TRANSPORT AND ADSORPTION OF VOLATILE ORGANIC COMPOUNDS IN LOW WATER CONTENT SOILS

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Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
DOCTOR OF PHILOSOPHY
May, 1996

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ACKNOWLEDGMENTS

I wish to express my sincere appreciation to my major advisor, Dr. Glenn O. Brown, for his financial support, invaluable guidance and encouragement throughout this research. Thanks are also due my other graduate committee members, Dr. R. L. Elliott, Dr. C. T. Haan, and Dr. N. T. Basta, for their time and valuable assistance and coorperation. Special thanks go to Mr. Tom Underwood, who aided in the experiments and helped with my English. I also want to thank the Department of Biosystems and Agricultural Engineering for providing the laboratory facilities which made this study possible.

I would like to give my deeply appreciation to my personal friend, Dr. Jian Yue, for her life-long friendship and encouragement. I also extend my appreciation to her husband, Shaopin Tang, for his assistance. The special support from Qin Zhao and his wife Shuiyu Zhang, Hsuantsung Hsieh and his wife Meihua Koo are especially appreciated.

More over, I would like to express my special thanks to my parents, Kaiguo Li and Dinhe Yu, for their support and understanding throughout my life. I couldn't finish this thesis without the love and care of my aunt, Dinhu Yu, my brother, Youzhen Li, and sisters, Youquan Li, Xuejun Li. For this, I am especially appreciative.

Finally, I would like to give my special thanks to my husband, Zhongxiang Luo, and my daughter, Brooke T. Luo, for their love, patience, and support during this research. My husband's encouragement and faith always provided me strength and comfort. My daughter's love made me happy and helped me get through all difficulties. She always makes my life exciting and wonderful.

TABLE OF CONTENTS

Chapter **Page**

I. INTRODUCTION AND REVIEW 1

Introduction 1
Fate and Transport of VOCs in Low Water Content Soil 3
Objectives 5
References 6

II. VOLATILE ORGANIC VAPOR SORPTION ONTO LOW WATER CONTENT SOILS 8

Abstract 8
Introduction 9
Methods 17
Materials 24
Experimental Procedures 25
Results and Discussion 26
Conclusions 30
References 31

III. VOLATILE ORGANIC VAPOR PHASE DIFFUSION IN LOW WATER CONTENT SOILS 51

Abstract 51
Introduction 52
Materials and Experimental Apparatus 57
Experimental Procedures 59
Calculation of Vapor Phase Diffusion Coefficient 63
Experimental Results 70
Discussion 72
Conclusions 76
References 77

Chapter **Page**

IV. **VOLATILIZATION OF ORGANIC COMPOUNDS FROM SOIL SURFACES** 104

Abstract 104
Introduction 105
Method of Calculating Volatilization of VOCs 106
Experimental Results and Discussion 108
Conclusions 113
References 114

V. **SUMMARY AND RECOMMENDATIONS FOR FUTURE STUDY** 129

APPENDICES 131

Appendix A: Flow Chart and Computer Programs 131

Appendix B: Experimental Data from Soil Sorption Tests 142

Appendix C: Experimental Data from Soil Column Tests 162

LIST OF TABLES

Table **Page**

1-1 Physical-Chemical Parameters of Toluene 7

2-1 Characteristics of the Experimental Soils 34

2-2 Results of Teller Loam Sorption Tests 35

2-3 Results of Dougherty Sand Sorption Tests 36

2-4 Results of Measured Critical Moisture 37

3-1 Overview of Major Diffusivity Models 54

3-2 Toluene Adsorption of Materials 58

3-3 Preparation of Toluene Standards in Air 80

3-4 Test Parameters of Each Column Experiment 81

3-5 Results of Estimated Gaseous Diffusion Coefficients in Teller Loam 82

3-6 Results of Estimated Gaseous Diffusion Coefficients in Dougherty Sand .. 83

3-7 Estimated Lower and Upper Boundary of Diffusion Coefficient by Experimental Data 84

4-1 Impacts of Moisture on Volatilization Time and Initial Toluene Mass 115

4-2 Impacts of Moisture on Volatilization Time and Initial Toluene Concentration 116

B-1 Data from Teller Loam Sorption Test #1 143

B-2 Data from Teller Loam Sorption Test #2 144

Table **Page**

B-3 Data from Teller Loam Sorption Test #3 145

B-4 Data from Teller Loam Sorption Test #4 146

B-5 Data from Teller Loam Sorption Test #5 147

B-6 Data from Teller Loam Sorption Test #6 148

B-7 Data from Teller Loam Sorption Test #7 149

B-8 Data from Teller Loam Sorption Test #8 150

B-9 Data from Teller Loam Sorption Test #9 151

B-10 Data from Teller Loam Sorption Test #10 152

B-11 Data from Dougherty Sand Sorption Test #1 153

B-12 Data from Dougherty Sand Sorption Test #2 154

B-13 Data from Dougherty Sand Sorption Test #3 155

B-14 Data from Dougherty Sand Sorption Test #4 156

B-15 Data from Dougherty Sand Sorption Test #5 157

B-16 Data from Dougherty Sand Sorption Test #6 158

B-17 Data from Dougherty Sand Sorption Test #7 159

B-18 Data from Dougherty Sand Sorption Test #8 160

B-19 Data from Dougherty Sand Sorption Test #9 161

C-1 Data from Column Test Teller-1 163

C-2 Measured Data of Toluene Concentration Profiles in Column Test Teller-1 167

C-3 Measured Soil Moisture Data in Column Test Teller-1 168

C-4 Data from Column Test Teller-2 169

Table **Page**

C-5 Measured Data of Toluene Concentration Profiles in Column Test Teller-2 174

C-6 Measured Soil Moisture Data in Column Test Teller-2 175

C-7 Data from Column Test Teller-3 176

C-8 Measured Data of Toluene Concentration Profiles in Column Test Teller-3 179

C-9 Data from Column Test Dougherty-1 180

C-10 Measured Data of Toluene Concentration Profiles in Column Test Dougherty-1 184

C-11 Measured Sand Moisture Data in Column Test Dougherty-1 185

C-12 Data from Column Test Dougherty-2 186

C-13 Measured Data of Toluene Concentration Profiles in Column Test Dougherty-2 189

LIST OF FIGURES

Figure **Page**

2-1 Three Stages of Soil Adsorption 38

2-2 Vapor/Solid Partition Coefficient of Teller-1 39

2-3 Vapor/Solid Partition Coefficient of Teller-2 39

2-4 Vapor/Solid Partition Coefficient of Teller-3 40

2-5 Vapor/Solid Partition Coefficient of Teller-4 40

2-6 Vapor/Solid Partition Coefficient of Teller-5 41

2-7 Vapor/Solid Partition Coefficient of Teller-6 41

2-8 Vapor/Solid Partition Coefficient of Teller-7 42

2-9 Vapor/Solid Partition Coefficient of Teller-8 42

2-10 Vapor/Solid Partition Coefficient of Teller-9 43

2-11 Saturated Partition Coefficient of Teller-10 43

2-12 Vapor/Solid Partition Coefficient of Dougherty-1 44

2-13 Vapor/Solid Partition Coefficient of Dougherty-2 44

2-14 Vapor/Solid Partition Coefficient of Dougherty-3 45

2-15 Vapor/Solid Partition Coefficient of Dougherty-4 45

2-16 Vapor/Solid Partition Coefficient of Dougherty-5 46

2-17 Vapor/Solid Partition Coefficient of Dougherty-6 46

Figure **Page**

2-18 Vapor/Solid Partition Coefficient of Dougherty-7 47

2-19 Vapor/Solid Partition Coefficient of Dougherty-8 47

2-20 Saturated Partition Coefficient of Dougherty-9 48

2-21 Measured Relationships of Moisture and Partition Coefficients of Teller Loam 49

2-22 Measured Relationships of Moisture and Partition Coefficients of Dougherty Sand 50

3-1 PVC Cylinder and Locations of Sampling Ports 58

3-2 Experimental Apparatus 61

3-3 Measured and Best-fit Toluene Gas Phase Concentration Profiles in Column Test Teller-1 85

3-4 Measured and Best-fit Toluene Gas Phase Concentration Profiles in Column Test Teller-2 86

3-5 Measured and Best-fit Toluene Gas Phase Concentration Profiles in Column Test Teller-3 87

3-6 Measured and Best-fit Toluene Gas Phase Concentration Profiles in Column Test Dougherty-1 88

3-7 Measured and Best-fit Toluene Gas Phase Concentration Profiles in Column Test Dougherty-2 89

3-8 Measured Soil Moisture Profiles of Column Test Teller-1 90

3-9 Measured Soil Moisture Profiles of Column Test Teller-2 91

3-10 Measured Soil Moisture Profiles of Column Test Dougherty-1 92

3-11 Optimum K^*_d and D^*_g Relationships of Column Test Teller-1 93

3-12 Optimum K^*_d and D^*_g Relationships of Column Test Teller-2 94

3-13 Optimum K^*_d and D^*_g Relationships of Column Test Teller-3 95

Figure **Page**

3-14 Optimum K^*_d and D^*_g Relationships of Column Test Dougherty-1 96

3-15 Optimum K^*_d and D^*_g Relationships of Column Test Dougherty-2 97

3-16 Typical Response Surface and Contour Map of Parameters 98

3-17 Measured and Simulated Toluene Gas Phase Concentration Profiles Using Millington-Quirk Diffusivity Model in Column Test Teller-1 99

3-18 Measured and Simulated Toluene Gas Phase Concentration Profiles Using Millington-Quirk Diffusivity Model in Column Test Teller-2 100

3-19 Measured and Simulated Toluene Gas Phase Concentration Profiles Using Millington-Quirk Diffusivity Model in Column Test Teller-3 101

3-20 Measured and Simulated Toluene Gas Phase Concentration Profiles Using Millington-Quirk Diffusivity Model in Column Test Dougherty-1 .. 102

3-21 Measured and Simulated Toluene Gas Phase Concentration Profiles Using Millington-Quirk Diffusivity Model in Column Test Dougherty-2 .. 103

4-1 Measured and Predicted Toluene Volatilization in Column Test Teller-1 117

4-2 Measured and Predicted Toluene Volatilization in Column Test Teller-2 118

4-3 Measured and Predicted Toluene Volatilization in Column Test Teller-3 119

4-4 Measured and Predicted Toluene Volatilization in Column Test Dougherty-1 120

4-5 Measured and Predicted Toluene Volatilization in Column Test Dougherty-2 121

4-6 Toluene Volatilization at Different Moisture With C_0=50 mg/L a. Teller Loam b. Dougherty Sand 122

4-7 Relationship of Toluene Volatilization Time and Moisture With C_0=50 mg/L a. Teller Loam b. Dougherty Sand 123

Figure **Page**

4-8 Initial Toluene Mass at Different Moisture With C_0=50 mg/L
a. Teller Loam b. Dougherty Sand 124

4-9 Volatilization at Different Moisture With Initial Toluene Mass 7000 mg
a. Teller Loam b. Dougherty Sand 125

4-10 Relationship of Volatilization Time and Moisture With Initial Toluene Mass 7000 mg a. Teller Loam b. Dougherty Sand 126

4-11 Initial Gas Phase Concentration at Different Moisture With Toluene Mass 7000 mg a. Teller Loam b. Dougherty Sand 127

4-12 Volatilization of Teller and Dougherty at Different Moisture
a. theta=0.2 v/v b. theta=0.3 v/v 128

LIST OF SYMBOLS

Variable	Definition	Dimension
θ_w	Soil moisture by weight	M/M
θ_v	Soil moisture by volume	L^3/L^3
θ'_w	Soil critical moisture	M/M
ε	Volumetric gas-filled porosity	L^3/L^3
ϕ	Volumetric total porosity	L^3/L^3
γ	Solution activity coefficient	none
ρ_l	Liquid phase density	M/L^3
ρ_s	Solid phase density	M/L^3
C_0	Initial gas phase concentration	M/L^3
C_g	Gas phase concentration	M/L^3
C_l	Liquid phase concentration	M/L^3
C_s	Solid phase concentration	M/M
$C_{gs}(i)$	Simulated gaseous concentration at the ith sampling port	M/L^3
$C_{gm}(i)$	Measured gaseous concentration at the ith sampling port	M/L^3
D_g	Gaseous diffusion coefficient	L^2/T
$D_g{}^*$	Optimum gaseous diffusion coefficient	L^2/T
D_o	Diffusion coefficient in pure air	L^2/T

Variable	**Definition**	**Dimension**
D_l	Liquid phase diffusion coefficient	L^2/T
E	Biodegradation rate	M/L^3T
ET	Volatilization of organic compound	M
F	Mass flux of compound from soil column	L/T
f_{oc}	Soil organic carbon content	M/M
H_c	Henry's constant	none
K_d	Liquid/solid partition coefficient	L^3/M
K_d*	Optimum liquid/solid partition coefficient	L^3/M
K'_d	Vapor/solid partition coefficient	L^3/M
K_{dm}	Upper boundary of K_d	L^3/M
K_{oc}	Soil sorption per unit of organic carbon	L^3/M
M	Oven dry sorbent mass in vial	M
M_T	Total compound mass in vial	M
N	Number of water molecule layers	none
q_g	Volumetric gas flux	L/T
q_l	Volumetric liquid flux	L/T
S	Soil specific surface area	L^2/M
TM	Total compound mass in soil column	M
V	Total volume of PVC column	L^3
V_l	Liquid volume in vial	L^3

Variable	Definition	Dimension
V_T	Total volume of vial	L^3
X	Organic mass sorbed in the sorbent	M

Chapter I

INTRODUCTION AND REVIEW

Introduction

Increasing ground water contamination by volatile organic compounds (VOCs), such as benzene, trichloroethylene, toluene, chlorobenzene, and many pesticides, has been reported in recent years (Pionke and Glotfelty, 1989; McCann et al., 1994). Because of their abundance in industrial materials and domestic products, these nonpolar, hydrophobic organic compounds are major ground water contaminants. Since the top soil layer is usually dry, especially in summer, the transport and sorption of VOCs in low water content soil is important in simulation and prediction of the volatilization and the concentration of VOCs in soils.

Generally, if VOCs are released to soil, they can be adsorbed by the soil, lost by volatilization at the surface, degraded by the microorganisms or transported to the ground water. The dominant process will depend on temperature, mixing conditions, and the existence of acclimated microorganisms at the site. Their half-lives will depend on the types of chemicals and may range from days to several weeks. Since they are relatively mobile in soil, they can leach into the ground water where biodegradation may be slow.

If VOCs are released into the atmosphere, most will degrade moderately rapidly by reaction with photochemically produced hydroxyl radicals. Their half-lives vary depending on the chemicals and weather, but typically range from hours to days. Volatilization to the atmosphere is a major pathway for the removal of most VOCs from soil systems. However, little is known about their adsorption onto soils and the transport rate at which they diffuse through complex and heterogeneous natural materials. The transport process of VOCs within low water content soils can be influenced by several processes, including sorption, diffusion, advection, and biodegradation. Each process is complex and varies with the soil and weather. The dominant processes are adsorption and gaseous diffusion when soil is dry and contains a large amount of organic matter. Biodegradation of most VOCs in soils is usually small.

Volatile organic compounds have many common characteristics in transport and adsorption in soils. In this research toluene was chosen as a model solute to investigate their properties. Toluene is a petroleum derivative, has a low health hazard and is moderately soluble. Its vapor pressure or Henry's constant allows a suitable distribution of toluene between liquid phase and gas phase, with gas phase concentrations ranging from 0 to about 110 mg/L at 20°C. This concentration range matches the linear response of gas chromatography normally used to measure gas phase concentrations. The main sources of contaminant toluene are from petroleum spills and leaks from underground gasoline storage tanks.

The physical and chemical properties of toluene are listed in Table 1-1.

Fate and Transport of Volatile Organic Compounds in Low Water Content Soil

Once volatile organic chemicals penetrate into soil systems, they can move into the groundwater, or their vapors may spread in the vadose zone (unsaturated soil) and contaminate soil over a wide area. The fate and transport of organic vapor in unsaturated soil are very complex and several processes occur including advection, diffusion, dispersion, soil sorption, and biodegradation.

Usually VOCs exist in gas, liquid, and solid phases in unsaturated soil. An organic compound can be present in the solid phase by its adsorption onto soil, dissolved in the liquid aqueous phase, and volatilized into the gas phase. Advection, diffusion, and dispersion of an organic compound can occur in both liquid and gas phases. If large amounts of the organic are present, a fourth phase of the pure compound may also occur. Advection is caused by the movement of phases. In unsaturated soil, liquid and gas phase movement is very small and it is reasonable to assume that advection caused by the movement of phases is negligible compared to gaseous diffusion. Liquid and vapor diffusion are caused by the concentration gradient in liquid phase and gas phase respectively. Usually the liquid phase diffusion is several orders of magnitude less than the vapor phase diffusion. For example, diffusion coefficients of toluene are 0.972×10^{-6} and 0.76×10^{-1} cm^2/sec in water and in air respectively. Therefore, diffusion in the liquid phase is negligible compared with vapor phase diffusion. Dispersion is due to advective mixing and is a function of the phase flow velocity. If the phase flow is small, dispersion can be ignored. Therefore, the predominant processes for volatile compounds in unsaturated soil usually are considered to be vapor diffusion and soil adsorption if the soil is dry and contains a high organic matter content.

Adsorption of organic compounds is usually considered to be a linear and kinetic process. A partition coefficient (K_d) is defined to describe the distribution of chemicals between solid and liquid phases. Numerous experiments measuring the soil partition coefficient have been done in saturated soil conditions. The saturated partition coefficient has been widely used in the modeling and simulation of organic vapor transport in unsaturated or low water content soil. Recent research (Peterson et al., 1988; Ong and Lion, 1991; Petersen et al., 1994) has found that the partition coefficient in a low water content soil can be several orders of magnitude greater than the partition coefficient measured for the saturated soil. Furthermore, it is highly dependent on the soil water content, especially when soil water content is small. The constant liquid/solid partition coefficient (K_d) is not adequate to describe the adsorption of chemicals onto soil when water content is lower than a "critical water content." With this limited information, no conclusions can be drawn about the "critical water content" content or if this "critical water content" content exists in all soils.

Compared with soil adsorption, more work has been done on organic vapor diffusion in low water content soil. It has been found that vapor diffusion of volatile organic compounds in dry soils is strongly influenced by soil temperature, water content, porosity, contaminant characteristics, and soil properties. The Millington-Quirk diffusivity model (Millington, 1959) is considered to give the best predictions of vapor diffusivity and is widely used in the modeling of organic vapor transport in the vadose zone, but little experimental data are available to verify it, especially at low water contents.

Likewise, volatilization of organic chemicals to the atmosphere is found to be strongly affected by soil boundary conditions, weather, soil and chemical properties. Due to the difficulties of measuring volatilization of organic chemicals, little experimental data is available to verify the results of model predictions.

Objectives

This research will investigate the transport of volatile organic compounds in low water content soil, including adsorption onto soils, vapor diffusion, and volatilization from soil surfaces. The objectives are:

1) Experimentally measure the partition coefficients of toluene in two types of soils at different soil water contents and test the existence of the "critical water content" and quantify it for soils.

2) Measure gaseous diffusion coefficients in two types of soils at different soil water content and compare the experimental results with the values of the Millington-Quirk diffusivity model.

3) Investigate and quantify the effects of soil types and water content on volatilization of toluene from soil surfaces.

The dissertation is organized as follows: Chapter 2 presents a literature review of soil adsorption and the experimental results of partition coefficients of toluene onto two soils (Teller loam and Dougherty sand). An analysis of the data obtained and the other data found in the literature is also included. Chapter 3 addresses vapor phase diffusion of toluene in low water content soils, and contains the methods used for measuring gaseous diffusion coefficients of toluene in two soils. Included also is a comparison of experimental data with the values of the Millington-Quirk diffusivity model. In Chapter 4 toluene volatilization is calculated from measured soil gas phase concentration changes. The effects of soil types and water contents are also studied from toluene volatilization data and model prediction. Finally, Chapter 5 summarizes and provides future research recommendations.

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Table 1-1

PHYSICAL-CHEMICAL PARAMETERS OF TOLUENE*

Parameter	Unit	Value
Molecular weight (C_7H_8)	--	92
Molecular cross-sectional area (x 10^{-10})	m^2	34.34
Diffusion coefficient in pure water (x10^{-5})	cm^2/sec	0.0972
Diffusion coefficient in pure air	cm^2/sec	0.076
Henry's law constant (20°C)	--	0.270
Saturated aqueous solubility (20°C)	mg/L	515
Saturated vapor concentration (20°C)	mg/L	110
Saturated vapor pressure (20°C)	mm Hg	22
Liquid density (20°C)	g/mL	0.867
K_{oc}	cm^3/g	259

* From Ong et al. (1992)

Chapter II

VOLATILE ORGANIC VAPOR SORPTION ONTO LOW WATER CONTENT SOILS

Abstract

Vapor adsorption onto soil is an important process affecting the transport and fate of volatile organic compounds in soil. A constant saturated liquid/solid partition coefficient K_d is widely used in modeling of organic vapor transport in unsaturated soil. However, recent research indicates the equilibrium partition coefficient in low water content soil conditions can be several orders of magnitude greater than the value measured for the saturated soil. The partition coefficient in dry soil was observed to be highly dependent on soil water content, when water content is lower than the "critical water content". Since the top soil layer is usually dry, the sorption of VOCs in low water content soil is of importance. There has been little research investigating the sorption mechanisms and quantifying the relationship of the partition coefficient and soil water content. Three stages of soil sorption are proposed from this research. In stage 1, from oven dry to a monolayer of water molecule coverage, water molecules and organic molecules compete for dry sites and soil sorption depends on soil specific surface area.

In stage 2, between a monolayer coverage to "critical water content", soil sorption is strongly dependent on the water content. In stage 3, extending from "critical water content" to a saturated condition, soil sorption coefficient remains constant and is equal to the saturated liquid/solid partition coefficient. Soil "critical water content" varies with respect to the types of soil and the soil surface area. It was found that soil sorption in low water content soil varies significantly with the two soils tested and the water content. The adsorption of organic compounds onto low water content soil may be several orders of magnitude greater than the adsorption onto high water content soil. The application of saturated partition coefficient in low water content soil is not correct and can cause significant error in the prediction of volatile transport.

Introduction

The adsorption of volatile organic compounds onto soil is an important process that determines VOCs fate and transportation in both saturated and unsaturated soils. Usually an equilibrium liquid/solid partition coefficient (K_d) is defined to describe the distribution of volatile organic compound between liquid and solid phases after equilibration. K_d is measured using a batch technique in a saturated soil condition. A small error in soil sorption coefficient will cause a significant difference in predicting the process of VOC transport and fate in soil. Peterson et al. (1988) found that the model predictions of transport down through the unsaturated zone vary markedly with the values used for the partition coefficient. This result was confirmed later by Culver et al. (1991).

Much of the previous research has focused on the soil sorption of VOCs in saturated condition and little research has been performed to quantify the sorption of VOCs in unsaturated or low water content soil conditions. It is found that, under saturated condition, adsorption of most volatile organic compounds is dominated by soil organic matter content. Empirical relationships between saturated liquid/solid partition coefficient and soil organic carbon content have been developed to predict the liquid/solid partition coefficient. A widely used laboratory method of measuring liquid/solid partition coefficient was developed by Garbarini and Lion (1985). In most investigations of modeling and simulation of the fate and transport process of VOCs in unsaturated soil, it was assumed that the equilibrium partition coefficient in unsaturated or low water content soil is equal to the value measured in saturated soil condition (Stephanatos, 1985; Pinder and Abriola, 1986; Corapcioglu and Baehr, 1987; Baehr and Corapcioglu, 1987; Sleep and Sykes, 1989). But recent research found that the soil partition coefficient in low water content soil can be several orders of magnitude greater than the value measured for saturated soil (Ong, 1991a). Soil sorption of VOCs in low water content soil is highly dependent on the soil water content. The saturated partition coefficient used to describe sorption in low water content soil zone results in model predictions of much faster transport than is predicted when any of the unsaturated partition coefficients is used (Peterson et al., 1988).

Little research was accomplished on soil sorption of vapor. Most researchers defined a vapor sorption coefficient to describe the distribution of chemicals between vapor phase and solid phase for unsaturated soil. Wade (1954) investigated the vapor sorption of ethylene dibromide (EDB) onto several soils over the field range of water contents, and found that soil vapor sorption could be related to the organic content of soil. Call (1957a&b) investigated the mechanisms of sorption of EDB and found that the sorption coefficients of EDB vapors on 20 soils at water contents corresponding to field capacity could be predicted with reasonable accuracy from their water content. Jurinak (1957) investigated the adsorption of 1,2-dibromo-3- chloropane vapor on oven-dried soils and indicated that the adsorptive capacity was determined to be a function of the external surface area. Rhue et al. (1988) confirmed this result.

As the pollution of petroleum products became increasingly serious, more research was performed on the vapor adsorption mechanism of VOCs including quantification of the adsorption values. Chiou and Shoup (1985) investigated the soil sorption of organic vapors and effects of humidity on sorptive mechanisms and capacity. He evaluated the effects of water on the sorption of a series of volatile chlorobenzene compounds onto soil. Soil water content was found to be a strong competitor for mineral sorption sites relative to nonionic organic compounds. The high sorption of organic compounds at low water content was attributed to available surface "sites" on the soil minerals. So it was concluded that soil mineral surfaces "prefer" polar water molecules over nonpolar organic compounds.

Later, Peterson and coworkers (1988) measured trichloroethylene (TCE) vapor phase partition coefficients onto a porous aluminum oxide surface coated with humic acid at 8.2% and 11.6% water contents (by weight), and under oven-dry and saturated conditions. They found that vapor phase sorption of TCE by alumina coated with humic acid was highly dependent on water content. Linear partition coefficients for the binding of TCE vapor under a range of unsaturated conditions were 1-4 orders of magnitude greater than the value measured for the saturated sorbent. They divided sorbent surface as dry and wet sorption sites in unsaturated conditions and tried to find the distribution of these two sites in different water contents. They found by the calculation of their experimental data that the site distribution was a highly nonlinear function of the water content. Shoemaker et al. (1990) proposed a two-phase sorption model and defined an "effective partition coefficient" for unsaturated soil conditions based on Peterson's experimental data. They thought that simply replacing the saturated partition coefficient with a vapor phase partition coefficient in a transport model is not adequate since both liquid and vapor phase sorption occur in unsaturated conditions simultaneously. Their two phase sorption model consists of two parts (liquid/solid sorption and vapor/solid sorption). However, the vapor phase sorption coefficient of oven dried soil can not be used for other water contents because the vapor/solid sorption strength is highly dependent on the water content. Actually this idea is the same as Peterson's dry and wet sites idea. Shoemaker's analysis assumed the vapor/solid sorption coefficient was two times the liquid/solid sorption coefficient. But this factor could be in a wide range (0-20) for the soil at 40% saturation that they were interested in. Any small error of this factor can cause significant difference in prediction of the VOCs' transport process. In reality, there would exist some water content below which Henry's Law is invalid and the value of liquid/solid sorption coefficient would decrease due to insufficient water coverage of the soil particles (Yeh and Ward, 1983). But Shoemaker's model could not account for this and simply assumed that the water content of most soils at common environmental conditions is above this critical water content.

Ong and Lion (1991a) measured the partition coefficient of TCE vapor for several minerals over a wide range of water contents. They concluded that surface area is a good indicator of the sorptive capacity of solid phase for oven-dried minerals, and application of Henry's Law to model TCE interaction with the soil water was possible only after five layers of water molecules have formed. They further found that as water content increased, the partition coefficients of TCE vapor decreased by several orders of magnitude, attained a minimum and then gradually increased. He proposed an idea of three regions of sorbent water content. In Region 1, from oven-dried conditions to one monolayer coverage of water on the solid surface, direct solid-vapor sorption was evident with strong competition between water and TCE for adsorption sites on the sorbents. In Region 2, between a monolayer coverage to approximately five layers of water molecules, likely interactions between TCE vapor and water include adsorption of TCE onto surface-bound water and limited TCE dissolution into sorbed water with some "salting out" effects caused by water structure. In Region 3, extending from a minimum of approximately five layers of water molecules to the water retention capacity of the soil, TCE dissolution into condensed water dominated vapor uptake along with sorption at the water-solid interface. Ong and Lion (1991b) also stated that under air-dried conditions, at field capacity and for saturated conditions, organic carbon content controls sorption.

Petersen et al. (1994) measured vapor phase partition coefficients for toluene and TCE on Yolo silt loam at a soil water content of 0.02 and 0.10 g H_2O/g soil respectively. They found that for water contents higher than four molecular layers of water surface coverage, vapor/solid partition coefficients were consistent with values predicted by Henry's Law constants and liquid/solid partition coefficients. However, for less than four molecular layers of water, sorption increased by orders of magnitude.

It is clear that the soil sorption of VOCs at water contents lower than a "critical water content" value is highly dependent on the water content and can be several orders of magnitude greater than saturated soil sorption. Previous research (Peterson et al., 1988; Lion et al., 1990; Ong et al., 1991a) classified soil as saturated and unsaturated soil. For saturated soil they used a constant liquid/solid partition coefficient (K_d) to describe the soil sorption as the portions of the solid phase behave as though they are surrounded by liquid water. For unsaturated soil they defined a vapor/solid partition coefficient (K_d') to describe the soil sorption on a portion of the soil to behave as though it is in contact with both water and organic vapor. Actually it is quite possible that all the soil surface is covered by water molecules even when the soil is very dry and no soil surface is exposed directly to organic vapor. Therefore, in this research soil that has water content lower than the "critical water content" is defined as low water content soil and those soils having water content higher than the "critical water content" are defined as high water content soils. It is assumed that there are two types of sites: organic and mineral. The organic matter sites prefer any VOC, while the mineral sites prefer water. In high water content soil, all mineral sites are saturated with water molecules, and only the organic matter sites can adsorb the nonpolar organic chemical molecule. The soil sorption depends on the organic matter content only, not the water content, and can be described by a constant liquid/solid partition coefficient equal to the partition coefficient in saturated soil. In low water content soil the mineral sites are not saturated with water. So, in addition to organic matter sites, mineral sites will have some capacity to adsorb VOC's. Therefore, the constant liquid/solid partition coefficient K_d is not adequate to describe VOC sorption. Sorption is a function of not only the soil organic matter sites, but also the "available" mineral sites. Thus K_d is a function of both organic matter content and water content. Henry's Law is assumed to be valid at all water contents in this research because there is not enough evidence to invalidate it.

Although some research work has been done on the sorption of organic vapor onto soil, the relative importance of soil surface area, water content and organic matter content in sorption of organic vapors is not clear. There is not enough experimental evidence to support the existence of "critical water content" and no method to quantify the value of "critical water content." Also, the mechanisms responsible for the observed impact of water content on the vapor phase partition coefficient at low water content soil requires further study. The objectives of this chapter are (1) to investigate the mechanisms of toluene vapor phase sorption onto soils, (2) to quantify the relationship between the vapor phase sorption coefficient and soil water content, and (3) to test the existence of a "critical water content" and quantify it for soils.

In this research three stages of soil sorption shown in Figure 2-1 were suggested. Stage 1: Very dry soil. Soil water content is from oven-dry soil to one monolayer water molecule coverage. So there are two types of sites in this stage: dry site and wet site. The dry site is exposed directly to gas phase. Water molecules and organic molecules strongly compete for adsorption sites of soil. Organic compound molecules can be adsorbed by organic matter site and by available dry mineral site, even bounded to water molecules by the adsorption force of the soil surface. The adsorption capacity of soil depends on the soil specific surface area, water, and organic carbon content. In this stage, the liquid/solid partition coefficient has no meaning because there is no true liquid water phase.

Stage 2: Water content ranges from one monolayer water molecule coverage to "critical water content". In this stage soil surface is all covered by at least one monolayer of water molecules and no dry site is exposed directly to gas phase. Since there are not enough water molecules to satisfy the surface adsorption force of soil, adsorption potential can attract organic molecules. The available extra force for organic compound molecules depends on the abundance of water molecules. Henry's Law is assumed to be valid in this stage. Therefore, organic molecules can be adsorbed by organic matter sites, which follows the saturated liquid/solid partition rule, and bonded to water molecules by the extra adsorption force of the soil surface.

Stage 3: Water content ranges from "critical water content" to saturated soil. In this stage all the soil surface is deeply covered by water and there is no extra adsorption force for organic molecules to bind to water. The organic molecules can be only dissolved in the surrounding water phase and adsorbed at soil organic matter sites, which follows the saturated liquid/solid partition rule. The soil sorption is not a function of water content but only dependent on the soil organic matter content. Therefore, when water content is greater than "critical water content" the partition coefficient is a constant equal to the saturated partition coefficient.

Methods

Two soils (Teller loam and Dougherty sand) were used in this research to investigate the mechanisms of organic vapor sorption onto soils. Toluene was chosen in this research as it is a common volatile organic contaminant often found in the ground, inexpensive, and relatively safe. Toluene partition coefficients were measured in saturated and unsaturated conditions for each soil. The experiment and calculation of toluene partition coefficients in saturated and unsaturated conditions are different.

(a) Calculation of Partition Coefficient in Saturated Soil

The basic method of determining the partition coefficient in saturated soil was extended by Garbarini and Lion (1985) from the determination of Henry's constant of a volatile organic compound in water proposed by Lincoff and Gossett (1984). This method applied an equilibrium headspace technique in closed systems. The saturated partition coefficient or liquid/solid partition coefficient is determined by comparing mass balances in two similar systems containing the same liquid volume (V_l), total compound mass (M_T), and total vial volume (V_T), but one system (vial 2) contains a sorbent, the other (vial 1) none. Under such situations the equilibrium partition coefficient between solid and liquid phase is given by Henry's Law,

$$\frac{C_g}{C_l} = \gamma H_c \tag{2-1}$$

where C_g and C_l are the gas phase (headspace of closed system) and liquid phase concentrations of volatile compound respectively, H_c is the Henry's constant (dimensionless), and γ is the activity coefficient that relates the concentration of a compound in solution to its thermodynamic activity.

For vial 1 without sorbent,

$$M_T = C_{g1} V_{g1} + C_{l1} V_l = C_{g1}\left(V_{g1} + \frac{V_l}{\gamma H_c}\right) \tag{2-2}$$

and vial 2 with sorbent,

$$M_T = C_{g2} V_{g2} + C_{l2} V_l + X = C_{g2}\left(V_{g2} + \frac{V_l}{\gamma H_c}\right) + X \tag{2-3}$$

$$C_s = \frac{X}{M} = K_d C_{l2} = K_d \frac{C_{g2}}{\gamma H_c} \tag{2-4}$$

where C_s is the solid phase organic concentration, C_{g1} and C_{g2} are the volatile compound gas phase concentrations of vial 1 and 2, V_{g1} and V_{g2} are the headspace volumes of vial 1 and 2, C_{l1} and C_{l2} are the volatile compound liquid concentrations of vial 1 and 2, X is the mass of volatile compound sorbed in the sorbent, M is the mass of oven-dry sorbent in vial 2, and K_d is the saturated liquid/solid partition coefficient. Setting equation (2-2) equal to equation (2-3) gives,

$$X = C_{g1}\left(V_{g1} + \frac{V_l}{\gamma H_c}\right) - C_{g2}\left(V_{g2} + \frac{V_l}{\gamma H_c}\right) \tag{2-5}$$

Substituting equation (2-5) into equation (2-4) generates,

$$C_{g1}\left(V_{g1} + \frac{V_l}{\gamma H_c}\right) - C_{g2}\left(V_{g2} + \frac{V_l}{\gamma H_c}\right) = K_d M \frac{C_{g2}}{\gamma H_c} \tag{2-6}$$

Equation (2-6) is rearranged to,

$$C_{g1}(V_l + \gamma H_c V_{g1}) - C_{g2}(V_l + \gamma H_c V_{g2}) = K_d M C_{g2} \tag{2-7}$$

Equation (2-7) divided by the second term on the left hand side forms,

$$\frac{C_{g1}\left(V_l + \gamma H_c V_{g1}\right)}{C_{g2}\left(V_l + \gamma H_c V_{g2}\right)} - 1 = K_d[M/(V_l + \gamma H_c V_{g2})] \tag{2-8}$$

Assuming,

$$C_{g2_{normalized}} = C_{g2}\frac{V_l + \gamma H_c V_g}{V_l + \gamma H_c V_g} \tag{2-9}$$

where $C_{g2\ \mathrm{normalized}}$ is the gas concentration of the volatile compound in vial 2. Equation (2-9) assumes a sorbent can adsorb compound only but doesn't occupies space. The combination of equation (2-8) and equation (2-9) yields the desired form,

$$\frac{C_{g1}}{C_{g2_{normalized}}} - 1 = K_d[M/(V_l + \gamma H_c V_{g2})] \tag{2-10}$$

Define two lumped parameters,

$$X_s = M/(V_l + \gamma H_c V_{g2}) \tag{2-11}$$

$$Y_s = \frac{C_{g1}}{C_{g2_{normalized}}} - 1 \tag{2-12}$$

So equation (2-10) becomes,

$$Y_s = K_d X_s \tag{2-13}$$

The saturated liquid/solid partition coefficient K_d may be determined by calculating the slope of the linear relationship between X_s and Y_s with an intercept of 0. When the gas chromatography peak area or peak height response is linearly related to the gas concentrations being examined, the peak data may be directly substituted for gas concentrations in equation (2-9) and equation (2-12). Thus, there is no need to make standard solutions in the sorption experiment and the error caused by an inaccurate calibration curve is avoided.

(b) Calculation of Partition Coefficient in Unsaturated Soil

The method for determining the partition coefficient in unsaturated soils proposed by Peterson et al. (1988) was adapted in this research. The liquid/solid partition coefficient for unsaturated soil may also be obtained by mass balance principles. A system with known total volume and moist sorbent (sample vial 2) may be compared with another control system, which has the same total volume but contains no sorbent (control vial 1). If the same mass of organic compound (M_T) is introduced into each system, the relationships can be developed for determining the equilibrium liquid/solid partition coefficient in unsaturated soil as follows:

For vial 1 without moist sorbent,

$$M_T = C_{g1} V_{g1} \tag{2-14}$$

and vial 2 with moist sorbent,

$$M_T = C_{g2} V_{g2} + C_{l2} V_{l2} + X \tag{2-15}$$

$$V_{l2} = \frac{\theta_w M}{\rho_l} \tag{2-16}$$

where V_{l2} is liquid phase volume of vial 2, θ_w is the water content by weight, and ρ_l is the liquid phase density.

From equations (2-14), (2-5), and (2-16) the following relationship can be derived,

$$X = C_{g1} V_{g1} - C_{g2} V_{g2} - \frac{\theta_w M}{\rho_l} C_{l2} \tag{2-17}$$

At low vapor pressures of the adsorbate gas, the liquid/solid partition coefficient in unsaturated soil (K_d) can be defined as a linear isotherm,

$$C_s = \frac{X}{M} = K_d C_{l2} \tag{2-18}$$

Rearranging equation (2-18) yields,

$$X = MK_d C_{l2} \tag{2-19}$$

Setting equation (2-17) equal to (2-19) gives,

$$C_{g1} V_{g1} - C_{g2} V_{g2} = (K_d + \frac{\theta_w}{\rho_l}) M C_{l2} \tag{2-20}$$

By Henry's Law (see 2-1),

$$C_{l2} = \frac{C_{g2}}{\gamma H_c} \tag{2-21}$$

Substituting equation (2-21) into equation (2-20) generates,

$$C_{g1} V_{g1} - C_{g2} V_{g2} = (K_d + \frac{\theta_w}{\rho_l}) M \frac{C_{g2}}{\gamma H_c} \tag{2-22}$$

Dividing equation (2-22) by the second term on the left hand side and rearranging results in the following desired form,

$$\frac{C_{g1}V_{g1}}{C_{g2}V_{g2}} - 1 = \left(\frac{K_d}{\gamma H_c} + \frac{\theta_w}{\gamma H_c \rho_l}\right)(M/V_{g2}) \tag{2-23}$$

Now define three lumped parameters,

$$K_d' = \frac{K_d}{\gamma H_c} + \frac{\theta_w}{\gamma H_c \rho_l} \tag{2-24}$$

$$X_{un} = M/V_{g2} \tag{2-25}$$

$$Y_{un} = \frac{C_{g1}V_{g1}}{C_{g2}V_{g2}} - 1 \tag{2-26}$$

So equation (2-23) becomes,

$$Y_{un} = K_d' X_{un} \tag{2-27}$$

From inspection it can be shown that,

$$K_d' = \frac{C_s}{C_g} = \frac{X/M}{C_g} \tag{2-28}$$

That is, when K_d' is defined as equation (2-28) the same equation as (2-27) can be obtained. K_d' is called the vapor phase partition coefficient.

