This is to certify that the

dissertation entitled

Retention, Enhanced Volatilization and
Leaching of Gasoline in Unsaturated Soils

presented by

Nancy Joan Hayden

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Environmental
Engineering

Thomas C Voice

Major professor

Date January 30, 1992

RETENTION, ENHANCED VOLATILIZATION AND LEACHING OF GASOLINE IN UNSATURATED SOILS

By

Nancy Joan Hayden

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Civil and Environmental Engineering

1992

LE

Gasoli
contaminati
an attracti
gasoline co
information
gasoline in
ents from re
optimize in
main objecti
of SVE in
water perco

The fi
better unde
soils. Cap
two differe
different in
tion and air
ray analysis
nonaqueous-p

ABSTRACT

RETENTION, ENHANCED VOLATILIZATION AND LEACHING OF GASOLINE IN UNSATURATED SOILS

By

Nancy Joan Hayden

Gasoline contaminated soil can be a long-term source of contamination to groundwater. Soil vapor extraction (SVE) is an attractive in-situ technique that can significantly reduce gasoline contamination in vadose zone soils. Fundamental information regarding the factors affecting the retention of gasoline in the vadose zone and the mass transfer of constituents from residual gasoline is critical to better utilize and optimize in-situ remediation technologies such as SVE. The main objective of this research was to determine the efficacy of SVE in reducing gasoline constituent concentrations in water percolating through contaminated soils.

The first phase of study concentrated on obtaining a better understanding of gasoline retention in unsaturated soils. Capillary pressure-saturation data were obtained for two different soils (with and without organic matter) at two different initial moisture conditions (residual water saturation and air-dry). Cryo-scanning electron microscopy with x-ray analysis was employed to visually observe the retained nonaqueous-phase liquid (NAPL) in unsaturated soils.

The re

gasoline wh

air dry. D

the two s

observed wh

Microscopic

acts as an i

The se

the mass-tr

water. Ga

coefficient

brought to r

plates, and

leachate and

soils were u

A loca

were employe

venting. A

air mass tr

behavior was

depletion in

Venting

trations of

magnitude.

soils was ev

for various d

ed using air

The results showed that soils retained significantly less gasoline when starting with an initially wet state than when air dry. Differences in residual gasoline saturations between the two soils (observed at air-dry conditions) were not observed when soils at residual water saturations were used. Microscopic observation substantiates the theory that a NAPL acts as an intermediate wetting fluid in a three-phase system.

The second phase of this research involved determining the mass-transfer behavior from residual gasoline to air and water. Gasoline constituent mole fractions and partition coefficients were determined. Packed soil columns were brought to residual liquid saturations using ceramic pressure plates, and then vented and leached or leached only. Air, leachate and soil concentrations were measured. Two different soils were used (with and without organic matter present).

A local equilibrium model and experimental techniques were employed to evaluate mass transfer to air during soil venting. A local equilibrium assumption was deemed valid for air mass transfer at early venting times. Rate limited behavior was observed at later venting times when constituent depletion in the NAPL had occurred.

Venting was effective in reducing aqueous-phase concentrations of BTEX in column leachate by two or three orders of magnitude. Differences in leaching behavior for different soils was evident only after venting. Leachate concentrations for various gasoline constituents could be adequately predicted using air and soil concentration measurements.

There
assistance
Ph.D. Now
that they
dissertatio

I woul
committee m
provided me
past years;
research, e
Masten, who
ment in both
Boyd, who di

I woul
Environmenta
incredible j
as an Envirc
answered all
my lab); Dav
agement in m
trained me i
who first go

ACKNOWLEDGMENTS

There have been so many people who have provided me with assistance during the long and often tortuous road toward the Ph.D. Now that I finally made it, I think it only fitting that they be remembered on the first few pages of this dissertation.

I would like to express my greatest appreciation to my committee members; my major advisor, Thomas Voice, who has provided me with encouragement, support and friendship these past years; Roger Wallace, for his time and advice on my research, especially this past year in Tom's absence; Susan Masten, who has provided me with sound advice and encouragement in both my research and outside activities; and Stephen Boyd, who directed me in all my questions regarding soils.

I would also like to thank the other MSU Civil and Environmental Engineering Faculty that have aided me on my incredible journey: Mackenzie Davis, who helped me get started as an Environmental Engineer, way back when; Simon Davies, who answered all my analytical questions (and let me put a GC in my lab); David Wiggert, who gave me extra support and encouragement in my job search; Arthur Corey, visiting scholar, who trained me in immiscible fluid flow; and Reinier Bouwmeester, who first got me interested in fluid mechanics.

Workin
I have beer
Crop and So
in answerin
my gratitud
did he dire
digging; Ma
Joanne Whal
Raymond Kur
it didn't w
and soil pc
Specia
pressure ce
and friends
tion to: Ti
that the mo
my good fr
persistence
office mate,
never compla
I would
at the Depa
office and t
running smoo
I grat
CoBioRem, In
and the MSU

Working with real soils is always a challenge. Luckily, I have been able to find a vast number of experts in the MSU Crop and Soil Science Department that have been able to help in answering my numerous questions. I would like to express my gratitude to the following people: Delbert Mokma, not only did he direct me to the soil I wanted, he even did most of the digging; Max Mortland, for his expertise on clays and soils; Joanne Whallon, for the use of her fluorescent microscope; Raymond Kunze, for the use of his pressure membrane (even if it didn't work); and Francis Pierce, for information on resins and soil pores.

Special thanks also goes out to my colleague (and fellow pressure cell sufferer) George Zalidis for his advice, humor and friendship. I would like to express my sincere appreciation to: Timothy Vogel, for being a reference and showing me that the most important thing in a job is to enjoy yourself; my good friend Walter Boylan-Pett for his assistance and persistence with the scanning electron microscope; and my office mate, Pan, for analyzing all the water samples (and never complaining about it).

I would also like to thank the secretarial personnel both at the Department of Civil and Environmental Engineering office and the Engineering Research Complex for keeping things running smoothly.

I gratefully acknowledge the financial support of CoBioRem, Inc., the National Institute of Environmental Health and the MSU Division of Engineering Research.

The
without g
never cea
years, so
greatly a
Heuer, fo
elevating
keeping me
great frie
find out a
new timers
for measur
Lizette Ch
assistance

Last o
would like t
all the gra
easily shave
candidate, v
advice, assi
and leaching

Finally
the support,
the adaptabi
and Nolan.
all.

The best aspect of working and studying at MSU has been without question, my fellow students. Their diversity has never ceased to amaze me. So many have helped me over the years, some in big ways and some in small, but all has been greatly appreciated. Thanks goes to some old timers: Janice Heuer, for her down to earth attitude; Barry Christian, for elevating the groups social consciousness; Dave Filipiak, for keeping me in touch with the real world; and especially my great friend and office mate, Myung Chang, for helping me to find out about my past life as a Korean. Thanks also to some new timers (compared to me anyway): Xianda Zhao; Zhizhen Lzu for measuring drops, drops and more drops; Munjed Maraqa; Lizette Chevalier; Carolann Beigan; and Mark Dixon for his assistance with purge and trap.

Last of my fellow students, but certainly not least, I would like to express my sincere gratitude to Hung Nguyen, for all the graphs, tables and vials he provided for me and who easily shaved six months off the Ph.D.; and my fellow Ph.D. candidate, venting aficionado and lab mate, Mike Annable, for advice, assistance and intense conversations on NAPLs, venting and leaching for the past four years.

Finally, this work would not have been possible without the support, love and encouragement of my husband John, and the adaptability and easy going attitudes of my sons, Connor and Nolan. It's been one hell of a ride but fun. Thanks to all.

TABLE OF CONTENTS

TABLE

LIST OF TABLES

5-10. Initi
colu

5-11. Fina
naph
(µg/

6-1. Exper
base

6-2. Measu
coeff
parti

6-3. Avera
efflu
$C_{w,1}^{\theta}$,

6-4. Compa
conce
from

7-1. Predi
Henry
$C_{w,1}^{\theta}$,

7-2. Henry
value
and w

8-1. Compa
predi
exper
value

8-2. Measu
to pr
and s
extra
vente

8-3. Compa
the a
Law a
24°C,

8-4. Parti

8-5. Compa
taker
leach

8-6. Compa
sampl

take

8-7. Meas
to p

8-8. Meas
comp

FIGURE

LIST OF FIGURES

FIGURE

$C_{air,i}$ concer

$C_{oil,i}$ concer

$C_{s,i}$ satura

$C_{w,i}$ aqueo

$C_{w,i}^{s}$ aqueou
exper

$C_{w,i}^{c}$ aqueou

d_e diamet

d_s width

f_{om} fracti

f_{oil} fracti

g gravi

h_c capi

$K_{air,i}$ air

$K_{d,i}$ dist

K_d dis

$K_{w,i}$ Henr

K_{ow} octar

M_i mass

MW molecu

P_c capilla

$P_c(S)$ capil

P_d displac

NOMENCLATURE

$C_{air,i}$ concentration in air-phase

$C_{oil,i}$ concentration in oil-phase

$C_{s,i}$ saturated pure-phase vapor concentration

$C_{w,i}$ aqueous-phase concentration

$C_{w,i}^{B}$ aqueous-phase concentration from batch experiments

$C_{w,i}^{C}$ aqueous-phase concentration from columns

d_e diameter of a drop

d_s width of drop at distance d_e from the apex

f_{om} fraction of organic matter

f_{oil} fraction of oil

g gravitation constant

h_c capillary pressure head

$K_{air,i}$ air partition coefficient

$K_{d,i}$ distribution coefficient, aqeuous-phase

K_d distribution ceofficient, solid-phase

$K_{H,i}$ Henry's Law constants

K_{ow} octanol-water partition coefficient

M_i mass removed

MW molecular weight

P_c capillary pressure

$P_c(S)$ capillary pressure-saturation relations

P_d displacement pressure

P_e en

P_i pa

P_{nw} pr

P_w pr

Q ai

R_1, R_2 p

r_{ct} rad

R uni

S sat

S_e eff

S_r resi

S_w wate

$S_{w,i}$ pure

t time

T tempe

X_i mole

V_p vapor

β scalin

σ interf

θ contac

ϕ fluid

ϕ_b bulk d

ϕ poros

P_e entry pressure

P_i partial pressure

P_{nw} pressure of the nonwetting phase

P_w pressure of wetting phase

Q air flow rate

R_1, R_2 principle radii of curvature

r_{ct} radius of capillary tube

R universal gas constant

S saturation

S_e effective saturation

S_r residual saturation

S_w water saturation

$S_{w,i}$ pure-phase solubility

t time

T temperature

X_i mole fraction

V_p vapor pressure

β scaling factor, ratio of interfacial tensions

σ interfacial tension

θ contact angle

ρ fluid density

ρ_b bulk density

ϕ porosity

I

1.1. INTR

Gaso

serious n

approximat

in the Uni

or no pro

Environmen

these syste

odor thresh

small amoun

unsafe for

gasoline ar

threaten hu

poses a sig

supplies.

Gasoli

volatile hy

aromatics.

is immiscib

a non-aqueo

CHAPTER 1

INTRODUCTION AND RESEARCH OBJECTIVES

1.1. INTRODUCTION

Gasoline contamination of soil and groundwater is a serious national and international problem. There are approximately two million underground gasoline storage tanks in the United States alone. The majority of these have little or no protection against corrosion. The United States Environmental Protection Agency (EPA) estimates that 10-35% of these systems are leaking (EPA 1988). The very low taste and odor threshold of gasoline (1-2 ppm) makes it possible for small amounts of gasoline to render large volumes of water unsafe for human and animal consumption. Many constituents of gasoline are suspected carcinogens and repeated exposure could threaten human health. Spilled gasoline in soil, therefore, poses a significant threat to groundwater and drinking water supplies.

Gasoline is a complex mixture of volatile and semi-volatile hydrocarbons, mostly C-5 through C-10 alkanes and aromatics. It is less dense and less viscous than water. It is immiscible with water and is often referred to generally as a non-aqueous phase liquid (NAPL). The term gasoline will be

used in

constitu

Aro

toluene,

concern.

constitue

on a mass

much high

often fou

compounds

contamina

threat to

ents, such

health sta

Gasol

therefore

spilled or

largely by

the vadose

spreading

reaches the

spilled and

tions exist

be immobili

migrates th

referred to

Residu

used in this text to refer to the NAPL and not individual constituents of gasoline that may partition into the water.

Aromatic compounds found in gasoline such as benzene, toluene, ethylbenzene and xylenes (BTEX) are of particular concern. They are generally the most soluble of the gasoline constituents and constitute a fairly large percentage (15-30% on a mass basis) of the total gasoline. BTEX concentrations much higher than allowed by EPA drinking water regulations are often found in groundwater near the spill site. Since these compounds are carcinogens or suspected carcinogens, BTEX contamination of groundwater may pose a serious chronic health threat to humans. Other heavier aromatic gasoline constituents, such as naphthalene, are also of concern from a human health standpoint.

Gasoline is essentially immiscible with water and therefore it moves as a separate phase in the soil. Gasoline spilled or leaked from underground storage systems moves largely by gravitational and pressure forces downward through the vadose zone. There may also be some lateral and vertical spreading due to capillary forces. Whether the gasoline reaches the water table depends on the amount of gasoline spilled and the physical, chemical and environmental conditions existing at the spill site. Some of the gasoline will be immobilized in the vadose zone as the bulk of the NAPL migrates through the soil. The retained portion is often referred to as residual gasoline.

Residual gasoline in both the unsaturated and saturated

zones

Tradit

removal

cal an

threate

soluble

of reme

exposure

goal, re

subsurfa

for the r

NAPL such

extractio

biodegrad

residual

effort is

The ap

ogies for

lack of und

important s

NAPL mass

partially a

It is

and immobil

of the NAPL;

as well as

water satur

zones poses a serious and complex contamination problem. Traditional pump and treat methods are ineffectual in its removal, and excavation processes are often costly, impractical and simply relocate the problem. Residual gasoline threatens groundwater because it can be a long-term source of soluble contaminants, such as BTEX and naphthalene. The goal of remediation efforts is to reduce the risk of chemical exposure to human and animal populations. To attain this goal, reduction or elimination of residual gasoline in the subsurface environment must be achieved. In-situ technologies for the remediation of soil and groundwater contaminated with NAPL such as: soil venting, also referred to as soil vapor extraction (SVE); surfactant/water flushing; and accelerated biodegradation have the potential to solve the problem of residual gasoline. A substantial research and development effort is currently being devoted to these technologies.

The application, evaluation and success of these technologies for contaminated field sites are often hampered by the lack of understanding regarding NAPLs in porous media. Many important scientific questions regarding NAPL retention and NAPL mass transfer to various phases in the soil are only partially answered.

It is known that a variety of factors affect the movement and immobilization of NAPL in soil. These include properties of the NAPL; such as density, viscosity and interfacial forces as well as properties of the soil; such as pore geometry and water saturation. However, the relative importance of these

facto
exampl
conte
specul
moveme
using
gasoli
has oc

Qu
immobil
answers
when mod
air and
complex
observed
heterogen
mixture.
a NAPL is

A bet
retained N
mizing reme
and transpo

The ma
as a remedi
the vadose
to the appl
this resear

factors in affecting immobilization is not clear. For example, the effects of water saturation and organic matter content on residual saturation are, for the most part, speculative. Information regarding NAPL retention and movement in a soil is needed because cost and cleanup times using in-situ technologies often depends on the amount of gasoline retained and its location in the soil after a spill has occurred.

Questions governing mass transfer of constituents of immobilized NAPL to air and water in soil are also in need of answers. A local equilibrium assumption (LEA) is often made when modeling the mass-transfer process from retained NAPLs to air and water and some experiments support this. However, in complex field situations, mass-transfer limitations are often observed and it is unclear whether this is due solely to heterogeneities at the site or in part to the complex NAPL mixture. The importance of soil-contaminant interactions when a NAPL is present is also not known.

A better understanding of the mass transfer process from retained NAPL in soil, to air and water is needed for optimizing remediation technologies as well as predicting the fate and transport of contaminants in the environment.

The main purpose of this research was to investigate SVE as a remediation technique for gasoline contaminated soils of the vadose zone. The important scientific questions related to the application of SVE to gasoline contaminated sites that this research addressed were: 1) How much gasoline is retained

in unsat

matter fr

this rete

of gasoli

soil-wate

1.2. RESE

The

investiga

primary ob

1.) I

gasoline s

a) initial

tion.

2.) I

NAPL reten

The s

investigate

residual ga

venting exp

3.) De

coefficient

compare to

4.) Ch

lene to a

unsaturated

and b) expe

in unsaturated soil (with and without significant organic matter fractions), and how does residual water content affect this retention; and 2) What processes affect the mass transfer of gasoline constituents from residual NAPL to soil-air and soil-water.

1.2. RESEARCH OBJECTIVES

The initial stage of this research was conducted to investigate gasoline retention in unsaturated soils. The primary objectives of the first phase were to:

1.) Determine the effect of organic matter on residual gasoline saturation in soils at different moisture contents: a) initially dry soil and b) soils at residual water saturation.

2.) Investigate the use of visual methods for studying NAPL retention in a three-fluid-phase soil.

The second stage of this research was designed to investigate the mass transfer of gasoline constituents from residual gasoline in soils to air and water during laboratory venting experiments. The primary objectives were:

3.) Determine gasoline-air and gasoline-water partition coefficients for the gasoline used in this research and compare to predicted values using Raoult's Law.

4.) Characterize the mass transfer of BTEX and naphthalene to air and water from residually held gasoline in unsaturated soils using: a) a local equilibrium based model; and b) experimental techniques.

5.)

transfer

The

study to

objective

6.)

concentra

aqueous-p

5.) Determine the effect of organic matter on mass transfer during venting and leaching experiments.

The final stage of this work was to apply results of this study toward solving a practical problem. The primary objective was to:

6.) Determine the appropriateness of using air and soil concentration measurements of BTEX and naphthalene to predict aqueous-phase contamination of gasoline contaminated soils.

Con

other pe

occurren

significa

occurred.

and costl

long-term

optimizing

groundwate

This

important

gasoline c

section is

individual

current res

2.1. SUBSU

Petro

characteris

alkanes an

CHAPTER 2

BACKGROUND

Contamination of soil and groundwater by gasoline and other petroleum products has become a widespread and common occurrence. Often leaks or spills remain undetected until significant groundwater and soil contamination have already occurred. After discovery of the spill, cleanup is difficult and costly. Retained gasoline in the subsurface represents a long-term contamination source, therefore, developing and optimizing remediation technologies is imperative to safeguard groundwater and drinking water supplies.

