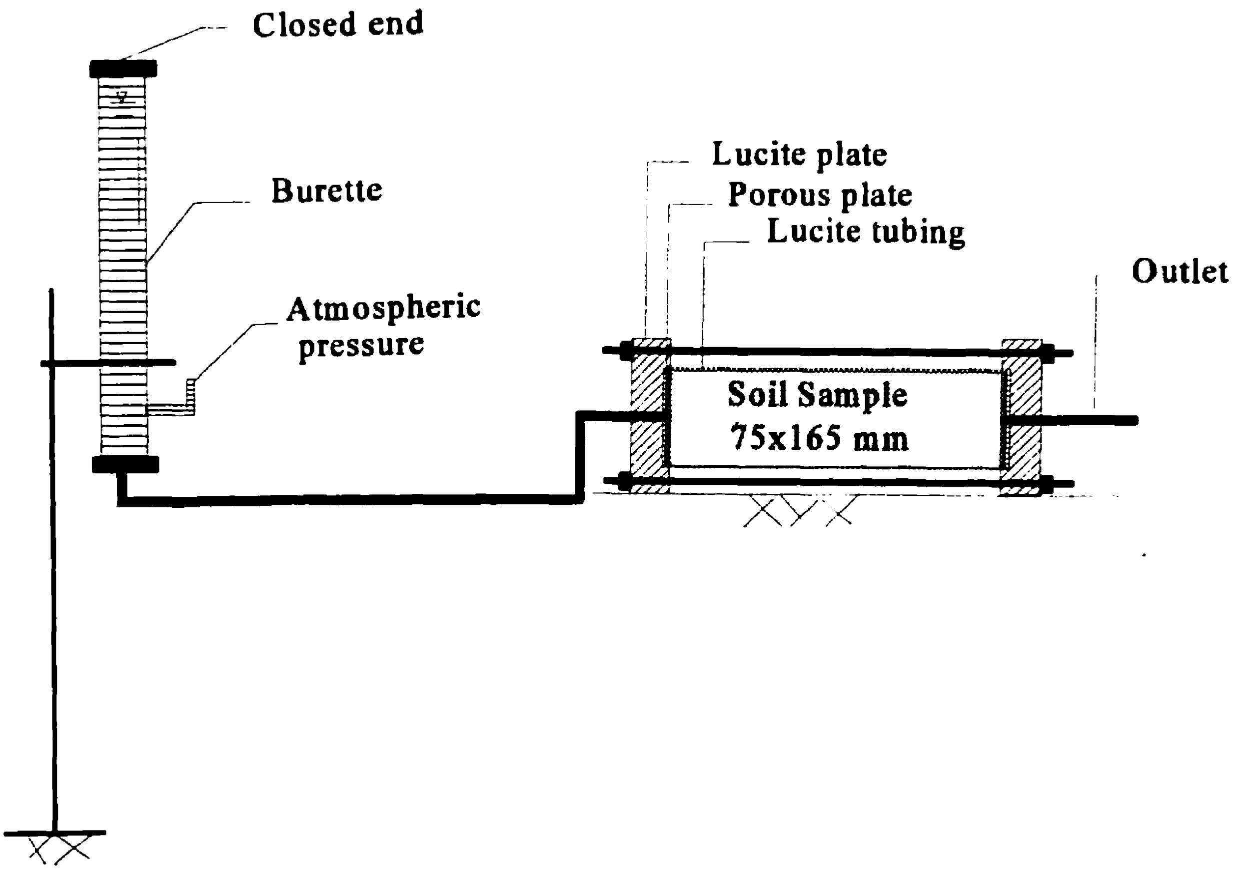


Figure 3.1 A schematic Representation of the Laboratory Leaching Cell.

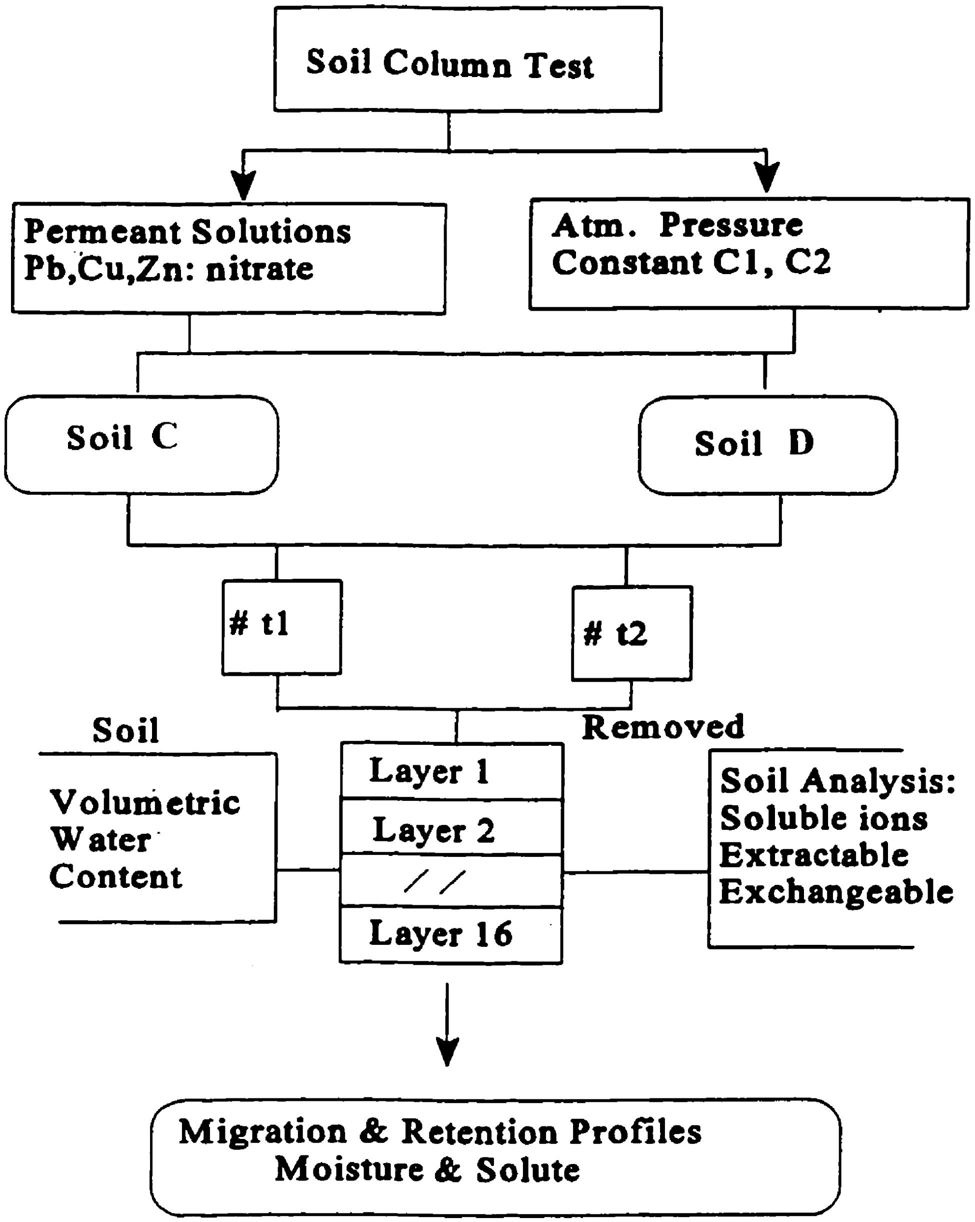


Figure 3.2 Schematic Diagram Showing Leaching Column Test Procedures

the soluble, and total concentration profiles.

Finally, volumetric water content variations and concentration distributions in the liquid and solid phases of the soil with distance were determined for different time durations for each section. Concentrations of adsorbed heavy metals were determined using the acid digestion method of the United States Environmental Protection Agency (USEPA, 1986). Concentrations of cations and heavy metals were determined using Atomic Absorption Spectrophotometry (AAS).

A schematic diagram showing leaching column test procedures for determination of contaminant migration and adsorption profiles of soils is shown in Figure 3. 2.

3.4 Soil Characterization Study

This section presents full details of the technique employed to characterize the soil. Section 3.4.1 deals with the geotechnical aspects - i.e. measurements of grain size distribution, specific gravity, water content, Atterberg limit, hydraulic conductivity, optimum moisture content and maximum dry density relationships. Section 3.4.2 deals with the geochemical characterization - i.e. soil pH, organic and amorphous content measurement, cation exchange capacity (CEC), the specific surface area (SSA), and the carbonate content. Concentrations of adsorbed heavy metals in the solid and the soluble phases were determined using the acid digestion method and the pore fluid removal or the batch shaker techniques in accordance with the United States Environmental Protection Agency. Concentrations of cations and heavy metals were determined using the Perkin Elmer Model 3110 atomic absorption spectrophotometer (AAS). All results pertaining to physical and chemical analysis, including initial and final soil property test results are presented in Chapter 4.

3.4.1 Geotechnical characterization

Measurements of grain size distribution were performed experimentally using the mechanical (sieve analysis) and the hydrometer method according to ASTM standards method D422. Two materials were used as dispersing agents to neutralize the soil particle charge: sodium hexa-metaphosphate was used as a dispersion agent in alkaline soil with pH higher than 7 and sodium silicate which is efficient in acidic soils whose pH is less than 7.

The specific gravity, water content and Atterberg limits were performed experimentally according to ASTM standard methods D854, D2216-80 and D4318-84, respectively.

Determination of optimum moisture content and maximum dry density relationships for soils were carried out following ASTM standard D698-78, impact method, using a 2.49 kg rammer and 305 mm drops.

Hydraulic conductivity tests were performed on various illitic soils using the constant head system with a graduated pipette connected to the leaching cell. The hydraulic gradient (i) used in this study varied between 7.76 and 51.2. Tests were conducted according to ASTM standard D5084-90. Before testing , the dry soil was mixed with distilled water to reach optimum moisture content and then placed in the humid room for at least 24 hours to allow for uniform moisture distribution. The soil was then statically compacted directly into the leaching cell to its maximum density and optimum moisture content. Each cell was leached with three different permeants: 200 mg/l of calcium sulfate, $CaSO_4$ (pH 5.6), and 2500 mg/l and 5000 mg/l (pH 2.8) of lead nitrate solutions. The concentration of each heavy metal was kept constant during the leaching. The pH of the solutions was adjusted to 2.8 by adding nitric acid to the prepared solutions in order to keep an acidic environment and prevent metal precipitation in the solution (Cabral, 1992). 200 mg/l of calcium sulfate was used as a control liquid which had a pH between 5.6 and 5.8, as recommended by ASTM 5084-90. It is thought that this solution will neither decrease nor increase significantly the hydraulic conductivity of clayey soils.

3.4.2 Geochemical Analysis

3.4.2.1 Cation exchange capacity

The cation exchange capacity (CEC) for the soil was determined using two different methods: the silver-thiourea method described by Chhabra et al. (1975) and the barium chloride method described by Hendershot and Duquette (1993). The first method is more reliable, particularly for illite-rich samples, than the barium chloride method. Using the first method, the silver solution was prepared in the dark to prevent oxidation, and its pH was adjusted to pH 7 by adding acetic acid if pH > 7 or NaOH if pH < 7. 30 ml of the silver reagent were added to 0.5 g of dried soil and pipetted into a plastic 40 ml centrifuge tube and shaken for 4 hours in an end-over-end-shaker. The supernatant was then separated from the soil by centrifugation at 10,000 rpm for 20 min. Concentrations of cations such as: Ca^{+2}, Na^{+}, K^{+}, Mg^{+2} and Ag^{+2} were measured in the supernatant by atomic absorption spectrophotometry.

The second method, which is the barium chloride method, is often preferable to measure the CEC of low pH soils. This method provides a rapid means of determining the exchangeable cations and the CEC of a wide range of soil types and gives comparable results when compared to other methods of determining the CEC at the soil pH (Hendershot et al., 1993). Barium is a good flocculant and is able to displace the trivalent cations.

Both of these methods were used to obtained the CEC which is the sum of the exchangeable cations (Ca, Mg, K, Na) found on the clay surface. The amount of the exchangeable cation is found by substracting the soluble cation concentration from the extractable cation concentration. Where:

Exchangeable cation (meq/100g)= Extractable cation (meq/100g) - Soluble cation (meq/100g).

For both methods, cation exchange capacity was expressed in meq/100g and the detection limit for both methods is 0.1 meq/100g.

3.4.2.2 Specific surface area determination

The specific surface area of the materials was determined using the Ethylene Glycol-Monoethyl Ether method, following the procedures described by Eltantaway and Arnold (1973), and Carter et al. (1986). This method is based on the assumption that the ethylene glycol monoethyl ether (EGME) will be adsorbed on a particle surface and forms a single or mono-molecular layer of polar fluid on the soil particle. The packing area of the mono-molecular layer of the adsorbate or EGME to cover 1m^2 of the soil surface area is estimated to be equal to 2.86 x 10^{-4} g of EGME per m^2 of the surface. The specific surface area of the soil (SSA) was calculated from the variation of the soil sample before and after the application of the EGME, by dividing the adsorbate sample mass ratio by the packing area and can be expressed as:

Surface area (m^2/g) = (wt.of EGME retained (mg) x 1 m^2) / (wt. of dry soil (g) x 0.286 (mg) EGME)

3.4.2.3 Soil carbonate content determination

The carbonate content of the soil was determined in accordance with the titration method described by Hesse (1971) in the soil chemical analysis handbook.

The rapid titration method is suitable for the routine analysis of a large number of samples where an accuracy of about 1% is sufficient. The results are referred to as the calcium carbonate equivalent. They indicate the amount of the acid required to dissolve the carbonate component.

To measure the carbonate content of the soil, 100 cm^2 of 1.0 M of hydrochloric acid were slowly added from a burette to 5 g of 2-mm soil placed into a tall beaker which was allowed to stand with occasional stirring for 1 hour and then to settle after its final agitation. After the soil had settled, 20 cm^3 of the supernatant liquid was pipetted into a conical flask and titrated with 1M of sodium hydroxide using six drops of bromthymol blue indicator solution. As a blank, 20 cm^3 of the original acid was titrated. Finally, the carbonate content was calculated by subtracting the blank titre from the actual titre.

$$\%\ CaCO_3 \text{ equivalent} = (\text{Blank titre} - \text{Actual titre}) \times 5$$

3.4.2.4 Soil pH , organic and amourphous content measurement

Soil pH was measured in a 1:2 ratio of soil to distilled water solution. 20 ml of distilled water was added to 10 g weight of 2 mm soil and shaken for 30 minutes. Then, the suspension was allowed to settle for 30 minutes. The pH of the soil was measured using a Beckman I™ 12/pH/ISE meter, according to the method described in the analytical methods manual edited by Sheldrick (1984). The organic content of the soil was determined using the titration method described by Jackson (1956). The presence of amorphous materials such as: silicon dioxide (SiO_2), iron oxide (Fe_2O_3), and aluminum oxide (Al_2O_3), was determined using the method described by Segalen (1968).

3.5 Metal Partitioning Analysis

The metal partitioning analyses were conducted according to the Environmental Protection Agency procedures and ASTM standards. Two different soil suspension methods were used to determine the concentration of heavy metals in the soil: (a) the pore fluid removal or the batch shaker test was used to determine the soluble cations concentration in the liquid phase, and (b) the acid digestion method was used to measure the metals concentration in the solid phase. For both methods, analysis of the fluid for heavy metal ions (Zn^{+2}, Pb^{+2}, Cu^{+2}) associated with the sample solution was performed using the Perkin Elmer Model 3110 atomic absorption spectrophotometer (AAS). The cation concentrations were expressed in mg/100g.

3.5.1 Soluble Phase

Soluble cations were determined using the pore fluid removal method or the batch shaker test. Duplicate suspensions with a ratio of 1:10 soil weight to solution volume of distilled water were prepared as recommended by the United States Environmental Protection Agency (USEPA, 1987) to estimate the attenuation of chemicals from batch tests. For each batch test, 30 ml of distilled water was added to 3 g of soil and mechanically shaken in the end-over-end shaker for 24 hours. After agitation, the sample was then centrifuged in plastic Nalgene centrifuge tubes at 10,000 rpm for 20 min and the clear supernatant was collected for cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and heavy metals (Zn^{2+}, Pb^{2+}, Cu^{2+}) analysis by means of atomic absorption spectrophotometry. The concentration of a particular species found in the supernatant or in the pores of each slice was calculated using the following formula:

$$C_{mg/100g} = \frac{DF \; x \; Cs_{mg/l} \; x \; V_{ml} \; x \; 100_g}{1000_{ml} \; x \; WDS_g} \qquad (3.1)$$

where C is the soluble species concentration found in the supernatant and is expressed in mg per 100 g of the soil, DF is the dilution factor, Cs (ppm) or (mg/l) is a particular species concentration in the pore fluid which is obtained from AAS readings, V is the volume of distilled water used during the test (where 30 ml was used, 1000 ml is used to convert from 1 liter to ml) and WDS is the weight of dry soil in grams (where 3 g was used).

3.5.2 Solid Phase

Heavy metals and existing cations in the solid phase were measured using the pore fluid extraction or the acid digestion method (3050) of the United States Environmental Protection Agency (USEPA, 1986). This method is an acid digestion method used to dissolve all the sample metal and to prepare soil samples for analysis by atomic absorption spectrophotometry (AAS) in order to determine the background level of the trace metals in soil. Hot diluted nitric acid (HNO_3) was used to dissolve the inorganic-metal bonds and to ensure complete oxidation. Hydrogen peroxide (H_2O_2) was added to the soil, and was warmed until the effervescence was minimal or the general sample appearance was unchanged – to ensure complete destruction of the organic-metals bonds. After cooling, the sample was diluted up to 100 ml and then allowed to settle overnight. The sample was then centrifuged at 5,000 rpm for 10 min to clear the supernatant of any particulates that may clog the nebulizer. The concentration of a particular species adsorbed by the clay and found in the supernatant for each slice was obtained using the following formula:

$$Ct_{mg/100g} = \frac{DF \ x \ Cs_{mg/l} \ x \ V_{ml} \ x \ 100_g}{1000_{ml} \ x \ WDS_g} \tag{3.2}$$

where Ct is the total concentration of metals by the clay which was found in the supernatant and is expressed in mg per 100 g of the soil, DF is the dilution factor, Cs (ppm) or (mg/l) is a particular species concentration in the supernatant and is obtained from AAS readings, V is the volume of distilled water used during the test (100 ml was used), 1000 ml is used to convert from 1 liter to 1 ml and WDS is the weight of dry soil expressed in g (where 1 g or 2 g was used). Thus,

$$S = Ct - C \tag{3.3}$$

where (S) is the total adsorbed or retained concentration of metals in the solid phase which can be obtained by subtracting the soluble species concentration C from the total concentration (Ct) of metals by the clay. The units of S, Ct and C are expressed in mg of constituent per 100 g of dry soil.

3.6 Partitioning Coefficient Determination

K_d is the distribution coefficient or the partition coefficient. It is used to describe contaminant partitioning between the liquid and solids only if the reactions that cause the partitioning are fast and reversible, and only if the isotherm is linear, (Yong et al., 1992a).

$$K_d = \frac{S}{C'} \tag{3.4}$$

S represents the ratio between the mass of the contaminant adsorbed onto the solid phase divided by the mass of the soil to obtain a measure of the relative mass of the constituent adsorbed on the solid phase. The units of the numerator are expressed in mg of adsorbed constituent/100g of soil. The denominator C' represents the concentration of the contaminant in solution and its unit is expressed in mass of constituent / volume of moisture or g/ml. The distribution coefficient (K_d) unit is expressed in ml/g. According to Yong et al. (1992a) and Mohsen (1993), the mass of constituent in moisture / volume can be computed from:

$$C' = \frac{C}{n\,S\,V} = \frac{C}{\theta\,V} = C\,\frac{\rho_d}{\theta} \tag{3.5}$$

C is the concentration of the contaminant in the solution and is expressed in (mass/mass) or (mg/100g), ρ_d is the bulk density of the soil (g/ml), θ is the volumetric water content (fraction), n is the porosity (fraction), S (fraction) is the water saturation and V (ml) is the total volume of soil.

The volumetric water content (θ) is defined as the volume of water per volume of moist soil:

$$\theta = \frac{V_w}{(V_s + V_v)} = \frac{V_w}{V} \tag{3.6}$$

where V_s is the solid volume and V_v is the void volume.

The relation between the water content (w) and the volumetric water content (θ) is:

$$\theta = \frac{w}{100}\,\rho_d\,\frac{1}{\rho_w} \tag{3.7}$$

where ρ_w is the water density and ρ_d is the bulk density or the dry density, and is defined as the weight of soil divided by the total volume of the soil (Yong and Warkentin, 1975).

$$\gamma_d = \frac{W_s}{V_s + V_V} \tag{3.8}$$

In this research, the leaching column test was used to determine the sorption characteristics of the soils. Previous research showed that batch tests give only rough estimates of the partitioning coefficient K_d, because the adsorption characteristics of the compacted material are not the same as that of soil in a suspension (Cabral and Yong, 1993). The batch technique did not reflect the leachate soil interaction which exist in landfills. The ratio of solution to soil and the time required to attain equilibrium did not give a good estimate of the migration and the adsorption of heavy metals through the clay barrier (Darban, 1997).

CHAPTER 4

SOIL CHARACTERIZATION RESULTS AND DISCUSSION

4.0 General

This chapter presents the soil characterization results of all experiments described in the previous chapter. Discussion of the results is also included. Section 4.1 deals with the geotechnical aspects: measurements of grain size distribution, specific gravity, water content, Atterberg limit, hydraulic conductivity, optimum moisture content and maximum dry density relationships. Section 4.2 deals with the geochemical characterization: soil pH, organic and amorphous content measurement, cation exchange capacity (CEC), the specific surface area (SSA), and the carbonate content.

All results pertaining to physical and chemical analysis, including initial and final soil property test results are presented in this chapter. All results pertaining to the leaching column tests are presented in Chapter 5.

4.1 Geotechnical Aspects

The geotechnical properties of the illitic (Domtar sealbond) soil (A) before carbonate treatment are summarized in Table 4.1. The physico-chemical and mineralogical composition of illite soil (A) are summarized in Table 4.2. The physico-chemical properties of the illitic soil (B) , (C), and (D) after carbonate extraction are summarized in Table 4.3.

Table 4.1. Geotechnical Properties of Illitic Soil(A)

	Soil A
Soil Type	Illite (Domtar sealbond)
Specific Gravity	2.76
Soil pH	9.5
Dry Density (Mg/m^3)	
pH 9.5	1.80
pH 6.9	1.88
Optimum Moisture Content %	
pH 9.5	16.6
pH 6.9	14.6
Particle Size Distribution	
Gravel	0%
Sand	16%
Silt	40%
Clay	44%

Table 4.2. Soil Physico-Chemical Characteristics of Soil A

	Soil A
Soil Type	Illite (Domtar Sealbond)
Soil pH	9.5
Soluble Cations (mg/100g)	
Al^{+3}	-
Ca^{2+}	3
Mg^{2+}	1.46
K^{+}	57
Na^{+}	29
Cation exchange capacity (meq/100g)	34.2
Carbonate content (% by weight)	15.18
Surface area (m^2/g)	76.41
Organic Matter w%	0.8
Amorphous Contents	
SiO_2	2.2
Fe_2O_3	3.1
Al_2O_3	1.1
Mineralogical Composition*	
(in decreasing abundance)	Illite Chlorites Quartz Feldspar Calcite

* after MacDonald (1994)

Table 4.3. Soil Physico-Chemical Characteristics of Soil B, C, and D

	Soil B	Soil C	Soil D
Soil	Illite*	Illite*	Illite*
Specific Gravity	2.80	2.83	2.87
Soil pH	6.9	4.0	3.5
Liquid limit	32.0	38.5	39.0
Soluble Cations(mg./100g)			
Al^{+3}	-	23	90
Ca^{2+}	848	573	631
Mg^{2+}	47	110	170
K^{+}	38	22	25
Na^{+}	23	12	13
Cation exchange capacity (meq./100g)	7.94	6.81	5.34
Carbonate content (% by weight)	11.73	5.22	4.60
Surface area (m^2/g)	86.09	100.41	101.91
Particle Size Distribution			
Gravel	0%	0%	0%
Sand	19%	24%	24%
Silt	40%	38%	41%
Clay	41%	38%	35%

* Illitic soil treated with acid for carbonate extraction.

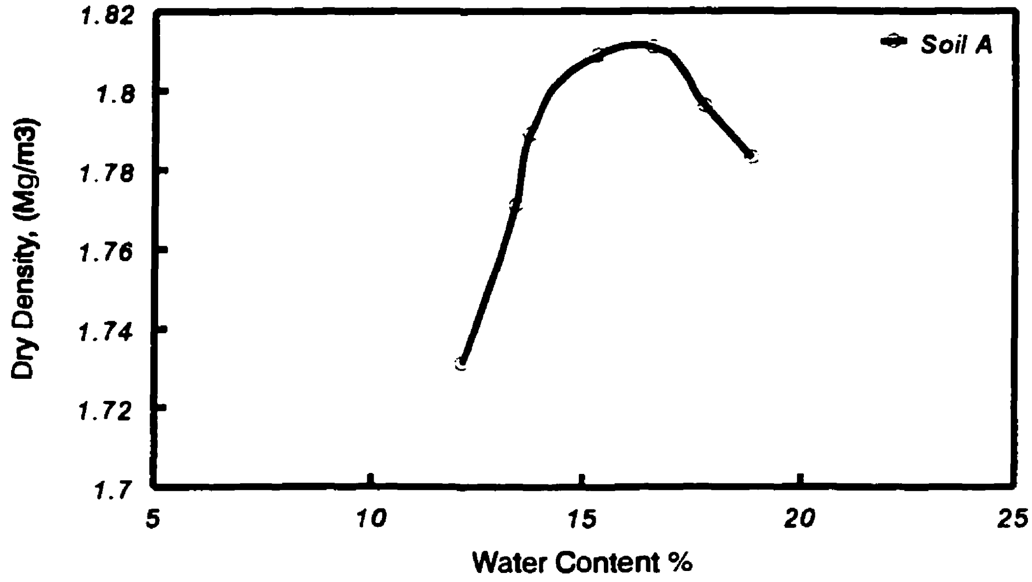


Figure 4a Dry Density-Water Content Relationship for Soil A (Illite at pH 9.5)

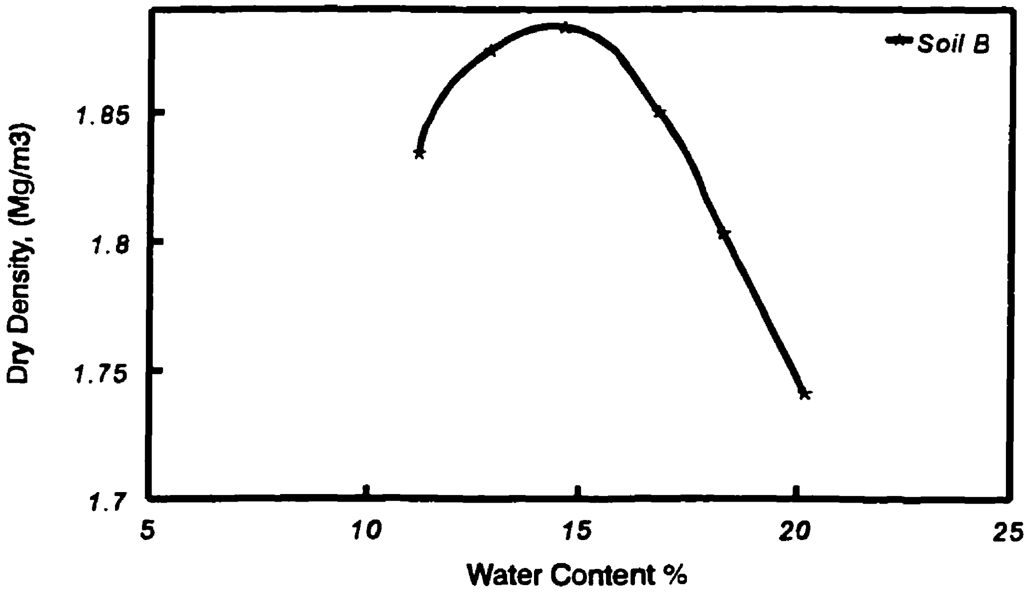


Figure 4b Dry Density-Water Content Relationship for Soil B (Illite at pH 6.9)

The predominant mineral used in this study is illite with varying amounts of chlorite, quartz, feldspar and calcite. The results of the soil properties and composition analysis are close to those found by Macdonald (1994). A similar study by Karczewska (1987), showed that the mineralogical analysis of soil samples after acid leaching revealed no significant changes in the soil composition. The reduction of the soil pH does not alter the mineralogical composition. The predominant minerals for both treated and untreated soil were unchanged and these minerals are: illite, chlorite and carbonates such as calcite, and dolomite.

The standard proctor compaction test was used according to ASTM D698 to determine the maximum dry density and the optimum moisture content of soil A at pH 9.5 and soil B at pH 6.9. Results showed that at low soil pH, the maximum dry density and moisture content revealed no significant changes. The maximum dry density and optimum moisture content results for soil A and B are presented in Figure 4a and Figure 4b respectively.

The carbonate contents in soil A and B were considered to be significant and varied between 15.18% and 11.73%. This may explain their high values of soil pH. The carbonate contents for soil C and D decreased with decreasing soil pH and ranged between 5.22% and 4.60%.

4.1.1 Particle size distribution

Particle size disribution affects the surface area for adsorption of heavy metals. The results of the grain size distributions are presented in Figure 4.1. The particle size distributions were obtained by using mechanical sieves analysis in combination with the hydrometer method. Sieves were used to obtain the percentages of the following soil components: a) Sieve No.4 (4.75 mm), gravel; b) Sieve No. 4 (4.75 mm) and No. 40 (0.420 mm), coarse to medium sand; c) Sieve

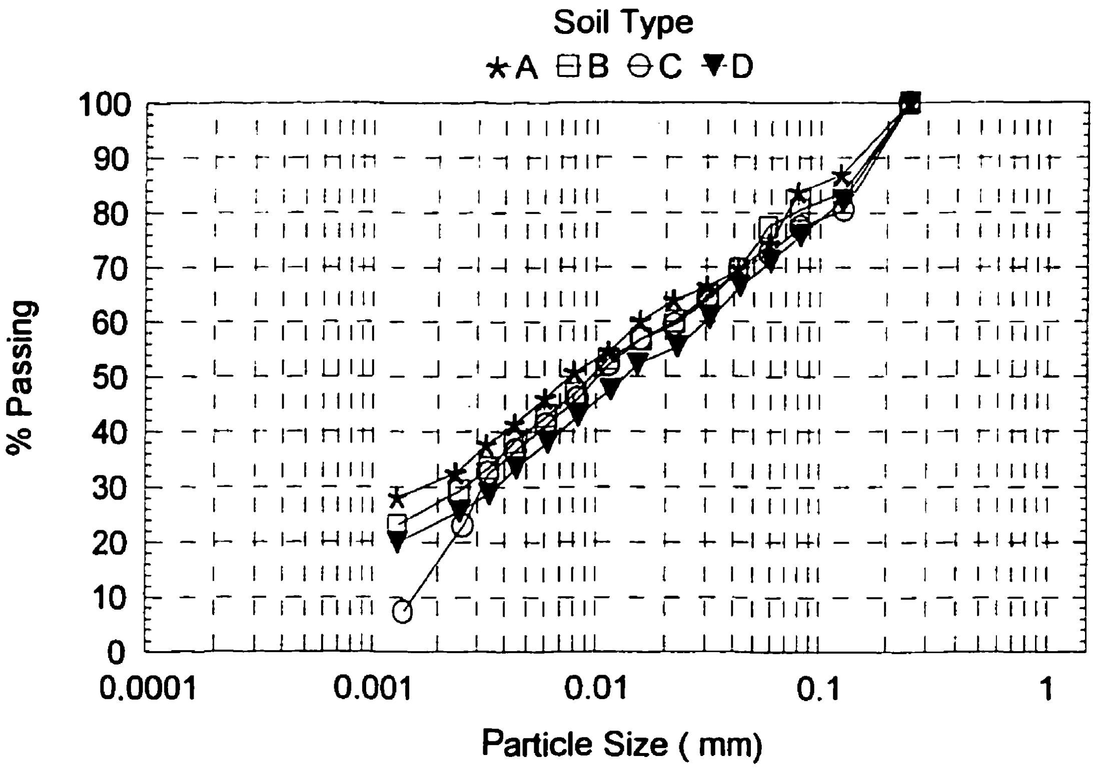


Figure 4.1 Particle Size Distribution for Soils A, B, C and D

{No. 40 (0.420 mm) to No. 200 (0.075 mm)}, fine sand; and d) silt passes through sieve No. 200. For clay, where particles are less than 0.002 mm, the hydrometer method was used to determine the fraction down to 0.001 mm.

Grain size analysis of the samples A, B, C, and D showed the following composition:

Soil A : clay 44%, silt 40%, sand 16%, gravel 0 %
Soil B: clay 41%, silt 40%, sand 19%, gravel 0%
Soil C : clay 38%, silt 38%, sand 24%, gravel 0%
Soil D: clay 35%, silt 41%, sand 24%, gravel 0%

It was found that during the washing stages as the carbonates were extracted, the soil lost some fine clay particles and the portion of the silt and the sand was slightly increased. The significance of this factor is how it is likely to affect the movement of H.M. along the soil column. Variations in adsorption between different size fraction is mostly a reflection of their carbon content (Yong et al., 1992a). The capacity for H.M. movement is increased not only by low pH and low carbonate content but also by large particle size.

4.1.2 Atterberg limits

Liquid limits (LL) and plastic limits (PL) of soils were determined using ASTM D4318-84. The relation between Atterberg limits, soil pH and carbonate content for soil A (pH 9.5), soil B (pH 6.9), soil C (pH 4.0) and soil D (pH 3.5) are illustrated in Figure 4.2. Results show that when the soil is mixed with distilled water, the liquid limits and the plastic limits of the soil increase slightly with a decrease in soil pH and carbonates content (soil D & soil C). This might occur due to an increase in the amount of water trapped between particles and due to the flocculated arrangement of acidic soil, where the edges of clay particles become positively

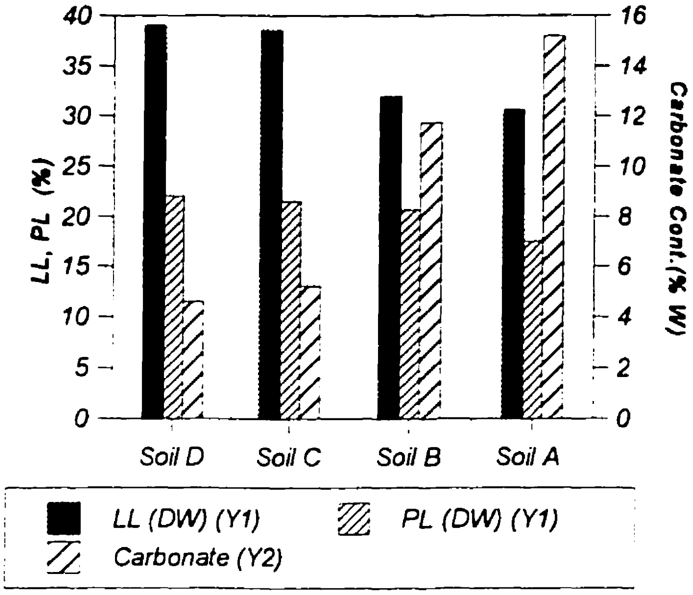


Figure 4.2 Results of Some Atterberg Limit tests

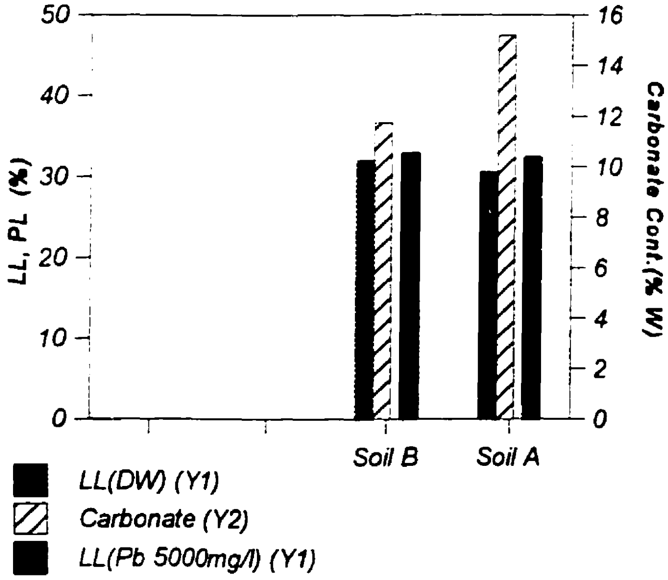


Figure 4.3 Liquid Limits obtained with DW and 5000 mg/l Pb-solution

charged after attracting extra hydrogen ions (Hoppe, 1986). Changes of the LL may be used as a first indicator of the effect of a liquid on a soil (Bowders and Daniel, 1987) whereas a drastic change in the LL indicates that the structure of the clay may be affected by contact with the specific leachate. Figure 4.3 compares the LL of soil A at pH 9.5 and soil B at pH 6.9, mixed with distilled water and lead solution. It is observed that the LL of soil A (pH 9.5) and soil B (pH 6.5) was not affected by the soil mixing with a high lead solution (5000mg/l). This indicates that the percolation of high concentrated Pb solutions did not affect the structure of the illitic clay.

4.1.3 Hydraulic conductivity test

Hydraulic conductivity tests were carried out on different illitic soil mixtures at various soil pH and the results are presented in Table 4.4 to Table 4.6. There are slight differences in the permeability response between calcium sulfate, and lead with different concentrations. The hydraulic conductivity test results on compacted illitic soils B (pH 6.9), C (pH 4.0) and D (pH 3.5) show that when soils B, C, and D were permeated with calcium sulfate, the hydraulic conductivity values ranged from 1.56×10^{-10}m/s to 2.5×10^{-10}m/s. The range of hydraulic conductivities, K, for soil B is from 2.5×10^{-10} m/s when leached with calcium sulfate to 2.61×10^{-10} m/s when leached with 5000 mg/l of lead nitrate solution. The hydraulic conductivity for soil C ranged from 1.56×10^{-10} m/s when leached with calcium sulfate to 1.62×10^{-10} m/s when leached with 5000 mg/l of lead nitrate. When compared with the hydraulic conductivity results obtained when leached with calcium sulfate permeant solution, the hydraulic conductivity for soils B and C increased when leached with lead concentration and showed a slight decrease with increasing lead concentration. However, soil D showed a slight increase in the hydraulic conductivity values for samples leached with high concentrations of lead nitrate compared with low lead concentrations.

This particular case shows that the slight variations in the overall hydraulic conductivity results cannot be considered important as they fall within the same order of magnitude. This indicates that reducing the soil pH by dissolving some of the carbonate bonds did not alter significantly the hydraulic conductivity of the illitic soil. The latter means that the mineralogical composition of the treated soils remain unchanged.

Table 4.4 - Hydraulic Conductivity Test Results on Compacted Illitic Soils (B).

Soil Type	Soil pH	Permeant Type	Concentration	Hydraulic Conductivity	Total pore vol.of flow
100% Illite	6.9	$CaSO_4$	0.005 N	2.50×10^{-10} m/sec	2.84
100% Illite	6.9	Pb	2500 mg/l	5.72×10^{-10} m/sec	5.49
100% Illite	6.9	Pb	5000 mg/l	2.61×10^{-10} m/sec	3.12

Soil B: L = 16.5 cm, H = 128 cm, i = 7.76, A = 45.94 cm^2

Table 4.5 - Hydraulic Conductivity Test Results on Compacted Illitic Soils (C).

Soil Type	Soil pH	Permeant Type	Concentration	Hydraulic Conductivity	Total pore vol.of flow
100% Illite	4.0	$CaSO_4$	0.005 N	1.56×10^{-10} m/sec	19.94
100% Illite	4.0	Pb	2500 mg/l	2.41×10^{-10} m/sec	33.5
100% Illite	4.0	Pb	5000 mg/l	1.62×10^{-10} m/sec	22.3

Table 4.6 - Hydraulic Conductivity Test Results on Compacted Illitic Soils (D).

Soil Type	Soil pH	Permeant Type	Concentration	Hydraulic Conductivity	Total pore vol. of flow
100% Illite	3.5	$CaSO_4$	0.005 N	2.17×10^{-10} m/sec	30.64
100% Illite	3.5	Pb	2500 mg/l	1.07×10^{-10} m/sec	13.50
100% Illite	3.5	Pb	5000 mg/l	3.20×10^{-10} m/sec	43.70

Soil C & D: $\gamma_{dry} = 1.88 Mg/m^3$, Wc = 14%, L = 2.5cm, H = 128cm, i = 51.2, A = $45.94 cm^2$

- The effective pore volume (PV) of flow for a saturated soil is the cumulative volume of flow divided by the volume of the void space, (Yong et al., 1992a).

4.2 Geochemical Aspects

4.2.1 Cation exchange capacity

The Cation Exchange Capacity (CEC) of soil A (pH 9.5) was determined using the silver thiourea method while the barium chloride method was used for soil B (pH 6.9), soil C (pH 4.0) and soil D (pH 3.5). The Cation Exchange Capacity values for soil A, B, C. and D, as a function of soil pH and carbonate content are presented in Figure 4.4. The CEC value of soil A, rich in carbonates, was calculated to be 34.20 meq/100g. The results show that the dissolution of carbonates and the acidification of the soil cause a decrease in the CEC values obtained, ranging from 34.20 meq/100g (Soil A, illite at pH 9.5) to 7.94 meq/100g (soil B, pH 6.9), to 6.81 meq/100g (soil C, pH 4) and to 5.34 meq/100g (soil D. pH 3.5).

The CEC obtained for soil A, fall well within the range of reported values which are usually between 20 to 40 meq/100g (Grim,1968; Yong et al., 1992a; and Hausenbuiller, 1985; Ouhadi,1997). The CEC measured on the illitic untreated soil is much higher than the CEC of the soil with carbonates extracted. It is clear that the loss of the CEC is associated with the presence of carbonates in the soil. Some researchers have reported similar decreases in the CEC. MacDonald and Yong (1997) indicated that the removal of carbonates resulted in a drop in the CEC from 24 meq/100g to 8.2 meq/100g. This drop might be explained as a result of the dissolution of soil carbonates during CEC measurement causing an artificially high CEC when the carbonates are present. The carbonate dissolution process showed a great excess in Ca^{2+} and Mg^{2+} cations in the pore fluid. Karczewska (1987) studied the effect of acid leaching on the illitic soil properties. He demonstrated that acid precipitation has a major effect on soil pH and on CEC. Clayey samples showed the greatest changes in the soil pH (up to 46%) and revealed a large decrease in the cation exchange capacity (up to 73%) especially when soil is leached with strong acid of pH 2.0.

Furthermore, it is observed from Figure 4.4 that the CEC was found to be pH dependent. It increases with increasing the soil pH and decreases with decreasing soil pH and increasing soil acidity (Robitaille, 1982; Yong et al., 1992a). The influence of pH on the CEC is well known by many researchers. The pH-dependent cation exchange capacity data measured by Pratt (1961) showed that the CEC for some soil samples changed continuously with pH and increased from pH 4.5 to 8.0. CEC measured in other soil samples with pH 3 to 4.5 gave a constant value. The present study agrees with this finding as the CEC measured between soil pH 4 and soil pH 3.5 is only slightly different.

Moreover, exchangeable cations and soluble cations for soil A, B, C, and D are presented in Figures 4.5 and 4.6 respectively. Results showed that by lowering the soil pH, the soluble cations such as Ca^{2+}, Na^+ and K^+ were reduced and leached out during the soil preparation procedures and their amounts decreased with the soil pH adjustment. Only calcium and magnesium cations, released from the soil structure, significantly increased with lower soil pH. It is observed from Figures 4.5 and Figure 4.6 that the amount of Ca^{2+} released from the soil structure to the soluble phase increases with decreasing the soil pH, and reaches its maximum at soil pH 6.9, then decreases with decreasing soil pH and carbonate content. The amount of Mg^{2+} released from the soil structure shows an increase with decreasing soil pH, whereas, the amount of Na^+ and K^+ released to the soluble phase shows only a slight decrease with decreasing the soil pH.

Furthermore, these research results showed that the accumulation of nitrate leads to an increase in H^+ ion concentration which replaces the basic cations such as Na^+, Ca^{2+} and Mg^{2+} on the clay surface and increases their leaching out of the soil. Leaching of cations leads to an increase in soil acidity and therefore, lowers the soil pH, as demonstrated by Robitaille (1982). In addition to leaching of nutrients, an increase in soil acidification leads to the mobility of other toxic elements such as Al, Mn, etc. (Dale and Turner, 1982). One might expect a significant decrease in the CEC at soil pH 3.5. However, instead, with the presence of exchangeable cations and the increase in calcium and magnesium exchangeable cations, the CEC of the soil only decreased slightly (Pratt, 1961) and was still able to almost completely retain the introduced metals under unsaturated conditions as demonstrated in Chapter 5.

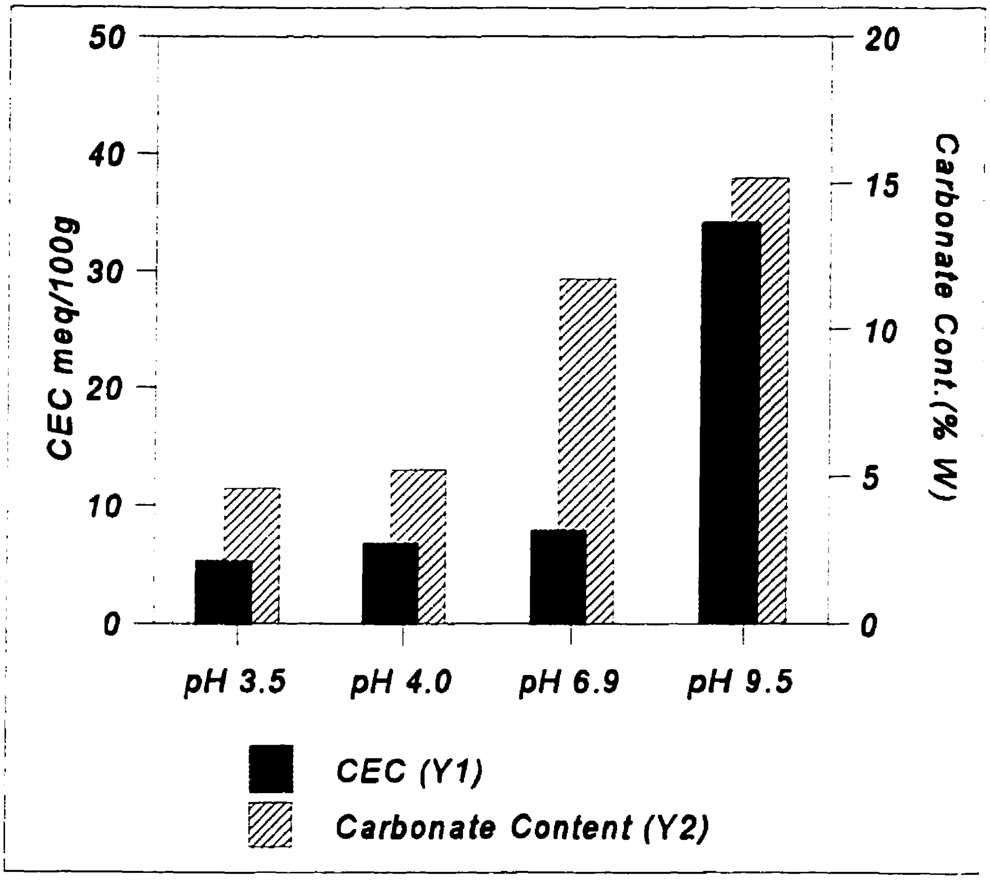


Figure 4.4 Cation Exchange Capacity

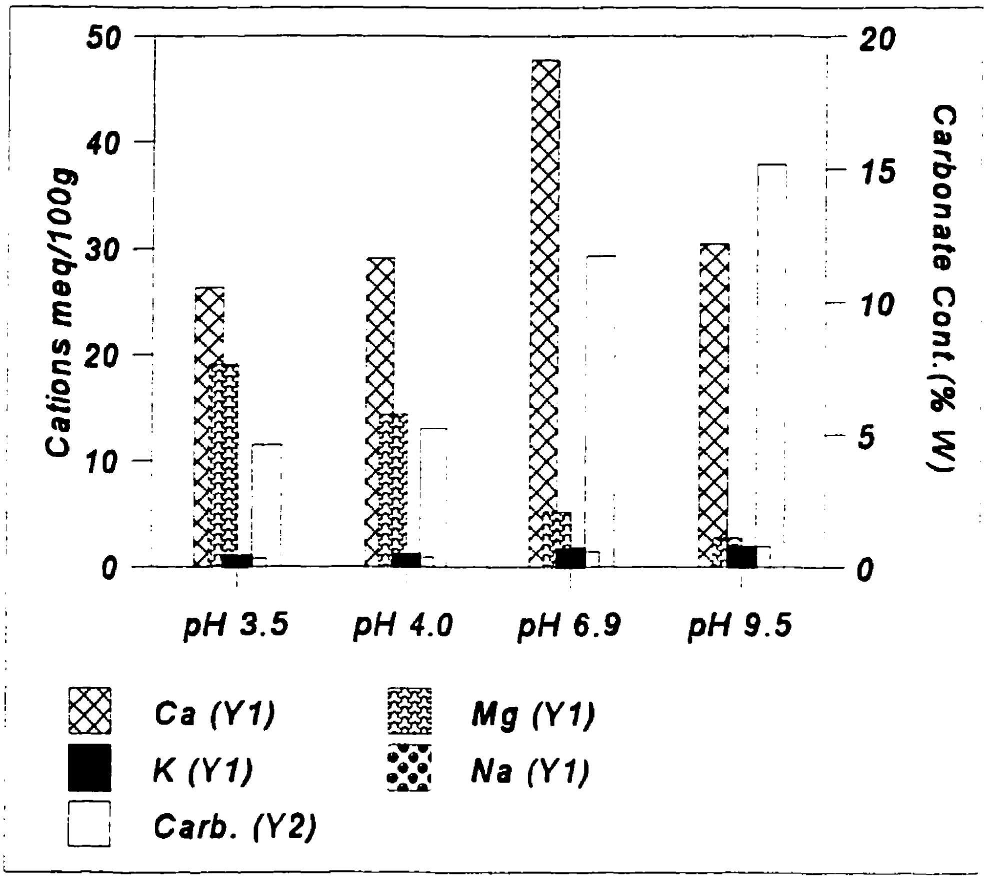


Figure 4.5 Exchangeable Cations

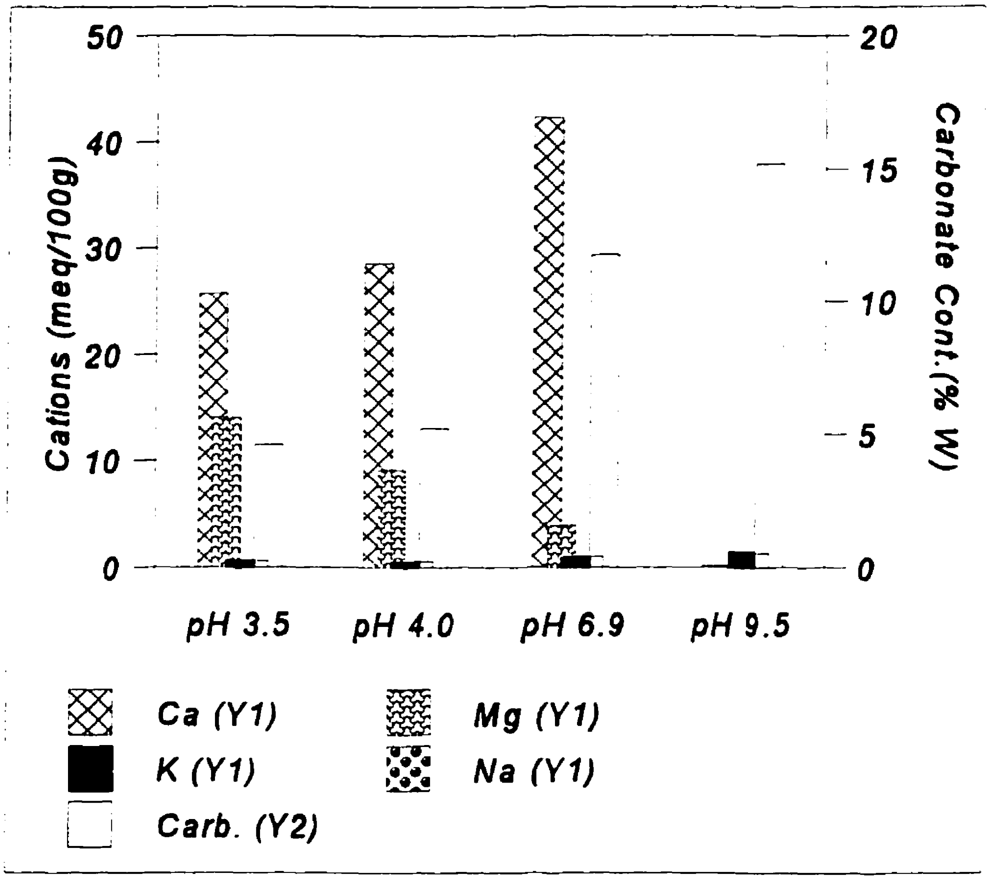


Figure 4.6 Soluble Cations

4.2.2 Specific surface area

The SSA results are presented in Figure 4.7 in terms of soil pH and carbonate content. It was observed that the SSA increases with decreasing the soil pH and the presence of the carbonate content in the soil. As shown, a SSA of 76.41 m^2/g (soil A, pH 9.5) was measured when soil carbonates were present. However, the decrease of soil pH and the removal of soil carbonates resulted in an increase in the soil SSA to 86.09 m^2/g (soil B, pH 6.9), to 100.41 m^2/g (soil C, pH 4) and to 101.91 m^2/g (soil D, pH 3.5). The extraction of carbonates resulted in a SSA which was greater than the SSA of the illitic soil A. The surface area of the acidic soil tends to increase as the carbonate content and the pH of the soil decrease. This increase in the surface area when the soil pH decreases and soil carbonates solubilize was expected given that soil carbonates act as a strong bonding agent in soil.The removal of the carbonate bonding provided the opportunity for greater particle dispersion and thus provided a larger SSA as recorded by many researchers (Yong and Warkentin ,1975; Mitchell, 1993; Kersten and Förstner, 1989; MacDonald and Yong,1997). The resulting increase in SSA due to particle dispersion is likely to affect the sorption of heavy metal metal. In fact, it should be noted that retention of heavy metal is due to the availability of exposed clay particle surface. Bear in mind that the formation of clusters in the case of compacted materials will considerably decrease the effective SSA, resulting in less adsorption.