So the vapor phase partition coefficient K_d' may be determined by calculating the slope of the linear relationship between X_{un} and Y_{un} with an intercept of 0. Then the liquid/solid partition coefficient K_d in unsaturated soil can be calculated as,

$$K_d = \gamma H_c K_d^{\prime} - \frac{\theta_w}{\rho_l} \qquad (2\text{-}29)$$

Equation (2-29) is derived from equation (2-24). Similarly, when the gas chromatography peak area or peak height response is linearly related to the gas concentrations being examined, the peak data may be directly substituted for gas concentrations in equation (2-26).

Materials

Soils used in the experiments were Teller loam and Dougherty sand. Teller loam was collected from the top 20 cm of a Oklahoma State University research field near Perkins, Oklahoma. Dougherty sand was collected from about 3 meters below the soil surface in the barrow pit of Kerns Construction Company also near Perkins, Oklahoma. These two soils were chosen because they have much different physical and chemical properties. Teller loam has a moderate organic carbon content and Dougherty almost none. Neither soil has ever been exposed to anthropogenic organic compunds. Soils were air dried and mixed thoroughly to obtain a homogeneous mixture. Then air dried Teller loam was ground using a machine grinder and both soils passed through a 1-mm sieve (No. 18). Uniform moist soil was obtained by mixing air dried soil and a solution of calcium sulfate and sodium azide. Oven dried soil was mixed with air dried soil to obtain a soil with water content less than air dried water content. Sodium azide was used to kill microbes to avoid biodegradation of the toluene.

The characteristics of the experimental soils are summarized in Table 2-1. The specific area of the soil was determined using the BET water adsorption method (Quirk, 1955). Organic carbon was determined by the acid dichromate wet digestion method. Soil pH was measured in a 1:1 (by volume) soil/water suspension. The ammonium acetate method (Thomas, 1982) was used to determine the cation exchange capacity of the soils. The water contents of the soil samples (by weight) were determined by weighing the sample before and after drying for at least 24 hours in an oven at 105°C. Soil texture was determined by dry sieving.

Experimental Procedures

For each adsorption isotherm, five different sorbent masses were used with three replicates for each mass. Three blank vials were used as controls. The oven dry or moist sorbent was placed into oven dry clean glass EPA vials with volume of 40 mL. Sorbent masses ranged from 3 to 15 g with an interval of 3 g. 1.5 uL or 2 uL liquid pure toluene (depending on the adsorption capacity) was introduced into sample vials and control vials with a high precision gas-tight syringe. The vial was sealed immediately with a Teflon-lined rubber septum and threaded cap after delivering liquid pure toluene. With the rubber side against the cap and the Teflon side facing the soil no toluene would be adsorbed by rubber. Liquid toluene evaporated inside the vials quickly and produced a headspace concentration of between 20 and 40 mg/L, which is lower than the saturated toluene concentration of about 130 mg/L at 20°C. Thus, there was no toluene condensation inside the vials. All vials were tumbled about 36 hours in a constant temperature (21°C) and, after equilibration, the vials were removed from the tumbler and allowed to set still for another 12 hours. The vials were covered with paper to prevent photodecomposition of toluene. Fifteen microliters of the headspace was withdrawn from each vial using 25 uL gas-tight Hammilton syringes and analyzed immediately by a Hewlett Packard 5890 gas chromatograph (GC) with a flame ionization detector (FID). The GC column was 30 M x 0.53 mm x 1.5 mM J & W Scientific DB^{TM}-1 packed with dimethylpolysiloxane and was operated at 150°C for the oven and injector, and 225°C for the detector. Three gas samples were withdrawn and analyzed by GC for each vial and the average peak area was taken in the calculation.

Results and Discussion

The adsorption of toluene onto Teller loam soil at ten water contents was measured. Figures 2-2 to 2-10 present the experimental data and the vapor/solid partition coefficient K'_d as a function of water content. Figure 2-11 shows the experimental data and K'_d at saturated soil condition. The adsorption of toluene onto Dougherty sand at eight water contents and at saturated sand condition was measured. Figures 2-12 to 2-19 present the experimental data and the vapor/solid partition coefficient K'_d at different sand water contents, while Figure 2-20 presents the experimental data and K'_d at saturation. The raw data of all sorption tests are listed in Appendix B. The vapor/solid partition coefficient K'_d was obtained by calculating the slope of the linear relationship between variables X_{un} and Y_{un}. The liquid/solid partition coefficient K_d was calculated by equation (2-29). Table 2-2 shows the results for Teller loam, while Table 2-3 shows the results for Dougherty sand. The measured relationships between soil water content and the partition coefficients in Teller loam and in Dougherty sand are provided in Figures 2-21 and 2-22. Water content is in weight of water per weight of soil. The correlation coefficient r of soil sorption data of Teller loam decreases with the increasing soil water content. It is above 0.88 when soil water content is smaller than 6.58% g/g. The measured vapor/solid partition coefficient is quiet reliable for dry Teller loam. Soil sorption decreases rapidly with increasing water content and reaches a minimum when water content is larger than 6.58% g/g. The correlation coefficient decreases to about 0.6 with increasing water content, but the graphs still have a good linear relationship. The adsorption data of Dougherty sand at oven and air dry conditions shows a large adsorption capacity. When water content is greater than 0.74% g/g the soil sorption is around zero and several calculated liquid/solid partition coefficients are even negative. This is caused by measurement error in the GC, because the adsorption of sand is so small.

All data were obtained at a constant temperature of 20± 1°C. More data at different temperature will be helpful to determine if temperature affects K_d.

Sorption Mechanism The mechanism of organic vapor sorption onto soil is complicated. Assuming there are two types of sites, organic matter and mineral, it is apparent that not only organic matter sites, but also mineral sites can adsorb organic vapor. This can be verified by the large adsorption coefficient in dry Teller and Dougherty shown in Figures 2-21 and 2-22. In the absence of water, mineral sites adsorb the organic compound. Dougherty sand has almost no organic matter but the adsorption when water content is below 1.64% g/g is quite significant. Figure 2-20 and 2-21 show that organic vapor adsorption onto soil is strongly dependent on the soil water content when soil water content is lower than a "critical water content." Above the "critical water content" the partition coefficient equals the saturated partition coefficient. The liquid/solid partition coefficient of Teller loam at oven-dry condition is as high as 511 mL/g, which is 1280 times the saturated liquid/solid partition coefficient of 0.4 mL/g. When water content increases, the soil sorption decreased rapidly until water content reaches about 6.58% g/g. The adsorption of oven-dry Dougherty sand is 9.93 mL/g and decreases dramatically with increasing water content until it reaches zero at 1.64% g/g.

By the theory of three stages of soil sorption proposed in this research, the liquid/solid partition coefficient is suitable for stage 3 and stage 2 soil, but not suitable for stage 1 soil. In stage 1 soil the vapor/solid partition coefficient may describe the soil sorption better than the liquid/solid partition coefficient because some dry sites are directly expose to gas phase, and Henry's Law may be invalid due to the insufficiency of water molecules. As soil water content of one monolayer water molecule coverage is too small and difficult to obtain without special laboratory instrument, stage 1 is a conceptual stage and not validated by data.

Critical Water Content By the analysis above the critical water content is a breakpoint of the constant and variable liquid/solid partition coefficient for the soil. Each soil has a different critical water content for the same organic compound. For toluene the measured critical water content is about 6.58% g/g in Teller loam and about

1.64% g/g in Dougherty sand. Water content of 6.58% g/g in Teller loam corresponds to about 6 layers of coverage of water molecules and 1.64% g/g in Dougherty sand corresponds to about 3 layers of coverage of water molecules. The number of water molecule layers was calculated based on the measured soil specific surface area assuming that a water molecule would occupy a surface area of 10.8 x 10^{-20} m^2 (Livingston, 1949). The number of water molecules per gram is about 3.346 x 10^{22} and one gram could occupy a surface area of 3613.7 m^2. Therefore the number of water molecule layers (N) in moist soil can be calculated by,

$$N = \frac{\theta_w}{\frac{S}{3613.7}} = 3613.7\frac{\theta_w}{S} \tag{2-30}$$

where θ_w is the soil water content in g water/g soil, and S is the soil specific surface area in m^2/g soil.

Based on their experimental results Ong and Lion (1991a) concluded that in the region of soil water content less than five layers surface coverage by water the sorption of TCE vapor was decreased with increasing water content and attained a minimum value at about 5 layers water molecule coverage. This means that their measured "critical water content" of TCE onto five simulated soils was five layers water molecule coverage. Petersen et al. (1994) found that for water contents higher than four molecular layers of water surface coverage, vapor/solid partition coefficient were consistent with values predicted by Henry's Law constant and saturated liquid/solid partition coefficient. For less than four molecular layers of water, sorption increased by orders of magnitude. This means that their measured "critical water content" is four layers of water coverage. This conclusion were obtained based on the adsorption of freon, toluene, and TCE onto Yolo silt loam. The "critical water content" is independent on the volatile organic compound. Table 2-4 shows the measured "critical water content" of several researchers. From the experimental data of Ong (1991) and Peterson (1994) and Yu (1995) it can be found that the value of "critical water content" is only dependent on the soil particle size but not the organic compound. The "critical water content" can be determined by

$$\theta_w' = \frac{N \cdot S}{3613.7} \tag{2-31}$$

where N is 3 for sand, and N is about 6 for silt loam, loam or high surface area soil. Attention must be paid to the measurement of soil specific surface area. Different methods of measuring soil surface area may have different results. The result of BET method is suggested in equation (2-31).

Conclusions

Soil sorption in low water content soil observed in this research varies significantly with the two soils tested and the water content. The adsorption of an organic compound onto low water content soil may be several orders of magnitude greater than the adsorption onto high water content soil. Therefore, care must be paid to the use of saturated liquid/solid partition coefficient in the modeling and simulation of organic vapor transport in low water content soil. The use of saturated liquid/solid partition coefficient in low water content soil may predict a much quicker transport process of organic vapor than the real process. When soil water content is smaller than "critical water content", soil sorption must be determined by experiment. There is no model available so far to predict soil sorption for all soils and all organic compounds. More work is needed to develop a soil sorption model.

Soil "critical water content" is defined as the content below which the saturated liquid/solid partition coefficient can not be used. It exists in all soils, even in sand. Data collected here and by Ong (1991a) and Petersen (1994) indicates soil "critical water content" varies only with soil specific surface, but the data set is limited in size and materials. The method of determining "critical water content" proposed in this research is semi-empirical. Further studies with different sorbent and sorbates are needed to verify this conclusion.

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Table 2-1

CHARACTERISTICS OF THE EXPERIMENTAL SOILS

Characteristics	Teller Loam	Dougherty Sand	Analysis Method
Texture[+]			Dry sieving
sand (%)	52	98	
silt (%)	31	2	
clay (%)	17		
Particle Density (g/cm^3)	2.65	2.65	
pH	6.4	5.9	Glass electrode (1:1 soil:water)
Organic C (%)	1.7	0.1	Acid dichromate wet digestion
Surface Area (m^2/g)[+]	37.8	21.8	BET-water
CEC (meq/100g)[+]	~14	~5	Ammonium acetate

[+] From Allred (1995)

Table 2-2

RESULTS OF TELLER LOAM SORPTION TESTS

Moisture g/g %	Vapor/Solid Partition Coef. K_d' mL/g soil	Liquid/Solid Partition Coef. K_d mL/g soil	Correlation Coefficient r
0	1960	521	0.96
1.85	28.7	7.58	0.96
2.57	8.74	2.29	0.96
3.54	4.49	1.15	0.97
3.89	2.85	0.72	0.95
5.02	2.61	0.64	0.85
6.58	1.74	0.40	0.88
9.88	1.84	0.39	0.71
12.82	1.71	0.32	0.62
saturated		0.40	0.79

Table 2-3

RESULTS OF DOUGHERTY SAND SORPTION TESTS

Moisture g/g %	Vapor/Solid Partition Coef. K_d' mL/g soil	Liquid/Solid Partition Coef. K_d mL/g soil	Correlation Coefficient r
0	37.49	9.935	0.93
0.12	3.270	0.865	0.94
0.74	0.017	-0.002	0.25
1.64	0.0058	-0.015	0.02
1.74	0.0073	-0.015	0.16
5.11	0.065	-0.034	0.24
7.95	0.44	0.037	0.61
11.23	0.402	-0.006	0.27
saturated		0.00	0.08

Table 2-4

RESULTS OF MEASURED CRITICAL MOISTURE

Author	Year	Organic Compound	Sorbent	Critical Moisture Layers of Water Molecules
Ong et al.	1991	TCE	Alumina	5
			Humic Coated Alumina	
			Iron Oxide	
			Montmorillonite	
			Kaolinite	
Petersen et al.	1994	Freon	Yolo Silt Loam	4
		Toluene		
		TCE		
Yu	1995	Toluene	Teller Loam	6
			Dougherty Sand	3

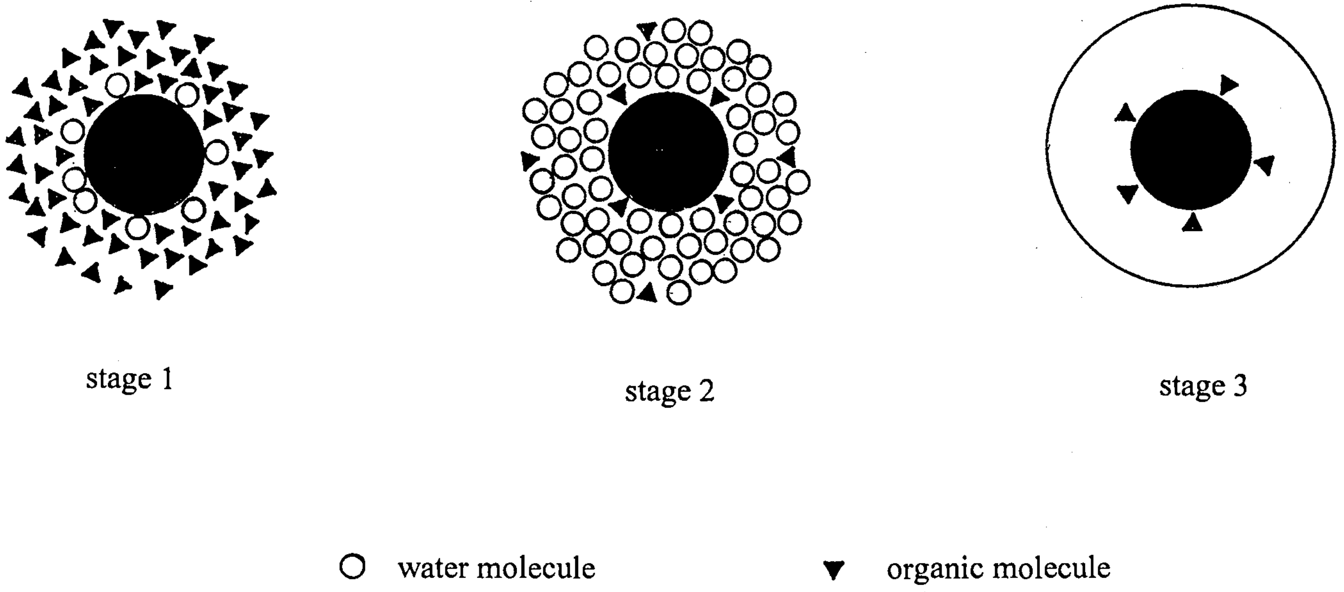

Figure 2-1. Three stages of soil sorption.

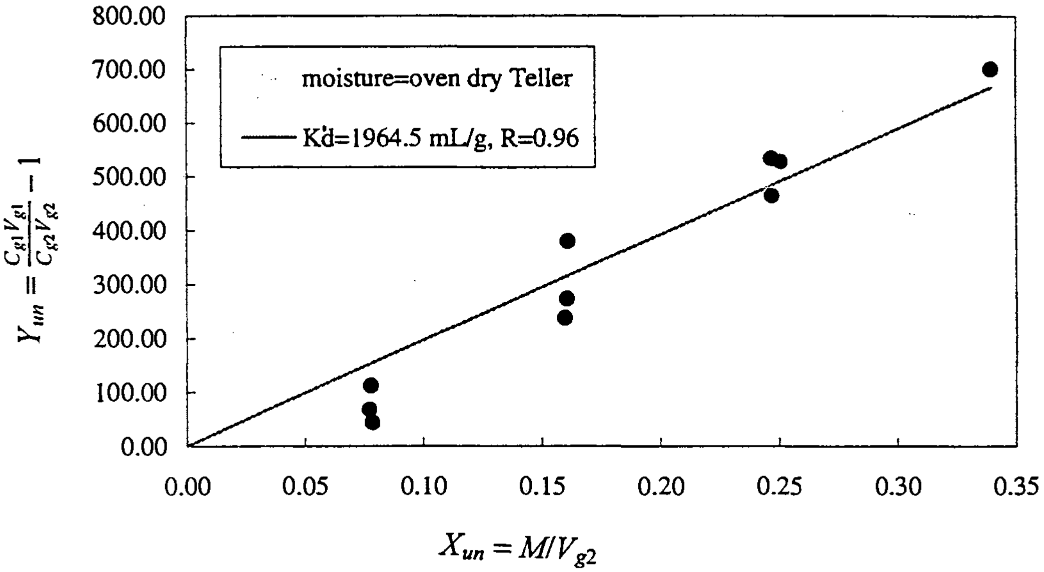

Figure 2-2. Vapor/solid partition coefficient of Teller at oven dry.

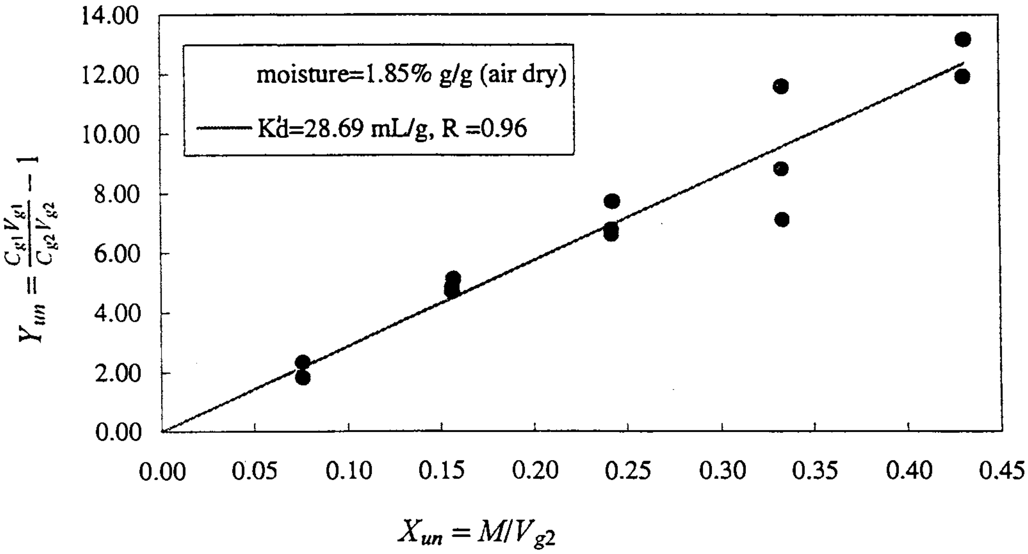

Figure 2-3. Vapor/solid partition coefficient of Teller at 1.85% moisture.

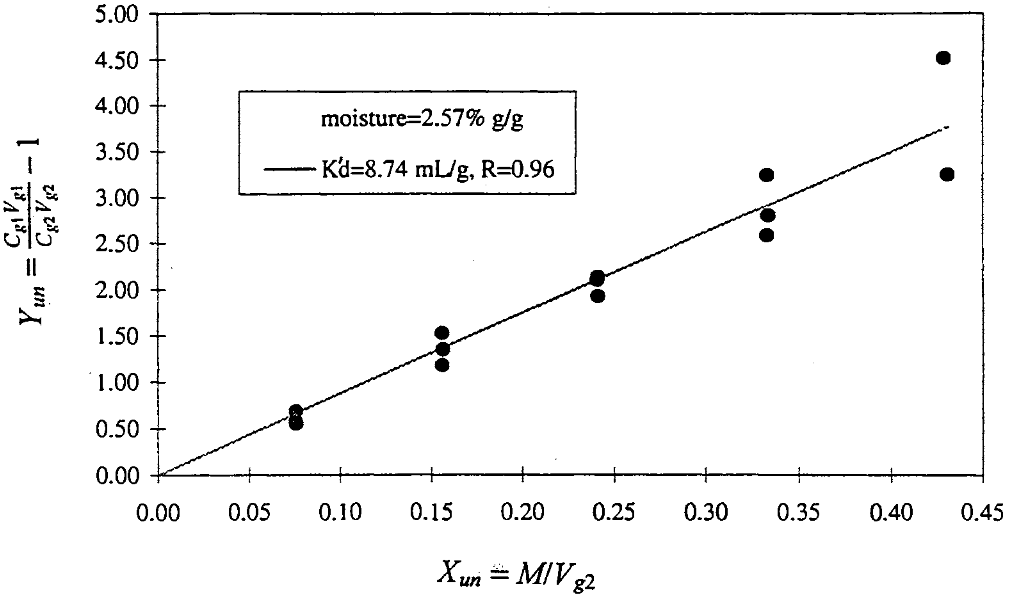

Figure 2-4. Vapor/solid partition coefficient of Teller at 2.57% moisture.

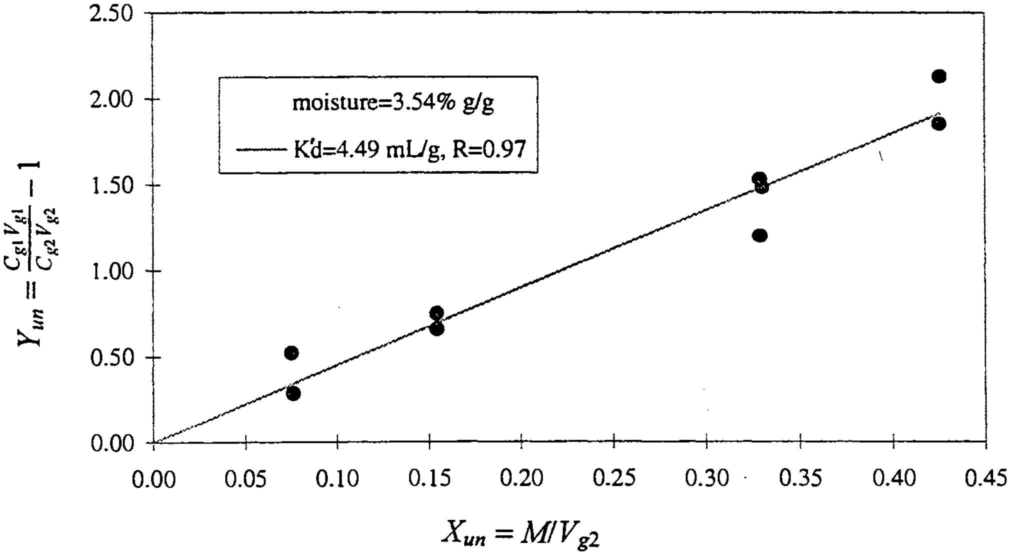

Figure 2-5. Vapor/solid partition coefficient of Teller at 3.54% moisture.

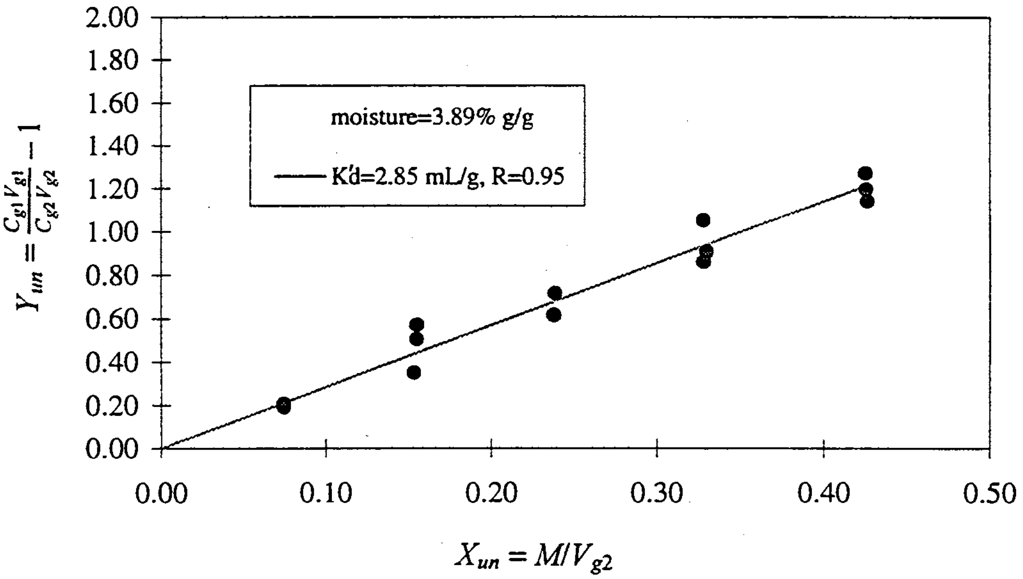

Figure 2-6. Vapor/solid partition coefficient of Teller at 3.89% moisture.

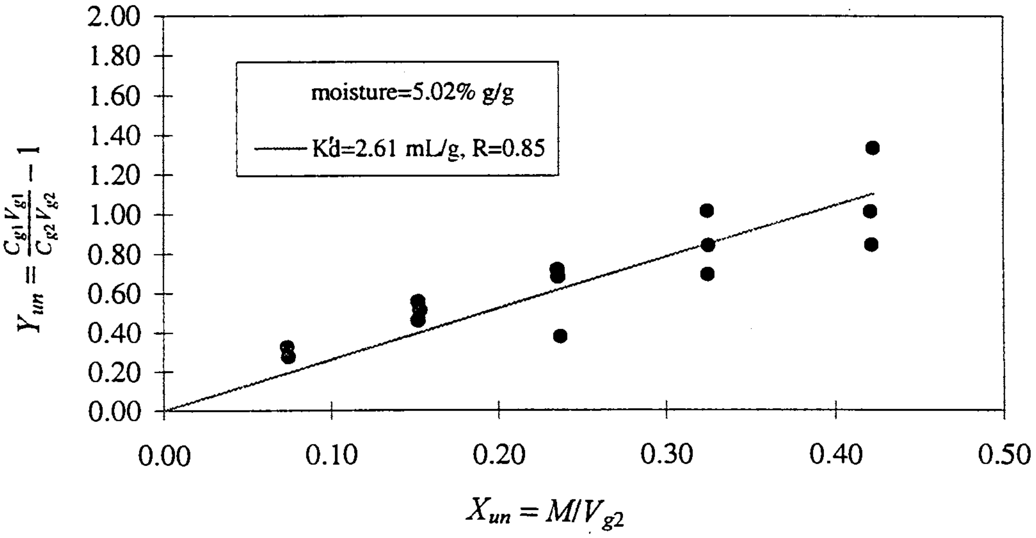

Figure 2-7. Vapor/solid partition coefficient of Teller at 5.02% moisture.

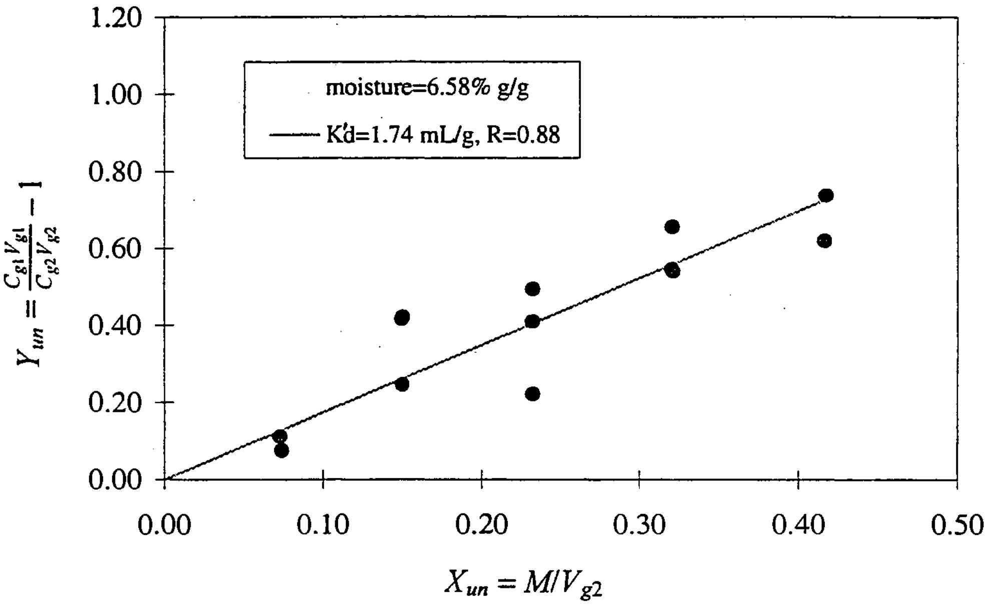

Figure 2-8. Vapor/solid partition coefficient of Teller at 6.58% moisture.

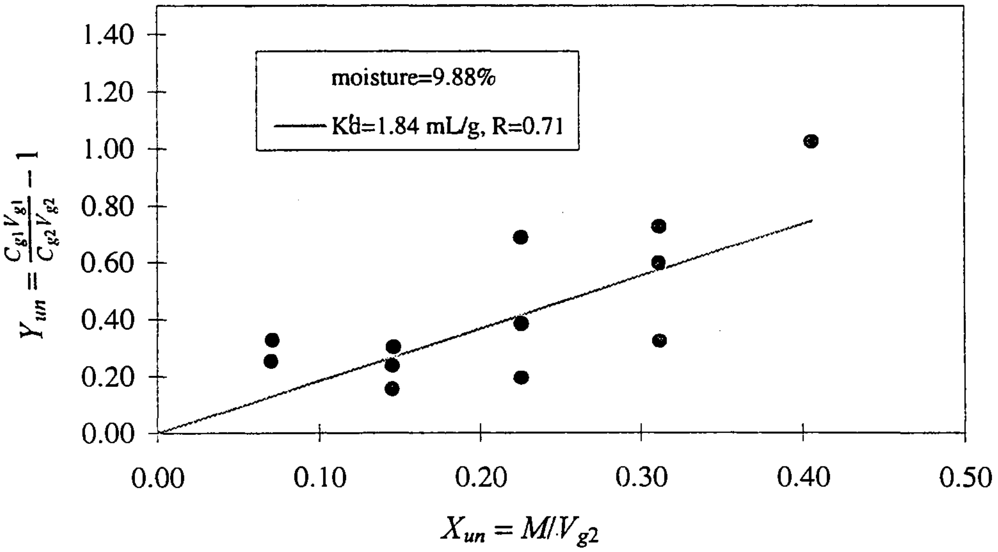

Figure 2-9. Vapor/solid partition coefficient of Teller at 9.88% moisture.

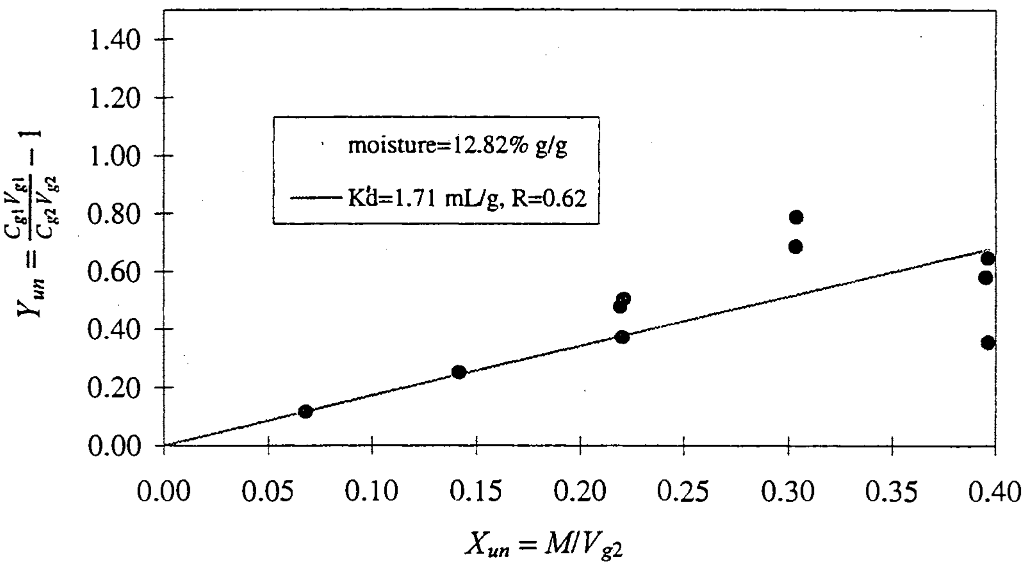

Figure 2-10. Vapor/solid partition coefficient of Teller at 12.82% moisture.

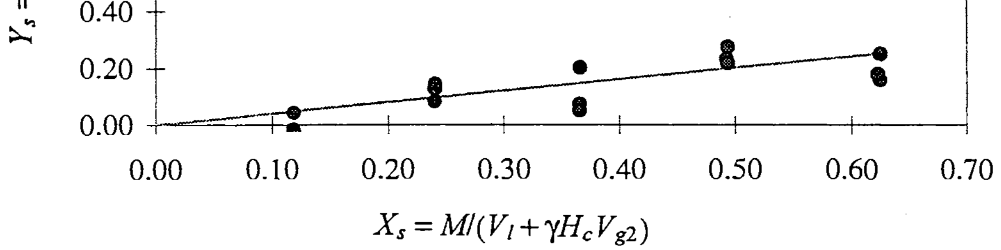

Figure 2-11. Saturated partition coefficient of Teller loam.

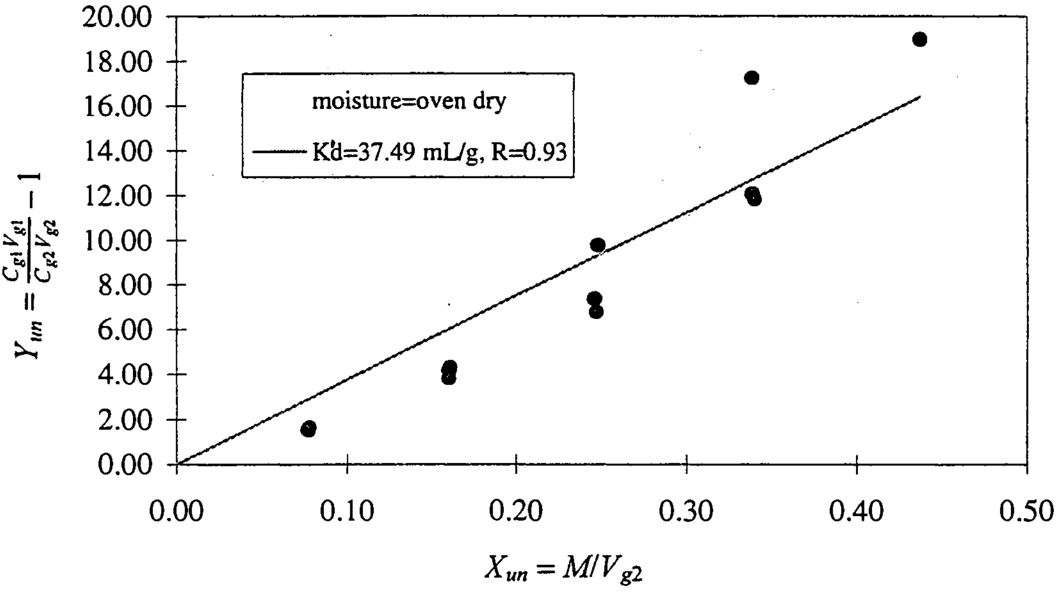

Figure 2-12. Vapor/solid partition coefficient of Dougherty at oven dry.

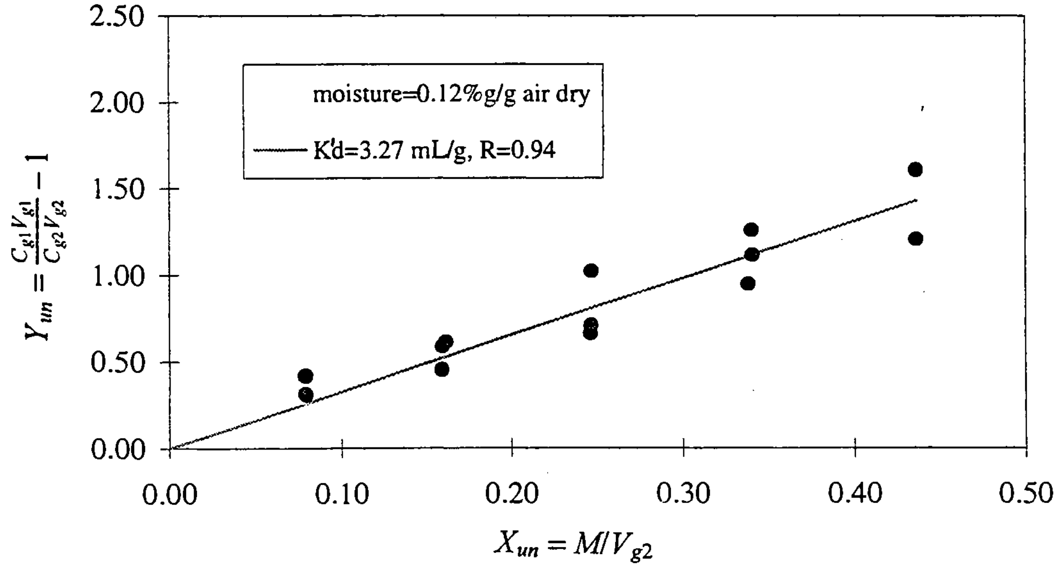

Figure 2-13. Vapor/solid partition coefficient of Dougherty at 0.12% moisture.

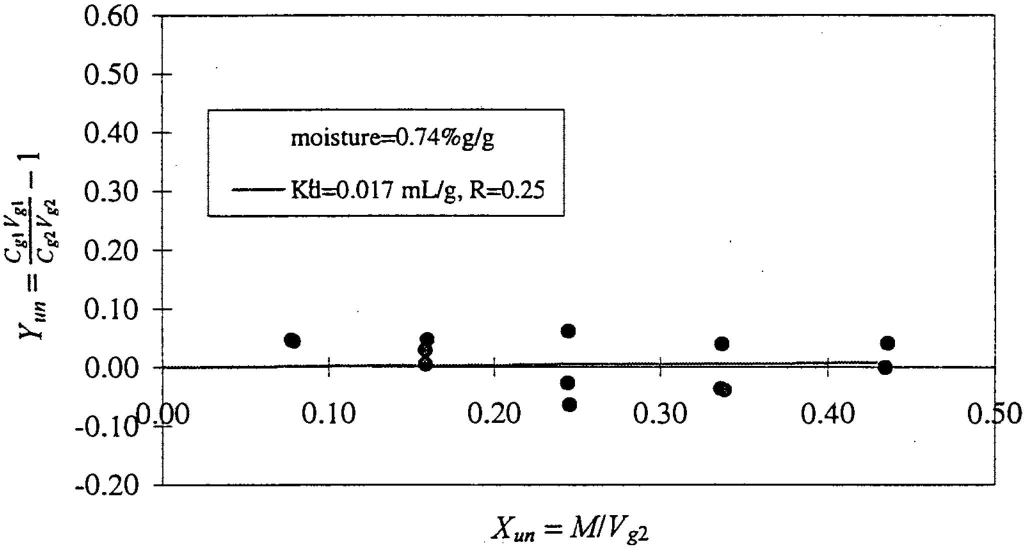

Figure 2-14. Vapor/solid partition coefficient of Dougherty at 0.74% moisture.

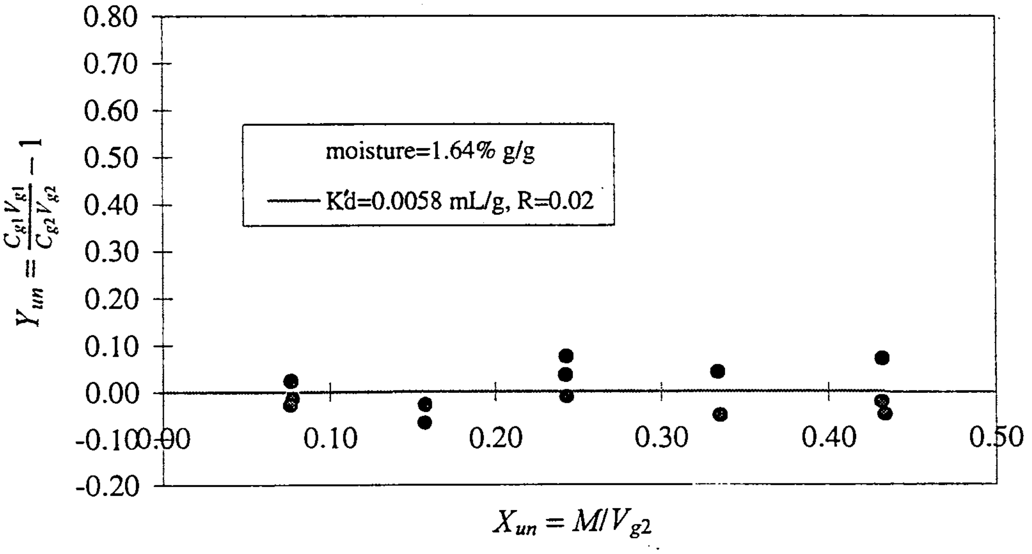

Figure 2-15. Vapor/solid partition coefficient of Dougherty at 1.64% moisture.