This chapter is intended to present a general summary of important concepts and research studies pertaining to SVE and gasoline contaminated porous media. A short background section is also found at the beginning of each chapter. The individual background sections will focus more specifically on current research related to each chapter.

2.1. SUBSURFACE CONTAMINATION BY PETROLEUM PRODUCTS

Petroleum products vary in their physical and chemical characteristics. Gasoline is a complex mixture of volatile alkanes and aromatics, while diesel and fuel oils consist

pri
fue
thes
ther
fuel
gaso
nate
it's
hydro

Fig

Disco
water fro
soluble gas
late in nei

primarily of higher boiling point hydrocarbons. Diesel and fuel oils may possess a large proportion of aromatics but these are mostly in the form of naphthalenes. Gasoline, therefore, may contaminate larger amounts of soil than diesel fuels because of the transport of volatile compounds of gasoline to uncontaminated soils. Gasoline may also contaminate larger volumes of water due to the higher solubilities of it's various aromatic fractions. Figure 2-1 shows the hydrocarbon distribution in various petroleum products.

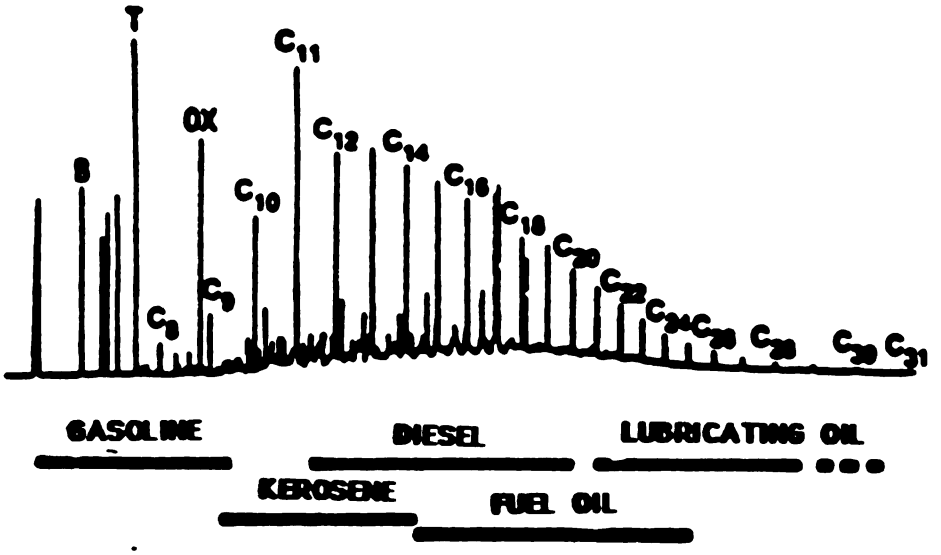


Figure 2-1. Carbon distribution for various petroleum products (Senn and Johnson 1985).

Discovery of a gasoline spill or leak is often made when water from nearby wells is found to be contaminated with soluble gasoline constituents or when gasoline vapors accumulate in neighboring buildings and basements. New regulations

regard
in Se
corros
monthl
existi
suffici
environ
signifi
of leak

2.2. REM

Once
site rem
contamina
groundwat
the ground
ate for s

Often
ization is
and subseq
drawdown c
usually don
pump and tr
ter restora
rate at wh
1989). Tuc
contaminant

regarding underground storage tanks were set forth by the EPA in September 1988 (EPA 1988). These rules now require corrosion control for tanks and piping systems as well as monthly monitoring or monthly inventory control for new or existing tanks. It remains to be seen whether this will be sufficient to prevent continued contamination of subsurface environments by petroleum products. Hopefully, it will significantly reduce both the number and the time to discovery of leaks or spills.

2.2. REMEDIATION OF PETROLEUM CONTAMINATED SITES

Once a spill or leak has been discovered, preparation for site remediation would include determination of: 1) the contaminant or contaminants present; 2) the extent of soil and groundwater contamination; 3) the presence of free product on the groundwater table; and 4) the method or methods appropriate for site specific cleanup.

Often the initial remediation steps after site characterization is made, are the pumping and treating of groundwater and subsequent pumping of free product accumulated at the drawdown cone. Treatment of contaminated groundwater is usually done by air stripping or activated carbon. The use of pump and treat systems as a practical technology for groundwater restoration is in doubt. It has virtually no effect on the rate at which the contaminant is released (Tucker et al. 1989). Tucker et al. (1989) suggest that the high levels of contaminant removal observed early in the restoration opera-

tion ar
the aqu
achieve
nants a
may als
with co
better t
contamin

The
critical
soils of
water con
treated a
number of
and cost
therefore,
ation tec
also calle
3) water o
the most p
organic co

SVE i
It is succe
compounds.
gasoline be
The techni
pressure in

tion are the result of removal of contamination that was in the aquifer when remediation was initiated. Asymptotic levels achieved at later times reflect the rate at which the contaminants are released from the residual NAPL in the soil. They may also be the result of dilution as clean water is mixed with contaminated water. A pump and treat system may be better thought of as a method to contain offsite migration of contaminants than as a remediation technique.

The removal of the residual NAPL in unsaturated soil is critical to the success of a cleanup operation. Contaminated soils of the vadose zone can be a long-term source of groundwater contamination. Often contaminated soil is excavated and treated above ground or disposed of in a landfill. In a large number of cases, however, excavation of soil is impractical and cost prohibitive. In-situ remediation techniques, therefore, are highly desirable. The three in-situ remediation techniques currently of interest are 1) soil venting also called soil vapor extraction (SVE), 2) bioremediation and 3) water or surfactant flushing. Of these, SVE is currently the most practical and common for use dealing with volatile organic compounds (VOC's) in unsaturated soil.

SVE is used to enhance volatilization of a spilled NAPL. It is successful in increasing the removal rates of volatile compounds. It is applicable to sites contaminated with gasoline because of the large volatile fraction of gasoline. The technique involves actively decreasing the soil air pressure in relation to atmospheric air pressure thus inducing

convect
The inc
reducti
soil.

Soi
for the
contamin
Hoag and
informat
regard t
SVE has
nants in

Figu
system, w
and vapor
a practica
of soil ve
presented

Compu
feasibilit
scenarios
1989, Baeh

Altho
sites and
for further
technique i

Johnso

convective air flow into the soil and through the spill site. The increased volatilization can result in a significant reduction in the amount of residual gasoline remaining in the soil.

Soil venting has been applied to contaminated field sites for the removal of harmful vapors as well as to reduce soil contaminant levels (Crow et al. 1987, Batchelder et al. 1986, Hoag and Cliff 1980). Hutzler et al. (1989) have summarized information pertaining to full-scale venting operations in regard to current practices and site conditions. They found SVE has been effective in reducing a wide range of contaminants in different field settings.

Figure 2-2 represents a "basic" in-situ soil venting system, which consists of vacuum extraction well, vacuum pump and vapor treatment unit (Johnson et al. 1989). They present a practical approach to the design, operation and monitoring of soil venting systems. A good review of SVE systems is also presented by Hutzler et al. (1989).

Computer models have also been developed to determine the feasibility of using SVE for different chemicals and site scenarios (Johnson et al. 1990, Wilson et al. 1988, Massman 1989, Baehr et al. 1989).

Although soil venting is currently being used at field sites and has been effective, information that is important for further optimization and the widespread application of the technique is still needed.

Johnson et al. (1989) summarized the three main factors


Vapor
Flow

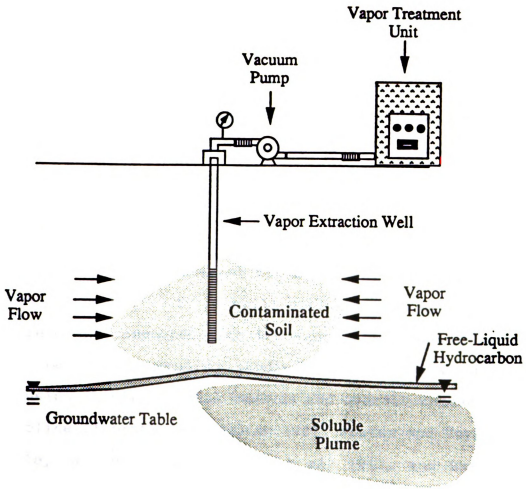


Figure 2-2. "Basic" in-situ soil venting system. (Johnson et al. 1989).

affec
compo
path.
engine
Both m
ties.

C
conside
petrole
over 20
possess
affect t
compound
out" of t
at removi

Labo
focusing
gasoline
Marley and
1989). In
constituen
not looke
investigat
component
as emphas
hydrocarbo
individual

affecting the efficiency of a venting operation as chemical composition of contaminants, vapor flow rate and vapor flow path. Vapor flow rate and flow path are often determined by engineering design, such as pump capacity and well placement. Both may also be affected by soil type and soil heterogeneities.

Contaminant composition is an important factor when considering soil venting as a remediation technique of petroleum product spills. Gasoline is a complex mixture of over 200 different hydrocarbon compounds. These compounds possess a wide range of volatilities, which will ultimately affect the duration of the venting operation, since heavier compounds with lower vapor pressures will be slower to "vent out" of the soil. It is still not clear how effective SVE is at removing compounds with low vapor pressures.

Laboratory venting studies have also been performed, focusing mainly on total removal and overall removal rates of gasoline (Thornton and Wootan 1982, Wootan and Voynick 1983, Marley and Hoag 1984, Brown et al. 1987, and Baehr et al. 1989). Information related to the mass transfer of specific constituents to air or water from residual NAPLs in soils was not looked at. In fact, there has been very little work investigating mass transfer to air and water from multi-component NAPLs in soil. This, however, is an important area as emphasis is shifting from monitoring total petroleum hydrocarbons to understanding the fate and transport of individual constituents of gasoline and petroleum products.

techn
unsat
used.
this
mass
in so
tion
these

2.3. G

Sp
through
retaine
table.
a compli
gasoline
preferent
In a two
nonwetting
series gen

The w
fluids in
and retent
example, a
in the sma
nonwetting

Bioremediation and surfactant/water flushing are other technologies that may become increasingly important in unsaturated soils, although at this time they are not widely used. These techniques are not specifically dealt with in this dissertation, however, fundamental information related to mass transfer processes from a multi-component NAPL retained in soil as well as a better understanding of gasoline retention in unsaturated soil would aid in optimizing and applying these technologies to a wide variety of field situations.

2.3. GASOLINE RETENTION AND MOBILIZATION IN POROUS MEDIA

Spilled gasoline in the vadose zone moves downward through the soil as a separate fluid phase. Some of it is retained as the bulk of the gasoline migrates to the water table. The presence of gasoline elevates the vadose zone to a complicated system involving three fluid phases; water, gasoline and air. In typical soil porous media the water will preferentially wet the soil and is called the wetting fluid. In a two-phase system the air or gasoline would be the nonwetting phase and in a three-phase system the wettability series generally follows the order of water, gasoline and air.

The wettability series dictates the general location of fluids in a multiphase system and therefore, influences flow and retention characteristics. The wetting liquid, water for example, at low saturations in the vadose zone will be present in the small soil pores and as thin films on the soil. The nonwetting phase, such as air, would occupy and move through

the c
would
of the
wettin
U
fluid
transp
remedi
a spil
complex
develop
liquids
Faust et
Faust et
mostly f
useful f
because a
the limit
actual sit
Numer
media will
vadose zo
tension, i
tion, satu
of the int
difficulty
complex na

the center of the large pores. In the vadose zone, gasoline would be of intermediate wetting and would be present on top of the water possibly as thin films or blobs but acting as a wetting fluid relative to the air.

Understanding the factors and mechanisms that affect fluid retention and flow is important for predicting the transport of NAPLs in porous media as well as developing remediation strategies. Predicting the movement of NAPL from a spill site is difficult and often hampered by geologic complexities and unknowns at the field site. Models have been developed to aid in predicting the movement of immiscible liquids in soil (Faust 1984, Kaluarachchi and Parker 1989, Faust et al. 1989 and Kaluarachchi and Parker 1990), however, Faust et al. (1989) suggested that flow models are useful mostly from conceptual and research standpoints and less useful from a predictive standpoint in the field. This is because application to field sites is often unrealistic due to the limited geologic and chemical data pertaining to the actual site.

Numerous parameters related to both the NAPL and porous media will affect the retention and movement of NAPLs in the vadose zone. These include density, viscosity, surface tension, interfacial tension, pore size, pore size distribution, saturation, saturation history and wettability. Because of the interrelationship among many of these parameters, the difficulty in isolating one parameter for study, and the complex nature of system as a whole, the relative importance

of each in regard to NAPL retention and movement in soil is still not clear.

2.4. CAPILLARITY IN MULTIPHASE FLOW AND NAPL RETENTION

Capillarity is central to the movement of liquids within a porous media because of its relationship to saturation and permeability. Permeability and saturation are dependent on capillary pressure. This subject will be discussed in more detail after the introduction of fundamental concepts related to capillarity.

Capillary pressure (P_c) is defined as the difference in pressure between the nonwetting (P_{nw}) and wetting (P_w) fluids:

$$P_c = P_{nw} - P_w \qquad (2\text{-}1)$$

Capillary pressure is related to surface or interfacial tension and the curvature of the interface by the Young-Laplace equation (Adamson 1990):

$$P_c = \sigma(1/R_1+1/R_2) \qquad (2\text{-}2)$$

where σ is surface tension (F/L), R_1 and R_2 are the principle radii of curvature (L). The curvature is affected by pore size and shape.

The surface tension or surface free energy is the free energy per unit area and is used to describe the boundary between a liquid and gas. A soap bubble is often used to illustrate the concept of surface tension. The term tension implies that the surface of the bubble acts as if it were covered by an elastic membrane. This gives rise to the units of force (needed to stretch the surface) per unit length.

Surfac

free e

consta

capilla

(Adamsc

In

describ

term, w

describe

In

defined

where σ i

r_{ct} is th

contact

relations

The

liquid an

forces of

between t

forces of

Capi

governed b

contact an

that are i

ing the t

different

Surface free energy, on the other hand, is the change in Gibbs free energy necessary to form a unit area of surface under constant conditions. Mathematically either concept holds in capillary phenomena such that either phrase may be used (Adamson 1990).

Interfacial tension will be used throughout this text to describe the boundary between two liquids and as the general term, while surface tension will be specifically used to describe the boundary between a liquid and a gas only.

In a circular capillary tube, the capillary pressure is defined by the following equation:

$$P_c = -2\sigma\cos\theta / r_{ct} \qquad (2\text{-}3)$$

where σ is the liquid surface tension, θ is the contact angle, r_{ct} is the radius of the capillary tube. The importance of contact angle to capillary pressure is evident from this relationship.

The contact angle is the angle made between a drop of liquid and a solid surface. This angle is dependent on the forces of cohesion between the liquid molecules, adhesion between the liquid molecules and solid molecules and the forces of attraction between a second fluid and the surface.

Capillary pressure, as shown in Equation 2-3, is governed by interfacial tension between the fluids and the contact angle. It relates the pressure in two fluid phases that are in physical contact and is of importance in determining the transport pathways as well as saturation of the different phases.

re

po

th

wat

tio

in

rese

reter

been

1987,

and Wi

Parker

cial te

pair to

conclude

tion, wh

system d

predict p

Zalidis et

true at s

At the cr

saturation

phase.

As m

related to

Capillary pressure-saturation, $P_c(S)$, curves depict the relationship between capillary pressure and saturation for a porous sample. Soil physicists have long been interested in these relationships because water availability for plants and water movement in unsaturated soil are tied to these relations. Petroleum engineers have also had a continued interest in $P_c(S)$ relations as they relate to recovery of oil from oil reservoirs.

Recently, engineers and scientists interested in NAPL retention and movement in the vadose zone and groundwater have been investigating $P_c(S)$ relationships (Lenhard and Parker 1987, Parker and Lenhard 1987, Parker et al. 1987, Demond 1988 and Wilson et al. 1990). Parker et al. (1987) and Lenhard and Parker (1987) used a scaling procedure based on fluid interfacial tension ratios and a $P_c(S)$ curve for a reference fluid pair to predict $P_c(S)$ curves for other fluid pairs. They concluded by suggesting that using Leverett's (1941) assumption, which states that the air-oil interface in a three phase system determines the total liquid saturation, one could predict pressure-saturation relations of three-phase systems. Zalidis et al. (unpublished), however, found this not to hold true at saturations at or above a critical water saturation. At the critical water saturation and higher, residual NAPL saturation remained constant with increases in the wetting phase.

As mentioned earlier, relative permeability is also related to capillary pressure through its relationship with

saturat
two an
permeab
tion co
critica
experim
Recentl
saturat
mental
complic
methods
correlat
(1988),
predict
generall

Ove
environme
relations
Much of t
petroleum
to soil ar

2.5. RESI

Resid
retained
capillary
retention.

saturation. Relative permeability is important when discussing two and three-phase flow. Relative permeability is the permeability of a fluid relative to the presence and saturation content of another fluid in the media. Although it is a critical parameter for modeling two- and three-phase flow, experimental work related to environmental systems is limited. Recently Demond (1988) determined relative permeability-saturation data for water-organic liquid systems of environmental interest. Measurements of relative permeability can be complicated and time consuming to perform so estimation methods have been used based on $P_c(S)$ data and empirical correlations such as those discussed by Corey (1986). Demond (1988), however, found that the correlations she used to predict relative permeability of the nonwetting phase were generally inadequate.

Overall, there is limited experimental data related to environmental problems dealing with NAPL saturation and its relationship to capillary pressure or relative permeability. Much of the theory and evidence has been obtained from the petroleum engineering literature, which may not be applicable to soil and groundwater systems.

2.5. RESIDUAL NAPL SATURATION

Residual saturation, S_r, is the phrase given to the retained liquid in the soil when subsequent increases in capillary pressure result in virtually no decrease in liquid retention. This retained or residual NAPL is important

becaus
lifeti
duratio
Ca
which r
tional
from fo
surface
surface
size an
tance o
and rem
Inv
saturate
al. (19
saturate
columns,
They fou
dated sa
ages four
(three-ph
than in s
(Schiegg
is that ir
air acts
large pore
zone, the

because it is ultimately tied to source strength, source lifetime, application of remediation processes and remediation duration.