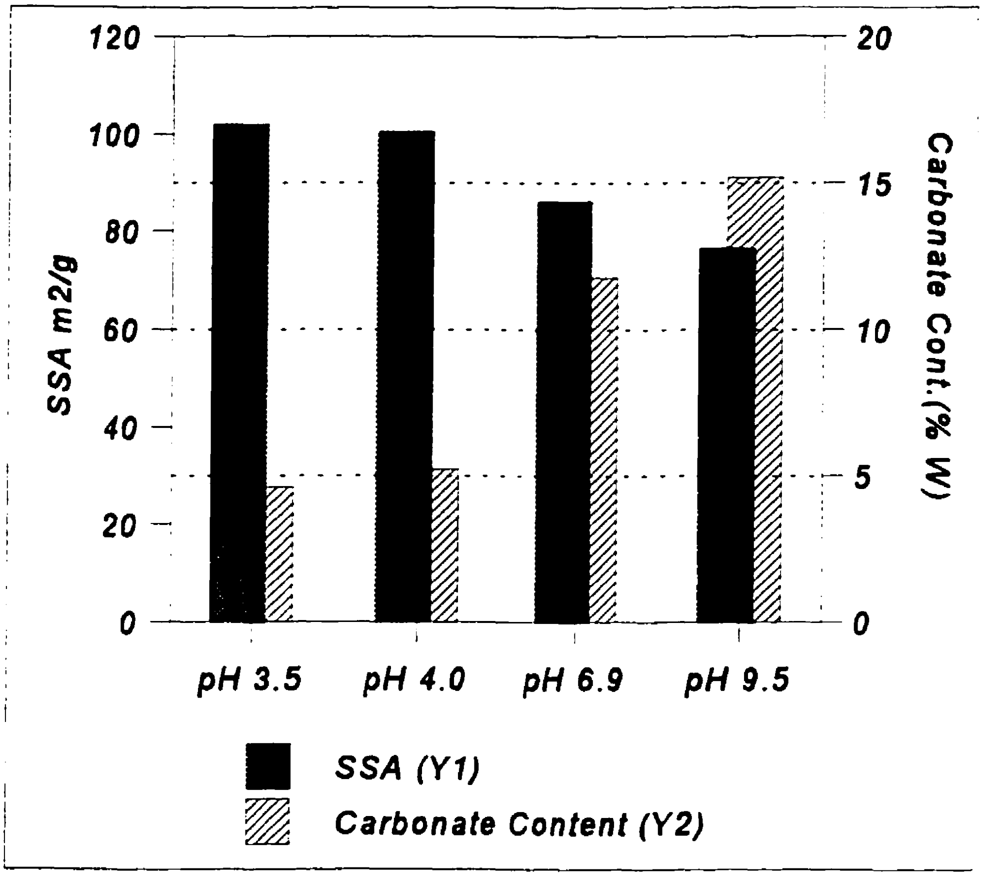


Figure 4.7 Specific Surface Area

4.3 Summary

The overall geotechnical properties of the treated soils revealed no significant changes after the washing procedures. The standard proctor compaction test results did not show any significant changes in the maximum dry density of the soil by lowering the soil pH. Only a slight decrease occurred in the optimum moisture content. The liquid limits of the soil show a slight increase with a decrease in the soil pH and carbonate content. In addition, it was observed that during the washing stages and as the carbonate content was extracted, the soil lost some fines clay particles and the portion of the silt and the sand increased slightly resulting in an increase in voids ratio. These changes might increase H.M. movement along the soil column. The slight variations in the overall hydraulic conductivity results cannot be considered important as they fall within the same order of magnitude. This indicates that reducing the soil pH by dissolving some of the carbonate bonds did not alter significantly the hydraulic conductivity of the illitic soil. Furthermore, the mineralogical composition of the treated soils remains unchanged.

Meanwhile, reducing the soil pH has a considerable effect on the geochemical aspects of the treated soils. The loss of CEC in the acidic soils is associated with the presence of carbonate, low soil pH, and the exchangeable cations in the soil. The removal of carbonates decreases the soil pH, increase the cations leaching and results in a drop of the CEC. In addition, the removal of the carbonate bonding provided the opportunity for greater particle dispersion and thus a larger SSA.

The significance of these factors is how they are likely to affect the movement of H.M. along the soil column. Variations in adsorption between different size fraction is mostly a reflection of their carbon content. The capacity for H.M.

movement is increased by low pH, low carbonate content, and large particle size. Furthermore, the resulting increased exposure of the effective SSA and the CEC may also be involved when an increase in heavy metal sorption has been observed. These factors are considered in the next chapter when sorption of heavy metal in unsaturated illitic soil is investigated.

CHAPTER 5

SORPTION CHARACTERISTICS RESULTS AND ANALYSIS

5.1 General

This chapter presents the results of the experimental investigation into heavy metal transport through unsaturated soil, under conditions of two different pH and constant temperature. The heavy metals investigated are lead, copper and zinc. The soil sorption characteristics of these metals are measured in terms of metal retention and migration.

A series of one dimensional coupled solute and moisture leaching column tests, using different heavy metal solutions, was conducted on an unsaturated illitic soil at varying pH values. Variations of volumetric water content with distance were measured for different time durations, and concentrations of heavy metals in the liquid and the solid phases were analysed. The migration and retention profiles of contaminants along the soil column were determined for each individual layer in the soil along with the partitioning coefficients.

The volumetric water content and the total heavy metal concentrations presented in this chapter provide the experimental information necessary for numerical analysis of the transport of H.M. in the vadose zone. Particular attention is given to the effect of degree of saturation, the presence of carbonate, soil pH and heavy metal concentration. The numerical analysis of most of the data obtained from the leaching column tests is contained and discussed in Chapter 6.

5.2 Moisture Distribution

The soil moisture distribution is central to sorption characteristics because heavy metals are transported in solution. Heavy metals in illite are retained mostly in the carbonate or hydroxide phase at soil pH values above 4. Below pH 4, retention of heavy metals is mostly by exchange mechanisms, (Yong et al., 1992a). In order to study the movement of heavy metals in acidic soil, the buffering capacity of the illitic soil was reduced by using nitric acid. Lowering the pH value of the soil increases the solubility of heavy metals in the soil water by redissolving the heavy metal precipitates (e.g., carbonates and hydroxides) into the soil water. The greater availability of ions will enhance mobilization and the rate of their loss by leaching (Yong and Phadungchewit, 1993; Yong et al., 1992a). The retention of heavy metals increases when the pH of the soil solution exceeds the value required for precipitation (Farrah and Pickering, 1976a, 1976b, 1977a, 1977b and 1979). Since the focus of this study is on the retention of heavy metals by exchange mechanisms, and since sorption of lead in illite soil at high pH values is by precipitation mechanisms (MacDonald and Yong, 1997; Yong et al., 1993), the soil pH in this study was reduced to values below pH 4 to avoid H.M. precipitation.

The degree of water connectivity between the various soil pore classes strongly impacts the hydrologic flux and the mass transfer of contaminants in the system. Contaminant migration from shallow land barrier sites is confined to micropore (matric) regions because it involves unsaturated transport processes unless perched water tables or downslope convergent processes are prevalent. Jardine et al., 1993. During unsaturated conditions, coupled processes of chemical and hydrologic factors control the subsurface transport of contaminants. The extent to which these coupled processes control the movement of contaminants in the vadose zone is largely unkown and is investigated herein. This section on unsaturated soil-contaminant interaction investigates experimentally, the effect of pH changes in the acidic range on the adsorption characteristics of the heavy metals: lead, copper and zinc.

In order to determine the sorption characteristics of the soils, one-dimensional coupled solute and moisture flow tests were conducted on an unsaturated illitic soil at varying pH values. Samples were tested in horizontal leaching columns designed to simulate slow flow of leachate through unsaturated clay. The soil was first statically compacted into the leaching column cell to its maximum dry density (1.88 Mg/m^3) and optimum moisture content (14.16%). The cell was then leached with a continuously supplied nitrate permeant solution of lead, copper or zinc. Two concentrations of each solution were used: 2500mg/l and 5000mg/l. A permeant solution of 200 mg/l of calcium sulfate was used as a control liquid. All trials were conducted at constant atmospheric pressure, under a negligible hydraulic gradient and at room temperature. Samples were tested after time durations of 52 hours and 17.8 days. For each time duration, the test sample was removed and sectioned into disc shapes for chemical analysis. Variations of volumetric water content with distance were measured for different time durations, and metal partitioning analyses of heavy metals in the pore fluid (soluble ions) and the solid phases (extractable ions) were carried out. The migration and retention profiles of contaminants along the soil column were determined for each individual section of soil along with the partition coefficients (K_d) and are investigated in the following sections of chapter 5.

Volumetric water content distribution profiles with time, distance and contaminant concentration for illitic soil at pH 6.9, pH 4.0 and pH 3.5 are presented in Figures 5.1, Figures 5.2a, 5.2b, 5.2c and Figures 5.3a, 5.3b, 5.3c, respectively. The variations of moisture content distributions within the soil columns are plotted in terms of volumetric water content as a function of space and time for various types of fluid. Generally, most test results show moisture distribution along the soil column due to the internal suction gradients. These two gradients are called the volumetric water content and concentration gradient. The volumetric water content along the soil column shows higher values near the source point. However, the volumetric water content decreases as one proceeds along the soil column. For longer time periods, the increase in volumetric water content is seen to be highly dependent on the soil pH and the input concentrations.

5.2.1 Analytical volumetric water content

The analytical saturated volumetric water content is calculated as follows:

Solid volume, $Vs = (\rho_{dry} \times Vt) / (Gs \times \rho_w)$

$Vs = (1.88 \times 1.0) / (2.76 \times 1.0) = 0.68\ m^3$

Void volume, $Vv = Vt - Vs = 1.0 - 0.68 = 0.32\ m^3$

Volumetric water content, $\theta = Vv / Vt = 0.32$ or 32%

Voids ratio, $e = Vv / Vs = 0.32 / 0.68 = 0.47$

The water density, $\rho_w = 1.0\ Mg/m^3$

The total volume is assumed to be, $Vt = 1.0\ m^3$

The analytical saturated water content is calculated in Table 5.1. At shallow depths (above 40mm), where the soil is considered to be fully saturated, volumetric water content profiles obtained experimentally show higher values near the source and exceed the values calculated in Table 5.1. Comparing the theoretical saturated volumetric water content with the experimental results in Tables 5.2, 5.3 and 5.4 one sees that the decrease along the soil column shows a clear dependence on the soil pH, the input concentration, the type of contaminant and the time of wetting. The higher experimental values are explained by particle or cation migration. However, as the distance and the time of wetting from the H.M. source increases, the migration of the existing cations in the soil pores, increases along the soil depth.

Table 5.1 Analytical Saturated Volumetric Water Content

	Soil A	Soil B	Soil C	Soil D
Dry Density, ρ Mg/m^3	1.88	1.88	1.88	1.88
Specific Gravity, Gs	2.76	2.80	2.83	2.87
Volume of Solid, Vs m^3	0.68	0.67	0.66	0.65
Volumetric Water Content, θ	0.32	0.33	0.34	0.35
Voids ratio, e	0.47	0.49	0.51	0.54

5.2.2 Volumetric water content results at high soil pH

In unsaturated soil, moisture moves along the soil columns due to the internal suction gradient, from a location of high concentration to low concentration. Referring to Figure 5.1, at initial time of wetting (52 hrs), the volumetric water content along soil column B (pH 6.9) follows the same profile shape for different input fluid concentrations, and decreases with a decreasing degree of saturation along the soil column. As the time of wetting increases (17.8 days), the increase in volumetric water content is seen to be highly dependent on the fluid input concentration and generally increases with time and concentration. However, the presence of carbonates in illite soil increases the retention of heavy metals at high soil pH and also enhances the buffering capacity of the soil. The higher the carbonate content of the soil, the greater is the retention of heavy metals by the carbonate phase (Yanful et al., 1988a and 1988b). So because of the high carbonate content and high cation exchange capacity, heavy metals were accumulated in the first section of soil A with pH 9.5 (Mazus, 1993) and soil B with pH 6.9, adjacent to the source of the fluid and there was no evidence of heavy metal movement to the soil pore fluid after the shaking procedure. The focus of this study is to investigate the retention and the migration of heavy metals along the soil column at low soil pH. Since sorption of heavy metals in illitic soil at high pH value showed no evidence of heavy metals movement far from the source point, the following sections of chapter 5 investigate mainly the variations of coupled moisture content and heavy metals migration along the soil column for acidic illitic soils (soil C with pH 4.0 and soil D with pH 3.5) leached with various concentrations of heavy metals (lead, copper and zinc). It should be noted that variations in sorption between different size fraction is mostly a reflection of their carbon content, (Westall et al., 1990, Yong et al., 1992a). The capacity for moisture and heavy metal movement is increased by low pH, low carbonate content, and large particle size (silt and sand portions increased in soil C and D, section 4.1.1). Refer to Figures 5.2 through 5.3 for volumetric water content gradients profiles and to Figures 5.4 through 5.16 for contaminant leaching gradients profiles. Also, the resulting increased exposure of SSA and CEC is also involved when an increase in heavy metal sorption has been observed.

5.2.3 Volumetric water content distributions in soil C

Results before and after leaching for illitic soil C at pH 4.0 due to 5000 mg/l of heavy metal input concentration are summarized in Table 5.2 and Figure 5.2. Results showed that at initial time of wetting (52 hrs) and for high input concentration of nitrate solution (5000 mg/l), the steepest gradients of the volumetric water content occurred near the source point. Also for lead the higher concentration solution resulted in a higher volumetric water content. This difference was most pronounced in the 52hours samples. For copper or zinc there was no apparent correlation between concentration and volumetric water content. The same conclusions may be drawn from soil D, Figure 5.3. The high average of the volumetric water content when leached with Cu is due to the high initial value of the volumetric water content before leaching, Figure 5.2b

Table 5.2 Summary of Volumetric Water Content Results for Illitic Soil at pH 4.0, (5000 mg/l input concentration)

input	5000 mg/l			5000 mg/l		
Time	52hrs			17.8 days		
H.M.	Pb	Cu	Zn	Pb	Cu	Zn
before leaching						
V.W.C %	26.69	27.26	26.32	26.69	27.26	26.32
after leaching: above 40mm						
V.W.C. %	35.81-31.06	37.15-31.45	35.87-31.43	38.30-33.58	37.79-33.29	37.97-33.28
below 40mm						
V.W.C. %	31.06-28.09	31.45-28.93	31.43-29.84	33.58-31.77	33.29-31.11	33.28-31.32
average along the soil						
V.W.C %	30.00	30.95	31.25	32.99	33.20	33.

above 40mm : depth between 0 and 40mm; below 40mm : depth between 40mm and 160mm

Generally, volumetric water content is higher in the longer time interval samples of soils C and D. The only exception is the soil D, high concentration of lead, in the first 40mm Sample. This may be explained by the longer diffusion time for more leachate solution and by the leachate lowering the soil pH. It seems natural to conclude that the presence of lead increases the volumetric water content in a way that is somewhat proportional to the concentration of lead. This conclusion explains the higher water content with concentration and the one noted exception to longer time intervals having higher water content (soilD, 5000mg/l, 52hr., first 40mm). Figure 5.5c shows the very high lead level in this sample, within the first 40mm.

Table 5.3 summarizes the volumetric water content variations before and after leaching for illitic soil C at pH 4.0 due to 2500 mg/l of heavy metal input concentration. The high average value of the volumetric water content when leached with Pb and Cu is due to the high initial value of the volumetric water content before leaching.

Table 5.3 Summary of Volumetric Water Content Results for Illitic Soil at pH 4.0, (2500 mg/l input concentration)

input	2500 mg/l			2500 mg/l		
Time	52hrs			17.8 days		
H.M.	Pb	Cu	Zn	Pb	Cu	Zn
before leaching						
V.W.C %	26.69	27.26	26.32	28.20	27.26	26.32
after leaching: above 40mm						
V.W.C. %	32.04-28.61	37.04-32.07	38.65-31.73	36.85-33.71	36.51-33.45	38.07-32.88
below 40mm						
V.W.C. %	28.61-27.60	32.07-30.47	31.73-29.46	33.71-31.94	33.45-30.47	32.88-31.68
average along the soil						
V.W.C %	28.40	31.73	31.69	33.01	33.05	33.13

5.2.4 Volumetric water content distributions in soil D

Table 5.4 summarizes the volumetric water content results before and after leaching for illitic soils D at pH 3.5 due to 5000 mg/l of heavy metal input concentration. It was observed that at initial time of wetting (52hrs) and high input concentration of nitrate solution (5000 mg/l), results show a significant increase in volumetric water content for soil D near the source point, where the soil is considered to be fully saturated for all trials.

Table 5.4 Summary of Volumetric Water Content Results for Illitic Soil at pH 3.5, (5000 mg/l input concentration)

input Time	5000 mg/l 52hrs			5000 mg/l 17.8 days		
H.M.	Pb	Cu	Zn	Pb	Cu	Zn
before leaching						
V.W.C %	26.69	26.32	26.32	26.69	26.32	26.32
after leaching: above 40mm						
V.W.C. %	41.75-32.28	38.31-31.02	38.67-32.09	38.86-32.67	38.90-33.11	39.24-33.09
below 40mm						
V.W.C. %	32.28-28.67	31.02-28.18	32.09-29.22	32.67-30.40	33.11-32.37	33.09-31.15
average along the soil						
V.W.C %	31.45	30.50	31.48	32.27	33.58	32.95

Table 5.5 summarizes the volumetric water content results before and after leaching for illitic soils D at pH 3.5 due to 2500 mg/l of heavy metal input concentration. The high average value of the volumetric water content when

leached Cu is due to the high initial value of the volumetric water content before leaching.

Interpretation of Figures 5.1, 5.2, and 5.3 should be made with the knowledge that the pH of the samples changed along the soil column length. The pH in the unsaturated zone (>40mm) increased over time with leaching. Refer to Figures 5.44 through 5.46 for pH distributions with time and distance in soils B, C and D.

Table 5.5 Summary of Volumetric Water Content Results for Illitic Soil at pH 3.5, (2500 mg/l input concentration).

input	2500 mg/l			2500 mg/l		
Time	52hrs			17.8 days		
H.M.	Pb	Cu	Zn	Pb	Cu	Zn
before leaching						
V.W.C %	26.32	26.32	26.32	26.69	27.26	26.32
after leaching: above 40mm						
V.W.C. %	33.01-29.08	36.94-31.87	36.92-31.45	37.60-32.92	38.84-33.05	38.71-34.27
below 40mm						
V.W.C. %	29.08-31.15	31.87-28.71	31.45-29.20	32.92-31.98	33.05-31.96	34.27-31.98
average along the soil						
V.W.C %	29.86	30.91	31.00	32.90	33.24	33.86

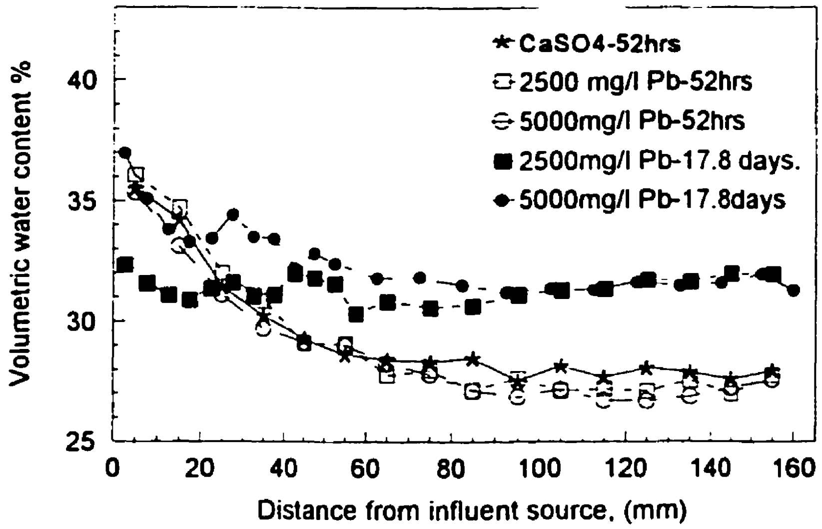


Figure 5.1 Volumetric Water Content Distributions with Time and Distance in Soil B.

(a)

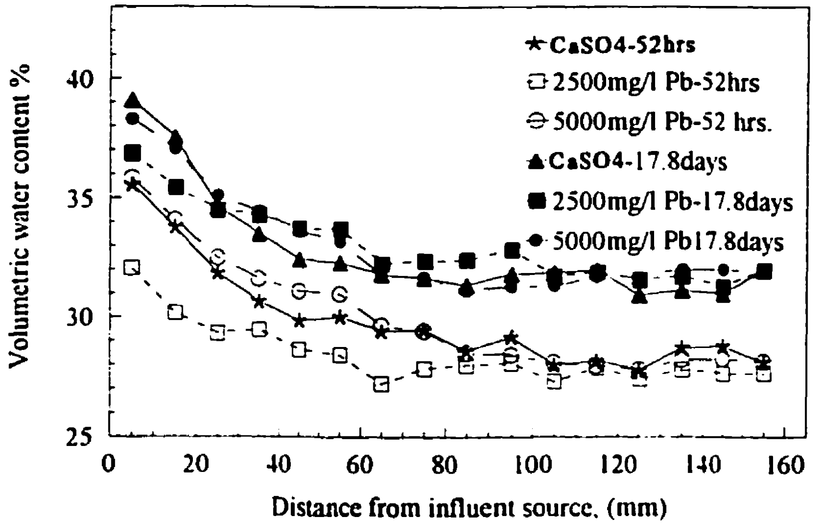
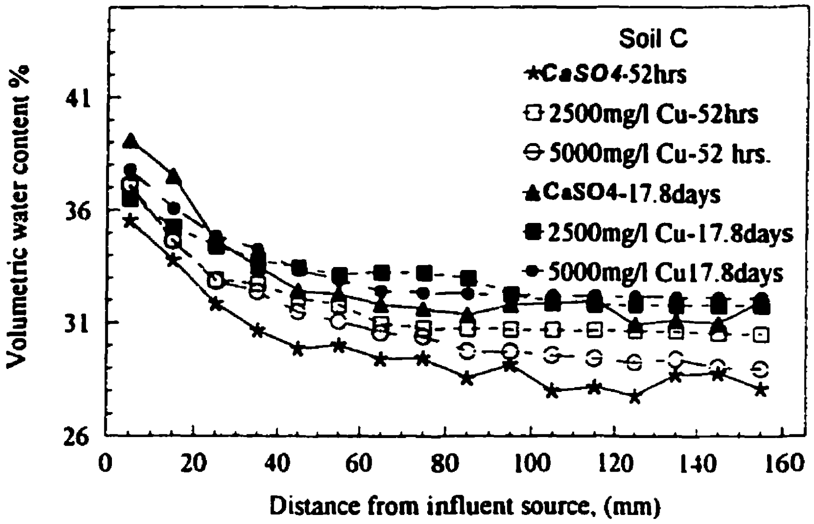


Figure 5.2 Volumetric Water Content Distributions with Time and Distance in Soil C.

(b)



(c)

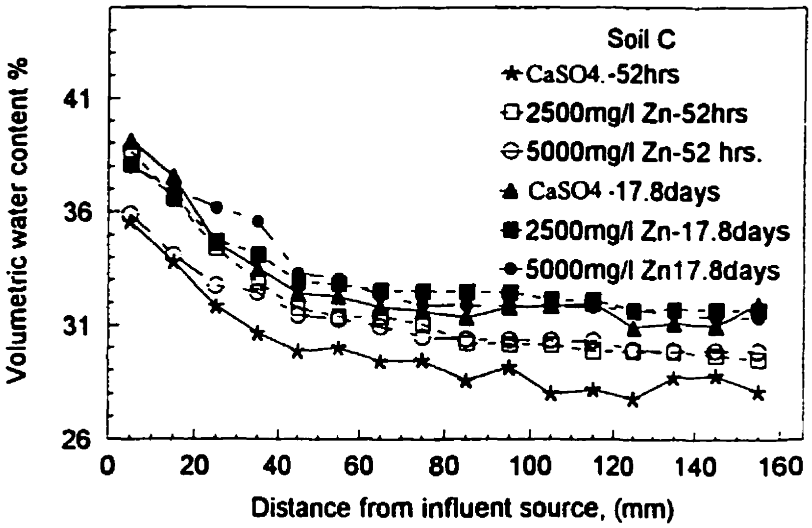


Figure 5.2 Volumetric Water Content Distributions with Time and Distance in Soil C for (a) Lead, (b) Copper and (c) Zinc.

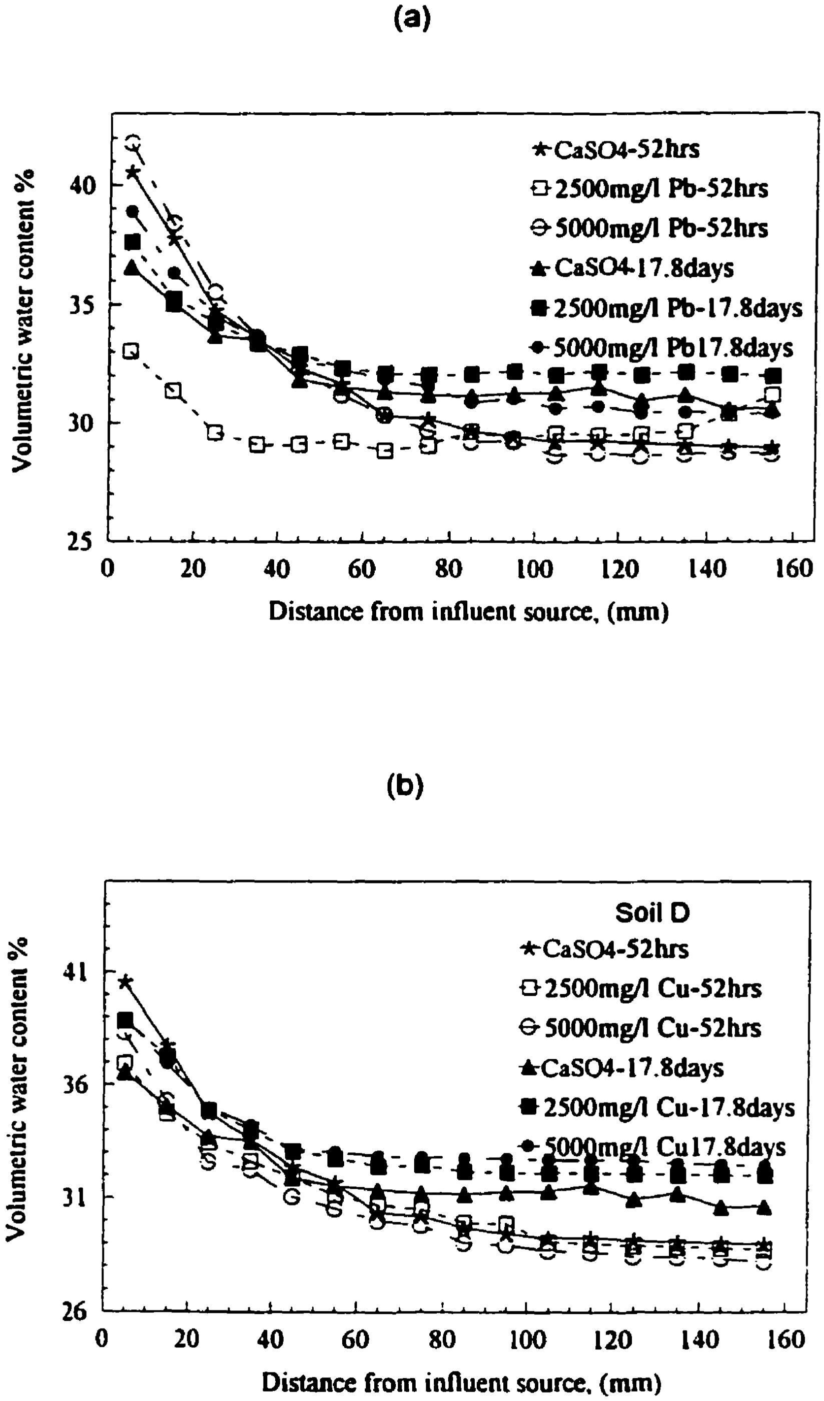


Figure 5.3 Volumetric Water Content Distributions with Time and Distance in Soil D.

(c)

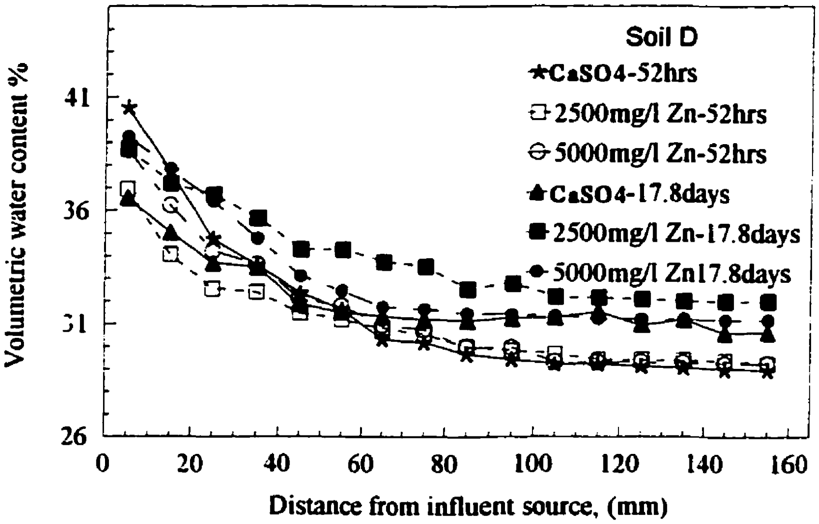


Figure 5.3 Volumetric Water Content Distributions with Time and Distance in Soil D for (a) Lead, (b) Copper and (c) Zinc.

5.3 Sorption Characteristics Results

5.3.1 Metal partitioning analysis

Following the test completion, and for each time duration, samples were extruded, sectioned into sixteen 10 mm thick discs and ground into powder form for chemical analysis, as described in section 3. Then, the samples were analysed for pore fluid contents, measurements of soluble cations and total extractable concentration ions profiles. Metal partitioning analysis was performed according to the Environmental Protection Agency and ASTM standards. Following the procedures described in section 3.5, two different soil suspension methods were used to determine the concentration of heavy metals in the soil: the pore fluid removal or the batch shaker test was used to determine the soluble cations concentration in the liquid phase, and the acid digestion method was used to measure the metals concentration in the solid phase. For both methods, analysis of the fluid for heavy metals ions (Zn^{2+}, Pb^{2+}, Cu^{2+}) associated with the sample solution was performed using the Perkin Elmer Model 3110 atomic absorption spectrophotometer (AAS). The cations concentrations in both phases were expressed in mg/100g. For each leaching test, water content and heavy metal concentrations were determined after 52 hours and after 17.8 days.

Laboratory evaluation of heavy metal migration using the leaching column test is used to determine the sorption characteristics of heavy metals such as lead, copper and zinc in the unsaturated soil, and to describe the migration and retention profiles of contaminants along the soil column for each layer in the soil column along with the partitioning coefficients. The results of these analyses provide the experimental information necessary for numerical analysis of heavy metals in the vadose zone. The model development and prediction is shown in Chapter 6.

5.3.2 Heavy metals profiles in the pore fluid

The pore fluid concentration or soluble cations were determined using the pore fluid removal method or the batch shaker test. Duplicate suspensions with a ratio of 1:10 soil weight to solution volume of distilled water were prepared as recommended by the United States Environmental Protection Agency (USEPA, 1987) to estimate the attenuation of chemicals from batch tests. The concentration of a particular species found in the supernatant or in the pores of each slice was calculated using the formula described in section 3.5 and is expressed in mg per 100g of the soil .

Migration profiles for various heavy metal concentrations of lead, copper and zinc for illitic soil at pH 3.5 are shown in Figures 5.4c, 5.4d, 5.5c and 5.5d, and for illitic soil at pH 4.0 are shown in Figures 5.4a, 5.4b, 5.5a, and 5.5b. Results are plotted between the pore fluid concentration in mg/100g of soil versus depth in mm for various time durations of wetting and input concentration.

5.3.2.1 Heavy metals concentrations in the pore fluid in soil C

5.3.2.1a Case of high input concentration

For high input concentrations of 5000mg/l , migration profiles of Pb, Cu and Zn as a function of distance for soil C (pH 4.0) after 52 hrs and 17.8 days are shown in Figures 5.5a, 5.5b respectively. Due to the low input pH in the influent leachate and the high input concentration of 5000 mg/l of heavy metal nitrate solution, one expects a reduction of the retention capacity of the soil in upper part of the soil column. However, results did not show any traces of H.M. collected in the effluent leachate indicating that the most of Pb, Cu and Zn are completely sorbed in the soils. The maximum sorption of H.M. occurred at the upper part of the soil column above 40mm indicating therefore the capability of the soil to resist any pH changes. It can be observed from Figures 5.5a and 5.5b that , the amount of heavy metals released to the soluble phase varies with heavy metal species, time of wetting and the degree of saturation. So, at initial time of wetting (52hrs) and high input concentration of (5000mg/l), the maximum migration of heavy metals to the soluble phase occurred near the source point and showed that only 1.48% Pb, 3.32% Cu, and 3.56% of Zn migrated to the soluble phase from the total amount sorbed in the first section. Between the source point and 40mm depth, the mobility of H.M. to the soluble phase tended to be in the order of Zn > Cu > Pb, as shown in Figure 5.5a.

In comparison with longer period of time (17.8 days), the amount of H.M. released to the soluble phase slightly increases for Zn and decreases for Cu and Pb. The mobility of H.M. to the soluble phase fell in the same order of Zn > Cu > Pb, as shown in Figure 5.5b. Below 40mm, within the unsaturated phase and as the distance and the time of wetting from H.M. source increases, the amount of H.M. released to the soluble phase decreased sharply indicating that H.M. (from the total amount of H.M. sorbed by the soil pores along the soil column), migrate only a very short distance from the input source after initial and longer periods of time, as shown in Figure 5.5a and Figure 5.5b respectively.

5.3.2.1b Case of low input concentration

For the case of low input concentration of 2500 mg/l , Figures 5.4a and 5.4b illustrate the migration profiles of Pb, Cu and Zn, after 52 hrs and 17.8 days respectively, as a function of H.M. species, and distance for soil C. Similarly to the case of high input concentration, results showed that the maximum sorption of H.M. occurred at the upper part of the soil column above 40mm, demonstrating almost a complete sorption of Pb, Cu and Zn by the soil pores, and there was no trace of

H.M. collected in the effluent leachate. In comparison with the case of high input concentration, the amount of heavy metals moved to the soluble phase decreased slightly indicating higher retention of H.M. by the soil. The data obtained at initial time of wetting (52hrs) and for low input concentration of (2500 mg/l), showed that only 0.41% of lead, 1.22% of zinc were released to the soluble phase from the total amount sorbed in the first section whereas copper showed a complete retention. The mobility of H.M. to the soluble phase tended to be in the order of Zn >Cu> Pb, as shown in Figure 5.5a

However, for longer time periods (17.8 days), in comparison with short time of leaching, the mobility of H.M. to the soluble phase tended to be in the order of Pb > Zn> Cu as shown in Figure 5.4b. The increase in the amount of Pb released to the soluble phase from the first section is due to the high accumulation of Pb near the source point initial value of the volumetric water content before leaching. Beyond that depth, and as the time of wetting increases, the amount of H.M. released to the soluble phase (as shown in Figures 5.4a,b) decreased sharply indicating that H.M. migrates only a short distance from the input source after longer periods of time.

5.3.2.2 Heavy metals concentrations in the pore fluid in soil D

5.3.2.2a Case of high input concentration

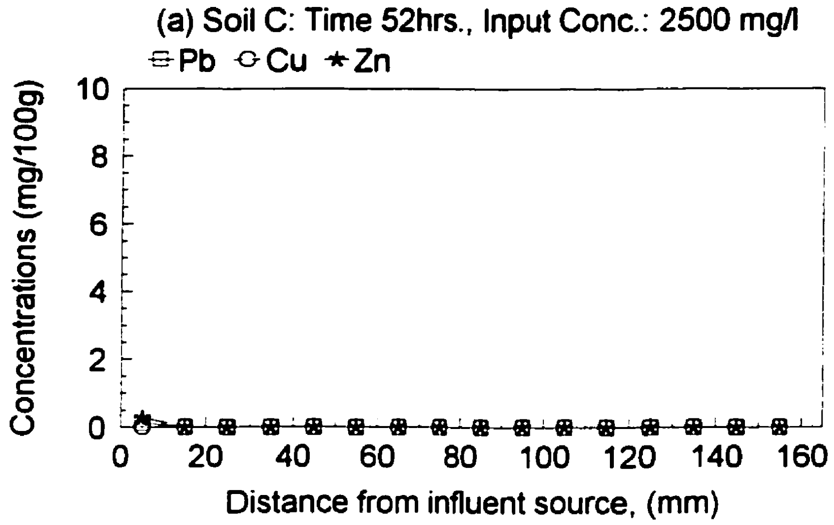
At initial time of wetting (52hrs) and high input concentration of (5000 mg/l), results showed that only 15.6% of lead migrated to the soluble phase from the total amount of lead sorbed (71.5%) in the first section, which is equal to 11.16% of the total amount of lead moved along soil column D (pH 3.5).The total amount moved to the soluble phase from the total sorbed in the first section fell in the order of Pb (15.6%) > Zn (3.6%)> Cu (1.38). The migration profiles of Pb, Cu and Zn to the soluble phase are illustrated in Figure 5.5c. The release of lead at initial time might be due to the amout of acidic water entrapped in the first section of the soil D, resulting in an increase of the volumetric water content to near saturation - i.e. the volumetric water content increased from 26.69% to 41.75% for Pb for the first section of soil D, while for soil C, the volumetric water content increased from 26.69% to 35.81% indicating higher retention of Pb with higher soil pH and less amount of Pb moved to the soluble phase.

However, It can be observed from Figure 5.5d that for longer time periods of 17.8 days and between the source point and 40mm depths, the amount of H.M. released to the soluble phase slightly increased for Cu and Zn due to the increase in the amount sorbed by the soil and tended to be in the order of (3.11) %Zn > (1.87%) Cu > (0.78%) Pb for soil D when leached with high input concentration of 5000 mg/l. Whereas, for higher soil pH as the case in soil C, the retention of H.M. increased, the amount of H.M. released to the soluble phase demonstrated lower values and the mobility of H.M. to the soluble phase falls in the order of (1.89%) Zn > (0.42%) Cu > (0.41%) Pb, as illustrated in Figure 5.5b. Similarly to soil C, the maximum sorption of H.M. also occurred above 40mm at the upper part of the soil column, indicating therefore a complete retention of H.M. below that depth.

5.3.2.2b Case of low input concentration

Migration profiles of Pb, Cu and Zn as a function of distance for soil D after 52 hrs. and 17.8 days are shown in Figures 5.4c and 5.4d respectively. In comparison with soil C, at initial time of wetting (52hrs), and low input concentration of (2500 mg/l), migration profiles of Pb show higher movement to the soluble phase with decreasing the soil pH. It is observed that 8.56% of lead migrated from the total mass moved along the soil column with 11.3% of lead migrated to the soluble phase from the total amount of lead sorbed in the first section of soil column D (pH 3.5). Whereas Zinc and copper did not show any significant increase in their movement to the soluble phase along the soil column, only values of 0.35% of zinc and 0.16% of copper were released to the soluble phase from the first section as illustrated in Figure 5.4c. The release of lead at initial time is also due to the low soil pH and the high percentage of lead sorbed in the upper part of the soil column above 40mm depth.

However, as the time of wetting increased as illustarted in Figure 5.4d, results showed an increase in Pb sorption or Pb movement towards the bottom of the soil column, so the amount of lead accumulated in the first part decreased resulting in a lower movement to the soluble phase from the upper part of the soil column above 40mm. Beyond that depth, results also showed a complete H.M. sorption in the soils with no H.M. movement to the soil solution, (as shown in Figures 5.4c and 5.4d).



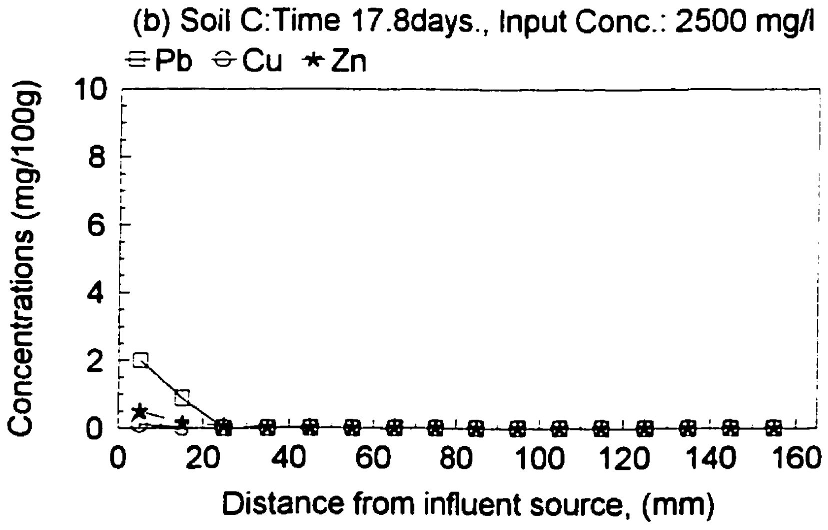
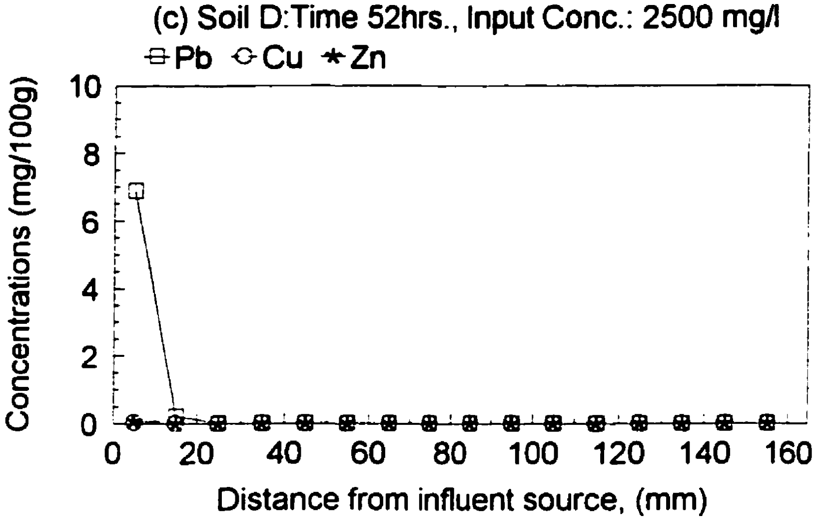


Figure 5.4 Migration of Pb, Cu and Zn, (2500mg/l).



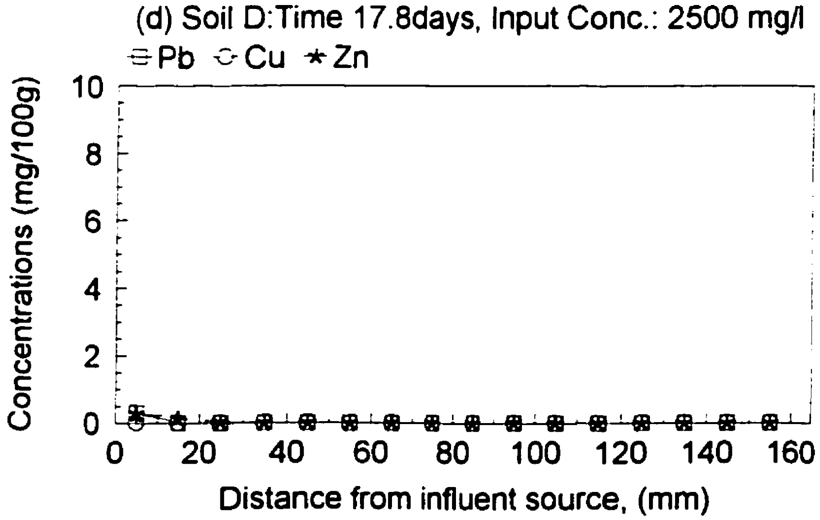
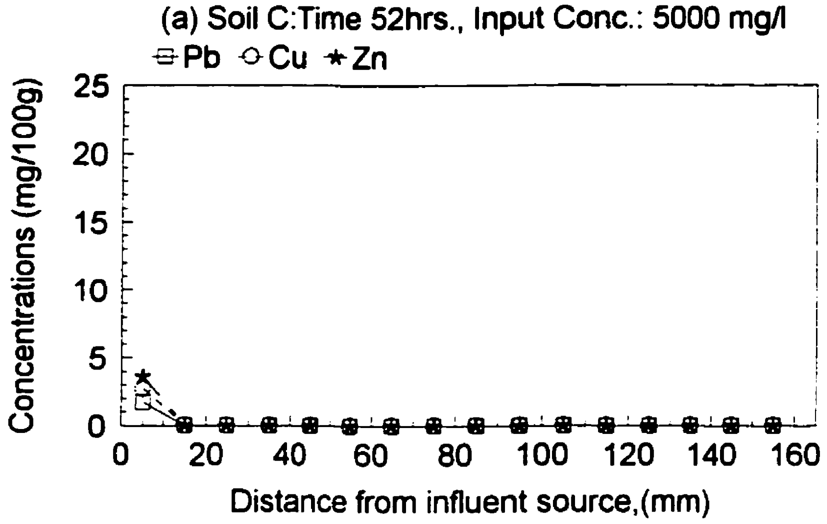


Figure 5.4 Migration of Pb, Cu and Zn, (2500mg/l).
(a) Soil C, 52 hrs, (b) Soil C, 17.8 days,
(C) Soil D, 52 hrs, (d) Soil D, 17.8 days.


(a) Soil C:Time 52hrs., Input Conc.: 5000 mg/l

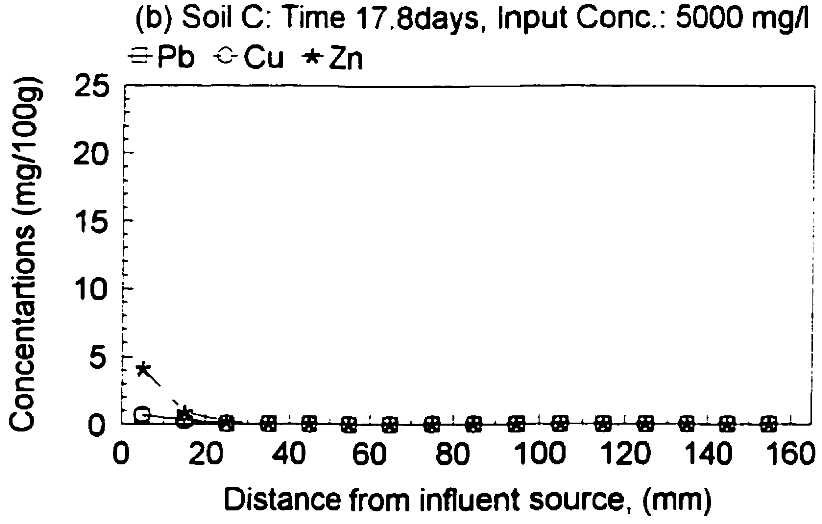

(b) Soil C: Time 17.8days, Input Conc.: 5000 mg/l

Figure 5.5 Migration of Pb, Cu and Zn, (5000mg/l).