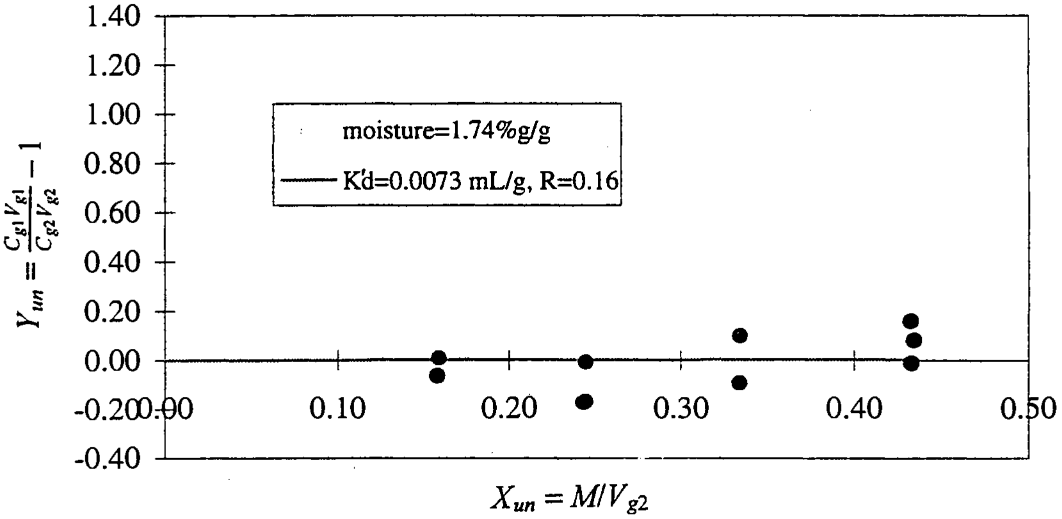

Figure 2-16. Vapor/solid partition coefficient of Dougherty at 1.74% moisture.

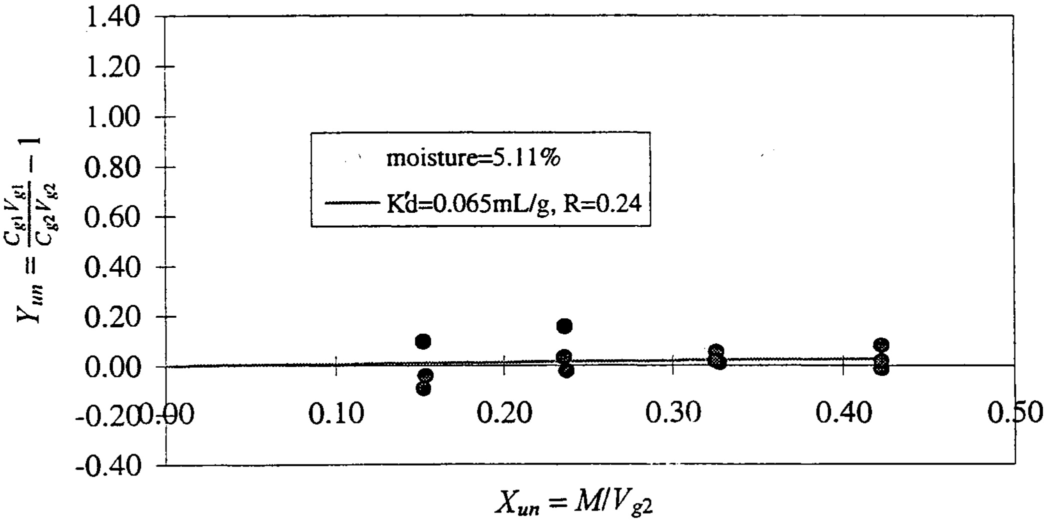

Figure 2-17. Vapor/solid partition coefficient of Dougherty at 5.11% moisture.

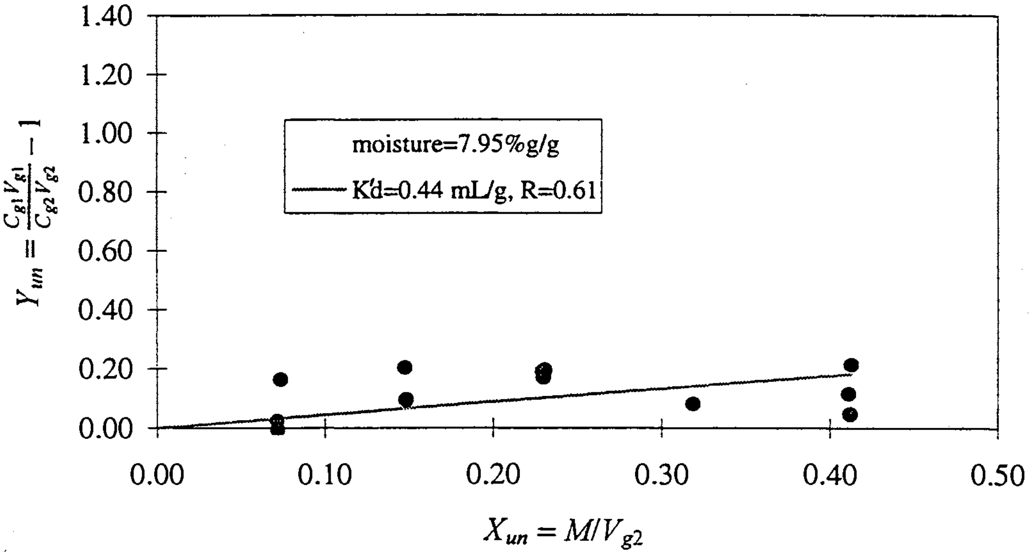

Figure 2-18. Vapor/solid partition coefficient of Dougherty at 7.97% moisture.

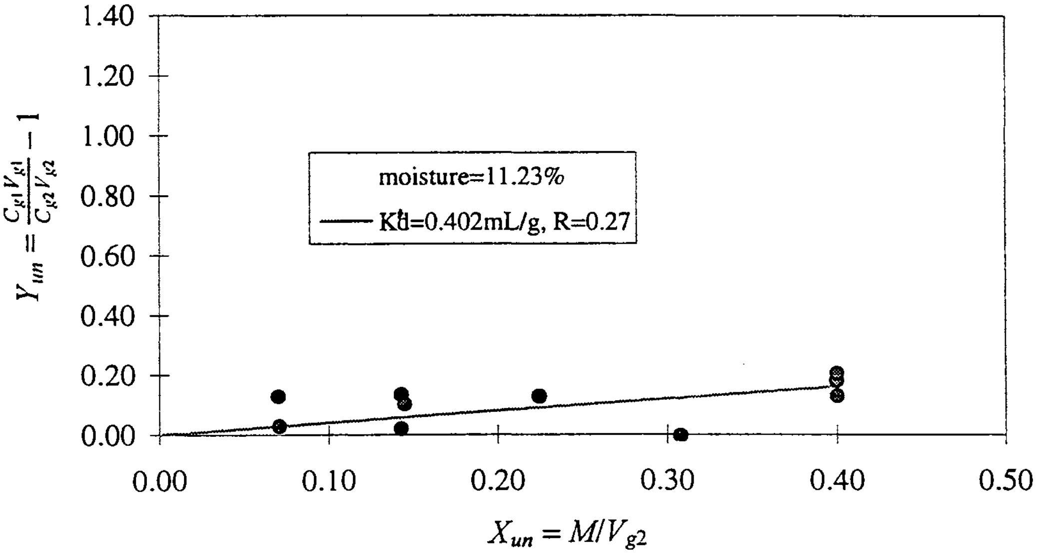

Figure 2-19. Vapor/solid partition coefficient of Dougherty at 11.23% moisture.

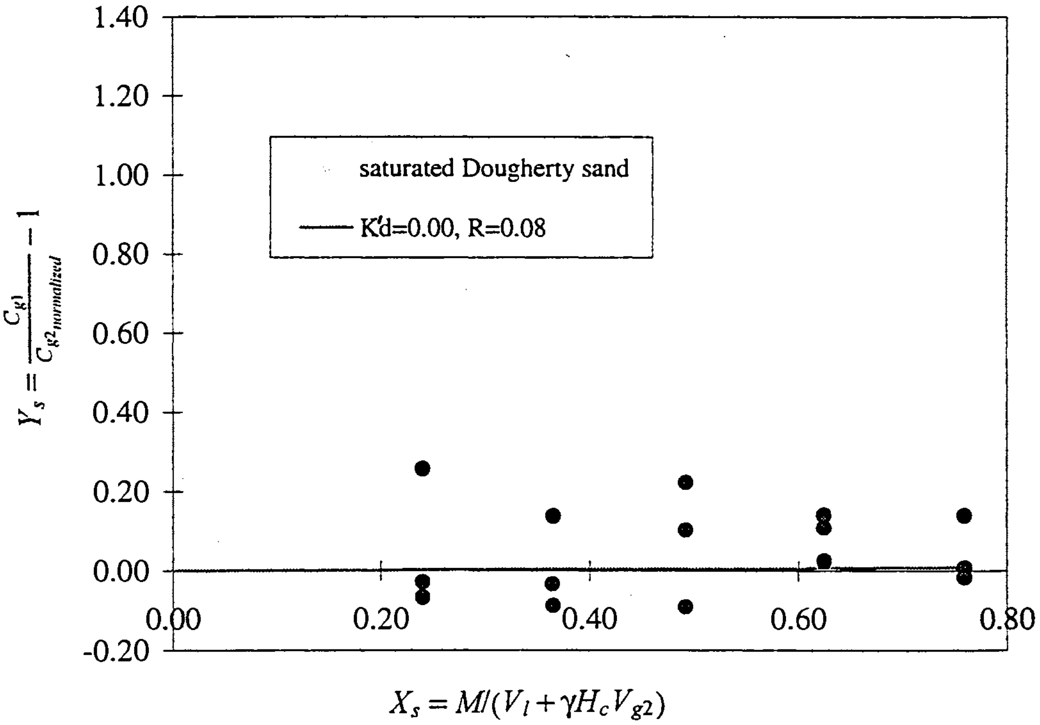

Figure 2-20. Saturated partition coefficient of Dougherty sand.

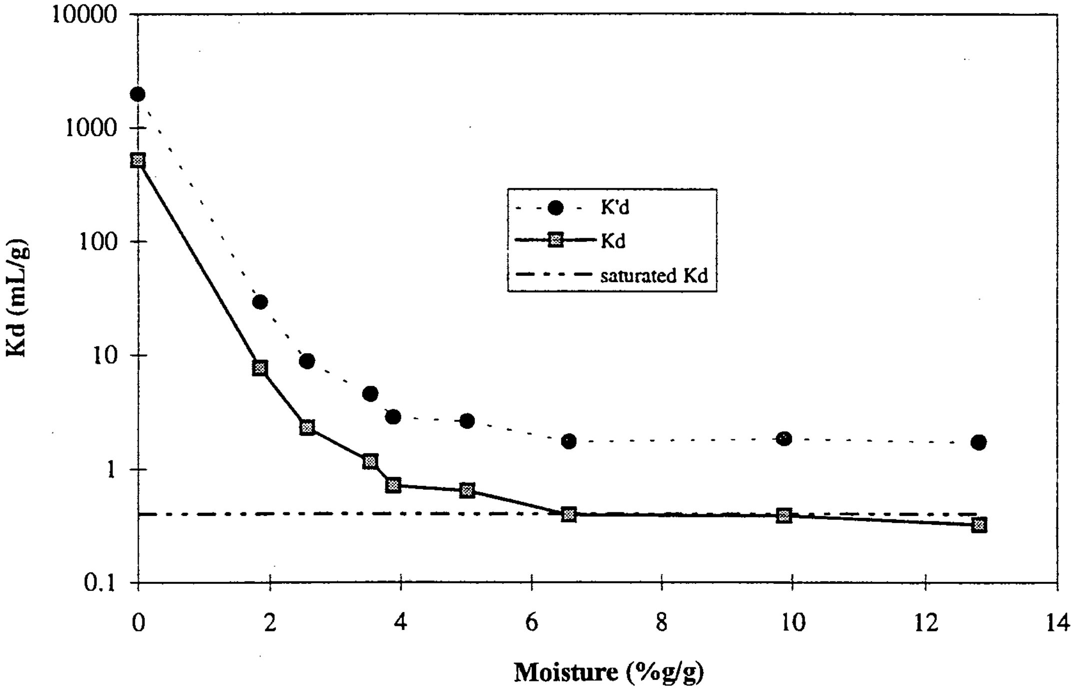

Figure 2-21. Measured relationships of moisture and partition coefficients of Teller loam.

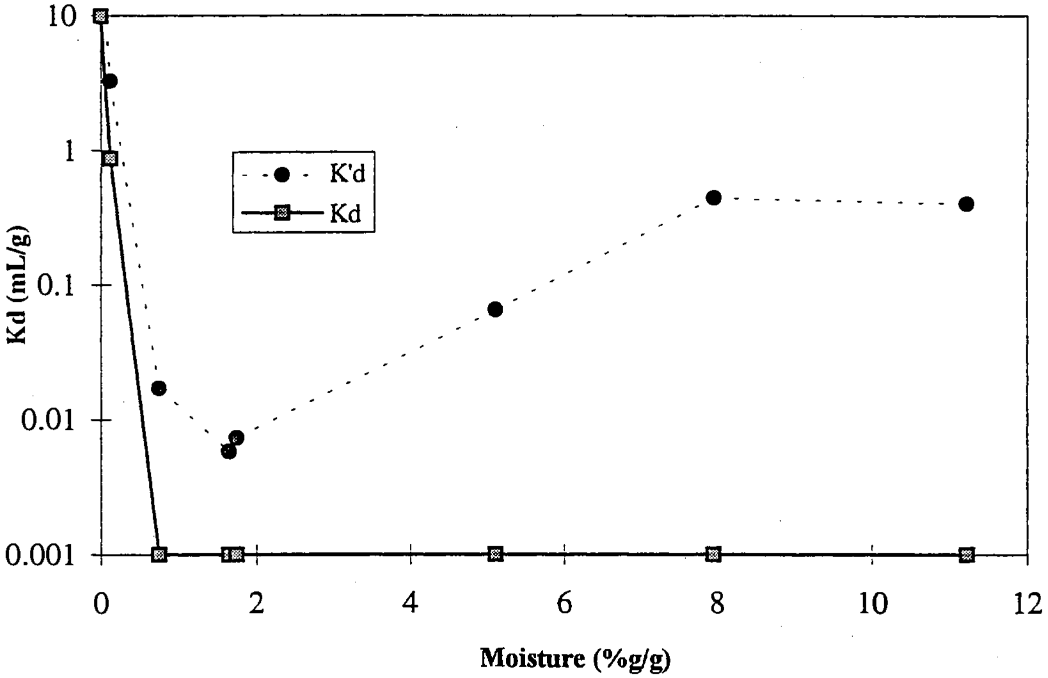

Figure 2-22. Measured relationships of moisture and partition coefficients of Dougherty sand.

Chapter III

VOLATILE ORGANIC VAPOR PHASE DIFFUSION IN LOW WATER CONTENT SOILS

Abstract

Vapor phase diffusion is an important process affecting the transport and fate of organic vapor in unsaturated soil. Vapor phase diffusion is the mass transport resulting from the concentration gradient of organic chemical in gas phase. Gaseous diffusion can be affected by many factors including soil temperature, water content, porosity, contaminant characteristics, and soil properties. Many researches have been done on this subject and empirical or semi-empirical diffusivity models have been developed to predict the diffusion coefficient in unsaturated soil. Based on the area "available" for flow in a porous medium and the probability of pore continuity in adjacent planes Millington and Quirk (1961) proposed a diffusivity model, which is considered to give the best predictions of the vapor diffusivity and is widely used in the modeling and simulation, but few experimental data are available to verify it. The objectives of this chapter are (1) to measure the diffusivity at different water contents in two soils, and (2) to test the Millington-Quirk model. A 25 cm x 45 cm PVC column was packed with toluene contaminant and soils and a gas chromatograph was used to measure vapor

concentrations of gas samples taken from different sample locations along the soil column. The experimental data was analyzed using optimization theory to estimate the vapor phase diffusion coefficient. It is found that the Millington-Quirk diffusivity model is a good predictor for soil or sand except in extremely dry soil ($\theta < 0.002$). In extremely dry soil, the Millington-Quirk model slightly underpredicted the diffusivity and the simulation using Millington-Quirk diffusivity would result in a slower prediction of transport of volatile organic compounds.

Introduction

The vapor phase diffusion coefficient is a function of temperature, porosity, fluid content and pore size distribution of porous media. It decreases rapidly with increasing water content and decreasing porosity. The cross-sectional area "available" for flow and a path-length are regarded as common determinants of diffusivity. Yue (1995) performed a parameter sensitivity analysis of a vapor transport model for the unsaturated zone. The analysis of parameters of water phase tortuosity, air phase tortuosity, Henry's constant, and soil partition coefficient indicated that the latter three have a significant impact on volatile organic transport model output. The air phase tortuosity and soil partition coefficient are more sensitive at their lower range. Peterson et al. (1988) also reported the high sensitivity of gaseous diffusion coefficient. In low water content soil the air-filled porosity is relatively larger than the high water content soil and the vapor diffusion inside soil could be a predominant process of vapor transport. So vapor phase diffusion coefficient is important to obtain accurate predictions of volatile contaminant transport in low water content soil.

Based on the area "available" for flow in a porous medium and the probability of pore continuity in adjacent planes Millington and Quirk (1961) proposed a diffusivity model:

$$\frac{D_g}{D_o} = \frac{(\varepsilon)^{10/3}}{\phi^2} = \frac{(\phi-\theta)^{10/3}}{\phi^2} \tag{3-1}$$

where D_g is the vapor phase diffusion coefficient in porous media, D_o is the diffusion coefficient in pure air, ϕ is the volumetric total porosity, θ is the volumetric water content, and ε is the volumetric gas-filled porosity. This model has been widely used (Baehr, 1987; Karimi et al., 1987; Shoemaker et al., 1990; Gierke et al., 1990; Culver et al., 1991; Amali and Rolston, 1993; Yue, 1995) since it was proposed. Many other diffusivity models have been proposed since 1904 to predict the gaseous diffusion coefficient in porous media. Each of them may be suitable in some specific conditions, however, no one can give the best prediction in all soil conditions. The major diffusivity models are listed in Table 3-1. In the table τ is the tortuosity which accounts for the tortuous path of real pores, δ is the constrictivity which accounts for the fact that the cross section of a pore segment varies over its length, ε_p is the intercrumb porosity, D' is the diffusivity when the intercrumb pore space is completely drained and the pores in the crumbs are water-filled, and u and v are fitting parameters.

Some research has been done to compare those diffusivity models (Sallam et al., 1984; Collin and Rasmuson, 1988; Xu et al., 1992; Petersen et al., 1994), but the

Table 3-1

OVERVIEW OF MAJOR DIFFUSIVITY MODELS

Author	Year	Model	Conditions
Buckingham	1904	$\frac{D_g}{D_0} \propto \varepsilon^2$	moist and dry soils
Penman	1940	$\frac{D_g}{D_0} = 0.66\varepsilon, \ (0 < \varepsilon < 0.6)$	moist and dry porous solids
Marshall	1959	$\frac{D_g}{D_o} = \varepsilon^{\frac{2}{3}}$	for porous media
Millington and Quirk	1959	$\frac{D_g}{D_o} = \frac{(\varepsilon)^{10/3}}{\phi^2}$	for porous media
Currie	1960	$\frac{D_g}{D_o} = \left(\frac{\delta}{\tau^2}\right)_{\theta=0} \phi(1-\theta)^4$	for solid particle
		$\frac{D_g}{D'} = \left(\frac{\varepsilon}{\varepsilon_p}\right)^4$	for porous particle, intercrumb pores were drained
Troeh et al.	1982	$\frac{D_g}{D_o} = \left(\frac{\varepsilon-u}{1-u}\right)^v$	for all soils
Sallam et al.	1984	$\frac{D_g}{D_o} = \frac{\varepsilon^{3.1}}{\phi^2}$	for porous media

conclusions are not consistent with each other. Data presented by Shearer et al. (1973) and Sallam et al. (1984) indicated that Millington-Quirk diffusivity is an appropriate representation. Collin and Rasmuson (1988) did a comparison among several diffusivity models using experimental data from Fluhler, Lindstrom, and McAfee for different materials at various water contents. He found that the estimation methods proposed by Millington and Shearer (1971) give the best predictions of the effective diffusivity. Nielson et al. (1984) point out that significant differences in estimated diffusion coefficients occur depending on the assumed model. They present a relatively complicated description of the diffusion coefficient based on pore space occupation by air and water phases to describe the diffusion of radon, a substance that significantly partitions in both air and water.

Peterson et al. (1988) measured the diffusion coefficient of TCE in the simulated aquifer material and he indicated that the Millington-Quirk model can be in error by as much as 400%, but his experiment used a simulated soil (alumina oxide coated with humic acid). Ryan and Cohen (1990) compared three diffusivity models using the experimental data of Ehlers et al. (1969) and Shearer et al. (1973). They concluded that the Millington-Quirk model was incapable of describing the diffusion coefficient over the entire range of water content, although it was adequate below a volumetric water content of 0.3. Xu et al. (1992) measured the diffusion coefficients of N_2 in four soils at four water contents and found that at an air-filled porosity of ~10%, the diffusion coefficient was close to zero, reflecting a discontinuity in the pathways at an air-filled pore space of 10% or lower. The exponent of the Millington-Quirk model corresponded to 3.29 (smaller than 3.33) for their data set and 2.58 in low air-filled porosity ($\varepsilon<0.15$). This means Millington-Quirk underpredicted D_g slightly when air-filled porosity is greater than 0.15, and significantly underpredicted when air-filled porosity is smaller than 0.15. Petersen et al. (1994) measured the diffusion coefficients of freon, TCE, and toluene. He also concluded that the Millington-Quirk model underestimates the measured data, but he indicated that at low air contents, the Millington-Quirk model is fairly accurate. This is in agreement with what Sallam et al. (1984) found for low air-filled porosity ($\varepsilon<0.15$), but is not consistent with the result of Xu et al. (1992). Their data were best fitted by the model introduced by Troeh et al. (1982).

The inconsistent results reported by previous researchers may be caused by inaccurate experimental data. There can be difficulty in keeping volatile gases from escaping experimental apparati. The experimental methods used by researchers were different. Most of the experiments used a diffusion chamber and measured the concentration change of the chemical vapor in the diffusion chamber. The size of soil columns was usually less than 8 cm in diameter and 7 cm in length. Most experiments applied GC or GC/MS to analyze the gas samples taken from the diffusion chamber. There were several common problems that may have caused data error in the previous experiments:

1) Boundary Effects. Almost all materials will adsorb organic vapor to a certain degree, so data error may be caused by the adsorption to the diffusion chamber or the sealing material. This is called boundary effects in this research.

2) Escape of Organic Vapor. It is usually difficult to keep organic vapor from escaping from the soil column. Leaks may go undetected.

3) Pressure Problem. The chemical gas flow introduced into a diffusion chamber may change the pressure of the chamber and form a pressure gradient in the soil column, greatly increasing mass transport.

To overcome these problems and improve the accuracy of diffusion data a large diameter PVC column and the method of direct sampling of gas phase from the soil column were used in this research.

Materials and Experimental Apparatus

To minimize the boundary effect the experimental materials were chosen carefully. Four materials: PVC, rubber, viton, and aluminum, were tested for their adsorption of organic vapor. Each material was tested in two environmental conditions, with and without water vapor. The tested material was placed into well-sealed EPA vials, four of them with 5 mL 0.01N calcium sulfate solution and four without. Then 2 uL pure toluene was introduced into the vials. After equilibrium was reached, the headspace toluene concentration was measured and the adsorption mass to material per mass of material was calculated by comparing the headspace toluene concentration with that in a blank vial. It was found that the adsorption on all materials with water is much smaller than without water. The sorption of PVC, viton, and aluminum with water were negligible, but the adsorption on rubber with or without water was large and could not be

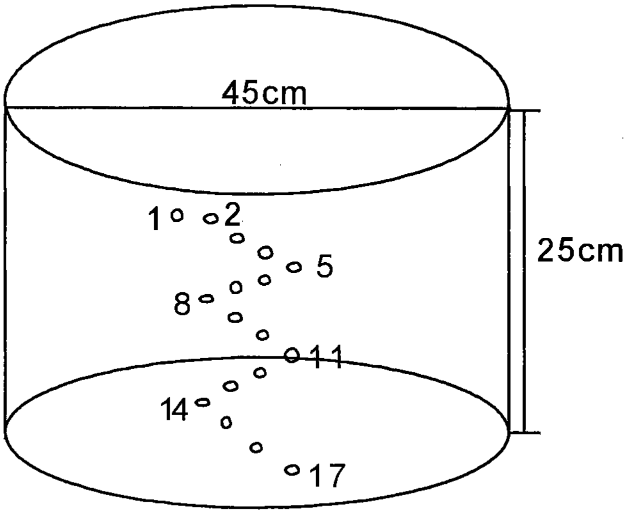

Figure 3-1. PVC Cylinder and Locations of Sampling Ports.

Table 3-2

TOLUENE ADSORPTION OF MATERIALS

Materials	with water mg/g	without water mg/g
Rubber	0.99	1.78
PVC	0.2	1.0
Viton	0.05	0.2
Aluminum	0.02	0.1

ignored. The sorption test results of four materials are shown in Table 3-2. Therefore, three materials: PVC, viton, and aluminum, were chosen for use in this experiment.

A PVC cylinder 45 cm in diameter by 25 cm in height formed the soil column. It was closed at the bottom and open at the top. Seventeen sampling ports, 1.5 cm in diameter were drilled 1.5 cm apart on a zig-zag pattern for sampling convenience. The ports were covered by a viton gasket and secured by a mounting bracket against the column with screws. Port 1 and port 2 were drilled at the same level, 3 cm from the top, for the convenience of top sealing. The sampling ports were used to take both gas samples during the tests and soil samples after the experiment. Figure 3-1 shows the PVC cylinder and the locations of sampling ports. The bottom plate and sampling ports were gas tight and after packing the soil and contaminating with toluene, the top was covered with aluminum foil.

Soils used in this experiment were the same as in the adsorption experiment, Teller loam and Dougherty sand. Soils were prepared following the same procedures as in Chapter 2, air drying, removal of roots, leaves, and other organic matter, and then grinding to less than 1 mm. The physical and chemical characteristics of soils are listed in Table 2-1. The large amount of uniform moist soil was obtained by mixing air-dry soil with 0.01N $CaSO_4$ and 1% NaN_3 (by weight) solution in ten five-gallon metal barrels. At least 24 hours was allowed to let water content equilibrate and to allow any microbes to die.

Experimental Procedures

Paking Soil Column The soil column was hand packed uniformly in density in lifts of 2.5 cm height. During the packing operation 25 cm long stainless tubing 1.5 mm in outer diameter was inserted into the column through the viton gasket of the sampling ports to prevent the clogging of the sampling needle. The tip of each tube was placed in the middle of the column and at the designed depth as the packing proceeded from bottom to top. Six holes, about 0.5 mm in diameter, were drilled around the tip of each tube to allow the gas phase to enter and the tube was crimped just in back of the holes to give a metal-to-metal seal against the gas sampling syringe needles. A 5 kg, round 10 cm hammer wrapped with aluminum foil was used to pack the soil to achieve the required porosity or density. Before adding another lift the soil surface was loosened by a small rake to minimize layering. Upon completion three dishes with pure toluene solution were set on the top of the soil to contaminate the soil, and the column top sealed rapidly with aluminum foil. Gas-tight syringes with 22s gauge needles approximately 23 cm long were inserted into the stainless tubes immediately after sealing the column top. The column was allowed to sit as the toluene volatilized into the soil until gas samples from the ports showed that the toluene concentration in the column was uniform. This usually took from 24 hours for Dougherty to several days for Teller.

Sampling and Analysis After a uniform gas concentration was achieved, the aluminum foil cover was removed and the toluene allowed to volatilize from the column. Gas samples were removed from each of the seventeen sampling locations using gas-tight syringes and analyzed on a Hewlett Packard 5890 Series II gas chromatograph (GC) for toluene concentration every few hours. When a sample was taken, the syringe plunger was pushed in and out slowly several times before about a 15 uL gas sample was drawn slowly. The needle barrel was unscrewed from the needle in the column and a clean

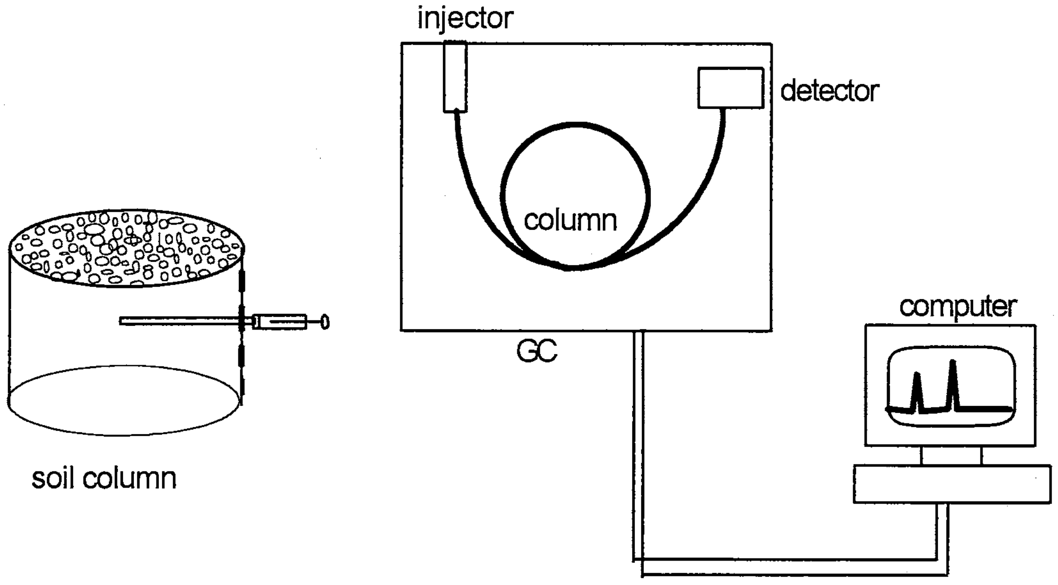

Figure 3-2. Experimental apparatus.

barrel was immediately screwed onto the soil needle. The collected sample had a 22s needle screwed on and gas volume reduced to 10 uL for immediate injection into the GC. After injection the syringe was flushed with methanol and dried with a heated vacuum syringe cleaner for additional use during the experiment. The GC has a flame ionization detector (FID), direct injector, megabore (0.530 mm) capillary column, and a microcomputer with HP Chemstation™ interface software. The GC was operated at 150°C for oven and injector, and 225°C for the FID detector. All data was collected by computer and reduced by the Chemstation software. The experimental apparatus is shown in Figure 3-2. All packing and sampling processes were carried out in a constant temperature of 21 ± 1°C.

Making Standards The GC required calibration at every use. The headspace method of making standards proposed by Roll (1995) was adapted in this research. The external standards were made up in the concentration range of the linear response of the GC and a calibration curve was determined through linear regression. Three 500 mL glass bottles and two 40 mL EPA glass vials were used to make standards. The large bottles were used for low concentration standards, while the EPA vials were used for high concentration standards. $CaSO_4$ solution was placed in the bottles or vials and then pure toluene was injected into each. After 24 hours, the partition of toluene between liquid phase and air phase reached equilibrium and the toluene concentration in the headspace could be calculated by Henry's constant and the known total mass injected into each container. By mass balance,

$$M_T = C_l V_l + C_g V_g \tag{3-2}$$

and by Henry's Law,

$$C_l = \frac{C_g}{H_c} \tag{3-3}$$

where M_T is the total toluene mass injected into each container, C_g and C_l are the toluene concentrations in the air phase and liquid phase respectively, V_g and V_l are the volumes of liquid phase and air phase, and H_c is the Henry's constant. Substituting (3-3) into (3-2) and rearranging yields,

$$C_g = \frac{M_T H_c}{V_l + H_c V_g} \tag{3-4}$$

The data for standards preparation is listed in Table 3-3.

Calculation of Vapor Phase Diffusion Coefficient

At low total mass concentrations, the VOCs in unsaturated soil will partition in three phases: gas, liquid and solid. It is assumed that the VOC is transported in the liquid phase by advection and dispersion, in the gas phase by advection and diffusion, and not transported in the solid phase. The one dimensional transport of VOCs can be modeled by the volatile solute transport model proposed by Brown (1987).

$$\frac{\partial}{\partial t}(\varepsilon C_g) + \frac{\partial}{\partial t}(\theta C_l) + \frac{\partial}{\partial t}(\rho_s C_s) = -\frac{\partial}{\partial z}(C_g q_g) - \frac{\partial}{\partial z}(C_l q_l)$$

$$+\frac{\partial}{\partial z}\left(D_l \frac{\partial C_l}{\partial z}\right) + \frac{\partial}{\partial z}\left(D_g \frac{\partial C_g}{\partial z}\right) + E \tag{3-5}$$

where C_s is the solute concentration in solid phase, ρ_s is the soil density, Z is the distance from the top of soil column, q_l and q_g are the volume flow of the liquid phase and the gas phase, D_l is the solute dispersion coefficient, and E is the biodegradation rate of solute.

Advection in the liquid phase and gas phase are neglected as both phase flows were small. Liquid dispersion is usually several orders of magnitude less than the vapor diffusion, so the liquid dispersion term can be dropped from equation (3-2). Likewise, the biodegradation term E, can be ignored since NaN_3 was used to kill microbes to avoid biodegradation of toluene. Therefore, equation (3-2) becomes,

$$\frac{\partial}{\partial t}(\varepsilon C_g) + \frac{\partial}{\partial t}(\theta C_l) + \frac{\partial}{\partial t}(\rho_s C_s) = \frac{\partial}{\partial z}\left(D_g \frac{\partial C_g}{\partial z}\right) \tag{3-6}$$

Since ρ_s, θ, ε, and D_g are constants in this experiment, they can be taken out from the partial derivatives. With Henry's Law (equation 3-3) and the definition of liquid/solid partition coefficient K_d, the solid phase concentration can be expressed by,

$$C_s = K_d C_l = K_d \frac{C_g}{H_c} \tag{3-7}$$

Using the definition of total porosity,

$$\varepsilon = \phi - \theta \tag{3-8}$$

substituting equations (3-3), (3-7), and (3-8) into equation (3-5) generates the desired form,

$$\left(\phi - \theta + \frac{\theta}{H_c} + \frac{\rho_s \cdot K_d}{H_c}\right)\frac{\partial C_g}{\partial t} = D_g \frac{\partial^2 C_g}{\partial Z^2} \tag{3-9}$$

The initial and boundary conditions for the soil column are:

$$I.C. \quad C_g|_{t=0} = Constant \tag{3-10}$$

$$B.C. \quad C_g|_{z=0} = 0 \tag{3-11}$$

When soil water content is greater than the critical water content, K_d is a constant equal to the saturated liquid/solid partition coefficient. When water content is less than the critical water content, K_d is a function of both organic matter content and the soil water content. K_d can be measured by experiment or predicted by a partition coefficient model. But so far no such model has been proposed which is applicable for all soils. The finite difference method is used to solve the second order partial derivative equation (3-9) with a time step of thirty minutes and a distance step of 1.5 cm.

The parameter sensitivity analysis for this model by Yue (1995) found the partition coefficient and vapor diffusion coefficient to be the most sensitive parameters. Fixing the other parameters, the optimum K_d and D_g were determined by minimizing the difference between measured and simulated results. The optimum K_d and D_g will minimize the error function f(x) stated as,

$$\textit{Minimize}: \quad f(x) = \sum_{i=1}^{n} [C_{gs}(i) - C_{gm}(i)]^2 \tag{3-12}$$

$$\textit{Subject to}: \quad 0 \leq D_g \leq D_o$$

$$0 \leq K_d \leq K_{dm}$$

where $C_{gs}(i)$ and $C_{gm}(i)$ are the simulated and measured gaseous toluene concentrations at the ith sampling port respectively, and n is the number of the sampling ports. K_{dm}, the upper limit of K_d, is dependent on the soil type and organic compound. The diffusion coefficient of toluene in free air (D_o) was calculated using the Fuller correlation (Fuller et al., 1966) to be 0.076 cm^2/sec at 21°C.

The following and the entire searching process was done by computer using a Quick Basic program. The flowchart and the computer program for searching optimum parameters are shown in Appendix A.

Complex Method

The optimization problem can be solved using the random searching Complex Method. This method was developed from the simplex method. The main idea of the method is to randomly search for optimum values in a feasible domain by effective rules. The procedures used were:

a. Select initial vertices $(V_1, V_2, V_3, V_4)_o$ by the relation:

$$V_{io} = a + r_{io}(b - a), \quad i = 1, 2, 3, 4 \tag{3-13}$$

where r_{io} is a random number between 0 and 1, a and b are the lower and upper limit of parameters. V_i, a, and b are two-dimensional vectors including K_d and D_g.

b. Calculate and evaluate the error function at each vertex

$R_i = f(V_i) \quad i=1,2,3,4$

c. Put R_i in a descendant order to find the worst vertex V_1 corresponding to R_1

$R_1 > R_2 > R_3 > R_4$

d. Replace the worst vertex V_1 by a new tentative vertex V_1' in the feasible domain

$V_1' = V_c + \kappa (V_c - V_1)$, where k is a coefficient greater than 1

$$V_c = \tfrac{1}{3}\left(\sum_{i=1}^{4} V_i - V_1\right) \tag{3-14}$$

e. Decide whether the tentative is the new worst vertex or the new best vertex.

<u>Contract</u>

If tentative vertex is the new worst vertex, contract by the following way:

$V_1' = V_c + \kappa (V_1 - V_c)$,

If the contracted vertex is still the worst vertex, replace all vertices except the best one by,

$$V_i = (V_i + V_4)/2, \quad i = 1, 2, 3 \tag{3-15}$$

<u>Extend</u>

If the tentative vertex is the new best vertex, extend further by step (d). If the extended vertex is better than the tentative vertex, use the extended vertex as the new vertex. If not, use the tentative vertex as the new vertex.

f. Repeat steps (b) through (e) until the tolerance value e is achieved.

$$|R_1 - R_4| \leq e \tag{3-16}$$

The Complex method can be shown to be better than the simplex. Assume there are n variables to be estimated Complex will form a polyhedron with more than n+1 vertices while Simplex will form a polyhedron with n+1 vertices. The Complex can avoid the decrease of dimensions by the withdrawal of the nonfeasible vertex in the Simplex and increases searching speed. Another advantage of the Complex method is that it decreases the probability of trapping in a local extreme since you can have as many initial vertices as you want.

Linear Relationship Between Optimum K_d and D_g**

To see the relationship of optimum K_d* and D_g* equation (3-9) is rearranged as,

$$\frac{\partial C_g}{\partial t} = \frac{D_g}{\phi - \theta + \frac{\theta}{Hc} + \frac{\rho \cdot K_d}{Hc}} \cdot \frac{\partial^2 C_g}{\partial Z^2} \tag{3-17}$$

Now define a lumped parameter,

$$D_g' = \frac{D_g}{\phi - \theta + \frac{\theta}{Hc} + \frac{\rho \cdot K_d}{Hc}} \tag{3-18}$$

equation (3-17) then becomes,

$$\frac{\partial C_g}{\partial t} = D_g' \cdot \frac{\partial^2 C_g}{\partial Z^2} \tag{3-19}$$

Assuming $D_g'^*$ is the optimum value of D_g', K_d^* and D_g^* are the optimum values corresponding to $D_g'^*$. Then,

$$D_g'^* = \frac{Dg^*}{\phi - \theta + \frac{\theta}{Hc} + \frac{\rho \cdot K_d^*}{Hc}} \tag{3-20}$$

$$D_g^* = D_g'^* \left(\phi - \theta + \frac{\theta}{H_c} + \frac{\rho \cdot K_d^*}{H_c} \right) = C_1 + C_2 K_d^* \tag{3-21}$$

$$C_1 = D_g'^* (\phi - \theta + \frac{\theta}{H_c}) \tag{3-22}$$

and,

$$C_2 = D_g'^* \frac{\rho}{H_c} \tag{3-23}$$

As porosity, water content, Henry's constant, soil density, and $D_g'^*$ are constants, C_1 and C_2 will be constants. Equation (3-21) shows a linear relationship between optimum K_d^* and D_g^*. Therefore, the gaseous diffusion coefficient D_g can be determined by the linear relationship since K_d is known. As the measured K_d may have measurement error, the true K_d value will fall into a small range. It is easy to find the corresponding D_g range from the linear relationship between optimum K_d^* and D_g^*.