Capillary forces are regarded as the key mechanism by which residual NAPL is retained in soils despite the gravitational forces acting on the liquid. The retention results from forces at the wetting-nonwetting interface and the solid surface. These forces are believed to be determined by surface or interfacial tension, wettability and the shape, size and continuity of the pore spaces. The relative importance of these factors is of interest from both a predictive and remediation standpoint.

Investigations related to residual NAPL saturation in the saturated and vadose zones are limited. Recently Wilson et al. (1990) investigated mechanisms of NAPL retention in both saturated and unsaturated systems using long and short columns, micromodels and polymerized styrene "blob casts". They found residual saturations in water saturated unconsolidated sands to be between 14% to 30%, with much lower percentages found in unsaturated soil. Residual NAPL in unsaturated (three-phase) systems has been found to be considerably lower than in saturated (two-phase) systems in other studies as well (Schiegg 1984, Wilson and Conrad 1984). The reason for this is that in a three-phase system, for example the vadose zone, air acts as the nonwetting phase, occupying the center of large pores. In a two-phase system, for example the saturated zone, the NAPL is the nonwetting fluid occupying the center of

the pores.

The NAPL in the unsaturated zone was observed using micromodel systems and found to reside as thin films and pendular rings around contact points (Wilson et al. 1990). They only found a few isolated organic liquid blobs trapped in water filled pore bodies.

In the saturated zone, however, the NAPL is found primarily as blobs. Wilson et al. (1990) summarized the major mechanisms of trapping in the saturated zone as "snap-off" and by-passing. These terms were originally presented by Chatzis et al. (1983).

Specific retention (the maximum amount of liquid a soil can retain under the influence of gravity) has been investigated for gasoline in aquifer materials (McKee et al. 1972, Convery 1979, Hoag and Marley 1986). The saturation was measured over the length of the column and, therefore, is not an equivalent definition of the term residual as previously described. Hoag and Marley (1986) noted that soil physical parameters have a very significant influence on gasoline retention even under residual water saturations. It is not clear if this was an artifact of their experiment because of the gravity drainage method or is generally applicable. They did find that initially dry soil had higher gasoline retention than soil at residual water saturations. Zalidis et al. (unpublished) also found lower residual gasoline saturations in moist vs. dry soils. Wilson et al. (1990), however, found no difference in residual gasoline saturations between dry and

moist

T

consid

Howeve

questi

satura

proper

Organic

influer

1988),

Mo

glass be

There is

an actua

would be

2.6. MASS

Unde

NAPLs in

remediatic

ing the fa

The two in

with in th

Both proce

nation at

processes

geometry,

moist soil conditions.

The recent study by Wilson et al. (1990) has added considerably to our understanding of NAPLs in porous media. However, there are still questions to be answered. The question of how initial water content affects residual saturation has conflicting answers. The influence of soil properties, including organic matter is also not clear. Organic matter has been hypothesized to possibly have an influence on NAPL retention in soils (Parker 1989 and Wilson 1988), but to date this hypothesis has not proven.

More work is also needed using real soils. Typically glass beads and sands are used in most experimental studies. There is a need to go beyond this. Observation of a NAPL in an actual unsaturated soil has not been performed although it would be a powerful learning example.

2.6. MASS TRANSFER FROM RESIDUAL GASOLINE

Understanding the mass-transfer process from residual NAPLs in soils is of critical importance in determining remediation strategies, interpreting field data, and predicting the fate and transport of contaminants in the environment. The two important mass-transfer processes that will be dealt with in this dissertation are volatilization and dissolution. Both processes can dramatically increase the zone of contamination at a spill site, and thus the factors that affect these processes are of importance. Characteristics such as pore geometry, wetting behavior and sorption or partitioning into

soil ma

immisci

constit

Th

ization

followi

of disso

2.6.1. V

Vol

a liquid

volatili

the solu

enhanced

air phas

could be

liquid ph

Vola

tion, the

liquid a

affecting

interface

matter ma

experimen

Gasc

hydrocarb

are chair

varying nu

soil may affect not only the movement and retention of the immiscible phase but also the mass transfer of gasoline constituents to the air and water phases.

The next section will discuss the importance of volatilization from the general context of soil venting. The section following volatilization will summarize the important aspects of dissolution as it relates to leaching in unsaturated soils.

2.6.1. Volatilization

Volatilization refers to the transfer of a substance from a liquid or solid to a vapor phase. The driving force for volatilization is the difference in the partial pressure of the solute between the two phases. Volatilization can be enhanced by reducing the partial pressure of the solute in the air phase, thereby creating a larger driving force. This could be performed by providing solute-free air above the liquid phase, which is the basic concept behind soil venting.

Volatilization will also depend on the liquid composition, the vapor pressure of individual constituents of the liquid and possible physical and environmental factors affecting the behavior of constituents at the gasoline-air interface, for example temperature. Partitioning into organic matter may also alter a constituent's vapor pressure. Actual experimental evidence in this area is lacking.

Gasoline consists of numerous aliphatic and aromatic hydrocarbons having high vapor pressures. Aliphatic compounds are chained, branched chains and cyclic compounds with a varying number of carbon atoms. Aromatic compounds consist of

the ba

attach

hydroc

varies

of com

than t

Sanders

Ex

gasolin

(1984)

columns

tal dat

based m

Raoult's

and Hoag

constitu

uents be

are brie

Raou

phase of

liquid mi

where p_i i

is mole f

pressure

Raou

structura

the base unit, benzene, with single or multiple carbon units attached or as multiple benzene rings (polynuclear aromatic hydrocarbons, PAHs or PNAs). The constituent mole fraction varies for different gasoline samples, however, the majority of compounds found in gasoline have vapor pressures higher than that of o-xylene, which is 5 mm at 20°C (Maynard and Sanders 1968).

Experimental work investigating mass transfer to air from gasoline contaminated soils has been limited. Marley and Hoag (1984) looked at the removal of total gasoline from soil columns during venting experiments. They compared experimental data for total gasoline removal to a local-equilibrium based model. The model employed the ideal gas law and Raoult's law to determine vapor phase concentrations. Marley and Hoag (1984) did not show data related to the individual constituents, however, to determine if the individual constituents behaved according Raoult's law. The laws of interest are briefly presented here for completeness.

Raoult's law states that the partial pressure in the gas phase of a constituent is related to its mole fraction in the liquid mixture by its pure phase vapor pressure:

$$P_i = X_i V_p \qquad (2\text{-}4)$$

where P_i is vapor pressure of the compound in the mixture, X_i is mole fraction of the compound in the mixture, V_p is vapor pressure of the pure compound.

Raoult's law is generally applicable to mixtures of structurally related compounds or for the solvent in a dilute

solutio

of dis

compon

Raoult

the pa

longer

For di

is now

where

consta

wide r

system

R

values

tions.

calcula

where C_a

molecula

constant

gases obe

The

the mass

solving t

where M_i

solution. Deviations from ideality may exist for constituents of dissimilar chemical structure. In ideal solutions a component present at low concentrations would still obey Raoult's law, however, in real solutions, the dependence of the partial pressure of the solute and mole fraction is no longer given by the pure-phase vapor pressure (Atkins 1986). For dilute ideal systems, the partial pressure of the solute is now governed by Henry's law:

$$P_i = X_i K_H \qquad (2\text{-}5)$$

where K_H is the constant of proportionality called Henry's law constant. Henry's law constants have been determined for a wide range of chemicals of environmental interest for aqueous systems (MacKay and Shiu 1981).

Raoult's law and Henry's law utilize partial pressure values, however, it is often desirable to deal in concentrations. The concentration of a compound in the vapor can be calculated using the ideal gas law:

$$C_{air,i} = P_i * MW_i / RT \qquad (2\text{-}6)$$

where $C_{air,i}$ is the concentration in the air phase, MW_i is the molecular weight of the constituent i, R is the universal gas constant and T is temperature. Generally at low pressure, all gases obey the ideal gas law (Atkins 1986).

The model developed by Marley and Hoag (1984) determined the mass removed for each constituent at each time step by solving the following differential equation numerically:

$$dM_i/dt = Q * V_p * X_i * MW_i / RT = Q * C_{air,i} \qquad (2\text{-}7)$$

where M_i is the mass of constituent i removed, Q is the air

flow ra
by summ
step.
and thi
of tota
gasolin
specifi
makes
individ
which
continu
result
Underst
may dic

Jo
they al
ent in
time.
could
valida

J
compon
removi
compou
tions
the sc
remedia

flow rate, t is time. The total mass removed was determined by summing the mass removed for each constituent at each time step. The new mole fraction in the gasoline was calculated, and this was continued in a step fashion to predict loss rates of total gasoline. They found the model to predict total gasoline removal quite well. However, our interest in specific individual constituents of gasoline, such as BTX, makes it paramount that we determine the removal rates of individual compounds. The model is based on Raoult's law, which assumes an ideal mixture. The residual gasoline is continually changing during the venting process, which may result in deviations from ideality at later venting times. Understanding the venting process at these later times (which may dictate the duration of venting) is important.

Johnson et al. (1990) developed a similar model, however, they also included terms to account for the mass of constituent in the air, water and solid phase in the soil at any given time. They postulated at later venting times, these sources could be important. They did not provide experimental data to validate their model or hypotheses.

Johnson et al. (1987) ran experiments using a three component NAPL in porous media noting the difficulty in removing low vapor-pressure compounds. These types of compounds are also found in gasoline in measurable concentrations which may be important when determining the duration of the soil venting process for gasoline contaminated soil remediation. Johnson et al. (1987) also investigated the

diffusi

and mo

through

soils d

they co

equilib

is not c

rates m

Mos

rated z

diffusiv

Baehr 19

1989).

the aque

section.

2.6.2. D

The

groundwat

Numerous

concentra

Corapcio

Typically

the resid

der Waard

hydrocarb

equilibri

readily a

diffusion of volatile organic vapors in porous media under dry and moist conditions. They found that contaminant breakthrough curves were delayed in moist soils compared to dry soils due to partitioning into the pore water. This exchange, they concluded was sufficiently rapid to be treated as an equilibrium process under their experimental conditions. It is not clear whether this conclusion would be valid using flow rates more typical of actual soil venting.

Most other work related to vapor movement in the unsaturated zone has been numerical in nature and related to diffusive transport (Baehr 1987, Robbins 1987, Corapcioglu and Baehr 1987, Baehr and Corapcioglu 1987, and Sleep and Sykes 1989). Some of these models also predict the contaminant in the aqueous-phase as well, which is the topic of the next section.

2.6.2. Dissolution

The transport of soluble contaminants in soil and groundwater has been an active area of study in recent years. Numerous numerical models have been developed for predicting concentration of contaminants in groundwater (Baehr and Corapcioglu 1984, Abriola and Pinder 1985 and Baehr 1987). Typically these models assume equilibrium partitioning between the residual NAPL and the aqueous solution. For example, van der Waarden et al. (1971), investigating the transfer of hydrocarbons from residual oil to trickling water, found that equilibrium conditions between oil and aqueous phases were readily approached. Similar findings have ben reported in

subseq

1988,

C

gasoli

litera

partit

solubi

tics an

of a va

few com

solubil

Solubil

compound

toluene

respecti

the samp

individu

aqueous-p

coefficie

different

trations

while dis

concluded

gasoline-

gasoline

involve r

Leac

subsequent studies (Pfannkuch 1984, Hunt et al. 1988, Schwille 1988, Miller et al. 1990 and Zalidis et al. 1991).

Constituent partitioning from complex mixtures such as gasoline to water has received little attention in the literature. Recently API (1985) investigated gasoline/water partitioning and concluded that gasoline exhibited low water solubility. This is due to gasoline's nonpolar characteristics and poor hydrogen bonding capability. Gasoline consists of a variety of alkanes, alkenes, and aromatic compounds. A few compounds, such as benzene and toluene, exhibit moderate solubility, 1800 and 550 mg/l respectively, as pure liquids. Solubility, however, is affected by the presence of other compounds. Aqueous-phase concentrations of benzene and toluene found in gasoline were found to be 58.7 and 33.4 mg/l respectively (API 1985). These values can change depending on the sample of gasoline used and the different fraction of individual components. Cline et al. (1991) determined the aqueous-phase concentrations and fuel-water distribution coefficients for various aromatic compounds in over 30 different gasoline samples. They found aqueous-phase concentrations to vary over an order of magnitude between samples while distribution coefficients varied less than 30%. They concluded that overall Raoult's law is generally valid for gasoline-water partitioning, for the aromatic constituents of gasoline that they studied. However, their study did not involve residual gasoline in soils.

Leaching of organic chemicals (NAPLs excluded) in soils

has tr

scienc

with a

(1986)

organi

Consid

biodeg

circum

The upt

the sol

into th

organic

correla

Chiou et

Aft

residual

related

into org

has not

has traditionally been of interest to researchers in the soil science field. Numerous leaching models have been developed with a good overview presented by Hern and Melancon (eds) (1986). These models are typically concerned with trace organic or inorganic contaminants in the vadose zone. Consideration of adsorption, organic matter partitioning and biodegradation perhaps warrant greater importance under these circumstances than when dealing with NAPLs in the vadose zone. The uptake of nonionic organic compounds (NOC) in solution by the solid phase of the soil is primarily due to partitioning into the soil organic phase (Chiou et al. 1981). The NOC organic matter-water partition coefficient has been highly correlated to the NOC octanol-water partition coefficient Chiou et al. (1983).

After a remediation process, such as forced venting, the residual and its remaining constituents may be more closely related to trace organic scenarios, in which case partitioning into organic matter may be considerably more important. This has not been specifically dealt with in the literature.

3.1.INT

In

is an ev

are sto

which ar

gasoline

downward

forces.

capillar

move to

horizonta

Wher

ceases,

This is

threatens

contamina

Eluc

teristics

products

CHAPTER 3

GASOLINE RETENTION IN UNSATURATED SOIL

3.1. INTRODUCTION

In the United States, as well as other countries, there is an ever increasing demand for petroleum fuels. These fuels are stored in millions of underground storage tanks; many of which are leaking or may leak in the future. Fuels, such as gasoline that enter the subsurface from spills and leaks, move downward through the soil due to gravitational and pressure forces. Some lateral and vertical movement also occurs due to capillary forces. A gasoline spill of sufficient size will move to the groundwater table, where it will generally spread horizontally along the capillary fringe.

When drainage of the majority of the spilled gasoline ceases, some gasoline will be retained in the vadose zone. This is often called residual gasoline. Residual gasoline threatens groundwater because it can be a long-term source of contaminants.

Elucidating the factors, such as soil and fluid characteristics, that affect the immobilization of petroleum products in soils has been of interest in recent years

(Conve
1983,
Unders
in ou
gasoli
NAPL r
optimi
effort
depend
the so

investi
retenti
has dra
size dis
the per
organic
mined.

Det
retentio
vapor ext

3.2. BAC

The
with thre
separated
interface

(Convery 1979, Morrow and Songkran 1981, Chatzis and Dullien 1983, Wilson and Conrad 1984 and Wilson et al. 1990). Understanding what factors affect gasoline retention will aid in our ability to predict the fate and transport of spilled gasoline in the subsurface soil environment. Investigation of NAPL retention in soils is also important for developing and optimizing remediation strategies. The success of remediation efforts, such as soil vapor extraction or water flushing, will depend on the amount and location of the residual gasoline in the soil.

The focus of study reported in this chapter is the investigation of the effect of soil organic matter on gasoline retention in sandy soils after the majority of the gasoline has drained. The soils used in this study had similar grain size distributions, pH and other characteristics but varied in the percent organic matter content. Thus, the effect of organic matter on residual NAPL saturation could be determined.

Determination of the effect of organic matter on gasoline retention was prerequisite to my investigation of the soil vapor extraction process with the same soils.

3.2. BACKGROUND

The vadose zone contaminated with gasoline is a system with three fluid phases; air, gasoline and water. These are separated by abrupt boundaries between the fluids called interfaces. Interfacial forces are the result of an imbalance

of coh

interf

is us

interf

fluids

throug

B

fluid

equatio

where σ

bubble.

always

Imm

example

by a curv

solid su

is calle

of highe

than the

face). T

is calle

where P_{∞}

pressure

pressure

(Adamson

of cohesive forces between molecules for a given phase at an interface and those within the bulk fluids. Surface tension is used to describe liquid-gas interfacial forces, while interfacial tension is often used as the general term when the fluids are both liquids. The same convention will be used throughout this text.

Balancing the forces between the fluid inside and the fluid surrounding a spherical droplet leads to the Laplace equation:

$$P_{in} = P_{out} + 2\sigma/r \qquad (3\text{-}1)$$

where σ is the interfacial tension and r is the radius of the bubble. For a bubble to exist, the pressure on the inside is always larger than the pressure on the outside of the bubble.

Immiscible fluids in contact with solid surfaces, for example in soil pores or capillary tubes, are also separated by a curved interface. The fluid that preferentially wets the solid surface is designated the wetting fluid, the other fluid is called the nonwetting fluid. The nonwetting fluid will be of higher pressure (on the inside of the curved interface) than the wetting fluid (on the outside of the curved interface). The difference in fluid pressure across an interface is called capillary pressure, P_c, and is defined by:

$$P_c = P_{nw} - P_w \qquad (3\text{-}2)$$

where P_{nw} is the pressure of the nonwetting fluid and P_w is the pressure of the wetting fluid. The equation for capillary pressure can be described by the Young-Laplace equation (Adamson 1990):

where

depen

prese

the f

Equat

would

This m

nonwet

functi

satura

betwee

hystere

imbibit

functio

As

wetting

and eve

result i

This fin

the resi

saturati

are also

that the

system is

through e

The

$$P_c = \sigma(1/R_1 + 1/R_2) \qquad (3\text{-}3)$$

where R_1 and R_2 are the principle radii of curvature. The dependency of P_c on pore size and the proportion of fluid present (these being related to R_1 and R_2) and the nature of the fluids present (as characterized by σ) is easily seen in Equation 3-3. An increase in P_c for two fluids in a soil pore would result in a smaller radii of curvature at the interface. This means that the wetting phase would be displaced by the nonwetting phase. This statement reveals the intimate functional relationship between capillary pressure, P_c, and saturation, S. It should be mentioned that the relationship between P_c and S depends on the saturation history. Thus, hysteresis results in two main sets of curves, drainage and imbibition. Fluid saturations, therefore, are not a unique function of capillary pressure.