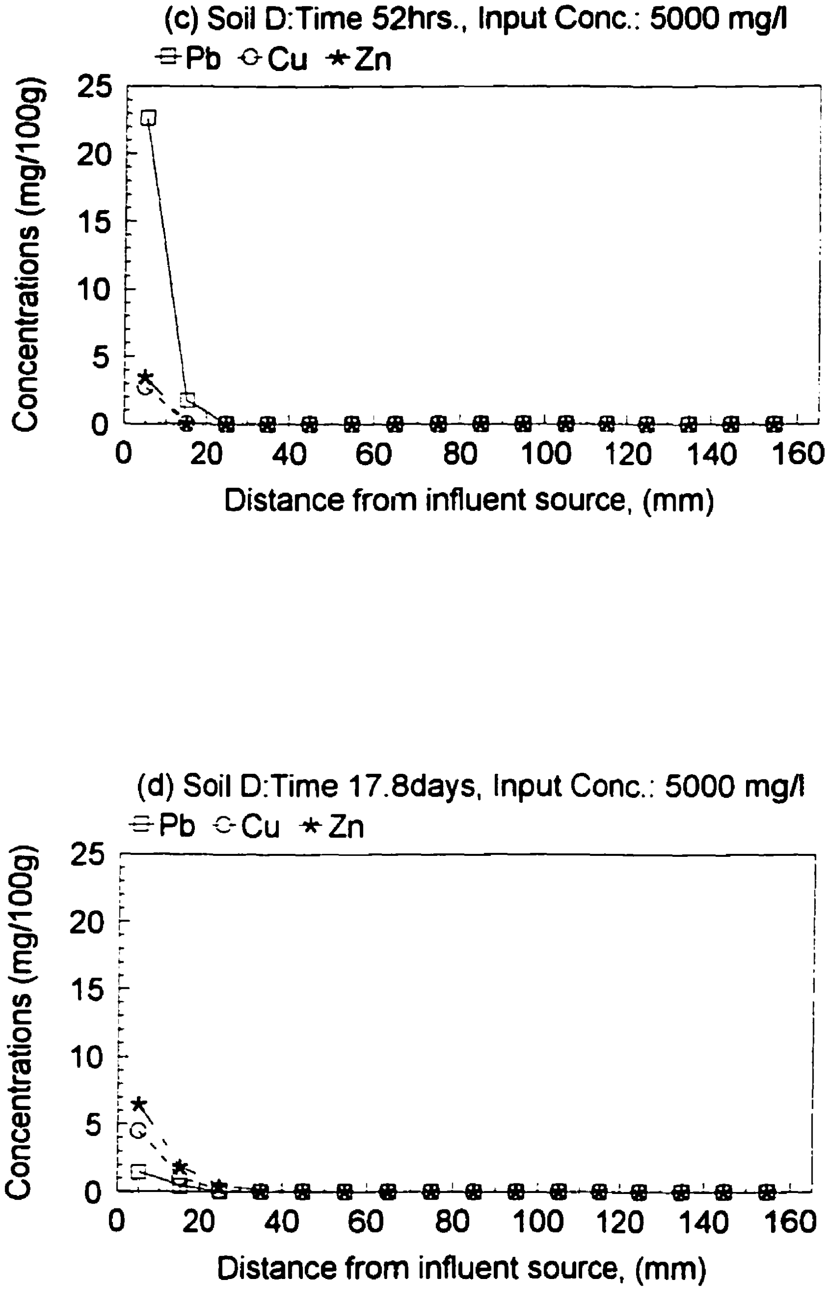


Figure 5.5 Migration of Pb, Cu and Zn, (5000mg/l).
(a) Soil C, 52 hrs, (b) Soil C, 17.8 days,
(C) Soil D, 52 hrs, (d) Soil D, 17.8 days.

5.3.3 Heavy metals sorbed profiles

Heavy metals and existing cations in the solid phase were measured using the pore fluid extraction or the acid digestion method (3050) of the United States following the procedures described by the Environmental Protection Agency (USEPA, 1986). This method is used to dissolve all the sample inorganic-metal bonds. It is used to ensure complete oxidation and destruction of the organic-metal bonds and to prepare soil samples for analysis by atomic adsorption spectrophotometry (AAS) in order to determine the background level of the trace metals in soil. The concentration of a particular species adsorbed by the clay and found in the supernatant for each slice was obtained using the formula described in section 3.5. The total adsorbed (S) concentration of metals in the solid phase was obtained by subtracting the soluble species concentration (C) from the total concentration (Ct) of metals by the clay which was found in the supernatant . The units of S, Ct and C are expressed in mg of constituent adsorbed per 100 g of dry soil.

Retention profiles of lead, copper and zinc within the soil column as a function of time of wetting and soil depth for various soil pH (soil C & D) are shown in Figures 5.6 to 5.11. In order to examine the selectivity order of heavy metals retention in the unsaturated soil, the amounts of heavy metals retained in soil C and D were replotted and are shown in Figures 5.12a, 5.12b, 5.14a, 5.14b, and 5.13a, 5.13b, 5.15a, 5.15b, respectively, in terms of time duration, concentration and heavy metals retention for easy comparison between heavy metals single species movements.The results are plotted using the retained concentration of metals in the solid phase (S) expressed in mg/100g of soil, versus soil depth in mm for various times, duration of wetting, and two different input concentrations of lead copper and zinc.

Generally, as mentioned before, results show that there were no heavy metals collected in the effluent leaching, indicating that heavy metals are mostly retained in the soil. Since heavy metals are highly soluble in acidic saturated conditions, one expects to have a total desorption from the soil to the soluble phase at low soil pH. However, results showed that the migration of H.M. is highly dependent on the presence of carbonate, the degree of saturation, the influent concentration and the time duration.The presence of carbonates in the illite soil (A & B) increases the retention of heavy metals at high pH and also enhances the buffering capacity of the soil. The higher the carbonate content of the soil, the greater the retention of heavy metals by the carbonate phase (Yanful et al.. 1988a and 1988b; Yong et al., 1992a).

Furthermore, due to the low input pH in the influent leachate, one expects a reduction of the retention capacity of the soil in upper part of the soil column. However, results did not show any traces of H.M. collected in the effluent leachate indicating that most of the Pb, Cu and Zn are completly sorbed in the soils. The maximum sorption of H.M. occurred in the initial sections of the soil column between 0 - 40mm (shallow depths) indicating therefore the capability of the soil to resist any pH changes.

As the time of wetting increases, the amount of H.M. released to the soluble phase increased slightly with the mobility of H.M. along the soil column . The overall migration test results showed that at shallow depths and when the soil is near saturation, Zn is more mobile along the soil column than other H.M. species. and smaller amounts of Zn are retained than Cu and Pb in the saturated phase or the upper part of the soil column near the source point. However, the mobility along the soil column species tended to be in the order of Zn > Pb > Cu. This agreed well with previous findings by several authors, Yong and Phadungchewit, 1993; Elliott et al., 1986; Bohn et al., 1979; and Farrah and Pickering, 1977a and 1977b.

Generally, heavy metals precipitate at high soil pH's (e.g., Pb precipitates at pH > 5). Since the initial soil pH is 3.5 and 4.5 for soils D and C, respectively, further H.M. leaching slightly decreases the soil pH of the upper part and enhances the mobility of H.M. along the soil column. In the top part of the soil column, H.M. was retained by cation exchange.

However, as the distance and the time of wetting from H.M. source increases, (as shown in Figures 5.4a,b,c,d and Figures 5.5a,b,c,d) and within the unsaturated phase (below 40mm), the amount of H.M. released to the soluble phase decreased sharply indicating that H.M. migrates only a short distance from the input source after longer periods of time. This might be explained by the cation exchange capacity of the soil and their replacements with the exchangeable cations along the soil column, which are still able to almost completely retain the introduced H.M. under unsaturated conditions. As the distance and the time of wetting from the H.M. source increases, the mobility of the existing cations such as Na^+, K^+, Ca^{+2}, Mg^{+2}, far from the source point and towards the bottom of the soil column, increases along the soil depth resulting in an increase in the soil pH along the soil column. The latter will increase the presence of carbonate which favors the retention of heavy metals. In addition, the decrease in the degree of saturation, as one proceeds along the soil column and far from the source point, can be another significant reason for H.M. retention and the discontinuity to migrate to the soluble phase.

5.3.3.1 Heavy metals sorbed in soil C

5.3.3.1a Case of high input concentration

For soil C, at initial time of wetting (52 hrs), and high input concentration of (5000 mg/l), results showed a maximum sorption and retention of heavy metals near the source point. Sorption decreases in absolute terms, along the soil column. It is observed from Table 5.6 and Figure 5.12a that, at initial time of wetting and for the case of 5000 mg/l of input concentration, the selectivity order of heavy metals sorbed at shallow depths (above 40mm) in soil C, fell in the order of (89.68%) Pb > (63.19%) Cu > (59.11%) Zn, while the amount retained tended to fall in the order of (88.46%) Pb > (61.52%) Cu > (57.51%) Zn, indicating, as mentioned before, very little migration of heavy metals to the soluble phase and almost a complete sorption by the soils. Below that depth, where the soil becomes less saturated, and due to the decrease in volumetric water content movement, sorption of heavy metals decreases and followed the order (10.32%) Pb < (36.81)% Cu < (40.89)% Zn. This indicates a complete retention of heavy metals and a higher mobility of zinc along the soil column. The mobility of heavy metal along the soil column followed the order (139mg/100g) Pb < (163mg/100g) Cu < (225mg/100g) Zn.

For the 17.8 time days period, the amount of heavy metal retained as a function of heavy metal selectivity and distance in soil C, and due to a 5000 mg/l input concentration is shown in Table 5.6 and Figure 5.12b. It was observed that as the time of wetting increased, and at 0 - 40mm, the sorption of heavy metals associated with high input concentration increases and followed the order (89%) Pb> (66.67)% Cu >(62.82)% Zn, while the amount retained fell in the order (88.59)% Pb > (66.25)% Cu > and (60.93)% for Zn. For depths below 40mm, the amount of heavy metal sorbed and retained fell in the order of (11%) Pb < (33.33)% Cu < (37.18)% Zn indicating the discontinuity of heavy metal movement to the soluble phase and the increase in Zn mobility and sorption towards the end of the soil column. The mobility of heavy metals along the soil column after 17.8 days tended to be in the order of (237mg/100g) Pb, (216mg/100g) Cu and (269mg/100g) Zn. A summary of Heavy metals sorption results for illitic soil C at pH 4.0 due to 5000mg/l of heavy metal input concentration is presented in Table 5.6.

Table 5.6 Percentage of Heavy Metal Sorption by Soil Region and Phase. Illitic Soil at pH 4.0, (5000 mg/l input concentration).

input	2500	mg/l		5000	mg/l	
Time		52hrs		17.8	days	
H.M.	Pb	Cu	Zn	Pb	Cu	Zn
			above	40mm		
Sorbed	89.68%	63.19%	59.11%	89%	66.67%	62.82%
Retained	88.46%	61.52%	57.51%	88.59%	66.25%	60.93%
Soluble	1.23%	1.67%	1.6%	0.41%	0.42%	1.89%
			below	40mm		
Sorbed	10.32	36.81%	40.89%	11%	33.33%	37.18%
Retained	10.32	36.81%	40.89%	11%	33.33%	37.18%
Soluble	0%	0%	0%	0%	0%	0%
	Total	Sorbed	along	the Soil		
mg/100g	139	163	225	237	216	269

5.3.3.1b Case of low input concentration

In comparison to the case of high input conentration, results revealed that, for low input concentration and at initial time of wetting, the maximum sorption and retention of Pb occurred above 40mm depth. However, the maximum retention of Cu and Zn occurred beyond that depth indicating the increase in Cu and Zn movement along the soil column with lowering the input concentration. The selectivity order of heavy metal sorbed above 40mm depth fell in the order of (75.93%) Pb , (37.62%) Cu, (37.93%) Zn and the amount retained fell in the order of (75.64%) Pb, (37.62%) Cu and (37.7%) Zn as shown in Table 5.7 and Figure 5.14a. The low value of Cu sorbed in the upper part of the soil column near the source point is due to the high initial volumetric water content before leaching which increases slightly the mobility of Cu towards the end of the soil column. However, for depths below 40mm, the selectivity order of heavy metal sorbed and retained tended to be in the order of (24.07%) Pb , (62.37)% Cu and (62.07) Zn. The mobility of heavy metals sorbed along the soil column fell in the order of (38mg/100g) Pb < (101mg/100g) Cu < (116 mg/100g) Zn indicating a decrease of heavy metal movement along the soil column with lowering of the input concentration.

In the case of longer time periods of leaching (17.8 days), and as the time of wetting increased, the movement of heavy metals along the soil column increased resulting in an increase of heavy metal sorption at shallow depths above 40mm (as shown in Table 5.7 and Figure 5.14b). The sorption of heavy metals associated with low input concentration tended to be in the order of (67.28%) Pb , (46.55%) Cu and (43.87%) Zn and the amount retained fell in the order of (63.9%) Pb , (46.46%) Cu and (43.40%) Zn. Whereas, beyond 40mm depth, sorption and retention of heavy metals fell in the order of (32.71) Pb < (53.45%) Cu and (56.13%) Zn . Also, results show higher mobility of Zn and complete retention of Pb, Cu and Zn towards the end of the soil column C. The mobility of heavy metals sorbed along the soil column due to 2500 mg/l of heavy metal input concentration after 17.8 days tended to be in the order of (87 mg/100g) Pb < (116 mg/100g) Cu and (155 mg/100g) Zn.

Table 5.7 Percentage of Heavy Metal Sorption by Soil Region and Phase. Illitic Soil at pH 4.0, (2500 mg/l input concentration).

input	2500 mg/l			2500 mg/l		
Time	52hrs			17.8 days		
H.M.	Pb	Cu	Zn	Pb	Cu	Zn
above 40mm						
Sorbed	75.93%	37.62%	37.93%	67.28%	46.55%	43.87%
Retained	75.64%	37.62%	37.7%	63.9%	46.46%	43.40%
Soluble	0.29%	0%	0.23%	3.3%	0.085%	0.47%
below 40mm						
Sorbed	24.07%	62.37%	62.07%	32.71%	53.45%	56.13%
Retained	24.07%	62.37%	62.07%	32.71%	53.45%	56.13%
Soluble	0%	0%	0%	0%	0%	0%
Total Sorbed along the Soil						
mg/100g	38	101	116	87	116	155

5.3.3.2 Heavy metals sorbed in soil D

5.3.3.2a Case of high input concentration

Heavy metal retention profiles for Pb, Cu and Zn in soil D at high input concentration of 5000 mg/l and after 52 hrs and 17.8 days are shown in Table 5.8 and Figures 5.13a and 5.13b respectively. Results showed that for a high input concentration of (5000 mg/l) and at initial time of wetting (52hrs), Pb is more retained than Cu and Zn. These results are similar to those of soil C using a 5000mg/l permeant solution with the following exceptions. The total weight of sorbed heavy metal is significantly higher at this lower pH for Pb and Cu at 52 hrs and for Cu at 17.8 days. Never-the-less, the distribution of the sorbed metal is approximately the same except that more Pb is found in the soluble state in the saturated zone at 52hrs, and a greater percentage of Cu is found in the 0 - 40mm saturated zone. The high value obtained for Pb at initial time of wetting is due to the increase in the amout of acidic water entrapped in the first section of the soil resulting in an increase in the volumetric water content from 26.69% to 41.75%. The high value of Cu sorbed along the soil column is due to the increase in its sorption above 40mm depth.

Table 5.8 Percentage of Heavy Metal Sorption by Soil Region and Phase. Illitic Soil at pH 3.5, (5000 mg/l input concentration).

input	5000	mg/l		5000	mg/l	
Time		52hrs		17.8	days	
H.M.	Pb	Cu	Zn	Pb	Cu	Zn
			above	40mm		
Sorbed	90.57%	67.85%	56.46%	88%	75%	61.6%
Retained	78.56%	66.47%	54.97%	87.22%	73.13%	58.49%
Soluble	12%	1.38%	1.49%	0.78%	1.87%	3.11%
			below	40mm		
Sorbed	9.43%	32.14%	43.54%	12%	25%	38.4%
Retained	9,43%	32.14%	43.54%	12%	25%	38.35%
Soluble	0%	0%	0%	0%	0%	0.046%
	Total	Sorbed	along	the Soil		
mg/100g	202	196	232	238	300	284

5.3.3.2b Case of low input concentration

Low input concentration results for soil D are given in Table 5.9 and in Figures 5.15a and 5.15b. These results are similar to those for soil C, low input concentration, with the following exceptions. The sorption results for soil D show a significant increase in the total Pb, sorbed in the 0 - 40mm, saturation region compared to soil C. Cu and Zn show a slight increase in total sorption and, for the 17.8 day time interval, a significant increase in transport from the 0 - 40mm saturated zone to the unsaturated zone. This indicates an increase in the movement along the soil column for Cu and Zn at lower pH. The migration of Pb, Cu and Zn along the soil column increases with time and with decreasing soil pH.

Table 5.9 Percentage of Heavy Metal Sorption by Soil Region and Phase. Illitic Soil at pH 3.5, (2500 mg/l input concentration).

input	2500	mg/l		2500	mg/l	
Time		52hrs		17.8	days	
H.M.	Pb	Cu	Zn	Pb	Cu	Zn
			above	40mm		
Sorbed	87.10%	36.80%	37.00%	78%	39.50%	36.30%
Retained	78.54%	36.77%	16.74%	77.77%	39.50%	36.03%
Soluble	8.56%	0.03%	0.058%	0.23%	0%	0.27%
			below	40mm		
Sorbed	12.90%	63.20%	63.00%	22%	60.50	63.69%
Retained	12.90%	63.20%	63.00%	22%	60.50	63.69%
Soluble	0%	0%	0%	0%	0%	0%
	Total	Sorbed	along	the Soil		
mg/100g	83	106	119	127	119	168

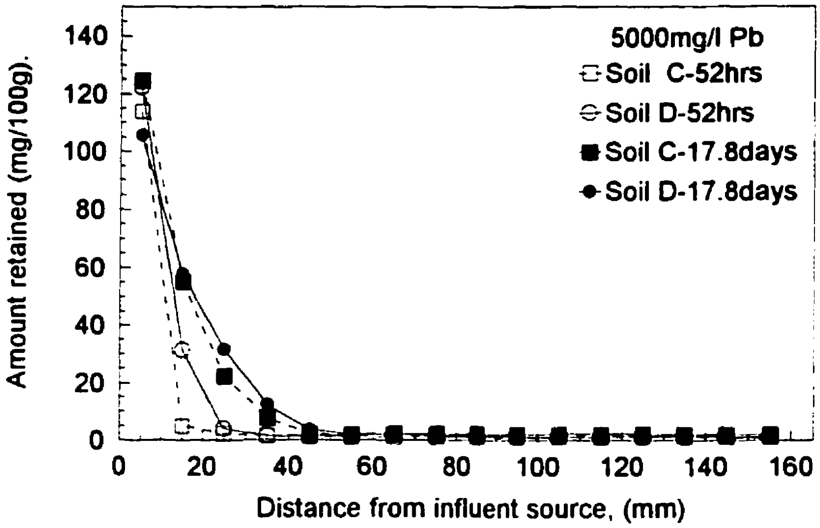


Figure 5.6 Amount of Lead Retained as a function of Time, Soil pH and Distance, (5000mg/l input).

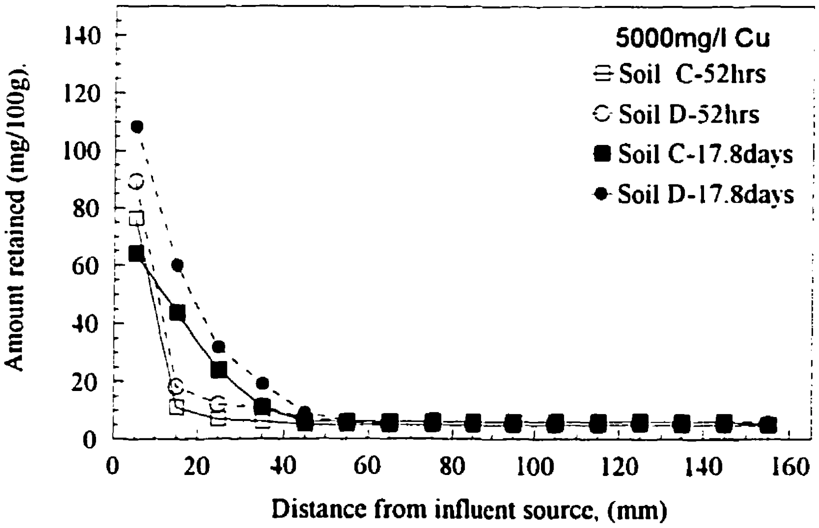


Figure 5.7 Amount of Copper Retained as a function of Time, Soil pH and Distance, (5000mg/l input).

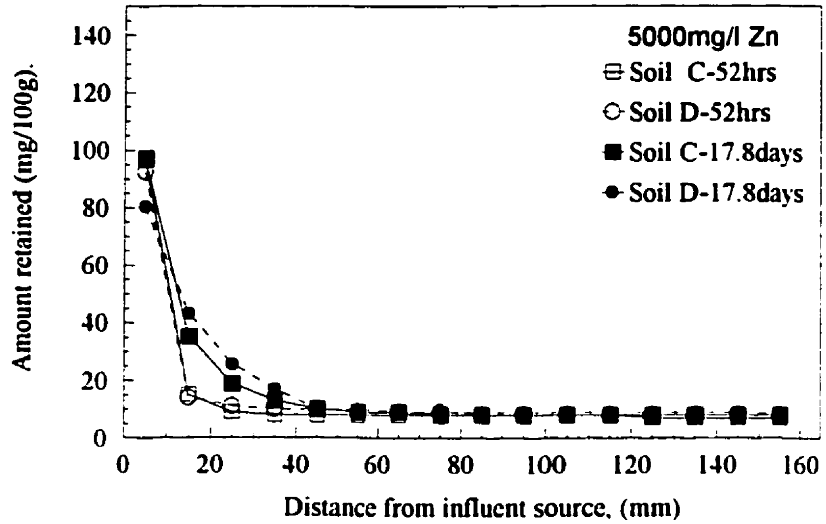


Figure 5.8 Amount of Zinc Retained as a function of Time, Soil pH and Distance, (5000mg/l input).

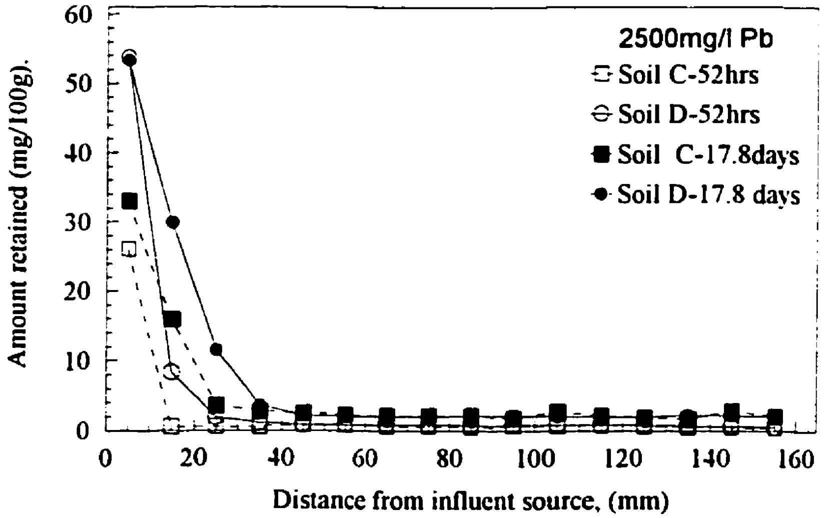


Figure 5.9 Amount of Lead Retained as a function of Time Soil pH and Distance, (2500mg/l input).

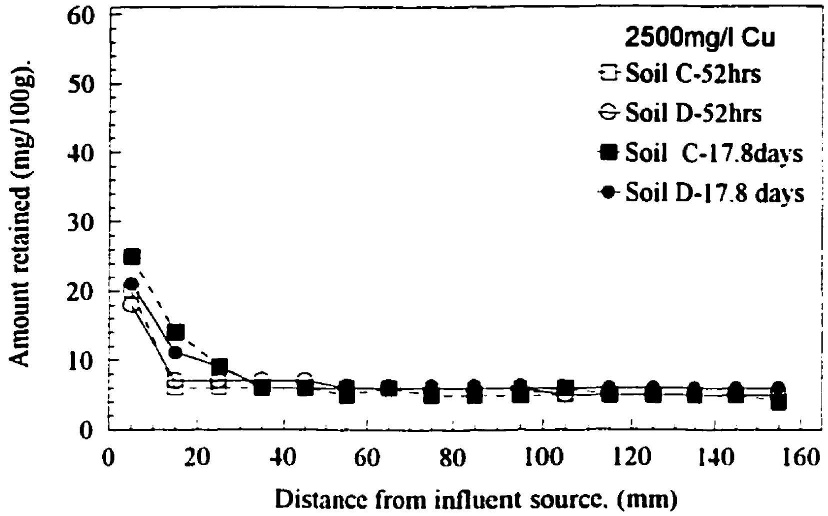


Figure 5.10 Amount of Copper Retained as a function of Time, Soil pH and Distance, (2500mg/linput).

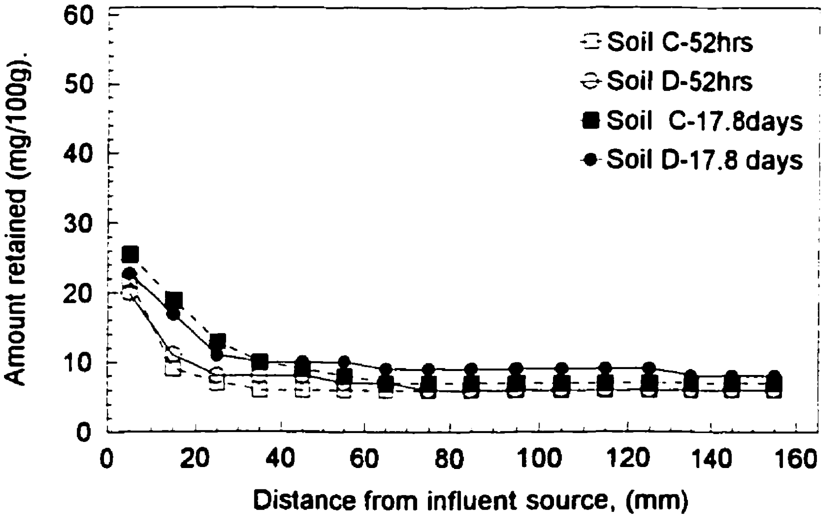
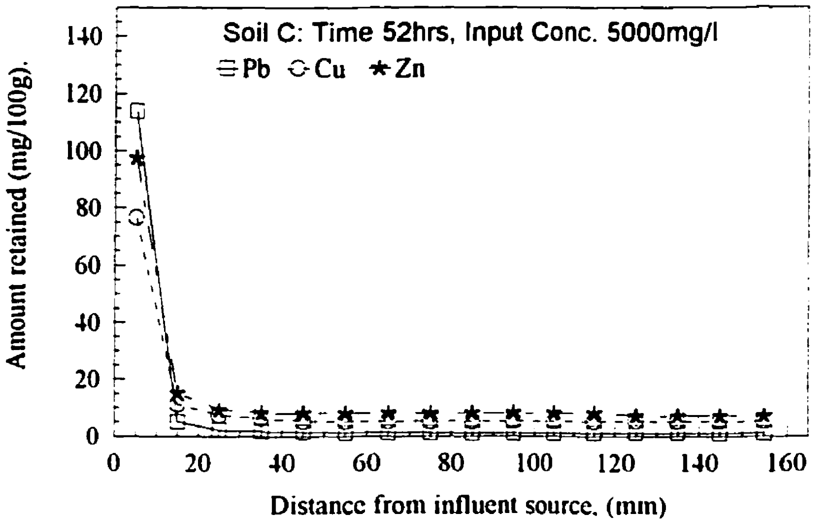


Figure 5.11 Amount of Zinc Retained as a function of Time, Soil pH and Distance,(2500mg/l input).

(a)



(b)

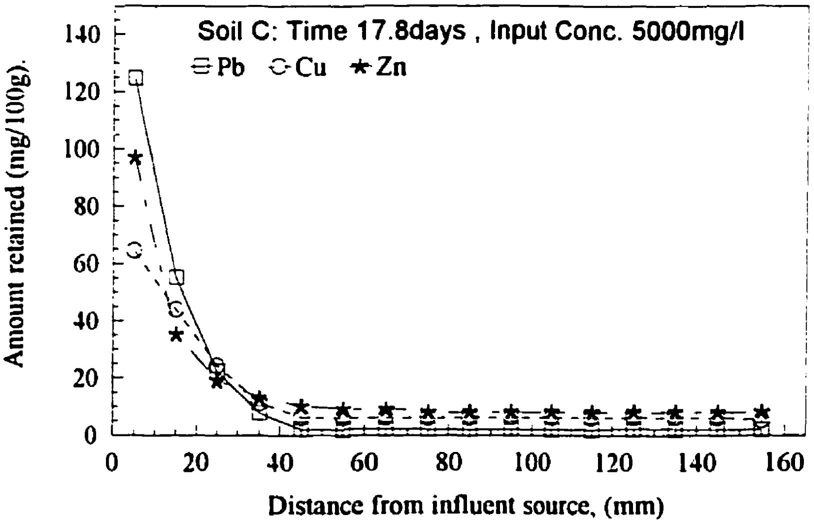
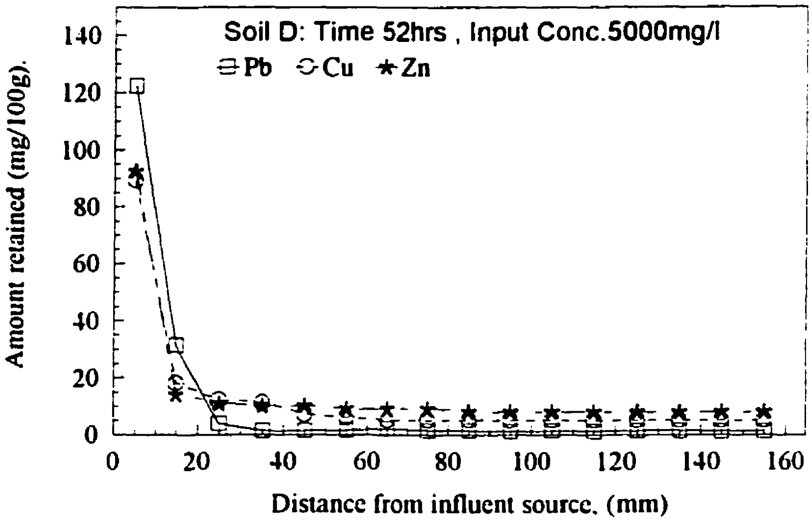


Figure 5.12 Amount of Heavy Metals Retained as a function of Distance in Soil C, (5000mg/l input).

(a)



(b)

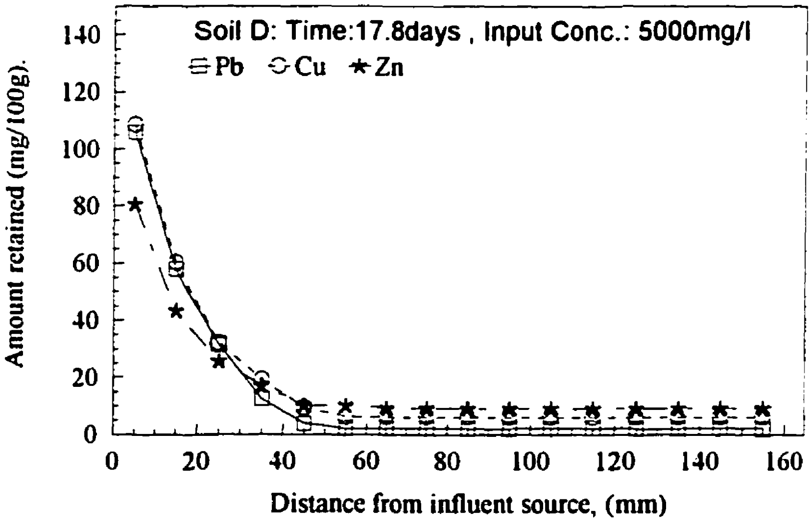
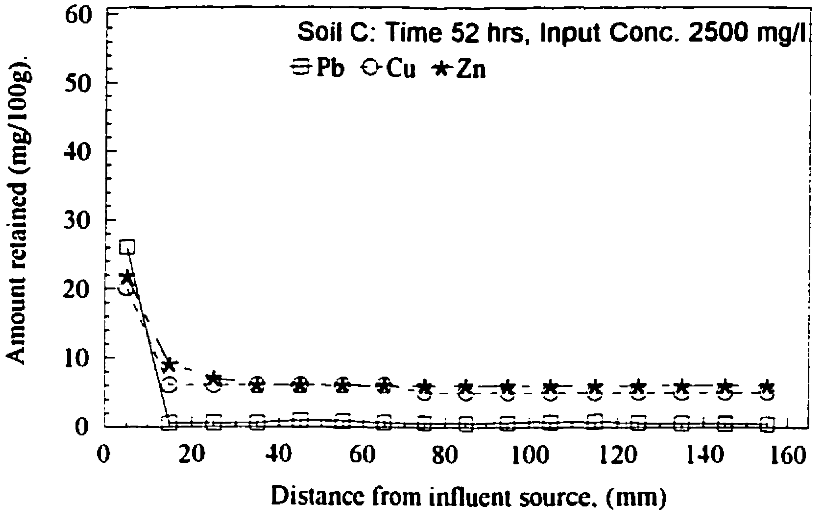


Figure 5.13 Amount of Heavy Metals Retained as a function of Distance in Soil D, (5000mg/l).

(a)



(b)

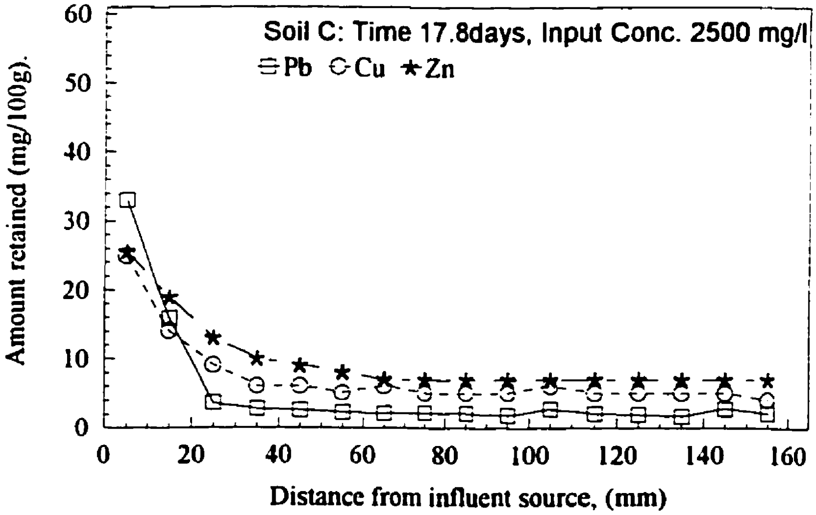
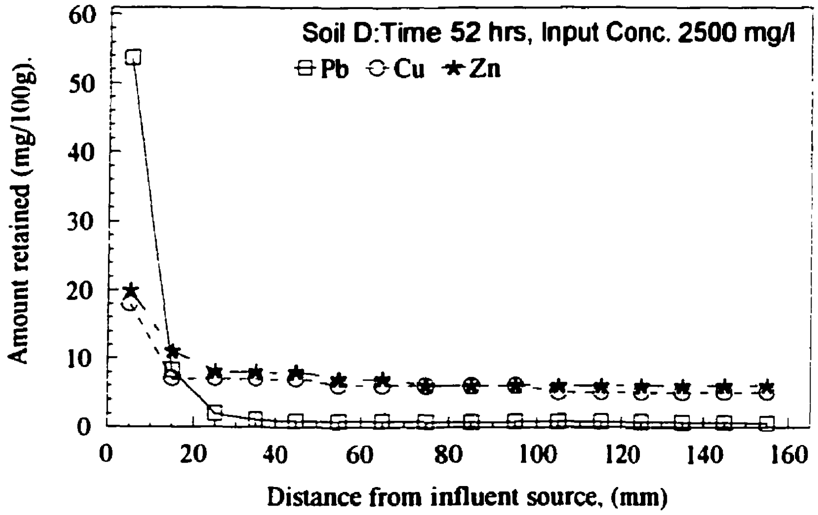


Figure 5.14 Amount of Heavy Metals Retained as a function of Distance in Soil C, (2500mg/l input).

(a)



(b)

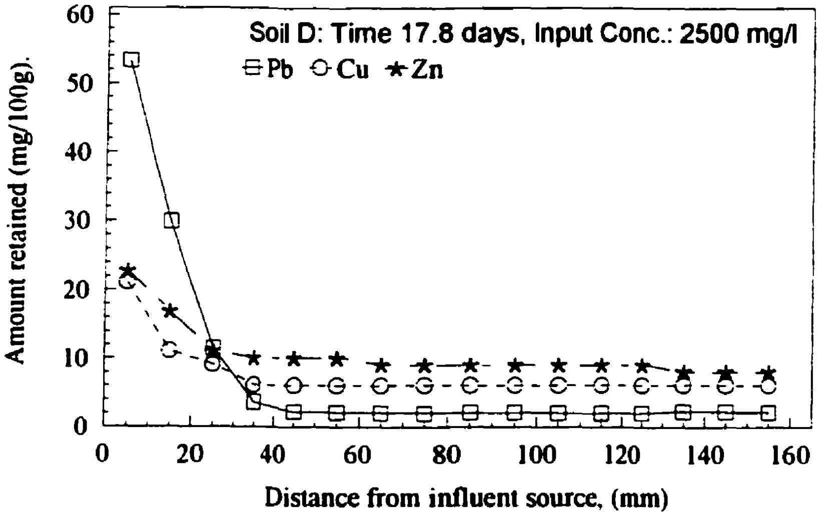


Figure 5.15 Amount of Heavy Metals Retained as a function of Distance in Soil D, (2500mg/l input).

5.4 Partitioning Coefficient Profiles (K_d)

As mentioned in Chapter 1, the partitioning coefficient is required in the contaminant transport equations and is calculated from test data. Most transport models use K_d obtained from 'linear' adsorption isotherms – i.e. as a constant parameter (Freeze and Cherry, 1979; Rowe, 1988). Simplification of (K_d) as a constant and linear function may lead to an improper evaluation of the adsorption/desorption phenomena, (Davidson et al.,1976).

A partitioning coefficient K_d is calculated for each section of the leaching soil column and the results are plotted as a function of soil depth and time of wetting for soil pH values of 3.5 and 4.0 and for two concentrations of lead, copper and zinc contaminants. Solid and liquid phases were determined from the soil sections, as given in section 3.5. The K_d profiles results for illitic soil are shown in Figures 5.16 through 5.19. Refer also to Figures 5.4 through 5.15 for contaminant leaching gradients profiles.

The partitioning coefficient K_d is seen to increase with soil pH and distance from leachate source. It decreases with an increase in time of wetting and in degree of satutation. The low value of K_d obtained when leached with high Pb concentration can be attributed to the high amount of lead released to the soluble phase as a result of the acidic water entrapped in the first section of the soil D, as discussed in section 5.3.3.2.a and section 5.3.2.2.

In comparison with soil D and at high input concentration, soil C (pH 4.0) showed an increase in K_d due to the increase of heavy metal attenuation. The selectivity order of K_d values fall in the order of 12.68 - infinite ml/g (Pb) > 5.58 - 101 ml/g (Cu) > 5.16-67.73 ml/g (Zn) were associated with high concentration (5000 mg/l) (Figure5.19a). While values of infinite - infinite (Cu) > 41.03 - infinite ml/g

(Pb) > 16.54 - infinite ml/g (Zn) were associated with low concentration (2500 mg/l) (Figure 5.18a). However, at shallow depths (above 40 mm) and as the time of wetting increased (17.8 days), the partitioning coefficient K_d decreased with an increase in the degree of saturation .

The overall test results revealed that as the distance and time of wetting from H.M. source increased, (Figures 5.16 through 5.19), and within the unsaturated phase (below 40mm depth), the amount of H.M. released to the soluble phase decreased sharply. This indicates that H.M. migrates only a very short distance from the input source during the specified migration time, and this causes infinite K_d values. The reason for the soluble phase decrease might be related to the decrease in the degree of saturation along the soil column and may also be explained by the cation exchange capacity of the soil. The CEC was still able to almost completely retain the introduced H.M. under unsaturated conditions.

Furthermore, the presence of carbonates in the illite soil increases the retention of heavy metals at high pH and also enhances the buffering capacity of the soil. The higher the carbonate content of the soil, the greater the retention of heavy metals by the carbonate phase (Yanful et al., 1988a and 1988b). Therefore, because of its high carbonate content and high cation exchange capacity, heavy metals were accumulated in the first section of soil with pH 6.9 resulting in a calculated partition coefficient value of "infinity".

Results showed that the sorption characteristics of heavy metals are controlled by many factors which should be taken into consideration - i.e. the presence of carbonate, volumetric water content or degree of saturation, soil pH, and the influent heavy metal concentrations. Therefore, one may conculde that K_d is not a proper approach to use in the design of clay barrier system. Furthermore, the assumption of a linear isotherm can lead to serious errors in predicting contaminant migration, (Darban,1997; Davidson, 1976; Fityus, 1999).

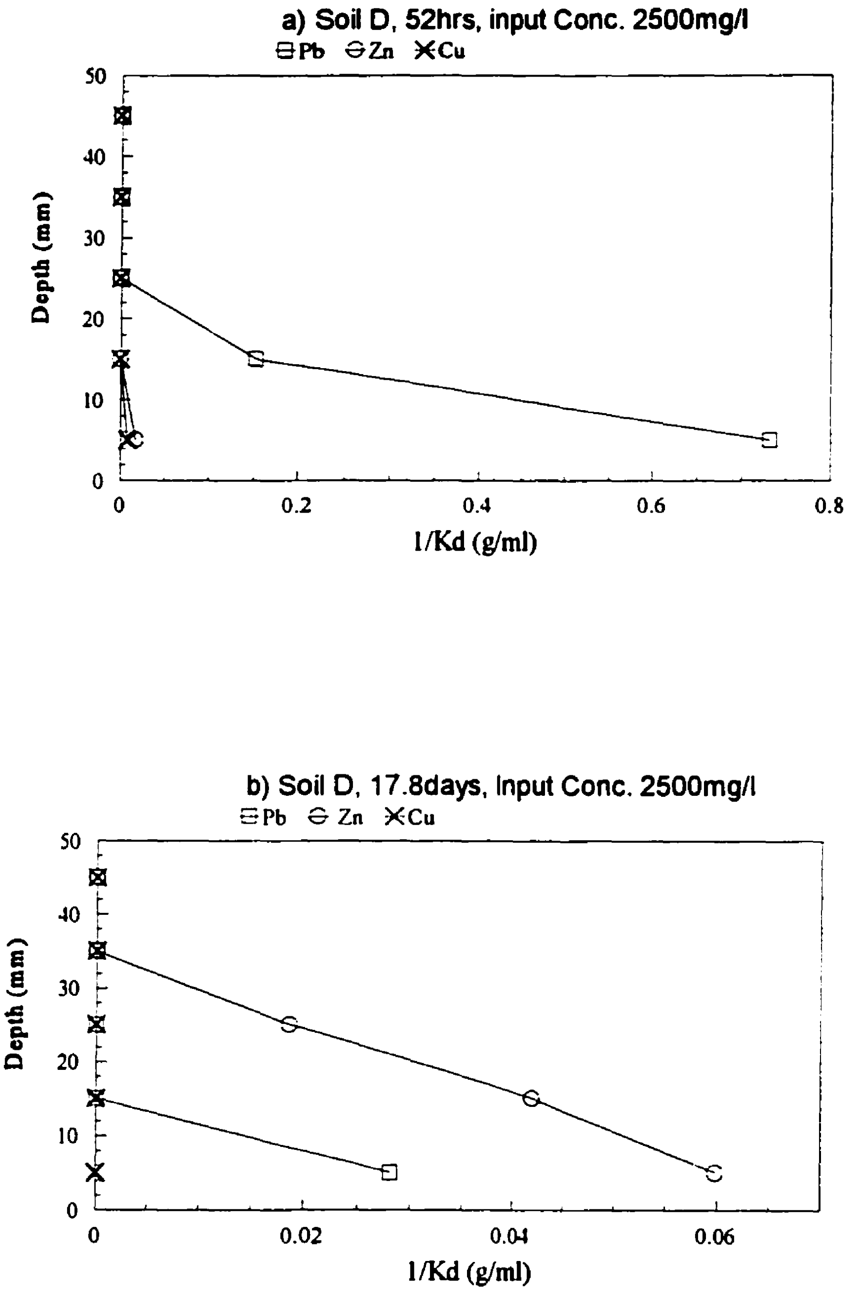
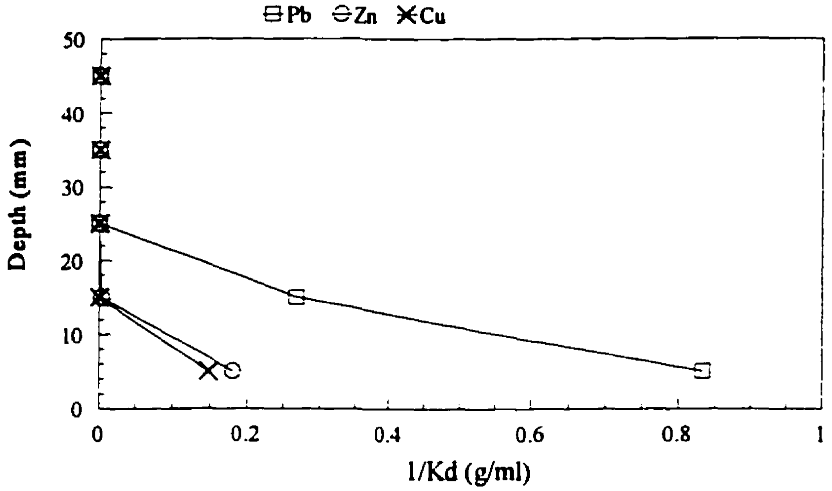


Figure 5.16 K_d Profiles of Pb, Cu and Zn for Soil D, (2500mg/l input).


a) Soil D, 52hrs, input Conc. 5000mg/l

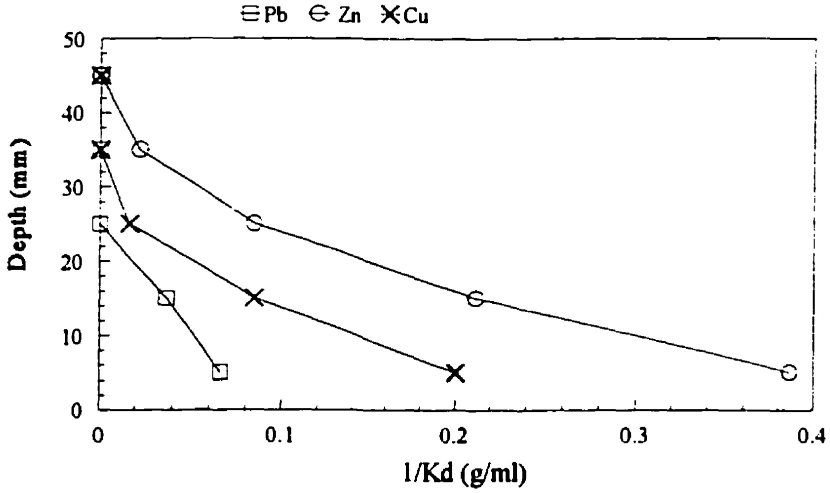
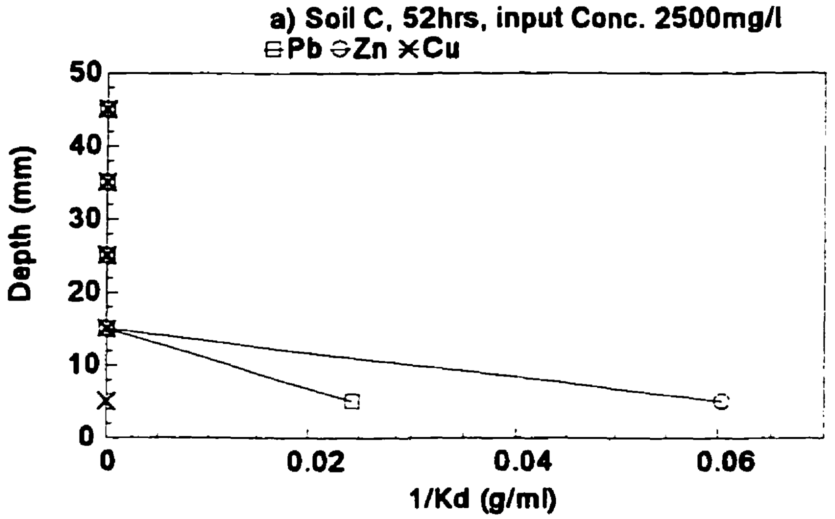

b) Soil D, 17.8days, Input Conc. 5000mg/l

Figure 5.18 K_d Profiles of Pb, Cu and Zinc for Soil D, (5000mg/l input).