Experimental Results

In this study, five column tests were run, including three with Teller loam and two with Dougherty sand. Parameters for each test are listed in Table 3-4. All soil columns had a porosity of 40%. Toluene transport was measured in the Teller loam at volumetric water contents of 0.15, 0.12, and 0.029. For the Dougherty sand, toluene transport was measured at two water contents, 0.12 and 0.003.

During testing, the toluene concentration profile along the column was measured at time intervals of approximately ten hours for Teller loam test and four hours for Dougherty sand test. Soil column liquid/solid partitioning and gaseous diffusion coefficient, K_d and D_g, were then determined using regression techniques to best fit the transport equation (3-9) governed by boundary conditions (3-10) and (3-11) to the measured toluene concentrations. Fitted curves along with measured toluene concentrations are shown in Figures 3-3, 3-4, and 3-5 for the Teller loam tests, and Figures 3-6 and 3-7 for the Dougherty sand tests.

Soil column water content profiles measured before and after testing were compared in order to determine water loss due to evaporation. The profile prior to testing was ascertained from samples of the soil used to pack each layer within the column. The water content profile at test completion was obtained by oven drying soil samples extracted from the column through side ports. Water content profiles for column tests Teller-1, Teller-2, and Dougherty-1 are shown in Figures 3-8 through 3-10, respectively. Water Content profiles from columns packed with air dried soil (Teller-3 and Dougherty-2) remained uniform during testing and consequently are not provided.

For each measured concentration profile the optimum K^*_d and D^*_g were searched in their domain using complex method that was carried out by a computer program listed in Appendix A and the relationship between optimum K^*_d and D^*_g can be obtained. As the K_d value was measured in the soil sorption experiment, the optimum D^*_g can be calculated through the linear relationship between K^*_d and D^*_g. Figures 3-11 to 3-13 display the K^*_d and D^*_g linear relationships of all measured concentration profiles of Teller loam column tests. Figures 3-14 and 3-15 present the K^*_d and D^*_g linear relationships of Dougherty sand column tests. The optimum parameter linear relationship shifts with the time.

The difference between measured and simulated data using different parameter combinations in the feasible parameter domain can be seen clearly in the error response surface shown in Figure 3-16. The response surfaces of all concentration profiles are similar. Figure 3-16a is the typical response surface and Figure 3-16b is the corresponding contour map. All response surfaces have the shape of a valley whose values of the objective function are the same. This optimum parameter valley corresponds to the linear relationship of K_d and D_g. The calculated D_g from experimental data, the predicted values by the Millington-Quirk model, and the comparison are shown in Table 3-5 for Teller loam and Table 3-6 for Dougherty sand.

To see the accuracy of Millington-Quirk diffusivity model the measured soil adsorption coefficient and the predicted Millington-Quirk diffusion coefficient were used to simulate the transport of toluene in five column tests. The measured and simulated toluene gas phase concentration profiles in Teller loam and Dougherty sand column tests are presented in Figures 3-17 to 3-21.

Discussion

The diffusion coefficient was measured at three water contents for Teller loam and at two water contents for Dougherty sand. The Teller-3 was air-dry soil and Dougherty-2 was air-dry sand. The total experimental time listed in Table 3-4 suggests that the toluene transport in Teller loam is much slower than in Dougherty sand. The soil porosity and water content of Teller-2 and Dougherty-1 are the same and the initial concentration of Dougherty-1 is even higher than that of Teller-2, but the total experiment time of Teller-2 is 115 hours and it is just 29 hours for Dougherty-1. This is because the toluene adsorption onto Dougherty is much smaller than onto Teller. As the soil sorption in low water content soil is several orders in magnitude greater than in high water content soil, the toluene transport at low water content is much slower than in high. In Teller-3 the total time needed for 3.8 mg/L of toluene to escape from the column is 312 hours, and in Teller-1 it is just 75 hours for 6.3 mg/L. The total experiment time of Dougherty-1 and Dougherty-2 are almost the same although the initial concentration of Dougherty-1 is ten times the initial concentration of Dougherty-2. If soil sorption is the same at any water content, it would be impossible for toluene to transport slower at low water content than in high because the diffusion coefficient in low water content soil should be larger. This implies that the organic contaminants will be much more difficult to remove from dry soil than from wet soil.

The calculated diffusion coefficients of five column tests listed in Tables 3-5 and 3-6 show that the Millington-Quirk diffusivity model is good. The gaseous diffusion coefficient from experimental data is close to the predicted value by Millington-Quirk model in all column tests except in Teller-1. This may be caused by the short incorporation time of toluene before the experiment. In Teller-1 the toluene vapor was allowed to incorporate for just about 24 hours compared to 100 hours in the other tests. Therefore, the soil adsorption in Teller-1 may have not reached equilibrium when the experiment started and the actual K_d is smaller than the expected K_d value. In this situation the calculated gaseous diffusion coefficient from experimental data may be larger than the real diffusion coefficient. The calculated gaseous diffusion coefficient tends to be 0.008 in Teller-2, 0.0216 in Teller-3, 0.0091 in Dougherty-1, and 0.0376 in Dougherty-2, while the expected value of Millington-Quirk model is 0.009, 0.0229, 0.009, and 0.0290 cm^2/sec. respectively. In Dougherty-2 Millington-Quirk appears to underestimate the diffusion coefficient. This slight underprediction by the Millington-Quirk model in dry soil was also observed by Xu (1992).

For all column tests the best-fit diffusion coefficient of the early data has the largest difference from the Millington-Quirk model. This is shown clearly in Figures 3-11 to 3-15. The linear optimum K^*_d and D^*_g relationship for early data is significantly different from later data in all five column tests. This might be caused by the large concentration gradient near soil surface at the beginning as the toluene concentration in the air above soil surface was zero. Later, toluene concentration in the air above the soil surface may not be zero and a thin transition layer was formed at the top. The real surface gradient became smaller than expected and the toluene loss was smaller. So the calculated optimum D_g was smaller than in the beginning. In Teller-1, Teller-2, and Dougherty-1 tests water loss from the soil surface might have contributed partly to the large D_g in the beginning due to the gas phase convection caused by the water evaporation. Therefore, volatilization of organic compounds is always more rapid at the beginning.

The linear optimum parameter relationship means that the best-fit concentration curve can be obtained using all parameters which meet this linear relationship. If either one is known another parameter can be obtained. The optimum valley of all response surfaces is narrow and steep which indicates that the probability of the real K_d and D_g falling in the valley is very large.

There are two factors which may affect the determination of true diffusion coefficient. First, as presented in Chapter II, the soil sorption coefficient was measured using a batch experiment. Due to the complication of soil adsorption and the experimental error the measured K_d value ranged in a small area. For Teller-1 and Teller-2 soil the measured K_d ranged from 0.35 to 0.45 cm^3/g, and from 0 to 0.05 cm^3/g for Dougherty-1 sand. For air-dry Teller-3 and Dougherty-2 K_d was assumed to fall into a small area. The change of K_d value will result in the change of the calculated optimum diffusion coefficient. The possible lower boundary and upper boundary for the optimum diffusion coefficient are presented in Table 3-7. From this table it can be seen that the Millington-Quirk diffusivity value falls into or close to the range of the estimated diffusion coefficient except for Teller-1. Second, the diffusion coefficient is a function of soil water content. Water evaporation during the experiment affected about 5 cm of the surface soil in tests Teller-1 and Teller-2 as shown in Figures 3-8 and 3-9. The surface soil became dry and the diffusion coefficient in the surface soil layer should be larger than the average value of the entire soil column. This will impact the data of the top three sampling locations. As the toluene concentration of the top layers decreased rapidly and remained small during the experiment, they will not have a significant effect in the concentration curve-fitting. The estimated and predicted diffusion coefficients in these two column tests match very well. In column test Dougherty-1, the water content profiles before and after the experiment show that the water content redistributed due to the high permeability of Dougherty sand. The soil water content increased at the bottom and decreased gradually going up to the soil surface. This may bring in error in the determination of diffusion coefficient, but the error may be small as the optimum diffusion coefficient obtained is an average value of the entire soil column. Since tests Teller-3 and Dougherty-2 used air-dry soil no error was caused by water evaporation or redistribution.

The predicted diffusivity by the Millington-Quirk model is used to simulate the transport of toluene in a soil column and the measured data is plotted in the same graph to see the accuracy of Millington-Quirk diffusivity model. The soil partition coefficient used in the simulation was taken from the measured relationship between soil water content and soil partition coefficient. Figure 3-17 shows a large lag of the simulation curve in column test Teller-1. The simulated toluene transport using Millington-Quirk model is much slower than the measured transport process. The simulated concentration profile of 35.5 hours fitted the measured concentration profile of 21 hours. But Figures 3-18 to 3-20 show a good match between the simulation and the measured data in Teller-2, Teller-3, and Dougherty-1. In Dougherty-2 the simulation is slower than the measured transport process as shown in Figure 3-21. It appears that Millington-Quirk may underestimate the diffusion coefficient when soil water content is small.

As discussed before in this chapter, there are three common problems in the diffusion experiment dealing with volatile organic compounds: boundary effects, escape of organic vapor, pressure problem. The large diameter PVC column used in this research certainly improved the accuracy of experimental data. The data error caused by the boundary effects and the escape of organic vapor was relatively small compared with the total chemical mass inside the large soil column. During the experiment the soil column was exposed directly to atmosphere, so no pressure differences existed. Seventeen gas samples were taken directly from the inside of the soil column and analyzed for each concentration profile. This could increase the reliability of the estimated diffusion coefficient because the result is based on all data instead of data from a single sampling location.

Conclusions

Three conclusions can be drawn from the above analysis. First, the Millington-Quirk diffusivity model slightly underpredicted the diffusivity when soil water content is low ($\theta < 0.002$). Second, for low water content soil ($\theta < 0.002$) any simulation using Millington-Quirk diffusivity would result in a slower prediction of transport of volatile organic compounds. Third, the Millington-Quirk diffusivity model is a good predictor for soil or sand except in extremely dry soil ($\theta < 0.002$).

Diffusion coefficient was measured at a constant temperature 20 ± 1 °C in this research. Data in high temperature would be necessary to better evaluate the Millington-Quirk model.

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Table 3-3

PREPARATION OF TOLUENE STANDARDS IN AIR

Container	Volume mL	$CaSO_4$ Solution mL	Toluene Mass uL*	Conc. in Headspace ppm
Bottle 1	506	130.0	0.5	0.49
Bottle 2	504	130.0	1.0	0.99
Bottle 3	529	130.0	5.0	4.82
Vial 4	40.0	16.0	1.0	10.14
Vial 5	40.0	16.0	5.0	50.70

* 1 uL toluene = 0.867 mg

Table 3-4

TEST PARAMETERS OF EACH COLUMN EXPERIMENT

Name	Porosity	Moisture	Initial Conc. mg/L	Total Experiment Time (hrs.)	Water Evaporated (g)
Teller-1	0.4	0.15	6.3	75	660
Teller-2	0.4	0.12	35.0	115	660
Teller-3	0.4	0.03	3.8	312	0.0*
Dougherty-1	0.4	0.12	48.0	29	816
Dougherty-2	0.4	0.002	4.0	26	0.0*

* Teller-3 and Dougherty-2 were air-dry soil and sand, so there was no water evaporated during the experiments.

Table 3-5

RESULTS OF ESTIMATED GASEOUS DIFFUSION COEFFICIENTS IN TELLER LOAM

Column	Parameter	Time Period (hour)	Measured Gaseous Diffusion Coefficient (cm^2/sec.)	Ratio of Measured to M-Q Model
		0-2	0.0188	3.03
	$\phi = 0.4$	0-5	0.0177	2.85
		0-13	0.0117	1.89
Teller-1	$\theta = 0.15$	0-21	0.0120	1.94
		0-27.5	0.0118	1.90
	$K_d = 0.4$	0-35.5	0.0127	2.05
		M-Q Model	0.0062	
		0-3	0.0056	0.62
	$\phi = 0.4$	0-8	0.0076	0.84
		0-18	0.0100	1.11
Teller-2	$\theta = 0.12$	0-32.5	0.0084	0.93
		0-48	0.0085	0.94
	$K_d = 0.4$	0-69	0.0080	0.89
		0-93	0.0077	0.86
		M-Q Model	0.0090	
	$\phi = 0.4$	0-13	0.0362	1.58
		0-38	0.0348	1.52
Teller-3	$\theta = 0.029$	0-72	0.0270	1.18
		0-117	0.0224	0.98
	$K_d = 7.58$	0-192	0.0216	0.94
		M-Q Model	0.0229	

Table 3-6

RESULTS OF ESTIMATED GASEOUS DIFFUSION COEFFICIENTS IN DOUGHERTY SAND

Column	Parameter	Time Period (hour)	Measured Gaseous Diffusion Coefficient (cm^2/sec.)	Ratio of Measured to M-Q Model
Dougherty-1	$\phi = 0.4$ $\theta = 0.12$ K_d =0.00	0-1	0.0108	1.20
		0-3	0.0117	1.30
		0-7	0.0096	1.07
		0-11	0.0096	1.07
		0-16.5	0.0098	1.09
		0-22	0.0094	1.04
		0-29	0.0091	1.01
		M-Q Model	0.0090	
Dougherty-2	$\phi = 0.4$ $\theta = 0.002$ $K_d = 0.865$	0-1	0.1085[+]	3.74
		0-4	0.0521	1.80
		0-10	0.0384	1.32
		0-17	0.0382	1.32
		0-26	0.0376	1.30
		M-Q Model	0.0290	

[+] This is not reasonable because it is greater than the upper limit 0.1 cm^2/sec.

Table 3-7

ESTIMATED LOWER AND UPPER BOUNDARY OF DIFFUSION COEFFICIENT BY EXPERIMENTAL DATA

Column	Soil Adsorption cm^3/g	Millington-Quirk $cm^2/sec.$	Experimental Results* $cm^2/sec.$
Teller-1	0.35 - 0.45	0.0062	0.0106 - 0.0139
Teller-2	0.35 - 0.45	0.0090	0.0070 - 0.0109
Teller-3	8.5 - 6.5	0.0229	0.0186 - 0.0406
Dougherty-1	0.00 - 0.05	0.0090	0.0091 - 0.0158
Dougherty-2	0.76 - 0.96	0.0290	0.0337 - 0.0420

* The early data is not considered.

Table 3-7

ESTIMATED LOWER AND UPPER BOUNDARY OF DIFFUSION COEFFICIENT BY EXPERIMENTAL DATA

Column	Soil Adsorption cm^3/g	Millington-Quirk $cm^2/sec.$	Experimental Results* $cm^2/sec.$
Teller-1	0.35 - 0.45	0.0062	0.0106 - 0.0139
Teller-2	0.35 - 0.45	0.0090	0.0070 - 0.0109
Teller-3	8.5 - 6.5	0.0229	0.0186 - 0.0406
Dougherty-1	0.00 - 0.05	0.0090	0.0091 - 0.0158
Dougherty-2	0.76 - 0.96	0.0290	0.0337 - 0.0420

* The early data is not considered.

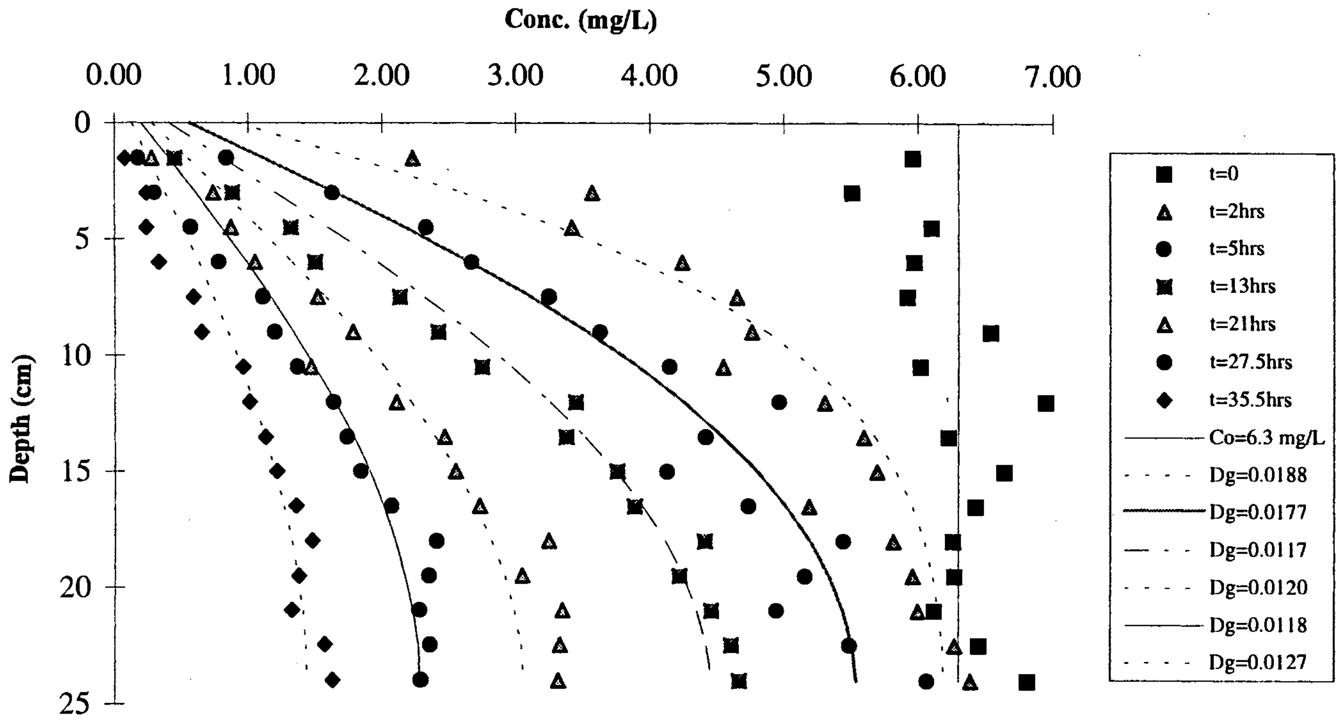


Figure 3-3. Measured and best-fit toluene gas phase concentration profiles in column test Teller-1 (water content = 0.15 v/v).

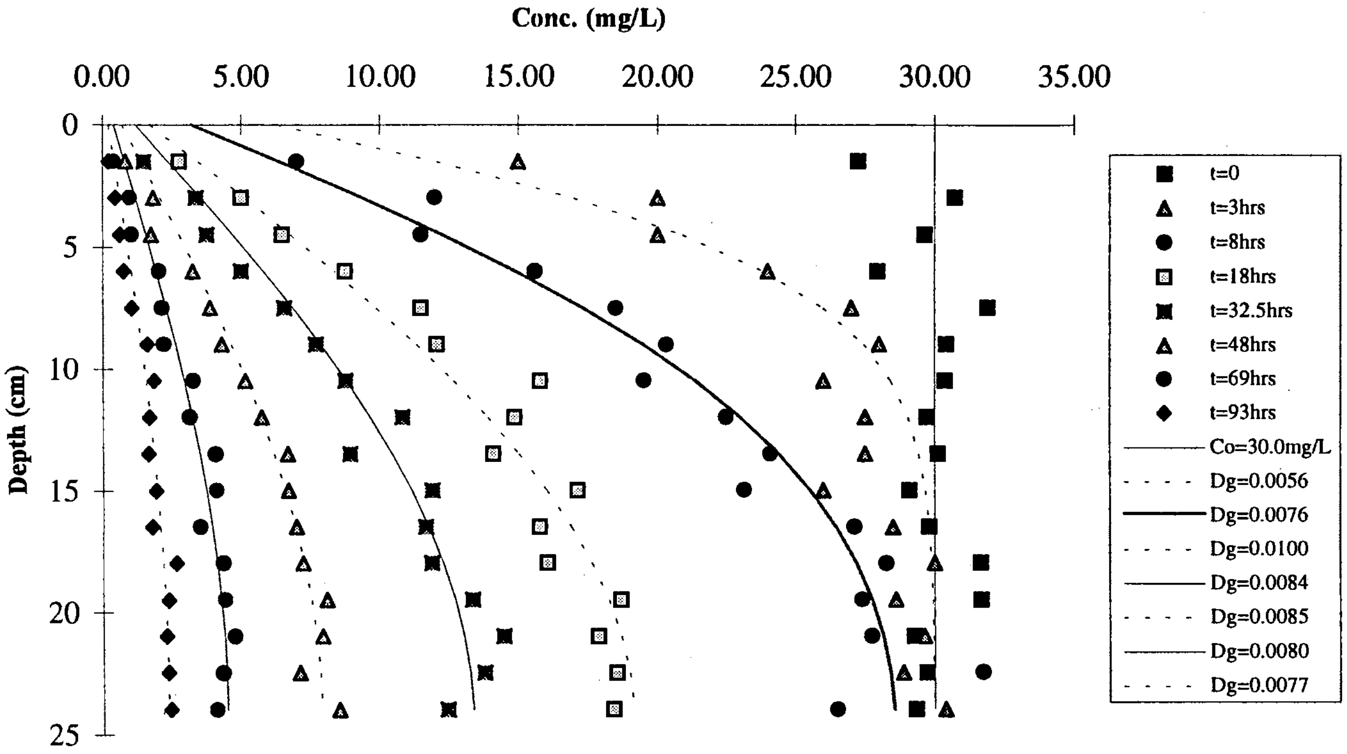


Figure 3-4. Measured and best-fit toluene gas phase concentration profiles in column test Teller-2 (water content = 0.12 v/v).

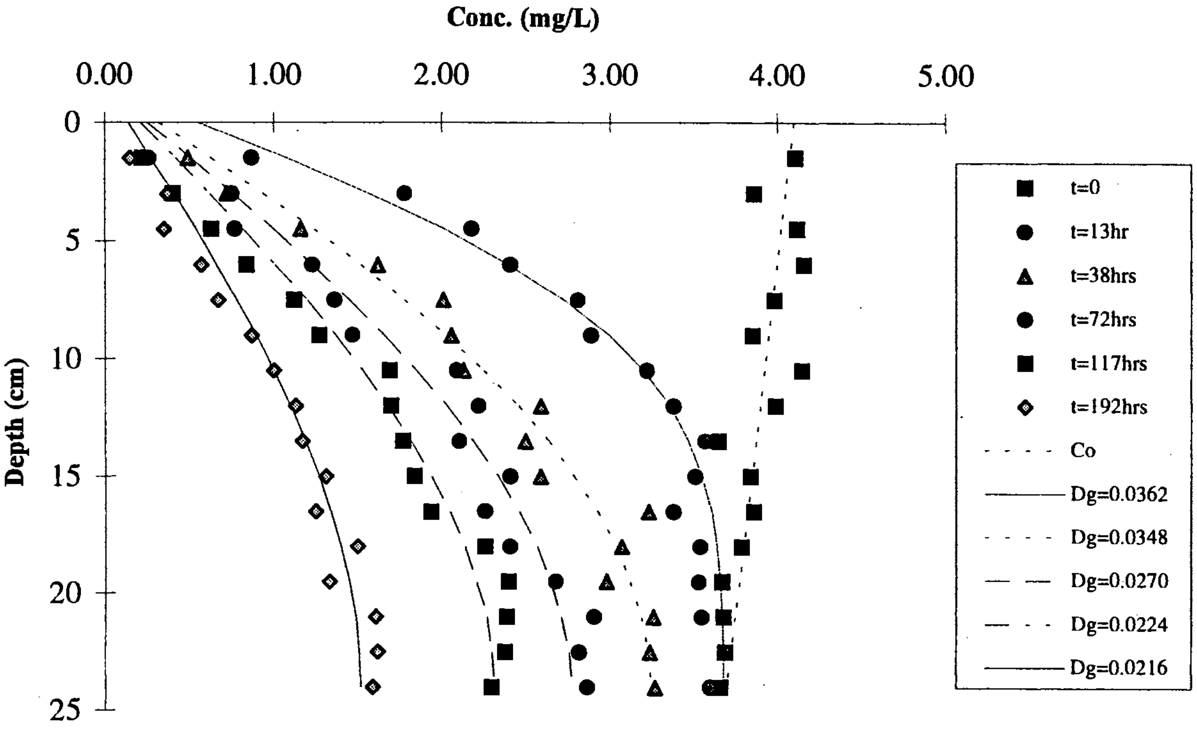


Figure 3-5. Measured and best-fit toluene gas phase concentration profiles in column test Teller-3 (water content = 0.029 v/v).

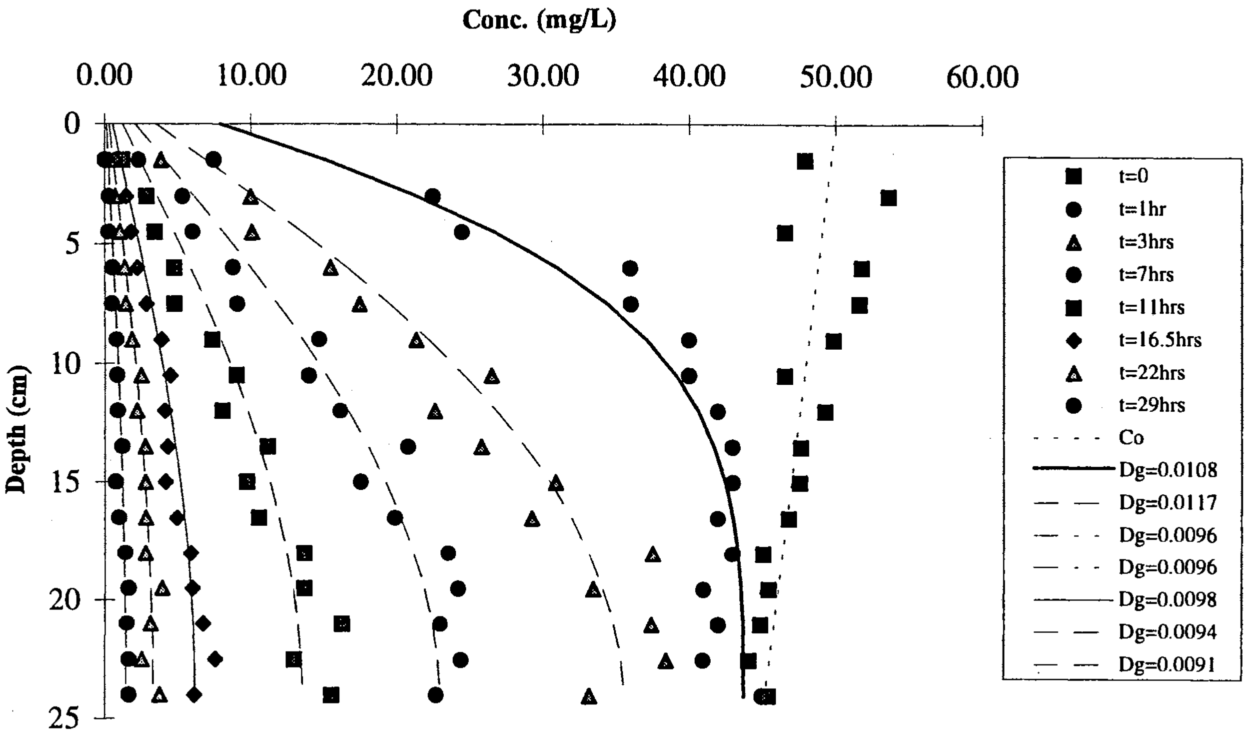


Figure 3-6. Measured and best-fit toluene gas phase concentration profiles in column test Dougherty-1 (water content = 0.12 v/v).

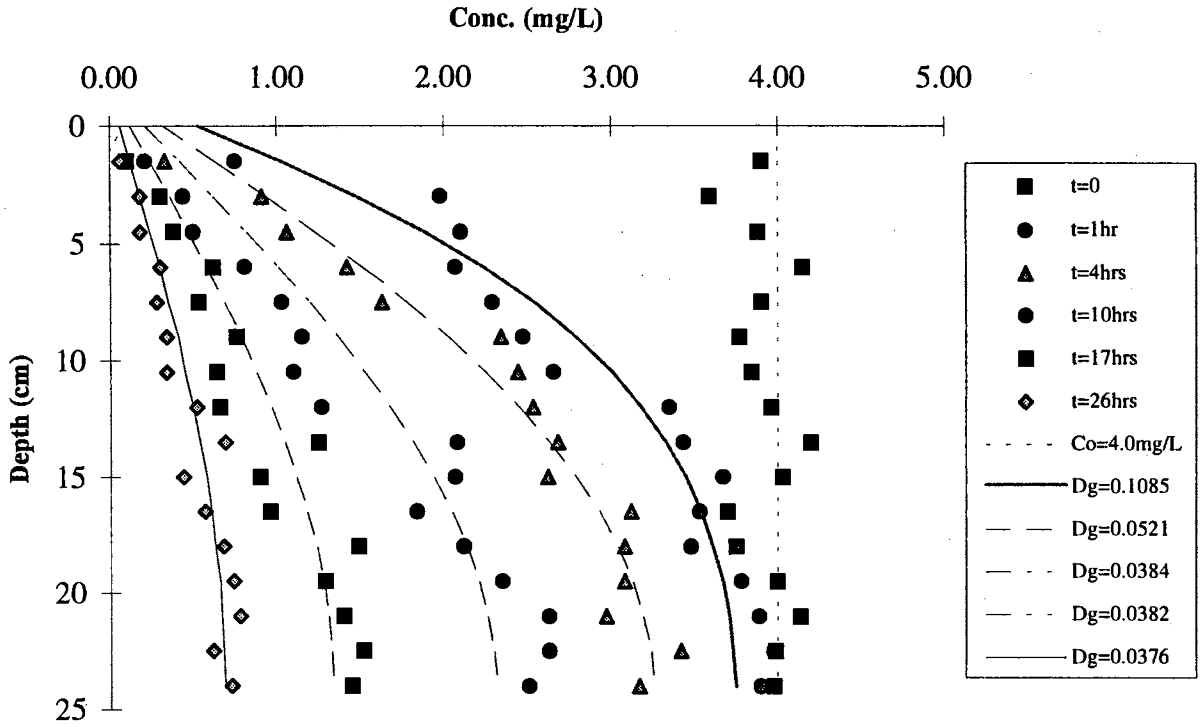


Figure 3-7. Measured and best-fit toluene gas phase concentration profiles in column test Dougherty-2 (water content = 0.002 v/v).

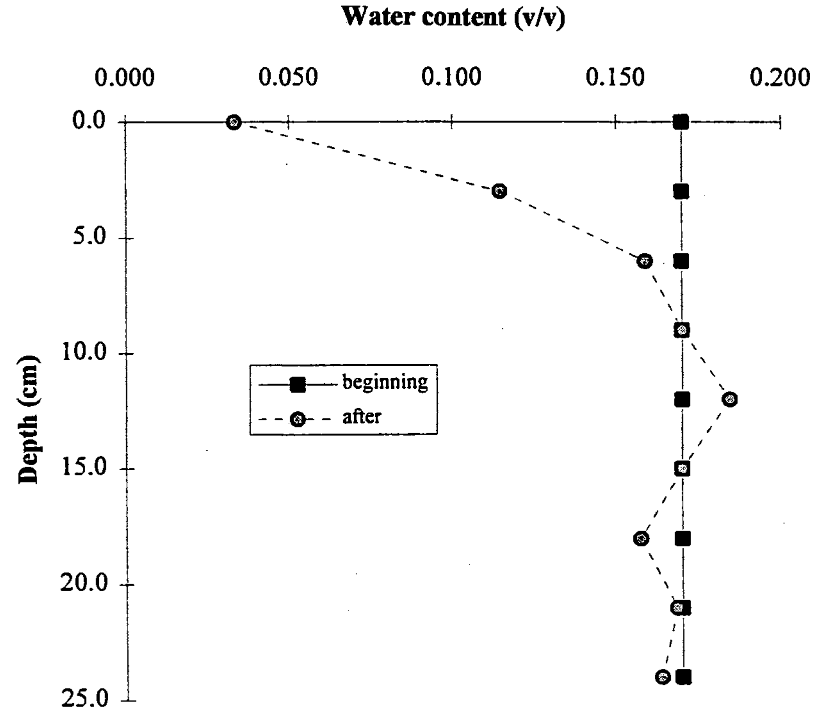


Figure 3-8. Measured soil water content profiles of column test Teller-1.

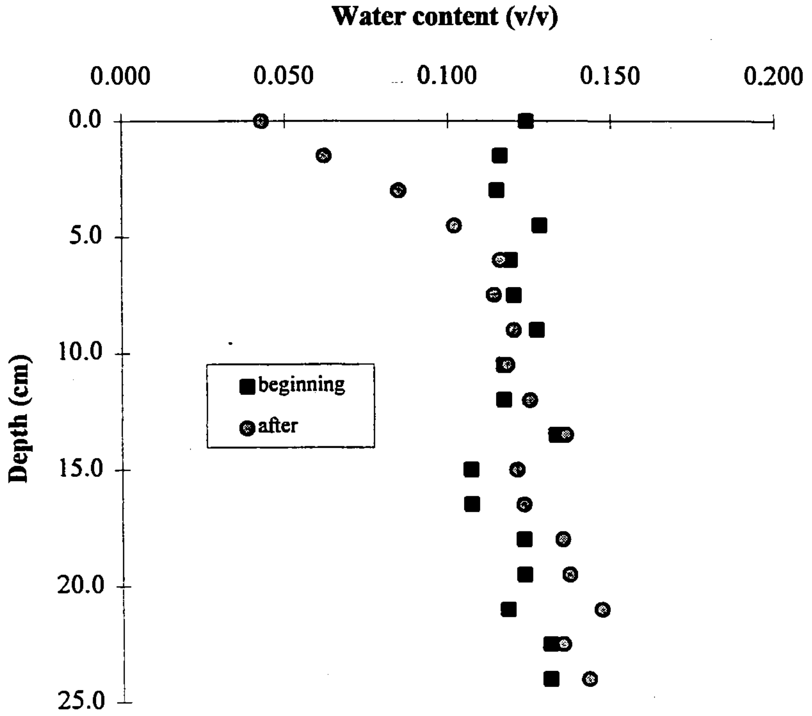


Figure 3-9. Measured soil water content profiles of column test Teller-2.

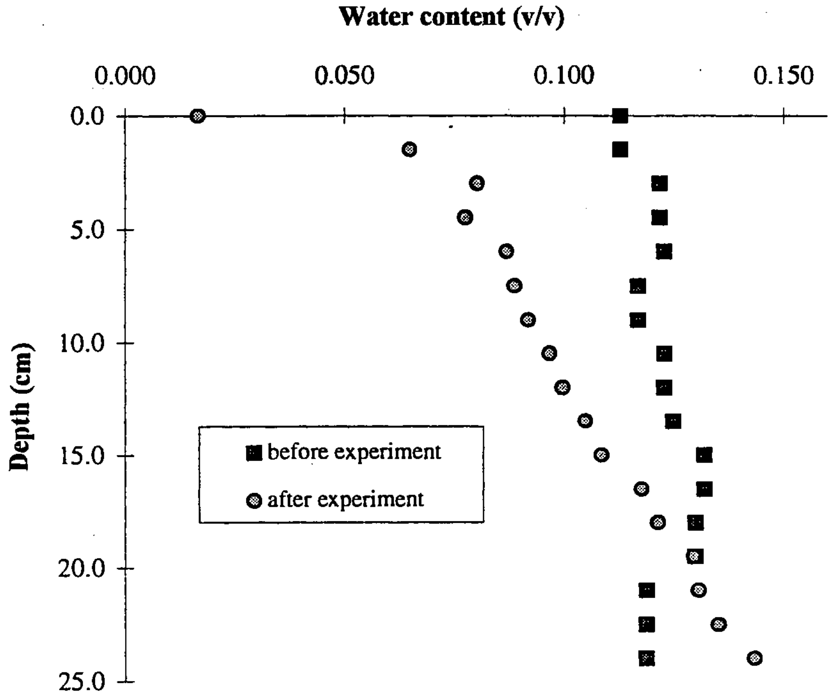


Figure 3-10. Measured soil water content profiles of column test Dougherty-1.

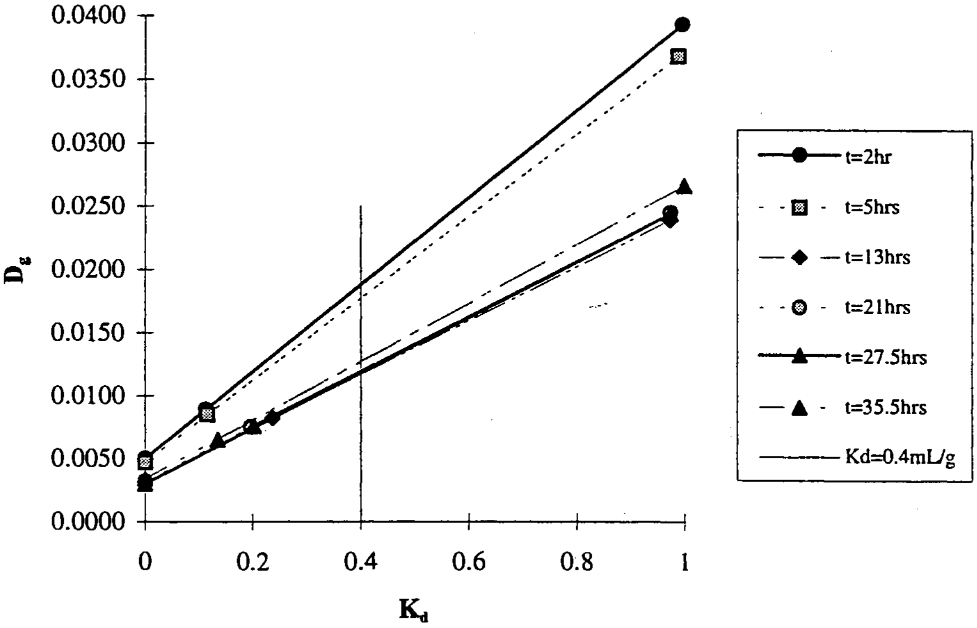


Figure 3-11. Optimum K^*_d and D^*_g relationships of column test Teller-1.

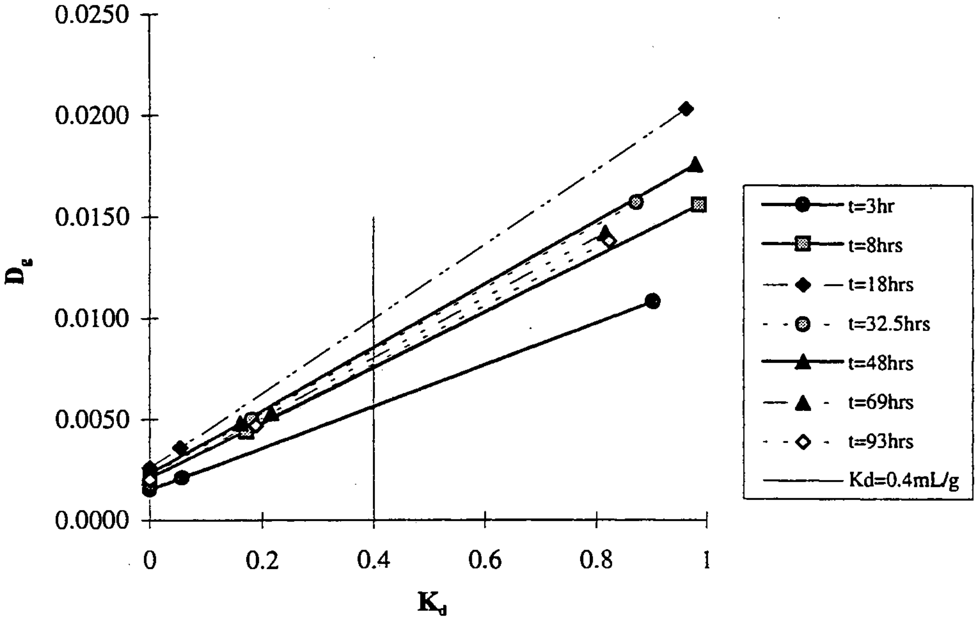


Figure 3-12. Optimum K^*_d and D^*_g relationships of column test Teller-2.