As the capillary pressure increases, drainage of the wetting fluid occurs. At some point, drainage begins to slow and eventually any increase in the capillary pressure will result in virtually no further removal of the wetting fluid. This final wetting fluid saturation is often referred to as the residual saturation, S_{rw}. Other terms, such as irreducible saturation (petroleum literature) and minimum water content are also used (Corey 1986). These terms may be misleading in that they imply that no further reduction in water from the system is possible (further water reduction may be possible through evaporation or removal by plants).

The definition of residual water saturation, S_{rw}, is not

cle
wil
unl
disc
nect
Wils
S_{rw}.
all t
only
state
capil
achiev
D
the S_{rw}
(Brooks
drainag
ing S_{rw}
acknowle
true S_{rw}.
the phys
tion of
high P_c,
used. T
academic
the perio
evapotran
the theo

clear either. Anderson (1987) states that the wetting phase will become discontinuous at sufficiently high P_c. This seems unlikely (i.e. that the water (wetting phase) will ever be discontinuous). The water phase will continue to be interconnected by a water film and can be drained (Corey 1986 and Wilson et al. 1990). Herein lies the difficulty in defining S_{rw}. If the water phase is interconnected then theoretically, all the water can be drained from the soil, to the point where only adsorbed water exists on the soil grains. Reaching this state may require such long equilibration times and high capillary pressures, that for practical purposes it may not be achievable in laboratory studies.

Different approaches have become common for determining the S_{rw} of a porous medium: extrapolation of the $P_c(S)$ curve (Brooks and Corey 1966); measuring water content after gravity drainage of soil columns (Hoag and Marley 1986); and determining S_{rw} at a high P_c (Wilson et al. 1990). Most researchers acknowledge the limitations of their method for describing the true S_{rw}. For example, Corey (1986) notes the uncertainty of the physical meaning of an extrapolated parameter. Determination of S_{rw}, when defined as the saturation at an arbitrarily high P_c, may ultimately depend on the final capillary pressure used. The definition of S_{rw} may be more important from an academic sense, than from a practical standpoint. In nature, the periodic infiltration of precipitation, the influences of evapotranspiration and the water table may mean that achieving the theoretical S_{rw} is uncommon. From an experimental

standpc
be ade
intende
Th
system)
in effe
The res
tinuous
air is
saturat
(Anders
1981) a
1990, M
In
air); w
nonwetti
This is
drainage
$P_c(S)$ re
may be a
because
gasoline
interconn
Wilson et
be possib
The
instead o

standpoint, defining S_{rw} in one of the ways stated above, may be adequate given the nature of the experiment and the intended application of the results.

The residual nonwetting phase saturation, S_{rnw}, (two-phase system) is the saturation at which an increase in P_c results in effectively no further drainage of the nonwetting phase. The residual nonwetting phase saturation does become discontinuous in the form of blobs and ganglia (trapped bubbles when air is the nonwetting fluid). Residual nonwetting phase saturation has been of interest to the petroleum industry (Anderson 1986, Chatzis et al. 1983 and Morrow and Songkran 1981) and recently in the environmental area (Wilson et al. 1990, Miller et al. 1990 and Demond 1988).

In a three-fluid-phase system (ie. water, gasoline and air); water is generally the wetting fluid; air is the nonwetting fluid; and gasoline is of intermediate wetting. This is a common situation in the vadose zone after some drainage of the spilled gasoline occurs. In determining the $P_c(S)$ relationship for air-gasoline on a water wet soil, it may be appropriate to think of gasoline as a wetting fluid, because in essence, this is how it behaves. The residual gasoline saturation, S_{rg}, is presumably present as thin interconnected films and pendular rings (Wilson et al. 1990). Wilson et al. (1990) also suggest that discontinuous blobs may be possible in some areas of the porous media.

The term, effective saturation (S_e), is often used instead of saturation, as defined by:

where

ing th

tive

simpl

wettin

wettin

may be

charac

matter

and NAP

Eq

saturat

in the s

are dif

pressure

tension

1986).

saturati

less thar

the drai

Seve

scaling p

$P_c(S)$ cur

the effec

scaled r

$$S_e = (S-S_r)/(1-S_r) \qquad (3-4)$$

where S_r is the residual saturation. The pore space containing the wetting phase at $S < S_r$ contributes little to convective flow processes, therefore, this is often a useful simplification (Corey 1986).

The use of effective saturation removes the residual wetting phase saturation term from the $P_c(S)$ curve. Residual wetting phase saturation, depending on how it is determined, may be related to the small soil pores as well as soil characteristics such as clay content (Corey 1986). Organic matter of soil has also been suggested as influencing water and NAPL saturation (Parker 1989 and Wilson 1988).

Equation 3-3 reveals that the capillary pressure-saturation relationships $P_c(S)$ for two different fluid pairs in the same medium are different if their interfacial tensions are different. The implication of this is that a capillary pressure-saturation relation can be scaled using interfacial tension as the scaling factor for capillary pressure (Corey 1986). Effective saturation could then be used to scale saturation. The reason for this is that saturation at levels less than residual saturation would contribute very little to the drainage process.

Several other considerations need to be made in the scaling process. For example, if one tries to scale air-water $P_c(S)$ curves to an air-solvent system but does not consider the effects of water induced swelling of the soil particles, scaled results for the air-solvent system could be in

co

cou

als

por

bec

wat

cons

numb

larg

remov

inter

addit

organi

amount

Pa

relatio

where S

capillar

saturati

fluid pa

($\beta=\sigma^{*}/\sigma_{w}$,

fluid pa

differen

Parker (1

cial tens

considerable error. Water induced swelling of soil particles could also mean that the scaled air-entry pressure (P_e) might also be in error. These are important considerations for porous media with considerable clay content present.

Soil organic matter may also cause scaling problems because of differences in its behavior in the presence of water or organic solvents. Organic matter is generally considered to be a hydrophilic material because of the large number of COOH and C=O bonds (Stevenson 1982). It may adsorb large amounts of water and prevent this water from being removed, even at high P_c. A large addition of solvent may not interact with the organic matter in the same manner. The addition of the solvent may also result in dehydration of the organic matter, thus causing the release of significant amounts of water (Boyd 1991).

Parker (1989) describes a scaling process for $P_c(S)$ relationships as:

$$S_w(\beta_{nw}h_{c,nw}) = S^*(h_c^*) \qquad (3\text{-}5)$$

where S_w is the effective wetting phase saturation, h is the capillary pressure head, $S^*(h^*)$ is the effective wetting fluid saturation versus capillary pressure function for a reference fluid pair, generally water-air, and β_{nw} is the scaling factor ($\beta=\sigma^*/\sigma_{nw}$, where σ^* is the interfacial tension of the reference fluid pair and σ_{nw} is the interfacial tension between a different set of nonwetting and wetting fluids). Lenhard and Parker (1987) found that scaling $P_c(S)$ curves using interfacial tension data worked well provided the interfacial tension

measurements were performed on fluids that were subject to the impurities occurring in the actual porous medium system and the effects of residual saturation are removed by scaling using effective saturation, S_e. The universal applicability of this scaling procedure is still being investigated. Soils containing organic matter and multicomponent NAPLs have not been employed.

The scaling procedure described above does not deal with hysteretic effects, therefore scaling can only be performed for the same type of curve, ie. primary drainage data can only be scaled to give the primary drainage curve for a different fluid pair. Scaling is also only appropriate for different fluid pairs in the same porous medium. Scaling the P_c as set forth by Lenhard and Parker (1987) involves only the interfacial tension ratios. As is evident in Equation 3-3, both interfacial tension and pore dimension (radii of curvature) are related to P_c. The general assumption is that the pore size distribution is the same. In order to scale $P_c(S)$ curves to other porous media, scaling of P_c must consider the pore size distribution, and other pore characteristics that influence the radii of curvature.

The question arises of what to do in a situation where three fluid phases are present, such as the case in the vadose zone when gasoline is spilled into a water wet soil. Leverett (1941) proposed that the total equilibrium liquid saturation would be fixed for a given system (the same geometry therefore the interfacial curvature would be fixed). This is written

mathema

In the
gasolin
rium li
spill i
zone it
line),
may be
assumpt
Th
detail
syntheti
Brusseau
matter i
influenc
outweigh
mechanis
matter i

3.3. RES

The

1.

retentio
nonwetti
for two
compared

mathematically as:

$$S_{tl}^{aow}(P_{ao}) = S_{o}^{ao}(P_{ao}) \qquad (3\text{-}6)$$

In the case of gasoline spilled in a water wet soil, the air-gasoline capillary pressure will determine the total equilibrium liquid saturation according to this theory. A gasoline spill in the vadose zone, because of the dynamic nature of the zone itself (changing water contents, evaporation of gasoline), may never reach a true thermodynamic equilibrium. This may be an important consideration when utilizing theoretical assumptions for practical applications.

The importance of organic matter has been investigated in detail as it relates to soil-water partitioning behavior of synthetic organic compounds (Chiou 1989, Bouchard et al. 1989, Brusseau et al. 1989, Chiou et al. 1983). The role of organic matter in NAPL retention, however, is not known. Clearly, the influence of capillarity on gasoline retention should far outweigh the importance of sorption as a NAPL retention mechanism, at least initially. However, the role of organic matter in affecting capillarity needs to be investigated.

3.3. RESEARCH OBJECTIVES

The specific objectives of this research were to:

1. Determine the effect of organic matter on gasoline retention in a three-fluid-phase system, with air as the nonwetting fluid. Capillary pressure-saturation relationships for two soils with different organic matter contents were compared at low moisture conditions (air dry) and residual

water saturations; and

2. Use measured interfacial tensions for air-gasoline and air-water to scale the data from an air-water system and compare with air-gasoline systems in both soils (with and without organic matter). The effect of initial soil moisture content in air-gasoline systems on scaling was also investigated.

3.4. MATERIALS AND METHODS

3.4.1. Soil and fluid measurements

Two sandy soils were collected from Clare County, Michigan in the spring of 1989. These were stored at field saturations in double plastic bags at 8°C. This was done to minimize possible changes that might occur to the organic matter during drying and long storage periods at room temperature. Two horizons were sampled for the Croswell soil, the C and Bs1 horizon. The Bs1 horizon was sampled for the AuGres soil.

Grain size analysis was determined following a mechanical method presented by Bowles (1986). This is presented in Figure 3-1. Specific gravity determinations for each soil were performed (Bowles 1986). Cation exchange capacity and pH were determined following the methods by Rhoades (1982) and McLean (1982), respectively. Total extractable iron and aluminum were performed using a citrate-dithionite extraction (Hayden 1987). Surface area was determined using ethylene glycol monoethyl ether retention (Heilman et al. 1965). Soil

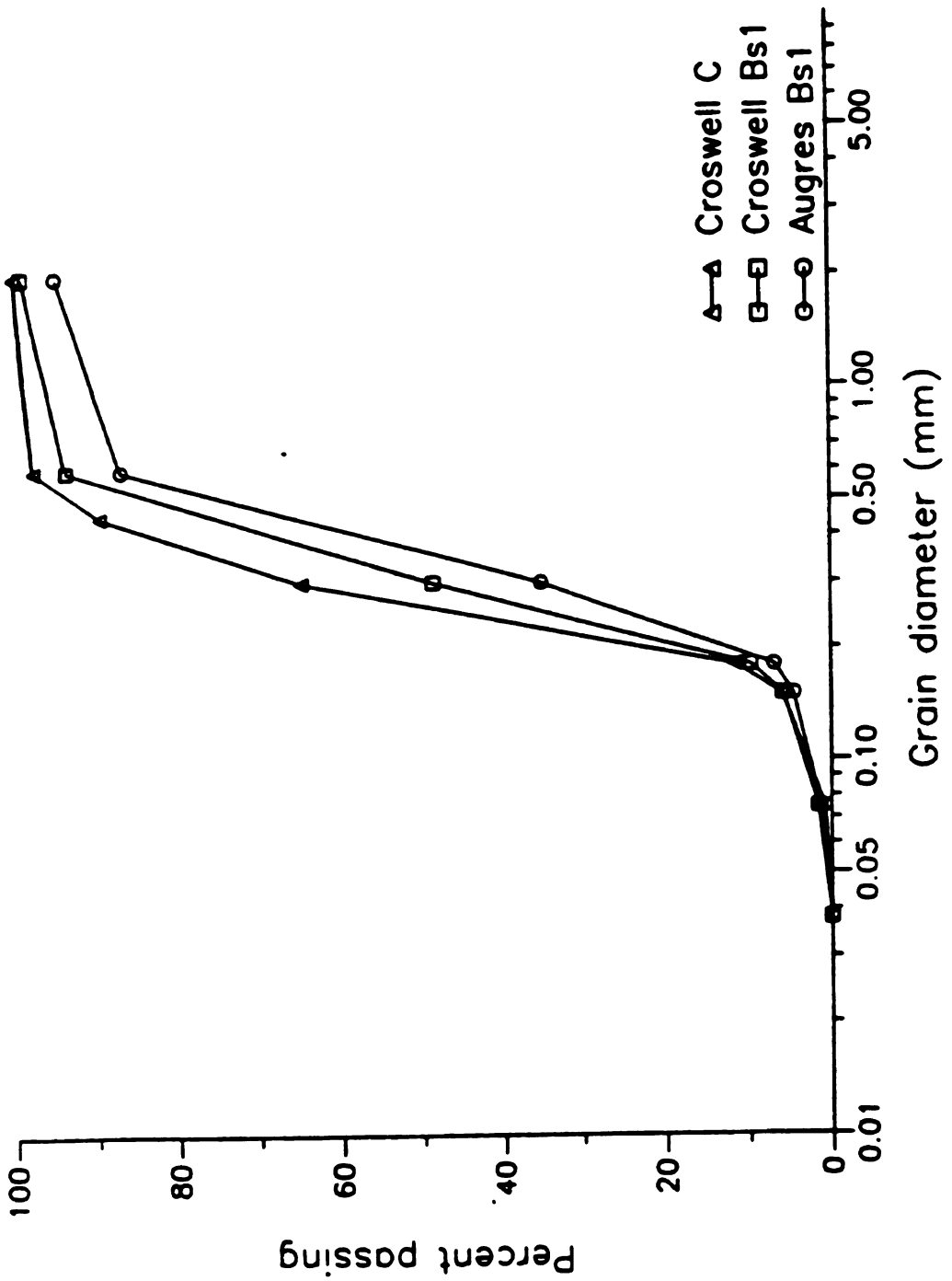


Figure 3-1. Sieve analysis.

prope

(Mode
placi
moist
ampul
volum
nitro
deter
of so
ampule
in the
for tw
ampule
are pre

Ap
April
contain
subdivi
vials w
the cont
until ne
to minim
insure
experime

Kin
followin

properties are presented in Table 3-1.

Total organic carbon was determined using a TOC analyzer (Model 7000, OI Analytical, Texas). The method involved placing twenty to thirty milligrams of soil (pre-determined moisture content) into a pre-weighed special pre-sealed glass ampule. Three hundred microliters of phosphoric acid (5 % by volume) were added to the ampule and purged with high grade nitrogen to remove carbonates in the soil. This amount was determined to be sufficient for these soils. Three milligrams of sodium persulfate oxidant (100 g/l) were added and the ampule was flamed sealed. Blanks and standards were prepared in the same manner. The ampules were placed in a 100°C oven for two hours. They were analyzed for TOC after breaking the ampule with a special attachment to the TOC analyzer. Results are presented in Table 3-1.

Approximately 30 liters of gasoline were collected in April 1988 and stored with minimal headspace in glass containers (four liter size). A four liter container was subdivided into 3 one liter glass containers and 50 headspace vials with crimp caps. Minimal headspace was maintained in the containers and they were stored in the refrigerator at 8°C until needed. This method of storage and usage was designed to minimize losses of volatile compounds from the gasoline and insure a consistent gasoline source over the months of experimentation.

Kinematic viscosities and densities were measured following procedures of ASTM (1990) and are presented in Table

Table 3-1. Soil properties.

Soil	Horizon	Density (g/cm^3)	Fe_T (mg/g)	Al_T (mg/g)	SA (m^2/g)	% OC (by wt)
Croswell	Bs1	2.65	3.42	2.94	35.5	0.885
Croswell	C	2.65	1.91	0.420	5.64	0.0861
AuGres	Bs1	2.62	3.65	5.12	62.2	1.65

3-2.

a pend

Fort (

liquid

immisc

diamet

distan

define

Fordha

term, H

cial te

A

Lakes,

to crea

and nee

with de

A typica

shown i

3.4.2. E

Mod

CA) were

gasoline

cell sup

in a bra

Viton o-

ceramic

3-2. Interfacial tension measurements were determined using a pendant drop technique following the method of Ambwani and Fort (1979). This technique involves photographing drops of liquids in either air (surface tension) or an equilibrated immiscible liquid (interfacial tension) and measuring the diameter of the drop, d_e, and width of the drop, d_s, at a distance d_e from the apex of the drop. The term S, which is defined as d_s/d_e can now be determined. Using Stauffer's and Fordham's Tables reprinted in Ambwani and Fort (1979), another term, H, was determined. The following equation for interfacial tension could now be used.

$$\sigma = \triangle\rho g d_e^2/H \qquad (3\text{-}7)$$

A goniometer (Model #100-00, Rame-Hart Inc., Mountain Lakes, NJ) with microsyringe and camera attachments was used to create and photograph the drops. All glassware, syringes and needles were cleaned in a chromic acid solution, rinsed with deionized water and stored in a 100°C oven until needed. A typical drop (gasoline in air) with important dimensions is shown in Figure 3-2.

3.4.2. Experimental design

Modified #1400 Tempe cells (Soil Moisture, Santa Barbara, CA) were used to determine $P_c(S)$ curves for air-water and air-gasoline systems (Figure 3-3). The inlet line on top of a cell supplied air at a positive pressure. The soil was packed in a brass cylinder (3.0 cm in height and 5.5 cm in diameter). Viton o-rings were used to maintain critical seals. A porous ceramic plate (nominal air-entry pressure of one bar for air-

Table 3-2. Fluid properties at 20°C.