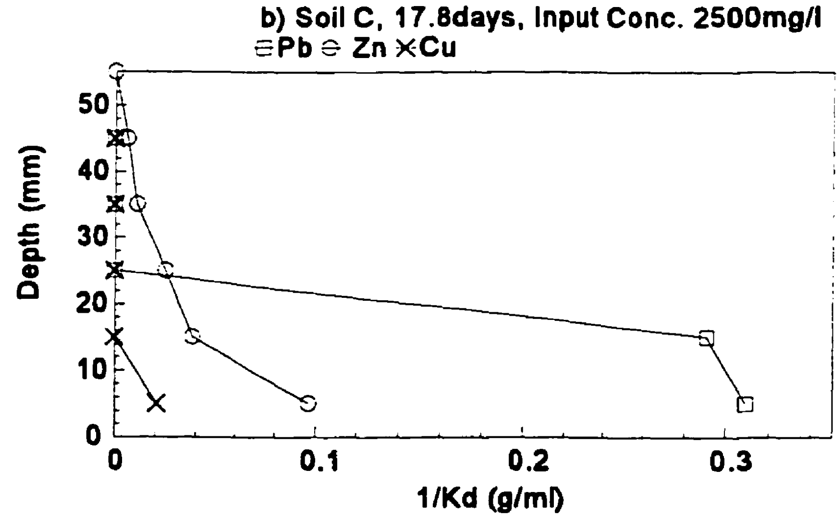
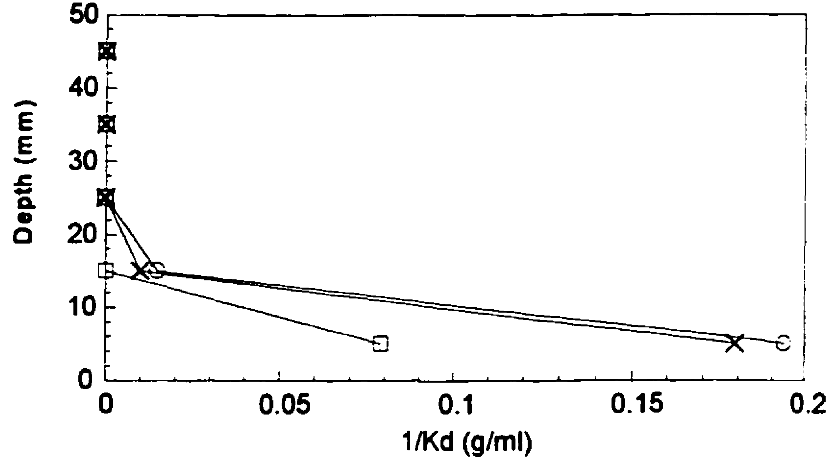


Figure 5.18 K_d Profiles of Pb, Cu and Zn for Soil C, (2500mg/l input).

a) Soil C, 52hrs, input Conc. 5000mg/l
⊟Pb ⊖Zn ×Cu



b) Soil C, 17.8days, Input Conc. 5000mg/l
⊟Pb ⊖ Zn ×Cu

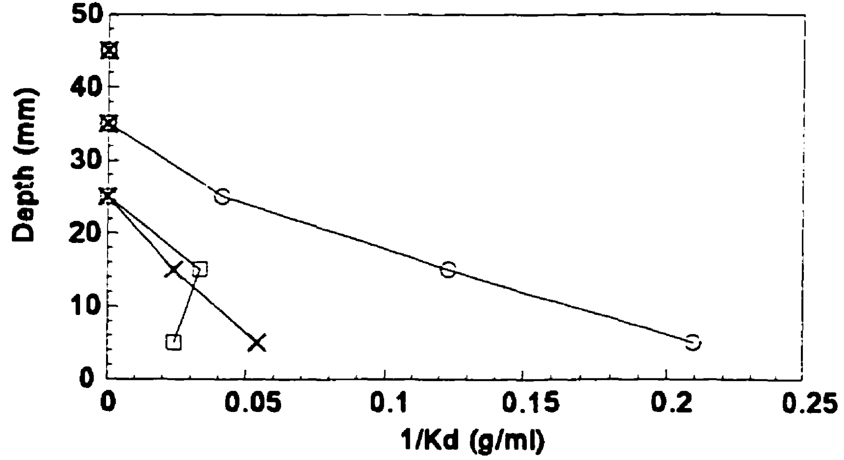


Figure 5.19 K_d Profiles of Pb, Cu and Zn for Soil C, (5000mg/l input).

5.5 Cation Migration and Redistribution

The migration and redistribution profiles of calcium, magnesium, potassium and sodium cations within the pore fluid as a function of time, depth, soil pH and various heavy metal input concentrations are presented in Figures 5.20 through 5.43, respectively. The migration profiles depict how a particular cationic species migrates through the soil column with increasing permeation of heavy metal solutions. In general, results showed that the migration profiles and the redistribution of the exchangeable cations along the soil column were leached out or reduced from the first sections of the soil column and increased toward the bottom of the soil with increasing time, depth and influent concentration due to the exchange reaction with heavy metals.

Generally, most test results show moisture and solute distribution maximums at the source. As expected, the profiles decline from a location of high concentration to low concentration. As the degree of saturation decreases, the volumetric water content and heavy metal retention and migration decrease along the soil column. For longer time periods, the increase in volumetric water content and heavy metal concentration is seen to be highly dependent on the soil pH and on the input concentrations, time of wetting and degree of saturation. Factors which control the migration of existing cations are carbonate presence, degree of saturation, time of wetting, soil pH and influent heavy metal concentration. However, at initial time of wetting (52 hrs), the volumetric water content and heavy metal retention distribution gradients follow a trend opposite to the existing cation redistribution for various soil and heavy metal input concentrations. The gradients decline with decreasing degree of saturation along the soil column. As the time of wetting increases (17.8 days), the increase in volumetric water content and heavy metal retention is seen to be highly dependent on the fluid input concentration and generally increases with time and concentration, as was demonstrated.

Generally, results showed that by lowering the soil pH, the initial presence of existing cations such as calcium (Ca^{2+}), sodium (Na^{+}), and potassium (K^{+}) was reduced and leached out when the soil was treated with nitric acid during preparations. Only magnesium cations, released from the soil structure, significantly increased with lowering the soil pH below 4. However, only traces of aluminum were found in the first section of soil after leaching. This may explain the variation in cation exchange capacity as reported in Table 4.3. One might expect a significant decrease in the cation exchange capacity at pH 3.5. However, instead with the presence of exchangeable cations and the increase in aluminum and magnesium exchangeable cations, the soil was still able to almost completely retain the introduced metals under unsaturated conditions. The exchangeable cation variations with depth indicated high retention at the upper part of the soil column, in particular when soil was leached with various heavy metal solutions of Pb . Cu and Zn.

Particularly, the loss of the carbonate in the illite soil due to the treatment of soil with acid reduced slightly the initial concentration of calcium for soil C and D. Thus, by decreasing the soil pH, calcium cations released from the structure to the soluble phase increased significantly for soil B, C and D (Figures 5.21 to 5.25), and followed almost the same trend for all cases leached with various heavy metal concentrations with a slight reduction in migration toward the bottom of the soil when leached with zinc nitrates. In addition, magnesium cations released to the soluble phase show similar behaviour to the calcium migration. This increased significantly with reduced soil pH for soil D and C and slightly increased toward the bottom of the cell when leached with copper and zinc nitrates (Figures 5.26 to 5.31).

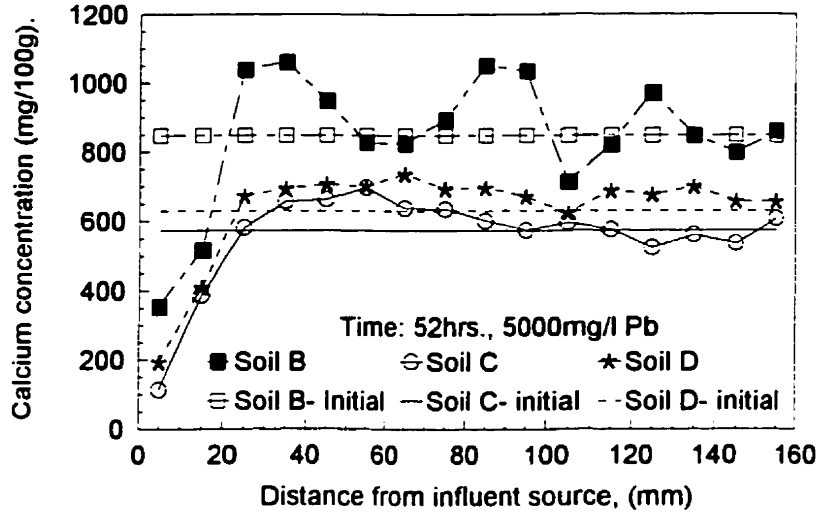
So, at initial time of wetting (52 hrs) and high input concentration of nitrate solution (5000 mg/l), results show a significant increase in calcium and magnesium at shallow depths (below 40mm), where the soil is considered to be fully saturated. However, the redistribution of both monovalent cations of potassium (K^+) (Figures 5.33 to 5.37) and sodium (Na^+) (Figures 5.38 to 5.43) followed almost the same trend with similar variations of heavy metal concentration along the soil column and no significant variations toward the bottom of the cell when leached with various heavy metal concentrations. At shallow depths (above 40mm) and as the time of wetting increases, the migration of cations towards the bottom of the cell increased. resulting in concentration values lower than the initial concentration in the upper part near the source and higher values below 40mm depth.

In addition, below 40mm depth and with an increase in time duration. the relative concentration, which is the ratio between the final (Cf) and the initial (Ci) concentration of cations in the soil before and after leaching (Cf/Ci). exceeded 1.0. This can be attributed to the ion migration and exchange reactions between monovalent and divalent cations and the continuous migration of both water and cations towards the bottom of the cell as a result of the water and osmotic potential gradients, indicating the elution of cations from the solid particles (Mohamed et al., 1994a). It should be noted that Na^+ and K^+ concentrations reached an approximate steady state along the soil column after 17.8 days. Whilest, for Mg^{2+} and Ca^{2+} steady state conditions were reached only in the lower part below 40mm after approximately 17.8 days. The low concentration of the K^+ ions which occurred in the pore fluid during the leaching process is due to the fact that K^+ is often adsorbed and incorporated into the inter-layer lattice of soils. As indicated before. the high movement of Ca^{2+} and Mg^{2+} can be also attributed to the cation exchange capacity or the replacement by Pb, Zn and Cu in the top part of the soil column.

Whereas, the interaction mechanism is due to the cation exchange process between calcium, magnesium, sodium and potassium at the bottom part of the soil. The replacement of sodium and potasium ions in the exchangeable sites by calcium and magnesium balances the charge deficit that occurs by the elution of sodium and potassium, (Yong et al. ,1986; Crooks and Quigly, 1984).

The selectivity order of soluble cation movements along the soil column within the unsaturated condition appears to be in the order of $Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$ for soils B, C and D, for various heavy metals input concentrations. While for soil A which is the original soil before treatment with acid for carbonate extraction, the selectivity order of soluble cations follows the order of $K^{+} > Na^{+} > Ca^{2+} > Mg^{2+}$. The initial soluble cation concentrations of sodium, potassium, calcium and magnesium and their selectivity are reported in Table 4.2.

(a)



(b)

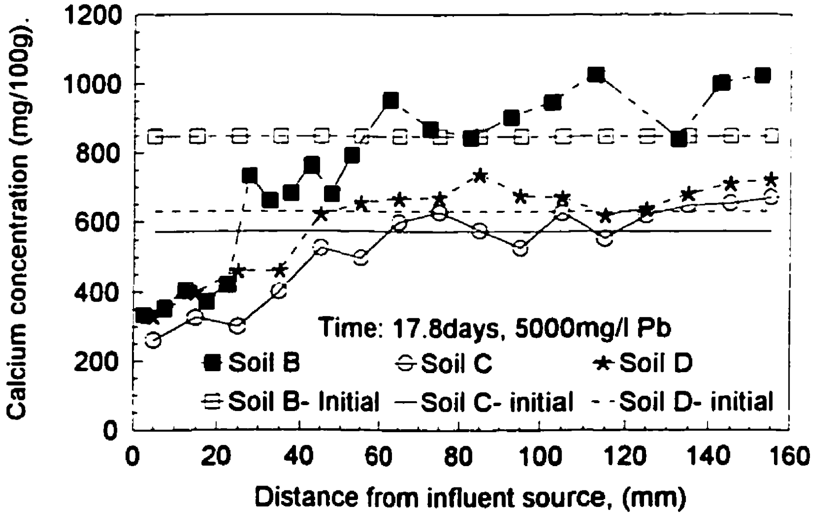
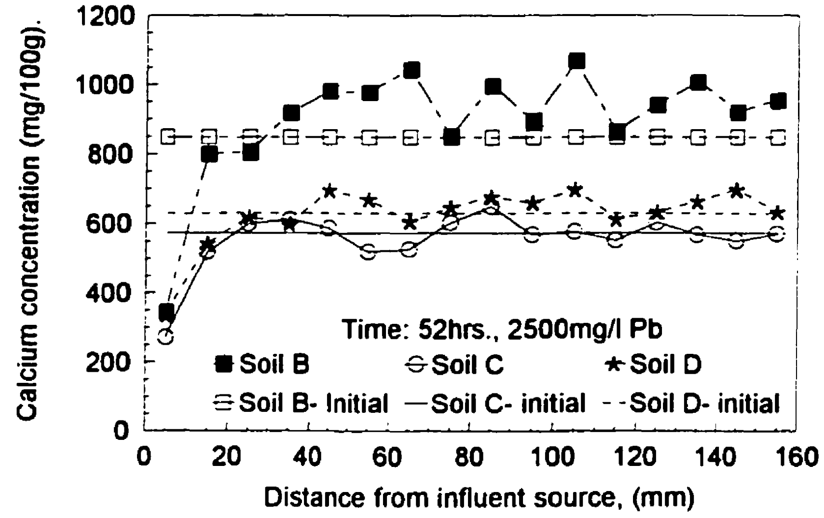


Figure 5.20 Migration of Calcium as a function of Soil pH and Distance for 5000mg/l input Concentration of Lead.

(a)



(b)

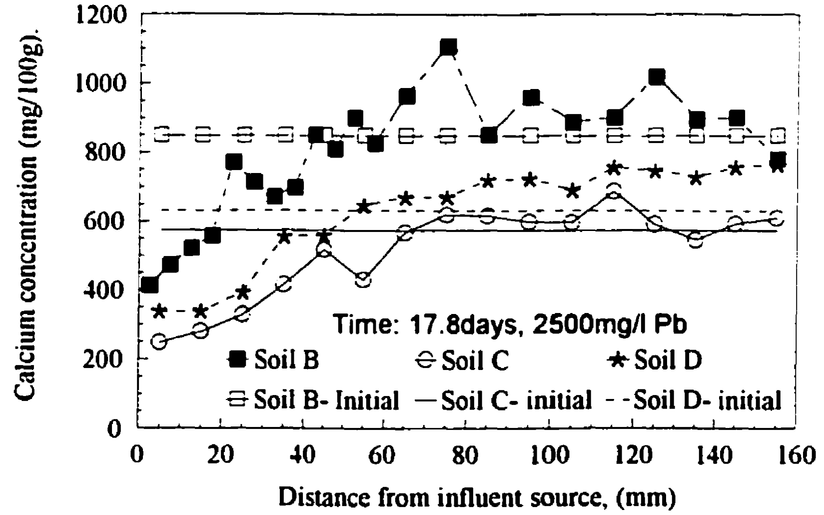


Figure 5.21 Migration of Calcium as a function of Soil pH and Distance For 2500mg/l input Concentration of Lead.

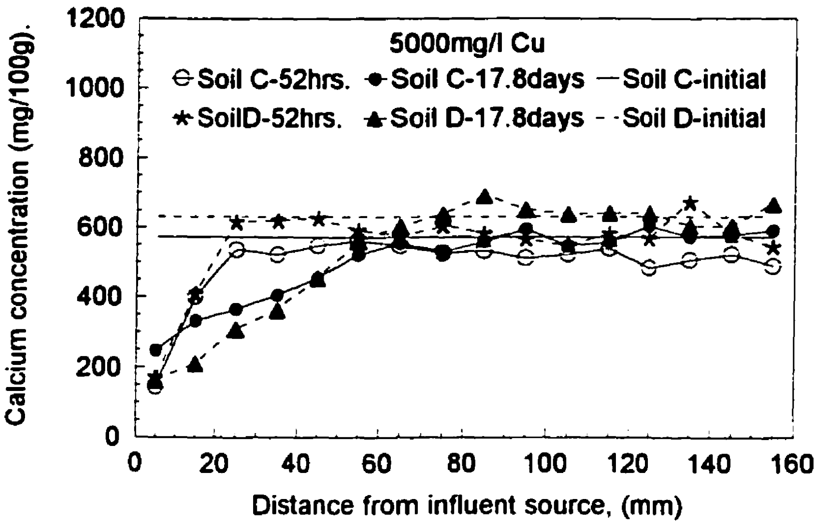


Figure 5.22 Migration of Calcium as a function of Soil pH and Distance for 5000mg/l input Concentration of Copper.

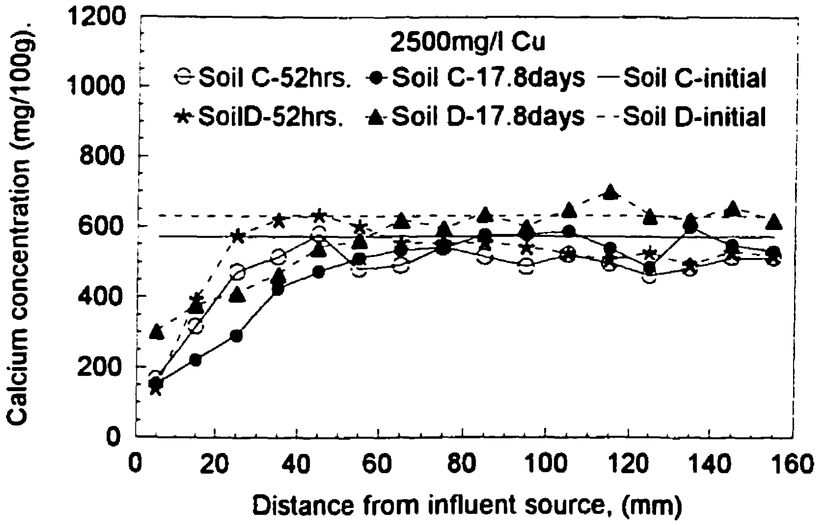


Figure 5.23 Migration of Calcium as a function of Soil pH and Distance for 2500mg/l input Concentration of Copper.

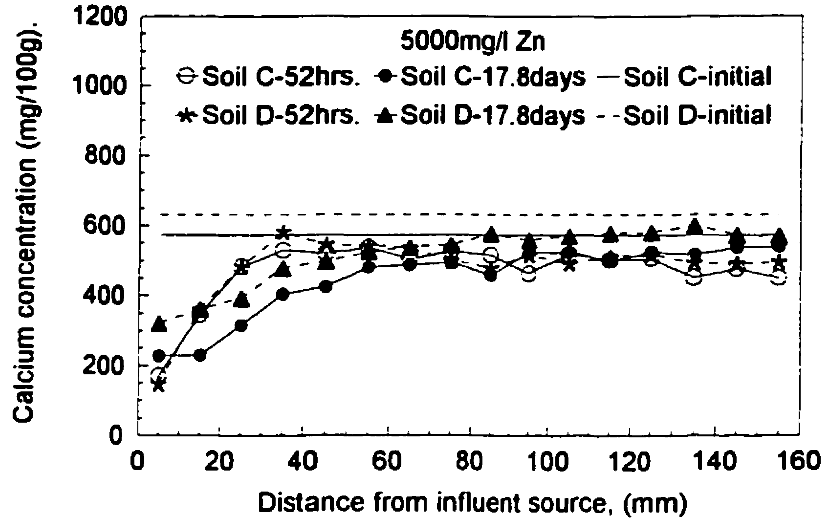


Figure 5.24 Migration of Calcium as a function of Soil pH and Distance for 5000mg/l input Concentration of Zinc.

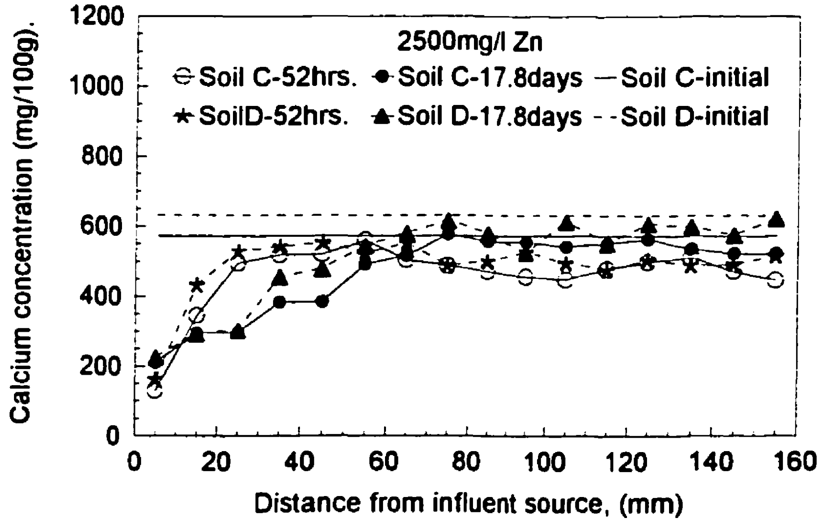


Figure 5.25 Migration of Calcium as a function of Soil pH and Distance for 2500mg/l input Concentration of Zinc.

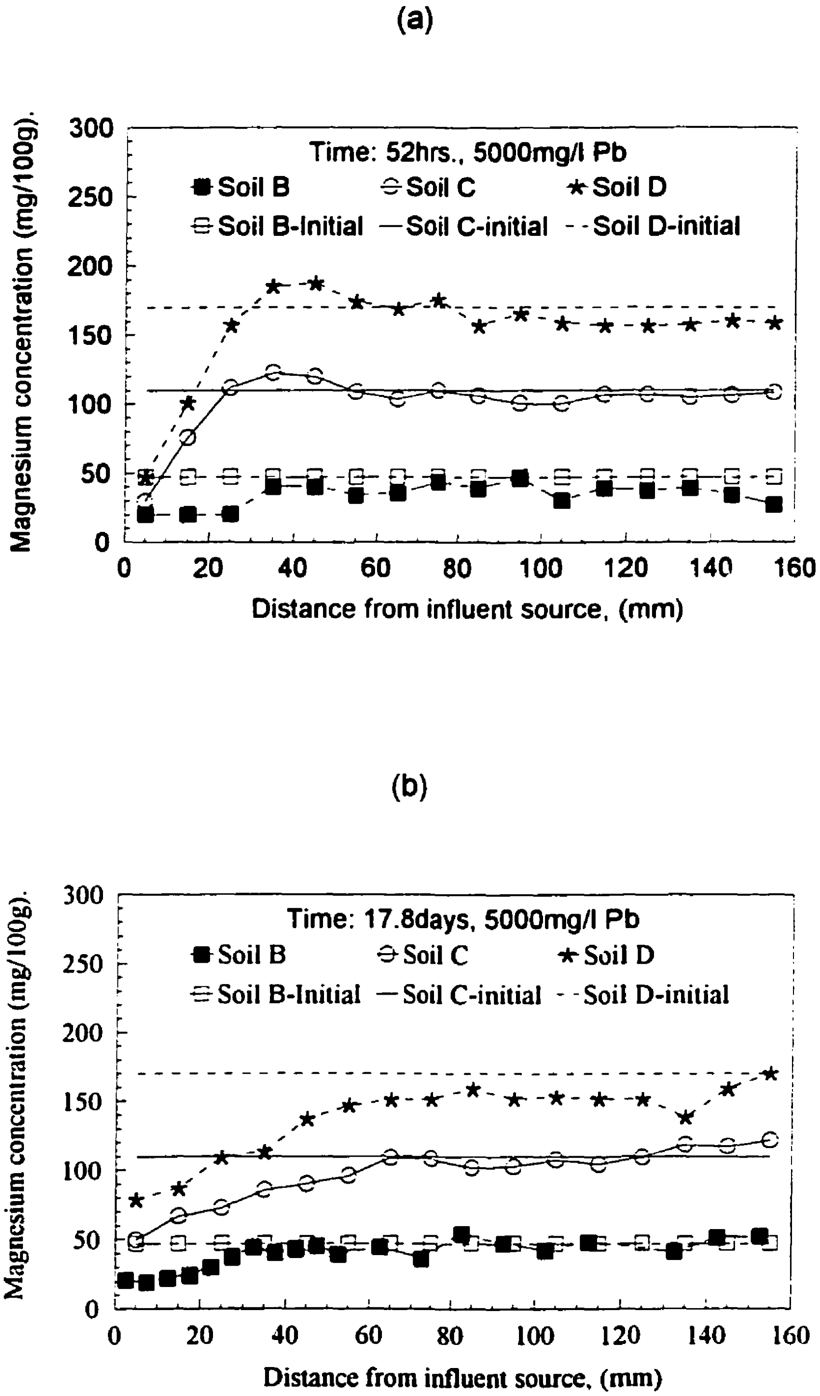
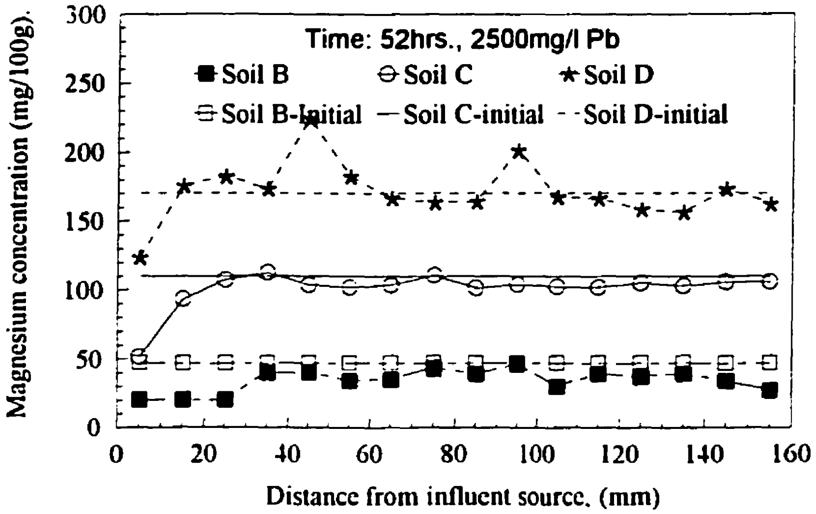


Figure 5.26 Migration of Magnesium as a function of Soil pH and Distance for 5000mg/l input Concentration of Lead.

(a)



(b)

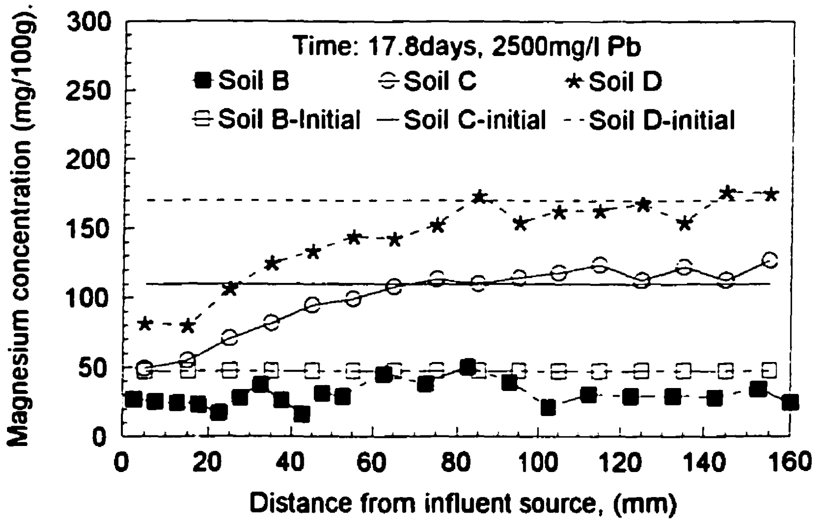


Figure 5.27 Migration of Magnesium as a function of Soil pH and Distance For 2500 mg/l input Concentration of Lead.

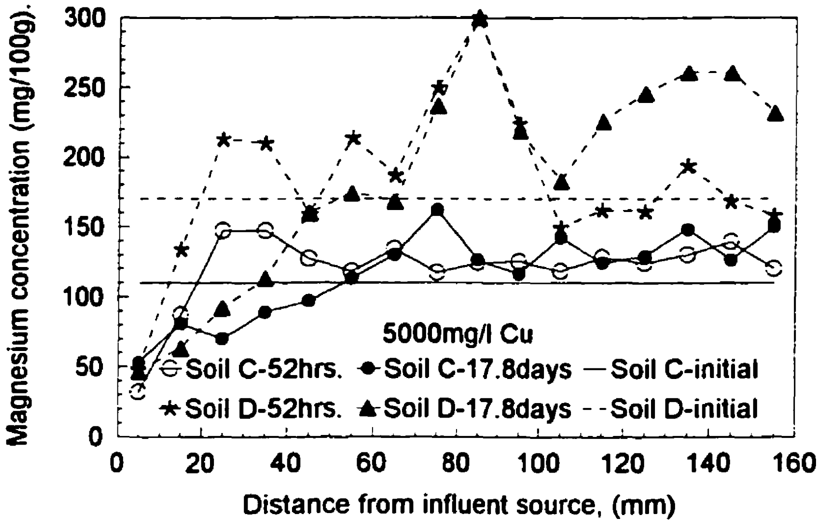


Figure 5.28 Migration of Magnesium as a function of Soil pH and Distance for 5000mg/l input Concentration of Copper.

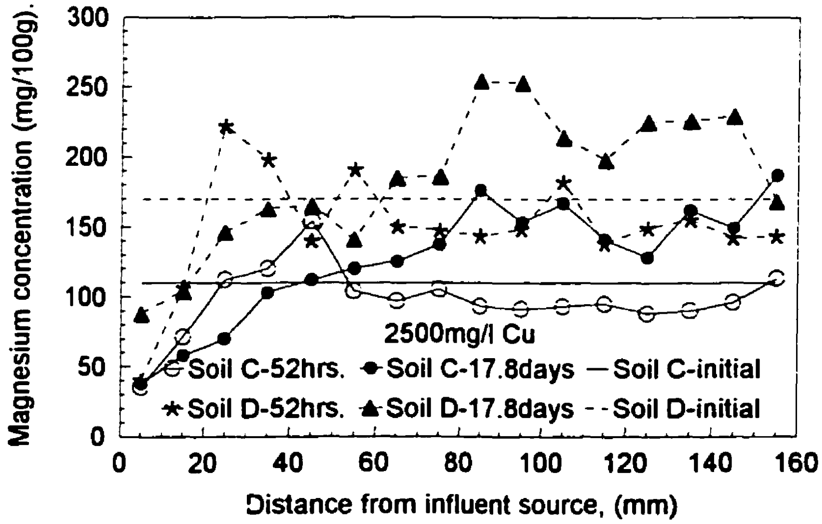


Figure 5.29 Migration of Magnesium as a function of Soil pH and Distance for 2500mg/l input Concentration of Copper.

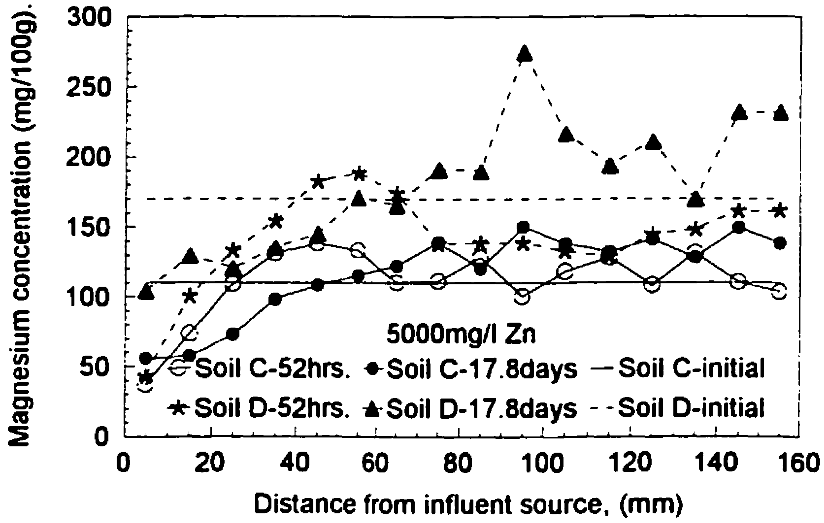


Figure 5.30 Migration of Magnesium as a function of Soil pH and Distance For 5000mg/l input Concentration of Zinc.

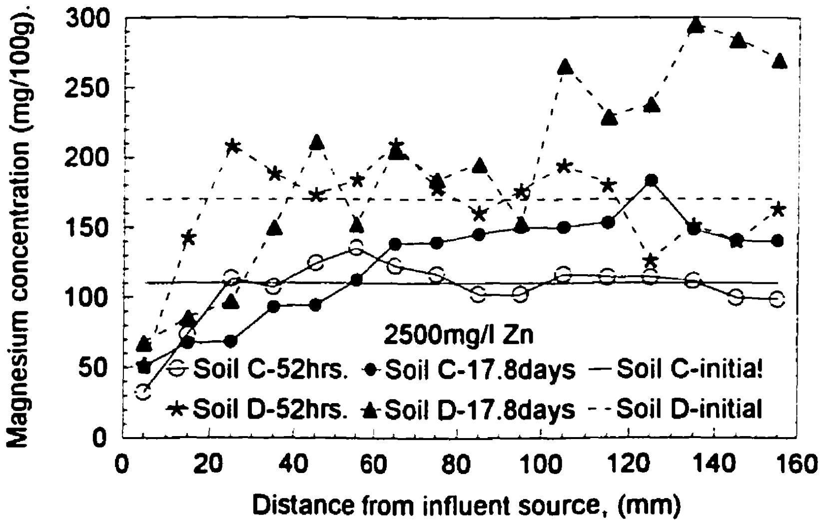


Figure 5.31 Migration of Magnesium as a function of Soil pH and Distance for 2500mg/l input Concentration of Zinc.

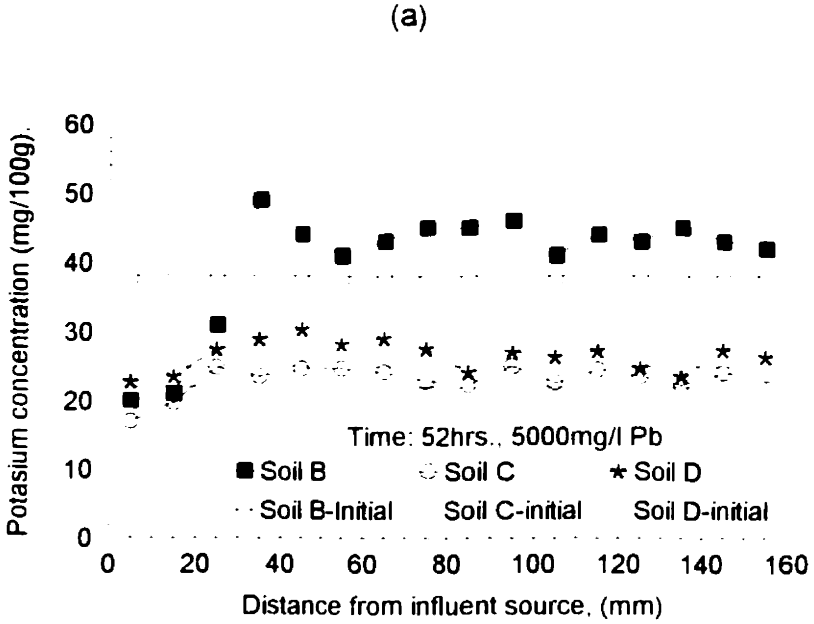


Figure 5.32 Migration of Potassium as a function of Soil pH and Distance For 5000mg/l input Concentration of Lead.

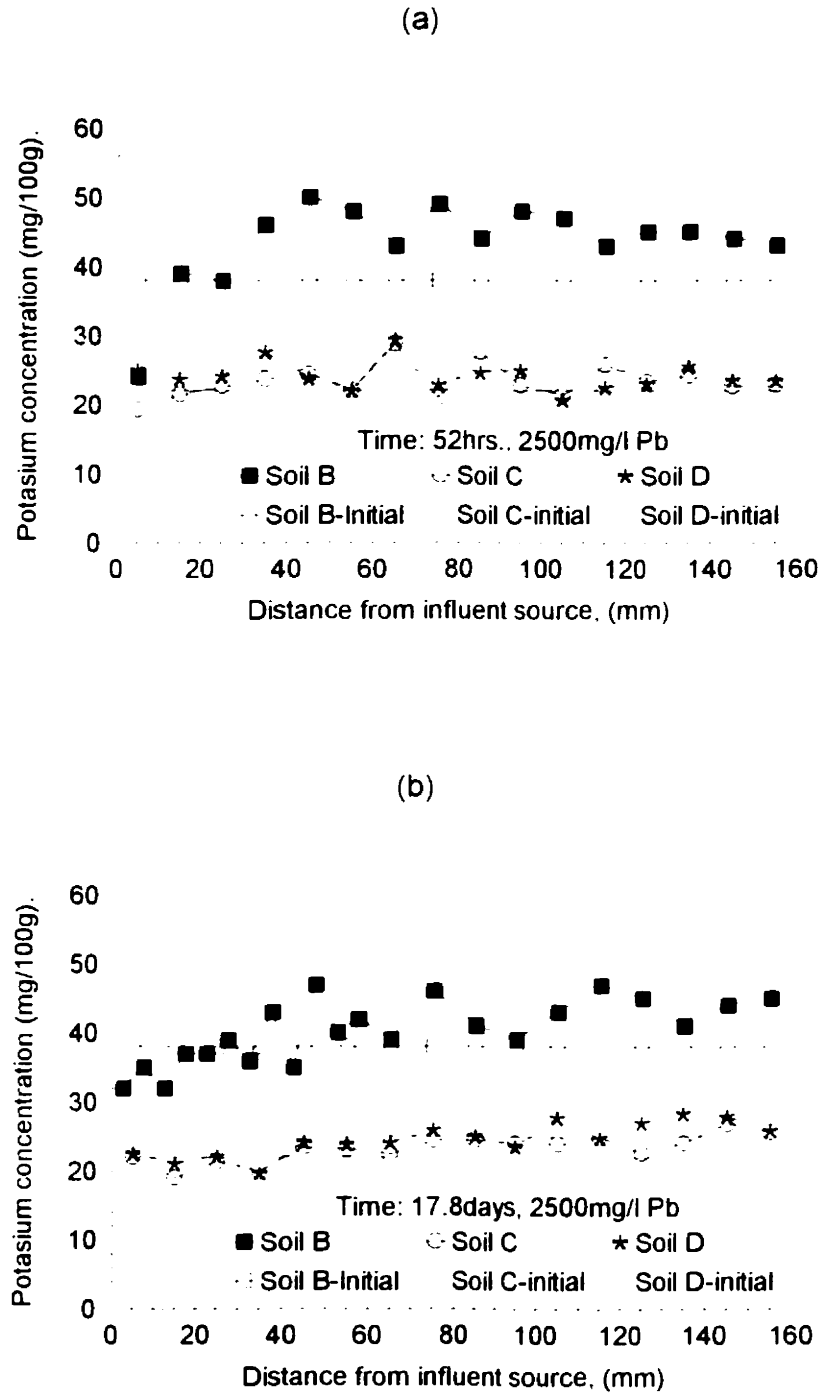


Figure 5.33 Migration of Potassium as a function of Soil pH and Distance for 2500mg/l input Concentration of Lead.

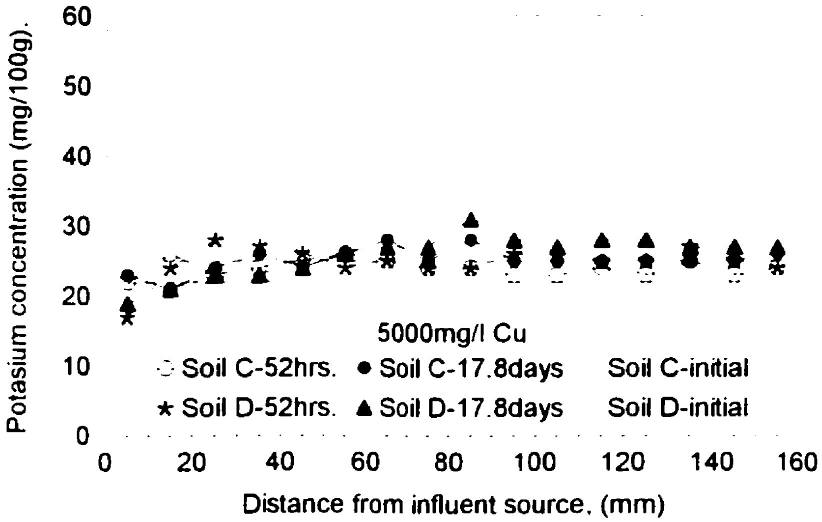


Figure 5.34 Migration of Potassium as a function of Soil pH and Distance for 5000mg/l input Concentration of Copper.

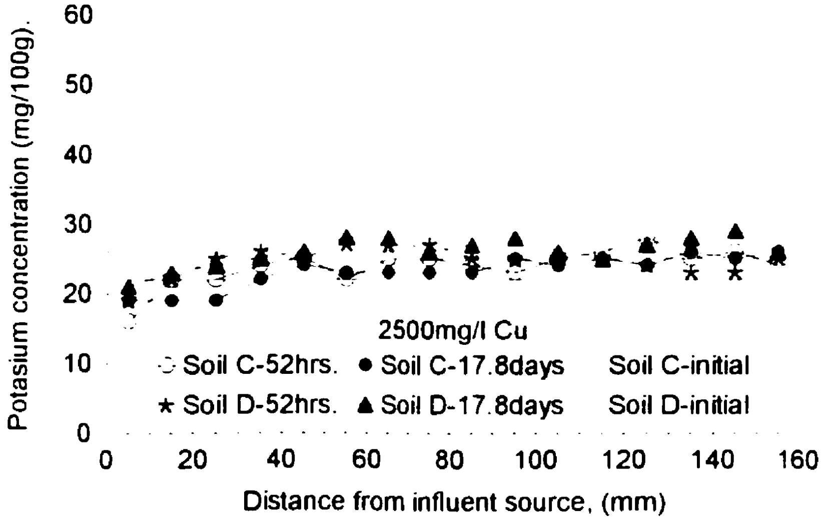


Figure 5.35 Migration of Potassium as a function of Soil pH and Distance for 2500mg/l input Concentration of Copper.

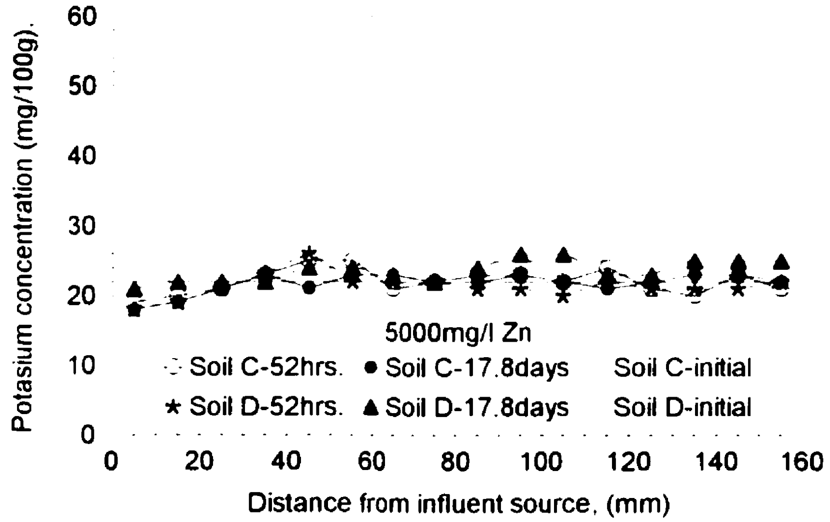


Figure 5.36 Migration of Potassium as a function of Soil pH and Distance for 5000mg/l input Concentration of Zinc.

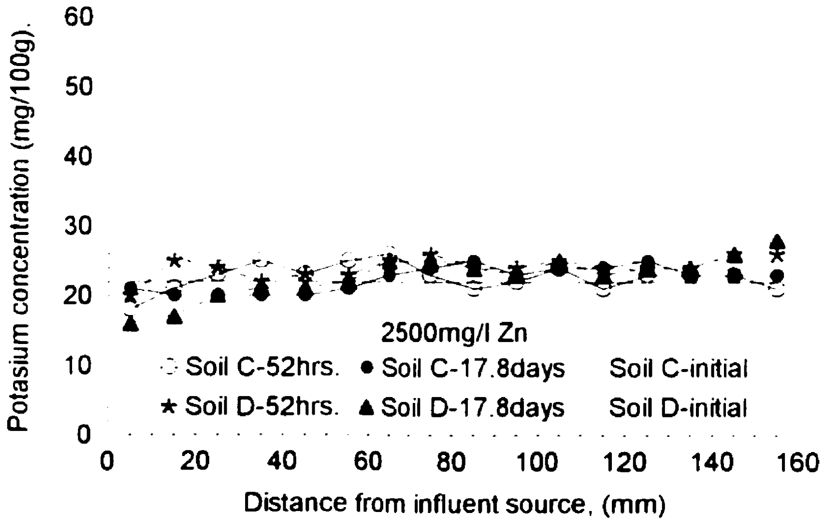
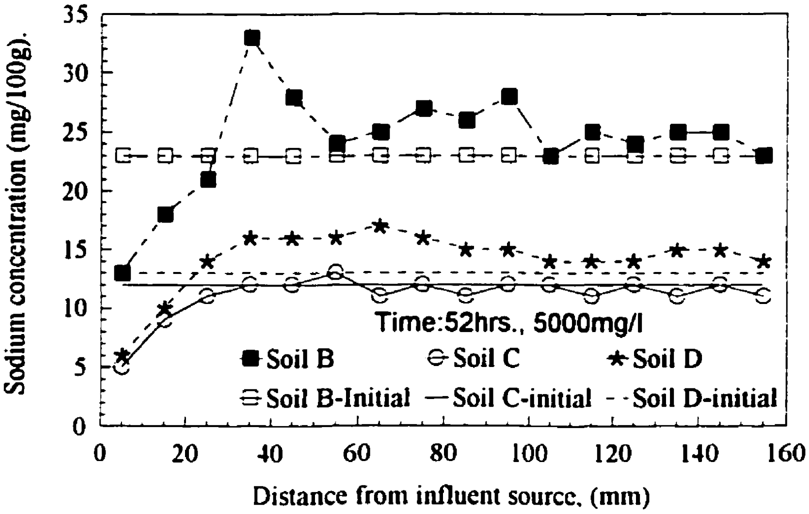


Figure 5.37 Migration of Potassium as a function of Soil pH and Distance for 2500mg/l input Concentration of Zinc.

(a)



(b)

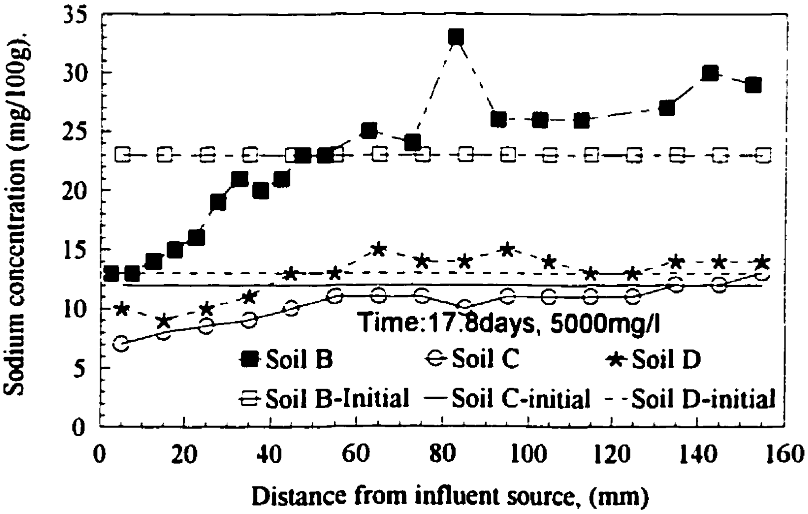
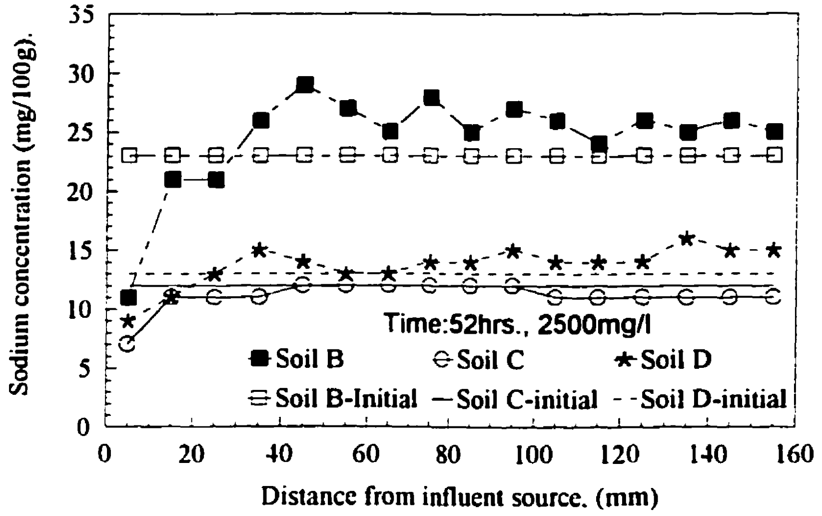


Figure 5.38 Migration of Sodium as a function of Soil pH and Distance for 5000mg/l input Concentration of Lead.

(a)



(b)

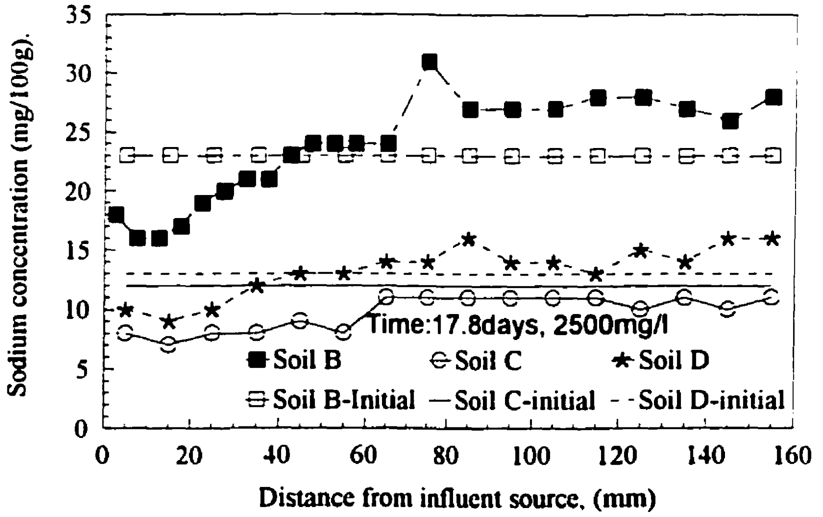


Figure 5.39 Migration of Sodium as a function of Soil pH and Distance for 2500mg/l input Concentration of Lead.

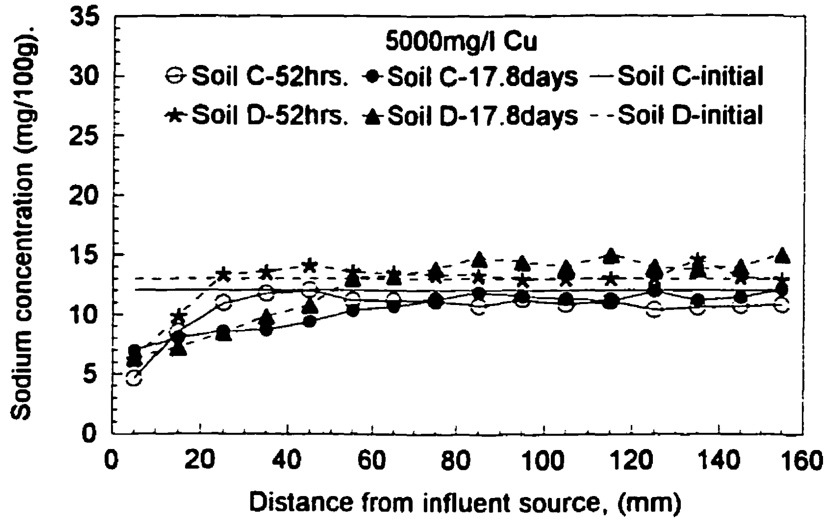


Figure 5.40 Migration of Sodium as a function of Soil pH and Distance for 5000mg/l input Concentration of Copper.