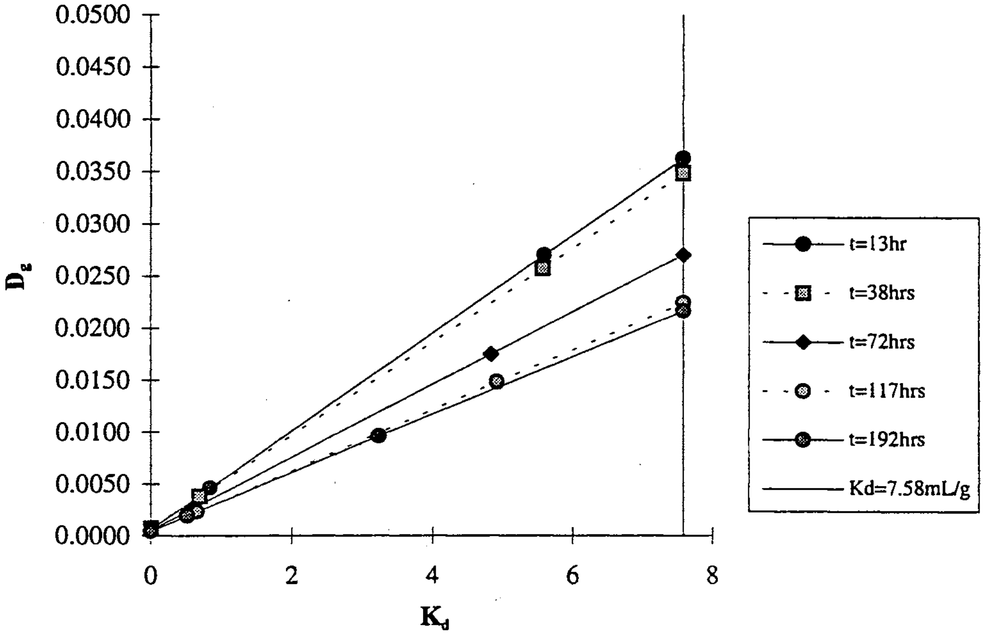


Figure 3-13. Optimum K^*_d and D^*_g relationships of column test Teller-3.

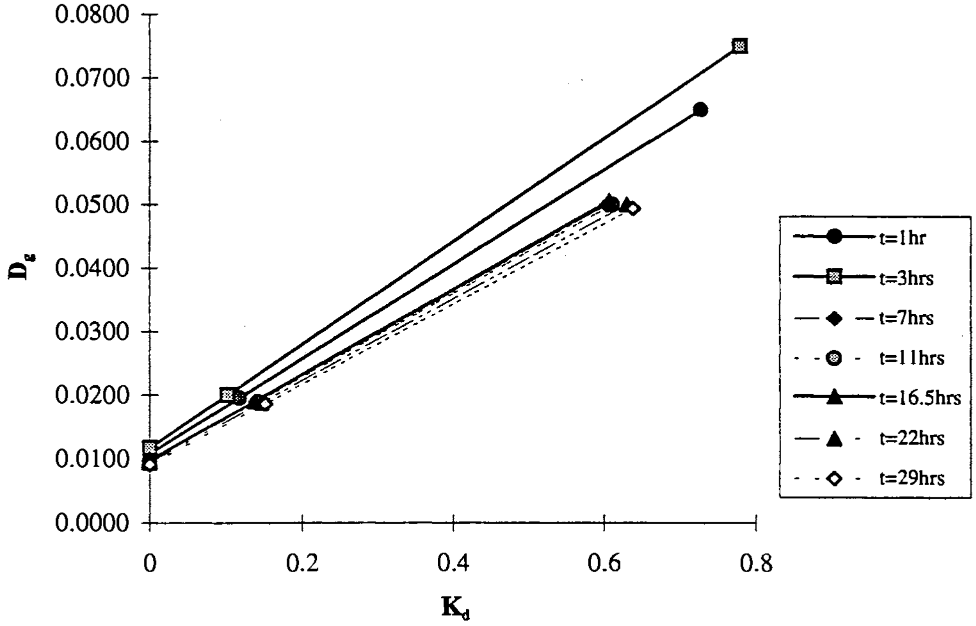


Figure 3-14. Optimum K^*_d and D^*_g relationships of column test Dougherty-1.

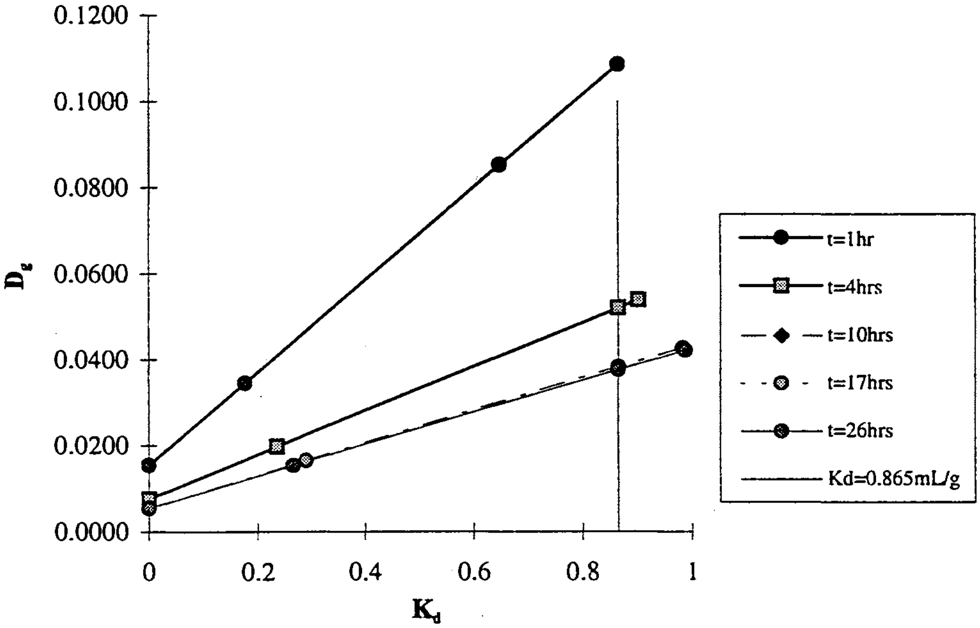
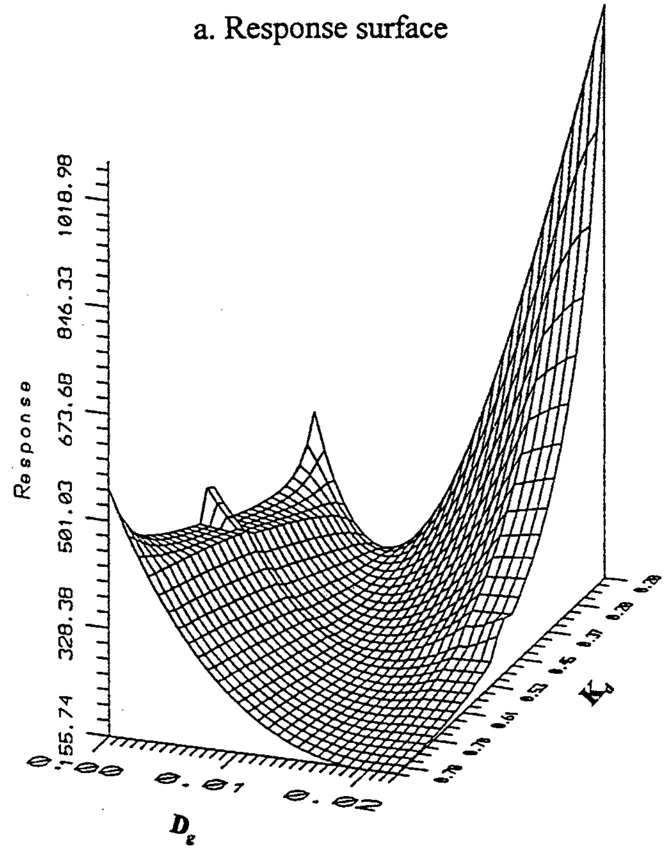


Figure 3-15. Optimum K^*_d and D^*_g relationships of column test Dougherty-2.

a. Response surface



b. Contour map

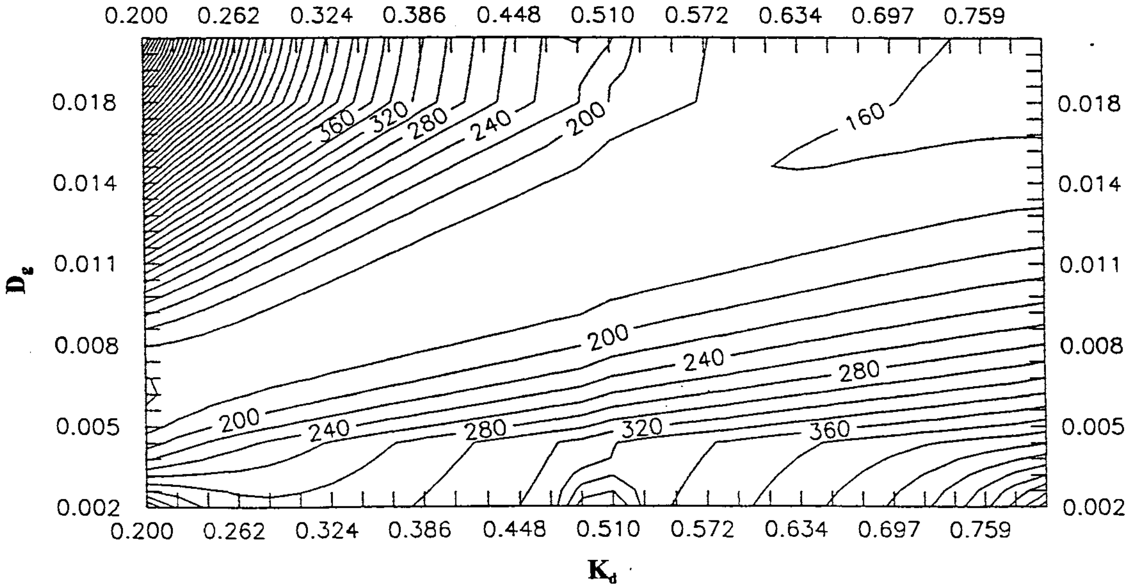


Figure 3-16. Typical response surface and contour map of parameters.

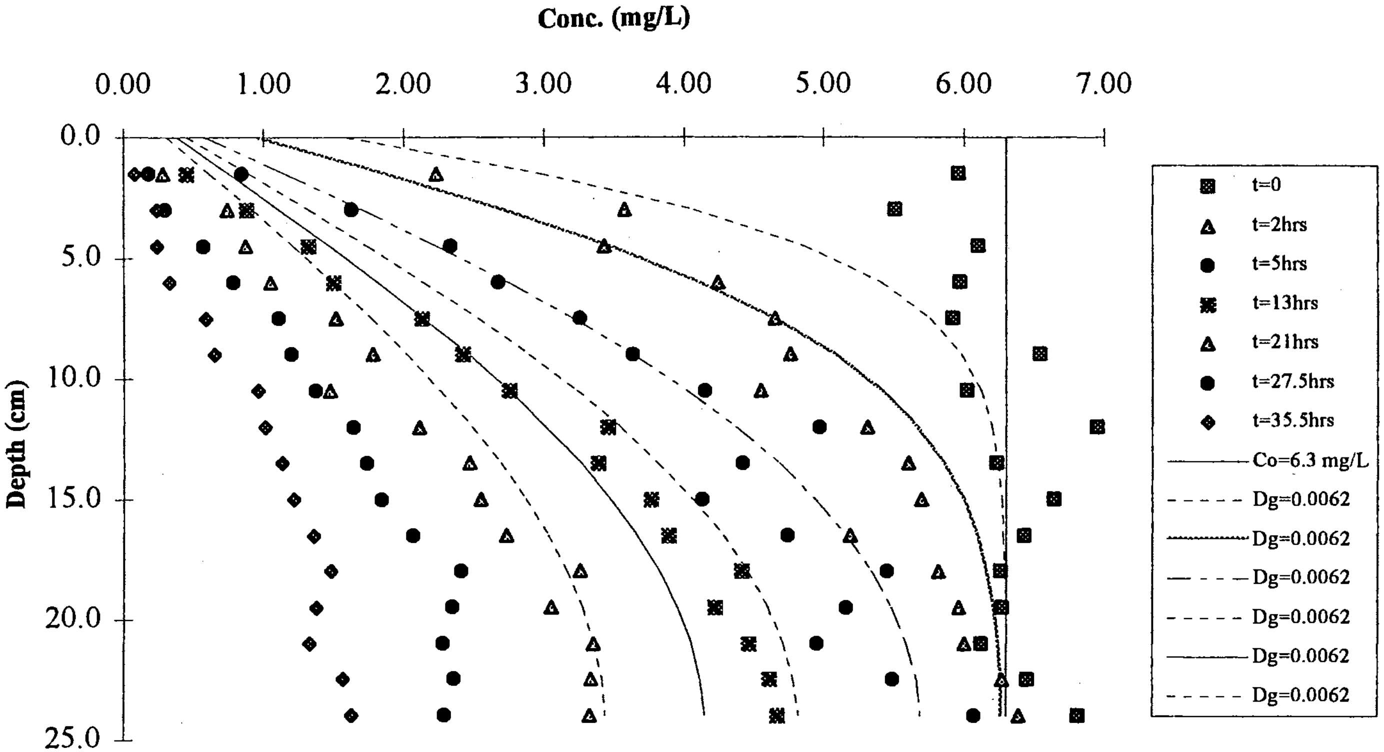


Figure 3-17. Measured and simulated toluene gas phase concentration profiles using Millington-Quirk diffusivity model in column test Teller-1. water content = 0.15 v/v

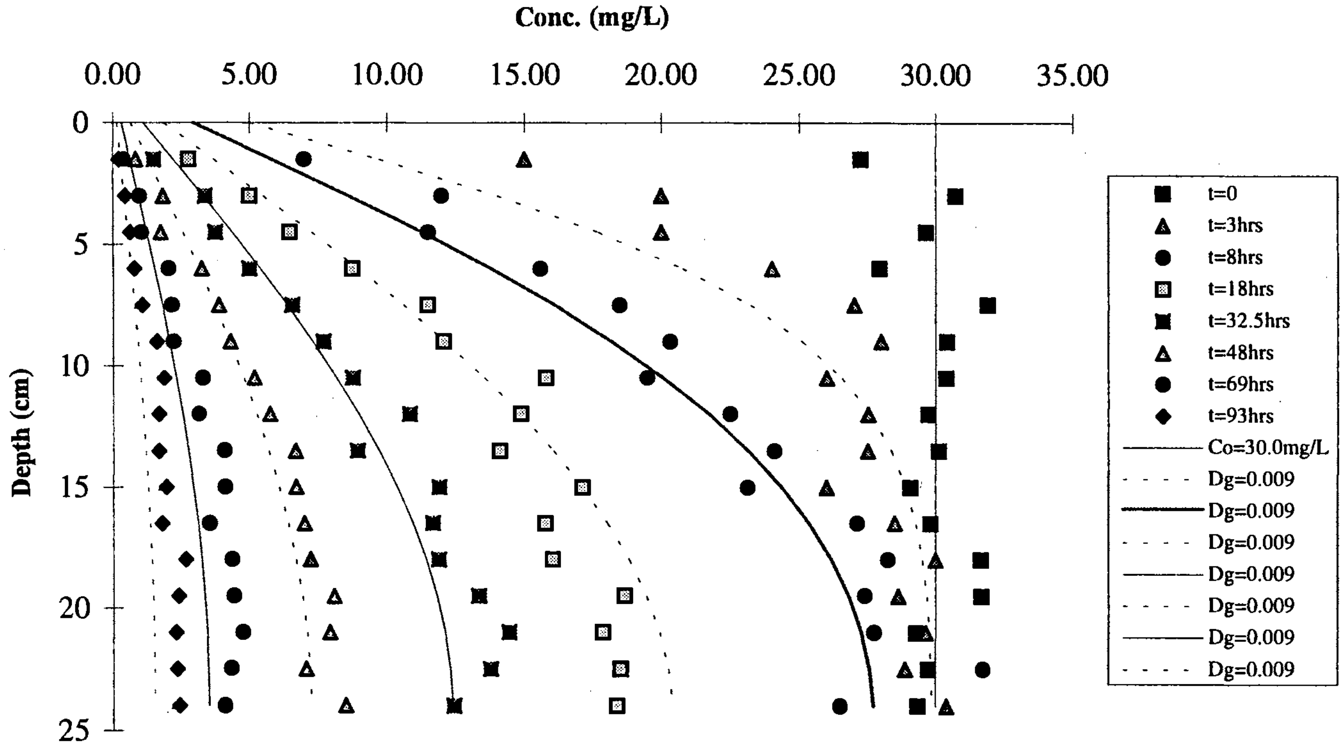


Figure 3-18. Measured and simulated toluene gas phase concentration profiles using Millington-Quirk diffusivity model in column test Teller-2. water content = 0.12 v/v

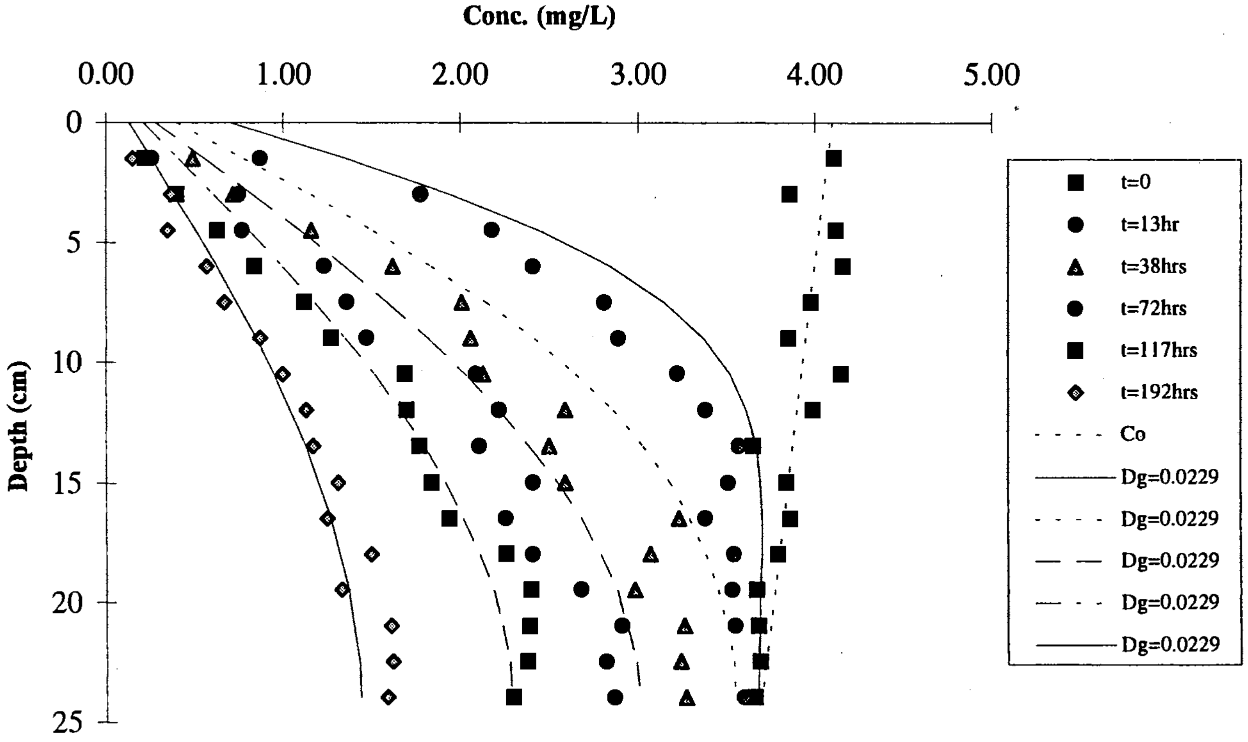


Figure 3-19. Measured and simulated toluene gas phase concentration profiles using Millington-Quirk diffusivity model in column test Teller-3. water content = 0.029 v/v

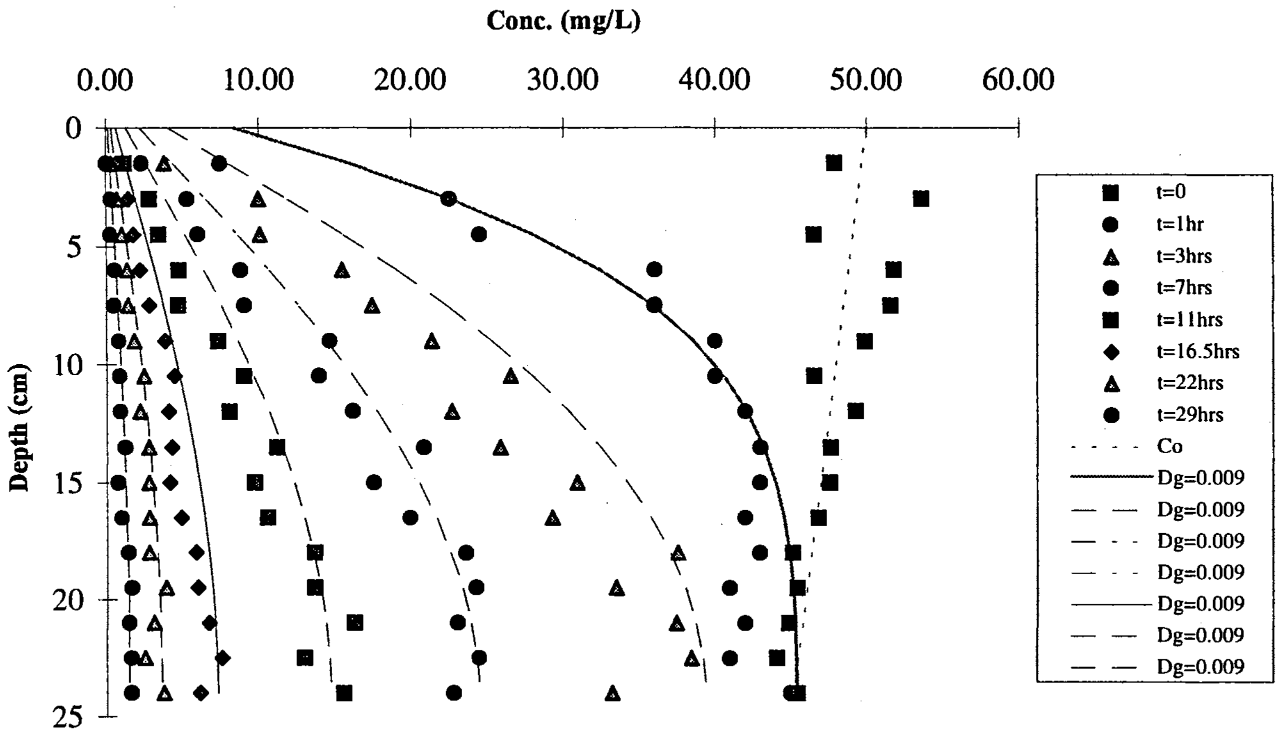


Figure 3-20. Measured and simulated toluene gas phase concentration profiles using Millington-Quirk diffusivity model in column test Dougherty-1. water content = 0.12 v/v

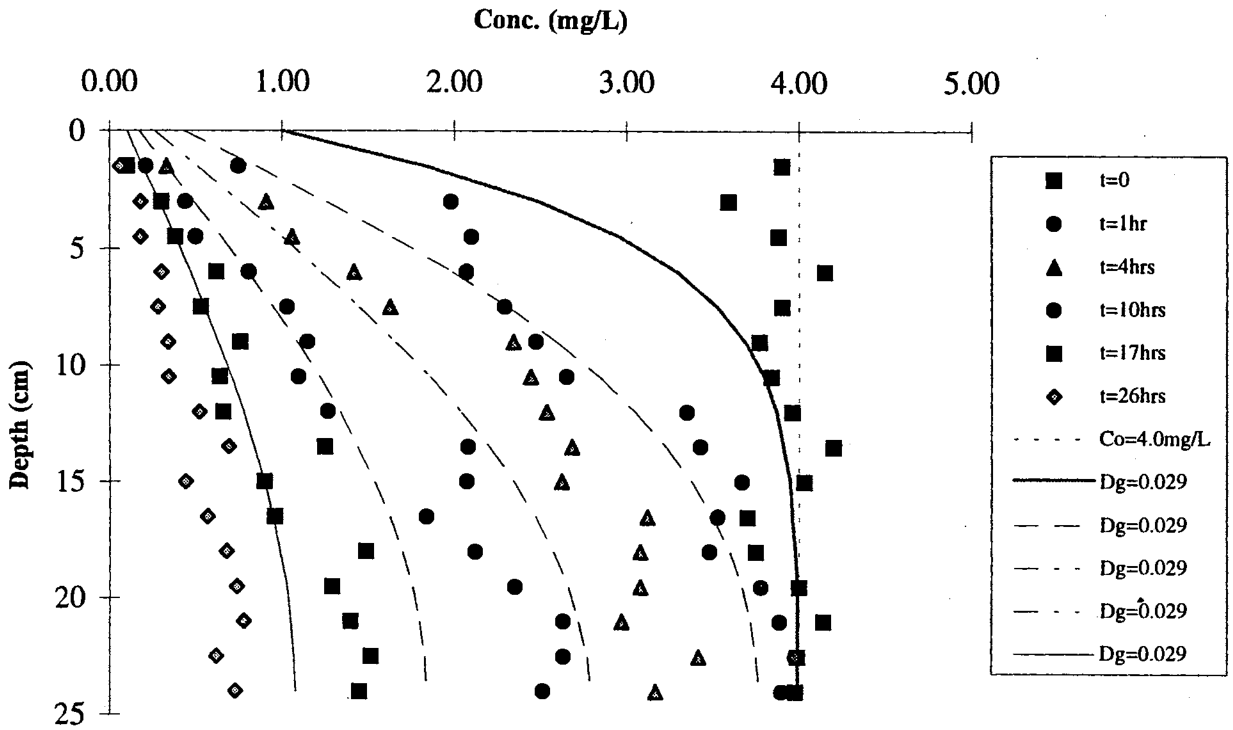


Figure 3-21. Measured and simulated toluene gas phase concentration profiles using Millington-Quirk diffusivity model in column test Dougherty-2, water content = 0.002 v/v

Chapter IV

VOLATILIZATION OF ORGANIC COMPOUNDS FROM SOIL SURFACES

Abstract

The accurate prediction of the volatilization of VOCs is important in the evaluation of soil quality and for predicting exposure for individuals living in the vicinity of waste repositories or landfills. Volatilization is significantly affected by soil type, water content, porosity, surface cover, wind velocity, and air temperature. Little research has been done on this subject due to the complexity and difficulty of the experimentation. The objective of this chapter is to quantify the effects of soil types and water contents on the volatilization of toluene from soil surfaces. Volatilization was measured over a period of two days for Dougherty sand, to thirteen days for Teller loam. The measured fluxes were compared with the predicted volatilization using a volatile organic transport model. The analysis of experimental data and model results reveal that the removal of volatile organic compounds from low or high water content soil is more difficult than from moderate water content soil, while the removal of these contaminants from the loam is more difficult than from sand. The fastest volatilization rate occurs around the soil critical water content.

Introduction

Although volatilization to the atmosphere is a major pathway for the removal of volatile organic compounds (VOCs) from the soil (Hanna and Drivas, 1993), little attention has been paid in the past to its estimation. Contamination by volatile organic compounds in groundwater and the unsaturated zone has brought a need to better predict the volatilization of the VOCs from soil surfaces. The volatilization of VOCs can be affected by many factors including soil type, porosity, water content, surface cover, physical and chemical properties of the compound, and weather (Lindhardt and Christensen, 1994b; Grass et al., 1994; Whang et al., 1993; Gowda et al., 1985; Glotfelty et al., 1984). Soil type can have a significant effect on volatilization. Grass et al. (1994) found that not one climate factor alone was responsible for a high volatilization rate, but that the whole set of climate parameters, affected the results of their test. Logan et al. (1983) measured the volatilization of ammonia from land applied sewage sludges and found that volatilization of ammonia was significantly affected by soil water content and temperature. Donaldson et al. investigated the loss of ten volatile organic compounds from 20-cm soil layers at five soil conditions and concluded that greater rates of loss occurred from wet soils than from dry soils. Ince and Inel (1991) found that the volatilization rates of organic chemicals were highly related to their physical properties, such as the octano/water partition coefficient, molecular weight, and the Henrry' constant. Jury et al. (1990) used a screening model to evaluate the relative volatilization losses of a number of organic compounds under standard soil conditions in two model soils with properties characteristic of sandy and clayey soil. The loss to the atmosphere was assumed to be governed by vapor diffusion through a stagnant air boundary layer. The results of their model prediction indicated that the volatilization of VOCs from the sand surface was much quicker than from the clay surface. They concluded that certain compounds may volatilize from deep subsurface locations or even groundwater unless the soil surface is sealed to prevent gas migration. There were no experimental data to verify the results and their model prediction can be only used to evaluate the relative volatilization of compounds, rather than the absolute volatilization of compounds at a particular site. The prediction of absolute volatilization is difficult and associated with substantial uncertainty (Lindhardt and Christensen, 1994b).

This research will focus on the effects of soil type and water content on the volatilization of toluene from Dougherty sand and Teller loam soil surfaces. The objective of this chapter is to quantify the effects of soil types and water contents on the volatilization of toluene from the soil surfaces. The objective was met in part by the use of a volatile organic transport model to simulate the transport and predict the volatilization of toluene. The measured volatilization of toluene was calculated by the experimental data obtained in the soil column test described in chapter III, while the predicted volatilization of toluene was calculated by the model simulation.

Method of Calculating Volatilization of VOCs

Volatilization was calculated by the change of total compound mass in the soil column. The volatilization of a compound from a soil column between time t and $t + \Delta t$ can be described as,

$$\Delta ET = TM^{t} - TM^{t+\Delta t} \tag{4-1}$$

where TM^t and $TM^{t+\Delta t}$ are the total compound mass in soil column at time t and $t+\Delta t$ respectively. The total compound mass was determined through the measured gas phase concentration in the column test described in chapter III. As volatile organic compounds in the soil usually can be present in the gas phase, dissolve in the liquid phase, and adsorbed by solid phase, the total compound mass in the soil column should be the sum of compound mass in the three phases,

$$C_T^t = \varepsilon C_g^t + \theta C_l^t + \rho_s C_s^t \qquad (4\text{-}2)$$

$$TM^t = C_T^t \cdot V = (\varepsilon C_g^t + \theta C_l^t + \rho_s C_s^t) \cdot V \qquad (4\text{-}3)$$

where C_T^t is the total concentration of the compound in the soil at time t, C_g^t, C_l^t, C_s^t are the compound concentrations in gas phase, liquid phase, and solid phase at time t, and V is the volume of the PVC column. By Henry's Law (3-3) and the definition of the liquid/solid partition coefficient (3-7) equation (4-2) becomes,

$$TM^t = (\phi - \theta + \tfrac{\theta}{H_c} + \rho_s \tfrac{K_d}{H_c}) \cdot C_g^t \cdot V \qquad (4\text{-}4)$$

The toluene gas phase concentration at time t (C_g^t) was measured data, and all the parameters in the right hand side of equation (4-4) can be determined from the literature or experiment. When water content is above the "critical water content", the partition coefficient K_d is a constant, which is equal to the liquid/solid partition coefficient under saturated soil condition. When water content is below the "critical water content", K_d is a function of both organic matter content and the soil water content. Henry's Law is assumed still to be valid in this situation and K_d can be determined either by experiment or by a partition coefficient model.

Since the gas phase concentration is not uniform along the depth of the soil column except in the beginning, the column was divided into seventeen layers to calculate the toluene mass accurately. Therefore, the compound volatilization from the soil column during time t to time $t+\Delta t$ can be calculated as,

$$\Delta ET = \sum_{i=1}^{n} [C_g^t(i) - C_g^{t+\Delta t}(i)]\left(\phi - \theta + \frac{\theta}{H_c} + \frac{\rho_s \cdot K_d}{H_c}\right) \cdot \Delta v \tag{4-5}$$

where n is the number of soil layers, (n=17), and $C_g^t(i)$, $C_g^{t+\Delta t}(i)$ are the gas phase compound concentrations in the ith soil layer at time t and $t+\Delta t$, respectively. Δv is the soil volume of each layer. The compound concentration above the soil surface was assumed to be zero in the calculation of gas flux.

Experimental Results and Discussion

The accuracy of predicted volatilization is illustrated by the plots of measured and predicted toluene volatilization. The evaluation of effects of soil types and water content on volatilization is based on the volatilization process, the required volatilization time, the initial toluene mass in the soil column, and the initial toluene gas phase concentration. Two scenarios of soil contamination by toluene were studied in this research:

a. equal initial toluene gas phase concentration in two contaminated soils at several water contents.

b. constant initial toluene mass in columns of two contaminated soils at several water contents.

The measured and predicted toluene volatilization calculated using equation 4-5 are shown in Figures 4-1 to 4-5. The cumulative volatilization from time 0 to time t was the difference of the initial total toluene mass in the column and the total toluene mass in the column at time t. The measured toluene volatilization was calculated using the measured data, while the predicted toluene volatilization was obtained using the simulated toluene transport data. Figures 4-1 to 4-5 show that the predicted toluene volatilization matches the measured value well except in column tests Teller-1 and Dougherty-2. In Teller-1 the model underpredicted the toluene volatilization, which may be caused by the short soil incorporation time with toluene as stated in chapter III. As a result of this short incorperation the toluene partition equilibrium among gas, liquid, and solid phases has not been reached during the experiment. Therefore, the measured toluene transport was faster than the simulated data and caused an underpredection of toluene volatilization. In Dougherty-2, air-dry sand has an extremely low water content of 0.0012 g/g and the underpredicting by Millington-Quirk may have caused the slight underprediction of toluene volatilization.

To evaluate the effects of soil types and the water contents on the volatilization, it is assumed that the initial gas phase toluene concentration is 50 mg/L. The volatilization process at different water content from two soils was calculated based on the simulated toluene transport process and presented in Figures 4-6a and 4-6b. The relationships between volatilization time needed for 99% of the toluene in the soil column to evaporate from the surfaces and the soil water content are provided in Figures 4-7a and 4-7b. The volatilization time was obtained by running the transport model until only 1% of the total toluene mass was left in the soil column. As toluene adsorption onto soil is a function of soil water content, the total toluene mass differs even though the initial gas phase toluene concentration was the same. Initial total toluene mass in the soil column versus soil water content in Teller and Dougherty is plotted in Figures 4-8a and 4-8b.

Soil water content has a significant effect on toluene volatilization in the two soils studied as shown in Figures 4-6a, 4-6b, 4-7a, and 4-7b. The toluene transport inside the soil and volatililzation rate from the surface is much slower at extremly low and high water content. Extremely low and high water content soil has a higher ability to retain the volatile organic, while those contaminants can not be retained as long in moderately dry or moderately wet soil. The fastest volatilization rate occurs around the soil critical water content, because beyond this water content soil adsorption is a constant while the diffusion coefficient decreases. This agrees with the studies of Donaldson et al. (1992), Jin and O'Connor (1990), and Lindhardt and Christensen (1994a). Donaldson et al. (1992) observed in their experiment that the volatilization when soil was wetted was quicker than when soil was dry. Jin and O'Connor (1990) concluded that the toluene volatilization flux was greatly reduced by increased soil water contents and soil OC contents based on their experimental results at field capacity and soil saturation. The measured naphthalene volatilization data of Lindhardt and Christensen (1994a) indicated a slower volatilization rate at high water content than at moderate water content.

The volatilization from Dougherty sand is much faster than from Teller loam, even at the same water content condition due to the high toluene adsorption onto Teller loam. Figures 4-8a and 4-8b suggest that due to the high soil adsorption coefficient in low water content soil, the total toluene mass could be several orders in magnitude greater than at higher water content. Table 4-1 lists the volatilization time and the initial toluene mass in two soils at different water content.

The effects of soil type and water content are also shown in Figures 4-9 to 4-12. Figures 4-9a and 4-9b present the toluene volatilization process at several water contents in two soils. For both cases 7000 mg of toluene contaminated two soil columns with Teller loam and Dougherty sand. It is apparent that soil water content has impacted the toluene volatilization and the volatilization rate in Dougherty is much faster than in Teller.

The time required for 99% of the toluene to evaporate from both soils as a function of soil water content are presented in Figures 4-10a and 4-10b. These two figures imply that the removal of the same amount of organic contaminant from extremely low and high water content soil or from high adsorption soil will take much longer than from moderate water content soil or from low adsorption soil (Taylor, 1978). For example, removal of 7000 mg toluene from a Teller loam column with water content at 0.0148 will take about 717 days, while the removal of the same amount of toluene at 0.08 water content will take only 4 days. The removal of 7000 mg of toluene from a Teller loam column at a water content of 0.3 will take about 212 days, but it will take only 56 days for Dougherty sand at the same water content. The fastest volatilization still occurs around the soil critical water content.

As toluene adsorption onto Teller is much larger than onto Dougherty, the initial gas phase concentration in the Teller loam column is smaller than that in Dougherty, even though the total toluene mass is the same. Figures 4-11a and 4-11b provide the initial concentration in Teller and Dougherty at different soil moistures. The initial gas phase concentration in the Dougherty sand column is much higher than in Teller loam at the same water content. At the same time the initial gas phase toluene concentration in low water soil is quite small compared with that in higher water content. For example, for 7000 mg of toluene in 0.015 water content Teller, the initial toluene gas phase concentration was as small as 0.11 mg/L, while the same amount of toluene in 0.08 v/v Teller loam column resulted in an initial toluene gas phase concentration of 56.2 mg/L. This amount of toluene produced an initial concentration of 46.2 mg/L in 0.3 water content Teller loam column and 136 mg/L in the same water content Dougherty sand column. Therefore, even though the measured gas phase concentrations of volatile organic contaminants in low water content soil are small, the soil contamination may be severe because large amounts of contaminant can be adsorbed by the soil solids and it will take a long time to remove them. When two soils were contaminated by 7000 mg toluene, the volatilization time and the initial gas phase concentration at different soil water content are provided in Table 4-2.

Toluene volatilization process in both Teller loam and Dougherty sand at water content 0.2 and 0.3 are plotted respectively in Figures 4-12a and 4-12b to show the impact of soil type on the volatilization of toluene caused by the different soil adsorption. These two figures show that high adsorption soil has a slower volatilization rate than low adsorption soil at any soil water content.

Conclusions

The following conclusions can be drawn by the study of toluene volatilization in this research:

a. The removal of volatile organic compounds from low or high water content soil is much more difficult than from the soil at moderate water contents. The removal of these contaminants from soil with high organic matter content is more difficult than from soil with relatively low organic matter content.

b. The fastest volatilization rate occurs around the soil critical water content.

c. Even though the measured gas phase concentrations are the same, the soil contamination is much more severe in low water content soil and in high organic matter soil than in high water content soil and in low organic matter soil.

d. The removal of the same amount of organic contaminant from low and high water content soil or from high adsorption soil would take much longer than from moderately water content soil or from low adsorption soil.

e. Even though the measured gas phase concentrations of volatile organic contaminants are small, the contamination in low water content soil or in high organic matter content soil may be severe because large amounts of contaminant could be adsorbed by soil and it will take long time to remove them from soil systems.

f. High organic matter soil has a slower volatilization rate than low organic matter soil at any soil water content.

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Table 4-1

IMPACTS OF WATER CONTENT ON VOLATILIZATION TIME

AND INITIAL TOLUENE MASS

C_0=50 mg/L

Soil	Water Content v/v	Volatilization Time day	Initial Toluene Mass mg
Teller Loam	0	1500	6270000
	0.0148	600	3180000
	0.0294	51	92200
	0.0563	8	14800
	0.0800	4	5970
	0.1000	6	6170
	0.2000	22	6730
	0.2500	56	7010
	0.3000	215	7290
Dougherty Sand	0	58	120000
	0.0012	4.5	11200
	0.0250	3.0	6130
	0.0500	1.0	1070
	0.1000	1.5	1350
	0.2000	4.5	1910
	0.2500	12	2190
	0.3000	46	2470

Table 4-2

IMPACTS OF WATER CONTENT ON VOLATILIZATION TIME AND INITIAL TOLUENE CONCENTRATION

Initial Mass=7000 mg

Soil	Water Content v/v	Volatilization Time day	Initial Toluene Conc. mg/L
Teller Loam	0	1130	0.05
	0.0148	717	0.11
	0.0294	35	3.64
	0.0563	7	22.6
	0.0800	4	56.2
	0.1000	6	54.5
	0.2000	22	49.9
	0.2500	55	47.9
	0.3000	212	46.2
Dougherty Sand	0	39	2.79
	0.0012	4.0	30.0
	0.0250	3.0	54.8
	0.1000	1.5	249
	0.2000	6.0	176
	0.2500	15	153
	0.3000	56.5	136

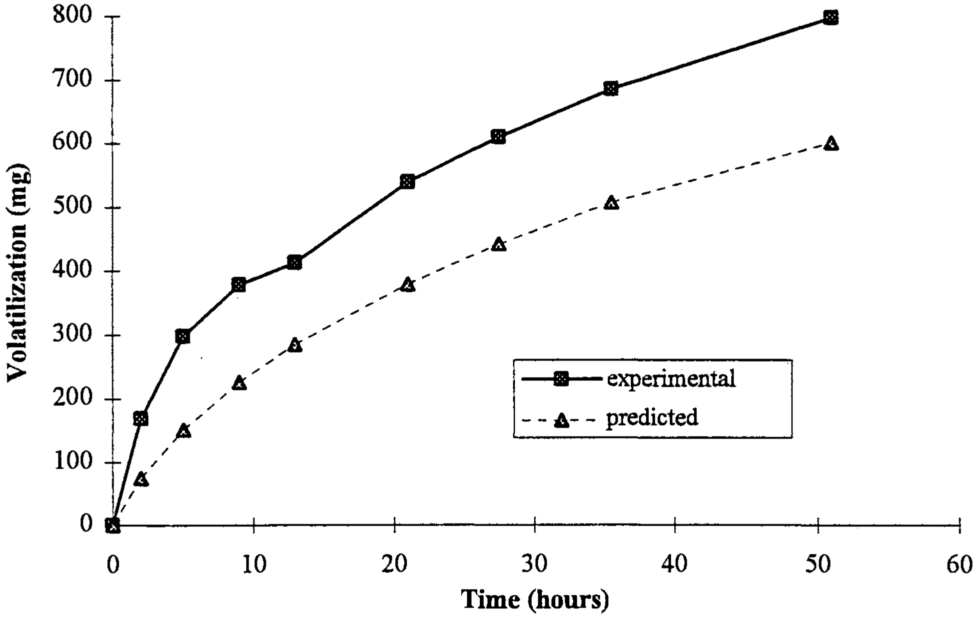


Figure 4-1. Measured and predicted toluene volatilization in test Teller-1.