Liquid	Density (g/cm^3)	(Standard deviation)	Kinematic viscosity (cP)	(Standard deviation)
0.001M $CaSO_4$ water	1.00	(0.002)	0.98	(0.01)
Fresh gasoline	0.72	(0.001)	0.035	(0.0006)
Pressure cell gasoline	0.75	(0.001)	ND	

ND not determined for this sample

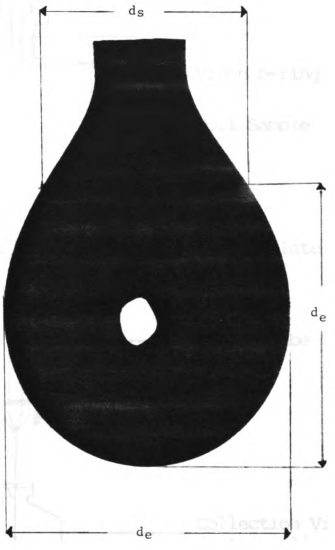


Figure 3-2. Gasoline drop in air.

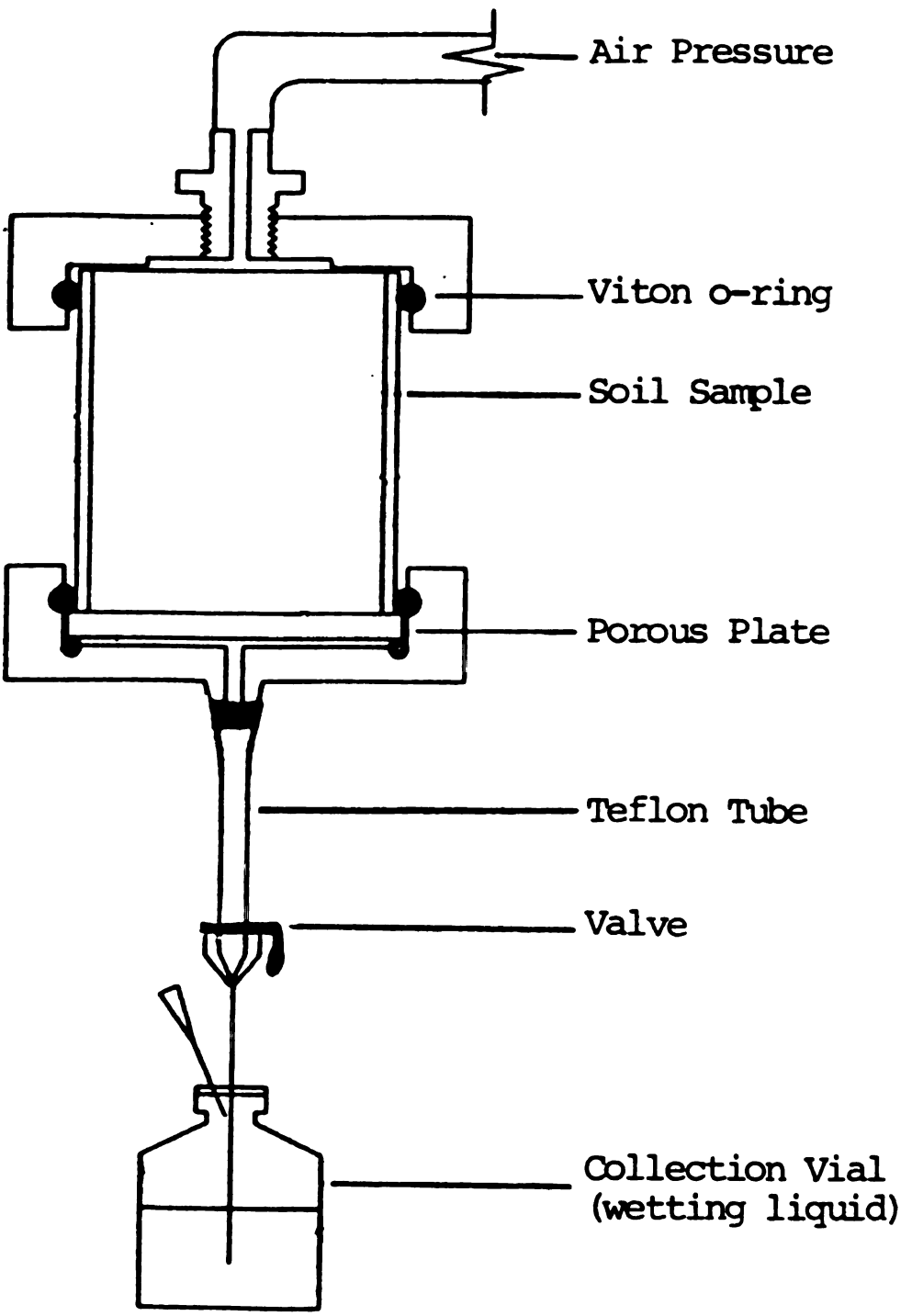


Figure 3-3. Modified Tempe pressure cell.

water
of the
the ce
steel
Teflon
A 30-g
mainta
S
but nc
standa
packed
assemb
plate a
ring wa
cell.
pre-cal
assembl
A solid
ring bu
weight
solid c
Tempe c
exact a
content
immedia
the Temp
was weig

water system) was used as a capillary barrier at the bottom of the cell. The brass fitting was attached to the outlet of the cell which was connected to a Teflon® tube with stainless steel valve and needle. The needle was inserted through a Teflon® lined septum that was used to seal a small glass vial. A 30-gauge needle was also inserted through the septum to maintain atmospheric pressure inside the vial.

Soil as needed was dried slightly to facilitate sieving but not dried completely. It was passed through a #10 standard sieve (2 mm mesh) into doubled plastic bags and packed moist into the brass rings. This was accomplished by assembling the bottom part of the Tempe cell with oven dry plate and brass ring and recording the weight. Another brass ring was taped to the one inside the bottom part of the Tempe cell. An approximate amount of soil necessary to achieve a pre-calculated bulk density was added to the double ring assembly. This was tapped several times to settle the soil. A solid brass cylinder slightly smaller than the top brass ring but the same height was placed on top of the soil. A weight was then dropped on the solid brass cylinder until the solid cylinder was flush with the top brass ring. The bottom Tempe cell assembly, complete with soil, was weighed and the exact amount of soil added was calculated. The moisture content of each soil was determined on separate soil samples immediately prior to setting up the cells. The top part of the Tempe cell was attached and the complete column with soil was weighed.

T

dry a

initia

approx

proces

conten

conten

that c

was de

F

column

soil a

and we

0.001

and dis

times

system

capilla

This we

5 mbar

Su

increas

to equi

determi

liquid

valve a

removed

The soil was air dried within the cell by passing clean dry air through the cell for several days depending on the initial moisture content of the soil. To determine the approximate moisture content of the soil during the drying process, the column was periodically weighed and the moisture content was calculated. Drying was complete when the moisture content of the soil in the pressure cells was approximately that of air dry soil. The moisture content of air dry soil was determined on separate samples dried in the laboratory.

Following air drying, carbon dioxide flowed through the column at 15 psi for 1 hour to displace air present in the soil as described by Demond (1988). The cell was then sealed and weighed. A vacuum was attached to the top and deaired 0.001 M Ca_2SO_4 water was flooded through the soil to dissolve and displace the carbon dioxide. The soil was flushed several times to remove the water containing carbon dioxide. The system was allowed to equilibrate 24 hours at 5 cm of capillary pressure, measured from the middle of the soil core. This weight was recorded and represented the soil moisture at 5 mbar of capillary pressure.

Subsequent capillary pressure increases were obtained by increasing the air pressure in steps and allowing the system to equilibrate for 24 hours. The total cell weight was determined after each step. To avoid back absorption of liquid into the soil from under the plate during weighing, the valve at the outlet end was closed, the inlet air line was removed and the top of the column was plugged. The outlet tube

was re
during
bottom
to the
weighi
losses
comple
plate
and af
initia
The amo
of the
experi
was al
saturat
gasolin
for the
gasolin
gasolin
deaired

Ai
determi
Upon co
core was
gasoline
water sa
cell.

was removed and any air bubbles that appeared under the plate during the step were removed by adding more liquid to the bottom of the cell. The cell was then weighed and reattached to the air. I believed this method to be more accurate than weighing the collection bottle because it accounted for small losses from the cell other than via the outlet tube. Upon completion of the experiment, o-rings and the liquid saturated plate were removed and weighed. The difference between before and after weights of the plate were subtracted from the initial cell weight to determine the initial water saturation. The amount of water beneath the plate at the beginning and end of the experiments was determined in a separate set of experiments when no soil was present in the core. This value was also subtracted from the initial cell weight upon saturation. Experiments were conducted at 22°C±2°C. Air-gasoline curves were obtained in a similar manner except that for the air-gasoline system carbon dioxide was not used and gasoline was supplied by applying positive air pressure to the gasoline in a gasoline reservoir. The gasoline was not deaired for obvious reasons.

Air-gasoline $P_c(S)$ curves for a water wet soil were determined using soil cores from the air-water experiments. Upon completion of the air-water $P_c(S)$ experiments, the soil core was carefully removed from the Tempe cell, a pre-weighed gasoline saturated pressure plate was inserted in place of the water saturated plate. The soil core was placed back into the cell. Gasoline was added to the bottom of the cell to

dislo

to f

press

and

descr

weigh

deter

3.5.

3.5.1

N

preser

water

tensio

column

measur

or 0.0(

gasolir

pressur

increas

however

gasolin

This is

molecul

cules.

compoun

have su

dislodge the air underneath the plate. Gasoline was allowed to flow into the bottom of the cell by applying positive pressure to the gasoline in a reservoir. The pressure steps and saturation measurements were determined as previously described. The gasoline saturated plate and o-rings were also weighed at the end of the experiment. Saturation was determined on a liquid volume per total void volume basis.

3.5. RESULTS AND DISCUSSION

3.5.1. Interfacial tension

Measured surface tensions of water and gasoline are presented in Table 3-3. Surface tension measurements for water matched closely with literature values. Water surface tension decreased slightly for water that had passed through columns containing AuGres soil, while virtually no change was measured for water that contained soluble gasoline components or 0.001 M $CaSO_4$. Surface tension was measured for both fresh gasoline and gasoline that had passed through Croswell Bs1 pressure cells during initial drainage. There was a slight increase in surface tension for the pressure cell gasoline, however, surface tension for both fresh and pressure cell gasoline was much lower than the surface tension of water. This is expected because the cohesive force between water molecules is much greater than that between gasoline molecules. Low surface tensions are also typical for pure compounds which are found in gasoline; o-xylene and n-dodecane have surface tensions of 30.0 and 25.6 dynes/cm respectively

Table

Compou

Deioni
Water

AuGres
Soil Wa
(0.01M

Water
With Ga

Fresh

Gasolin
Pressur
Experi
(passe
Cros Bs

Gasoli

N is t
value

[1] Wils

Table 3-3. Water and gasoline surface tension measurements at 20°C + 0.5°C (dynes/cm).

Compound	σ_{air}	% Relative Standard Dev.	N
Deionized Water	72.09	1.5	4
	72.10	2.5	5
AuGres Soil Water (0.01M $CaSO_4$)	70.03	2.4	4
Water Equilibrated With Gasoline	72.61	2.3	4
Fresh Gasoline	20.20	1.0	8
	20.15	1.4	7
Gasoline used in Pressure Cell Experiments (passed through Cros Bs1 soil)	21.99	2.0	7
	21.82	1.7	7
Gasoline[1]	20.5	1.5	unknown

N is the number of determinations used to obtain the average value reported for σ_{air}.

[1] Wilson et al. 1990 (Temperature 22-24°C)

(Ridd

are p

dodeca

the ac

compar

S

freshl

Ultra-

can de

attain

before

chemic

these

establ

interf

the in

in a l

the i

associ

mixtur

I

within

times

Presum

from t

Wilson

(Riddick et al. 1986).

Interfacial tension measurements for various liquid pairs are presented in Table 3-4. Two reference compounds, n-dodecane and tetrachloroethylene, were measured to determine the accuracy of the method and analyst. The measured values compared well to measurements made by Demond (1988).

Samples of the reference compounds were taken from new, freshly opened, uncontaminated bottles of these chemicals. Ultra-pure compounds are required because slight impurities can decrease the interfacial tension. Chemical equilibria is attained for the two immiscible liquids by sufficient mixing before measurements are made. However, if impurities or other chemicals are present in the liquids when the drop is formed, these impurities will migrate to or from the interface to establish a condition of minimum interfacial energy. The interfacial energy is primarily determined by the molecules at the interface and in a mixture, the constituents which result in a lower surface tension will have a higher concentration at the interface (Corey 1986). This suggests the difficulty associated with measuring interfacial tension for complex mixtures such as gasoline.

Interfacial measurements for fresh gasoline-water taken within 10 seconds after forming the drop were more than two times greater than measurements taken after two minutes. Presumably this is due to migration of constituents to and from the interface to establish a condition of minimum energy. Wilson et al. (1990) reported an interfacial tension value for

Table

Liquid

Dodeca	
TCE	
Gasoli (Fresh	
PC Gas (CC)	
PC Gas (CBsl)	
PC Gas (ABsl)	

σ_w^1 Der

σ_w^2 Wi

ND not

Table 3-4. Interfacial tension measurements at 20 + 0.5°C (dynes/cm) for liquid and water.

Liquid	σ_w (10^0 s)	(%RSD)	(N)	σ_w (2^0 m)	(%RSD)	(N)	σ_w (4^0 m)	(%RSD)	(N)	σ_w
Dodecane	46.7	5.4	11	ND			ND			45.8[1]
TCE	48.2	1.1	6	ND			ND			49.7[1]
Gasoline	28.5	0.47	3	12.5	31	3				
(Fresh)	28.8	5.6	5	12.5	3.1	5	ND			22.9[2]
PC Gasoline (CC)	27.0		2	13.0	4.3	5	12.6	3.6	7	ND
PC Gasoline (CBs1)	29.1		2	16.2	3.3	4	13.7	11	6	ND
PC Gasoline (ABs1)	27.6		2	13.7	6.5	6	ND			ND

σ_w[1] Demond (1988).

σ_w[2] Wilson et al. (1990). (Temperature 22-24°C)

ND not determined for this sample.

gasol
was n
over
this
surfa
effec

gasol
with
were
little
values
Change
the so
of the
interf
after
The pre
(e.g.
interfa
tensior
reduced
the rat
ing tha
a drop
trivial
off the

gasoline of 22.9 (Table 3-4). Although a determination time was not given, this value falls with the values determined over the 10 - 120 sec waiting period of the values reported in this dissertation. A waiting period was not possible for surface tension measurements because of volatilization effects.

Interfacial tension measurements are also presented for gasoline and water that passed through a pressure cell packed with Croswell soil. Although only a small number of drops were measured in each case, the results suggest there is little discernable difference between interfacial tension values from pressure cell or fresh gasoline-water systems. Changes in interfacial tension from impurities picked up in the soil will probably be overshadowed by the complex nature of the gasoline itself. The data do show slightly higher interfacial tension measurements for pressure cell gasoline after a two minute waiting period compared to fresh gasoline. The pressure cell gasoline has probably changed in composition (e.g. loss of volatile components) which may change its interfacial tension. After four minutes the interfacial tensions for pressure cell gasoline-water systems were further reduced, although not substantially. There is a decrease in the rate of change of interfacial tension over time, indicating that interface equilibrium is being attained. Maintaining a drop on the needle for four minutes, however, was not a trivial task because there was a tendency for the drop to fall off the needle. A two minute drop time is more practical and

may b

3.5.2

and A

at tw

satura

text,

the wa

experi

pressu

gasoli

mbar i

had th

Croswe

organi

in sma

highly

(four

in Tab

Croswel

symbols

Croswel

Other s

hence o

A

may be representative of the interfacial tension of gasoline.

3.5.2. Capillary pressure-saturation relationships

Air-water $P_c(S)$ relationships are presented for Croswell and AuGres soil in Figure 3-4. Croswell Bs1 soil was packed at two different bulk densities. Soil conditions and final saturation for each soil are shown in Table 3-5. In this text, the term residual saturation will be used to refer to the water saturation at the final capillary pressure of the experiments. In air-water systems the final capillary pressure was 700 mbar, while 300 mbar was used for the air-gasoline systems. For the purpose of comparison, S_w at 300 mbar is also shown in Table 3-5.

The AuGres soil, with an organic matter content of 3.0 %, had the highest average residual water saturation, while the Croswell C soil had the lowest. The hydrophilic nature of organic matter, its large surface area as well as the increase in small pores that organic matter creates in the soil make it highly water retentive.

The average final saturation from each of two trials (four replicates in each trial) are shown for Croswell C soil in Table 3-5. The replicate data for each trial using Croswell C soil are presented in Figure 3-4a using different symbols. The data are differentiated in this manner for Croswell C soil because of the differences in trial averages. Other soils did not show differences in trial averages and hence only one average is shown (Table 3-5).