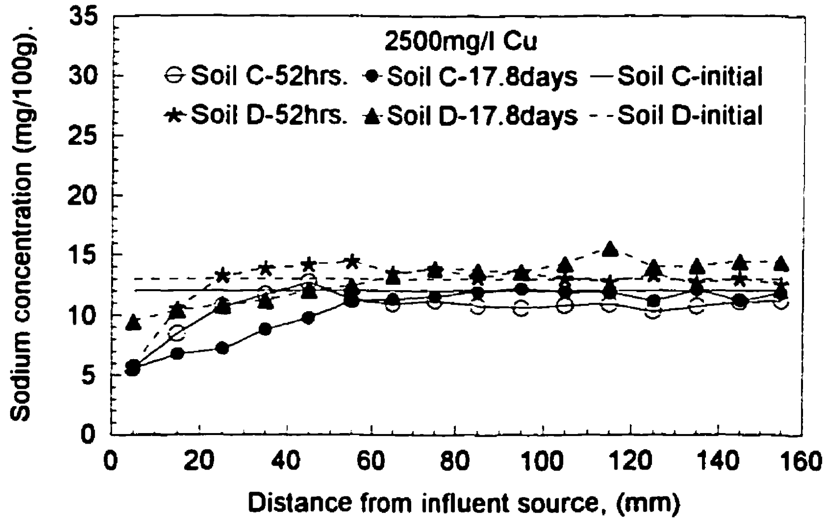


Figure 5.41 Migration of Sodium as a function of Soil pH and Distance for 2500mg/l input Concentration of Copper.

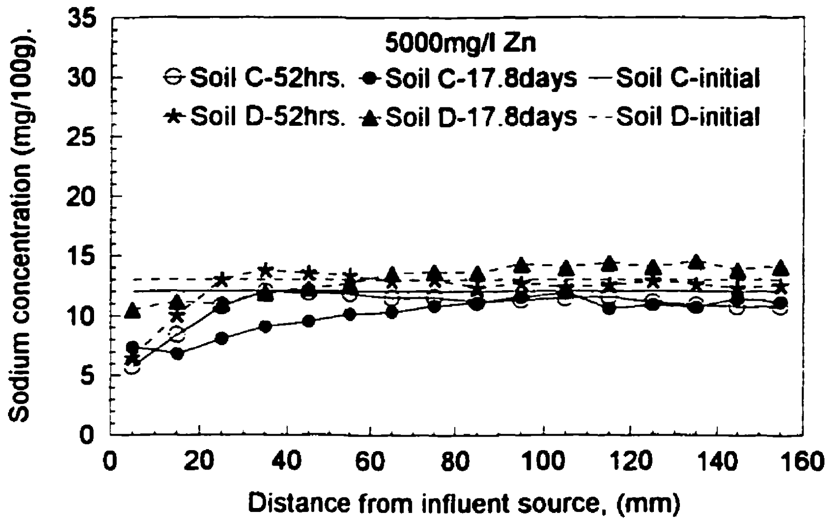


Figure 5.42 Migration of Sodium as a function of Soil pH and Distance for 5000mg/l input Concentration of Zinc.

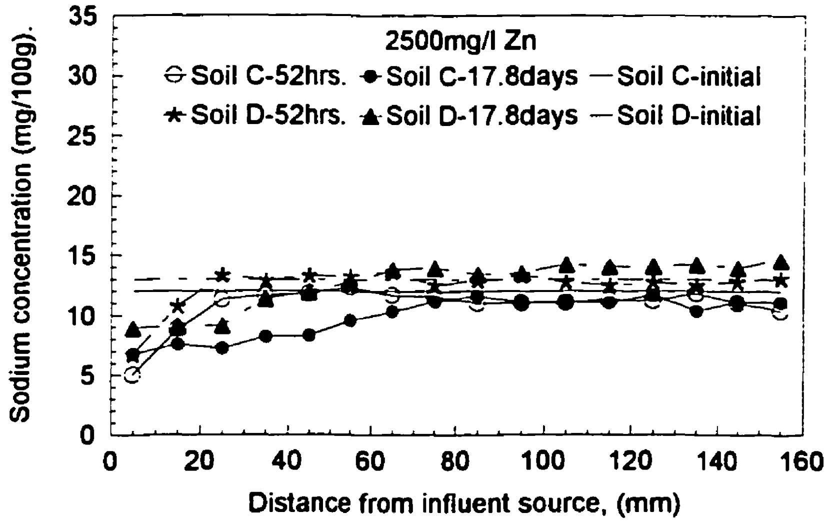


Figure 5.43 Migration of Sodium as a function of Soil pH and Distance for 2500mg/l input Concentration of Zinc.

5.6 pH Distribution

After leaching completion, measurements of the soil pH were performed on each soil section along the soil column. The Soil pH was measured in a 1:2 ratio of soil to distilled water solution where 20 ml of distilled water was added to 10 g weight of soil and shaken for 30minutes. Then, the suspension was allowed to settle for 30 minutes before soil pH measurement. The pH distribution profiles with time, distance and contaminant concentration for illitic soil at pH 5.5 (soil B), pH 4.0 (soil C) and pH 3.5 (soil D) are presented in Figures 5.44, 5.45 and Figure 5.46 respectively.

Generally, at initial time of wetting (52 hrs), most test results show lower pH distribution near the source point. However, as the distribution of the volumetric water content and solute concentration decreases, the soil pH increases slightly with depth as one proceeds along the soil column.

For longer periods of time (17.8 days), measurements of the soil pH performed on each soil section increase slightly with depth and time from the initial value showing a clear dependency on the soil material, the input concentration and the time of wetting. This might be explained by the elution of cations from the solid particles, as indicated by the pore fluid concentration profiles. Lead, copper and zinc replace these cations. On the other hand, the soil has a high attenuation capacity for Pb, Cu and Zn in the upper part near the source where the soil is considered to be fully saturated, as indicated by the concentration profiles of the pore fluid with depth after leaching.

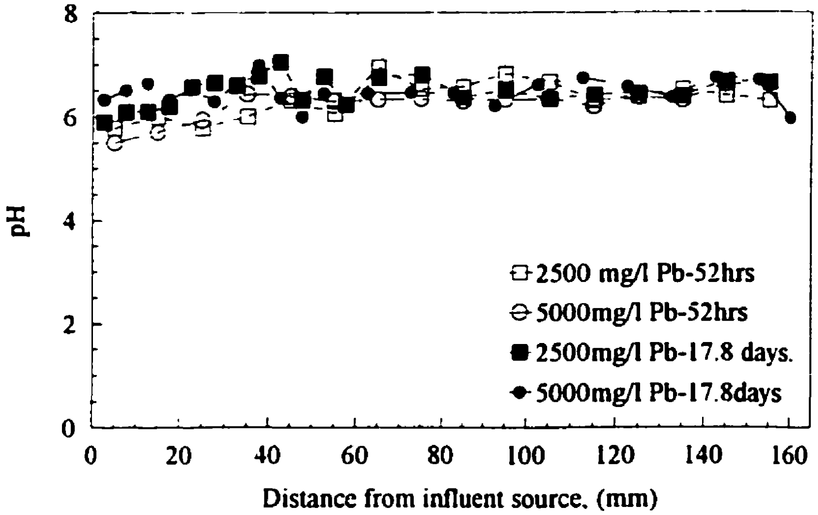


Figure 5.44 pH Distributions with Time and Distance in Soil B

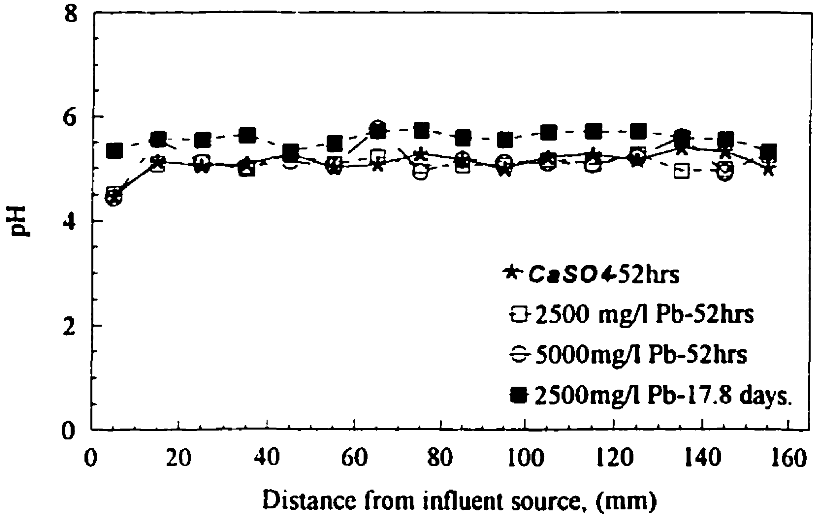


Figure 5.45 pH Distributions with Time and Distance in Soil C

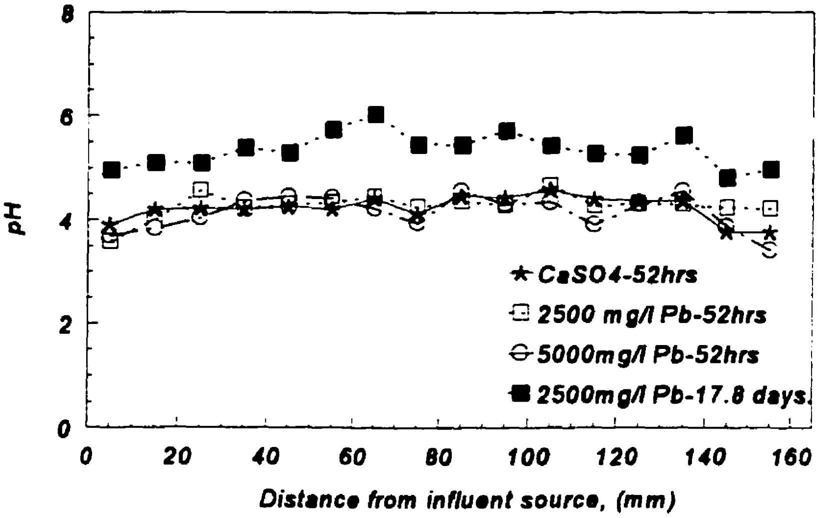


Figure 5.46 pH Distributions with Time and Distance in Soil D

5.7 Summary and General Discussion of Sorption Results

Many researchers have experimentally investigated the mechanism and process of heavy metal retention (Harter, 1983; Yanfulet al., 1988a and 1988b, Farrah and Pickering, 1977a and 1977b, 1978; Yong et al., 1990a). Heavy metals may be retained in soils in the form of oxides, hydroxides, carbonates, exchangeable cations bound to organic matter in soil, and are dependent on the local environmental conditions and on the kind of soil constituents present in the soil-water system. Heavy metal retention mechanisms in soils are different at different soil pH values and the soil's ability to retain them depends on its resistance to any change in soil pH. The retention of heavy metals increases with increasing pH and decreases with decreasing pH (Farrah and Pickering,1977a and 1977b; Allard et al., 1991; Phadungchewit, 1990). It is known that heavy metals in illite are mostly retained in the carbonate or hydroxide phase at soil pH values above 4. Below pH 4, the retention of heavy metals is mostly in the exchangeable phase, (Yong et. al., 1992a). In order to study the movement of heavy metals in acidic soil, the buffering capacity of the illitic soil was reduced by using nitric acid. Lowering the pH value of the soil increases the solubility of heavy metals in the soil water by redissolving the heavy metal precipitates (e.g., carbonate and hydroxides) into the soil water. The greater availibility of ions will enhance mobilization and the rate of their loss by leaching (Yong and Phadungchewit, 1993; Yong et al., 1992a). The retention of heavy metals increased when the soil pH of the soil solution exceeded the value required for precipitation (Farrah and Pickering, 1976a, 1976b, 1977a, 1977b, and 1979). Since the focus of this study is on the retention of heavy metals by the exchangeable mechanisms, and since sorption of lead onto illite soil at high soil pH is by precipitation mechanisms (MacDonald and Yong, 1997; Yong et al., 1993), the soil pH in this study was reduced to values below pH 4 in order to avoid heavy metal precipitation.

Sorption data are needed to determine the transport properties of the soil with respect to the contaminants under consideration. Test data permits one to calculate the partition coefficient K_d required in the contaminant transport equations. Most heavy metal partitioning studies are discussed in terms of selectivity (the ability of a surface to preferencially adsorb metals) and/or affinity (preference of a metal for a certain geochemical phase), using the batch equilibrium test. To compare results of this study with others, it should be noted that very few research studies were performed under the same type of conditions. There have been only a few studies that focussed on pH dependent partitioning, Yong et al., 1990e, Phadungchewit (1990), Galvez-Cloutier (1995) and Darban (1997).

It is known that batch equilibrium tests used for determination of adsorption isotherms utilize small portions of soil and representative contaminants. The problems arising therefore relate to the question of whether or not a small quantity of totally disturbed soil is appropriate to simulate the field conditions or situations, and the variability of the distribution coefficient (K_d) from one soil to another. The batch technique does not necessarily reflect the actual leachate-soil interaction. The ratio of solution to soil and the time required to attain equilibrium does not always give a good estimate of the migration and adsorption of heavy metals through the clay barrier, (Darban, 1997). Sorption characteristics obtained from leaching column tests provide a better means for evaluation of soil sorption performance. Leaching tests can illuminate the effects of partial soil saturation, and effective exposed surface area in the soil system. For these reasons leaching tests are more valuable than batch tests of soils.

This research obtained moisture and solute profiles along the soil column that were due to internal suction gradients. The gradients were, as expected, from a location of high concentration to low concentration. The volumetric water content and heavy metal retention and migration profiles along the soil column show higher values near the source point. As soil saturation and volumetric water content declined along the soil column, the heavy metal retention and migration also decreased. For longer time periods, the increase in volumetric water content and heavy metal concentration is seen to be highly dependent on the soil pH and the input concentrations, time of wetting and degree of saturation.

However, at initial time of wetting, most test results show lower pH distribution near the source point. The variations of volumetric water content and heavy metal retention distribution along the soil column for various types of soil follow a trend opposite to the existing cation redistribution, for various soil and heavy metals input concentrations. Cation movement decreases as the degree of saturation decreases along the soil column. Other factors which control the redistribution and migration of existing cations are carbonate presence, duration of wetting, soil pH and influent heavy metal concentration.

With the increased competition for sorption sites by various heavy metals, Ca^{2+} and Mg^{2+} show a significant increase in migration subject to time of wetting, input concentration and the decrease in soil pH. The selectivity order of soluble cation movements along the soil column within the unsaturated soil appears to be in the order of $Ca^{2+}>Mg^{2+}>K^{+}>Na^{+}$ for soil B, soil C, and soil D, for various heavy metal input concentrations. For soil A, which is the original soil before treatment with acid for carbonate extraction, the selectivity order of soluble cations follows the order of $K^{+}>Na^{+}>> Ca^{2+}>Mg^{2+}$.

In the unsaturated phase, results showed that as the distance and time of wetting from the heavy metal source increases, the volumetric water content and heavy metal retention is highly dependent on the fluid input concentration and generally increases with time and concentration. Moreover, the decrease in the amount of cations exchanged with decreasing degree of saturation may be due to a decrease in the diffusion flux rather than a decrease in the exchange capacity of the soil (Lim et al.,1995). However, as the volumetric water content and solute concentration decreasesd, the pH of each soil section increased slightly with distance along the soil column. This might be explained by the elution of cations from the solid particles, which is indicated by the pore fluid concentration profiles. Lead, copper and zinc replace soil cations. As explained before, the exchangeable cation variations with depth indicated high cation exchange capacity (CEC) or retention at the upper part of the soil column, in particular when soil was leached with solutions of Pb , Cu and Zn. High CEC increases the elution of cations from the solid phase and increases the movement of the cations replaced by heavy metals towards the bottom of the soil column. What result is a slight increase of the soil pH with time and depth from the initial value. The pH change shows a clear dependency on the soil material, the input concentration, the type of contaminant and the time of wetting. The increase of soil pH and the migration of cations will increase the presence of carbonate and this favors the retention of heavy metals. In addition, the decrease in the degree of saturation along the soil column away from the source point, can be another significant reason for heavy metal retention and their reluctance to migrate to the soluble phase, resulting in an "infinite" values of K_d.

It is concluded that there is a significant dependence of the partitioning coefficient on the volumetric water content, (Fityus et al., 1999). Results from column leaching tests also showed that besides the volumetric water content, there are other factors which should be considered in heavy metal retention, such as the presence of carbonate, and the influent heavy metal concentration. The capacity for moisture and heavy metal movement is increased by low pH, low carbonate content, and large particle size (silt and sand portions increased in soil C and D). Also, the resulting increased exposure of SSA and CEC is also involved when an increase in heavy metal sorption has been observed. The presence of carbonates in illite soil increases the retention of heavy metals at high soil pH and also enhances the buffering capacity of the soil. The higher the carbonate content of the soil, the greater the retention of heavy metals by the carbonate phase (Yanful et al., 1988a and 1988b). So because of the high carbonate content and high CEC, heavy metals were accumulated in the first section of soil B with pH 6.9, adjacent to the source of the fluid. There was no evidence of heavy metal movement to the soil pore fluid after the shaking procedure, resulting in a calculated partitioning coefficient value of "infinity".

Since heavy metals are highly soluble in acidic saturated conditions, one expects to have a total desorption from the soil to the soluble phase at low soil pH. However, within the acidic soil, results showed that the retention of lead, copper and zinc are highly dependent on the soil pH, the presence of carbonate, the degree of saturation, the influent concentration and the time of wetting. As the soil pH decreases, the dissolution of carbonates increases and the CEC becomes the more dominant process in heavy metal retention. It was observed that, in acidic soil, the CEC of the soil decreases slightly with a lowering the soil pH. This, however, does not detract from the ability of the soil to almost retain the heavy metals under unsaturated conditions. Furthermore, due to the low input pH in the influent leachate, one expects a reduction of the retention capacity of the soil in the upper part of the soil column. However, results did not show any traces of heavy metals collected in the effluent leachate indicating that most of the Pb, Cu and Zn are sorbed in the soils. The maximum sorption of heavy metals occurred at the upper part of the soil column above 40mm indicating therefore the capability of the soil to resist any pH changes. At that depth, the partitioning coefficient showed low values at initial time of wetting for soil D. This, however increases with an increase in the soil pH and the distance from the heavy metal source, and decreases with an increase in the time of wetting and the degree of saturation.

It is known that heavy metals precipitate at high soil pH's (e.g., Pb precipitates at pH > 5). Since the initial soil pH is 3.5 and 4.0 for soil D and C, respectively, further H.M. leaching slightly decreases the soil pH of the upper part and enhances the mobility of H.M. along the soil column. In the top part of the soil column, heavy metals were retained by cation exchange. Results show that the soil has a high attenuation capacity for Pb, Cu and Zn in the upper part above 40mm where the soil is considered to be almost fully saturated, as indicated by the concentration profiles of the pore fluid with depth after leaching.

However, one can relate the selectivity of heavy metals retention to the pK of the first hydrolysis product of the metals (Forbes et al., 1974). Where pK is the equilibrium constant for the reaction as described in the hydrolysis equation expressed below, when n=1.The general equation for the hydrolysis of aqueous metal divalent cations, as given by Elliot et al. (1986), is expressed as follows:

$$M^{2+}(aq) + n\,H_2O \rightleftharpoons M(OH)^{2-n}{}_n + nH^+$$

The selectivity order of heavy metals considering the pK values of Pb, Cu, Zn and Cd is ranked as follows: Pb (6.2) > Cu (8.0) > Zn (9.0) > Cd (10.1) (Swanson et. al., 1966, Baes and Messmer, 1976), Elliot et al., 1986). This order (Pb > Cu > Zn) held for test soil samples with low pH and for different concentrations of a single species.

Furthermore, the overall migration test results showed that at shallow depths and when the soil is near saturation, Zn is more mobile along the soil column than other H.M. species, and smaller amounts of Zn are retained than Cu and Pb in the saturated phase or the upper part of the soil column near the source point. As the time of wetting increased, the amount of H.M. released to the soluble phase increased slightly with increasing heavy metal sorption and with its mobility along the soil column. The mobility of H.M. along the soil column species was observed to fall in the order of Zn > Cu > Pb. This agreed well with previous findings of several authors, Yong and Phadungchewit, 1993; Elliott et al., 1986; Bohn, 1979; and Farrah and Pickering, 1977a and 1977b. Only at low soil pH (soil D) and initial time of wetting, did maximum accumulation of Pb occur in the first section of the soil column at maximum saturation, resulting in higher amounts of Pb released to the soluble phase than Zn and Cu.

Finally, this research work provides the experimental information necessary for numerical analyses on the transport of heavy metals in the vadose zone. Particular attention is given to the effect of degree of saturation, the presence of carbonate, soil pH and heavy metal concentrations. This analysis, which makes use of the diffusion coefficient and the volumetric water content, is presented in the next chapter.

CHAPTER 6

Coupled Moisture and Solute Equations for One Dimensional Flow Through Unsaturated Soil

6.1 Introduction

Recently, the application of nonequilibrium irreversible thermodynamics to the analysis of coupled flow problems related to transport phenomena in the soil system has been studied by many researchers such as: Taylor and Carry (1960 and1962), DeGroot and Mazur (1962), Fitts (1962), Olsen (1969,1972), Greenberg et al. (1973), Mitchell et al. (1973), Yong and Samani (1987), Selvadurai and Au (1986), Yong and Xu (1988), Yong et al. (1990a, 1990c,1990d,1992b and 1994), Mohamed et al. (1992 and 1994), Yeung and Mitchell (1992).

Irreversible thermodynamics are also termed non-equilibrium thermodynamics. It is a theory that can provide a basis for the description of a system that is out of equilibrium, Mitchell (1993). In a system, which is in a non-equilibrium state due to contaminant movement, thermodynamic forces and other forces (advectives) will cause the solutes to move toward the equilibrium state by balancing these forces, (Yong et al., 1992a).

6.2 Assumptions

The following assumptions were made:

- one dimensional moisture and solute flow
- no volume change
- isothermal condition
- horizontal flow, neglecting the effect of the gravity potential
- validity of Darcy's law (Richards 1931), Klute (1952)
- validity of Fick's law
- negligibility of the biological uptake of the minerals

6.3 Coupled Moisture and Solute Diffusion Equations Development

In a near state of equilibrium, and by applying the second postulate of irreversible thermodynamics (Onsager, 1931), thermodynamic forces and their fluxes can be described by a power series as follows:

$$J_i = L_{ij} X_j \tag{6.1}$$

J_i = Rate of flow (Flux)

X_i = Thermodynamic forces responsible for the fluxes

L_{ij} = Phenomenological coefficients

$$J_\theta = L_{\theta\theta} \frac{\partial\psi_\theta}{\partial x} + L_{\theta c} \frac{\partial\psi_c}{\partial x} \tag{6.2}$$

$$J_c = L_{c\theta} \frac{\partial\psi_\theta}{\partial x} + L_{cc} \frac{\partial\psi_c}{\partial x} \tag{6.3}$$

$\partial\psi_\theta/\partial x$ = Thermodynamic force due to soil water potential

$\partial\psi_c/\partial x$= Thermodynamic force due to chemical potential

J_θ = Fluid flux mole/l^2/t

J_c = Solute flux mole/l^2/t

x = Depth of soil column along the direction of flow (x-coordinate), $L_{\theta\theta}$, $L_{\theta c}$, $L_{c\theta}$, L_{cc} are phenomenological coefficients.

The relationship between the chemical potential gradient and concentration gradient is given by (Yong et al., 1992a):

$$\frac{\partial\psi_C}{\partial x} = \frac{RT}{C}\frac{\partial(-c)}{\partial x} \tag{6.4a}$$

R = gas constant

T = absolute temperature

C = solute concentration

t = time

Also, the relationship between the soil water potential gradient and the volumetric water content gradient is given by (Yong and Warkentin, 1975):

$$\frac{\partial\psi_\theta}{\partial x} = -\frac{\partial\psi_\theta}{\partial\theta}\frac{\partial\theta}{\partial x} \tag{6.4b}$$

Substitute equations 6.4a and 6.4b into 6.2 and 6.3 to obtain:

$$J_\theta = L_{\theta\theta}\frac{\partial(\psi_\theta)}{\partial\theta}\frac{\partial(-\theta)}{\partial x} + L_{\theta C}\frac{RT}{C}\frac{\partial(-C)}{\partial x} \tag{6.5}$$

$$J_c = L_{c\theta} \frac{\partial \psi_\theta}{\partial \theta} \frac{\partial(-\theta)}{\partial x} + L_{cc} \frac{RT}{C} \frac{\delta(-C)}{\partial x} \tag{6.6}$$

The mass conservation equation for diffusion involving the effect of adsorption reactions can be written as:

$$\frac{\partial \theta}{\partial t} = - \frac{\partial J_\theta}{\partial x} \tag{6.7}$$

$$\frac{\partial C}{\partial t} = - \frac{\partial J_C}{\partial x} - \frac{\rho_s}{\theta} \frac{\partial S_c}{\partial t} \tag{6.8}$$

ρ_s = Dry density

S = The adsorbed concentration of solute in the solid phase, which is directly proportional to the concentration

θ = Volumetric water content

Substituting equations 6.5 and 6.6 into equations 6.7 and 6.8 gives the final one dimensional solute and mass flow equations:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} [L_{\theta\theta} \frac{\partial \psi_\theta}{\partial \theta} \frac{\partial \theta}{\partial x} + L_{\theta c} \frac{RT}{C} \frac{\partial C}{\partial X}] \tag{6.9}$$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} [L_{c\theta} \frac{\partial \psi_\theta}{\partial \theta} \frac{\partial \theta}{\partial x} + L_{cc} \frac{RT}{C} \frac{\partial C}{\partial x}] - \frac{\rho_s}{\theta} \frac{\partial S}{\partial t} \tag{6.10}$$

Assume :

Moisture diffusivity:

$$D_{\theta\theta} = L_{\theta\theta} \frac{\partial \psi_\theta}{\partial x} \tag{6.11}$$

Solute diffusivity:

$$D_{c\,c} = L_{c\,c} \frac{RT}{C} \tag{6.12}$$

Solute moisture diffusivity:

$$D_{c\,\theta} = L_{c\,\theta} \frac{\partial \psi_\theta}{\partial \theta} \tag{6.13}$$

Moisture solute diffusivity:

$$D_{\theta\,c} = L_{\theta\,c} \frac{RT}{C} \tag{6.14}$$

By substituting equations 6.11 and 6.14 into equation 6.9 and 6.12 and 6.13 into equation 6.10, the coupled partial differential equations for one dimensional contaminant transport in an unsaturated soil boundary layer, due to variations in volumetric water content and contaminant concentration, can be written as:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} [\, D_{\theta\theta} \frac{\partial \theta}{\partial x} + D_{\theta c} \frac{\partial C}{\partial x} \,] \tag{6.15}$$

$$\frac{\delta C}{\delta t} = \frac{\delta}{\delta x} [D_{C\theta} \frac{\delta \theta}{\delta x} + D_C \frac{\delta C}{\delta x}] - \frac{\rho_s}{\theta} \frac{\delta S}{\delta t} \tag{6.16}$$

Furthermore, the relationship between the adsorbed components, S, and concentration, C, can be written as:

$$\frac{\delta C*}{\delta t} = \frac{\delta}{\delta x} [D_{C\theta} \frac{\delta \theta}{\delta x} + D_C \frac{\delta C}{\delta x}] \tag{6.17}$$

Where C* is the total concentration in mg/100g of soil.

6.4 Finite Difference Formulations

The diffusion coefficient will be calculated for each individual layer in the soil samples and for each pore volume passage of the contaminant by using the implicit finite difference method to solve the one dimensional parabolic second order differential coupled moisture and solute equations (6.15) and (6.17). This method is practical because the solution will permit a larger time step and require less time, which is more economical.

The finite difference formulations are discribed below as follows:

Time t and distance x are divided into j and i intervals, respectively, as shown in Figure 6.1, where:

$x = i\,\Delta x \quad \text{for } i = 1, I$

$t = j\,\Delta t \quad \text{for } j = 1, J$

The left side of equation 6.15, using the forward difference approximation of order Δt, can be written as follow:

$$\frac{\delta\theta}{\delta t} = \frac{\theta_i^{j+1} - \theta_i^{j}}{\Delta t} \qquad (6.18)$$

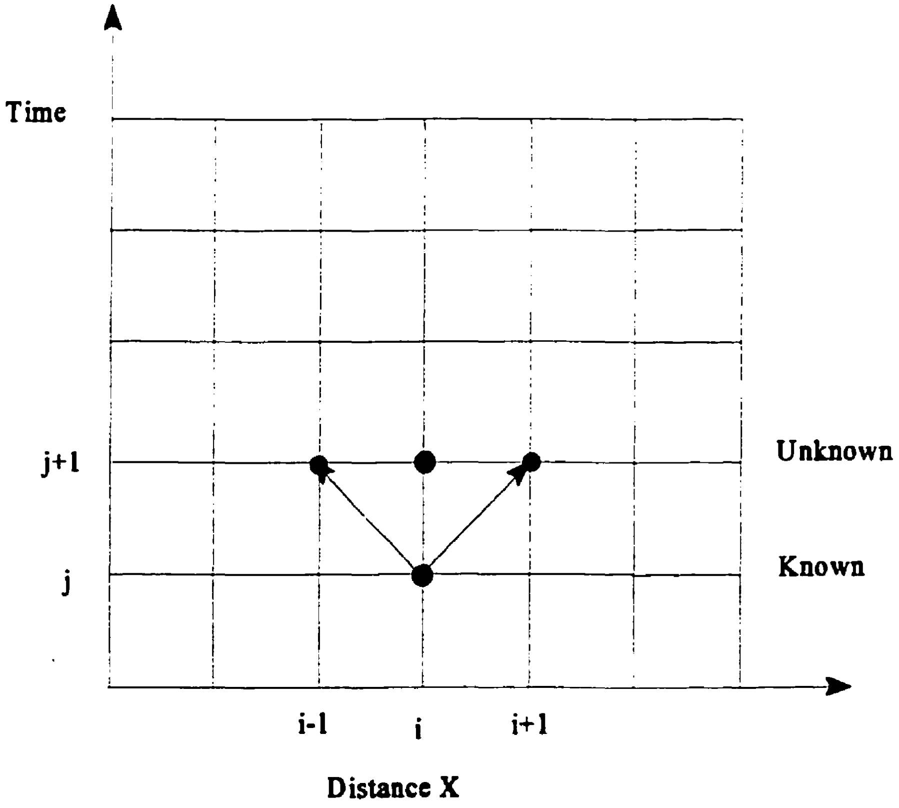


Figure 6.1 Grid Points for the Implicit Finite Difference Formulation

Using the second-order central difference approximation of the order of Δx^2, the first part of the right hand side of equation 6.15 can be written as:

$$\begin{aligned}\frac{\partial}{\partial x}\left(D_{\theta\theta}\frac{\partial\theta}{\partial x}\right) &= \frac{1}{\Delta x}\\ &\left[\omega\left(D_{\theta\theta(i+1/2)}\frac{\theta_{(i+1)}-\theta_i}{\Delta x} - D_{\theta\theta(i-1/2)}\frac{\theta_i-\theta_{(i-1)}}{\Delta x}\right)^j\right.\\ &\left.+ (1-\omega)\left(D_{\theta\theta(i+1/2)}\frac{\theta_{(i+1)}-\theta_i}{\Delta x} - D_{\theta\theta(i-1/2)}\frac{\theta_i-\theta_{i-1}}{\Delta x}\right)^{j+1}\right]\end{aligned} \tag{6.19}$$

Where :

$$D_{\theta\theta(i+1/2)}^{j} = \left(\frac{D_{\theta\theta(i+1)} + D_{\theta\theta i}}{2}\right)^{j} \tag{6.20}$$

$$D_{\theta\theta(i+1/2)}^{j+1} = \left(\frac{D_{\theta\theta(i+1)} + D_{\theta\theta i}}{2}\right)^{j+1} \tag{6.21}$$

$$D_{\theta\theta(i-1/2)}^{j} = \left(\frac{D_{\theta\theta i} + D_{\theta\theta(i-1)}}{2}\right)^{j} \tag{6.22}$$

$$D_{\theta\theta(i-1/2)}^{j+1} = \left(\frac{D_{\theta\theta i} + D_{\theta\theta(i-1)}}{2}\right)^{j+1} \tag{6.23}$$

Substituting equations 6.20, 6.21, 6.22, and 6.23 into equation 6.19 yields:

$$
\begin{aligned}
&\frac{\partial}{\partial x}\left(D_{\theta\theta}\frac{\partial\theta}{\partial x}\right)=\frac{1}{\Delta x}\\
&\Big[\,\omega\,\Big(\frac{D_{\theta\theta(i+1)}+D_{\theta\theta_i}}{2}\,\frac{\theta_{(i+1)}-\theta_i}{\Delta x}-\frac{D_{\theta\theta(i)}+D_{\theta\theta(i-)}}{2}\,\frac{\theta_i-\theta_{(i-1)}}{\Delta x}\Big)^{j}\\
&+(1-\omega)\Big(\frac{D_{\theta\theta(i+1)}+D_{\theta\theta_i}}{2}\,\frac{\theta_{(i+1)}-\theta_i}{\Delta x}-\frac{D_{\theta\theta(i)}+D_{\theta\theta(i-1)}}{2}\,\frac{\theta_i-\theta_{(i-1)}}{\Delta x}\Big)^{j+1}
\end{aligned}
\tag{6.24}
$$

Similarly, the second part of the equation 6.15 can be written as follow:

$$
\begin{aligned}
&\frac{\partial}{\partial x}\left(D_{\theta C}\,\frac{\partial C}{\partial x}\right)=\frac{1}{\Delta x}\\
&\Big[\omega\Big(\frac{D_{\theta C(i+1)}+D_{\theta C_i}}{2}\,\frac{C_{(i+1)}-C_i}{\Delta x}-\frac{D_{\theta C(i)}+D_{\theta C(i-)}}{2}\,\frac{C_i-C_{(i-1)}}{\Delta x}\Big)^{j}\\
&+(1-\omega)\,\Big(\frac{D_{\theta C(i+1)}+D_{\theta C_i}}{2}\,\frac{C_{(i+1)}-C_i}{\Delta x}-\frac{D_{\theta C(i)}+D_{\theta C(i-1)}}{2}\,\frac{C_i-C_{(i-1)}}{\Delta x}\Big)^{j+1}
\end{aligned}
\tag{6.25}
$$

After incorporating the implicit finite difference method, volumetric water content at time level j+1 can be obtained implicitly from the volumetric water content at time level j as given by substituting equations (6.18), (6.24) and (6.25) into equation (6.15):

Volumetric water content at time j+1

$$
\begin{aligned}
\theta_i^{j+1}=\frac{\Delta t}{2\,\Delta x^2}\,&\big[\omega[(D_{\theta\,\theta(i+1)}+D_{\theta\,\theta(i)})\,(\theta_{(i+1)}-\theta_{(i)})\\
&-(D_{\theta\,\theta(i)}+D_{\theta\,\theta\,(i-1)})\,(\theta_i-\theta_{(i-1)})\\
&+(D_{\theta\,C\,(i+1)}+D_{\theta\,C\,(i)})\,(C_{(i+1)}-C_{(i)})\\
&-(D_{\theta\,C\,(i)}+D_{\theta\,C\,(i-1)})\,(C_{(i)}-C_{(i-1)})\,]^{j}\\
&+(1-\omega)[\,(D_{\theta\,\theta(i+1)}+D_{\theta\,\theta(i)})\,(\theta_{(i+1)}-\theta_{(i)})\\
&-(D_{\theta\,\theta(i)}+D_{\theta\,\theta\,(i-1)})\,(\theta_i-\theta_{(i-1)})\\
&+(D_{\theta\,C\,(i+1)}+D_{\theta\,C\,(i)})\,(C_{(i+1)}-C_{(i)})\\
&-(D_{\theta\,C\,(i)}+D_{\theta\,C\,(i-1)})\,(C_{(i)}-C_{(i-1)})]^{j+1}\big]+\theta_i^{j}
\end{aligned}
\tag{6.26}
$$

The same procedure was used to find solute concentration at time j+1, where equation 6.16 can be written in implicit finite difference form as follows:

$$\begin{aligned} C_i^{j+1} = \frac{\Delta t}{2\ \Delta x^2} [\omega [& (D_{C\,C(i+1)} + D_{C\,C(i)})\ (C_{(i+1)} - C_{(i)}) \\ & - (\,D_{C\,C(i)} + D_{C\,C\,(i-1)})\ (C_i - C_{(i-1)}) \\ & + (\,D_{C\,\theta\,(i+1)} + D_{C\,\theta\,(i)})\ (\,\theta_{(i+1)} - \theta_{(i)}) \\ & - (\,D_{C\,\theta\,(i)} + D_{C\,\theta\,(i-1)})\ (\,\theta_{(i)} - \theta_{(i-1)})\ ]^{j} \\ & + (1-\omega)[\ (\,D_{C\,C(i+1)} + D_{C\,C(i)})\ (C_{(i+1)} - C_{(i)}) \\ & - (\,D_{C\,C(i)} + D_{C\,C\,(i-1)})\ (C_i - C_{(i-1)}) \\ & + (\,D_{C\,\theta\,(i+1)} + D_{C\,\theta\,(i)})\ (\,\theta_{(i+1)} - \theta_{(i)}) \\ & - (D_{C\,\theta\,(i)} + D_{C\,\theta\,(i-1)})\ (\theta_{(i)} - \theta_{(i-1)})]^{j+1}] + C_i^j \end{aligned} \qquad (6.27)$$

where : $x = i\ \Delta x$ for $i = 1, I$

$t = j\ \Delta t$ for $j = 1, J$

ω is considered 1/2, yielding the Crank-Nicolson implicit method, where the method is considered unconditionally stable for $1/2 \leq \omega \leq 1$.

Equations 6.26 and 6.27 are the final differential equations in the finite difference format and are used with the optimization technique to obtain the diffusion parameters.

6.5 Determination of Diffusion Parameters and Unkown Material Coefficients

Prediction of the moisture and concentration profiles at time j+1 can be found numerically once the concentration and moisture profile at time j are measured experimentally and the diffusion function is assumed. Thus, it is assumed that the diffusion parameters are expressed as an exponential function of volumetric water content and solute concentration and are described as follow:

$$D_{CC} = a_9 + a_1 \exp^{-a_{13} C_{NT}} + a_5 \exp^{-a_{17} \theta_{NT}} \tag{6.28}$$

$$D_{C\theta} = a_{11} + a_3 \exp^{-a_{15} C_{NT}} + a_7 \exp^{-a_{19} \theta_{NT}} \tag{6.29}$$

$$D_{\theta\theta} = a_{10} + a_2 \exp^{-a_{14} C_{NT}} + a_6 \exp^{-a_{18} \theta_{NT}} \tag{6.30}$$

$$D_{\theta C} = a_{12} + a_4 \exp^{-a_{16} C_{NT}} + a_8 \exp^{-a_{20} \theta_{NT}} \tag{6.31}$$

where a_1 to a_{20} are constant material parameters and can be obtained from the optimization procedures.

At time j, volumetric water content and concentrations at different depths and times were measured and under the same conditions the volumetric water content and concentrations were predicted numerically at time j+1 using the model described above.

If $C_{exp}(x,t)$ and $C_{cal}(x,t)$ are the measured and the calculated concentrations respectively, and $\theta_{exp}(x,t)$ and $\theta_{cal}(x,t)$ are the measured and calculated volumetric water content, respectively, then the best choice for these material parameter coefficients (a_1 to a_{20}) are those which minimize the following functions:

- For volumetric water content:

$$\sigma_2 = \sum_{i=1}^{m} \left| \theta_{exp}(x,t) - \theta_{cal}(x,t) \right| \tag{6.32}$$

- For solute concentration:

$$\sigma_1 = \sum_{i=1}^{m} \left| C_{exp}(x,t) - C_{cal}(x,t) \right| \tag{6.33}$$

where m represents the number of measured and calculated concentrations C and volumetric water content θ , and σ is a function of the unknown material coefficients. The best way to obtain the minimum of the function σ is to use Powell's conjugate directions method of non-linear optimization (Powell, 1964). So, the derivation of σ with respect to a specific unknown coefficient can be determined in a simple way. This makes Powell's method more useful because it does not require derivatives of the objective function.

6.6 Model Calibration

The migration and retention profiles of heavy metals along the soil column obtained from experiments were used for the calibration of the proposed model. To calibrate the model, a computer code called the Coupled Moisture and Solute Diffusion Parameter Technique (CMSDPT) has been developed (Appendix II) in conjunction with the application of the theory of irreversible thermodynamic, Fick's law, Darcy's law and equilibrium mass transfer principles. Two main procedures are used in this program to determine the unknown material parameters. The first one is to set the initial condition (initial moisture and concentration) and to find the time and space step size, based on the input data of the initial guess value of material parameters. The second is to keep revising the material parameters until the difference between experimental and theoretical moisture and solute values is minimized. Then, the diffusion parameter is calculated for each individual layer in the soil samples using Powell's optimization technique and the implicit finite difference method to solve the coupled diffusion equations. The implicit finite difference part starts with a guess value of the next time step. At each time step the numerical results are compared with the guess values. If the results agree within a specified criterion, they are accepted and the numerical process is continued for the next time step. If they do not, they are considered as the new guess values and repeated using the same procedure until results converge. A detailed technique of the calibration flow chart is shown in Figure 6.2.

In order to calibrate the model , experimentally measured moisture and metal concentrations were correlated with the corresponding calculated moisture concentrations through the following equations:

For volumetric water content:

$$r_1 = \sqrt{1 - \frac{\sum_{i=1}^{m} [\theta_{(Exp.i)} - \theta_{(Calc.i)}]^2}{\sum_{i=1}^{m} [\theta_{(Exp.i)} - \theta_{Avr.}]^2}} \tag{6.34}$$

For solute concentration:

$$r_2 = \sqrt{1 - \frac{\sum_{i=1}^{m} [\, C_{(Exp.i)} - C_{(Calc.i)} \,]^2}{\sum_{i=1}^{m} [\, C_{(Exp.i)} - C_{Avr.} \,]^2}} \tag{6.35}$$

Where r represents the correlation coefficients, $C_{avr.}$ is the average experimental concentration and $\theta_{avr.}$ is the average experimental volumetric water content. Experimental results from volumetric water content and total heavy metals concentration profiles of zinc, lead and copper after 52 hrs and 17.8 days for illitic soil at pH 3.5 were used to calibrate the model. The resulting diffusion and coefficient parameters for various heavy metals are tabulated in Appendix I. The experimental and the calibrated results calculated by the model for the volumetric water content and heavy metal variations with depth are shown in Figure 6.3 through Figure 6.8 and the calculated moisture, solute, solute moisture and moisture solute diffusivities as a function of time, distance from influent source, volumetric water content and heavy metal concentrations are presented in Figure 6.9 through Figure 6.32. The unknown parameters a_i of the diffusion coefficients for zinc copper and lead are presented in Appendix I. Experimental moisture and solute data used to calibrate the model, and the initial and boundary conditions are listed in the following section.