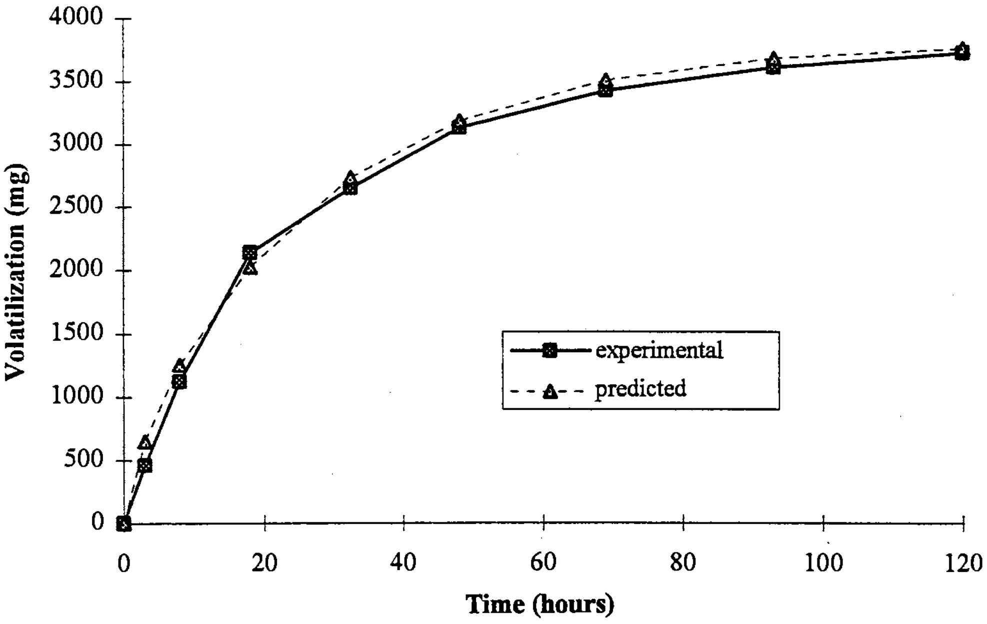


Figure 4-2. Measured and predicted toluene volatilization in test Teller-2.

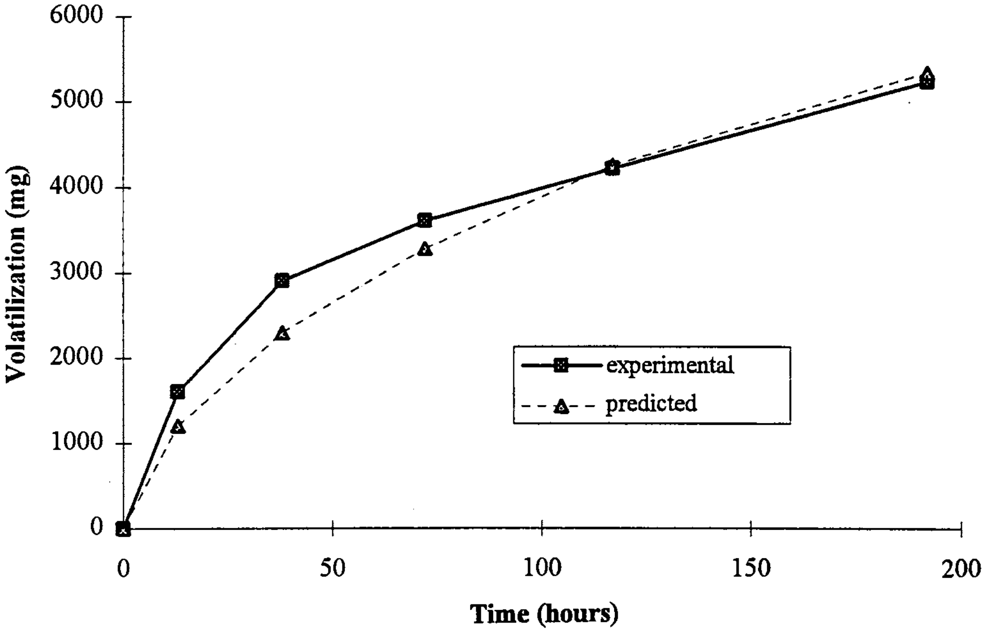


Figure 4-3. Measured and predicted toluene volatilization in test Teller-3.

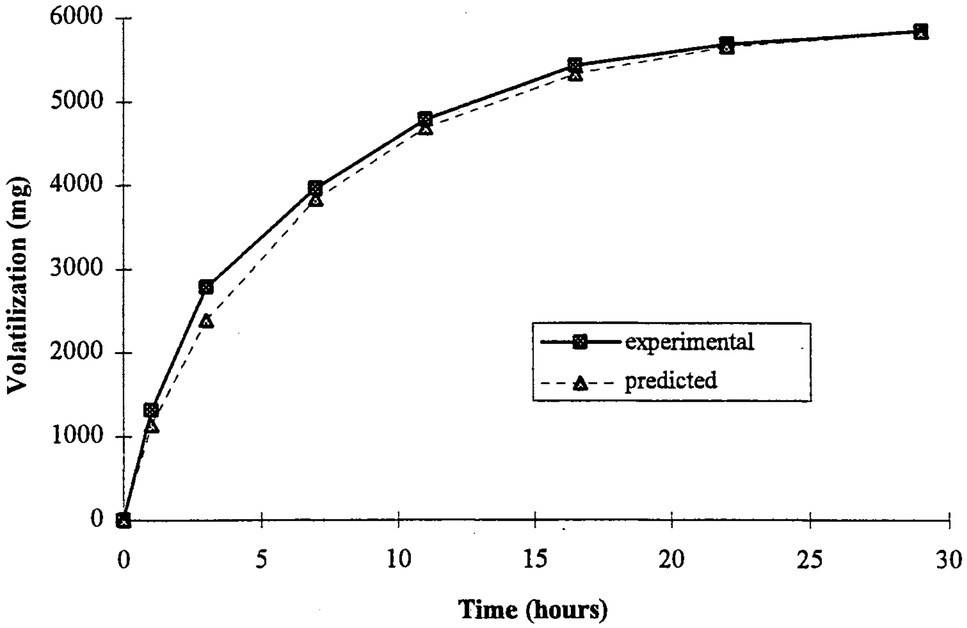


Figure 4-4. Measured and predicted toluene volatilization in test Dougherty-1.

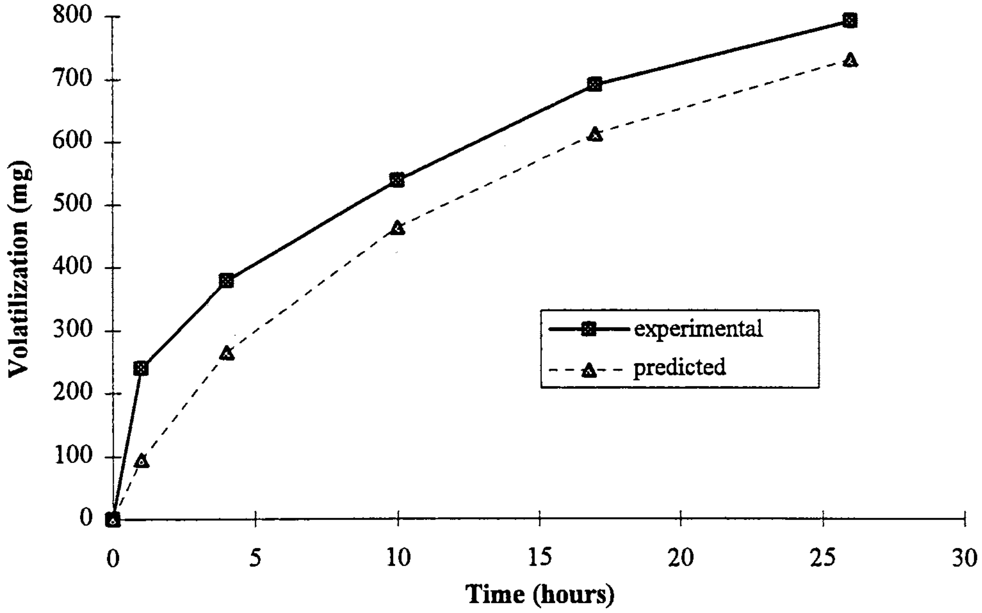
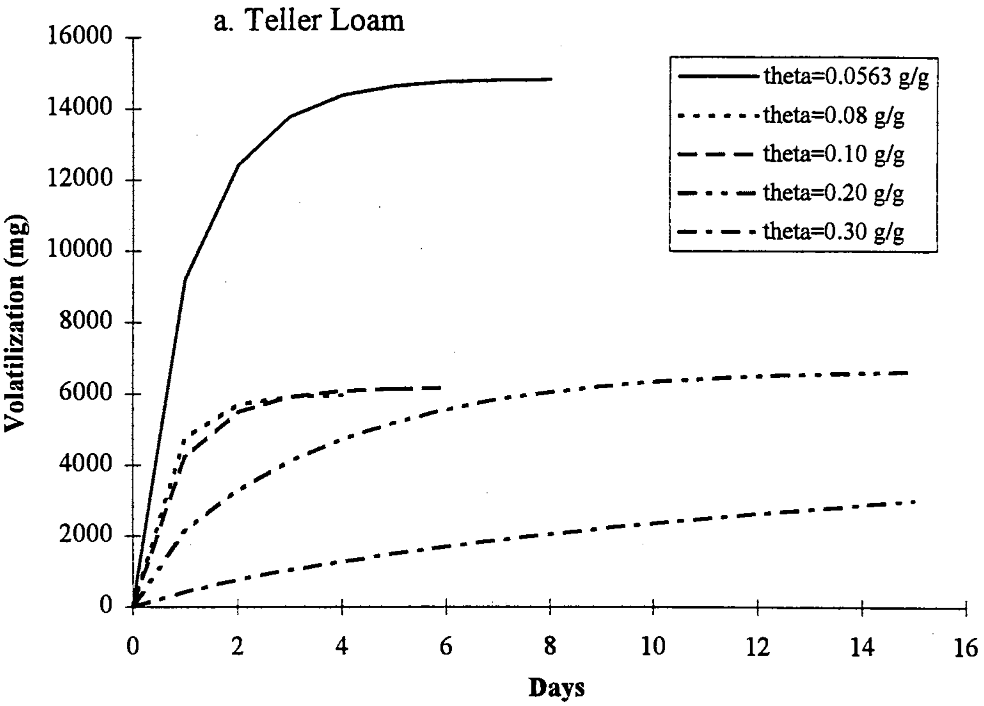


Figure 4-5. Measured and predicted toluene volatilization in test Dougherty-2.



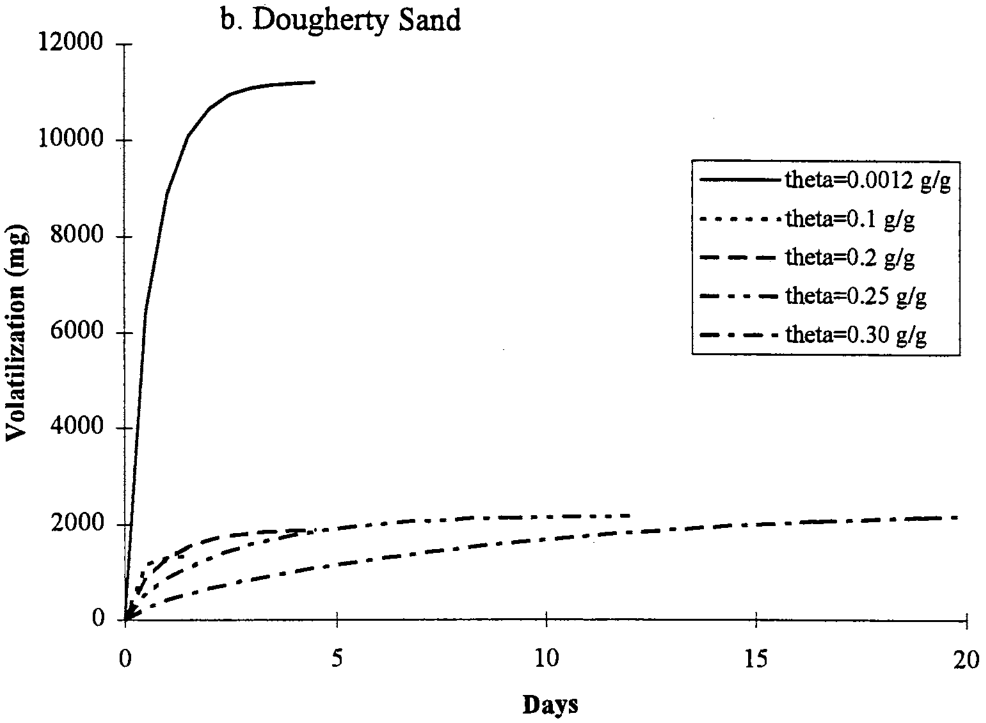


Figure 4-6. Toluene volatilization at different moisture with C_0=50 mg/L.

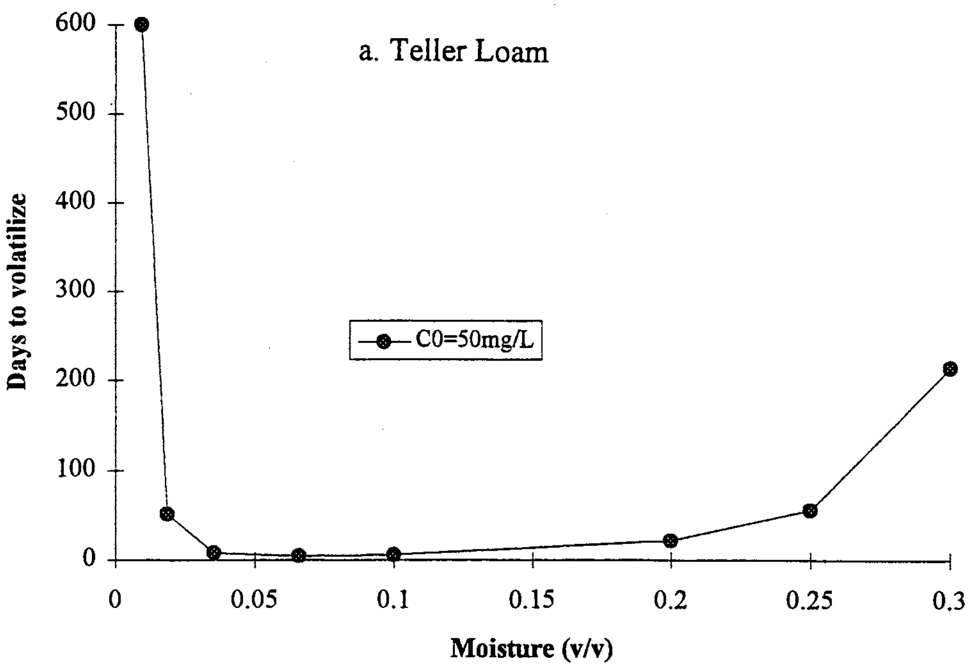


Figure 4-7. Toluene volatilization time at various soil moistures with C_0=50 mg/L.

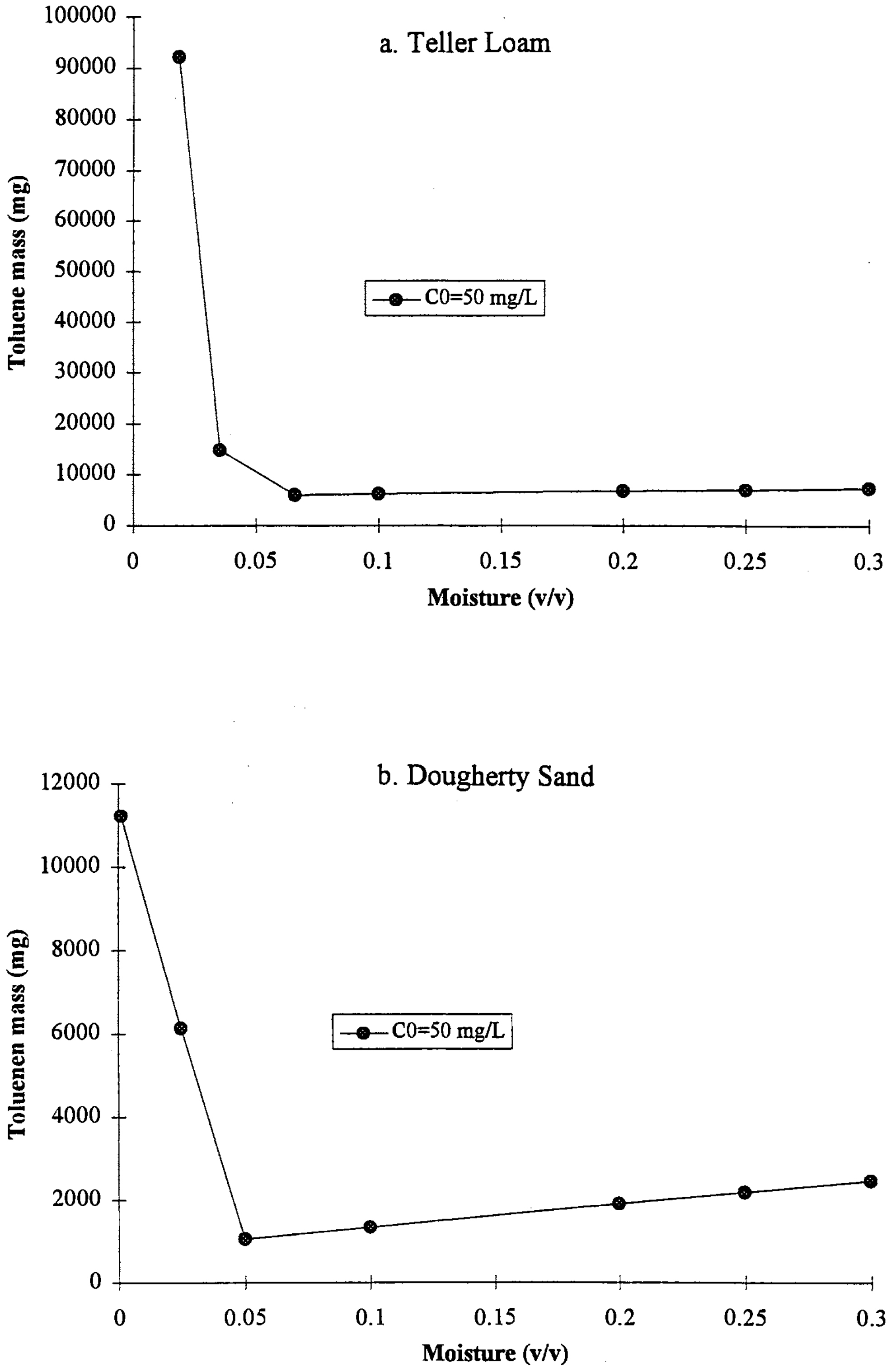
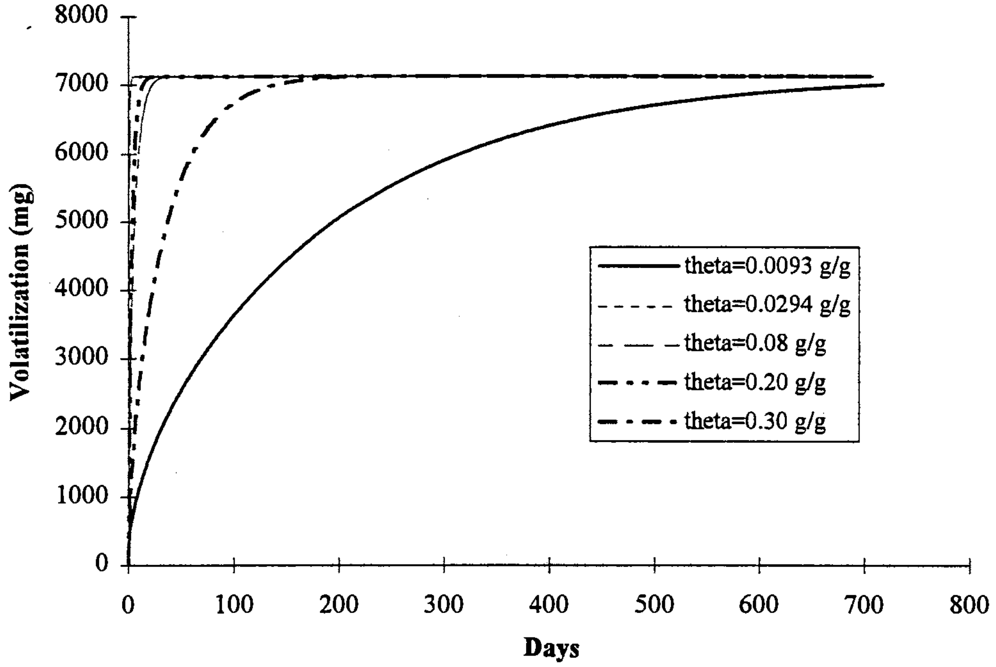


Figure 4-8. Initial toluene mass at different moisture wth Co=50 mg/L.

a. Teller Loam



b. Dougherty Sand

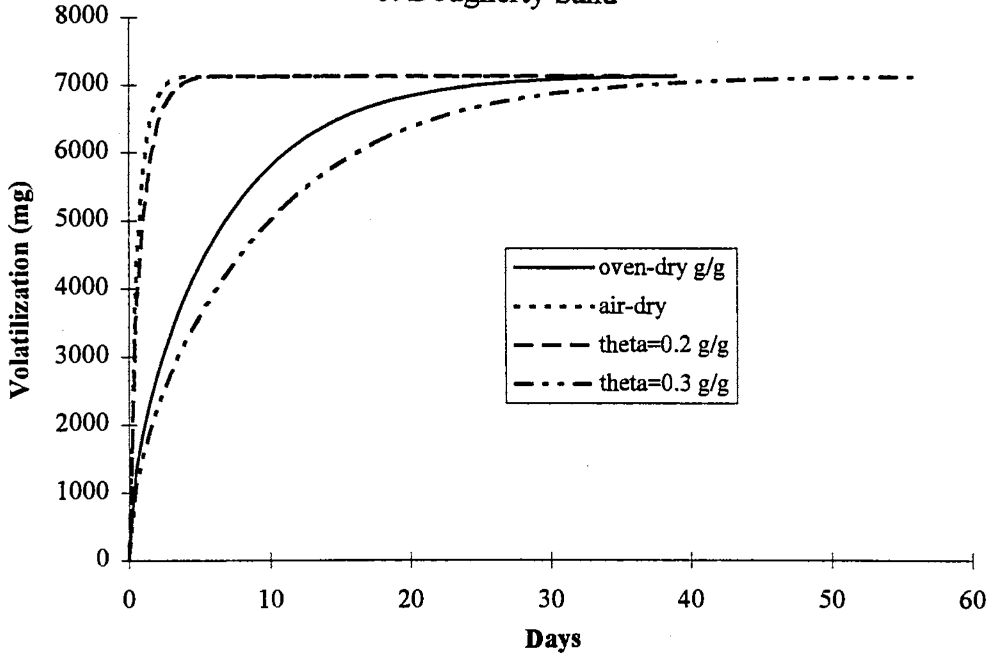
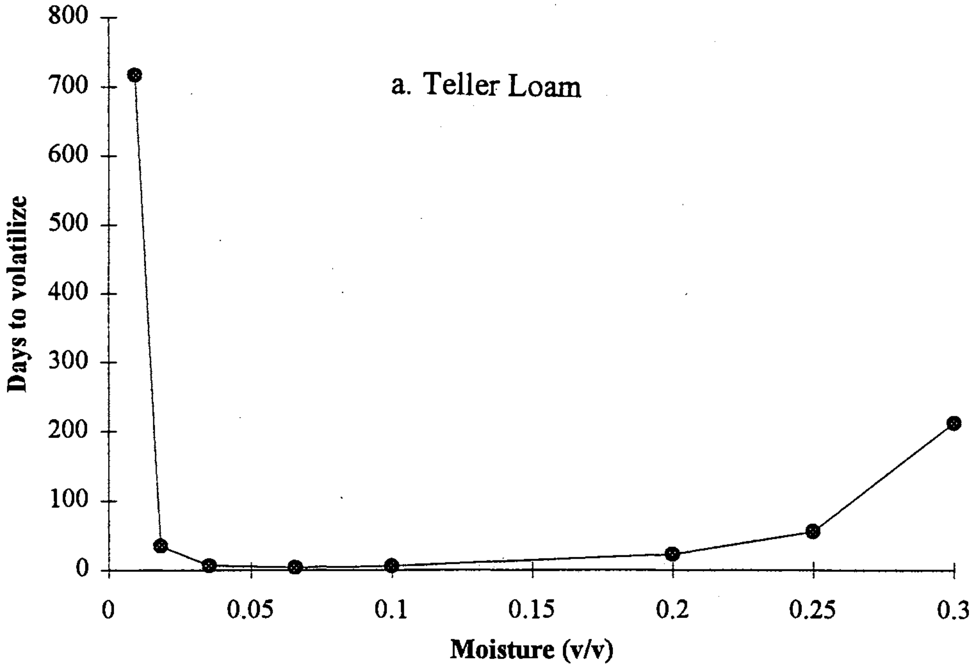


Figure 4-9. Volatilization at different moisture with equal initial toluene mass of 7000 mg.



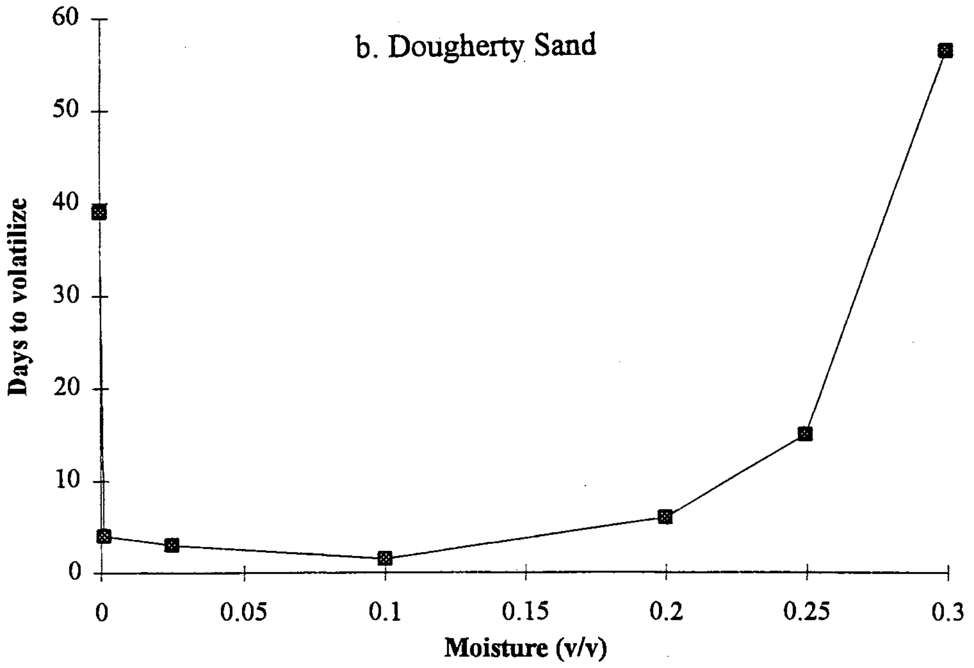


Figure 4-10. Volatilization time at various soil moistures with initial toluene mass of 7000 mg.

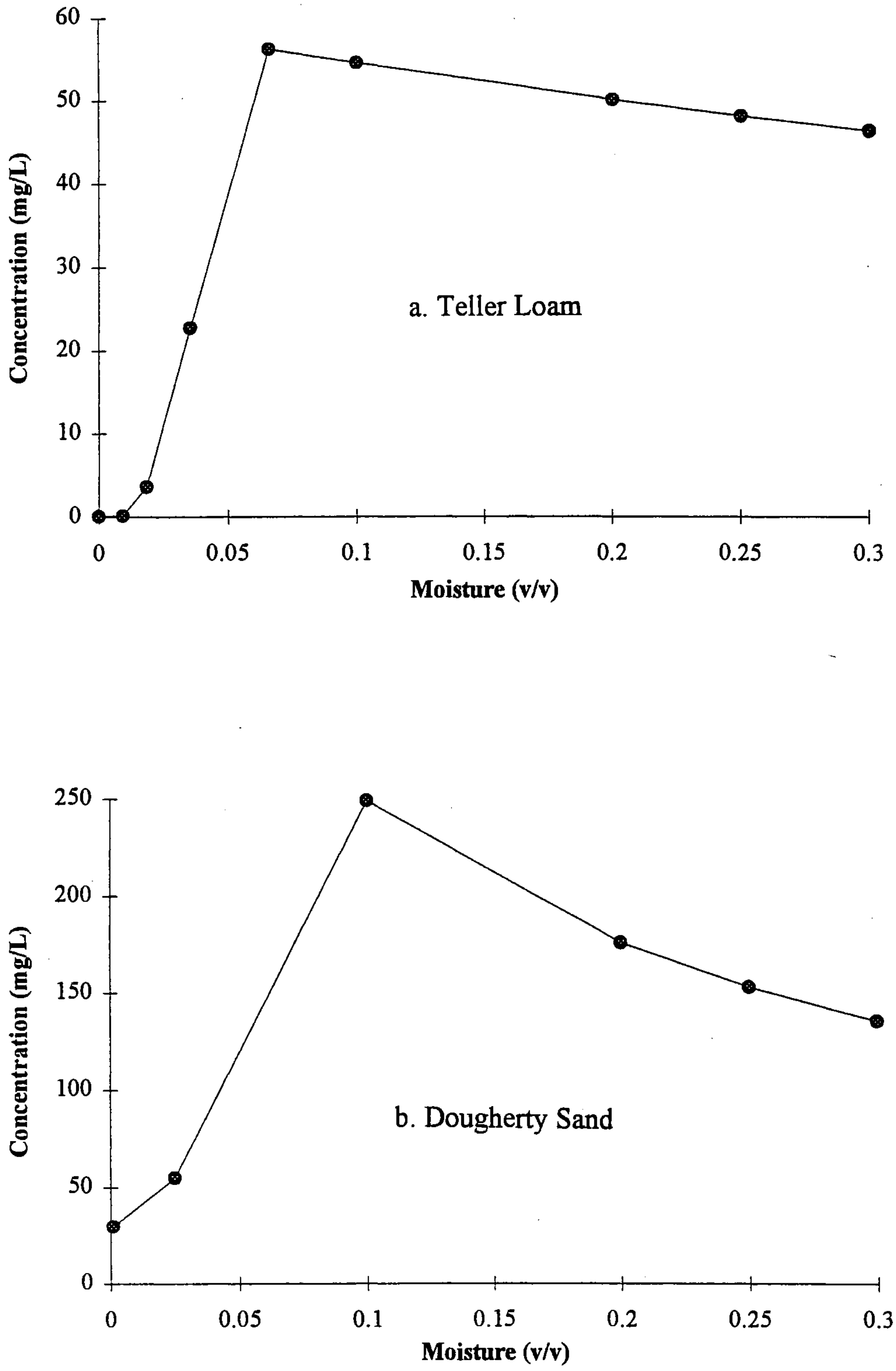
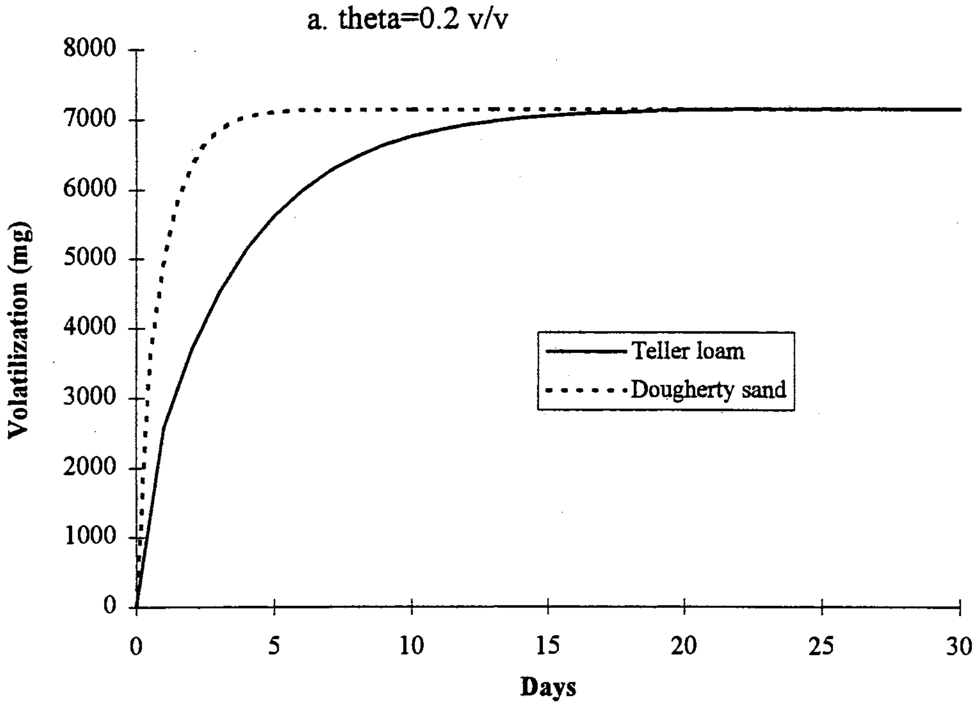
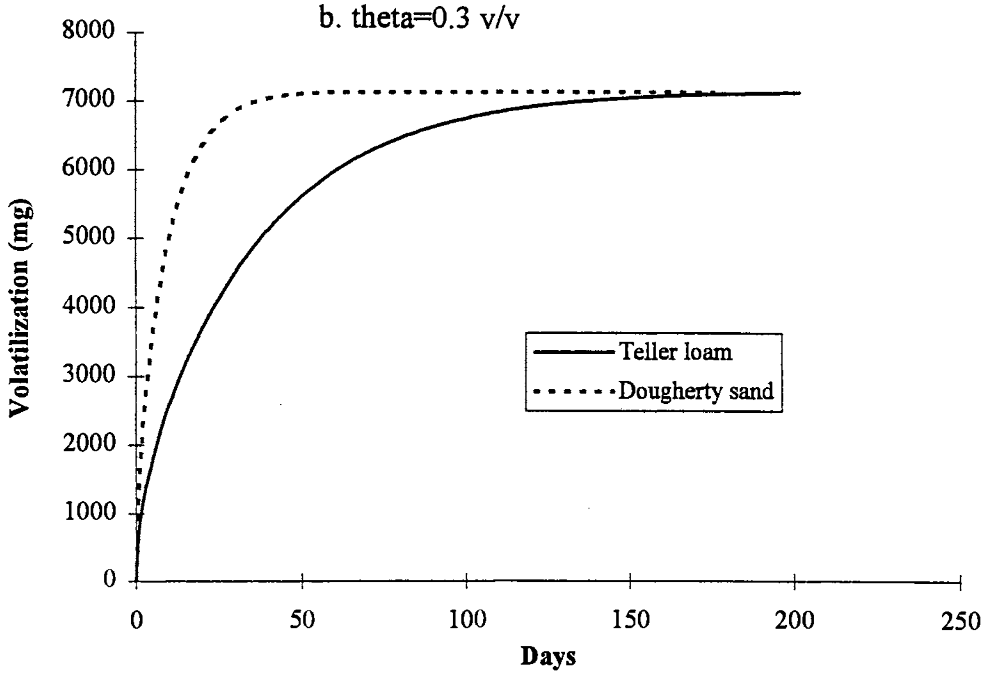


Figure 4-11. Initial gas phase concentration at different moisture with equal toluene mass of 7000 mg.



a. theta=0.2 v/v



b. theta=0.3 v/v

Figure 4-12. Volatilization of Teller and Dougherty at different moisutures.

Chapter V

SUMMARY AND RECOMMENDATIONS FOR FUTURE STUDY

The objective of this research was to investigate the adsorption and transport of volatile organic compounds in low water content soil. This investigation examined toluene vapor adsorption onto soil, diffusion within soil, and volatilization from soil surfaces. The measured soil sorption data was analyzed in Chapter II and used in Chapter IV, while in Chapter III the measured diffusion coefficient was compared with the Millington-Quirk diffusivity model. It is concluded that the Millington-Quirk model is a good predictor when soil water content is not too small. In Chapter IV the measured and predicted toluene volatilization were compared, and the volatilization from two contaminated soils at different water contents was estimated based on the simulated toluene transport data using partition coefficient obtained in Chapter II and the Millington-Quirk diffusivity value. The objective has been achieved and the results of this study should be useful in the modeling and prediction of volatile organic contaminant transport.

Future research should focus on the mechanism of soil sorption in low water content soil. Adsorption measurement of a variety of organic compounds is needed to develop a general model to predict the adsorption at different soil moistures. Further studies are also needed to conclude if critical water content varies with the type of organic compound. Additional data at extremely low and high water contents is needed to better quantify the error of Millington-Quirk.

Volatilization of organic contaminants from the soil surface could be affected by many factors, such as soil type, soil water content, porosity, surface cover, wind velocity, and air temperature. The impact of soil type and water content are studied in this research. Further studies are needed on the effects of other factors on volatilization. Soil water content was assumed to be constant in the prediction of toluene volatilization in chapter IV, this assumption may cause the underprediction of the toluene volatilization in high water content soil due to the neglect of the toluene volatilization caused by water loss at the soil surface. Further studies are needed to quantify the impact of water loss on volatilization.

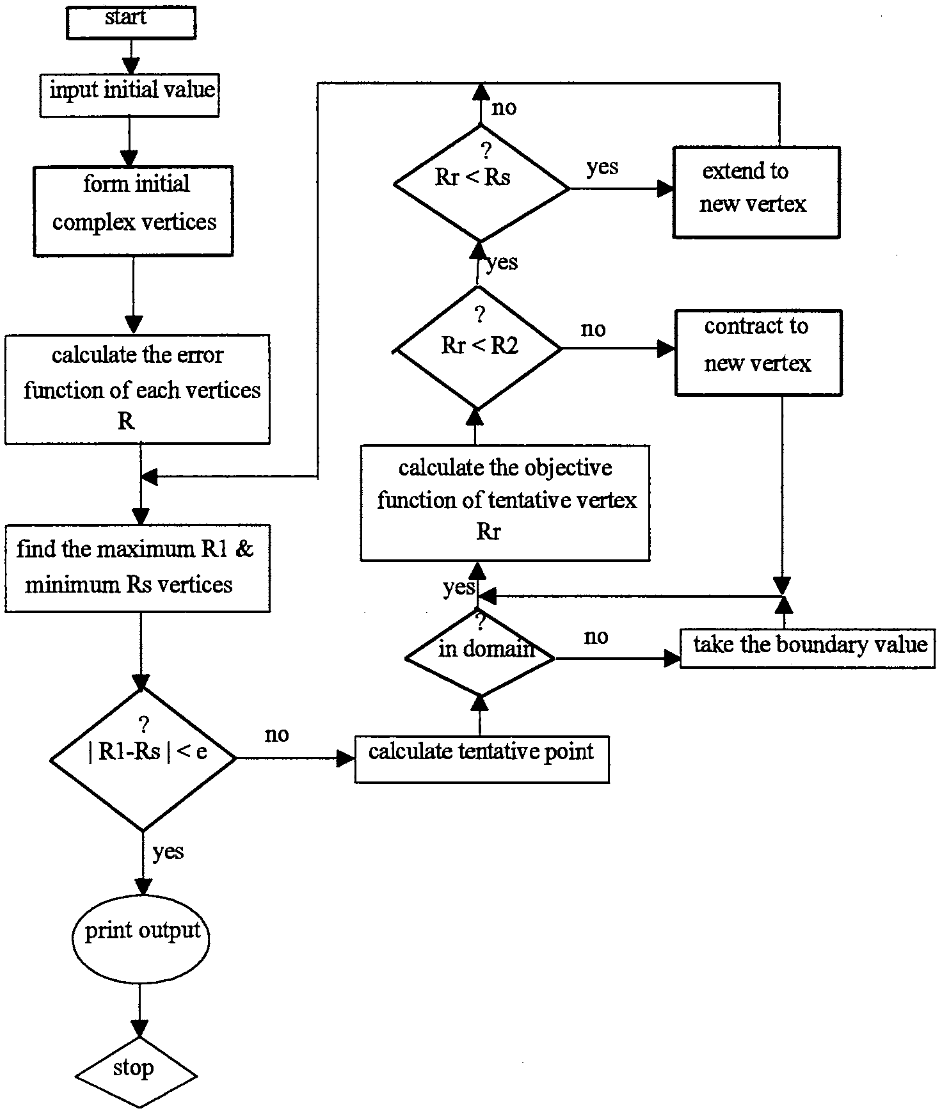
Finally, while the procedures used here were adequate, improvements would be welcome. Increases in accuracy could benefit the measurements of vapor diffusion. Standardization of laboratory measurements of soil specific surface area between water vapor or nitrogen may provide better consistency in the estimates of the critical water content.