A probable explanation for the difference in the two

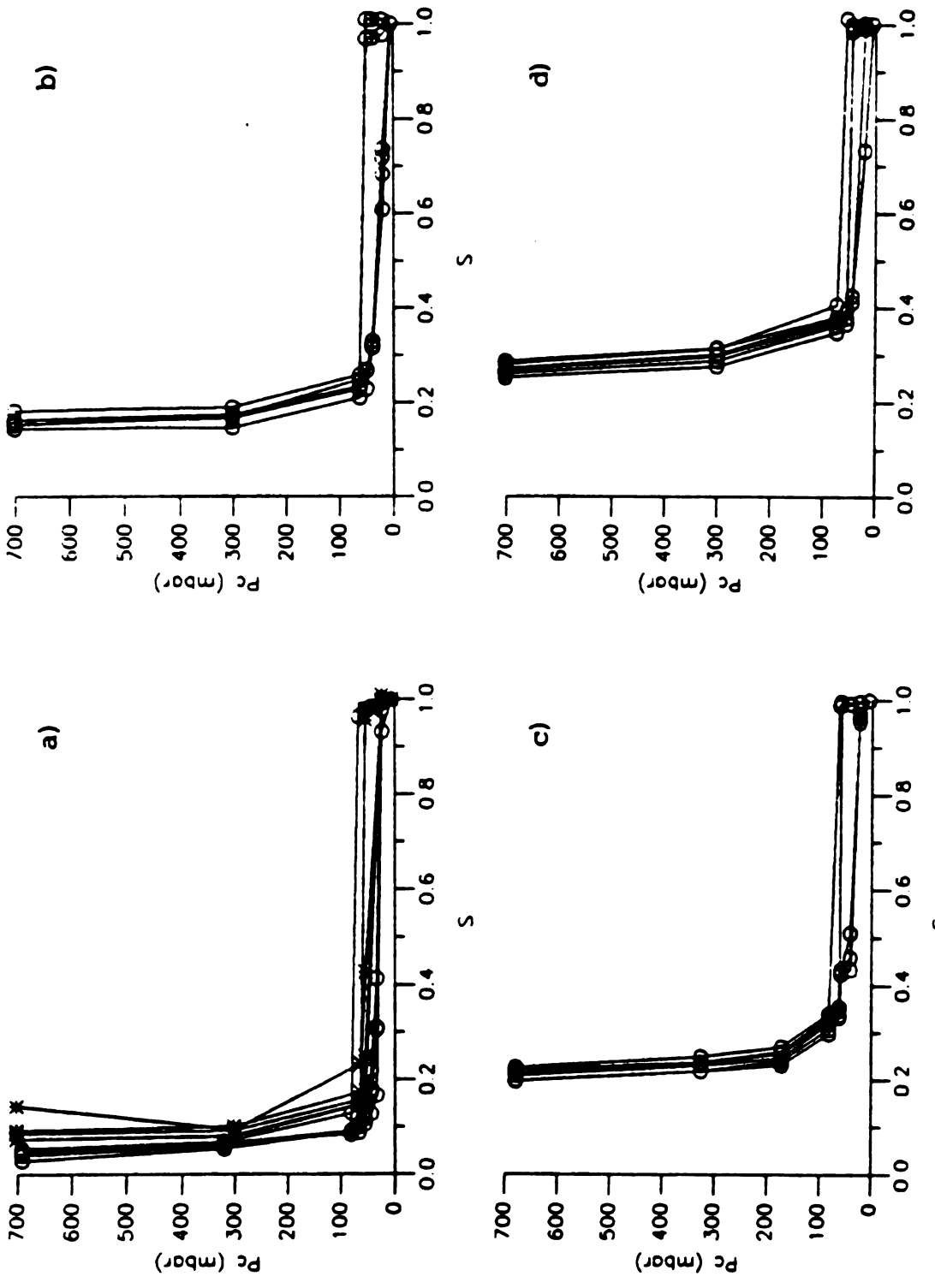


Figure 3-4. Air-water $P_c(S)$ curves for; a) Croswell C (ρ_b=1.55), b) Croswell Bs1 (ρ_b=1.55), c) Croswell Bs1 (ρ_b=1.34), and d) AuGres soil (ρ_b=1.34).

Table 3-5. Residual liquid saturation, S_r, and air-entry pressures, P_e (mbar), determined for various soils.

Soil	%OM (wt)	$\bar{\rho}_b$ (g/cm^3)	$\bar{\phi}$	$\bar{S}_{iw}$ air-dry	$\bar{S}_{rw}$ (aw) (.70bar)	$\bar{S}_{rw}$ (aw) (.30bar)	$\bar{S}_{rg}$ (ag) (.30bar)	$\bar{P}_{ew}$	$\bar{P}_{eg}$
Croswell C	0.16	1.55	0.42	0.0041	0.042	0.062 0.076	0.024 0.089	46	<5
Cros. Bs1	1.81	1.55	0.42	0.013	0.21	0.23	0.11	48	<5
Cros. Bs1	1.81	1.34	0.49	0.019	0.16	0.17	0.085	24	<5
AuGres Bs1	3.20	1.31	0.50	0.060	0.27	0.30	0.11	42	<5

(aw) air-water system
(ag) air-gasoline system

trial
resul
of th
could

tions
packe
resid
Crosw
tions
conte
packe
packe
total
in sm

amoun
adsor
in th
a cor

wate
a sh
the
larg
simi
dist

trials using Croswell C is soil packing. The trial which resulted in considerably larger residual saturations was one of the first experiments performed. Inexperience in packing could have been a source of error.

The Croswell Bs1 soil had intermediate residual saturations between the Croswell C and AuGres soil. The tighter packed Croswell Bs1 cores (higher bulk density) had higher residual water saturations than the more loosely packed Croswell Bs1 cores. The intermediate residual water saturations are probably due to the intermediate organic matter content. The higher residual water saturations in the tighter packed Croswell Bs1 soil cores compared to the more loosely packed Croswell Bs1 soil cores are probably due to the greater total amount of organic matter present, as well as an increase in smaller pores due to the tighter packing.

At high capillary pressures, much greater than 1 bar, the amount of water retained would be due predominantly to adsorption forces (Kunze 1990). At capillary pressures used in this study, residual water saturations probably result from a combination of capillary and adsorption effects.

The different soils generally exhibited the same type of water release for increases in pressure. There was generally a short pressure increase, usually about 20 mbars, in which the majority of water was released. This indicates volume of large pores between different soil types and packing was similar. This may be due to the similar nature, grain size distribution and packing procedure of the soils. The presence

of t

relea

P_e, i

the s

It th

P_e fo

This

soil.

50 mh

packe

these

the e

steps

this s

levels

From

curve

when t

or im

preser

T

residu

than i

increa

1982).

and po

residu

of the organic matter did not appear to affect the water released in the early pressure steps. The air-entry pressure, P_e, is the pressure that must be exceeded before air can enter the soil core, and subsequently displace the wetting liquid. It therefore, depends on the largest pore sizes. The average P_e for the water saturated soil cores is shown in Table 3-5. This was determined by inspection of the $P_c(S)$ curves for each soil. It is generally the same for all soils, between 40 and 50 mbar, although slightly lower, 24 mbar, for the looser packed (bulk density = 1.34) Croswell Bs1 soil. The nature of these soil (medium sand), made it difficult to characterize the early part of the $P_c(S)$ curves, i.e. very small pressure steps resulted in significant drainage. However, the goal of this study was to compare liquid contents at or near residual levels, which may be important from a practical standpoint. From a practical standpoint, the early portion of the $P_c(S)$ curve would be applicable to early times after the spill or when the negative pressure is low such as near the water table or impermeable barrier when a mobile gasoline phase is present.

The presence of organic matter did result in higher residual water saturations in the soils with organic matter than in Croswell C. The presence of organic matter generally increases the water retentive capabilities of soils (Hillel 1982). Organic matter may affect the number of small pores and pore sizes which in part may be responsible for the higher residual water saturations (at 700 mbar). Adsorption of

water

resid

shown

for t

air t

secti

moist

resid

soils

organ

satur

Crosw

satur

water

the

proba

satur

soils

in th

densi

satur

densi

Corre

Matte

water by organic matter may also be a significant factor in residual water saturation.

Air-gasoline $P_c(S)$ relationships for the same soils, are shown in Figure 3-5. It should be reiterated that soil cores for the air-gasoline study were air dried by passing clean dry air through the cell as previously described in the methods section for the air-water system. The average initial air-dry moisture contents for soil cores used to determine gasoline residual saturation are shown in Table 3-5.

The residual gasoline saturation measured in the air-dry soils also seems to be strongly related to the presence of organic matter in the soil. Average residual gasoline saturations are also presented in Table 3-5. The AuGres and Croswell Bs1 soils exhibited higher residual gasoline saturations than the Croswell C soil. The initial average water saturation (after air-drying) was generally higher in the organic soils. The remaining water in the soil is probably adsorbed water. The combined residual gasoline saturation and initial water saturation (air-dried) for all soils is considerably less than the residual water saturation in the air water system.

The Croswell Bs1 soil cores that had the higher bulk densities showed about a 30 % higher residual gasoline saturation than the lower bulk density cores. A larger bulk density means that more soil is present in the core. This corresponds to an increase in the total amount of organic matter present and also an overall reduction in the size of


700
600
a)
700
600
b)

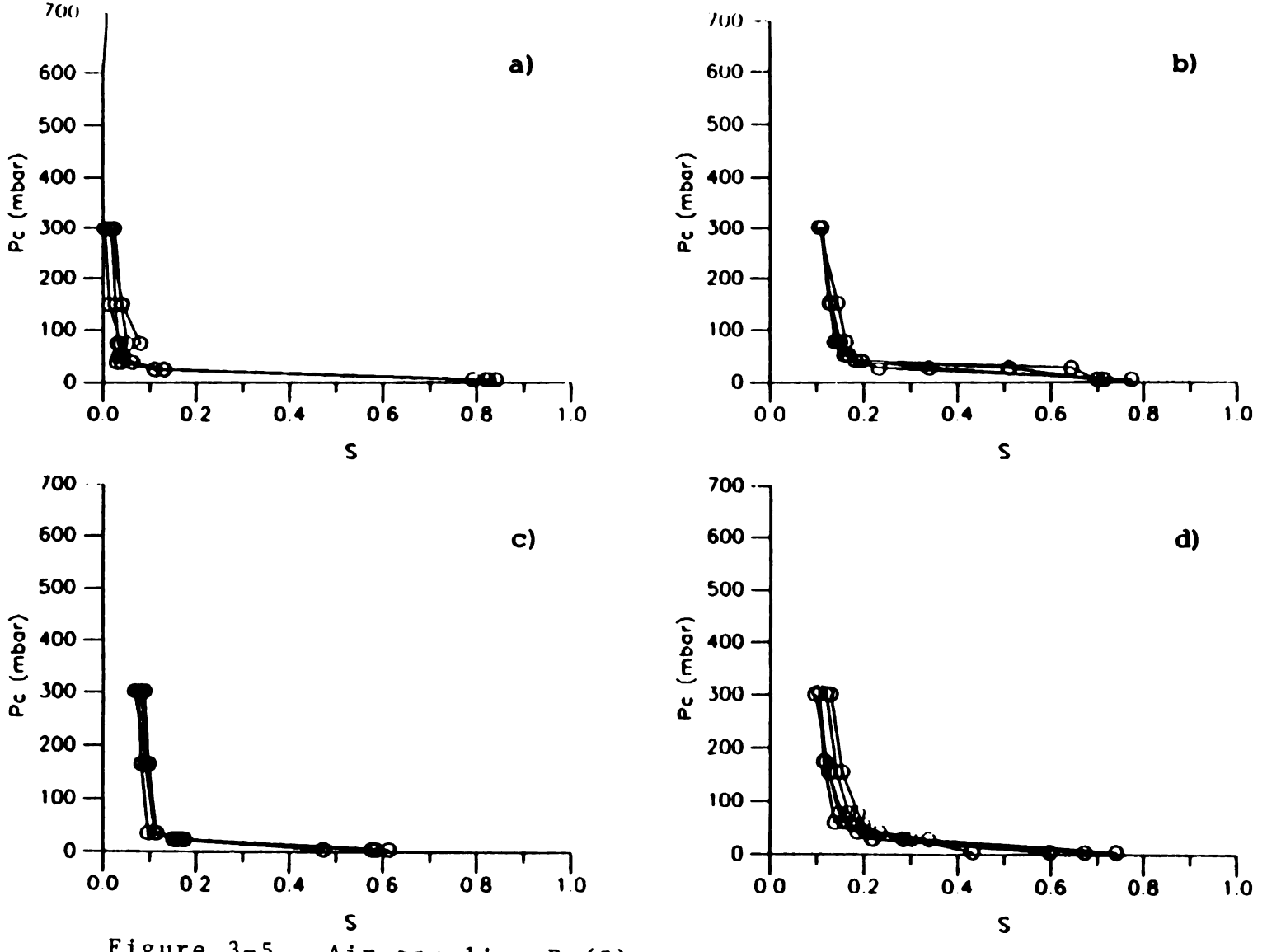


Figure 3-5. Air-gasoline Pc(S) curves for; a)Croswell C (ρ_b=1.55), b) Croswell Bs1 (ρ_b=1.55), c)Croswell Bs1 (ρ_b=1.34), and d) AuGres Bs1 (ρ_b=1.34).

the s

incre

soils

for w

resid

on:

resul

capil

organ

adsor

gasol

measu

weath

ratio

antic

would

case;

most

had su

such t

ly hig

be mer

the me

to red

of th

gasoli

the soil pores. Both of these factors would tend to result in increased residual gasoline saturations.

Residual gasoline saturations and gasoline P_e for these soils are summarized in Table 3-6. The residual saturations for water (at 300 mbars) are between two and three times the residual gasoline saturations which is to be expected based on: 1) the lower surface tension of gasoline which would result in gasoline draining from smaller pores for the same capillary pressures; and 2) the hydrophilic nature of most organic matter and soils resulting in greater amounts of water adsorbed. However, it would be expected that the residual gasoline saturations be even lower based on surface tension measurements. The surface tension of water is 72 dynes/cm and weathered gasoline surface tension was 22 dynes/cm giving a ratio of 3.3. Based on surface tension effects alone, it was anticipated that about 3.3 times more water than gasoline would be retained at a given P_c. This was clearly not the case; much more gasoline was retained that was expected. The most likely explanation for this is that the retained gasoline had sufficiently changed in composition due to volatilization, such that if it could be measured it would have a significantly higher surface tension than previously measured. It should be mentioned that a period of at least five days was used for the measurement of $P_c(S_g)$ curves. Although attempts were made to reduce volatilization effects, undoubtedly some weathering of the gasoline occurred. The effect of weathering on gasoline surface tension, as evidenced by measuring the

Table 3-6. Average residual gasoline saturation in soil with residual water saturation.

Soil	$\overline{S_r}$	ϕ_e	$\overline{S_{rg}}$	(SD)	N	time (days)
Croswell C	0.059	0.38	0.0071	(0.028)	8	5
Croswell Bs1 (ρ_b= 1.55)	0.21	0.21	0.015	(0.033)	4	5
Croswell Bs1 (ρ_b= 1.34)	0.16	0.33	0.0072	(0.0042)	4	7
AuGres	0.27	0.23	0.0080	(0.0075)	6	6

N is the number of determinations for calculating S_{rg}.

time is the number of days of experiment.

surf
cell
(Tab
that
unde
tion
tensi
highe

were
diffe
tion
swel
incr
wate
avoi
no a
satu

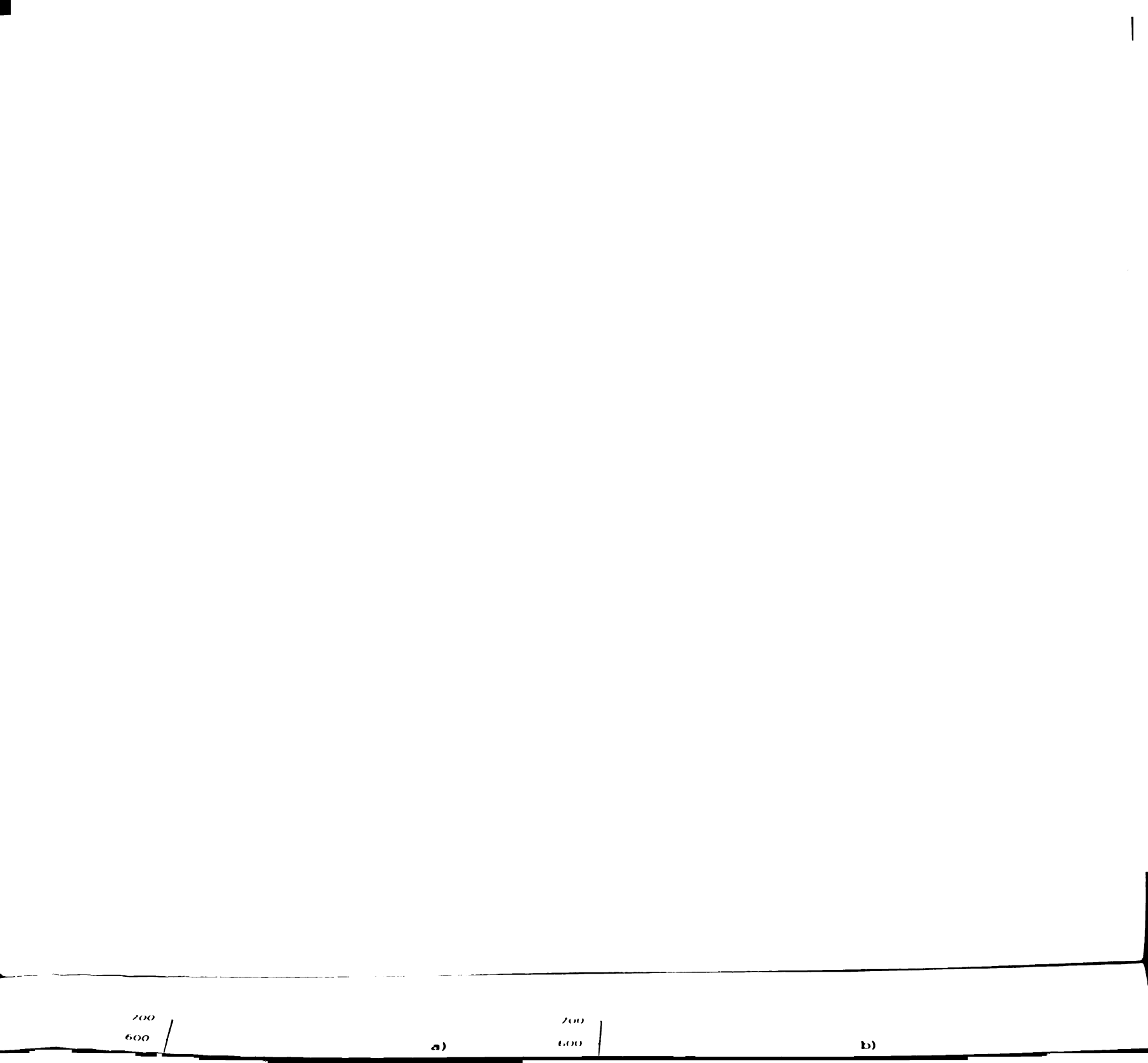
soil
mois
at
subs
Tabl
wate
impor

surface tension of gasoline that had passed through a pressure cell, was found to increase the gasoline surface tension (Table 3-3). In all likelihood the final residual gasoline that was present over the entire duration of the experiment underwent further compositional changes (through volatilization) that resulted in even greater increases in surface tension. A higher gasoline surface tension would result in higher residual gasoline saturations.

Air-entry pressures for the gasoline saturated media were considerably less than expected based on surface tension differences between gasoline and water. A possible explanation for this discrepancy may be that there was water-induced swelling of the filter paper residing on top of the soil increasing its air-entry pressure when it was saturated with water but not with gasoline. Filter paper should therefore be avoided in future experiments. The filter paper should have no affect on the other portion of the capillary-pressure saturation curve.

Figure 3-6 shows air-gasoline $P_c(S)$ curves in water wet soils (residual water saturation). Since very rarely do soil moisture contents reduce to air-dry levels in the field, soil at residual saturations may be more representative of subsurface situations in which a gasoline leak would occur. Table 3-6 summarizes the residual gasoline saturations in the water wet soils, total porosity, effective porosity and other important information regarding the soils.