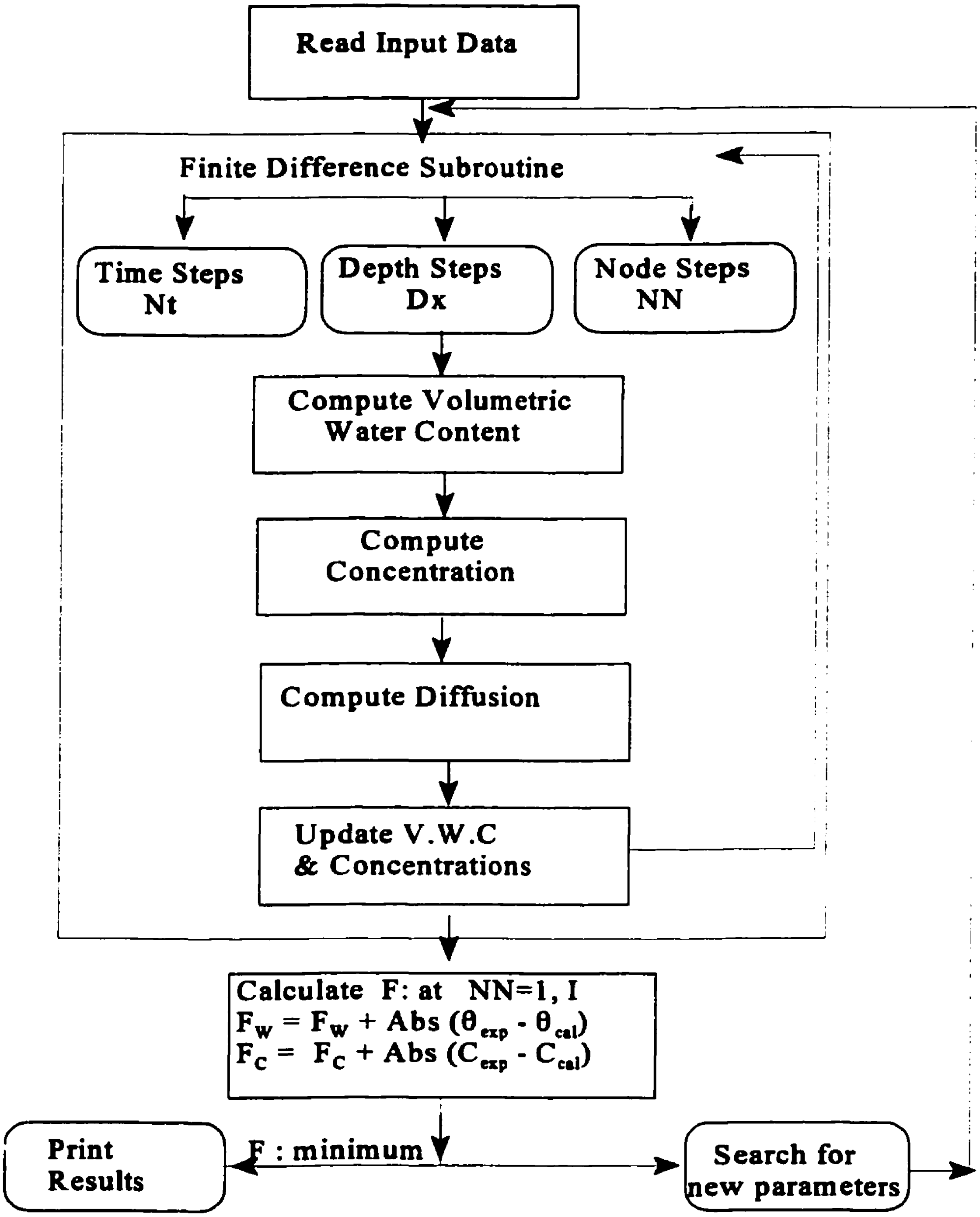


Figure 6.2 Calibration Program Flow Chart

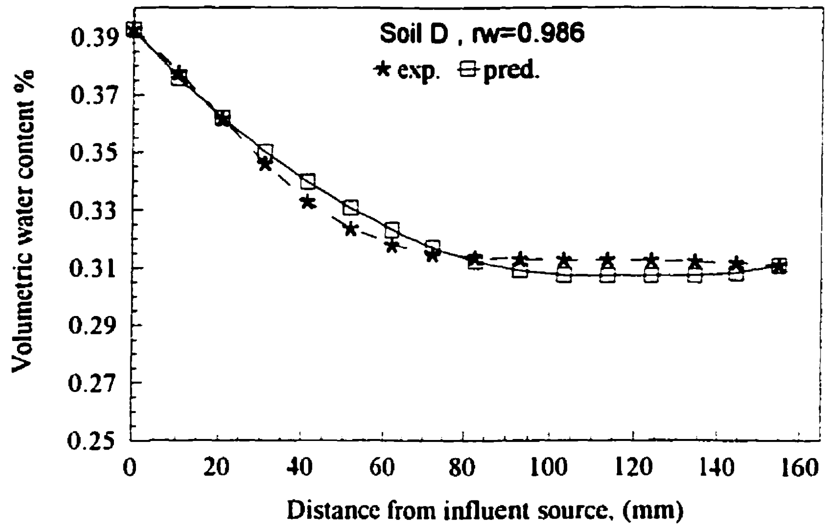


Figure 6.3 Volumetric Water Content Model Calibration for Soil D. (5000mg/l input Concentration of Zn)

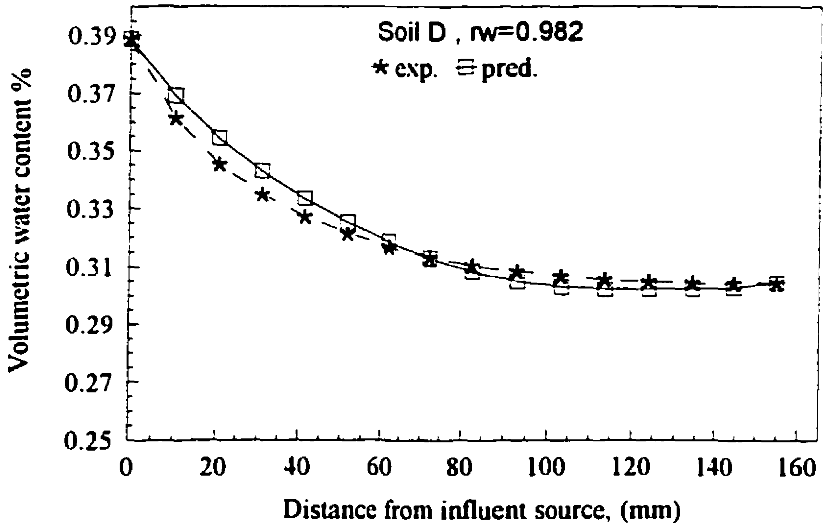


Figure 6.4 Volumetric Water Content Model Calibration for Soil D. (5000mg/l input Concentration of Pb)

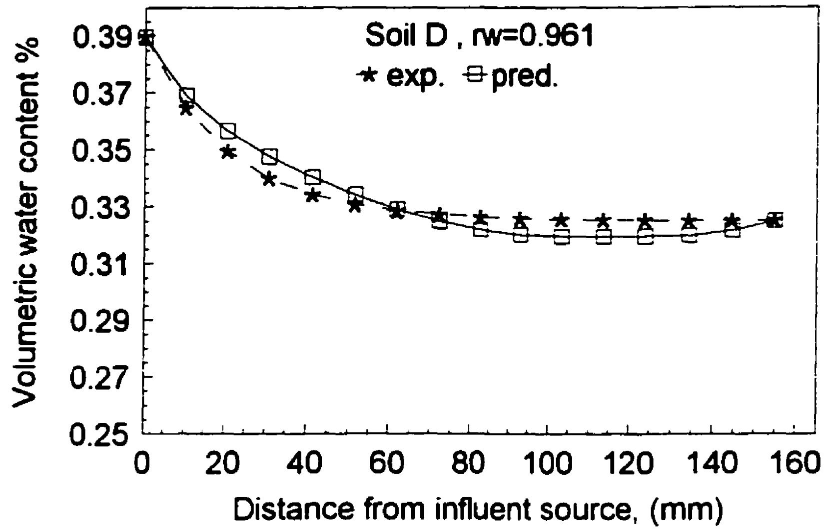


Figure 6.5 Volumetric Water Content Model Calibration for Soil D. (5000mg/l input Concentration of Cu)

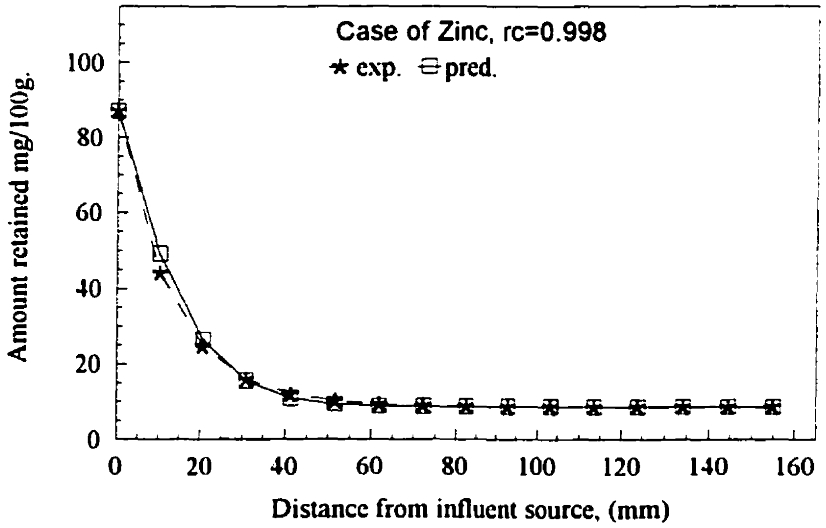


Figure 6.6 Model Calibration for Retained Zinc Concentration. (5000mg/l input)

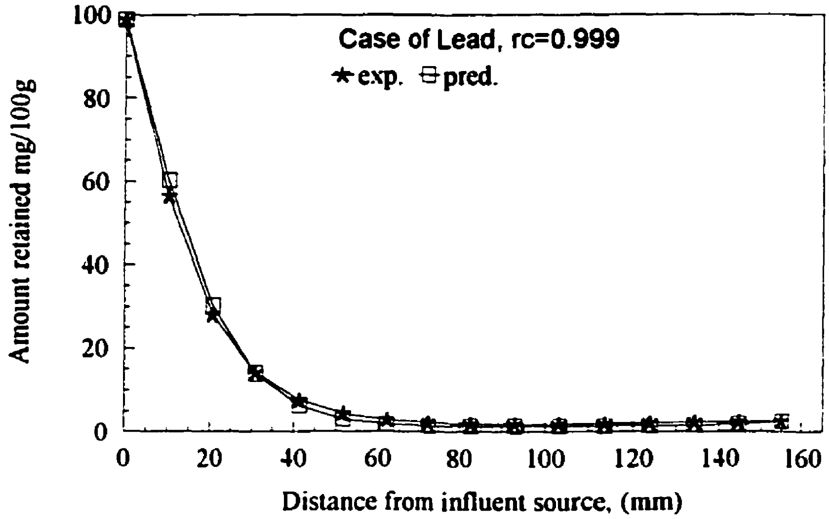


Figure 6.7 Model Calibration for Retained Lead Concentration. (5000mg/l input)

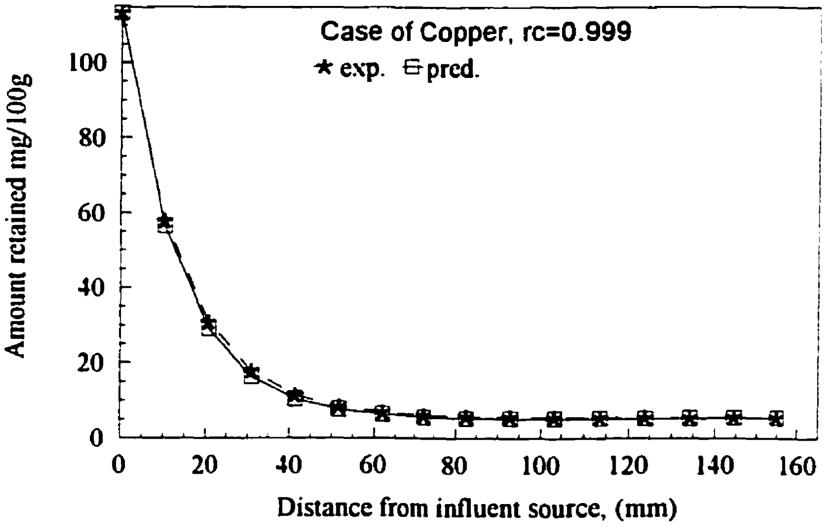


Figure 6.8 Model Calibration for Retained Copper Concentration. (5000mg/l input)

6.7 Initial and Boundary Conditions

The following initial and boundary conditions were used:

(1) initial conditions:

$$C = 5000\text{mg/l} \quad \text{for} \quad 0 \le x \le 165\text{mm} \tag{6.36}$$

$$\theta = 0.265 \quad \text{for} \quad 0 \le x \le 165\text{mm} \tag{6.38}$$

(2) boundary conditions:

$$C = C_0 \quad \text{for } 0 \le x \le 165\text{mm} \quad t=0 \tag{6.39}$$

$$\theta = \theta_0 \quad \text{for } 0 \le x \le 165\text{mm} \quad t=0 \tag{6.40}$$

$$C = C(x,t) \quad \text{for } 0 < x < 165\text{mm} \quad t>0 \tag{6.41}$$

$$\theta = \theta(x,t) \quad \text{for } 0 < x < 165\text{mm} \quad t>0 \tag{6.42}$$

The following equations were used to calibrate the model between 52 hrs. and 17.8 days as listed:

Case 1: Copper

a- Time t = 52 hrs.

$$\theta l = 0.403581328 + 0.000802637\, x - 0.01969281\, x^{0.5} - 0.02048126\, e^{-x} \tag{6.43}$$

$$Cl = 32.34149835 + 0.283868998\, x - 5.63992135\, x^{0.5} + 59.65851645\, e^{-x} \tag{6.44}$$

b- Time t = 17.8 days

$$\theta f = 0.324967829 + 0.064601219\, e^{(-x/21.28913618)} \tag{6.45}$$

$$Cf = 98.7192972 - 2.01424152\, x + 0.014450083\, (x^2 / (1+0.01776152\, x) + 0.002110884\, x^2 \tag{6.46}$$

Case 2 : Lead

a- Time t =52 hrs:

$$\theta\,I = 0.417652638 - 0.00490646\,x + 0.00042428\,x^{1.5} - 6.3264e\text{-}07\,x^{2.5} \quad (6.47)$$

$$CI = 1.301977886 + 143.7346457\,e^{(-x/6.393934567)} \quad (6.48)$$

b- Time t =17.8 days

$$\theta f = 0.411165472 + 0.000748414\,x - 0.01790256\,x^{0.5} - 0.02256545\,e^{-x} \quad (6.49)$$

$$Cf = 98.7192972 - 2.01424152\,x + 0.014450083\,(x^{2}/(1+0.01776152\,x)) \quad (6.50)$$
$$+0.002110884\,x^{2}$$

Case 3: Zinc

a- Time t=52 hrs.

$$\theta I = 0.289395401 + 0.096475303\,e^{(-x/37.61637976)} \quad (6.51)$$

$$CI = 8.668151957 + 87.32740871\,e^{(-x/3.641068278)} \quad (6.52)$$

b- Time t=17.8 days.

$$Cf = 8.618209996 + 78.43227136\,e^{-x/12.9868636} \quad (6.53)$$

$$\theta f = 0.392412593 - 0.00592318\,x + 8.95157e\text{-}05(x^{2}/(1-0.01170626\,x)) \quad (6.54)$$
$$+ 0.000217252\,x^{2} + 2.21355e\text{-}07\,x^{3}$$

Then, using the computer code CMSDPT, the volumetric water content and solute concentration as a function of space and time were predicted using the calculated diffusion parameters.

6.8 Diffusion Coefficient

Most existing transport models use an average diffusion coefficient in order to predict the movement of heavy metals. In fact, and as demonstrated in this section, it cannot be considered a good assumption. The diffusion coefficient varies with type of soil, time, distance, volumetric water content or degree of saturation, carbonate content and heavy metal influent concentration. The calculated moisture, solute moisture, and solute diffusivity parameters as a function of distance, volumetric water content and heavy metal concentration for illitic soil at pH 3.5 are discussed and presented in the following sections.

6.8.1 Moisture diffusivity

Moisture diffusivity, $D_{\theta\theta}$, and volumetric water content variations with distance for various heavy metal concentrations for illitic soil at pH 3.5 are shown in Figures 6.9, 6.10 and 6.11. Whereas, moisture diffusivity profiles and heavy metal concentration variations with depth are presented in Figures 6.12, 6.13 and 6.14. Test results show an increase in the moisture diffusivities, due to the internal suction gradients caused by coupled moisture and solute movement from the source point. The moisture diffusivities vary along the soil column and tend to be from 70 to 132 mm^2/day for Zinc (Figure 6.9), 66 to 142 mm^2/day for Pb (Figure 6.10) and from 116 to 382 mm^2/day for Copper (Figure 6.11).

6.8.2 Solute diffusivity

The solute diffusivity, D_{cc}, variations with distance, volumetric water content and heavy metal concentration retained along the soil column for different heavy metal species for illitic soil at pH 3.5 are presented in Figures 6.15 through 6.20. As also shown, the calculated solute diffusivities vary with type of soil, depth, the degree of saturation or volumetric water content variations along the soil column and various heavy metal input concentrations. Similar to the moisture diffusivity variations along the soil column, the solute diffusivity increases up to 30mm in depth and then continues steadily parallel to moisture and solute concentration movements along the soil column.

6.8.3 Solute moisture diffusivity

Solute moisture diffusivity, $D_{c\theta}$, and volumetric water content variations with distance for various heavy metal concentrations for illitic soil at pH 3.5 are shown in Figures 6.21, 6.22 and 6.23. Solute moisture diffusivity profiles and heavy metal concentration variations with depth are presented in Figures 6.24, 6.25 and 6.26. As shown, solute moisture diffusivity shows similar movement to moisture and solute diffusivities and increases up to 30mm and then continues steadily along the soil column.

6.8.4 Moisture solute diffusivity

Moisture solute diffusivity, $D_{\theta c}$, and volumetric water content variations with distance for various heavy metal concentrations for illitic soil at pH 3.5 are shown in Figures 6.27, 6.28 and 6.29. Moisture solute diffusivity profiles and heavy metal concentration variations with depth are shown in Figures 6.30, 6.31 and 6.32. As shown, the moisture solute diffusivity moves at a slow rate up to 40mm depth, reaches a maximun value at around 100mm depth and then decreases sharply for lead and decreases slowly for copper and zinc.

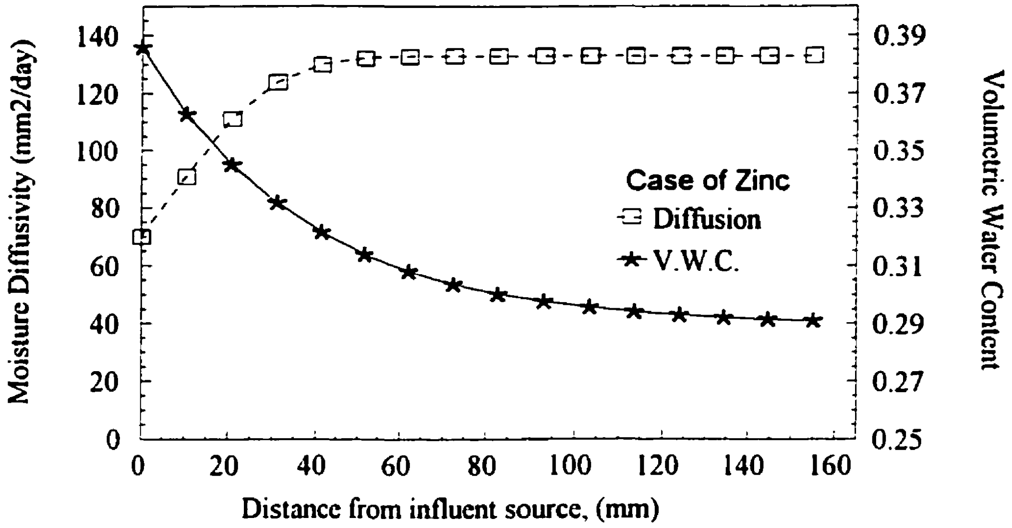


Figure 6.9 Moisture Diffusivity and Volumetric Water Content variations with Distance (Zinc).

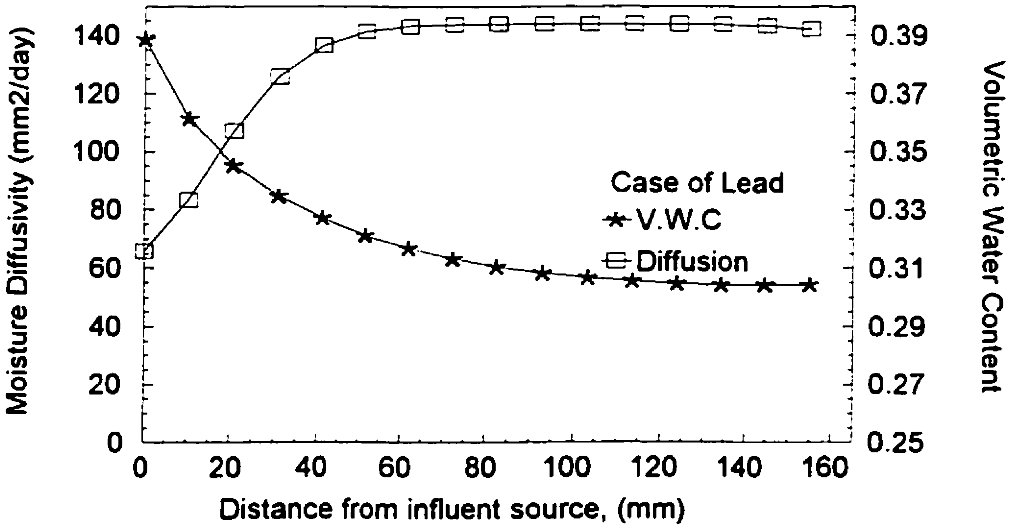


Figure 6.10 Moisture Diffusivity and Volumetric Water Content variations with Distance (Lead).

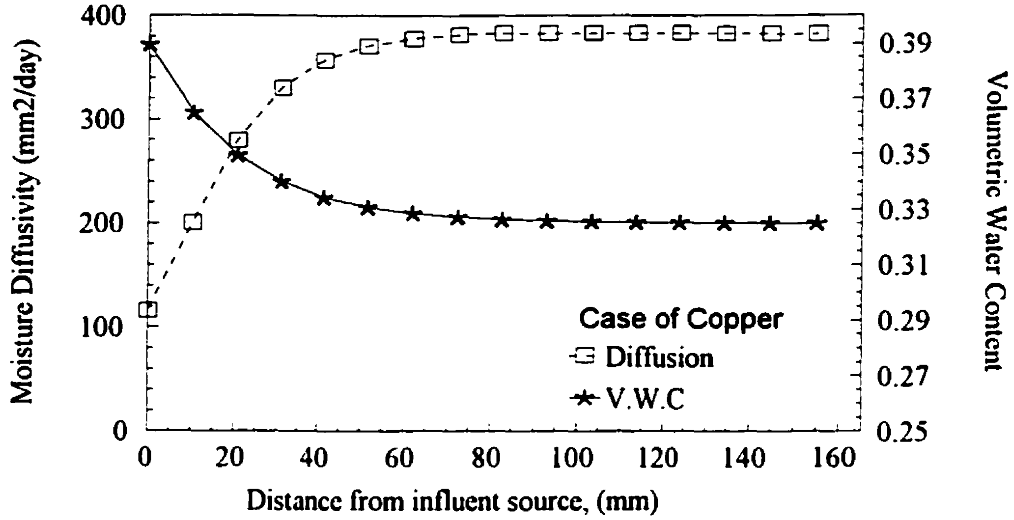


Figure 6.11 Moisture Diffusivity and Volumetric Water Content variations with Distance (Copper)

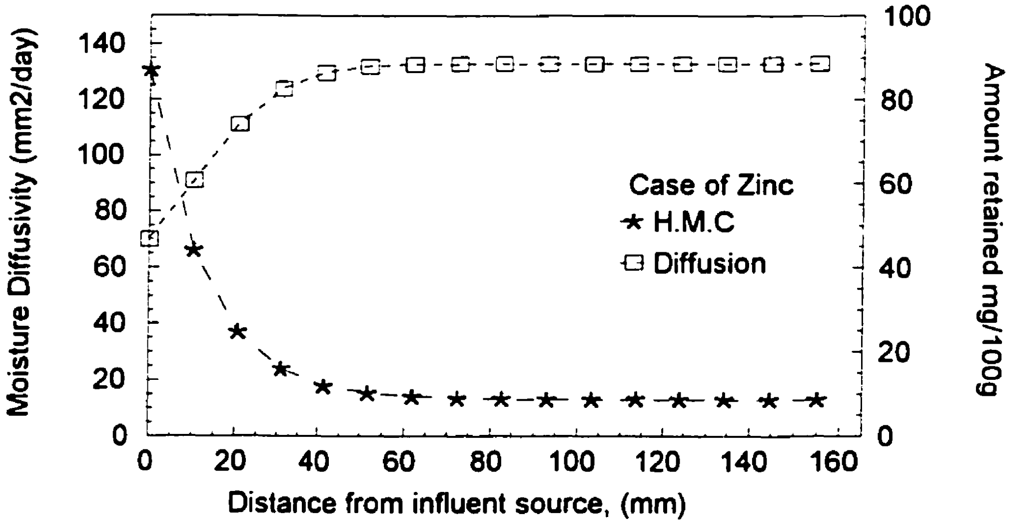


Figure 6.12 Moisture Diffusivity and Zinc Concentration Variations with Distance.

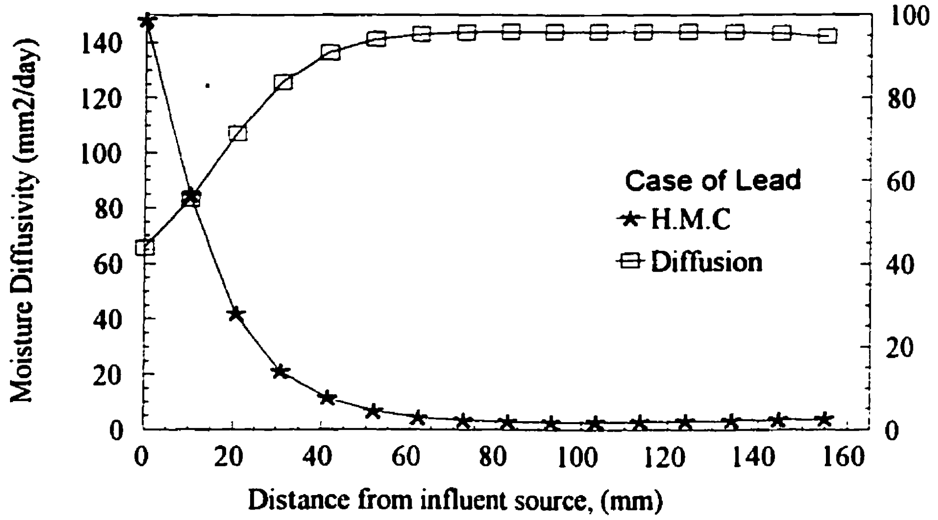


Figure 6.13 Moisture Diffusivity and Lead Concentration Variations with Distance.

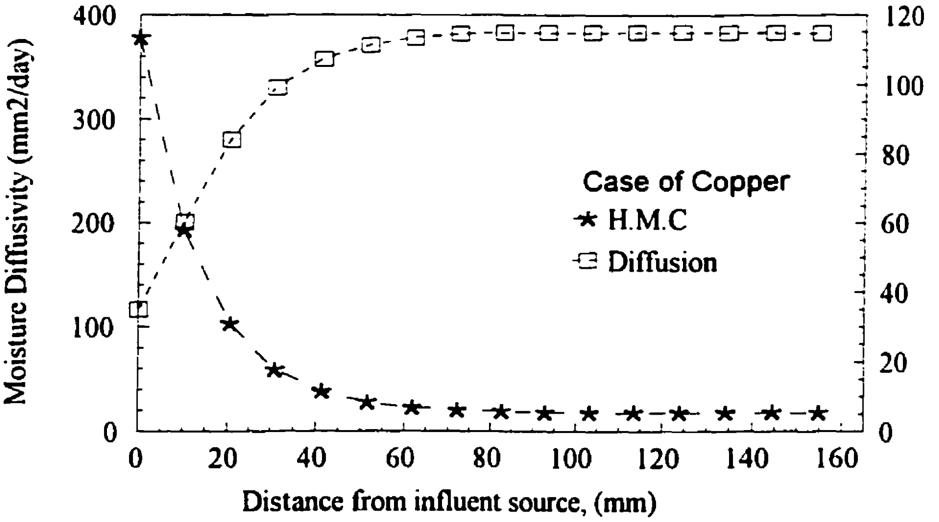


Figure 6.14 Moisture Diffusivity and Copper Concentration Variations with Distance.

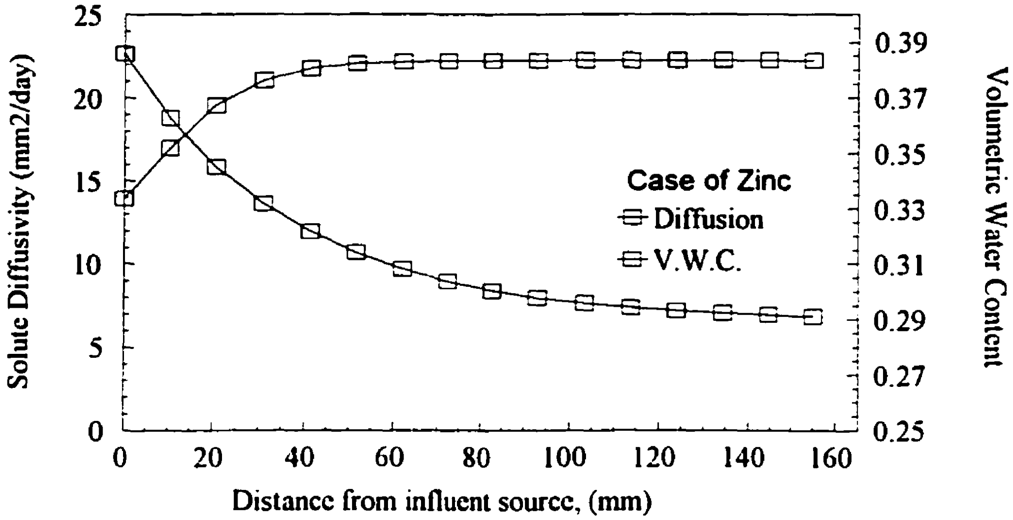


Figure 6.15 Solute Diffusivity and Volumetric Water Content Variations with Distance (Zinc).

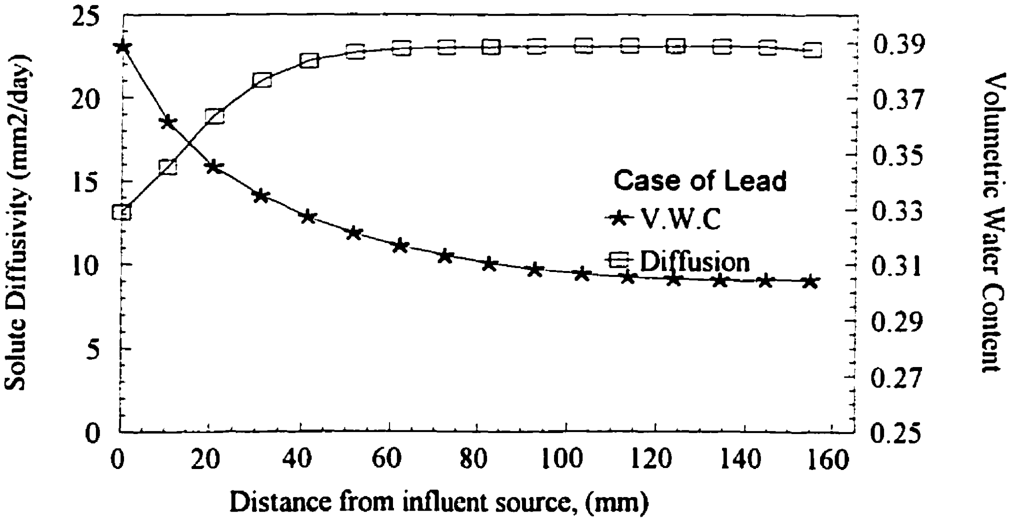


Figure 6.16 Solute Diffusivity and Volumetric Water Content Variations with Distance (Lead).

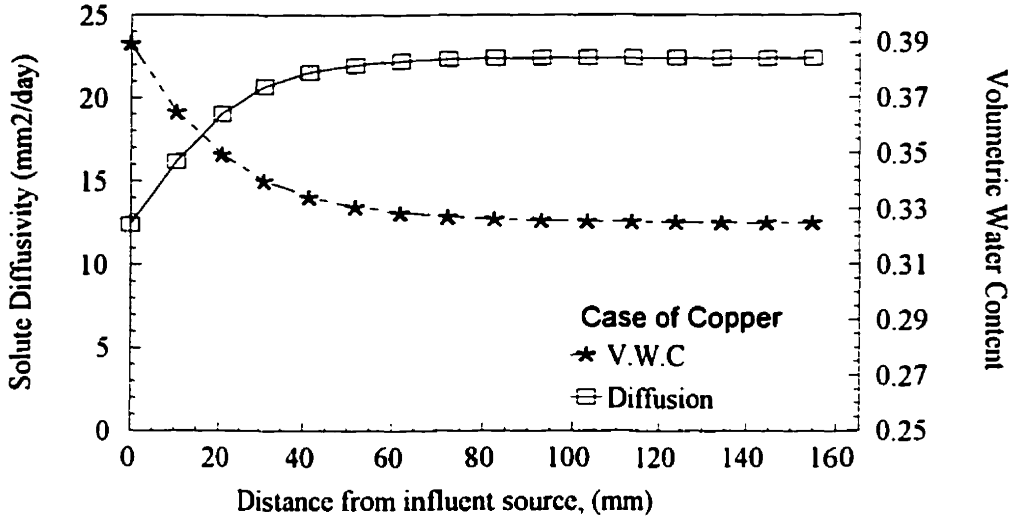


Figure 6.17 Solute Diffusivity and Volumetric Water Content Variations with Distance (Copper)

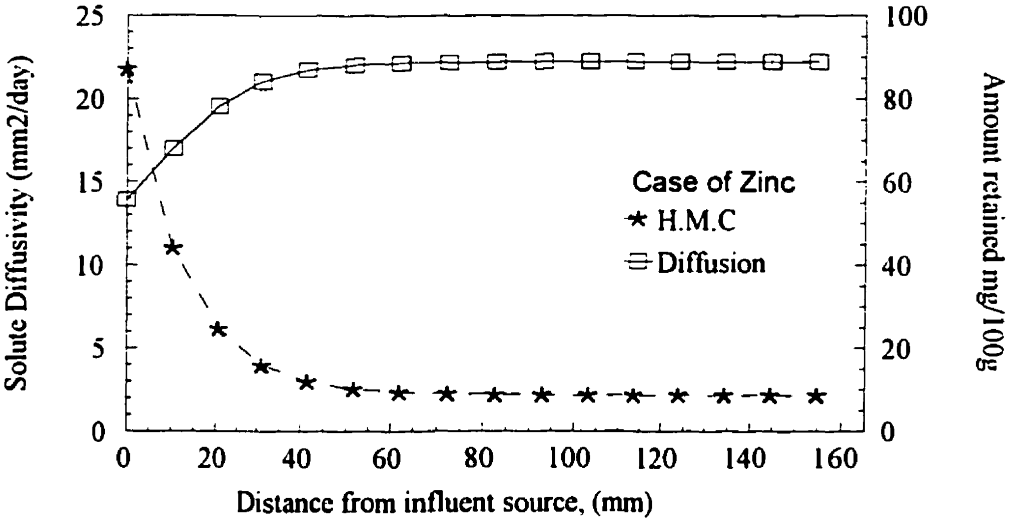


Figure 6.18 Solute Diffusivity and Zinc Concentration Variations with Distance.

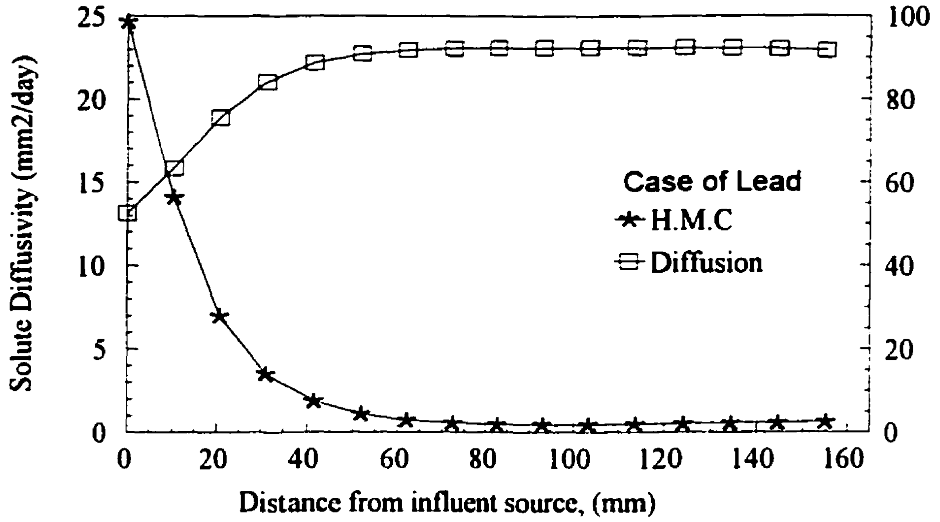


Figure 6.19 Solute Diffusivity and Lead Concentration Variations with Distance.

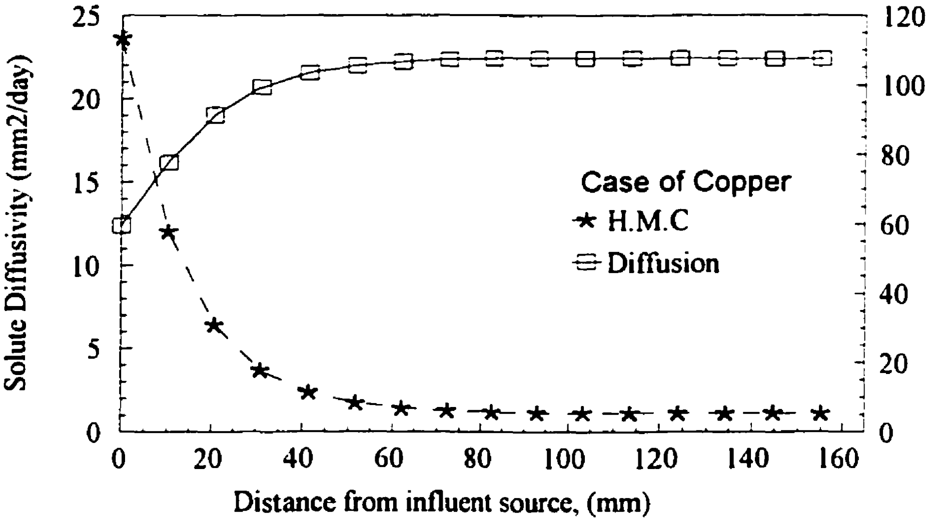


Figure 6.20 Solute Diffusivity and Copper Concentration Variations with Distance.

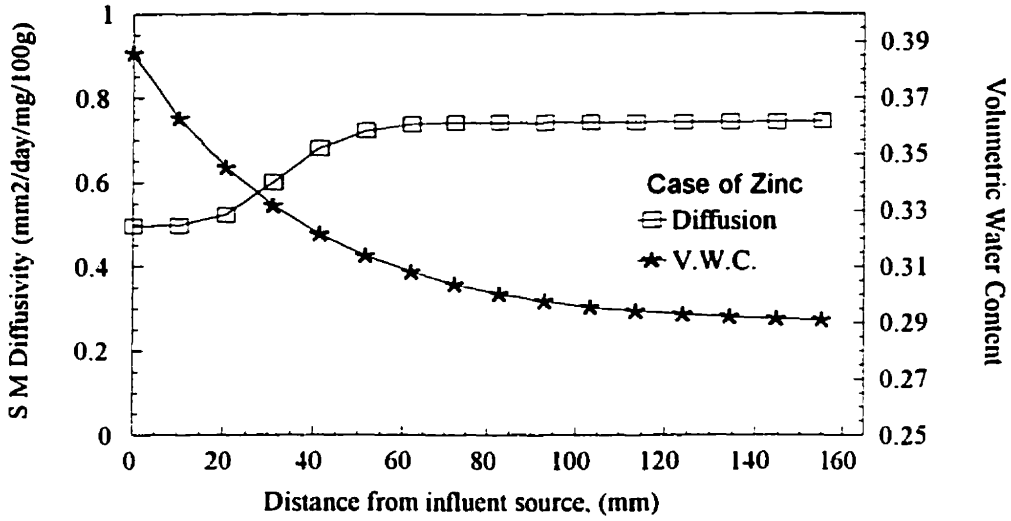


Figure 6.21 Solute Moisture Diffusivity and Volumetric Water Content Variations with Distance (Zinc).

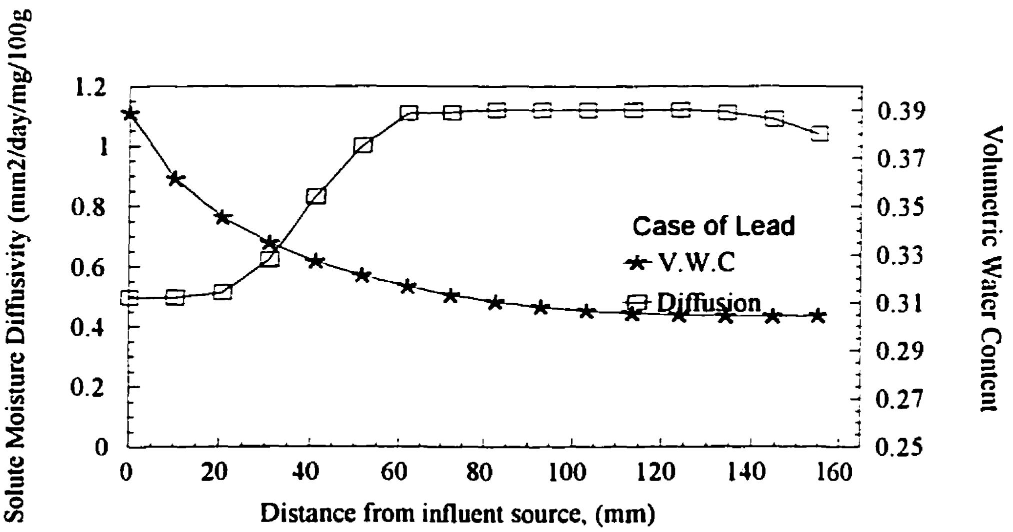


Figure 6.22 Solute Moisture Diffusivity and Volumetric Water Content Variations with Distance (Lead).

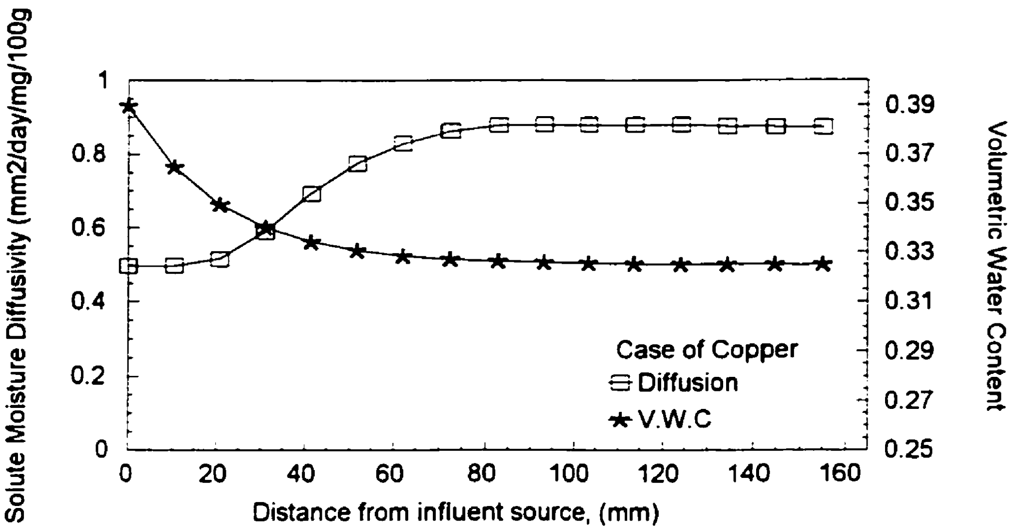


Figure 6.23 Solute Moisture Diffusivity and Volumetric Water Content Variations with Distance (Copper)

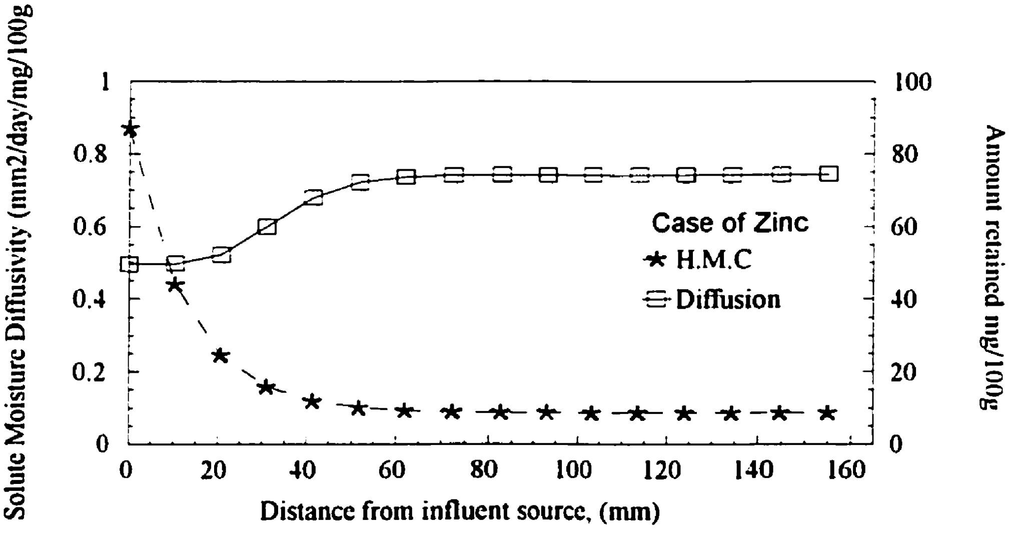


Figure 6.24 Solute Moisture Diffusivity and Zinc Concentration Variations with Distance.

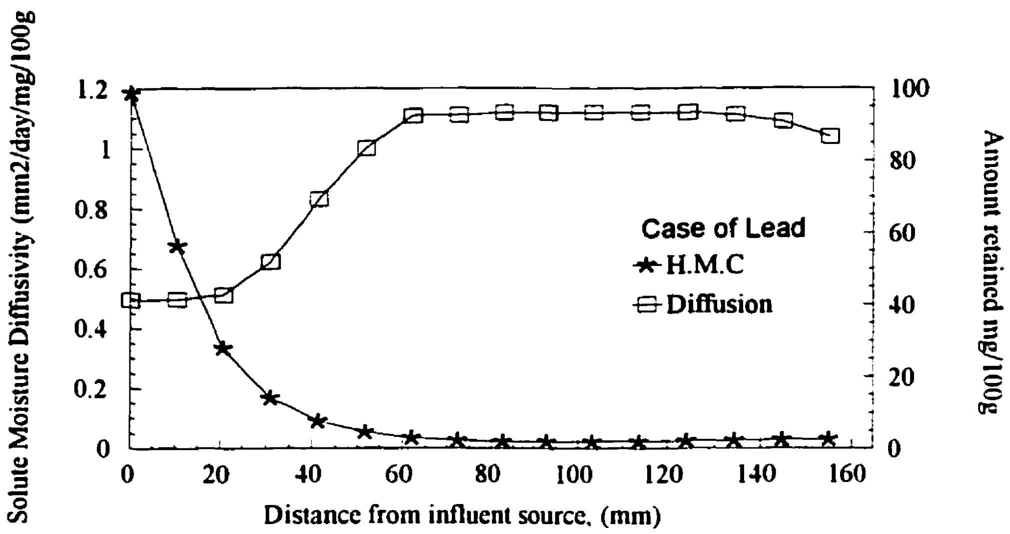


Figure 6.25 Solute Moisture Diffusivity and Lead Concentration Variations with Distance.

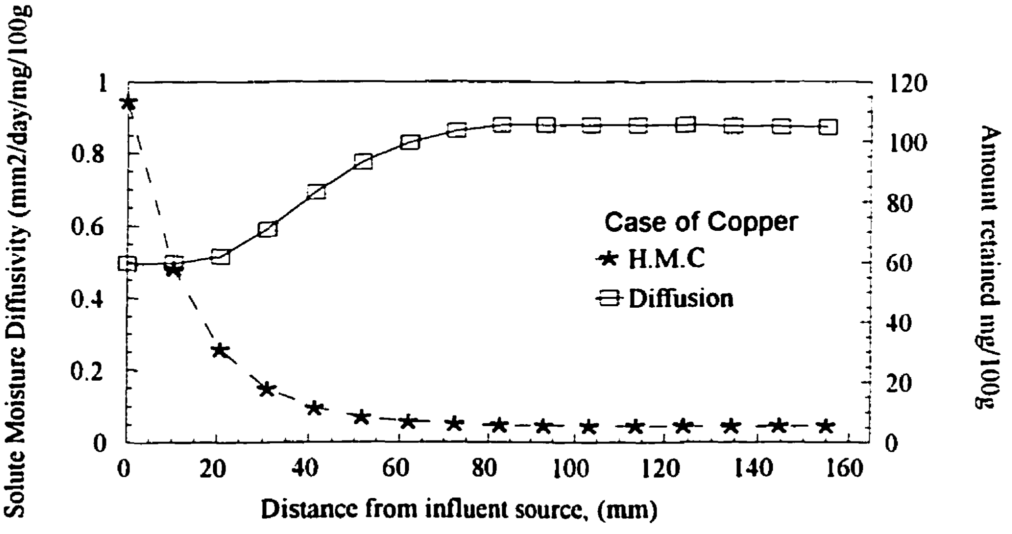


Figure 6.26 Solute Moisture Diffusivity and Copper Concentration Variations with Distance.

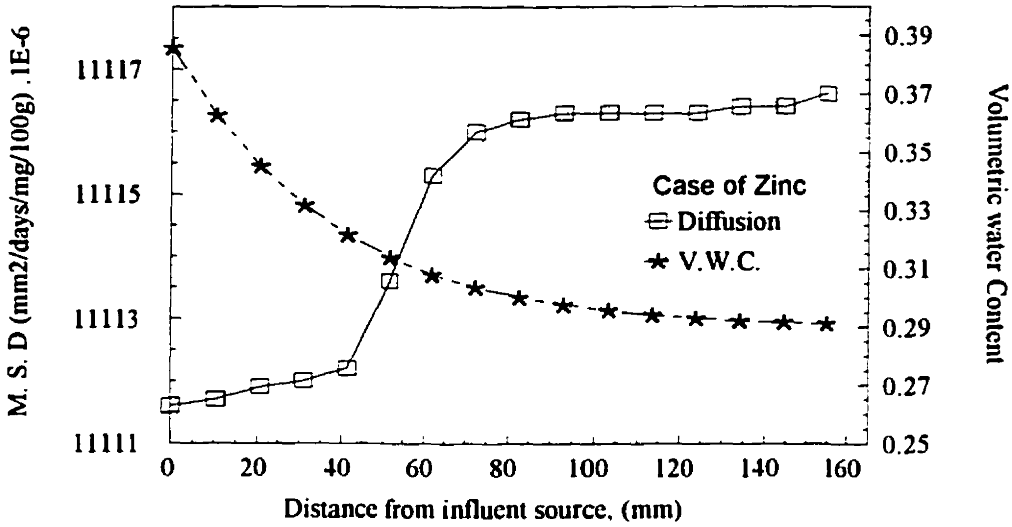


Figure 6.27 Moisture Solute Diffusivity and Volumetric Water Content Variations with Distance (Zinc).

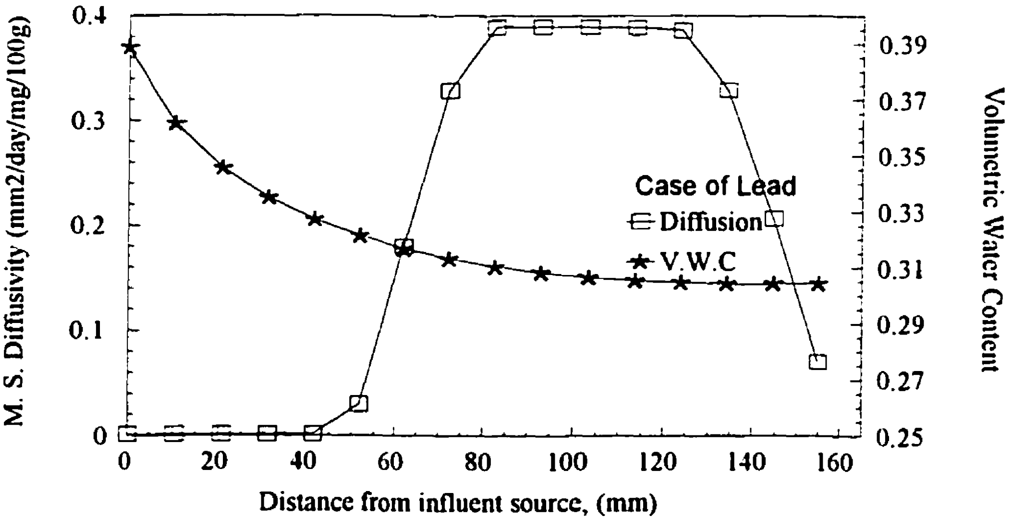


Figure 6.28 Moisture Solute Diffusivity and Volumetric Water Content Variations with Distance (Lead).

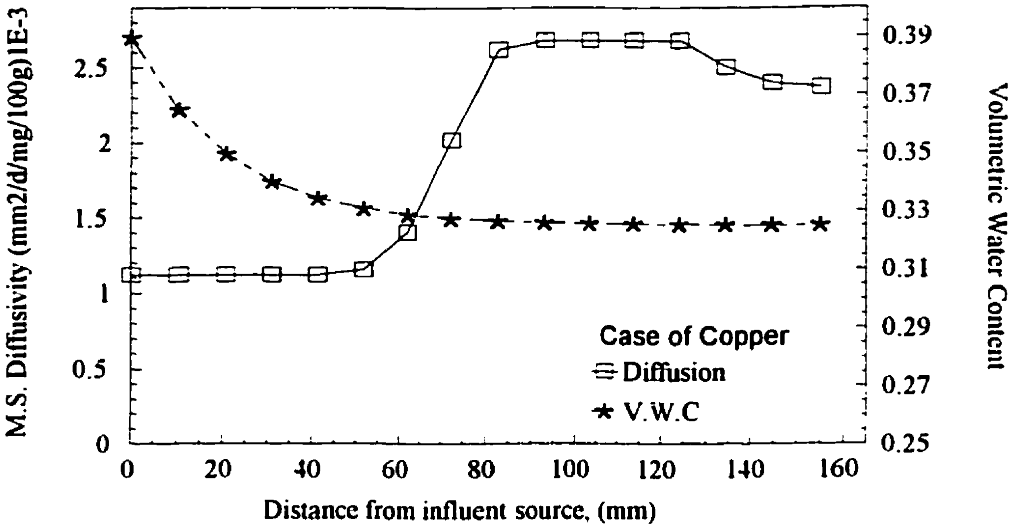


Figure 6.29 Moisture Solute Diffusivity and Volumetric Water Content Variations with Distance (Copper)

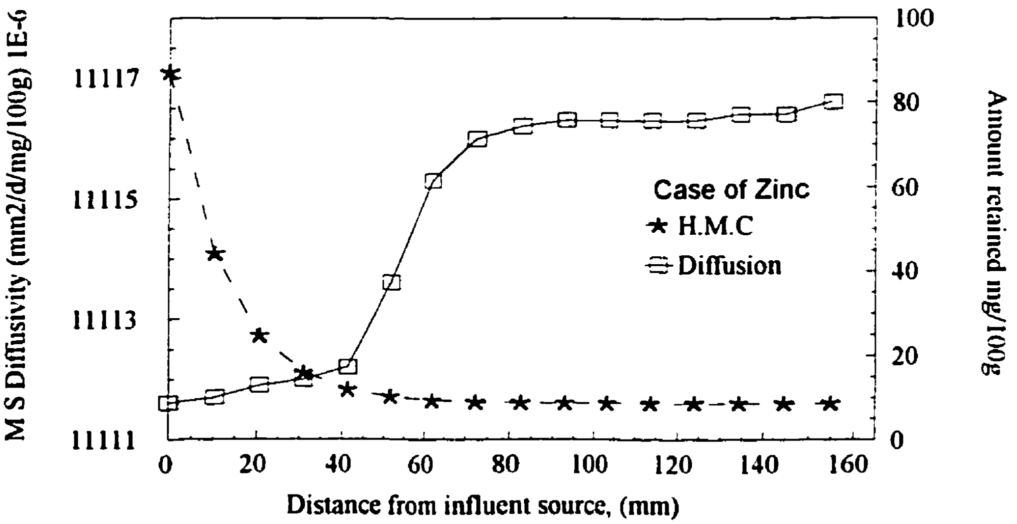


Figure 6.30 Moisture Solute Diffusivity and Zinc Concentration Variations with Distance.