Appendix A

FLOW CHART AND COMPUTER PROGRAMS

FLOW CHART OF OPTIMUM PARAMETERS SEARCH TECHNIQUE

- COMPLEX METHOD



PROGRAM OF SEARCHING OPTIMUM PARAMETERS

```
' This program was used to search optimum Kd and Dg parameters
' in multi-phase solute transport governing equation using complex
' search method.  Finite difference method was used to solve the
' governing equation.  Optimum Kd and Dg were searched for each
' concentration curve.  This program was run by MS-DOS QBasic
' and written by
'
'                  Ming Yu


DECLARE SUB condition (Kd!(), Dg!())
DECLARE SUB expend (Kd!(), Dg!(), z!(), Cg!(), RR!(), MCg!(), C0(), Ntime)
DECLARE SUB contract (Kd!(), Dg!(), z!(), Cg!(), RR!(), MCg!(), C0(), Ntime)
DECLARE SUB conc (i!, Kd!(), Dg!(), z!(), Cg!(), RR!(), MCg!(), C0(), Ntime)

    OPEN "i", #1, "c:\ming\paramet\optimum\input7.dat"
    OPEN "o", #2, "c:\ming\paramet\optimum\output7.dat"
    DIM z(17), MCg(17), Cg(17), Kd(4), Dg(4), RR(4), C0(17)

10  FOR k = 1 TO 8                   'input time parameters
    INPUT #1, k(k)
    NEXT k

20  FOR j = 1 TO 17                  'input the depth of each sampling ports on PVC column
    INPUT #1, z(j)
    NEXT j

30  FOR j = 1 TO 17                  'input initial concentration profile
    INPUT #1, C0(j)
    NEXT j

    k = 1
120 Ntime = k(k)
    IF Ntime = 0 THEN
    GOTO 150
    ELSE
40  FOR j = 1 TO 17                 'input measured gas phase
    INPUT #1, MCg(j)                'toluene concentration
    NEXT j
    END IF

    a(1) = .5                        'choose four initial vertices
    a(2) = .2                        'and each vertex includes two
    a(3) = .3                        'parameters Kd and Dg.  Calculate
    a(4) = .1                        'objective function value ERR of
    b(1) = .3                        'each vertices
    b(2) = .2
    b(3) = .4
    b(4) = .1
```

```
    FOR i = 1 TO 4
    Kd(i) = 0 + a(i) * (1 - 0)
    Dg(i) = 0 + b(i) * (.1 - 0)
    CALL conc(i, Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
    NEXT i

50  FOR i = 1 TO 3                    'put these four vertices in decendent
    FOR j = i + 1 TO 4                'order by the ERR value
    IF RR(i) < RR(j) THEN
       C1 = RR(i)
       C2 = Kd(i)
       C3 = Dg(i)
       RR(i) = RR(j)
       Kd(i) = Kd(j)
       Dg(i) = Dg(j)
       RR(j) = C1
       Kd(j) = C2
       Dg(j) = C3
      ELSE
      END IF
    NEXT j
    NEXT i

    IF RR(1) - RR(4) < .001 THEN      'if the max and min ERR is less than 0.01, stop searching and
    FOR i = 1 TO 4                    'print out the results
    CALL conc(i, Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
    PRINT #2, USING "i=##  Kd=#.###  Dg=#.####  RR=######.##"; i; Kd(i); Dg(i); RR(i)
    PRINT #2, "     Z(j)    Cg(j)      MCg(j)"
       FOR j = 1 TO 17
       PRINT #2, USING "     ##.#    ###.##      ###.##"; z(j); Cg(j); MCg(j)
       NEXT j
       NEXT i

   PRINT #2, USING "     RR= ######.##  ######.##  ######.##  ######.##"; RR(1); RR(2); RR(3);
RR(4)
   PRINT #2, USING "     Kd=#.###    #.###    #.###    #.###    #.###"; Kd(1); Kd(2); Kd(3); Kd(4)
   PRINT #2, USING "     Dg=#.####   #.####   #.####   #.####   #.####"; Dg(1); Dg(2); Dg(3);
Dg(4)

    k = k + 1
    PRINT , k(k)
    GOTO 120
    ELSE
     S1 = (Kd(2) + Kd(3) + Kd(4)) / 3          'find the tentative new point to
     Kd(1) = S1 + 1.3 * (S1 - Kd(1))           'replace the rejected vertex (Kd(1),Dg(1))
     S2 = (Dg(2) + Dg(3) + Dg(4)) / 3
     Dg(1) = S2 + 1.3 * (S2 - Dg(1))
    END IF

    CALL condition(Kd(), Dg())                 'determine if new vertex is in
                                               'the parameter domain
100  i = 1

    CALL conc(i, Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
```

```
60     IF RR(1) < RR(2) THEN                    'determine if the new vertex is the new best one
        IF RR(1) > RR(4) THEN                   'if yes, expend on that direction to new vertex
        GOTO 50                                 'if no, determing if it is the new worst one
        ELSE                                    if yes, contract to new vertex
        CALL expend(Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
        GOTO 50
        END IF
        ELSE
        CALL contract(Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
        GOTO 50
      END IF

150  STOP

'    The following subprogram SUB conc is used to solve the governing equation using finite difference
'    method.  The toluene concentration profile along column at every half hour can be obtained by runing
'    this subprogram.

SUB conc (i, Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
      DIM b(17), w(17), y(17), TC0(17)
      k = 1
      RR(i) = 0
      R = .4 - .17 + .17 / .26 + 1.59 * Kd(i) / .26
      alfa = Dg(i) / (R * 1.5 ^ 2)
      beta = -2 * Dg(i) / (R * 1.5 ^ 2) - 1 / (30 * 60)
      gama = Dg(i) / (R * 1.5 ^ 2)
      b(1) = beta
      w(1) = gama / b(1)
      FOR j = 2 TO 16
      b(j) = beta - alfa * w(j - 1)
      w(j) = gama / b(j)
      NEXT j
      b(17) = -Dg(i) / (R * 1.5 ^ 2) - 1 / (30 * 60) - alfa * w(16)
      FOR j = 1 TO 17
      TC0(j) = C0(j)
      NEXT j
20    y(1) = -TC0(1) / (30 * 60 * b(1))
      FOR j = 2 TO 17
      y(j) = (-TC0(j) / (30 * 60) - alfa * y(j - 1)) / b(j)
      NEXT j
      Cg(17) = y(17)
      FOR j = 16 TO 1 STEP -1
      Cg(j) = y(j) - w(j) * Cg(j + 1)
      TC0(j) = Cg(j)
      NEXT j
      TC0(17) = Cg(17)
      k = k + 1
      IF k = Ntime THEN
      GOTO 30
      ELSE
      GOTO 20
      END IF
30    FOR j = 1 TO 17
      RR(i) = RR(i) + (Cg(j) - MCg(j)) ^ 2
      NEXT j
```

```
END SUB

'    The following subprogram SUB condition was used to determine if the new vertex was in the
'    parameter domain.  If not, let them take the boundary value.

SUB condition (Kd(), Dg())
     IF Kd(1) < 0 THEN
     Kd(1) = 0
     ELSEIF Kd(1) > 1 THEN
     Kd(1) = 1
     END IF

     IF Dg(1) <= 0 THEN
     Dg(1) = .00000001#
     ELSEIF Dg(1) > .1 THEN
     Dg(1) = .1
     END IF
END SUB

'     The following subprogram SUB contract was used to contract the new worst vertex to form an
'     another vertex.

SUB contract (Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
     G1 = (Kd(2) + Kd(3) + Kd(4)) / 3
     Kd(1) = G1 + .7 * (Kd(1) - G1)
     G2 = (Dg(2) + Dg(3) + Dg(4)) / 3
     Dg(1) = G2 + .7 * (Dg(1) - G2)
     CALL condition(Kd(), Dg())
     i = 1
     CALL conc(i, Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
5    IF RR(1) < RR(2) THEN
     GOTO 10
     ELSE
     FOR i = 1 TO 3
        Kd(i) = (Kd(i) + Kd(4)) / 2
        Dg(i) = (Dg(i) + Dg(4)) / 2
        CALL conc(i, Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
     NEXT i
     END IF
10   END SUB

'    The following subprogram SUB expend was used to expend the best vertex to new one.  If the
'    expended one  is the new best vertex, keep the expended one as the best vertex.  If not, keep the
'    original one as the best vertex.

SUB expend (Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
     Kd1 = Kd(1)
     Dg1 = Dg(1)
     RR1 = RR(1)
     G1 = (Kd(2) + Kd(3) + Kd(4)) / 3
     Kd(1) = G1 + 1.3 * (Kd(1) - G1)
     G2 = (Dg(2) + Dg(3) + Dg(4)) / 3
     Dg(1) = G2 + 1.3 * (Dg(1) - G2)
     CALL condition(Kd(), Dg())
     i = 1
```

```
    CALL conc(i, Kd(), Dg(), z(), Cg(), RR(), MCg(), C0(), Ntime)
15   IF RR(1) < RR1 THEN
      GOTO 25
      ELSE
      Kd(1) = Kd1
      Dg(1) = Dg1
      RR(1) = RR1
    END IF
25   END SUB
```

PROGRAM OF SOLUTE TRANSPORT SIMULATION

```
' This program was used to simulate the solute transport in unsaturated soil
' zone. The toluene concentration profile every half hour can be obtained by
' running this program. Kd and Dg parameters were required in this program.
' Finite difference method was used to solve the governing equation.
' This program was run using MS-DOS QBasic and written by
'
'                  Ming Yu

DECLARE SUB conc (Kd!, Dg!, z!(), Cg!(), MCg!(), C0!(), Ntime!)

    OPEN "i", #1, "c:\ming\paramet\optimum\input9.dat"
    OPEN "o", #2, "c:\ming\paramet\optimum\simu9.dat"
    DIM z(17), MCg(17), Cg(17), C0(17)

10  FOR k = 1 TO 6                  'input time parameters
    INPUT #1, k(k)
    NEXT k

20  FOR j = 1 TO 17                 'input the depth of each sampling ports on PVC column
    INPUT #1, z(j)
    NEXT j

30  FOR j = 1 TO 17                 'input initial concentration profile
    INPUT #1, C0(j)
    NEXT j

    k = 1
120 Ntime = k(k)
    IF Ntime = 0 THEN
    GOTO 150
    ELSE
40  FOR j = 1 TO 17                 'input measured gas phase
    INPUT #1, MCg(j)                'toluene concentration
    NEXT j
    END IF

     Kd = 7.58                      'liquid/solid partition coefficient
     Dg = .0229                     'gaseous diffusion coefficient
     CALL conc(Kd, Dg, z(), Cg(), MCg(), C0(), Ntime)              'calculate concentration profile
     PRINT #2, USING "Ntime=###  Kd=#.####  Dg=#.####"; Ntime; Kd; Dg
     PRINT #2, " Z(j)    Cg(j)    MCg(j)  "
     FOR j = 1 TO 17
     PRINT #2, USING "##.##   ###.##   ###.##   "; z(j); Cg(j); MCg(j)
     NEXT j

     k = k + 1
     GOTO 120

150  STOP
```

```
'    The following subprogram SUB conc was used to solve the governing equation using finite difference
'    method. The toluene concentration profile along column at every half hour can be obtained by runing
'    this subprogram.

SUB conc (Kd, Dg, z(), Cg(), MCg(), C0(), Ntime)
     DIM b(17), w(17), y(17), TC0(17)
     k = 1
     RR = 0
     R = .4 - .17 + .17 / .26 + 1.59 * Kd / .26
     alfa = Dg / (R * 1.5 ^ 2)
     beta = -2 * Dg / (R * 1.5 ^ 2) - 1 / (30 * 60)
     gama = Dg / (R * 1.5 ^ 2)
     b(1) = beta
     w(1) = gama / b(1)
5    FOR j = 2 TO 16
     b(j) = beta - alfa * w(j - 1)
     w(j) = gama / b(j)
     NEXT j
     b(17) = -Dg / (R * 1.5 ^ 2) - 1 / (30 * 60) - alfa * w(16)
15   FOR j = 1 TO 17
     TC0(j) = C0(j)
     NEXT j
20   y(1) = -TC0(1) / (30 * 60 * b(1))
     FOR j = 2 TO 17
     y(j) = (-TC0(j) / (30 * 60) - alfa * y(j - 1)) / b(j)
     NEXT j
     Cg(17) = y(17)
25   FOR j = 16 TO 1 STEP -1
     Cg(j) = y(j) - w(j) * Cg(j + 1)
     TC0(j) = Cg(j)
     NEXT j
     TC0(17) = Cg(17)
     k = k + 1
28   IF k = Ntime THEN
     GOTO 30
     ELSE
     GOTO 20
     END IF
30   FOR j = 1 TO 17
     RR = RR + (Cg(j) - MCg(j)) ^ 2
     NEXT j
     PRINT , USING "RR=####.## "; RR
END SUB
```

PROGRAM OF VOLATILIZATION CALCULATION

```
' This program was used to calculate the volatilization of organic solutes
' from soil surface.  Liquid/solid partition coefficient Kd was obtained
' through experiment, while gaseous diffusion coefficient Dg was
' estimated by Millington-Quirk diffusivity model.  Porosity and
' water content are input parameters.  Finite difference method was used
' to solve the governing equation.  This program was run by MS-DOS
' QBasic and written by
'
'                   Ming Yu

DECLARE SUB conc (Kd!, Dg!, z!(), Cg!(), C0!())

    OPEN "i", #1, "c:\ming\volatile\volin.dat"
    OPEN "o", #2, "c:\ming\volatile\volout21.dat"
    DIM z(17), Cg(17), C0(17)

10  FOR j = 1 TO 17                      'input the depth of each sampling ports on PVC column
    INPUT #1, z(j)
    NEXT j

20  FOR j = 1 TO 17                      'input initial concentration profile
    INPUT #1, C0(j)
    NEXT j

    A = 1641.73                                'column area in cm2
    Kd = .432                                  'partition coefficient
    fei = .4                                   'soil porosity
    theta = .025                               'soil water content
    Dg = .1 * ((fei - theta) ^ (10 / 3)) / fei ^ 2   'gaseous diffusivity
    day = 0
    ET0 = 0
30  FOR j = 2 TO 17                            'calculate initial chemical mass in column
    ET0 = ET0 + C0(j) * (fei - theta + theta / .26 + Kd * (1 - fei) * 2.65 / .26) * 1.5 * A / 1000
    NEXT j
    PRINT #2, USING "C0=###.##   theta=##.####   Kd=###.###    Dg=#.####"; C0(1); theta; Kd; Dg
    PRINT #2, "  day        ET   "
    PRINT #2, USING "####    #######.##    "; day; ET0
    GOTO 130
120 CALL conc(Kd, Dg, z(), Cg(), C0())         'calculate conc. profile at time t
40  TT = 0                                     'calculate total chemical mass in column at time t
    FOR j = 2 TO 17
    TT = TT + Cg(j) * (fei - theta + theta / .26 + Kd * (1 - fei) * 2.65 / .26) * 1.5 * A / 1000
    NEXT j

50  ET = ET0 - TT                              'EI is volatilization from beginning to time t
    PRINT #2, USING "#####.#    #######.##     "; day; ET
60  IF TT < 20 THEN
```

```
    GOTO 150
    ELSE
130 day = day + .5
    PRINT , USING "day=#####.#"; day
    GOTO 120
    END IF

150 STOP

'   The following subprogram SUB conc was used to solve the governing equation using finite difference
'   method. The toluene concentration profile along column at every half hour can be obtained by runing
'   this subprogram.

SUB conc (Kd, Dg, z(), Cg(), C0())
    DIM b(17), w(17), y(17), TC0(17)
    k = 1
    R = .4 - .17 + .17 / .26 + 1.59 * Kd / .26
    alfa = Dg / (R * 1.5 ^ 2)
    beta = -2 * Dg / (R * 1.5 ^ 2) - 1 / (30 * 60)
    gama = Dg / (R * 1.5 ^ 2)
    b(1) = beta
    w(1) = gama / b(1)
5   FOR j = 2 TO 16
    b(j) = beta - alfa * w(j - 1)
    w(j) = gama / b(j)
    NEXT j
    b(17) = -Dg / (R * 1.5 ^ 2) - 1 / (30 * 60) - alfa * w(16)
15  FOR j = 1 TO 17
    TC0(j) = C0(j)
    NEXT j
20  y(1) = -TC0(1) / (30 * 60 * b(1))
23  FOR j = 2 TO 17
    y(j) = (-TC0(j) / (30 * 60) - alfa * y(j - 1)) / b(j)
    NEXT j
    Cg(17) = y(17)
25  FOR j = 16 TO 1 STEP -1                    'calculate toluene concentration profile
    Cg(j) = y(j) - w(j) * Cg(j + 1)
    TC0(j) = Cg(j)
    NEXT j
    TC0(17) = Cg(17)
    k = k + 1

28  IF k = 25 THEN
    FOR j = 1 TO 17
    C0(j) = Cg(j)
    NEXT j
    GOTO 30
    ELSE
    GOTO 20
    END IF

30  END SUB
```

Appendix B

EXPERIMENTAL DATA FROM SOIL SORPTION TESTS

Table B-1

DATA FROM TELLER LOAM SORPTION TEST #1

Moisture=Oven Dry

VialNo. YM	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0258	2.0	23984
2	3.0481	2.0	60757
3	3.0028	2.0	39515
4	6.0592	2.0	10092
5	6.0217	2.0	11566
6	6.0654	2.0	7254
7	9.0314	2.0	5318
8	9.1602	2.0	5391
9	9.0349	2.0	6119
10	12.0655	2.0	2552
11	12.0451	2.0	4186
12	12.0541	2.0	1328
13	15.0279	2.0	1076
14	15.0131	2.0	2331
15	15.0585	2.0	2281
16	0	2.0	2555589
17	0	2.0	2812966
18	0	2.0	2443983

Table B-2

DATA FROM TELLER LOAM SORPTION TEST #2

Moisture=1.85% g/g (Air Dry)

VialNo. JR	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0126	2.0	786258
2	3.0041	2.0	413842
3	3.0079	2.0	930699
4	6.0006	2.0	460913
5	6.0284	2.0	441631
6	6.0004	2.0	474325
7	9.0073	2.0	358256
8	9.0109	2.0	366025
9	9.0307	2.0	319301
10	12.0178	2.0	354878
11	12.0048	2.0	293285
12	12.0135	2.0	228550
13	15.0184	2.0	210326
14	15.0024	2.0	230215
15	15.0247	2.0	222433
16	0	2.0	3140949
17	0	2.0	2376882
18	0	2.0	2114691

Table B-3

DATA FROM TELLER LOAM SORPTION TEST #3

Moisture=2.57% g/g

VialNo. JR	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0119	2.0	1573266
2	3.0126	2.0	1466112
3	3.0223	2.0	1590504
4	6.0200	2.0	1167957
5	6.0366	2.0	1084002
6	6.0220	2.0	1007890
7	9.0222	2.0	897107
8	9.0197	2.0	836880
9	9.0124	2.0	845292
10	12.0463	2.0	756443
11	12.0497	2.0	639110
12	12.0668	2.0	713320
13	15.0727	2.0	660611
14	15.0028	2.0	508297
15	15.0471	2.0	leak
16	0	2.0	2484419
17	0	2.0	2323571
18	0	2.0	2358485

Table B-4

DATA FROM TELLER LOAM SORPTION TEST #4

Moisture=3.54% g/g

VialNo. YM	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0627	1.5	1676682
2	3.0222	1.5	1416850
3	3.0668	1.5	103062
4	6.0172	1.5	1338597
5	6.0159	1.5	631441
6	6.0110	1.5	1271133
7	9.0401	1.5	30907
8	9.0154	1.5	76094
9	9.0164	1.5	14930
10	12.0474	1.5	955923
11	12.0070	1.5	1079057
12	12.0038	1.5	937347
13	15.0046	1.5	210642
14	15.0070	1.5	784723
15	15.0059	1.5	860680
16	0	1.5	1620941
17	0	1.5	2574995
18	0	1.5	2062273

Table B-5

DATA FROM TELLER LOAM SORPTION TEST #5

Moisture=3.89% g/g

VialNo. JR	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
19	3.0623	2.0	1738277
20	3.0014	2.0	2177287
21	3.0049	2.0	2205202
22	6.0625	2.0	1726143
23	6.0085	2.0	2007049
24	6.0585	2.0	1800983
25	9.0164	2.0	1733128
26	9.0118	2.0	1731411
27	9.0422	2.0	1631781
28	12.0779	2.0	1520786
29	12.0165	2.0	1557739
30	12.0136	2.0	1412047
31	15.0177	2.0	1321170
32	15.0547	2.0	1401957
33	15.0304	2.0	1365311
34	0	2.0	2490802
35	0	2.0	2785515
36	0	2.0	2363066

Table B-6

DATA FROM TELLER LOAM SORPTION TEST #6

Moisture=5.02% g/g

VialNo. YM	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
19	3.0122	1.5	1655815
20	3.0362	1.5	1721151
21	3.0089	1.5	2085252
22	6.0116	1.5	1457143
23	6.0552	1.5	1499998
24	6.0072	1.5	1551692
25	9.0267	1.5	1393326
26	9.0114	1.5	1363837
27	9.0628	1.5	1704185
28	12.0060	1.5	1202918
29	12.0265	1.5	1316728
30	12.0139	1.5	1432415
31	15.0621	1.5	1077776
32	15.0124	1.5	1249204
33	15.0289	1.5	1361759
34	0	1.5	1929083
35	0	1.5	2072539
36	0	1.5	2376644

Table B-7

DATA FROM TELLER LOAM SORPTION TEST #7

Moisture=6.58% g/g

VialNo. JR	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0183	1.5	1156207
2	3.0614	1.5	1841844
3	3.0095	1.5	1781716
4	6.0225	1.5	1642894
5	6.0299	1.5	1440398
6	6.0040	1.5	1445394
7	9.0108	1.5	1732899
8	9.0136	1.5	1501743
9	9.0131	1.5	1416638
10	12.0308	1.5	1423781
11	12.0163	1.5	1324185
12	12.0051	1.5	1417261
13	15.0314	1.5	1404967
14	15.0752	1.5	929417
15	15.0554	1.5	1309926
16	0	1.5	2144358
17	0	1.5	1667754
18	0	1.5	1937881

Table B-8

DATA FROM TELLER LOAM SORPTION TEST #8

Moisture=9.88% g/g

VialNo. JR	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
19	3.0441	2.0	2126280
20	3.0013	2.0	2977592
21	3.0051	2.0	2253151
22	6.0261	2.0	2364538
23	6.0172	2.0	2531532
24	6.0535	2.0	2244937
25	9.0131	2.0	1796805
26	9.0210	2.0	2538973
27	9.0231	2.0	2188172
28	12.0144	2.0	1821104
29	12.0258	2.0	2374173
30	12.0098	2.0	1967355
31	15.0422	2.0	1614719
32	15.0056	2.0	2197494
33	15.0098	2.0	1881334
34	0	2.0	2391554
35	0	2.0	3215208
36	0	2.0	2585111

Table B-9

DATA FROM TELLER LOAM SORPTION TEST #9

Moisture=12.82% g/g

VialNo. JR	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
19	3.0151	1.5	1732147
20	3.0114	1.5	break
21	3.0056	1.5	break
22	6.0552	1.5	1603419
23	6.0278	1.5	1287207
24	6.0321	1.5	2040382
25	9.0223	1.5	1407956
26	9.0601	1.5	1516936
27	9.0847	1.5	1383637
28	12.0407	1.5	1797580
29	12.0002	1.5	1280804
30	12.0171	1.5	1209300
31	15.0538	1.5	1369238
32	15.0538	1.5	1662226
33	15.0200	1.5	1424495
34	0	1.5	1782471
35	0	1.5	1981911
36	0	1.5	1829525

Table B-10

DATA FROM TELLER LOAM SORPTION TEST #10

Moisture=Saturated

VialNo. JR	Wt./Dry Soil g	CaSO4 mL	Toluene uL	GC areax10^4 per uL
1	2.9905	20	1.0	3.75
2	3.0064	20	1.0	3.78
3	3.0015	20	1.0	3.54
5	5.9974	20	1.0	3.32
6	6.0108	20	1.0	3.27
7	5.9938	20	1.0	3.46
9	9.0203	20	1.0	3.53
10	9.0210	20	1.0	3.15
11	9.0194	20	1.0	3.61
13	11.9975	20	1.0	3.11
14	12.0205	20	1.0	3.01
15	12.0145	20	1.0	3.15
17	15.0019	20	1.0	3.36
18	15.0088	20	1.0	3.11
19	14.9612	20	1.0	3.30
4	0.0000	20	1.0	3.59
8	0.0000	20	1.0	3.69
12	0.0000	20	1.0	3.82
16	0.0000	20	1.0	3.55
20	0.0000	20	1.0	3.58

Table B-11

DATA FROM DOUGHERTY SAND SORPTION TEST #1

Moisture=Oven Dry

VialNo. YM	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0032	2.0	leak
2	3.0280	2.0	1220072
3	3.0056	2.0	1266345
4	6.0480	2.0	639853
5	6.0457	2.0	686758
6	6.0672	2.0	622502
7	9.0847	2.0	315844
8	9.0508	2.0	438441
9	9.0247	2.0	407174
10	12.0226	2.0	267915
11	12.0636	2.0	273142
12	12.0120	2.0	192037
13	15.0184	2.0	181449
14	15.0216	2.0	84647
15	15.0245	2.0	112129
16	0	2.0	3080791
17	0	2.0	3413024
18	0	2.0	2825445

Table B-12

DATA FROM DOUGHERTY SAND SORPTION TEST #2

Moisture=0.12% g/g (Air Dry)

VialNo. JR	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0724	2.0	1959779
2	3.0561	2.0	1950583
3	3.0628	2.0	1812020
4	6.0174	2.0	1667249
5	6.0920	2.0	1641168
6	6.0053	2.0	1822871
7	9.0342	2.0	1642115
8	9.0474	2.0	1597958
9	9.0541	2.0	1351212
10	12.0939	2.0	1331780
11	12.0137	2.0	1444992
12	12.0809	2.0	1249182
13	15.0019	2.0	1114978
14	15.0052	2.0	1319120
15	15.0709	2.0	leak
16	0	2.0	2486532
17	0	2.0	2388122
18	0	2.0	2604422

Table B-13

DATA FROM DOUGHERTY SAND SORPTION TEST #3

Moisture=0.74% g/g

VialNo. JR	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0352	1.5	2150166
2	3.0268	1.5	1821394
3	3.0821	1.5	1826406
4	6.0568	1.5	1876711
5	6.0141	1.5	1954637
6	6.0126	1.5	1909027
7	9.0074	1.5	2080986
8	9.0287	1.5	1908670
9	9.0527	1.5	2163345
10	12.0092	1.5	2170451
11	12.0776	1.5	2178073
12	12.0246	1.5	2013109
13	15.0054	1.5	2161511
14	15.0496	1.5	2076889
15	15.0087	1.5	2431137
16	0	1.5	1815307
17	0	1.5	1765554
18	0	1.5	1969828

Table B-14

DATA FROM DOUGHERTY SAND SORPTION TEST # 4

Moisture=1.64% g/g

VialNo. YM	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0539	1.5	1927635
2	3.0032	1.5	1954039
3	3.0205	1.5	1855982
4	6.0301	1.5	2012735
5	6.0355	1.5	2388537
6	6.0143	1.5	2096285
7	9.0122	1.5	1950393
8	9.0266	1.5	1878609
9	9.0373	1.5	2041938
10	12.0140	1.5	2003694
11	12.0138	1.5	1410866
12	12.0530	1.5	2198223
13	15.0085	1.5	2203785
14	15.0643	1.5	2268029
15	15.0234	1.5	2015647
16	0	1.5	1736777
17	0	1.5	1859183
18	0	1.5	1935375

Table B-15

DATA FROM DOUGHERTY SAND SORPTION TEST #5

Moisture=1.74% g/g

VialNo. YM	Wt./Wet Soil g	Toluene uL (gas)	GC area per 15 uL
1	3.0054	300.0	90535
2	3.0446	300.0	84228
3	3.0226	300.0	leak
4	6.0848	300.0	67149
5	6.0495	300.0	72314
6	6.0145	300.0	leak
7	9.0736	300.0	83818
8	9.0308	300.0	84316
9	9.0772	300.0	70382
10	12.0095	300.0	79499
11	12.0211	300.0	65567
12	12.0210	300.0	leak
13	15.0934	300.0	69061
14	15.0376	300.0	64372
15	15.0496	300.0	75460
16	0	300.0	74656
17	0	300.0	63609
18	0	300.0	52811

Table B-16

DATA FROM DOUGHERTY SAND SORPTION TEST #6

Moisture=5.11% g/g

VialNo. YM	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0397	1.5	2024814
2	3.0489	1.5	2037901
3	3.0630	1.5	2000112
4	6.0029	1.5	1738693
5	6.0115	1.5	2100070
6	6.0561	1.5	1983995
7	9.0212	1.5	1702263
8	9.0613	1.5	2014217
9	9.0092	1.5	1904527
10	12.0958	1.5	2018482
11	12.0376	1.5	1932817
12	12.0223	1.5	2000698
13	15.0590	1.5	2141671
14	15.0556	1.5	2074403
15	15.0570	1.5	1954140
16	0	1.5	1779893
17	0	1.5	1675673
18	0	1.5	1897855

Table B-17

DATA FROM DOUGHERTY SAND SORPTION TEST #7

Moisture=7.95% g/g

VialNo. YM	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0117	1.5	2001051
2	3.0245	1.5	2060065
3	3.0895	1.5	1762558
4	6.0357	1.5	1936072
5	6.0453	1.5	1935205
6	6.0083	1.5	1760710
7	9.0098	1.5	1842189
8	9.0516	1.5	1836988
9	9.0280	1.5	1874685
10	12.0095	1.5	leak
11	12.0711	1.5	2104304
12	12.0522	1.5	leak
13	15.0323	1.5	2256683
14	15.0528	1.5	1946690
15	15.0057	1.5	2115990
16	0	1.5	1927237
17	0	1.5	1989889
18	0	1.5	2024366

Table B-18

DATA FROM DOUGHERTY SAND SORPTION TEST #8

Moisture=11.23% g/g

VialNo. YM	Wt./Wet Soil g	Toluene uL	GC area per 15 uL
1	3.0780	1.0	1351924
2	3.0852	1.0	1441459
3	3.0512	1.0	1232317
4	6.0117	1.0	1270132
5	6.0856	1.0	1307181
6	6.0042	1.0	1411779
7	9.0988	1.0	1517187
8	9.0869	1.0	1325663
9	9.0182	1.0	1617465
10	12.0102	1.0	1557178
11	12.0671	1.0	1577377
12	12.0005	1.0	1568170
13	15.0050	1.0	1366678
14	15.0120	1.0	1429494
15	15.0104	1.0	1338720
16	0	1.0	1281309
17	0	1.0	1368441
18	0	1.0	1376930

Table B-19

DATA FROM DOUGHERTY SAND SORPTION TEST #9

Moisture=Saturated

VialNo. JR	Wt./Dry Soil g	CaSO4 mL	Toluene uL	GC area per 15uL
4	6.00	20	2.0	961172
5	6.00	20	2.0	1000492
6	6.00	20	2.0	742922
7	9.00	20	2.0	978274
8	9.00	20	2.0	1037804
9	9.00	20	2.0	831879
10	12.00	20	2.0	1054917
11	12.00	20	2.0	784125
12	12.00	20	2.0	869638
13	15.00	20	2.0	875992
14	15.00	20	2.0	851950
15	15.00	20	2.0	947568
16	18.00	20	2.0	976504
17	18.00	20	2.0	863048
18	18.00	20	2.0	1000107
19	0.00	20	2.0	893612
20	0.00	20	2.0	927167

Appendix C

EXPERIMENTAL DATA FROM SOIL COLUMN TESTS

Table C-1

DATA FROM COLUMN TEST TELLER-1

Soil column was packed on January 27, 1994.
Starting time: 12:00 a.m. January 28,1994
Stopping time: 3:00 p.m. January 31, 1994
Total time: 75 hour
Soil porosity: 0.4
Water content: 0.15 v/v
Calibration curve is: Area=3.1308*Conc. (R squared =0.99)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
2	1.5	1.00	0.194	158515	5.06
2	1.5	120.00	0.018	69799	2.23
2	1.5	300.00	0.011	26404	0.84
2	1.5	540.00	0.008	19274	0.62
2	1.5	780.00	0.007	14035	0.45
2	1.5	1260.00	0.005	8892	0.28
2	1.5	1650.00	0.005	5547	0.18
2	1.5	2130.00	0.004	2445	0.08
2	1.5	3060.00	0.004	774	0.02
3	3.0	1.00	0.387	172551	5.51
3	3.0	120.00	0.035	111717	3.57
3	3.0	300.00	0.022	50973	1.63
3	3.0	540.00	0.017	43921	1.40
3	3.0	780.00	0.014	27495	0.88
3	3.0	1260.00	0.011	23085	0.74
3	3.0	1650.00	0.010	9441	0.30
3	3.0	2130.00	0.008	7482	0.24
3	3.0	3060.00	0.007	540	0.02
4	4.5	1.00	0.581	190864	6.10
4	4.5	120.00	0.053	107092	3.42
4	4.5	300.00	0.034	72874	2.33
4	4.5	540.00	0.025	52823	1.69
4	4.5	780.00	0.021	22643	0.72
4	4.5	1260.00	0.016	27389	0.87
4	4.5	1650.00	0.014	17931	0.57
4	4.5	2130.00	0.013	7595	0.24
4	4.5	3060.00	0.011	1200	0.04
5	6.0	1.00	0.775	155493	4.97
5	6.0	120.00	0.071	132772	4.24
5	6.0	300.00	0.045	83722	2.67
5	6.0	540.00	0.033	59233	1.89
5	6.0	780.00	0.028	75282	2.40

Table C-1 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	Conc. (mg/L)
5	6.0	1260.00	0.022	32781	1.05
5	6.0	1650.00	0.019	24339	0.78
5	6.0	2130.00	0.017	10277	0.33
5	6.0	3060.00	0.014	1465	0.05
6	7.5	1.00	0.968	185215	5.92
6	7.5	120.00	0.088	145543	4.65
6	7.5	300.00	0.056	101613	3.25
6	7.5	540.00	0.042	58882	1.88
6	7.5	780.00	0.035	66704	2.13
6	7.5	1260.00	0.027	47617	1.52
6	7.5	1650.00	0.024	34702	1.11
6	7.5	2130.00	0.021	18445	0.59
6	7.5	3060.00	0.018	2363	0.08
7	9.0	1.00	1.162	204741	6.54
7	9.0	120.00	0.106	149173	4.76
7	9.0	300.00	0.067	113760	3.63
7	9.0	540.00	0.050	86411	2.76
7	9.0	780.00	0.042	75701	2.42
7	9.0	1260.00	0.033	55761	1.78
7	9.0	1650.00	0.029	37719	1.20
7	9.0	2130.00	0.025	20360	0.65
7	9.0	3060.00	0.021	937	0.03
8	10.5	1.00	1.356	188464	6.02
8	10.5	120.00	0.124	142600	4.55
8	10.5	300.00	0.078	130075	4.15
8	10.5	540.00	0.058	108304	3.46
8	10.5	780.00	0.049	86107	2.75
8	10.5	1260.00	0.038	46007	1.47
8	10.5	1650.00	0.033	42936	1.37
8	10.5	2130.00	0.029	30156	0.96
8	10.5	3060.00	0.025	6722	0.21
9	12.0	1.00	1.549	217457	6.95
9	12.0	120.00	0.141	166343	5.31
9	12.0	300.00	0.089	155747	4.97
9	12.0	540.00	0.067	108300	3.46
9	12.0	780.00	0.055	107898	3.45
9	12.0	1260.00	0.044	66179	2.11
9	12.0	1650.00	0.038	51457	1.64
9	12.0	2130.00	0.034	31717	1.01
9	12.0	3060.00	0.028	4534	0.14
10	13.5	1.00	1.743	195131	6.23
10	13.5	120.00	0.159	175304	5.60
10	13.5	300.00	0.101	138393	4.42
10	13.5	540.00	0.075	128784	4.11

Table C-1 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	Conc. (mg/L)
10	13.5	780.00	0.062	105901	3.38
10	13.5	1260.00	0.049	77373	2.47
10	13.5	1650.00	0.043	54556	1.74
10	13.5	2130.00	0.038	35402	1.13
10	13.5	3060.00	0.032	4495	0.14
11	15.0	1.00	1.936	207731	6.64
11	15.0	120.00	0.177	178460	5.70
11	15.0	300.00	0.112	129152	4.13
11	15.0	540.00	0.083	117875	3.77
11	15.0	780.00	0.069	117870	3.76
11	15.0	1260.00	0.055	79828	2.55
11	15.0	1650.00	0.048	57718	1.84
11	15.0	2130.00	0.042	38186	1.22
11	15.0	3060.00	0.035	5630	0.18
12	16.5	1.00	2.130	201375	6.43
12	16.5	120.00	0.194	162547	5.19
12	16.5	300.00	0.123	148291	4.74
12	16.5	540.00	0.092	141525	4.52
12	16.5	780.00	0.076	121739	3.89
12	16.5	1260.00	0.060	85377	2.73
12	16.5	1650.00	0.052	64724	2.07
12	16.5	2130.00	0.046	42563	1.36
12	16.5	3060.00	0.039	6387	0.20
13	18.0	1.00	2.324	196020	6.26
13	18.0	120.00	0.212	182124	5.82
13	18.0	300.00	0.134	170697	5.45
13	18.0	540.00	0.100	147148	4.70
13	18.0	780.00	0.083	138173	4.41
13	18.0	1260.00	0.065	101676	3.25
13	18.0	1650.00	0.057	75547	2.41
13	18.0	2130.00	0.050	46229	1.48
13	18.0	3060.00	0.042	4735	0.15
14	19.5	1.00	2.517	196307	6.27
14	19.5	120.00	0.230	186567	5.96
14	19.5	300.00	0.145	161501	5.16
14	19.5	540.00	0.108	158995	5.08
14	19.5	780.00	0.090	132231	4.22
14	19.5	1260.00	0.071	95590	3.05
14	19.5	1650.00	0.062	73538	2.35
14	19.5	2130.00	0.055	43322	1.38
14	19.5	3060.00	0.046	4862	0.16
15	21.0	1.00	2.711	179124	5.72
15	21.0	120.00	0.247	187962	6.00
15	21.0	300.00	0.157	155042	4.95

Table C-1 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	Conc. (mg/L)
15	21.0	540.00	0.117	131286	4.19
15	21.0	780.00	0.097	139761	4.46
15	21.0	1260.00	0.076	104960	3.35
15	21.0	1650.00	0.067	71313	2.28
15	21.0	2130.00	0.059	41652	1.33
15	21.0	3060.00	0.049	4719	0.15
16	22.5	1.00	2.905	202010	6.45
16	22.5	120.00	0.265	208707	6.67
16	22.5	300.00	0.168	171772	5.49
16	22.5	540.00	0.125	149812	4.79
16	22.5	780.00	0.104	144321	4.61
16	22.5	1260.00	0.082	104135	3.33
16	22.5	1650.00	0.072	73963	2.36
16	22.5	2130.00	0.063	49006	1.57
16	22.5	3060.00	0.053	4193	0.13
17	24.0	1.00	3.098	213320	6.81
17	24.0	120.00	0.283	199914	6.39
17	24.0	300.00	0.179	190000	6.07
17	24.0	540.00	0.133	160795	5.14
17	24.0	780.00	0.111	146128	4.67
17	24.0	1260.00	0.087	82011	2.62
17	24.0	1650.00	0.076	71744	2.29
17	24.0	2130.00	0.067	50963	1.63
17	24.0	3060.00	0.056	4414	0.14