The residual gasoline saturations in water-wet soils are


700
600
a)
700
600
b)

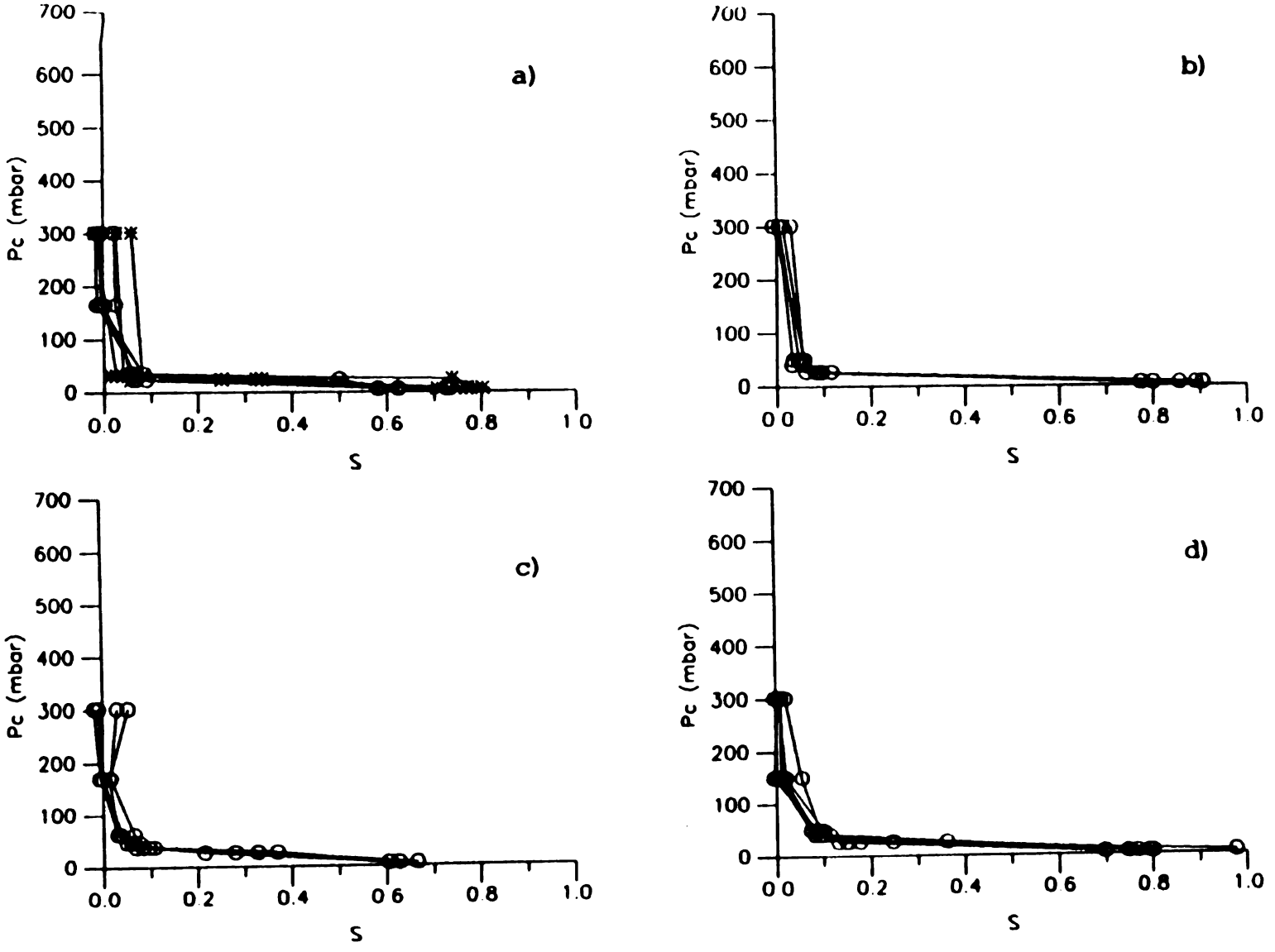


Figure 3-6. Air-gasoline Pc(S) curves for soil with residual water saturation; a) Croswell C (ρ_b=1.55), b) Croswell Bs1 (ρ_b=1.55), c) Croswell Bs1 (ρ_b=1.34), and d) AuGres Bs1 (ρ_b=1.34).

sign
soil
the
leav
gaso
of l
Duri
rema
wate
gaso
thin
suff
soil.

(at r
stand
with
havin
devia
from
soils
to ai
these
This r
syste
water
relati

significantly lower (over an order of magnitude) than the same soils at air-dry conditions. The water is probably covering the soil particles and filling in the smaller soil pores leaving these places unavailable for gasoline occupation. The gasoline in a water-wet system would be located in the center of large pores when the soil is saturated with gasoline. During drainage of the gasoline, it is removed and the remaining gasoline would be in the form of thin films on the water wet soil. This results in only a small amount of gasoline being retained in the soil, perhaps present as very thin films or as a discontinuity. It is possible that given sufficient time all the gasoline would have drained from the soil.

The average residual gasoline saturation between soils (at residual water saturations) appears to be similar. The standard deviations for all soil averages were quite large with Croswell C and Croswell Bs1 (higher bulk density cores) having the highest standard deviations. The high standard deviations make it difficult to draw any strong conclusions from these data pertaining to differences in retention among soils. The magnitude of the standard deviations are similar to air-water and air-gasoline (air-dry) systems, however, in these two systems the amount of liquid retained was high. This resulted in small relative standard deviations for these systems. The amount of gasoline that was retained in residual water saturated soils was very low, which resulted in large relative standard deviations for these cores. The large

stan
diff
more
core

gaso
vola
reas
satu
gaso
in s
The
resi
expe
afte
plat
plat
disr
dist
henc
expe

repl
for
evid
subs
orga

standard deviations in all systems may be due in part to differences in packing, resulting in some soil cores retaining more liquid than others. Local soil heterogeneities in the cores may also cause differences.

Other considerations for the systems with low residual gasoline saturation may be that losses of gasoline through volatilization would be more significant. This may be the reason why some negative values were recorded for gasoline saturation in water wet soils. Another difficulty with the gasoline on water wet soils procedure, which may have resulted in some variability was the extra handling of the soil cores. The soil cores used in the air-gasoline experiments at residual water saturation were the ones used in the air-water experiments. These cores had to be removed from the cell after the air-water experiment so that a gasoline saturated plate could be put in the cell replacing the water saturated plate. The cores were difficult to handle and some amount of disruption was inevitable. Often a core would be sufficiently disturbed to exclude it from the air-gasoline experiments, hence the number of replicates is generally lower in these experiments than the air-water experiments.

It may be possible with a much greater number of replicates that a difference in residual gasoline saturation for an organic and inorganic water wet soil would become evident. Based on these data, however, it would not be a substantial difference. The data suggest that the presence of organic matter does not affect residual gasoline saturation in

the

(unp

incr

resi

the

resu

orga

gaso

mech

gaso

3.5.3

gasol

press

scale

satur

capil

for a

water

soil)

resul

3-8 (a

air-wa

satura

in a g

the water wet soils used in these experiments. Zalidis et al. (unpublished) found that above a critical water saturation, increases in water content did not affect the amount of residual gasoline. Thus capillarity no longer seemed to be the predominant mechanism for residual saturation. The results presented in this chapter suggest that sorption to organic matter does not significantly contribute to residual gasoline saturation in water wet soils either. Other mechanisms such as hydraulic discontinuity of the films or gasoline entrapment may be responsible.

3.5.3. Scaling $P_c(S)$ relationships

Air-water $P_c(S)$ curves were scaled and compared to air-gasoline curves. The scaling factor for the capillary pressure was $\beta = \sigma_g/\sigma_w$ (gasoline to water) and saturation was scaled using effective saturation, S_e, Equation 3-5. Residual saturation was defined as the saturation at the final capillary pressure used, 700 mbar for air-water and 300 mbar for air-gasoline.

Figure 3-7 shows the set of three $P_c(S)$ curves (air-water, air-gasoline (air-dry soil) and air-gasoline (water-wet soil)) for the Croswell Bs1 soil prior to scaling.

Scaling of the data resulted in a single curve. The results for Croswell C and AuGres Bs1 are presented in Figure 3-8 (a and b). The results show good agreement between scaled air-water and air-gasoline data except at high liquid saturations. As mentioned previously, the air-entry pressure in a gasoline saturated soil was much lower than in a water

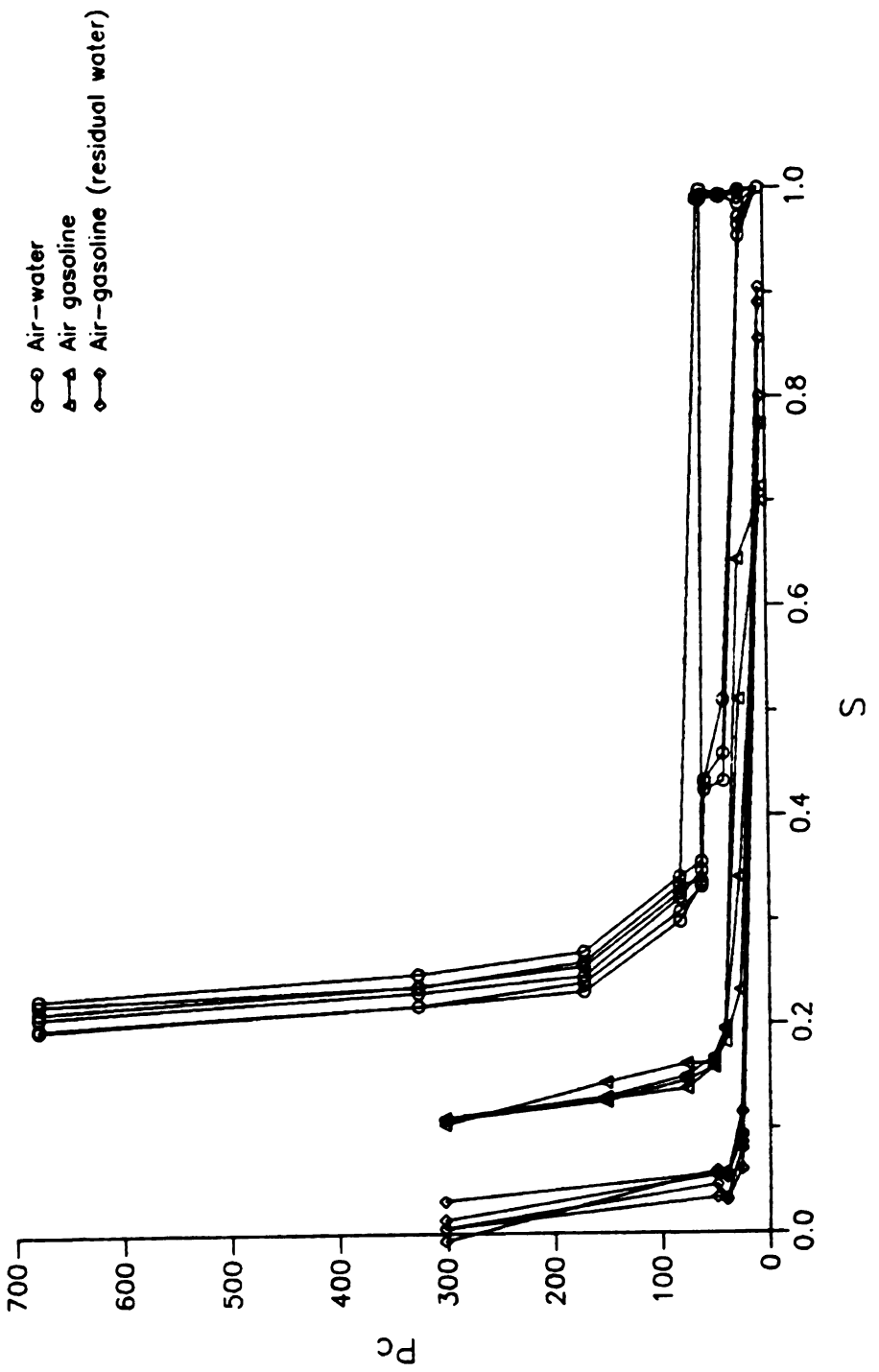


Figure 3-7. Pc curves for Croswell Bsl soil (ρ_b = 1.55).

log Pc (mbars)

log Pc (mbars)

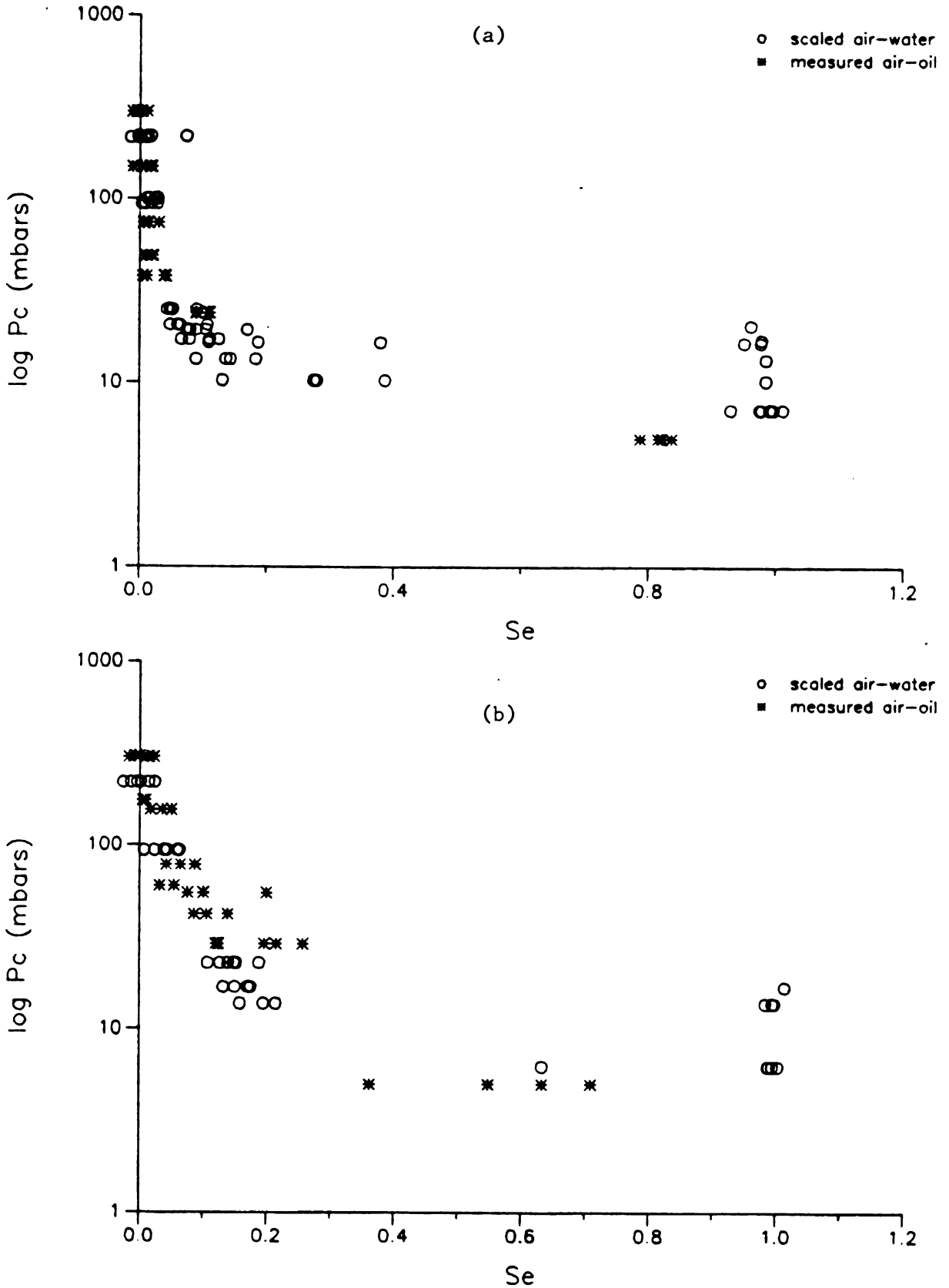


Figure 3-8. Scaled and measured air-oil curves; a) Croswell C soil, b) AuGres soil.

satu

tens

data

comp

at a

AuGr

This

the

suff

beha

dry

drai

affe

accou

these

pores

devia

devia

3.6.

for t

conte

highe

quanti

simila

saturated soil, more so than could be attributed to surface tension differences. This becomes quite evident in the scaled data.

Figure 3-9 (a and b) shows the scaled air-water results compared to air-gasoline curves in soils at S_r for water and at air-dry moisture contents for both the Croswell C and AuGres soil. The data for each soil generally form one curve. This is somewhat surprising, because it might be expected that the presence of the water would alter the porous media sufficiently such that gasoline drainage would no longer behave in a similar fashion to that of water or gasoline in a dry soil. However, as suggested earlier, the bulk of the drainage occurs from the larger pores, which may not be affected by the presence of the residual water. The S_e accounts for the differences in residual saturation, which in these soil experiments may also include liquid filled small pores. Scaling shows more clearly the similar standard deviations for various fluid pairs and how the standard deviation becomes more significant at low S_r.