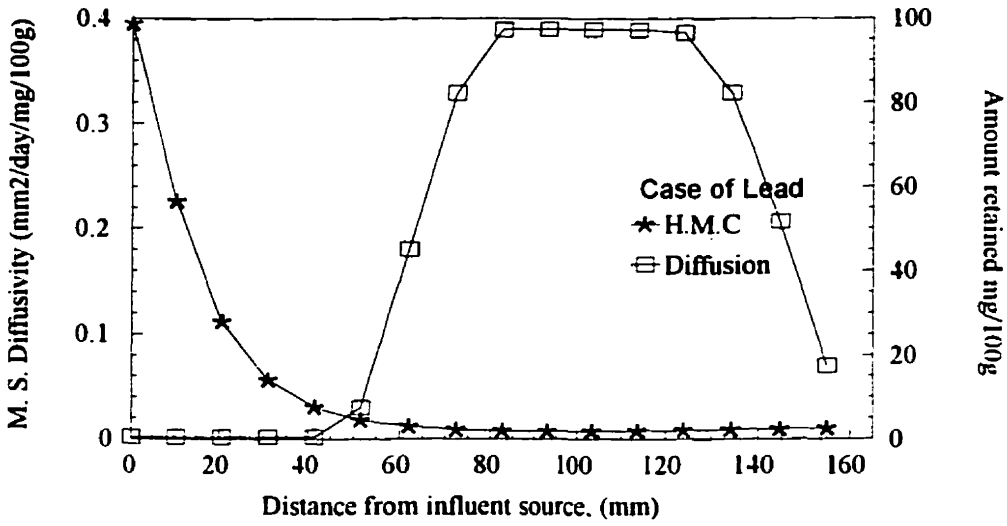


Figure 6.31 Moisture Solute Diffusivity and Lead Concentration Variations with Distance.

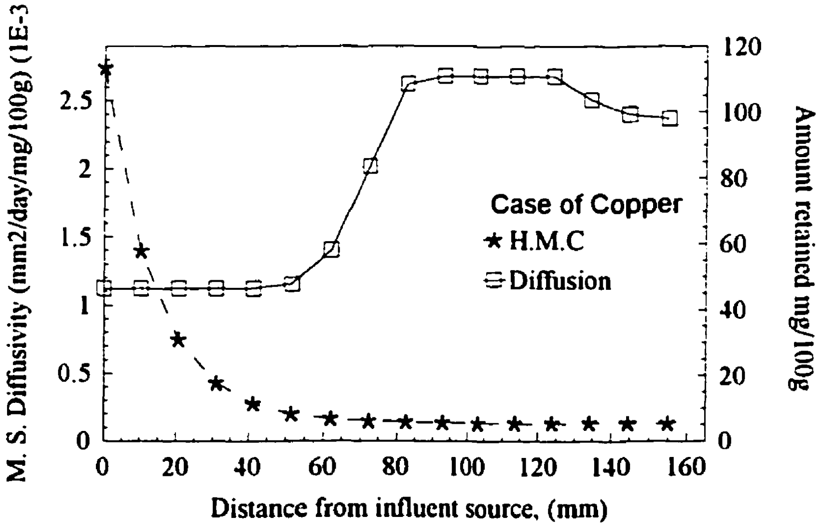


Figure 6.32 Moisture Solute Diffusivity and Copper Concentration Variations with Distance.

6.9 Model Validation and Prediction

With the known material coefficients and the calculated moisture, solute, solute moisture and moisture solute diffusivity coefficients, one can predict volumetric water content and solute variations along the soil column for different time durations by applying the implicit finite difference method combined with Powell's optimization technique.

In order to validate the calculated diffusion parameters, experimentally measured concentration and volumetric water content were compared with the predicted volumetric water content and the concentration under the same conditions to check the capability of the model to predict heavy metal movement for different time durations– as shown in Figure 6.33 through Figure 6.42. Comparison between the measured and the calculated moisture and solute profiles shows a good agreement and increases the level of confidence in predicting coupled solute and moisture profiles in the vadose zone.

6.10 Summary

The migration and retention profiles of heavy metals along the soil column obtained from experiments were used for the calibration of the proposed model. A computer code called the Coupled Moisture and Solute Diffusion Parameter Technique (CMSDPT) has been developed in conjunction with the application of the theory of irreversible thermodynamic, Fick's law, Darcy's law and equilibrium mass transfer principles. Then, the diffusion parameter was calculated for each individual layer in the soil samples using Powell's optimization technique and the implicit finite difference method to solve the coupled diffusion equations. Furthermore, experimentally measured concentrations and volumetric water content were compared with the predicted volumetric water content and concentrations under the same conditions to check the capability of the model to predict heavy metal movement and to validate the calculated diffusion parameters for different time durations. Finally, volumetric water content and solute concentration as a function of space and time, were predicted using the calculated diffusion parameters.

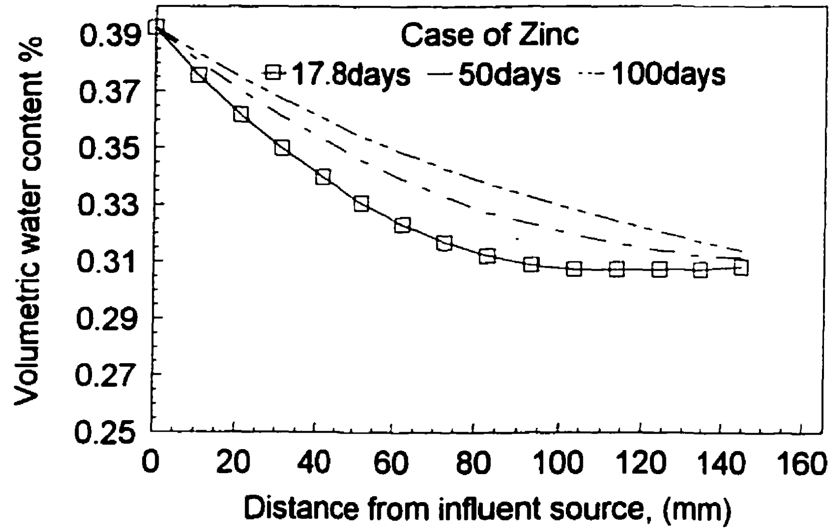


Figure 6.33 Predicted Volumetric Water Content for Soil D. (5000mg/l input Concentration of Zn)

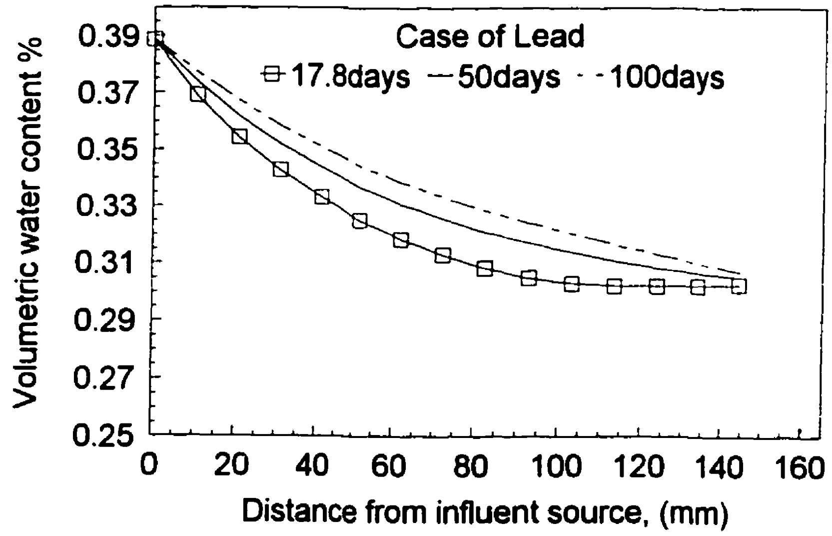


Figure 6.34 Predicted Volumetric Water Content for Soil D. (5000mg/l input Concentration of Pb)

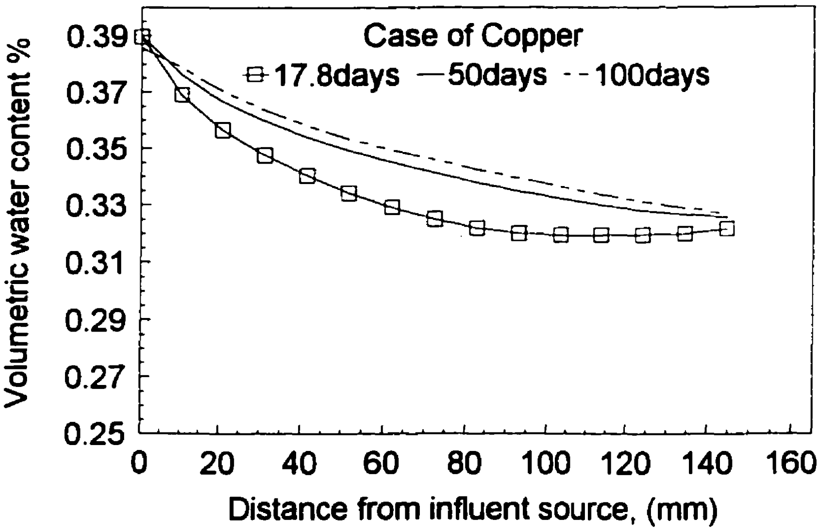


Figure 6.35 Predicted Volumetric Water Content for Soil D.
(5000mg/l input Concentration of Cu)

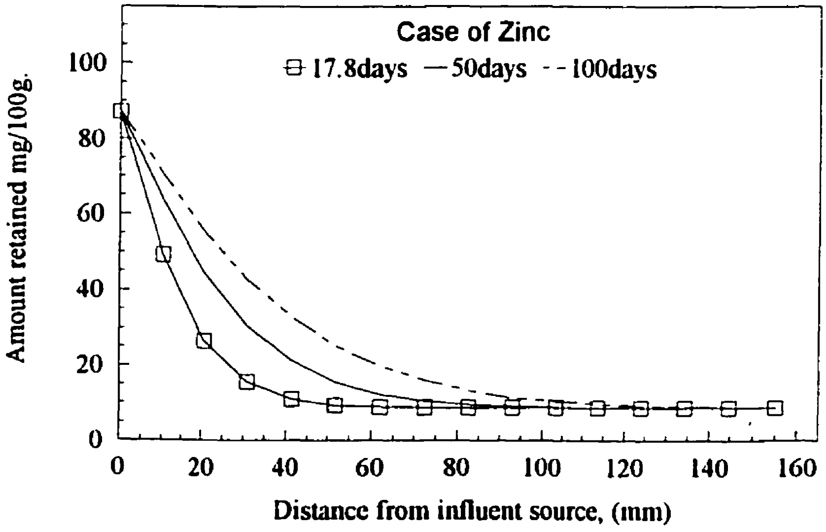


Figure 6.36 Prediced Zinc Concentration.

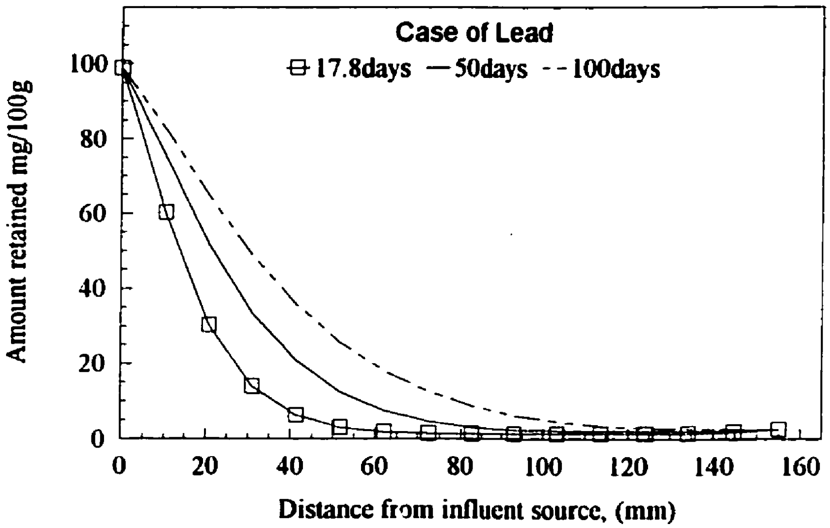


Figure 6.37 Predicted Lead Concentration.

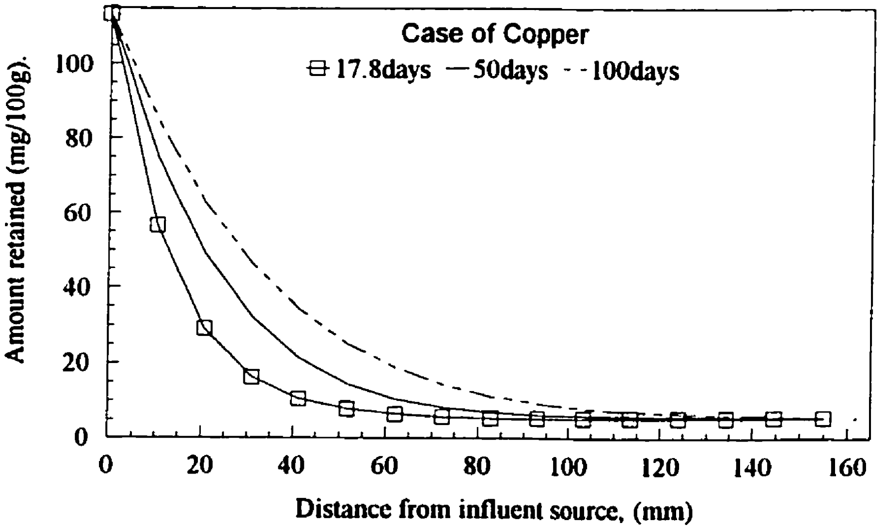


Figure 6.38 Predicted Copper Concentraion

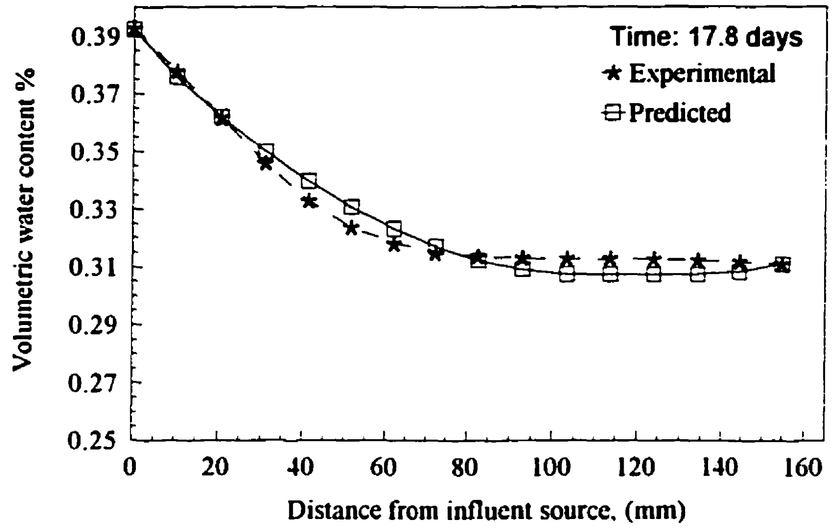


Figure 6.39 Comparison between Predicted and Measured Volumetric Water Content (Case of Zinc after 17.8days).

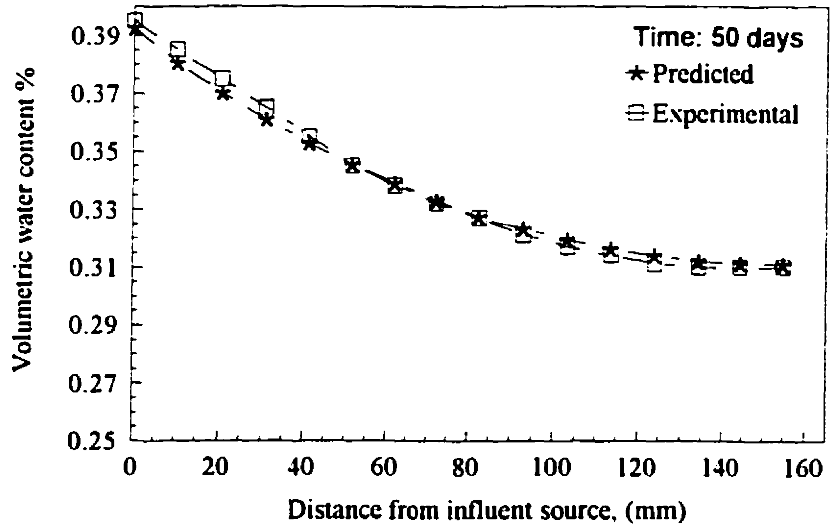


Figure 6.40 Comparison between Predicted and Measured Volumetric Water Content (Case of Zinc after 50 days).

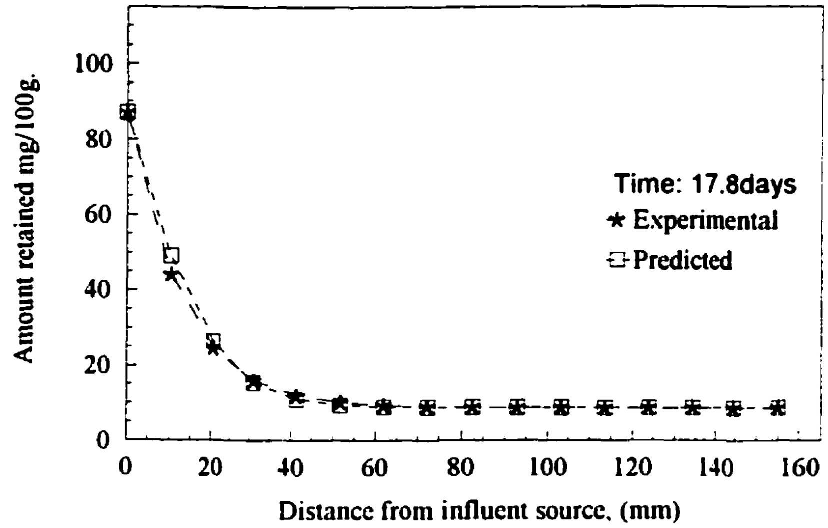


Figure 6.41 Comparison between Predicted and Measured H.M. Concentration Profiles (Case of Zinc after 17.8 days).

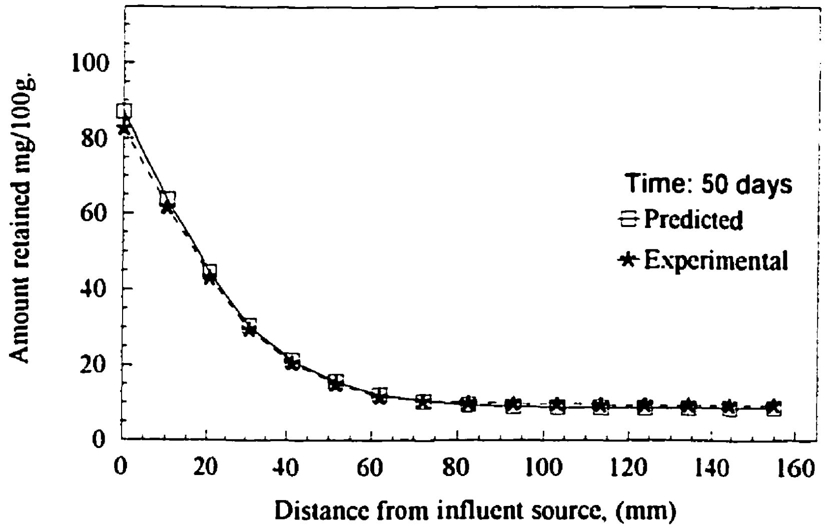


Figure 6.42 Comparison between Predicted and Measured H.M. Concentration Profiles (Case of Zinc after 50 days).

CHAPTER 7

SUMMARY AND CONCLUSIONS

7.1 Summary

This research study examines, experimentally, the transport of heavy metals in the vadose zone as a function of space and time, with particular attention to the effect of degree of saturation, the presence of carbonate, soil pH and heavy metal concentrations. One-dimensional coupled solute and moisture flow (leaching) tests, using different heavy metal permeants, were conducted on an unsaturated illitic soil at varying pH values. Variations of moisture content with distance were measured for different time durations, and concentrations of heavy metals in the liquid and solid phases were analyzed. The migration and retention profiles of contaminants along the soil column were determined for each individual layer in the soil.

Generally most test results show moisture and solute distribution along the soil column from the source point, due to the internal suction gradients, from a location of high energy to low energy. It was found that volumetric water content increases as a function of time and depth, and is highly dependent on the soil pH and the fluid input concentration.The volumetric water content and heavy metal retention and migration profiles along the soil column show higher values near the source point. However, as the degree of saturation decreases, the volumetric water content and heavy metal retention and migration decrease along the soil column. For longer time periods, the increase in volumetric water content and heavy metal concentration is seen to be highly dependent on the soil pH and the input concentrations, time of wetting, and degree of saturation.

Other factors which control the sorption characteristics of heavy metals, redistribution, and migration of existing cations are carbonate presence, degree of saturation, time of wetting, soil pH and influent heavy metal concentration. However, at initial time of wetting , the variations of volumetric water content and of the heavy metal retention distribution along the soil column for various types of soil follow a trend opposite to the existing cation redistribution for various soil and heavy metal input concentrations. They then decrease with a decreasing degree of saturation along the soil column. As the time of wetting increases, the increase in volumetric water content and heavy metal retention is seen to be highly dependent on the fluid input concentration and generally increases with time and concentration.

Retention and migration of heavy metals is highly dependent on the soil pH, the presence of carbonates, the volumetric water content or degree of saturation, the influent concentration and the time duration. The capacity for moisture and heavy metal movement is increased by low pH, low carbonate content, and large particle size (silt and sand portions increased in soil C and D). Also, the specific surface area and cation exchange capacity of the soil are also involved when an increase in heavy metal sorption has been observed. The presence of carbonates in the illitic soil increased the retention of heavy metals at high pH and also enhanced the buffering capacity of the soil. At high soil pH and carbonate content, heavy metals are retained in the soils if the buffering capacity is high enough to resist the acidic leachate input, and sorption processes will prevail in the carbonate phase. As the soil pH decreases, the dissolution of carbonates increases and cation exchange capacity becomes the more dominant process in heavy metal retention. In acidic soil, the cation exchange capacity of the soil decreases slightly with a lowering of the soil pH. This however does not affect the ability of the soil to retain the heavy metal under unsaturated conditions.

Results show that for lower soil pH (C&D) and different concentrations of single species, the selectivity for the retention of heavy metal species followed closely the order of Pb > Cu > Zn on a mass basis. This agrees well with previous findings of several authors. The selectivity order of migrated heavy metal cations seems to follow a similar order to those retained by the saturated zone. No significant migrations of heavy metals to the soluble phase were detected along the soil column. The migration and redistribution of exchangeable cations along the soil column increase with time, depth, influent concentration and soil pH and can be explained by the exchange reaction with heavy metals. One concludes that the mechanisms and processes governing the transport of inorganic chemicals through unsaturated soils are relevant to those of saturated soils. The key difference between them lies in the definition of the transport parameters (Lim et al., 1995).

Also, the partitioning coefficient K_d was computed for each section of the soil sample along the soil column and is plotted as a function of soil depth and time of wetting for various soil pH values and for two different contaminant concentrations of lead, copper and zinc. Results show that as the distance and time of wetting from the H.M. source increased, and within the unsaturated phase, the amount of H.M. released to the soluble phase decreases sharply indicating that H.M. migrates only a very short distance from the input source during the specified migration time, resulting in infinite K_d values. This might be related to the decrease in the degree of saturation along the soil column and may also be explained by the cation exchange capacity of the soil, which was still able to almost completely retain the introduced H.M. under unsaturated conditions. Most transport models use K_d obtained from 'linear' adsorption isotherms as a constant parameter. Simplification of (K_d) as a constant and linear function may lead to an improper evaluation of the adsorption/desorption phenomena. Results show that the sorption characteristics of heavy metals are controlled by many factors which should be taken into consideration such as the presence of carbonate, volumetric water content or degree of saturation, soil pH, and the influent heavy metal concentrations. Therefore, one may conclude that K_d is not a proper approach to use in the design of a clay barrier system. The assumption of a linear isotherm can lead to serious errors in predicting contaminant migration.

In addition, results show that the migration profiles and the redistribution of the exchangeable cations along the soil column were leached out or reduced from the first sections of the soil column and increased toward the bottom of the soil with increasing time, depth, and influent concentration due to the exchange reaction with heavy metals. The high movement of Ca^{2+} and Mg^{2+} can be also attributed to the cation exchange capacity or the replacement by Pb, Zn and Cu in the top part of the soil column. Whereas, the interaction mechanism is due to the cation exchange process between calcium, magnesium, sodium and potasium at the bottom part of the soil. The replacement of sodium and potasium ions in the exchangeable sites by calcium and magnesium balances the charge deficit that occurs by the elution of sodium and potasium. The selectivity order of soluble cation movements along the soil column within the unsaturated condition appears to be in the order of Ca>Mg>K>Na for soil B, C and D, for various heavy metal input concentrations. While for soil A, which is the original soil before treatment with acid for carbonate extraction, the selectivity order of soluble cations follows the order of K>Na>>Ca>Mg.

After leaching, measurements of soil pH for each soil section increased slightly with depth and time. This might be explained by the elution of cations from the solid particles. This is indicated by the pore fluid concentration profiles which result from the retention of lead, copper and zinc. On the other hand, the soil has a high attenuation capacity for Pb, Cu and Zn near the source, where it is considered to be fully saturated, as indicated from the concentration profiles of the pore fluid with depth after leaching.

The migration and retention profiles of heavy metals along the soil column obtained from experiments were used for the calibration of the proposed model. A computer code called the Coupled Moisture and Solute Diffusion Parameter Technique (CMSDPT) has been developed in conjunction with the application of the theory of irreversible thermodynamic, Fick's law, Darcy's law and equilibrium mass transfer principles. The diffusion parameter is calculated for each individual layer in the soil samples using Powell's optimization technique and the implicit finite difference method is used to solve the coupled diffusion equations.

Besides the partitioning coefficient, the diffusion of heavy metals in unsaturated soil is also highly dependent on the moisture content or the degree of saturation. However, most existing transport models use an average diffusion coefficient without considering the degree of saturation in order to predict the movement of heavy metals along the soil column. Simplification of the diffusion coefficient as a constant, and of the degree of saturation as a linear function, cannot be considered a good assumption and may lead to an improper evaluation of the sorption phenomenan in the vadose zone and also to serious errors in predicting contaminant migration. Therefore, an adequate characterization of moisture content dependence on the diffusion coefficient is essential for realistic modelling of diffusive mass transport through the unsaturated zone. In fact, results show that the diffusion coefficient cannot be constant, it is an exponentiai function of heavy metal concentration and volumetric water content and varies with type of soil, time, pH and depth of soil, volumetric water content or degree of saturation, carbonate content and heavy metal influent concentration.

Experimentally measured concentration and volumetric water content were compared with the predicted volumetric water content and concentration under the same conditions to check the capability of the model to predict heavy metal movement and to validate the calculated diffusion parameters for different time durations. Comparison between the measured and the calculated moisture and solute profiles shows a good agreement and increases the level of confidence in predicting coupled solute and moisture profiles in the vadose zone. Finally, volumetric water content and solute concentration as a function of space and time were predicted using the calculated diffusion parameters.

One may conclude that this research work provides the experimental information necessary for future numerical analyses which can be structured to account for vadose zone transport of heavy metals, with particular attention to the effect of degree of saturation, the presence of carbonate, soil pH and heavy metal concentrations. In addition, another significant reason for the need to study the vadose zone transport is the fact that the "initial conditions" established at the saturated zone interface will be affected considerably by vadose zone results, thereby impacting directly on the success of models designed to predict transport in the saturated zone. A new method that describes the full coupling effects on transport coefficients based on experimental evidence is applied to the unsaturated transport theory which provides successful predictions of the rate of transport of the heavy metals through the unsaturated soil in a pH-controlled environment.

7.2 Conclusions

1. The volumetric water content increases with time, decreases with depth, and is highly dependent on the soil pH and the fluid input concentration.
2. Heavy metals were accumulated in the first section of soil B (pH=6.9) because of its high carbonate content and high cation exchange capacity.
3. Retention and migration of H.M. is highly dependent on the soil pH, the presence of carbonates, the degree of saturation, the influent concentration and the time duration (soil C&D).
4. With the presence of exchangeable cations and the increase in aluminum and magnesium exchangeable cations, the CEC of the soil only decreases slightly for C&D and was still able to almost completely retain the introduced metals under unsaturated conditions.
5. The order of heavy metal migration in the unsaturated zone follows to Zn>Cu>Pb, while no significant concentration was detected along the soil column in the unsaturated zone.
6. The sorption characteristics of heavy metals are controlled by many factors which should be taken into consideration, SSA and CEC, the presence of carbonate, volumetric water content or degree of saturation, soil particle size distribution and pH, and the influent heavy metal concentrations.
7. K_d is not a proper approach to use in the design of a clay barrier system. The assumption of a linear isotherm can lead to serious errors in predicting contaminant migration.
8. The migration and redistribution of the exchangeable cations along the soil increase with time, depth and influent concentrations, and are explained by the exchange reaction with heavy metals.
9. The retention of heavy metals increases the movement of cations toward the

bottom of the soil and increases slightly the soil pH after leaching.

10. Only aluminum and magnesium cations released from the soil structure significantly increased with the lowering of soil pH.
11. The diffusivity coefficient is an exponential function of heavy metal concentration and volumetric water content.
12. A good agreement between experimentally measured and calibrated volumetric water content and heavy metal concentration shows the accuracy of the selected diffusion parameters and increases the level of confidence in predicting coupled solute and moisture profiles in the vadose zone.
13. Powell's optimization technique is appropriate to calculate the material parameters that govern the diffusion process.
14. The numerical technique is well developed to determine the diffusion parameters for different conditions and to predict the coupled moisture and solute movement.
15. A new method that describes the full coupling effects on transport coefficients based on experimental evidence was applied to the unsaturated transport theory providing successful predictions of the rate of transport of the heavy metals through the partially saturated zone in a pH-controlled environment.

7.3 Statement of Originality

The originality of the present study can be summarized as follows:

1. This research study provides the experimental information necessary for a numerical analysis structured to account for vadose zone transport of heavy

metals, with particular attention to the effect of volumetric water content or degree of saturation, the presence of carbonate, soil pH and heavy metal concentrations.

2. An experimental method was developed to represent the partitioning of heavy metals between the solid and the liquid phases and to evaluate solute and moisture flow problems in unsaturated soil.
3. A numerical technique was developed to evaluate the diffusivity parameters and to predict the migration of heavy metals along the clay liner in the partially saturated zone.

7.4 Suggestions for Further Studies

Further studies can be conducted on the following items:

- Continued investigation of the geochemistry contaminant reactions in unsaturated soil.
- Increasing our understanding of the diffusion dispersion process in groundwater transport which is important for the prediction of contaminant transport.
- Improving our understanding of retention mechanisms in unsaturated soil involving multi-component species and different soils.
- Examine how soil fractions can contribute to adsorption mechanisms and pollutant migration in unsatutated soil.
- Study the effect of initial degree of saturation, the effect of temperature and soil composition on contaminant migration.
- Further examination of the model should be performed on more

representative industrial pollutants and landfill leachate using actual field conditions to better simulate the natural system.

CHAPTER 8

REFERENCES

Airey, D.W., 1993. Migration of a pollutant through a natural clay liner. In Geotechnical Management of Waste and Contamination, Fells, Phillips, and Gerrard, pp. 323-328

Allard, B., Hakansson, K., Karlsson, S. and Sigas, E., 1991. A field study of diffusion controlled migration of copper, zinc and cadmium in a clay formation. Water, Air, and Soil Pollution 57-58:259-268.

American Society for Testing and Materials, 1995. Annual Book of ASTM Standards ASTM, Philadelphia.

Anderson, M.P., 1979. Using models to simulate the movement of contaminants through groundwater flow systems. CRC Critical Reviews in Environmental Control, 9:97-156.

Badv K. and Rowe, R.K., 1996. Contaminant transport through a soil liner underlain by an unsaturated stone collection layer. Canadian Geotechnical Journal 33:416-430

Baes, C.F. and Messmer, R.E., 1976. The Hydrolysis of Cations. John Wiley & Sons, New York.

Banks, R.B. and Ogata A., 1961. A solution of the differential equation of longitudinal dispersion in porous media. Fluid Movement in Earth Materials, Geological Survey Professional Paper 411-A, U.S.G.R.O., Washington, pp. 585211-61-2.

Barone, F.S., 1993. Description of diffusion and adsorption coefficient used for modelling contaminant migration through clayey soil. Geotechnical News 11-4:47-49.

Barry, D.A., 1993. Time dependence of solute dispersion in aquifers. Geotechnical Management of Waste and Contamination, Fells, Phillips, and Gerrard, pp. 329-332.

Best, R.J., Booker, J.R. and Mackie, C., 1993. Analysis of contaminant transport. Geotechnical Management of Waste and Contamination, Fells, Phillips, and

Gerrard, pp. 39-57.

Bohn, H. L., 1979. Soil Chemistry. John Wiley & Sons, New York.

Bowders, J.J., Jr. and Daniel, D.E. , 1987. Hydraulic conductivity of compacted clay to dilute organic chemicals. Journal of Geotechnical Engineering, ASCE 113-12:1432-1448.

Buckingham, E., 1907. Studies on the movement of soil moisture. U.S. Dep. Agr., Bur. Soils, Bull. 38:61.

Cabral, A.R., 1992. A Study of compatibility to heavy metal transport in permeability testing. Ph.D. Thesis, McGill University.

Cabral, R. A. and Yong, R. N., 1993. Mobility and retention of Pb and Zn in sand bentonite. CSCE, ASCE National Conference on Environmental Engineering, July 12-14, Montreal, Quebec, Canada, pp 1135-1143.

Carter, D.L., Mortland, M.M. and Kemper, W.D. 1986. Specific surface area measurement in methods of soil analysis. Klute, A. et al., 2nd ed., Part I, American Society of Agronomy, Madison, Wisconsin, pp. 413-423.

Cheremisinoff, N.P., Ellerbush, P. and Perna, A.J., 1979. Industrial and hazardous waste impoundment. Ann Arbor Science, Ann Arbor, MI.

Cherry, J.A., Gillham, R.W. and Barker J.F., 1984. Contaminants in groundwater: chemical process. Studies In Geophysics, Groundwater Contamination, pp. 46-64. Edited by National Academy Press. Washington, D.C.

Chhabra, R., Pleysier, J. and Cremers, A., 1975. The measurement of the cation exchange capacity and exchangeable Cations in soil: a new method. Proceedings of the International Clay Conference. pp. 439-448. Applied Publishing Ltd., Illinois, U.S.A.

Childs E. C. And Collins-George N., (1950). The permeability of porous materials. Proc. Royal Soc. 201 A:392-405.

Childs, E.C., 1969. An Introduction to the Physical Basis of Soil Water Phenomena. 493 pp. Wiley, New York, N.Y.

Chlopecka A., Bacon J.R., Wilson M.J. and J. Kay, 1996. Heavy metals in the environment. J. Environ. Qual. 25:69-79.

Cooke, A.B., 1993. Physical modelling of contaminant transport in the unsaturated zone. Geotechnical Management of Waste and Contamination, Fells, Phillips, and Gerrard, pp.343-348.

Crooks, V.E. and Quigley, R.M., 1984. Saline leachate migration through clay: a comparative laboratory and field investigation. Canadian Geotechnical Journal 21:349-362

Dale J. And Turner J., 1982. The effects of acid rain on forest nutrient status. J. Water Resources Research. 18-3.

Darban, A. K., 1997. Multi-component transport of heavy metals in clay barriers. Ph.D. thesis, McGill University, Montreal.

Darcy, Henry, 1856. Les fontaines publiques de la ville de dijon: Exposition et Applications des Principes à suivre et des Formules à Employer dans les Questions de Distribution d'Eau. Edited by Victor dalmont, Paris, 590-594.

Das, M. Braja, 1983. Soil Mechanics. Washington: McGraw Hill.

Davidson, J.M., Ou L.T. and Rao, P.S.C., 1976. Behavior of high pesticide concentrations in soil water systems. Proceedings of the Hazardous Waste Research Symposium, Residual Management by Land Disposal, EPA-600/9-76-015, pp. 206-212. U.S. Environment Protecton Agency, Washington D.C.

DeGroot, S.R. and Mazur, P., 1962. Non-Equilibrium Thermodynamics. North Holland Pub. Co., Amsterdam.

Desaulniers D.E. and Cherry, J.A., 1989. Origin and movement of groundwater and major ions in a thick deposit of champlain sea clay near montreal. Canadian Geotechnical Journal 26:80-89

Elliott, H.A., Liberati, M.R. and Huang, C.P., 1986. Competitive adsorption of heavy metals by soils. J. Environ. Qual. 15:214-219.

Eltantaway, I.N. and Arnold, P.W., 1973. Reappraisal of ethylene glycol mono-ethylether (EGME) method for surface area estimations of clays. Soil Science 24:23-238

Elzahabi M. and Yong R.N., 1997. Vadose zone transport of heavy metals. Proceedings of the first geoenvironmental engineering conference organized by the British Geotechnical Society and the Cardiff School of Engineering, University of Wales, Cardiff, September 1997, pp. 173-180.

Farrah, H. and Pickering, W.F., 1976a. The sorption of copper species by clays I. Kaolinite. Aust. J. Chem. 29:1167-1176.

Farrrah, H. and Pickering, W.F., 1976b. The sorption of copper species by clays. II. Illite and Montmorillonite. Aust. J. Chem., 29:1177-1184.

Farrah, H. and Pickering, W.F., 1977a. Influence of clay-solute interactions on aqueous heavy metal ion levels. Water, air, and Soil Pollution 8:189-197.

Farrah, H. and Pickering, W.F., 1977b. The sorption of lead and cadium species by clay minerals. Aust.J.Chem. 30:1417-1422.

Farrah, H. and Pickering, W.F., 1978. Extraction of heavy metal ions sorbed on clays. Water, Air, and Soil Poll. 9:491-498.

Farrah, H. and Pickering, W.F., 1979. pH effects in the adsorption of heavy metal ions by clays. Chem. Geol. 25:317-326

Fick, Adolf, 1855. Uber Diffusion, Annalen der Physik und chemie 94, ed. In Berlin by Poggendorff, J. C., (a.k.a. Poggendorffer Annalen), Leipzig.

Fitts, D.D., 1962 . Non-Equilibrium Thermodynamics, McGraw-Hill, New York.

Fityus, S.G., Smith, D.W. and Booker, J.R.,1999. Contaminant transport through an unsaturated soil liner beneath a landfill. Canadian Geotechnical Journal 36:330-354

Forbes, E. A., Posner, A. M. and Quirk, J. P., 1974. The specific adsorption of inorganic Hg(II) species and Co(III) complex ions on goethite. J. Colloid Interface Science. 49:403-409.

Freeze, R. A. and Cherry, J. A., 1979. GroundWater. Prentice-Hall, Inc. Englewood Cliffs, N.J.

Galvez-Cloutier, R., 1995. Study of heavy metal accumulation mechanisms in the lachine canal sediments. Doctorate Thesis, McGill University,Montreal.

Gillham, R.W. and Cherry, J.A., 1982. Contaminant migration in saturated unconsolidated geologic deposits. Recent Trends in Hydrogeology, Ed. T.N. Narasimhan, Geological Society of America Special Paper 189, pp.31-62.

Greenberg, J.A., Mitchell, J.K. and Witherspoon, P.A., 1973. Coupled salt and water flows in a groundwater basin. Journal of Geophysical Research 78-27:6341-6353.

Grim, R.E., 1968. Clay Mineralogy. 2nd edition, McGraw-Hill, N.Y., 596.

Hare, F.K. and Hutchinson, T.C., 1989. Human environmental disturbances. Environmental Science and Engineering Handbook, edited by Henry J.G. and Heinke G.W., pp.114-142.

Harter, R.D., 1983. Effect of soil pH on adsorption of lead, copper, zinc and nickel. Soil Sci. Soc. Am. J. 47:47-51

Hausenbuiller, R.L., 1985. Soil Science, Principles and Practice, Third Edition, Wm.C.Brown Publishers, Dubuque, IA.

Hendershot, W.H., Lalande, H. and Duquette, M., 1993. Ion exchange and exchangeable cations. Chapter 19. Soil Sampling and Methods Analysis. Canadian Society of Soil Science Press. pp. 167-176.

Hesse, P.R., 1971. A Textbook of Soil Chemical Analysis. William Clowes and Sons, London, 519 pp.

Hoppe, E., 1986. The influence of acid rain on the engineering properties of a sensitive clay. Msc. Thesis, Department of Civil Engineering and Applied Mechanics, McGill University, Montreal.

Iwata, S., Tabuchi, T. and Warkentin B., Soil water interactions mechanisms and application. Unsaturated Water Movement, pp.277-326.

Jackson, M.L., 1956. Soil chemical analysis- advance course. Published by the Author. University of Winsconsin, Madison.

Jardine, P.M., Jacobs, G. K. and Wilson, G.V., 1993. Unsaturated transport processes in undisturbed heterogeneous porous media: I- Inorganic contaminants. Soil Sci. Soc. Am. J. 57:945-953.

Jeffries Dean S., 1991. Southern Canada: An overview of the effect of acidic deposition on aquatic resources. In Acidic Deposition and Aquatic Ecosystems. Edited by Donald Charles, pp. 273-290.

Jonathan, G. and Hermann, B., 1987. Influental factors in soil liner construction for waste disposal facilities. Geotechnical Practice for Waste Disposal

'87/GT.

Karczewska, H., 1987. The effect of acid leaching on some physico-chemical properties of quebec soil. Master of Engineering Thesis, Department of Civil Engineering and Applied Mechanics, McGill University, Montreal.

Kersten, M. and Förstner, U. 1989. Speciation of trace elements in sediments. In Trace Element Speciation, Analytical Methods, and Problems (G.E. Batley, ed.) pp. 245-317.

Klute, A.1952. A numerical method for solving the flow equation for water in unsaturated materials. Soil Sci., pp. 73:105-116.

Lim, P.C., Barbour , S.L. and Fredlund D.G.,1995. Effect of degree of saturation on the adsorption characteristics of inorganic chemicalS in unsaturated soils. 2000 Geoenvironment, Vol. 1, Geotechnical Special Publication No. 46 , Edited by Yalcin, B., and Daniel, D., pp. 816-817.

MacDonald E., 1994. Aspects of competitive adsorption and precipitation of heavy metals by a clay soil. Msc. Thesis, Department of Civil Engineering and Applied Mechanics, McGill University, Montreal.

MacDonald E. and Yong R.N., 1997. On the retention of lead by illitic soil fractions. Proceedings of the First Geoenvironmental Engineering Conference organized by the British Geotechnical Society and the Cardiff School of Engineering, University of Wales, Cardiff, September 1997, pp. 116-127.

Mannings, S., Smith, S. and Bell, J.N.B. 1996. Effect of acid deposition on soil acidification and metal mobilisation. Applied Geochemistry 11:139-143.

Mazus, M.T., 1993. Contaminant migration in unsaturated soil subjected to subfreezing temperatures. Msc. Thesis, Department of Civil Engineering and Applied Mechanics, McGill University, Montreal.

Mitchell, J. K.,1993. Fundamentals of Soil Behavior.John Wiley and Sons, Inc. Toronto, 437pp.

Mitchell, J.K., Greenburg, J.A. and Witherspoon, P.A. 1973. Chemico-osmotic effects in fine-grained soils. Journal of the Soil Mechanics and Foundation Division, A.S.C.E. 99-SM 4:307-322.

Mitchell, J.K. and Madsen, F.T., 1987. Chemical effects on clay hydraulic conductivity. Proc. of Geotechnical Practice for Waste Disposal '87/GT Div. ASCE, pp. 87-116

Mohamed, A.M.O., Shooshpasha, I., Yong, R.N. and Onofrei, C., 1994. Moisture movement in clay based buffer material under isothermal conditions, Material Research Society, Symposium Proceeding 333:pp.925-932.

Mohamed, A.M.O. and Yong, R.N. 1993. Diffusion of contaminants through clay barriers under acidic conditions. Engineering Geology of Waste Disposal, Geological Society Engineering Geology Special Publication No.11, pp 279-289.

Mohamed, A.M.O., Yong, R.N. and Cheung, S.C.H. 1992. Temperature dependence of soil water potential. Geotechnical Testing Journal, GTODJ, 15-4:330-339.

Mohamed, A.M.O., Yong, R.N., Tan, B.K., Farkas, A. and Curtis, L.W., 1994a. Geo-environmental assessment of a micaceous Soil for Its potential use as an engineering clay barrier. Geotechnical Testing Journal, GTJODJ, 17-3: 291-304.

Mohsen, Mohamed F.N. 1993. Adsorbed concentration vs. Lab-reported concentration in soil. Technicale Notes in Ground Water. 32-3:499-500.

Oakley, R.E., 1987. Design and performance of earth lined contaminant systems. Proc. of Geotechnical Practice for Waste Disposal '87/GT Div. ASCE, pp. 117-136.

Ouhadi, V.R., 1997. The role of marl components and ettringite on the stability of stabilized marl. Ph.D. Thesis, McGill University, Montreal.

Olsen, H.W.,1969. Simultaneous fluxes of liquid and charge in saturated kaolinite. Soil Science Society of America, Proceedings 33:3:338-344

Olsen, H.W., 1972. Liquid movement through kaolinite under hydraulic, electric and osmotic gradients. The American Association of Petroleum Geologists Bulletin 56-10:2022-2028.

Onsager, L. 1931. Reciprocal relations in irreversible processes. Physical Review 37: 405-426 and 38:2265-2279.

Phadungchewit, Y. 1990. The role of pH and soil buffer capacity in heavy metal retention in clay soils. Doctorate Thesis, McGill University, Montreal.

Porter, L.K., Kemper, W.D., Jackson, R.D. and Stewart, B.A.,1960. Chloride diffusion in soils as influenced by moisture content. Proceeding Soil Science Society of America, 24, pp 460-463.

Powell, M.J.D., 1964. An efficient method for finding the minimum of a function of several variables calculating deriviatives. Computer Journal 7:155-162.

Pratt, P.F., 1961. Effect of pH on cations exchange capacity of surface soil. Proceedings of American Soil Science Society, No. 25.

Quigley, R.M., 1993. Clay minerals against contaminant migration. Geotechnical News 11-4:44-47

Quigley, R.M., Gwyn, Q.H.J., White, O.L., Rowe, R.K., Haynes, J.E. and Bohdanowicz, A.,1983. Leda clay from deep boreholes at hawkesbury, Ontario. Part I : geology and geotechnique. Canadian Geotechnical Journal, 20:288-298.

Richards, L.A., 1931. Capillary conduction of liquid through porous medium. Physics, pp. 1:318-333.

Robitaille, G, 1982. The effect of acid deposits on soil. Environment Canada-Quebec.

Rowe, R. K., 1987. Pollutant transport though barriers. Proc. of Geotechnical Practice for Waste Disposal '87/GT Div. ASCE, pp. 35-42, pp. 159-179

Rowe, R. K., 1988. Eleventh Canadian Geotechnical Colloquim:Contaminant Migration Through Groundwater- The role of modelling in the design of barriers. Canadian Geotechnical, J. 25:779-798.

Rowe, R. K., 1993. Contaminants migration in soils introduction. Geotechnical News 11-4:39-40.

Samani, H.M.V., 1987. Mathematical modelling of contaminant transport through clay soils using irreversible thermodynamics. Ph.D Thesis, Department of Civil Engineering and Applied Mechanics, McGill University, Montreal.

Segalen, P., 1968. Note sur une methode de determination des produits mineraux amorphes dans certains sols a hydroxides tropicaux. Cah, Orstom ser. Pedel 6:105-126.

Selvadurai, A.P.S. and Au, M.C. 1986. Coupled heat and moisture flow in buffer materials used in nuclear waste disposal Vault. A Report Submitted to Atomic Energy of Canada Limited, Pinawa, Manitoba.

Shackelford, C.D. 1988. Diffusion as a transport process in fine grained barrier Materials. Geotechnical News 6-2:24-27

Shackelford, C.D., 1994. Waste -soil interactions that alter hydraulic conductivity. Hydraulic conductivity and waste contaminant transport in soil. ASTM STP 1142, David E. Daniel and Stephen J. Trautwein, Eds., American Society for Testing and Materials, pp111-183.

Sheldrick, B.H, 1984. Analytical Methods Manual 1984. Land Resource Research Institute, Ottawa, Ontario. No:84-30. pp.2.

Swanson, L. E., Frost, J. C., Roder, L. F. Jr. and Huffman, C. Jr., (1966). Metal sorption by northwest florida humate. In: Geological Survey Research. U.S. Geological Survey. Professional Paper 550 - C174 - C177.

Taylor, S.A. and Cary, J.W., 1960. Analysis of simultaneous flow of water and heat or electricity with the thermodynamics of irreversible processes. Seventh International Congress of Soil Science Transactions 1:80-90.

Taylor, S.A. and Cary, J.W., 1962. The interactions of the simultaneous Diffusion of heat and water vapor. Soil Sci., Soc. Am. Proc. 26:413-416

USEPA, 1986. Method 3050, Acid digestion of sediments, sludges and soils. In Test Methods for Evaluating Solid Wastes, SW846, 3rd ed. U.S. Government Printing Offices, Washington, D.C.

USEPA, 1987. Batch type adsorption procedures for estimating soil attenuation of chemicals. Office of Solid Waste and Emergency Response, U.S.E.P.A., Washington, D.C., EPA/530-SW-87-006

Van Genuchten, M. Th. and Wierenga, P.J., 1976. Mass transfer studies in sorbing porous media, analysis solutions. Soil Science Society of America Journal 40:473-480.

Wang, B.W., 1990. A study of the role and contribution of amorphous materials in marine soils of eastern canada. Ph.D. Thesis, McGill University, Montreal.

Westall, J. C., Brownawell, B.J., Chen, H., Collier, J.M., and Hatfield, J. ,1990). Adsorption of organic cations to soils and surface materials. EPA/60/s2-90/004.

Yanful, E.K., Quigley, R.M. and Nesbitt, H.W., 1988a. Heavy metal migration at landfill site, Ontario, Canada-I. Thermodynamic assessment and chemical nterpretations. Applied Geochemistry 3:523-533.

Yanful, E.K., Quigley, R.M. and Nesbitt, H.W., 1988b. Heavy metal migration at landfill site, Ontario, Canada-II: Metal partitioning and geotechnical implications applied geochemistry. Applied Geochemistry 3:623-629

Yeung, A.T-C. and Mitchell, J.K., 1992. Coupled fluid, chemical, and electrical flows in soil. Geotechnique 42-4.

Yong, R.N., 1985. Interaction of clay and industrial waste: A summary review. Proceedings, Second Canadian/American Conference on Hydrogeology. Eds.B. Hitchon and M. Trudell. pp.13-15

Yong, R.N., and Di perno, N., 1991. Sources and characteristics of waste with specific reference to canada. McGill University. Geotechnical Research Centre. Geo-Engineering Series 91-1.

Yong, R.N., Galvez-Cloutier, R., and Phadungchewit, Y., 1993. Selective sequential extraction analysis of heavy metal retention in soil. Canadian Geotechnical Journal 30:834-847.