Table C-2

MEASURED DATA OF TOLUENE CONCENTRATION PROFILES IN COLUMN TEST TELLER-1

Sample Location no.	Sample depth (cm)	X-axis (cm)	Concentration (mg/L)								
			t=0hr	t=2hr	t=5hr	t=9hr	t=13hr	t=21hr	t=27.5hr	t=35.5hr	t=51hr
2	1.5	23.5	5.96	2.23	0.84	0.62	0.45	0.28	0.18	0.08	0.02
3	3.0	22.0	5.51	3.57	1.63	1.4	0.88	0.74	0.3	0.24	0.02
4	4.5	20.5	6.10	3.42	2.33	1.69	1.32	0.87	0.57	0.24	0.04
5	6.0	19.0	5.97	4.24	2.67	1.89	1.50	1.05	0.78	0.33	0.05
6	7.5	17.5	5.92	4.65	3.25	2.38	2.13	1.52	1.11	0.59	0.08
7	9.0	16.0	6.54	4.76	3.63	2.76	2.42	1.78	1.20	0.65	0.03
8	10.5	14.5	6.02	4.55	4.15	3.46	2.75	1.47	1.37	0.96	0.21
9	12.0	13.0	6.95	5.31	4.97	3.46	3.45	2.11	1.64	1.01	0.14
10	13.5	11.5	6.23	5.60	4.42	4.11	3.38	2.47	1.74	1.13	0.14
11	15.0	10.0	6.64	5.70	4.13	3.77	3.76	2.55	1.84	1.22	0.18
12	16.5	8.5	6.43	5.19	4.74	4.52	3.89	2.73	2.07	1.36	0.20
13	18.0	7.0	6.26	5.82	5.45	4.70	4.41	3.25	2.41	1.48	0.15
14	19.5	5.5	6.27	5.96	5.16	5.08	4.22	3.05	2.35	1.38	0.16
15	21.0	4.0	6.12	6.00	4.95	4.89	4.46	3.35	2.28	1.33	0.15
16	22.5	2.5	6.45	6.27	5.49	4.79	4.61	3.33	2.36	1.57	0.13
17	24.0	1.0	6.81	6.39	6.07	5.14	4.67	3.32	2.29	1.63	0.14

Table C-3

MEASURED SOIL MOISTURE DATA IN COLUMN TEST TELLER-1

Sample #	Sample Depth (cm)	Moisture (v/v) t=0	Moisture (v/v) t=120hrs
1	0.0	0.170	0.033
3	3.0	0.170	0.114
5	6.0	0.170	0.159
7	9.0	0.170	0.170
9	12.0	0.170	0.184
11	15.0	0.170	0.170
13	18.0	0.170	0.157
15	21.0	0.170	0.169
17	24.0	0.170	0.164

Table C-4

DATA FROM COLUMN TEST TELLER-2

Soil column was packed on July 10, 1994.
Starting time: 5:00 p.m. July 13,1994
Stopping time: 5:00 p.m. July 18, 1994
Total time: 120 hours
Soil porosity: 0.4
Water content: 0.12 v/v
Calibration curve is: Conc.=0.03085*Area (R squared =0.99)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
2	1.5	0.0	1.936	883419	27.25
2	1.5	6.0	0.079	865191	26.69
2	1.5	17.0	0.047	1064388	32.84
2	1.5	88.2	0.021	615407	18.99
2	1.5	157.2	0.015	472431	14.57
2	1.5	214.0	0.013	356840	11.01
2	1.5	450.0	0.009	209435	6.46
2	1.5	501.7	0.009	236756	7.30
2	1.5	1063.0	0.006	81849	2.53
2	1.5	1107.0	0.006	90071	2.78
2	1.5	1928.0	0.004	47201	1.46
2	1.5	1974.5	0.004	50982	1.57
2	1.5	2858.0	0.004	27292	0.84
2	1.5	4145.0	0.003	13036	0.40
2	1.5	5553.0	0.003	7003	0.22
2	1.5	7200.0	0.002	2193	0.07
3	3.0	0.0	3.873	996028	30.73
3	3.0	7.5	0.141	976303	30.12
3	3.0	19.1	0.089	1092695	33.71
3	3.0	89.5	0.041	849602	26.21
3	3.0	159.0	0.031	622609	19.21
3	3.0	215.5	0.026	618264	19.07
3	3.0	451.6	0.018	384037	11.85
3	3.0	504.0	0.017	404502	12.48
3	3.0	1065.0	0.012	209372	6.46
3	3.0	1109.3	0.012	173982	5.37
3	3.0	1930.5	0.009	109343	3.37
3	3.0	1977.0	0.009	68601	2.12
3	3.0	2860.0	0.007	59517	1.84
3	3.0	4090.0	0.006	31894	0.98
3	3.0	5555.0	0.005	14845	0.46
3	3.0	7200.0	0.005	6569	0.20

Table C-4 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
4	4.5	0.0	5.809	960880	29.64
4	4.5	9.4	0.189	992761	30.63
4	4.5	23.3	0.120	1029591	31.76
4	4.5	99.0	0.058	938242	28.94
4	4.5	160.2	0.046	729129	22.49
4	4.5	217.2	0.039	624462	19.26
4	4.5	453.3	0.027	407030	12.56
4	4.5	506.5	0.026	353755	10.91
4	4.5	1096.0	0.018	195635	6.04
4	4.5	1112.0	0.017	209687	6.47
4	4.5	1932.5	0.013	121653	3.75
4	4.5	1983.0	0.013	108867	3.36
4	4.5	2862.0	0.011	57172	1.76
4	4.5	4092.0	0.009	33512	1.03
4	4.5	4127.0	0.009	34058	1.05
4	4.5	5607.0	0.008	20492	0.63
4	4.5	7200.0	0.007	6265	0.19
5	6.0	0.0	7.746	905453	27.93
5	6.0	11.6	0.227	1105811	34.11
5	6.0	26.6	0.150	1009403	31.14
5	6.0	93.5	0.080	985886	30.41
5	6.0	164.2	0.060	799694	24.67
5	6.0	219.6	0.052	782603	24.14
5	6.0	508.3	0.034	508165	15.68
5	6.0	1069.0	0.024	283656	8.75
5	6.0	1934.3	0.018	161693	4.99
5	6.0	2864.0	0.014	105715	3.26
5	6.0	4096.0	0.012	66518	2.05
5	6.0	5560.5	0.010	25027	0.77
5	6.0	7200.0	0.009	10743	0.33
6	7.5	0.0	9.682	1034226	31.91
6	7.5	14.2	0.257	996917	30.75
6	7.5	28.7	0.181	1103968	34.06
6	7.5	95.3	0.099	1023655	31.58
6	7.5	166.0	0.075	772247	23.82
6	7.5	221.5	0.065	762917	23.54
6	7.5	457.3	0.045	630540	19.45
6	7.5	510.0	0.043	575492	17.75
6	7.5	1071.0	0.030	372157	11.48
6	7.5	1116.0	0.029	371275	11.45
6	7.5	1936.0	0.022	212163	6.55
6	7.5	2897.0	0.018	125495	3.87
6	7.5	4130.0	0.015	69745	2.15
6	7.5	5562.5	0.013	34833	1.07
6	7.5	7200.0	0.011	14162	0.44

Table C-4 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
7	9.0	0.0	11.619	986075	30.42
7	9.0	38.0	0.188	1083145	33.42
7	9.0	101.2	0.115	1055268	32.56
7	9.0	167.5	0.090	872689	26.92
7	9.0	223.5	0.078	682104	21.04
7	9.0	459.0	0.054	658911	20.33
7	9.0	1098.0	0.035	391234	12.07
7	9.0	1962.5	0.026	249669	7.70
7	9.0	2870.0	0.022	139459	4.30
7	9.0	4101.0	0.018	71868	2.22
7	9.0	5596.0	0.016	52487	1.62
7	9.0	7200.0	0.014	13485	0.42
8	10.5	0.0	13.555	984686	30.38
8	10.5	33.6	0.234	982002	30.29
8	10.5	171.2	0.104	832092	25.67
8	10.5	225.5	0.090	798198	24.62
8	10.5	461.0	0.063	612134	18.88
8	10.5	514.0	0.060	649230	20.03
8	10.5	1074.5	0.041	511860	15.79
8	10.5	1940.0	0.031	283823	8.76
8	10.5	2872.0	0.025	167329	5.16
8	10.5	4103.0	0.021	106403	3.28
8	10.5	5568.0	0.018	60667	1.87
8	10.5	7200.0	0.016	21154	0.65
9	12.0	0.0	15.492	963847	29.73
9	12.0	35.0	0.262	934355	28.82
9	12.0	172.6	0.118	882053	27.21
9	12.0	227.5	0.103	933286	28.79
9	12.0	463.0	0.072	701710	21.65
9	12.0	516.0	0.068	772207	23.82
9	12.0	1077.0	0.047	481647	14.86
9	12.0	1942.2	0.035	350798	10.82
9	12.0	2874.0	0.029	186152	5.74
9	12.0	4132.0	0.024	102257	3.15
9	12.0	5571.5	0.021	54762	1.69
9	12.0	7200.0	0.018	26056	0.80
10	13.5	0.0	17.428	976429	30.12
10	13.5	40.0	0.276	913394	28.18
10	13.5	68.0	0.211	972626	30.01
10	13.5	192.0	0.126	1100747	33.96
10	13.5	465.0	0.081	819499	25.28
10	13.5	518.0	0.077	747801	23.07
10	13.5	1079.0	0.053	456720	14.09
10	13.5	1100.5	0.053	449765	13.88
10	13.5	1118.7	0.052	382295	11.79

Table C-4 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
10	13.5	1944.6	0.040	289821	8.94
10	13.5	2876.0	0.032	216395	6.68
10	13.5	4107.0	0.027	132317	4.08
10	13.5	5574.0	0.023	54271	1.67
10	13.5	7200.0	0.021	27100	0.84
11	15.0	0.0	19.365	942950	29.09
11	15.0	64.1	0.242	970175	29.93
11	15.0	193.5	0.139	761340	23.49
11	15.0	499.5	0.087	749987	23.14
11	15.0	1081.5	0.059	554809	17.12
11	15.0	1965.0	0.044	385879	11.90
11	15.0	2878.0	0.036	217217	6.70
11	15.0	4135.0	0.030	133663	4.12
11	15.0	5576.0	0.026	63334	1.95
11	15.0	7200.0	0.023	25846	0.80
12	16.5	0.0	21.301	966304	29.81
12	16.5	45.0	0.318	902206	27.83
12	16.5	195.5	0.152	985597	30.41
12	16.5	493.5	0.096	878993	27.12
12	16.5	1084.0	0.065	510697	15.76
12	16.5	1949.5	0.048	378272	11.67
12	16.5	2893.0	0.040	226525	6.99
12	16.5	4137.0	0.033	114843	3.54
12	16.5	5599.0	0.028	58082	1.79
12	16.5	7200.0	0.025	29677	0.92
13	18.0	0.0	23.238	1090977	33.66
13	18.0	47.7	0.336	916954	28.29
13	18.0	198.1	0.165	968962	29.89
13	18.0	472.0	0.107	915780	28.25
13	18.0	1085.6	0.071	520060	16.04
13	18.0	1951.5	0.053	385151	11.88
13	18.0	2882.0	0.043	233797	7.21
13	18.0	4114.0	0.036	141486	4.36
13	18.0	5581.0	0.031	86115	2.66
13	18.0	7200.0	0.027	33914	1.05
14	19.5	0.0	25.174	1092207	33.69
14	19.5	50.0	0.356	993857	30.66
14	19.5	183.1	0.186	928239	28.64
14	19.5	491.2	0.114	888304	27.40
14	19.5	1126.0	0.075	605104	18.67
14	19.5	1967.0	0.057	432396	13.34
14	19.5	2895.0	0.047	261938	8.08
14	19.5	4143.0	0.039	143155	4.42
14	19.5	5601.5	0.034	77649	2.40
14	19.5	7200.0	0.030	25792	0.80

Table C-4 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
15	21.0	0.0	27.111	851651	26.27
15	21.0	52.3	0.375	954367	29.44
15	21.0	185.0	0.199	960430	29.63
15	21.0	484.3	0.123	899167	27.74
15	21.0	1089.5	0.082	579291	17.87
15	21.0	1956.0	0.061	468832	14.46
15	21.0	2886.0	0.050	256585	7.92
15	21.0	4119.0	0.042	154429	4.76
15	21.0	5588.0	0.036	75039	2.31
15	21.0	7200.0	0.032	36809	1.14
16	22.5	0.0	29.047	834181	25.73
16	22.5	59.0	0.378	1045214	32.24
16	22.5	187.4	0.212	935755	28.87
16	22.5	486.5	0.132	1029207	31.75
16	22.5	1091.5	0.088	600618	18.53
16	22.5	1970.0	0.065	446697	13.78
16	22.5	2888.0	0.054	229573	7.08
16	22.5	4121.0	0.045	140591	4.34
16	22.5	5590.0	0.039	77164	2.38
16	22.5	7200.0	0.034	32580	1.01
17	24.0	0.0	30.984	918168	28.33
17	24.0	61.0	0.397	1046216	32.28
17	24.0	200.0	0.219	985361	30.40
17	24.0	489.0	0.140	859453	26.51
17	24.0	1104.5	0.093	596540	18.40
17	24.0	1972.5	0.070	403534	12.45
17	24.0	2900.0	0.058	276282	8.52
17	24.0	4140.0	0.048	133227	4.11
17	24.0	5604.5	0.041	79192	2.44
17	24.0	7200.0	0.037	29421	0.91

Table C-5

MEASURED DATA OF TOLUENE CONCENTRATION PROFILES IN COLUMN TEST TELLER-2

Sample Location no.	Sample depth (cm)	X-axis (cm)	Concentration (mg/L) t=0hr	t=3hr	t=8hr	t=18hr	t=32.5hr	t=48hr	t=69hr	t=93hr	t=120hr
2	1.5	23.5	27.25	15.00	7.00	2.78	1.50	0.84	0.40	0.22	0.07
3	3.0	22.0	30.73	20.00	12.00	5.00	3.37	1.84	0.98	0.46	0.20
4	4.5	20.5	29.64	20.00	11.50	6.47	3.75	1.76	1.05	0.63	0.19
5	6.0	19.0	27.93	24.00	15.60	8.75	4.99	3.26	2.05	0.77	0.33
6	7.5	17.5	31.91	27.00	18.50	11.48	6.55	3.87	2.15	1.07	0.44
7	9.0	16.0	30.42	28.00	20.33	12.07	7.70	4.30	2.22	1.62	0.42
8	10.5	14.5	30.38	26.00	19.50	15.79	8.76	5.16	3.28	1.87	0.65
9	12.0	13.0	29.73	27.50	22.50	14.86	10.82	5.74	3.15	1.69	0.80
10	13.5	11.5	30.12	27.50	24.10	14.09	8.94	6.68	4.08	1.67	0.84
11	15.0	10.0	29.09	26.00	23.14	17.12	11.90	6.70	4.12	1.95	0.80
12	16.5	8.5	29.81	28.50	27.12	15.76	11.67	6.99	3.54	1.79	0.92
13	18.0	7.0	31.66	30.00	28.25	16.04	11.88	7.21	4.36	2.66	1.05
14	19.5	5.5	31.69	28.60	27.40	18.67	13.34	8.08	4.42	2.40	0.80
15	21.0	4.0	29.27	29.63	27.74	17.87	14.46	7.92	4.76	2.31	1.14
16	22.5	2.5	29.73	28.87	31.75	18.53	13.78	7.08	4.34	2.38	1.01
17	24.0	1.0	29.33	30.40	26.51	18.40	12.45	8.52	4.11	2.44	0.91

Table C-6

MEASURED SOIL MOISTURE DATA IN COLUMN TEST TELLER-2

Sample #	Sample Depth (cm)	Moisture (v/v) t=0	Moisture (v/v) t=120hrs
1	0.0	0.124	0.043
2	1.5	0.116	0.062
3	3.0	0.115	0.085
4	4.5	0.128	0.102
5	6.0	0.119	0.116
6	7.5	0.120	0.114
7	9.0	0.127	0.120
8	10.5	0.117	0.118
9	12.0	0.117	0.125
10	13.5	0.133	0.136
11	15.0	0.107	0.121
12	16.5	0.107	0.123
13	18.0	0.123	0.135
14	19.5	0.123	0.137
15	21.0	0.118	0.147
16	22.5	0.131	0.135
17	24.0	0.131	0.143
avg.		0.12	0.12

Table C-7

DATA FROM COLUMN TEST TELLER-3

Soil column was packed on Sept. 20, 1995.
Starting time: 8:00 p.m. Oct. 1, 1995
Stopping time: 8:00 p.m. Oct. 8, 1995
Total time: 192 hours
Soil porosity: 0.4
Water content: 0.0294 v/v
Calibration curve is: Conc.=0.02081*Area (R squared =0.99)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
2	1.5	0.0	6.124	197438	4.11
2	1.5	780.0	0.007	41593	0.87
2	1.5	2280.0	0.004	23591	0.49
2	1.5	4320.0	0.003	12720	0.26
2	1.5	7020.0	0.002	10649	0.22
2	1.5	11520.0	0.002	7303	0.15
3	3.0	0.0	12.247	185688	3.86
3	3.0	780.0	0.014	85377	1.78
3	3.0	2280.0	0.008	34421	0.72
3	3.0	4320.0	0.006	35954	0.75
3	3.0	7020.0	0.005	19312	0.40
3	3.0	11520.0	0.004	17550	0.37
4	4.5	0.0	18.371	198077	4.12
4	4.5	780.0	0.021	104538	2.18
4	4.5	2280.0	0.012	55541	1.16
4	4.5	4320.0	0.009	36774	0.77
4	4.5	7020.0	0.007	30135	0.63
4	4.5	11520.0	0.005	16613	0.35
5	6.0	0.0	24.495	199711	4.16
5	6.0	780.0	0.028	115989	2.41
5	6.0	2280.0	0.016	77645	1.62
5	6.0	4320.0	0.012	59288	1.23
5	6.0	7020.0	0.009	40416	0.84
5	6.0	11520.0	0.007	27420	0.57
6	7.5	0.0	30.619	191133	3.98
6	7.5	780.0	0.035	135110	2.81
6	7.5	2280.0	0.020	96737	2.01
6	7.5	4320.0	0.015	65420	1.36
6	7.5	7020.0	0.012	54027	1.12
6	7.5	11520.0	0.009	32271	0.67
7	9.0	0.0	36.742	185023	3.85
7	9.0	780.0	0.042	138995	2.89

Table C-7 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
7	9.0	2280.0	0.024	98796	2.06
7	9.0	4320.0	0.018	70505	1.47
7	9.0	7020.0	0.014	60999	1.27
7	9.0	11520.0	0.011	41677	0.87
8	10.5	0.0	42.866	199657	4.15
8	10.5	780.0	0.049	154707	3.22
8	10.5	2280.0	0.028	102203	2.13
8	10.5	4320.0	0.021	100418	2.09
8	10.5	7020.0	0.016	81055	1.69
8	10.5	11520.0	0.013	47984	1.00
9	12.0	0.0	48.990	191951	3.99
9	12.0	780.0	0.055	162637	3.38
9	12.0	2280.0	0.032	124096	2.58
9	12.0	4320.0	0.024	106444	2.22
9	12.0	7020.0	0.018	81926	1.70
9	12.0	11520.0	0.014	54492	1.13
10	13.5	0.0	55.114	175496	3.65
10	13.5	780.0	0.062	171660	3.57
10	13.5	2280.0	0.036	120100	2.50
10	13.5	4320.0	0.027	101334	2.11
10	13.5	7020.0	0.021	85101	1.77
10	13.5	11520.0	0.016	56121	1.17
11	15.0	0.0	61.237	184763	3.84
11	15.0	780.0	0.069	168831	3.51
11	15.0	2280.0	0.041	124605	2.59
11	15.0	4320.0	0.029	115836	2.41
11	15.0	7020.0	0.023	88296	1.84
11	15.0	11520.0	0.018	62882	1.31
12	16.5	0.0	67.361	185316	3.86
12	16.5	780.0	0.076	162331	3.38
12	16.5	2280.0	0.045	155049	3.23
12	16.5	4320.0	0.032	108761	2.26
12	16.5	7020.0	0.025	93066	1.94
12	16.5	11520.0	0.020	60016	1.25
13	18.0	0.0	73.485	182070	3.79
13	18.0	780.0	0.083	170340	3.54
13	18.0	2280.0	0.049	147758	3.07
13	18.0	4320.0	0.035	115788	2.41
13	18.0	7020.0	0.028	108706	2.26
13	18.0	11520.0	0.022	71927	1.50
14	19.5	0.0	79.608	176194	3.67
14	19.5	780.0	0.090	169792	3.53
14	19.5	2280.0	0.053	143294	2.98
14	19.5	4320.0	0.038	128856	2.68
14	19.5	7020.0	0.030	115370	2.40

Table C-7 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
14	19.5	11520.0	0.023	64141	1.33
15	21.0	0.0	85.732	176796	3.68
15	21.0	780.0	0.097	170524	3.55
15	21.0	2280.0	0.057	156451	3.26
15	21.0	4320.0	0.041	140004	2.91
15	21.0	7020.0	0.032	114810	2.39
15	21.0	11520.0	0.025	77568	1.61
16	22.5	0.0	91.856	177319	3.69
16	22.5	780.0	0.104	177372	3.69
16	22.5	2280.0	0.061	155839	3.24
16	22.5	4320.0	0.044	135463	2.82
16	22.5	7020.0	0.035	114399	2.38
16	22.5	11520.0	0.027	77625	1.62
17	24.0	0.0	97.980	175711	3.66
17	24.0	780.0	0.111	172974	3.60
17	24.0	2280.0	0.065	157332	3.27
17	24.0	4320.0	0.047	138059	2.87
17	24.0	7020.0	0.037	110521	2.30
17	24.0	11520.0	0.029	76250	1.59

Table C-8

MEASURED DATA OF TOLUENE CONCENTRATION PROFILES IN COLUMN TEST TELLER-3

Sample Location no.	Sample depth (cm)	X-axis (cm)	Concentration (mg/L)					
			t=0hr	t=13hr	t=38hrs	t=72hrs	t=117hrs	t=192hrs
2	1.5	23.5	4.11	0.87	0.49	0.26	0.22	0.15
3	3.0	22.0	3.86	1.78	0.72	0.75	0.40	0.37
4	4.5	20.5	4.12	2.18	1.16	0.77	0.63	0.35
5	6.0	19.0	4.16	2.41	1.62	1.23	0.84	0.57
6	7.5	17.5	3.98	2.81	2.01	1.360	1.12	0.67
7	9.0	16.0	3.85	2.89	2.06	1.47	1.27	0.87
8	10.5	14.5	4.15	3.22	2.13	2.09	1.69	1.00
9	12.0	13.0	3.99	3.38	2.59	2.22	1.70	1.13
10	13.5	11.5	3.65	3.57	2.50	2.11	1.77	1.17
11	15.0	10.0	3.84	3.51	2.59	2.41	1.84	1.31
12	16.5	8.5	3.86	3.38	3.23	2.26	1.94	1.25
13	18.0	7.0	3.79	3.54	3.07	2.41	2.26	1.50
14	19.5	5.5	3.67	3.53	2.98	2.68	2.40	1.33
15	21.0	4.0	3.68	3.55	3.26	2.91	2.39	1.61
16	22.5	2.5	3.69	3.69	3.24	2.82	2.38	1.62
17	24.0	1.0	3.66	3.60	3.27	2.87	2.30	1.59

Table C-9

DATA FROM COLUMN TEST DOUGHERTY-1

Soil column was packed on April 5, 1995.
Starting time: 1:00 p.m. April 7, 1995
Stopping time: 6:00 p.m. April 8, 1995
Total time: 29 hours
Soil porosity: 0.4
Water content: 0.12 v/v
Calibration curve is: Conc.=0.03125*Area (R squared =0.99)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
2	1.5	0.0	6.124	1533762	47.93
2	1.5	4.5	0.091	1205280	37.67
2	1.5	11.5	0.057	499284	15.60
2	1.5	22.0	0.041	566579	17.71
2	1.5	44.0	0.029	186014	5.81
2	1.5	53.0	0.027	283798	8.87
2	1.5	164.0	0.015	122848	3.84
2	1.5	416.0	0.009	74998	2.34
2	1.5	671.0	0.007	39110	1.22
2	1.5	986.0	0.006	22095	0.69
2	1.5	1340.0	0.005	11532	0.36
2	1.5	1747.0	0.005	711	0.02
3	3.0	0.0	12.247	1715659	53.61
3	3.0	7.0	0.146	1514555	47.33
3	3.0	23.5	0.080	1078709	33.71
3	3.0	46.0	0.057	753672	23.55
3	3.0	166.0	0.030	320410	10.01
3	3.0	414.0	0.019	171375	5.36
3	3.0	668.0	0.015	91441	2.86
3	3.0	979.0	0.012	47236	1.48
3	3.0	1342.0	0.011	23394	0.73
3	3.0	1749.0	0.009	9769	0.31
4	4.5	0.0	18.371	1489412	46.54
4	4.5	9.5	0.188	1450027	45.31
4	4.5	26.0	0.114	904497	28.27
4	4.5	76.5	0.066	759261	23.73
4	4.5	173.0	0.044	323078	10.10
4	4.5	405.0	0.029	193309	6.04
4	4.5	665.0	0.023	109990	3.44
4	4.5	984.0	0.019	57564	1.80
4	4.5	1336.0	0.016	33012	1.03
4	4.5	1752.0	0.014	8970	0.28

Table C-10 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
5	6.0	0.0	24.495	1656610	51.77
5	6.0	14.5	0.203	1556185	48.63
5	6.0	29.0	0.144	1290407	40.33
5	6.0	59.0	0.101	1044984	32.66
5	6.0	171.0	0.059	495169	15.47
5	6.0	403.0	0.039	282315	8.82
5	6.0	663.0	0.030	152760	4.77
5	6.0	989.0	0.025	71393	2.23
5	6.0	1325.0	0.021	43735	1.37
5	6.0	1754.0	0.018	18077	0.56
6	7.5	0.0	30.619	1650900	51.59
6	7.5	31.0	0.174	961533	30.05
6	7.5	80.0	0.108	890516	27.83
6	7.5	175.0	0.073	558063	17.44
6	7.5	400.0	0.048	290561	9.08
6	7.5	673.0	0.037	151671	4.74
6	7.5	991.0	0.031	90507	2.83
6	7.5	1344.0	0.026	46237	1.44
6	7.5	1756.0	0.023	16127	0.50
7	9.0	0.0	36.742	1596449	49.89
7	9.0	34.0	0.199	969010	30.28
7	9.0	105.0	0.113	1035898	32.37
7	9.0	177.0	0.087	682549	21.33
7	9.0	398.0	0.058	469163	14.66
7	9.0	657.0	0.045	235373	7.36
7	9.0	993.0	0.037	123734	3.87
7	9.0	1321.0	0.032	59339	1.85
7	9.0	1758.0	0.028	26375	0.82
8	10.5	0.0	42.866	1489619	46.55
8	10.5	39.0	0.217	1345583	42.05
8	10.5	88.5	0.144	1085098	33.91
8	10.5	184.0	0.100	848384	26.51
8	10.5	394.0	0.068	446576	13.96
8	10.5	659.0	0.053	289027	9.03
8	10.5	995.0	0.043	143353	4.48
8	10.5	1319.0	0.037	79360	2.48
8	10.5	1760.0	0.032	27422	0.86
9	12.0	0.0	48.990	1576803	49.28
9	12.0	41.0	0.242	1349949	42.19
9	12.0	91.0	0.162	1141667	35.68
9	12.0	182.0	0.115	724364	22.64
9	12.0	390.0	0.078	516446	16.14
9	12.0	653.0	0.061	258912	8.09
9	12.0	999.0	0.049	131585	4.11
9	12.0	1316.0	0.043	70538	2.20

Table C-10 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
9	12.0	1784.0	0.037	29260	0.91
10	13.5	0.0	55.114	1524406	47.64
10	13.5	94.0	0.180	1253950	39.19
10	13.5	189.0	0.127	826325	25.82
10	13.5	388.0	0.088	665869	20.81
10	13.5	651.0	0.068	357820	11.18
10	13.5	1001.0	0.055	137773	4.31
10	13.5	1314.0	0.048	88503	2.77
10	13.5	1765.0	0.041	39119	1.22
11	15.0	0.0	61.237	1523109	47.60
11	15.0	109.0	0.185	1305984	40.81
11	15.0	194.0	0.139	988785	30.90
11	15.0	380.0	0.099	561872	17.56
11	15.0	648.0	0.076	311643	9.74
11	15.0	1003.0	0.061	133495	4.17
11	15.0	1312.0	0.053	89340	2.79
11	15.0	1767.0	0.046	24581	0.77
12	16.5	0.0	67.361	1370970	42.84
12	16.5	98.5	0.215	1114870	34.84
12	16.5	196.0	0.152	936049	29.25
12	16.5	378.0	0.110	476862	14.90
12	16.5	644.0	0.084	338663	10.58
12	16.5	1006.0	0.067	158031	4.94
12	16.5	1310.0	0.059	90148	2.82
12	16.5	1790.0	0.050	31987	1.00
13	18.0	0.0	73.485	1379789	43.12
13	18.0	150.0	0.190	1201233	37.54
13	18.0	383.0	0.119	818388	25.57
13	18.0	646.0	0.091	436917	13.65
13	18.0	1011.0	0.073	188611	5.89
13	18.0	1307.0	0.064	89164	2.79
13	18.0	1772.0	0.055	45964	1.44
14	19.5	0.0	79.608	1325333	41.42
14	19.5	152.0	0.204	1071345	33.48
14	19.5	373.0	0.130	775416	24.23
14	19.5	640.0	0.100	436917	13.65
14	19.5	1013.0	0.079	191863	6.00
14	19.5	1355.0	0.068	125574	3.92
14	19.5	1774.0	0.060	53091	1.66
15	21.0	0.0	85.732	1371918	42.87
15	21.0	155.0	0.218	1293407	40.42
15	21.0	371.0	0.141	736479	23.01
15	21.0	638.0	0.107	520075	16.25
15	21.0	1023.0	0.085	215321	6.73
15	21.0	1303.0	0.075	100261	3.13

Table C-10 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
15	21.0	1791.0	0.064	47832	1.49
16	22.5	0.0	91.856	1314982	41.09
16	22.5	161.0	0.229	1358414	42.45
16	22.5	369.0	0.151	781986	24.44
16	22.5	633.0	0.115	415302	12.98
16	22.5	1018.0	0.091	242760	7.59
16	22.5	1350.0	0.079	81307	2.54
16	22.5	1778.0	0.069	53255	1.66
17	24.0	0.0	97.980	1454221	45.44
17	24.0	159.0	0.246	1062663	33.21
17	24.0	366.0	0.162	727987	22.75
17	24.0	630.0	0.123	497426	15.54
17	24.0	1025.0	0.097	196902	6.15
17	24.0	1294.0	0.086	120404	3.76
17	24.0	1780.0	0.073	52947	1.65

Table C-10

MEASURED DATA OF TOLUENE CONCENTRATION PROFILES IN COLUMN TEST DOUGHERTY-1

Sample Location no.	Sample depth (cm)	X-axis (cm)	Concentration (mg/L)							
			t=0hr	t=1hr	t=3hrs	t=7hrs	t=11hrs	t=16.5hrs	t=22hrs	t=29hrs
2	1.5	23.5	47.93	7.50	3.84	2.34	1.22	0.69	0.36	0.02
3	3.0	22.0	53.61	22.50	10.01	5.36	2.86	1.48	0.73	0.31
4	4.5	20.5	46.54	24.50	10.10	6.04	3.44	1.80	1.03	0.28
5	6.0	19.0	51.77	36.00	15.47	8.82	4.77	2.23	1.37	0.56
6	7.5	17.5	51.59	36.00	17.44	9.080	4.74	2.83	1.44	0.50
7	9.0	16.0	49.89	40.00	21.33	14.66	7.36	3.87	1.85	0.82
8	10.5	14.5	46.55	40.00	26.51	13.96	9.03	4.48	2.48	0.86
9	12.0	13.0	49.28	42.00	22.64	16.14	8.09	4.11	2.20	0.91
10	13.5	11.5	47.64	43.00	25.82	20.81	11.18	4.31	2.77	1.22
11	15.0	10.0	47.60	43.00	30.90	17.56	9.74	4.17	2.79	0.77
12	16.5	8.5	46.84	42.00	29.25	19.9	10.58	4.94	2.82	1.00
13	18.0	7.0	45.12	43.00	37.54	23.57	13.65	5.89	2.79	1.44
14	19.5	5.5	45.42	41.00	33.48	24.23	13.65	6.00	3.92	1.66
15	21.0	4.0	44.87	42.00	37.42	23.01	16.25	6.73	3.13	1.50
16	22.5	2.5	44.09	41.00	38.45	24.44	12.98	7.59	2.54	1.66
17	24.0	1.0	45.44	45.00	33.21	22.75	15.54	6.15	3.76	1.66

Table C-11

MEASURED SOIL MOISTURE DATA IN COLUMN TEST DOUGHERTY-1

Sample #	Sample Depth (cm)	Moisture (v/v) t=0	Moisture (v/v) t=120hrs
1	0.0	0.113	0.017
2	1.5	0.113	0.065
3	3.0	0.122	0.080
4	4.5	0.122	0.078
5	6.0	0.123	0.087
6	7.5	0.117	0.089
7	9.0	0.117	0.092
8	10.5	0.123	0.097
9	12.0	0.123	0.100
10	13.5	0.125	0.105
11	15.0	0.132	0.109
12	16.5	0.132	0.118
13	18.0	0.130	0.122
14	19.5	0.130	0.130
15	21.0	0.119	0.131
16	22.5	0.119	0.135
17	24.0	0.12	0.143

Table C-12

DATA FROM COLUMN TEST DOUGHERTY-2

Soil column was packed on Sept. 9, 1995.
Starting time: 6:00 p.m. Sept. 11, 1995
Stopping time: 8:00 p.m. Sept. 12, 1995
Total time: 26 hours
Soil porosity: 0.4
Water content: 0.0019 v/v
Calibration curve is: Conc.=0.01659*Area (R squared =0.99)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
2	1.5	0.0	6.124	234781	3.90
2	1.5	60.0	0.025	44960	0.75
2	1.5	240.0	0.013	19816	0.33
2	1.5	600.0	0.008	12545	0.21
2	1.5	1020.0	0.006	6301	0.10
2	1.5	1560.0	0.005	3873	0.06
3	3.0	0.0	3.873	216365	3.59
3	3.0	60.0	0.050	119634	1.98
3	3.0	240.0	0.025	54644	0.91
3	3.0	600.0	0.016	26271	0.44
3	3.0	1020.0	0.012	18313	0.30
3	3.0	1560.0	0.010	10566	0.18
4	4.5	0.0	5.809	233622	3.88
4	4.5	60.0	0.075	126543	2.10
4	4.5	240.0	0.038	63790	1.06
4	4.5	600.0	0.024	30199	0.50
4	4.5	1020.0	0.018	22719	0.38
4	4.5	1560.0	0.015	10732	0.18
5	6.0	0.0	7.746	250434	4.15
5	6.0	60.0	0.100	125000	2.07
5	6.0	240.0	0.050	85440	1.42
5	6.0	600.0	0.032	48892	0.81
5	6.0	1020.0	0.024	37328	0.62
5	6.0	1560.0	0.020	18095	0.30
6	7.5	0.0	9.682	235299	3.90
6	7.5	60.0	0.125	137916	2.29
6	7.5	240.0	0.063	98209	1.63
6	7.5	600.0	0.040	62247	1.03
6	7.5	1020.0	0.030	31827	0.53
6	7.5	1560.0	0.025	16874	0.28
7	9.0	0.0	11.619	227524	3.77
7	9.0	60.0	0.150	148905	2.47

Table C-13 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
7	9.0	240.0	0.075	141082	2.34
7	9.0	600.0	0.047	69314	1.15
7	9.0	1020.0	0.036	45980	0.76
7	9.0	1560.0	0.029	20595	0.34
8	10.5	0.0	13.555	231401	3.84
8	10.5	60.0	0.175	159661	2.65
8	10.5	240.0	0.088	147080	2.44
8	10.5	600.0	0.055	66376	1.10
8	10.5	1020.0	0.042	38758	0.64
8	10.5	1560.0	0.034	20555	0.34
9	12.0	0.0	15.492	238560	3.96
9	12.0	60.0	0.200	201930	3.35
9	12.0	240.0	0.100	152294	2.53
9	12.0	600.0	0.063	76497	1.27
9	12.0	1020.0	0.049	39811	0.66
9	12.0	1560.0	0.039	31459	0.52
10	13.5	0.0	17.428	253208	4.20
10	13.5	60.0	0.225	212750	3.53
10	13.5	240.0	0.113	161497	2.68
10	13.5	600.0	0.071	125158	2.08
10	13.5	1020.0	0.055	75606	1.25
10	13.5	1560.0	0.044	41550	0.69
11	15.0	0.0	19.365	242909	4.03
11	15.0	60.0	0.250	221337	3.67
11	15.0	240.0	0.125	157774	2.62
11	15.0	600.0	0.079	124734	2.07
11	15.0	1020.0	0.061	54526	0.90
11	15.0	1560.0	0.049	26769	0.44
12	16.5	0.0	21.301	222928	3.70
12	16.5	60.0	0.275	212998	3.53
12	16.5	240.0	0.138	188116	3.12
12	16.5	600.0	0.087	110860	1.84
12	16.5	1020.0	0.067	57629	0.96
12	16.5	1560.0	0.054	34446	0.57
13	18.0	0.0	23.238	226089	3.75
13	18.0	60.0	0.300	209820	3.48
13	18.0	240.0	0.150	185869	3.08
13	18.0	600.0	0.095	127942	2.12
13	18.0	1020.0	0.073	90072	1.49
13	18.0	1560.0	0.059	41158	0.68
14	19.5	0.0	25.174	241172	4.00
14	19.5	60.0	0.325	227953	3.78
14	19.5	240.0	0.163	185754	3.08
14	19.5	600.0	0.103	141610	2.35
14	19.5	1020.0	0.079	77494	1.29

Table C-13 (continued)

sample site no.	sample depth (cm)	sample time (min)	lanbta=Z/t^0.5 Z(cm) t(seconds)	GC peak area/10ul	conc. (mg/L)
14	19.5	1560.0	0.064	44446	0.74
15	21.0	0.0	27.111	249715	4.14
15	21.0	60.0	0.350	234553	3.89
15	21.0	240.0	0.175	178848	2.97
15	21.0	600.0	0.111	158385	2.63
15	21.0	1020.0	0.085	84265	1.40
15	21.0	1560.0	0.069	46815	0.78
16	22.5	0.0	29.047	240421	3.99
16	22.5	60.0	0.375	240059	3.98
16	22.5	240.0	0.188	206444	3.42
16	22.5	600.0	0.119	158803	2.63
16	22.5	1020.0	0.091	91686	1.52
16	22.5	1560.0	0.074	37418	0.62
17	24.0	0.0	30.984	239762	3.98
17	24.0	60.0	0.400	235270	3.90
17	24.0	240.0	0.200	191168	3.17
17	24.0	600.0	0.126	151426	2.51
17	24.0	1020.0	0.097	96747	1.61
17	24.0	1560.0	0.078	44211	0.73

Table C-13

MEASURED DATA OF TOLUENE CONCENTRATION PROFILES IN COLUMN TEST DOUGHERTY-2

Sample Location no.	Sample depth (cm)	X-axis (cm)	Concentration (mg/L) t=0hr	t=1hr	t=4hrs	t=10hrs	t=17hrs	t=26hrs
2	1.5	23.5	3.90	0.75	0.33	0.21	0.10	0.06
3	3.0	22.0	3.59	1.98	0.91	0.44	0.30	0.18
4	4.5	20.5	3.88	2.10	1.06	0.50	0.38	0.18
5	6.0	19.0	4.15	2.07	1.42	0.81	0.62	0.30
6	7.5	17.5	3.90	2.29	1.63	1.030	0.53	0.28
7	9.0	16.0	3.77	2.47	2.34	1.15	0.76	0.34
8	10.5	14.5	3.84	2.65	2.44	1.1	0.64	0.34
9	12.0	13.0	3.96	3.35	2.53	1.27	0.66	0.52
10	13.5	11.5	4.20	3.43	2.68	2.08	1.25	0.69
11	15.0	10.0	4.03	3.67	2.62	2.07	0.90	0.44
12	16.5	8.5	3.70	3.53	3.12	1.84	0.96	0.57
13	18.0	7.0	3.75	3.48	3.08	2.12	1.49	0.68
14	19.5	5.5	4.00	3.78	3.08	2.35	1.29	0.74
15	21.0	4.0	4.14	3.89	2.97	2.63	1.40	0.78
16	22.5	2.5	3.99	3.98	3.42	2.63	1.52	0.62
17	24.0	1.0	3.98	3.90	3.17	2.51	1.45	0.73

VITA

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