Yong, R.N., Mohamed, A.M.O. and Cheung, S.C.H., 1990a. Thermal behaviour of backfill material for a nuclear fuel waste disposal vault. Proceedings Materials Research Society Symposium 176:649-656.

Yong, R.N., Mohamed, A.M.O. and Samani, H.M.V., 1990b. Adsorption /desorpion in multi-component contaminant transport in clay barriers.CSCE Proceedings Annual Conference and 1st Biennial Environmemtal Speciality Conference, Hamilton, Ontario, Vol.1, Groundwater, pp. 689-706.

Yong R.N., Mohamed, A.M.O., and Shooshpasha, I., 1994. Thermal and moisture diffusivity in buffer material due to temperature and hydraulic gradients. Report Prepared for Atomic Energy of Canada Limited, Pianawa, Manitoba.

Yong R.N., Mohamed, A. M. O. and Warkentin, B. P., 1992a. Principles of contaminant transport in soils. Elsevier, Amsterdam, pp.211.

Yong, R.N., Mohamed, A.M.O. and Xu, D.M., 1990c. Coupled heat-mass transport effects on moisture redistribution prediction in clay barriers. Engineering Geology 28:315-324

Yong, R.N., Mohamed, A.M.O. and Xu, D.M., 1990d. Application of an identification technique to evaluate diffusion parameters in a coupled flow. Proceedings, IASTED International Symposium on Modelling, Simulation and Optimization. pp.103-106 .

Yong, R.N. and Phadungchewit, Y.,1993. PH influence on selectivity and retention of heavy metals in some clay soils. Canadian Geotechnical J. 30:821-830.

Yong., R.N. and Samani, H.M.V., 1987. Modelling of contaminant transport in clays via irreversible thermodynamics. Proceedings of Geotechnical Practice for Waste Disposal, '87/GT Div. ASCE, pp. 846-860

Yong, R.N. and Warith, M.A., 1990. Contaminant migration effect on dispersion coefficients. Physio-Chemical Aspects of Soil and Related Materials ASTMSTP 1095, pp. 69-80.

Yong, R.N., Warith, M.A. and Boonsinsuk, P., 1986. Migration of leachate solution through clay liner and substrate. Hazardous and Industrial Solid Waste Testing and Disposal: Six Volume, ASTM STP 933, D. Lorenzen, et.al., 208-225.

Yong, R. N. and Warkentin, B. P., 1975. Soil Properties and Behaviour. Elsevier, New York.

Yong , R.N., and Warkentin, B.P., Phadungchewit, Y., and Galvez, R., 1990e. Buffer capacity and lead retention in some clay materials. J. Water, Air, and Soil Pollution 53:53-67.

Yong, R.N. and Xu, D.M., 1988. An identification technique for evaluation of phenomenological coefficients in coupled flow in unsaturated soils. International Journal for Numerical and Analytical Methods in Geomechanics 16:233-246

Yong, R.N., Xu, D.M., Mohamed, A.M.O., 1992b. " An Analytical Technique for Evaluation of Coupled Heat and Mass Flow Coefficients in Unsaturated Soil", International journal for Numerical and Analytical Methods in Geomechanics. Vol.12 pp.283-299..

APPENDIX I

A Sample of Input and Output Data

1.CASE OF LEACHING WITH 5000 mg/l OF ZINC NITRATE IN SOIL D:

A. INPUT DATAFILE:

```
 20    15     8     5     5  155.000000    0.000000
 0.007000    17.800000    2.166667    0.0100000   0.50   0.50
0.100000000000000E-001  0.100000000000000E-001
 14.6339515806898        1.006008757662410E+002
0.100000000000000E-001  0.100000000000000E-001
0.738061068920222         3.26780675767410
0.100000000000000E-001  0.100000000000000E-001
 10.2762220989918        4.544792438742190E+001
0.100000000000000E-001  0.100000000000000E-001
0.509256083663560       0.100111702871250E-001
0.100000000000000E-001  0.100000000000000E-001
0.589113247997574E-001  0.129631027664813
0.100000000000000E-001  0.100000000000000E-001
0.538868589490000E-002  0.110472064862822E-002
0.100000000000000E-001  0.100000000000000E-001
0.111100099909999E-001  0.162265281927829E-001
0.100000000000000E-001  0.100000000000000E-001
0.128131441020897       1.57550011702871
0.100000000000000E-001  0.100000000000000E-001
0.589113247997574       0.129631027664813E-001
0.100000000000000E-001  0.100000000000000E-001
0.100538868589490       0.110472064862822E-002
```

B. OUTPUTS RESULTS:

```
DX            =  10.3333333333333
DT            = 0.700000000000000E-002
No. of nodes    =      16
No. of parameters=      20
No. of time steps=     2233
RW             =  0.986117134191611
RC            = 0.998643225038868

   XX(I)          WI(I)          WU(I)          WN(I)
0.000000E+00  0.385871E+00  0.392413E+00  0.392413E+00
0.103333E+02  0.362697E+00  0.377588E+00  0.375660E+00
0.206667E+02  0.345090E+00  0.361430E+00  0.361784E+00
0.310000E+02  0.331712E+00  0.345837E+00  0.349911E+00
0.413333E+02  0.321547E+00  0.332826E+00  0.339547E+00
0.516667E+02  0.313824E+00  0.323512E+00  0.330543E+00
0.620000E+02  0.307957E+00  0.317769E+00  0.322923E+00
0.723333E+02  0.303498E+00  0.314714E+00  0.316744E+00
0.826667E+02  0.300111E+00  0.313337E+00  0.312049E+00
0.930000E+02  0.297537E+00  0.312835E+00  0.308870E+00
0.103333E+03  0.295581E+00  0.312688E+00  0.307230E+00
0.113667E+03  0.294095E+00  0.312594E+00  0.307177E+00
0.124000E+03  0.292966E+00  0.312399E+00  0.307161E+00
0.134333E+03  0.292109E+00  0.312034E+00  0.307175E+00
0.144667E+03  0.291457E+00  0.311479E+00  0.308053E+00
0.155000E+03  0.290962E+00  0.310736E+00  0.310736E+00

   XX(I)          CI(I)          CU(I)          CN(I)
0.000000E+00  0.959956E+02  0.870505E+02  0.870505E+02
```

```
0.103333E+02   0.137806E+02   0.440128E+02   0.490895E+02
0.206667E+02   0.896745E+01   0.245910E+02   0.263546E+02
0.310000E+02   0.868567E+01   0.158263E+02   0.154105E+02
0.413333E+02   0.866918E+01   0.118711E+02   0.109032E+02
0.516667E+02   0.866821E+01   0.100861E+02   0.931273E+01
0.620000E+02   0.866816E+01   0.928065E+01   0.883105E+01
0.723333E+02   0.866815E+01   0.891715E+01   0.870464E+01
0.826667E+02   0.866815E+01   0.875312E+01   0.867551E+01
0.930000E+02   0.866815E+01   0.867909E+01   0.866951E+01
0.103333E+03   0.866815E+01   0.864568E+01   0.866832E+01
0.113667E+03   0.866815E+01   0.863061E+01   0.866774E+01
0.124000E+03   0.866815E+01   0.862380E+01   0.866631E+01
0.134333E+03   0.866815E+01   0.862073E+01   0.866175E+01
0.144667E+03   0.866815E+01   0.861935E+01   0.864901E+01
0.155000E+03   0.866815E+01   0.861872E+01   0.861872E+01

    XX(I)           DS              DV              DW              DZ
0.000000E+00   0.139113E+02   0.494955E+00   0.698460E+02   0.111116E-01
0.103333E+02   0.169810E+02   0.497139E+00   0.907158E+02   0.111117E-01
0.206667E+02   0.195445E+02   0.521662E+00   0.110961E+03   0.111119E-01
0.310000E+02   0.210485E+02   0.599499E+00   0.123715E+03   0.111120E-01
0.413333E+02   0.217481E+02   0.680096E+00   0.129666E+03   0.111122E-01
0.516667E+02   0.220295E+02   0.721804E+00   0.131875E+03   0.111136E-01
0.620000E+02   0.221401E+02   0.736429E+00   0.132558E+03   0.111153E-01
0.723333E+02   0.221902E+02   0.740623E+00   0.132741E+03   0.111160E-01
0.826667E+02   0.222182E+02   0.741760E+00   0.132785E+03   0.111162E-01
0.930000E+02   0.222351E+02   0.742105E+00   0.132795E+03   0.111163E-01
0.103333E+03   0.222436E+02   0.742223E+00   0.132798E+03   0.111163E-01
0.113667E+03   0.222440E+02   0.742244E+00   0.132799E+03   0.111163E-01
```

```
0.124000E+03   0.222443E+02   0.742289E+00   0.132801E+03   0.111163E-01
0.134333E+03   0.222449E+02   0.742431E+00   0.132807E+03   0.111164E-01
0.144667E+03   0.222424E+02   0.742785E+00   0.132825E+03   0.111164E-01
0.155000E+03   0.222334E+02   0.743599E+00   0.132866E+03   0.111166E-01
```

2.CASE OF LEACHING WITH 5000 mg/l OF LEAD NITRATE IN SOIL D:

A. INPUT DATAFILE:

```
 20    15    10     5     5   155.000000    0.000000
 0.007000   17.800000    2.166667    0.0100000    0.50    0.50
0.100000000000000E-001  0.100000000000000E-001
 14.6581380336767        1.006008757662410E+002
0.100000000000000E-001  0.100000000000000E-001
0.738061068920222        3.26780675767410
0.100000000000000E-001  0.100000000000000E-001
 10.2762220989918        4.544792438742190E+001
0.100000000000000E-001  0.100000000000000E-001
0.509256083663560        0.151117028712500E-003
0.100000000000000E-001  0.100000000000000E-001
0.589113247997574E-001  0.129631027664813
0.100000000000000E-001  0.100000000000000E-001
0.538868589490000E-002  0.110472064862822E-002
0.100000000000000E-001  0.100000000000000E-001
0.111100099909999E-001  0.162265281927829E-001
0.100000000000000E-001  0.100000000000000E-001
0.128131441020897        1.57550011702871
0.100000000000000E-001  0.100000000000000E-001
```

```
  0.589113247997574         0.129631027664813E-001
  0.100000000000000E-001   0.100000000000000E-001
  0.100538868589490         0.110472064862822E-002

B. OUTPUTS RESULTS :
DX            =   10.3333333333333
DT            =  0.700000000000000E-002
No. of nodes     =        16
No. of parameters=         20
No. of time steps=       2233
RW             =  0.982233665937321
RC            =  0.999037853182122

    XX(I)           WI(I)           WU(I)           WN(I)
0.000000E+00 0.417653E+00 0.388600E+00 0.388600E+00
0.103333E+02 0.380829E+00 0.361350E+00 0.369030E+00
0.206667E+02 0.354886E+00 0.345247E+00 0.354222E+00
0.310000E+02 0.335398E+00 0.334689E+00 0.342750E+00
0.413333E+02 0.320650E+00 0.327003E+00 0.333220E+00
0.516667E+02 0.309581E+00 0.321151E+00 0.325003E+00
0.620000E+02 0.301432E+00 0.316602E+00 0.318270E+00
0.723333E+02 0.295612E+00 0.313041E+00 0.312807E+00
0.826667E+02 0.291639E+00 0.310262E+00 0.308218E+00
0.930000E+02 0.289104E+00 0.308122E+00 0.304770E+00
0.103333E+03 0.287653E+00 0.306517E+00 0.302784E+00
0.113667E+03 0.286972E+00 0.305368E+00 0.302113E+00
0.124000E+03 0.286779E+00 0.304614E+00 0.302108E+00
0.134333E+03 0.286819E+00 0.304208E+00 0.302106E+00
0.144667E+03 0.286855E+00 0.304109E+00 0.302494E+00
```

```
0.155000E+03 0.286671E+00 0.304285E+00 0.304285E+00

     XX           CI(I)        CU(I)        CN(I)
0.000000E+00 0.145037E+03 0.987193E+02 0.987193E+02
0.103333E+02 0.298576E+02 0.563891E+02 0.602154E+02
0.206667E+02 0.697510E+01 0.278859E+02 0.301548E+02
0.310000E+02 0.242905E+01 0.140156E+02 0.138501E+02
0.413333E+02 0.152589E+01 0.751828E+01 0.620180E+01
0.516667E+02 0.134646E+01 0.439901E+01 0.301942E+01
0.620000E+02 0.131082E+01 0.287627E+01 0.184505E+01
0.723333E+02 0.130373E+01 0.214770E+01 0.146025E+01
0.826667E+02 0.130233E+01 0.183249E+01 0.135323E+01
0.930000E+02 0.130205E+01 0.173963E+01 0.135251E+01
0.103333E+03 0.130199E+01 0.176851E+01 0.135276E+01
0.113667E+03 0.130198E+01 0.186400E+01 0.135356E+01
0.124000E+03 0.130198E+01 0.199493E+01 0.135812E+01
0.134333E+03 0.130198E+01 0.214326E+01 0.145987E+01
0.144667E+03 0.130198E+01 0.229844E+01 0.175668E+01
0.155000E+03 0.130198E+01 0.245424E+01 0.245424E+01

    XX(I)         DS           DV           DW           DZ
0.000000E+00 0.131275E+02 0.495134E+00 0.656228E+02 0.125577E-02
0.103333E+02 0.158355E+02 0.496426E+00 0.832286E+02 0.125578E-02
0.206667E+02 0.188850E+02 0.512319E+00 0.107045E+03 0.125578E-02
0.310000E+02 0.210238E+02 0.622529E+00 0.125731E+03 0.125578E-02
0.413333E+02 0.221857E+02 0.831279E+00 0.136354E+03 0.144233E-02
0.516667E+02 0.227191E+02 0.999543E+00 0.141180E+03 0.293281E-01
0.620000E+02 0.229389E+02 0.108128E+01 0.143027E+03 0.179829E+00
0.723333E+02 0.230279E+02 0.111099E+01 0.143642E+03 0.328677E+00
```

```
0.826667E+02 0.230682E+02 0.111967E+01 0.143815E+03 0.388814E+00
0.930000E+02 0.230858E+02 0.111990E+01 0.143819E+03 0.389254E+00
0.103333E+03 0.230958E+02 0.111998E+01 0.143819E+03 0.389097E+00
0.113667E+03 0.230991E+02 0.111995E+01 0.143819E+03 0.388611E+00
0.124000E+03 0.230984E+02 0.111959E+01 0.143811E+03 0.385836E+00
0.134333E+03 0.230820E+02 0.111156E+01 0.143649E+03 0.328876E+00
0.144667E+03 0.230326E+02 0.108869E+01 0.143177E+03 0.206505E+00
0.155000E+03 0.229126E+02 0.103822E+01 0.142075E+03 0.696453E-01
```

3.CASE OF LEACHING WITH 5000 mg/l OF COPPER NITRATE IN SOIL D:

A. INPUT DATAFILE:

```
  20    15    15    5    5  155.000000    0.000000
  0.007000   17.800000    2.166667    0.0100000   0.50   0.50
 0.100000000000000E-001  0.100000000000000E-001
  14.6581380336767         3.5082087577250000E+001
 0.100000000000000E-001  0.100000000000000E-001
 0.738061068920222        5.26780675767410
 0.100000000000000E-001  0.100000000000000E-001
  10.2762220989918        6.044792438742200E+001
 0.100000000000000E-001  0.100000000000000E-001
 0.509256083663560        0.151117028712500D-004
 0.100000000000000E-001  0.100000000000000E-001
 0.589113247997574E-001  0.129631027664813
 0.100000000000000E-001  0.100000000000000E-001
 0.538868589490000E-002  0.110472064862822E-002
 0.100000000000000E-001  0.100000000000000E-001
 0.111100099909999E-001  0.162265281927829E-001
```

```
  0.100000000000000E-001  0.100000000000000E-001
  0.128131441020897        1.57550011702871
  0.100000000000000E-001  0.100000000000000E-001
  0.589113247997574        0.129631027664813E-001
  0.100000000000000E-001  0.100000000000000E-001
  0.100538868589490        0.110472064862822E-002
```

```
B. OUTPUTS RESULTS :
DX            =  10.3333333333333
DT            = 0.700000000000000E-002
No. of nodes    =      16
No. of parameters=       20
No. of time steps=     2233
RW             =  0.960845949218878
RC            =  0.999748810137060

     XX           WU(I)          WN(I)          WI(I)
0.000000E+00 0.383100E+00 0.389569E+00 0.389569E+00
0.103333E+02 0.348571E+00 0.364727E+00 0.369028E+00
0.206667E+02 0.330644E+00 0.349438E+00 0.356624E+00
0.310000E+02 0.318818E+00 0.340029E+00 0.347633E+00
0.413333E+02 0.310150E+00 0.334237E+00 0.340338E+00
0.516667E+02 0.303500E+00 0.330673E+00 0.334185E+00
0.620000E+02 0.298283E+00 0.328479E+00 0.329033E+00
0.723333E+02 0.294153E+00 0.327129E+00 0.324893E+00
0.826667E+02 0.290883E+00 0.326298E+00 0.321838E+00
0.930000E+02 0.288316E+00 0.325786E+00 0.319966E+00
0.103333E+03 0.286337E+00 0.325472E+00 0.319424E+00
0.113667E+03 0.284860E+00 0.325278E+00 0.319343E+00
```

```
0.124000E+03 0.283818E+00 0.325159E+00 0.319450E+00
0.134333E+03 0.283158E+00 0.325085E+00 0.319791E+00
0.144667E+03 0.282836E+00 0.325040E+00 0.321656E+00
0.155000E+03 0.282817E+00 0.325012E+00 0.325012E+00

     XX          CI(I)        CU(I)        CN(I)
0.000000E+00 0.920000E+02 0.113389E+03 0.113389E+03
0.103333E+02 0.171469E+02 0.577751E+02 0.565359E+02
0.206667E+02 0.125687E+02 0.307746E+02 0.289717E+02
0.310000E+02 0.973969E+01 0.176659E+02 0.161895E+02
0.413333E+02 0.781513E+01 0.113017E+02 0.103676E+02
0.516667E+02 0.646858E+01 0.821190E+01 0.763176E+01
0.620000E+02 0.553259E+01 0.671180E+01 0.624104E+01
0.723333E+02 0.490772E+01 0.598351E+01 0.550832E+01
0.826667E+02 0.452916E+01 0.562993E+01 0.518214E+01
0.930000E+02 0.435189E+01 0.545826E+01 0.515707E+01
0.103333E+03 0.434314E+01 0.537492E+01 0.515705E+01
0.113667E+03 0.447816E+01 0.533445E+01 0.515706E+01
0.124000E+03 0.473775E+01 0.531481E+01 0.515768E+01
0.134333E+03 0.510661E+01 0.530527E+01 0.523334E+01
0.144667E+03 0.557234E+01 0.530064E+01 0.528248E+01
0.155000E+03 0.612474E+01 0.529839E+01 0.529839E+01

     XX           DS           DV           DW           DZ
0.000000E+00 0.123867E+02 0.495085E+00 0.116012E+03 0.111983E-02
0.103333E+02 0.161488E+02 0.496624E+00 0.200508E+03 0.111983E-02
0.206667E+02 0.190119E+02 0.514735E+00 0.279607E+03 0.111983E-02
0.310000E+02 0.206773E+02 0.589879E+00 0.330162E+03 0.111983E-02
0.413333E+02 0.215315E+02 0.693023E+00 0.356904E+03 0.112025E-02
```

```
0.516667E+02 0.219652E+02 0.775412E+00 0.370372E+03 0.115143E-02
0.620000E+02 0.222006E+02 0.829815E+00 0.377453E+03 0.140252E-02
0.723333E+02 0.223330E+02 0.862673E+00 0.381249E+03 0.201656E-02
0.826667E+02 0.223984E+02 0.878377E+00 0.382954E+03 0.261900E-02
0.930000E+02 0.224116E+02 0.879693E+00 0.383087E+03 0.267940E-02
0.103333E+03 0.224143E+02 0.879721E+00 0.383088E+03 0.267944E-02
0.113667E+03 0.224147E+02 0.879724E+00 0.383088E+03 0.267942E-02
0.124000E+03 0.224141E+02 0.879688E+00 0.383084E+03 0.267788E-02
0.134333E+03 0.224008E+02 0.875994E+00 0.382688E+03 0.250280E-02
0.144667E+03 0.223839E+02 0.873532E+00 0.382430E+03 0.239977E-02
0.155000E+03 0.223646E+02 0.872602E+00 0.382344E+03 0.236808E-02
```

Appendix II

Coupled Moisture and Solute Diffusion Parameter Technique

```
**********************************************************************************
*A Program to Solve Coupled Diffusion Equations of Volumetric Water Content *
*  and Solute Concentration using Powell's Optimization Technique and the    *
*                     Implicit Finite Difference Method                       *
**********************************************************************************
```

List of variables

Input Data

N = Number of Unknown Coefficients
N+1 = Number of Nodes
Xu = Maximum X Co-Ordinate
ML = Any Arbitrary Number to Stop the Program
NS = Any Number to Change the Optimizing Direction
Max = Maximum Global Iteration
X(N) = Initial Value of Unknown Parameters
E(N) = Accuracy Requirement of Unknown Parameters
P = Accuracy Parameter
V = Crank Nicolson factor
DT = Time Step Increment
TI = Initial Time
TU = Final Time
WI(I) = Volumetric water Content Variations with Distance at Time TI
WU(I) = Volumetric water Content Variations with Distance at Time TU
CI(I) = Initial total Concentration with Distance at Time TI
CU(I) = Final Total Concentration with Distance at Time TU

Output Data

XX(I) = X Xoordinate (depth interval)
Y(I) = Final value of Unknown parameters
NT = Number of Time Steps
DX = Space Step Increment
DT = Time Step Interval
N = Number of Unknowns
N1+1 = Number of Nodes
RW = Correlation Coefficient of water content
RC = Correlation Coefficient of Concentration
WO(I) = Predicted Volumetric water Content at Time Step J
WN(I) = Predicted Volumetric water Content at Time Step J+1
CO(I) = Predicted Concentration at Time Step J
CN(I) = Predicted Concentration at Time Step J+1
DS = Solute Diffusivity Parameter
DV = Solute Moisture Diffusivity Parameter

DW = Moisture Diffusivity Parameter
DZ = Moisture Solute Diffusivity Parameter

```
C$DEBUG
    IMPLICIT REAL*8(A-H,O-Z)
    DIMENSION  CO(555),CN(555),WU(555),CU(555),WO(555),WN(555),AG(555)
   *,X(50),E(50),W(555),Y(50),CI(555),WI(555),XX(555)
    OPEN(10,FILE='ID1')
    OPEN(11,FILE='ROP')
    OPEN(12,FILE='ROP.DAT')
    OPEN(13,FILE='RO.DAT')

C   *******************  READ INPUT DATA  ******************
    READ(10,*) N,N1,ML,MAX,NS,XU,XI
    READ(10,*) DT,TU,TI,P,SCAL,V
    DO 5 J=1,N/2
    L=(J-1)*2
    READ(10,*) E(L+1),E(L+2)
    READ(10,*) X(L+1),X(L+2)
  5 CONTINUE
    DO 4 J=1,N
    Y(J)=X(J)
  4 CONTINUE

C   *************  CALCULATE TIME AND SPACE INCREAMENT  ************
    DX=(XU-XI)/N1
    NT=(TU-TI)/DT
C   ****** READ INITIAL AND FINAL NODAL VALUE FROM EQUATIONS  ******
    DO 13 I=1,N1+1
    XX(I)=XI+DX*(I-1)

c copper 52hrs and 17.8 days
    WI(I)=0.403581328+0.000802637*(XX(I))-0.01969281*(XX(I))**0.5
   *-0.02048126*EXP(-XX(I))
    CI(I)=32.34149835+0.283868998*(XX(I))-5.63992135*(XX(I))**0.5
   *+59.65851645*EXP(-XX(I))
    WU(I)=0.324967829+0.064601219*EXP((-XX(I))/21.28913618)

C LEAD
    WI(I)=0.417652638-0.00490646*(XX(I))+0.00042428*(XX(I))**1.5
   *-6.3264e-07*(XX(I))**2.5
    CI(I)=1.301977886+143.7346457*EXP((-XX(I))/6.393934567)
    WU(I)=0.411165472+0.000748414*(XX(I))-0.01790256*(XX(I))**0.5
   *-0.02256545*EXP(-XX(I))
    CU(I)=(98.7192972-2.01424152*(XX(I))+0.014450083*(XX(I))**2)/
   *(1+0.01776152*(XX(I))+0.002110884*(XX(I))**2)

C ZINC
    WU(I)=(0.392412593-0.00592318*(XX(I))+8.95157e-05*(XX(I))**2)/
   *(1-0.01170626*(XX(I))+0.000217252*(XX(I))**2+2.21355e-07*
   *(XX(I))**3)
    WI(I)=0.289395401+0.096475303*EXP((-XX(I))/37.61637976)
```

```
      CU(I)=8.618209996+78.43227136*EXP((-XX(I))/12.9868636)
      CI(I)=8.668151957+87.32740871*EXP((-XX(I))/3.641068278)
      CAV=CAV+CU(I)/(N1+1)
      WA=WA+WU(I)/(N1+1)
   13 CONTINUE
      WRITE(*,*)  '                No. of time step =',NT
      WRITE(*,*)  '                No. of node step =',N1+1
      IPRINT=1
      CALL OPM(N,N1,DT,NT,MAX,SCAL,X,E,CO,CU,CN,WN,WO,AG,TI,CI,WI,
     *CA,WA,ML,Y,XI,XU,TU,IT,DX,V,P,W,WU,NS,RW,RC)
      IF(IT.EQ.1) ML=ML+10
      IF(IT.GT.1) ML=IT+5
      CLOSE (10)
      OPEN(10,FILE='ID1')
      WRITE(10,24) N,N1,ML,MAX,NS,XU,XI
      WRITE(10,27) DT,TU,TI,P,SCAL,V
   24 FORMAT(5(I6,1X),2(F12.6,1X))
   27 FORMAT(3(F12.6,1X),F14.7,1X,2(F7.2,1X))
      DO 1 J=1,N/2
      L=(J-1)*2
      WRITE(10,*) E(L+1),E(L+2)
      WRITE(10,*) Y(L+1),Y(L+2)
    1  CONTINUE

C     ***************    PRINT OUT PUT  ******************
      WRITE(11,*)  "OUTPUTS RESULTS  "
      WRITE(11,*)  'DX             =',DX
      WRITE(11,*)  'DT             =',DT
      WRITE(11,*)  'No. of nodes     =',N1+1
      WRITE(11,*)  'No. of parameters=',N
      WRITE(11,*)  'No. of time steps=',NT
      WRITE(11,*)  'RW              =',RW
      WRITE(11,*)  'RC              =',RC
      WRITE(11,*)"XX(I),WI(I),WU(I),WN(I)"
      WRITE(12,*)"XX,CI(I),CU(I),CN(I)"
      WRITE(13,*)"XX(I),DS,DV,DW,DZ"
      DO 35 I=1,N1+1
      DS= X(9)+X(1)*EXP(-(X(13))*CN(I))+X(5)*EXP(-(X(17))*WN(I))
      DV=X(11)+X(3)*EXP(-(X(15))*CN(I))+X(7)*EXP(-(X(19))*WN(I))
      DW= X(10)+X(2)*EXP(-(X(14))*CN(I))+X(6)*EXP(-(X(18))*WN(I))
      DZ=X(12)+X(4)*EXP(-(X(16))*CN(I))+X(8)*EXP(-(X(20))*WN(I))
      WRITE(12,46) XX(I),CI(I),CU(I),CN(I)
      WRITE(11,42) XX(I),WI(I),WU(I),WN(I)
      WRITE(13,43) XX(I),DS,DV,DW,DZ
   43 FORMAT(5(E12.6,2X))
   42 FORMAT(4(E12.6,2X))
   46 FORMAT(4(E12.6,2X))
   47 FORMAT(7(E12.6,2X))
   35 CONTINUE
      CLOSE(11)
      CLOSE(10)
      CLOSE(12)
      CLOSE(13)
```

```
      STOP
      END
C     ******************************************************************************************
C     *                                                                                        *
C     *     A SUBROUTINE TO OPTIMIZE THE UNKNOWN PARAMETERS                                    *
C     *                                                                                        *
C     *                 USING POWELL'S OPTIMIZATION METHOD                                     *
C     *                                                                                        *
C     ******************************************************************************************
      SUBROUTINE OPM(N,N1,DT,NT,MAX,SCAL,X,E,CO,CU,CN,WN,WO,AG,TI,CI,WI,
     *CA,WA,ML,Y,XI,XU,TU,IT,DX,V,P,W,WU,NS,RW,RC)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION  CO(555),CN(555),WU(555),CU(555),WO(555),WN(555),AG(555)
     *,X(50),E(50),W(555),Y(50),CI(555),WI(555)
      IPRINT=1
      NOLUCK=1
      DDMAG=0.1*SCAL
      SCER=0.05/SCAL
      JJ=N*N+N
      JJJ=JJ+N
      K=N+1
      NFCC=1
      IND=1
      INN=1
      DO 1 I=1,N
      DO 2 J=1,N
      W(K)=0.0
      IF((I-J).NE.0.0) GO TO 92
      W(K)=ABS(E(I))
      W(I)=SCAL
   92 K=K+1
    2 CONTINUE
    1 CONTINUE
      ITERC=1
      ISGRAD=2
      CALL IMP(N1,DT,NT,N,F,X,CO,CU,CN,ITERD,TI,V,P,CA,WA,CI,WI,
     *Y,XI,XU,TU,ML,MAX,SCAL,E,IT,DX,WO,WU,AG,WN,mp,mn,NS,FN,RW,RC)
      IF(ITERD.EQ.ML) GO TO 320
      FKEEP=ABS(F)+ABS(F)
  101 ITONE=1
      FP=F
      SUM=0.0
      IXP=JJ
      DO 3 I=1,N
      IXP=IXP+1
      W(IXP)=X(I)
    3 CONTINUE
      IDIRN=N+1
      ILINE=1
      KLINE=1
  112 DMAX=W(ILINE)
      DACC=DMAX*SCER
```

```
   IF(DDMAG.LT.(0.1*DMAX)) DMAG=DDMAG
   IF(DDMAG.GE.(0.1*DMAX)) DMAG=0.1*DMAX
   IF(DMAG.LT.(20*DACC)) DMAG=20*DACC
   DDMAX=10*DMAG
   IF(ITONE.EQ.3) GO TO 184
   DL=0.0
   D=DMAG
   FPREV=F
   IS=5
   FA=F
   DA=DL
124 DD=D-DL
   DL=D
126 K=IDIRN
   DO 4 I=1,N
   X(I)=X(I)+DD*W(K)
   K=K+1
  4 CONTINUE
   CALL IMP(N1,DT,NT,N,F,X,CO,CU,CN,ITERD,TI,V,P,CA,WA,CI,WI,
  *Y,XI,XU,TU,ML,MAX,SCAL,E,IT,DX,WO,WU,AG,WN,mp,mn,NS,FN,RW,RC)
   IF(ITERD.EQ.ML) RETURN
   NFCC=NFCC+1
   IF(IS.EQ.1) GO TO 191
   IF(IS.EQ.2) GO TO 180
   IF(IS.EQ.3) GO TO 176
   IF(IS.EQ.4) GO TO 170
   IF(IS.EQ.5) GO TO 141
   IF(IS.EQ.6) GO TO 258
141 IF(F-FA) 147,142,150
142 IF((ABS(D)-DMAX).GT.0.0) GO TO 145
   D=D+D
   GO TO 124
145 NOLUCK=2
   GO TO 320
147 FB=F
   DB=D
   GO TO 154
150 FB=FA
   DB=DA
   FA=F
   DA=D
154 IF(ISGRAD.EQ.1) GO TO 158
155 D=DB+DB-DA
   IS=1
   GO TO 124
158 D=0.5*(DA+DB-(FA-FB)/(DA-DB))
   IS=4
   IF(((DA-D)*(D-DB)).GE.0.0) GO TO 124
161 IS=1
   IF((ABS(D-DB)-DDMAX).LE.0.0) GO TO 124
163 D=DB+(ABS(DDMAX))*SIGN(DB,DA)
   IS=1
   DDMAX=DDMAX+DDMAX
```

```
   DDMAG=DDMAG+DDMAG
   IF((DDMAX-DMAX).LE.0.0) GO TO 124
   DDMAX=DMAX
   GO TO 124
170 IF((F-FA).GE.0.0) GO TO 155
171 FC=FB
   DC=DB
173 FB=F
   DB=D
   GO TO 193
176 IF((F-FB).LE.0.0) GO TO 171
   FA=F
   DA=D
   GO TO 193
180 IF((F-FB).GE.0.0) GO TO 191
   FA=FB
   DA=DB
   GO TO 173
184 DL=1.0
   DDMAX=5.0
   FA=FP
   DA=-1.0
   FB=FHOLD
   DB=0.0
   D=1.0
191 FC=F
   DC=D
193 A=(DB-DC)*(FA-FC)
   B=(DC-DA)*(FB-FC)
   IF(((A+B)*(DA-DC)).GT.0.0) GO TO 201
   FA=FB
   DA=DB
   FB=FC
   DB=DC
   GO TO 163
201 D=0.5*(A*(DB+DC)+B*(DA+DC))/(A+B)
   DI=DB
   FI=FB
   IF((FB-FC).LE.0.0) GO TO 207
   DI=DC
   FI=FC
207 IF(ITONE.EQ.1) GO TO 212
   IF(ITONE.EQ.2) GO TO 212
   ITONE=2
   GO TO 214
212 IF((ABS(D-DI)-DACC).LE.0.0) GO TO 224
   IF((ABS(D-DI)-(0.03*ABS(D))).LE.0.0) GO TO 224
214 IF(((DA-DC)*(DC-D)).LT.0.0) GO TO 220
   FA=FB
   DA=DB
   FB=FC
   DB=DC
   GOTO 161
```

```
220 IS=2
    IF(((DB-D)*(D-DC)).GE.0.0) GO TO 124
    IS=3
    GO TO 124
224 F=FI
    D=DI-DL
    DD=SQRT((DC-DB)*(DC-DA)*(DA-DB)/(A+B))
    DO 5 I=1,N
    X(I)=X(I)+D*W(IDIRN)
    W(IDIRN)=DD*W(IDIRN)
    IDIRN=IDIRN+1
  5 CONTINUE
    W(ILINE)=W(ILINE)/DD
    ILINE=ILINE + 1
    IF((IPRINT-1).NE.0.0) GO TO 241
235 IF(IPRINT.EQ.1) GO TO 241
    IF(IPRINT.EQ.2) GO TO 300
241 IF(ITONE.EQ.1) GO TO 243
    IF(ITONE.EQ.2) GO TO 297
243 IF((FPREV-F-SUM).LT.0.0) GO TO 246
    SUM=FPREV-F
    JIL=ILINE
246 IF((IDIRN - JJ).LE.0.0) GO TO 112
    IF(IND.EQ.2) GO TO 299
    FHOLD=F
    IS=6
    IXP=JJ
    DO 6 I=1,N
    IXP=IXP+1
    W(IXP)=X(I)-W(IXP)
  6 CONTINUE
    DD=1.0
    GO TO 126
258 IF(IND.EQ.2) GO TO 262
    IF((FP-F).LE.0.0) GO TO 287
    D=2*(FP+F-2*FHOLD)/(FP-F)**2
    IF(((D*(FP-FHOLD-SUM)**2)-SUM).GE.0.0) GO TO 287
262 J=JIL*N+1
    IF((J-JJ).GT.0.0) GO TO 271
    DO 7 I=J,JJ
    K=I-N
    W(K)=W(I)
  7 CONTINUE
    DO 8 I=JIL,N
    W(I-1)=W(I)
  8 CONTINUE
271 IDIRN=IDIRN-N
    ITONE=3
    K=IDIRN
    IXP=JJ
    AAA=0.
    DO 9 I=1,N
    IXP=IXP+1
```

```
    W(K)=W(IXP)
    IF((AAA-ABS(W(K)/E(I))).GE.0.0) GO TO 281
    AAA=ABS(W(K)/E(I))
281 K=K+1
  9 CONTINUE
    DDMAG=1.
    W(N)=SCAL/AAA
    ILINE=N
    GO TO 112
287 IXP=JJ
    AAA=0.
    F=FHOLD
    DO 10 I=1,N
    IXP=IXP+1
    X(I)=X(I)-W(IXP)
    IF((AAA*ABS(E(I))-ABS(W(IXP))).GE.0.0) GO TO 10
    AAA=ABS(W(IXP)/E(I))
 10 CONTINUE
    GO TO 299
297 AAA=AAA*(1.+DI)
    IF(IND.EQ.2) GO TO 319
299 IF((IPRINT-2).GE.0.0) GO TO 235
300 KLINE=KLINE+1
    IF(IND.EQ.2) GO TO 306
    IF((AAA-0.1).LE.0.0) GO TO 320
    IF((F-FP).LT.0.0) GO TO 307
    NOLUCK=3
    GO TO 320
306 IND=1
307 DDMAG=0.4*SQRT(FP-F)
    ISGRAD=1
    ITERC=ITERC+1
    IF((ITERC-MAX).LE.0.0) GO TO 101
    NOLUCK=4
    IF((F-FKEEP).LE.0.0) GO TO 320
    F=FKEEP
    DO 11 I=1,N
    JJJ=JJJ+1
    X(I)=W(JJJ)
 11 CONTINUE
    GO TO 320
319 IF((AAA-0.1).LE.0.0) GO TO 320
    INN=1
    GO TO 307
320 RETURN
    END
```

```
C   ************************************************************************
C   *                                                                      *
C   *     A SUBROUTINE TO CoMPUTE THETA AT TIME J+1                        *
C   *                                                                      *
C   *     USING IMPLICIT FINITE DIFFERENCE METHOD                          *
C   *                                                                      *
C   ************************************************************************

      SUBROUTINE IMP(N1,DT,NT,N,F,X,CO,CU,CN,ITERD,TI,V,P,CA,WA,CI,WI,
     *Y,XI,XU,TU,ML,MAX,SCAL,E,IT,DX,WO,WU,AG,WN,MP,MN,NS,FN,RW,RC)
      IMPLICIT  REAL*8(A-H,O-Z)
      DIMENSION  CO(555),CN(555),WU(555),CU(555),WO(555),WN(555),AG(555)
     *,X(50),E(50),Y(50),CI(555),WI(555)
      ITERD=ITERD+1
C   **************  UPDATE C. AND W.   ***************
      DO 14 I=1,N1+1
      CO(I)=CI(I)
      CN(I)=CI(I)
      WO(I)=WI(I)
      WN(I)=WI(I)
   14 CONTINUE
C   **************  BOUNDARY CONDITIONS FOR  W. & C. ***********
      TIME=TI
      K1=0
      K2=0
      DO 50 N2=1,NT
      W2=(WU(N1+1)-WI(N1+1))/NT
      C1=((CU(1)-CI(1)))/Nt
      C2=((CU(N1+1)-CI(N1+1)))/NT
      IF(N2.NE.1) GO TO 2
      CN(1)=(CO(1)+C1)
      CN(N1+1)=CO(N1+1)+C2
      z=CU(N1+1)
      IF(CN(N1+1).GT.CU(N1+1))  CN(N1+1)=z
      WN(1)=WU(1)
      WN(N1+1)=WO(N1+1)+W2
      zz=wu(n1+1)
      if(wn(n1+1).gT.wu(N1+1))  wn(N1+1)=zz
      VV=(1-V)
    2 ff=0.
      DO 33 J=1,50
      K1=K1+1
      F=0.
C          *********************************************************************
C          *      O------O------O    TIME J+1                                  *
C          *      4      5      6                                              *
C          *                                                                   *
C          *      O------O------O    TIME J                                    *
C          *      1      2      3                                              *
C          *                                                                   *
C          * NODE I-1    I      I+1                                            *
C          *********************************************************************
```

```
C           ***********  COMPUTATION OF CONCENTRATION AT TIME J+1 ********
    DO 20 I = 2 , N1
C                  **************  DIFFUSION COMPUTATION ****************
    DS1=X(9)+X(1)*EXP(-(X(13))*CO(I-1))+X(5)*EXP(-(X(17))*WO(I-1))
    DS2=X(9)+X(1)*EXP(-(X(13))*CO(I))  +X(5)*EXP(-(X(17))*WO(I))
    DS3=X(9)+X(1)*EXP(-(X(13))*CO(I+1))+X(5)*EXP(-(X(17))*WO(I+1))
    DS4=X(9)+X(1)*EXP(-(X(13))*CN(I-1))+X(5)*EXP(-(X(17))*WN(I-1))
    DS5=X(9)+X(1)*EXP(-(X(13))*CN(I))  +X(5)*EXP(-(X(17))*WN(I))
    DS6=X(9)+X(1)*EXP(-(X(13))*CN(I+1))+X(5)*EXP(-(X(17))*WN(I+1))

    DV1=X(11)+X(3)*EXP(-(X(15))*CO(I-1))+X(7)*EXP(-(X(19))*WO(I-1))
    DV2=X(11)+X(3)*EXP(-(X(15))*CO(I))+X(7)*EXP(-(X(19))*WO(I))
    DV3=X(11)+X(3)*EXP(-(X(15))*CO(I+1))+X(7)*EXP(-(X(19))*WO(I+1))
    DV4=X(11)+X(3)*EXP(-(X(15))*CN(I-1))+X(7)*EXP(-(X(19))*WN(I-1))
    DV5=X(11)+X(3)*EXP(-(X(15))*CN(I))+X(7)*EXP(-(X(19))*WN(I))
    DV6=X(11)+X(3)*EXP(-(X(15))*CN(I+1))+X(7)*EXP(-(X(19))*WN(I+1))
C   *****************  HARMONIC  MEAN  *****************
      DVLb=2*DV1*DV2/(DV1+DV2)
      DVRb=2*DV2*DV3/(DV2+DV3)
      DSLb=2*DS1*DS2/(DS1+DS2)
      DSRb=2*DS2*DS3/(DS2+DS3)
      DVLt=2*DV4*DV5/(DV4+DV5)
      DVRt=2*DV5*DV6/(DV5+DV6)
      DSLt=2*DS4*DS5/(DS4+DS5)
      DSRt=2*DS5*DS6/(DS5+DS6)

      GO TO 56
C   *************    CONCENTRATION  AT TIME J+1    ****************
 56 WLb=WO(I)-WO(I-1)
   WRb=WO(I+1)-WO(I)
   CLb=CO(I)-CO(I-1)
   CRb=CO(I+1)-CO(I)
   WLt=WN(I)-WN(I-1)
   WRt=WN(I+1)-WN(I)
   CLt=CN(I)-CN(I-1)
   CRt=CN(I+1)-CN(I)
   AG(I)=CO(I)+DT*(V*((DSRb*CRb-DSLb*CLb)+(DVRb*WRb-DVLb*WLb))+
  *VV*((DSRt*CRt-DSLt*CLt)+(DVRt*WRt-DVLt*WLt)))/(2*DX**2)
   F=F+AG(I)/(N1+1)
 20 CONTINUE
   F=F+CN(1)/(N1+1)
   F=F+CN(N1+1)/(N1+1)
   AG(1)=CN(1)
   AG(N1+1)=CN(N1+1)
   DO 31 I=2,N1
   CN(I)=AG(I)
```

```
      IF((AG(I-1)-AG(I))*(AG(I)-AG(I+1)).LT.0.0) CN(I)=(2*AG(I)+
     *AG(I-1)+AG(I+1))/4.0
   31 CONTINUE
      IF(ABS(FF-f).LE.P*1.E-5)  GO TO 54
      FF=F
  33  CONTINUE
  54  DO 30 I=1,N1+1
      WO(I)=WN(I)
      IF(N2.EQ.1) GO TO 3
      WN(N1+1)=WO(N1+1)+W2
      if(WN(N1+1).gT.WU(N1+1))  WN(N1+1)=WU(n1+1)
  30  CONTINUE

C     *********** COMPUTATION OF VOLUMETRIC WATER CONTENT AT TIME J+1  ********

    3 ff=0.
      DO 43 J=1,50
      K2=K2+1
      F=0.
      DO 40 I = 2 , N1

C     **************   DIFFUSION COMPUTATION  ****************

      DW1=X(10)+X(2)*EXP(-(X(14))*CO(I-1))+X(6)*EXP(-(X(18))*WO(I-1))
      DW2=X(10)+X(2)*EXP(-(X(14))*CO(I))+X(6)*EXP(-(X(18))*WO(I))
      DW3=X(10)+X(2)*EXP(-(X(14))*CO(I+1))+X(6)*EXP(-(X(18))*WO(I+1))
      DW4=X(10)+X(2)*EXP(-(X(14))*CN(I-1))+X(6)*EXP(-(X(18))*WN(I-1))
      DW5=X(10)+X(2)*EXP(-(X(14))*CN(I))+X(6)*EXP(-(X(18))*WN(I))
      DW6=X(10)+X(2)*EXP(-(X(14))*CN(I+1))+X(6)*EXP(-(X(18))*WN(I+1))

      DZ1=X(12)+X(4)*EXP(-(X(16))*CO(I-1))+X(8)*EXP(-(X(20))*WO(I-1))
      DZ2=X(12)+X(4)*EXP(-(X(16))*CO(I))+X(8)*EXP(-(X(20))*WO(I))
      DZ3=X(12)+X(4)*EXP(-(X(16))*CO(I+1))+X(8)*EXP(-(X(20))*WO(I+1))
      DZ4=X(12)+X(4)*EXP(-(X(16))*CN(I-1))+X(8)*EXP(-(X(20))*WN(I-1))
      DZ5=X(12)+X(4)*EXP(-(X(16))*CN(I))+X(8)*EXP(-(X(20))*WN(I))
      DZ6=X(12)+X(4)*EXP(-(X(16))*CN(I+1))+X(8)*EXP(-(X(20))*WN(I+1))

C     *****************   HARMONIC  MEAN  ******************

        DWLb=2*DW1*DW2/(DW1+DW2)
        DWRb=2*DW2*DW3/(DW2+DW3)
        DZLb=2*DZ1*DZ2/(DZ1+DZ2)
        DZRb=2*DZ2*DZ3/(DZ2+DZ3)
        DWLt=2*DW4*DW5/(DW4+DW5)
        DWRt=2*DW5*DW6/(DW5+DW6)
        DZLt=2*DZ4*DZ5/(DZ4+DZ5)
        DZRt=2*DZ5*DZ6/(DZ5+DZ6)

C     ***************   MOISTURE AT TIME J+1
      WLb=WO(I)-WO(I-1)
      WRb=WO(I+1)-WO(I)
      CLb=CO(I)-CO(I-1)
      CRb=CO(I+1)-CO(I)
```

```
      WLt=WN(I)-WN(I-1)
      WRt=WN(I+1)-WN(I)
      CLt=CN(I)-CN(I-1)
      CRt=CN(I+1)-CN(I)
      AG(I)=WO(I)+DT*(VV*((DZRb*CRb-DZLb*CLb)+(DWRb*WRb-DWLb*WLb))+
     *V*((DZRt*CRt-DZLt*CLt)+(DWRt*WRt-DWLt*WLt)))/(2*DX**2)
      F=F+AG(I)/(N1+1)
   40 CONTINUE
      F=F+WN(1)/(N1+1)
      F=F+WN(N1+1)/(N1+1)
      AG(1)=WN(1)
      AG(N1+1)=WN(N1+1)
      DO 41 I=2,N1
      WN(I)=AG(I)
      IF((AG(I-1)-AG(I))*(AG(I)-AG(I+1)).LT.0.0) WN(I)=(2*AG(I)+
     *AG(I-1)+AG(I+1))/4.0
    41 CONTINUE
      IF(ABS(FF-f).LE.P*1.E-5)  GO TO 53
      FF=F
   43  CONTINUE
   53  DO 60 I=1,N1+1
      CO(I)=CN(I)
       IF(N2.EQ.1) GO TO 4
      CN(1)=CO(1)+C1
      CN(N1+1)=CO(N1+1)+C2
      if(CN(N1+1).GT.CU(N1+1))  CN(N1+1)=CU(N1+1)
   60  CONTINUE
    4  TIME=TIME+DT
   50   CONTINUE

C                   ********* CORRELATION COEFFICIENT FOR CONCENTRATION **********
      SUMD=0.0
      S2Y=0.0
      S2YE=0.0
      DO 52 I=1,N1+1
      SUMD=SUMD+ABS(CU(I)-CN(I))
      S2Y=S2Y+(CU(I)-CA)**2
      S2YE=S2YE+(CN(I)-CU(I))**2
    52 CONTINUE
      FY=1-S2YE/S2Y
      IF(FY.LT.0.0) FY=4.0
      RC=SQRT(FY)
      FT=SUMD

C                   ********* CORRELATION COEFFICIENT FOR MOISTURE **********
      SUMD=0.0
      S2Y=0.0
      S2YE=0.0
      DO 51 I=1,N1+1
      SUMD=SUMD+ABS(WU(I)-WN(I))
      S2Y=S2Y+(WU(I)-WA)**2
      S2YE=S2YE+(Wn(I)-WU(I))**2
   51 CONTINUE
```

```
      FY=1-S2YE/S2Y
      IF(FY.LT.0.0) FY=4.0
      RW=SQRT(FY)
      FW=SUMD
      F=FT+FW

C               ************  RECORDING THE OPTIMIZED PARAMETER  ************

      IF (ITERD.EQ.1) FN = F
      IF (ITERD.EQ.1) GO TO 199
      IF (F.GT.FN) GO TO 199
      FN=F
      IT=ITERD
      if(iterd-mn.ne.1)  go to 13
      mp=mp+1
      go to 16
 13   mp=1
      go to 12
 16   if(mp.ne.NS) go to 12
      f=fm
      fn=f
      mp=0
      go to 11
 12   fm=f
 11   mn=iterd
      write(*,*)'             =============================='
      DO 88 I=1,N
      Y(I)=X(I)
  88  CONTINUE
      CLOSE(10)
      OPEN(10,FILE='ID1')
      WRITE(10,24) N,N1,ML,MAX,NS,XU,XI
      WRITE(10,27) DT,TU,TI,P,SCAL,V
  24  FORMAT(5(I6,1X),2(F12.6,1X))
  27  FORMAT(3(F12.6,1X),F14.7,1X,2(F7.2,1X))
      DO 1 J=1,N/2
      L=(J-1)*2
      WRITE(10,*) E(L+1),E(L+2)
      WRITE(10,*) Y(L+1),X(L+2)
 1    CONTINUE
      CLOSE(10)
 199  IF(IT.EQ.0) IT=1
      IF(ITERD.EQ.1)   GO TO 96
      IF(ITERD/22*22.NE.ITERD)   GO TO 91
      WRITE(*,*)"      **************************************"
 96   WRITE(*,*) " ITER.     IT      k1      K2      RW
     *     RC        F"
 91   WRITE(*,23) ITERD,IT,k1/NT,K2/NT,RW,RC,f, mp
  23  FORMAT(4(I5,3x),3X,2(F5.2,5X),F12.3,3x,I1)
      RETURN
      END
```