3.6. SUMMARY AND CONCLUSIONS

Capillary pressure-saturation relations were determined for two soils, with and without significant organic matter contents for both air-water and air-gasoline systems. Much higher residual liquid (water and gasoline) saturations were quantified in air-dry soils that had organic matter than in a similar soil without a significant organic fraction. This

log Pc (mbars)

log Pc (mbars)

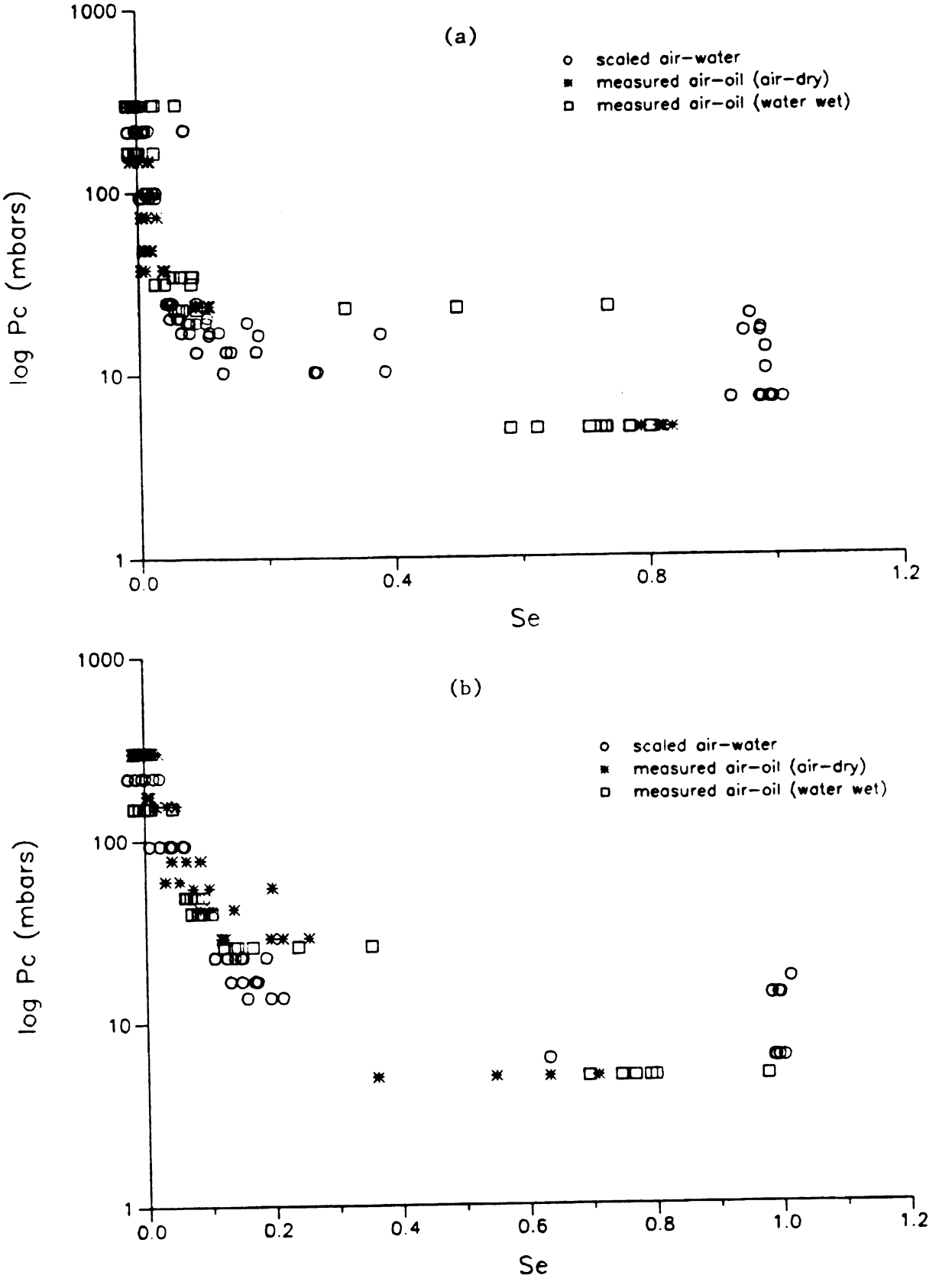


Figure 3-9. Scaled and measured air-oil curves; a) Croswell C soil, and b) AuGres soil.

diff
matt
resi
capi
stud
both
ther
wate
gaso
in l

5-10
ed t
tion,
conta
reduc

diffe
(with
conta
organ
resul
occup

scale
satur
satura

difference was attributed to the presence of the organic matter in the soil. The mechanisms responsible for the residual saturations measured were attributed to both capillary effects and sorption at the final P_c used in this study. The presence of organic matter is believed to increase both the surface area and volume of small pores present, thereby increasing residual liquid saturations. Residual water saturations were about two times greater than those of gasoline for air-dry soil, which was attributed to differences in liquid surface tension.

Residual gasoline saturation in air-dry soils were about 5-10 times greater than in water-wet soil. This was attributed to the fact that in the soils with residual water saturation, the water would occupy the small pores and be in direct contact with the particle surfaces, thereby, significantly reducing residual gasoline saturation.

The presence of organic matter did not result in differences in residual gasoline saturation between soils (with or without organic matter content) when the soils contained residual water saturation. The soils with higher organic matter contents had higher S_{rw}, which effectively resulted in no net increase in pores available for gasoline occupation.

The air-water capillary pressure-saturation data were scaled and compared to air-gasoline capillary pressure-saturation data for air-dry soil and soil with residual water saturations. A ratio of measured surface tensions was used to

scale the capillary pressure value and effective saturation was used to scale saturation. Scaling effectively collapsed all the curves, including the air-gasoline curves on water wet soil, into one curve. There were some differences at high saturations. The scaling procedure worked for both the soil with organic matter and that without, for the different bulk densities of the same soil, and different initial water contents for the same soil.

4.1.

impo
NAPL
reme
phys
and
trar
may
The
loca
dist

high
wedg
ofte
cont
howe
conc

CHAPTER 4

MICROSCOPIC OBSERVATION OF RETAINED NAPL IN SOIL

4.1. INTRODUCTION

The amount of NAPL retained in the porous media is important for understanding the fate and transport of soluble NAPL contaminants as well as estimating the duration of a remediation processes. The location in the soil and the physical characteristics of the residual NAPL, such as size and shape, may be equally important. For example, the mass transfer of constituents from a NAPL to either air or water may be dependent on the size and shape of the residual NAPL. The volume of water contaminated may ultimately depend on the location of the NAPL in the soil, i.e. whether it is uniformly distributed or located in isolated areas.

Typically visual descriptions of NAPL in soil utilize highly idealized models such as capillary tubes, v-shaped wedges, and spherical soil particles. These ideal systems often aid in our ability to mathematically characterize contaminant transport in the complex soil environment, however, to some degree they may limit our ability to conceptualize the true system. Without this ability to grasp

the true nature of the soil environment, experimental results may be misinterpreted and the importance of various processes and simplifying assumptions may not be identified properly.

The main focus of the research presented in this chapter was to qualitatively determine the location and nature of a NAPL in a water wet unsaturated soils using microscopic techniques.

4.2. BACKGROUND

Numerous visualization methods have been developed or modified over the past several to investigate fluid saturation and retention in soil from both macroscopic and microscopic perspectives.

Gamma ray attenuation has been used to measure fluid saturations (Schiegg and McBride 1987, Ferrand et al. 1989) in porous media. Although this technique can aid in our understanding of fluid saturations along the length or diameter of a soil column, it does not provide information at a microscale dimension.

Computed tomography is another promising technique for determining density differences in porous media and therefore could be used to determine bulk density, soil-liquid content and macropore characteristics (Petrovic et al. 1982, Anderson et al. 1988, Jenssen and Heyerdahl 1988, and Warner et al. 1989). This technique is limited to macropore size characterization due to resolution limits.

Nuclear magnetic resonance imaging (NMRI) has also been

used to determine soil-water content measurements (Paetzold et al. 1987) but is again limited by a pixel size, of about a few millimeters square.

Micromodels have been employed by Wilson et al. (1990) to investigate NAPL movement in both saturated and unsaturated systems. Micromodels are created by etching a model of a pore network onto two glass plates and fusing the plates together. They provide a visual method to observe two and three phase fluid behavior in a two dimensional network. Another method employed by Wilson et al. (1990) involved polymerizing styrene NAPL present in a porous medium and characterizing the pore and blob casts.

Scanning electron microscopy (SEM) has been used with image and x-ray analysis techniques to investigate macro and micro porosity characteristics of porous media (Bisdom and Thiel 1981 and Protz et al. 1987). SEM allows magnification between 20 and 200,000 times, with a resolving power of 3-6 nm. This instrument clearly allows investigation of porous media at the microscale. However, the scanning electron microscope requires a very high vacuum which has traditionally limited its use to samples with virtually no liquid content.

Recently, Sutanto (1988) and Sutanto et al. (1990) employed cryo-SEM with x-ray maps to investigate liquid distributions in porous rock under saturated liquid conditions. This technique allows observation of samples with liquid present because the sample is frozen at temperatures of -130^{o}C and kept frozen during observation. At this tempera-

ture, vaporization of liquids is minimal and the high vacuum necessary for SEM can be maintained.

Observation of liquids in a three-fluid-phase soil system on the microscale has not been accomplished. This study was designed with this goal in mind.

4.3. OBJECTIVES

The specific objectives of this research have been to:

1. Determine the applicability of using SEM to observe a NAPL in unsaturated, unconsolidated porous media.

2. Photograph the soils used in this research in a three-fluid-phase soil system and identify the location of NAPL from photomicrographs and x-ray dot maps.

4.4. MATERIALS AND METHODS

The AuGres and Croswell C soil were used in this investigation. Croswell C soil will be referred throughout the remainder of this text as Croswell, since Croswell Bs1 soil was not used in this study or subsequent studies. The two soils were initially observed without gasoline or water present, therefore freezing was not required. Preparation of the soils using SEM (without the cryostage) involves placing the soil sample in increasing concentrations of ethanol for 10 minutes. The sample is then allowed to stay in fresh 100 % ethanol for 10 minutes. This process of using increasing concentrations of ethanol allows for the total dehydration of the sample.

poi

sur

use

cha

abo

the

equ

ly c

allo

call

thin

cond

inco

defl

elec

and h

the s

is a

graph

photo

(JEOL

neces

Ashfo

One c

The soil samples were then transferred to a critical point dryer where the ethanol was removed in the absence of surface tension forces in the following manner. Liquid CO_2 is used to completely flush the ethanol from the specimen, the chamber containing the specimen and CO_2 is heated to slightly above the critical point, 33.1° at a pressure of 1071 psi. At the critical point, the liquid density and gas density are equal. The sample is now in a very dense gas and is completely dry but has not been significantly distorted as would be by allowing the sample to air dry.

The completely dry soils were mounted on a metal holder called a stub with graphite glue. They were coated with a thin layer of gold making the sample conductive. A non-conductive sample tends to build up negative charge from the incoming beam of electrons. A negatively charged sample can deflect both the incoming beam of electrons and the secondary electrons emanating from the sample. This causes distortions and bright spots that interfere with viewing and photographing the sample. A good connection between the sample and the stub is also required to prevent charging and is insured by the graphite or silver glue. The soils were observed and photographed using a JSM-35C scanning electron microscope (JEOL Inc., Tokyo, Japan).

To observe soils containing water and NAPL, it was necessary to use a cryo-stage (SP-2000 Sputter Cryo, Emscope, Ashford, Kent, England) with the scanning electron microscope. One of the criteria for operation of electron microscopes is

the necessity of an extremely high vacuum; molecules and vapors in the column can effectively limit the capability to observe a specimen. By maintaining a temperature of -130°C or lower, water in the sample will not vaporize and thus the sample can be viewed. This is the purpose of the cryo-stage.

Croswell and AuGres soil were packed into pressure cell cores and brought to residual water saturations as described in Chapter 3. However, the water in this case was saturated salt (NaCl) water. The chlorine in the water allows the location of the water to be determined by the x-ray analysis detector. Iodobenzene (Aldrich Chemical Co., Inc.) was used as the NAPL. It has a density of 1.823 g/cm^3, a boiling point of 188°C and a melting point of -29°C. This was selected because iodine can be detected by x-ray analysis. The melting point of -29°C also allows the retained NAPL in the soil to remain frozen at cryo-stage temperatures. NAPL saturations varied from nearly saturated to residual saturations.

Samples from pressure cell cores were taken by inserting a small diameter straw into the core and gently pushing down. The straw complete with soil sub-core was immediately immersed in liquid nitrogen and quick frozen. The straw was removed from around the frozen sub-core by cutting it lengthwise with a razor blade. Before the sub-core could thaw it was again immersed in the liquid nitrogen. Small pieces of the sub-core were obtained by fracturing it with a razor blade. Exposed areas of the fractured sample followed the natural shape of the soil grains. Graphite glue was placed on the sample

holder and several small pieces of sample were placed on the glue. The samples and sample holder were immediately placed in the sputter cryo-unit where a 7 nm chromium coat was applied to the sample. Chromium provides a continuous coat on the rough surfaces of the soil, whereas other coatings such as carbon or gold were not adequate. A more detailed discussion on the importance of chromium and coating is given in Sutanto et al. (1990). The sputter cryo unit maintains a high vacuum and -130°C temperature. After the sample was coated it was transferred to the cryo-stage of the scanning electron microscope (-150°C), where the sample could be observed and photographed.

Photomicrographs were taken of various samples from secondary electrons emanating from the subject. These will be referred to as secondary electron images (SEI). For some of the SEI, elemental scans were made of the subject being viewed. An example of an elemental scan is shown in Figure 4-1. The large silica peak represents the silica of the soil particles, the large chlorine peak is due to the residual salt water, and the three iodine peaks are from the retained iodobenzene NAPL. A large chromium peak is observed because this is the element that was used for coating the sample.

A subject that registered iodine peaks in the x-ray scan was used for generating elemental dot maps. These are generated by selecting the element of interest and taking a picture while in the x-ray mode. Small dots are exposed on the film in response to x-rays detected in that region of the

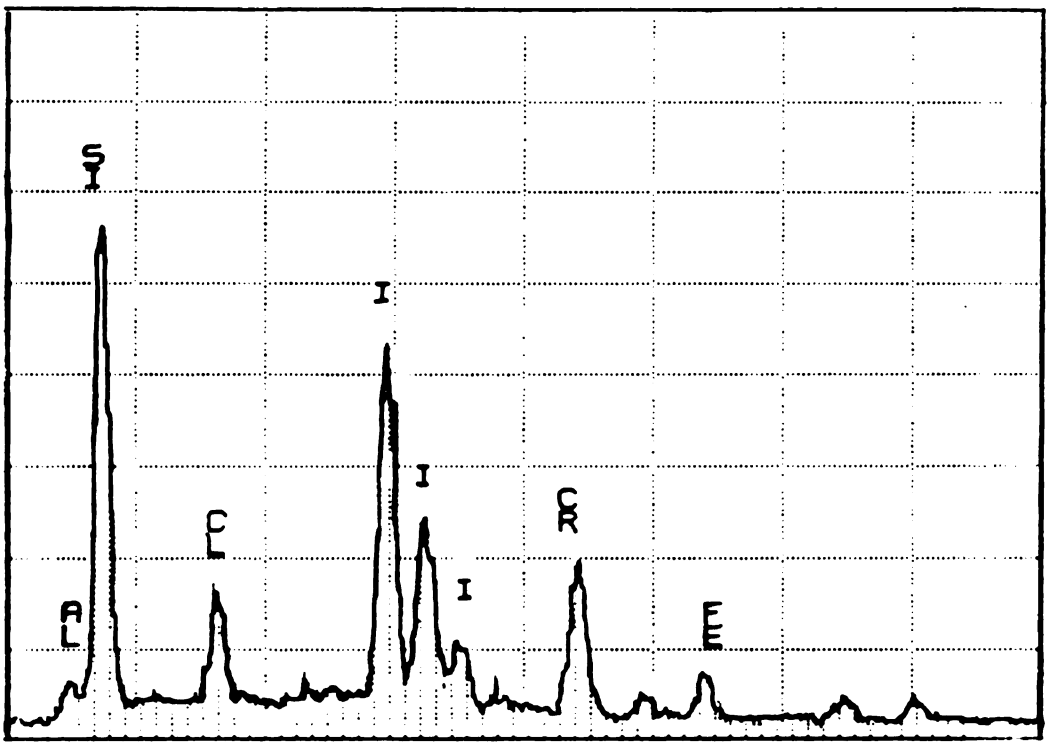


Figure 4-1. Elemental scan using x-ray analysis.

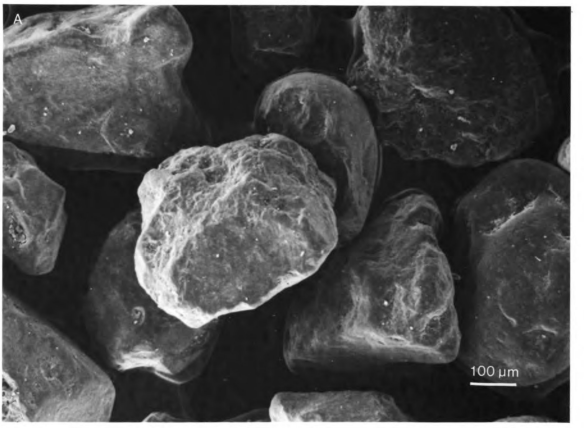
subject as the subject is slowly scanned. The dot maps can aid in determining the location of soil, water and NAPL in the photomicrograph.

4.5. RESULTS AND DISCUSSION

Photomicrographs of Croswell and AuGres soil are shown in Figure 4-2(a and b). As already discussed in Chapter 3, soils had similar grain size distribution and were also sieved to 2 mm in diameter and below. These photomicrographs qualitatively support this. As can be visually observed, the soil grains are similar in size. The presence of the organic matter on a gross scale, appears to smooth out the sharp edges and fill in the slight depressions on the sand grains, however, on closer inspection, it is observed that the organic matter results in numerous fissures, cracks and so adds more surface area to the soil particle. Although it is difficult to determine from this photomicrograph, the organic matter does not totally coat the sand grain. Under close scrutiny some surfaces of the sand grain can be seen in the AuGres soil. Observations using a light microscope allowed one to easily determine the portions of the sand surface that were covered with the organic material and those that were not.

Examples of Croswell and AuGres frozen sample fractures with residual liquid saturations are shown in Figure 4-3 (a and b). In both SEI photomicrographs it is nearly impossible to see any liquid present. The organic matter (Figure 4-3b) also tends to obscure the location of the soil pores. Soil

Figure 4-2. Photomicrographs of soils;a) Croswell, and b) AuGres using SEM.



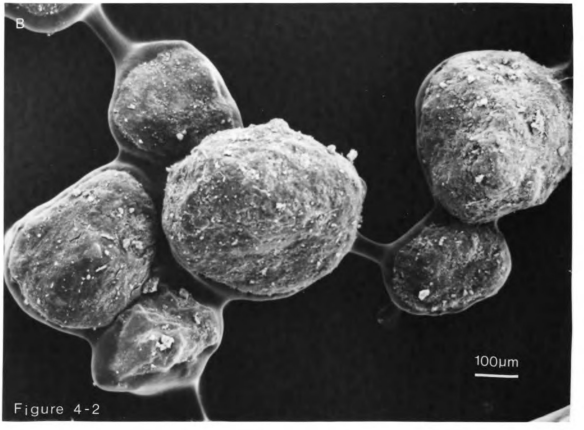
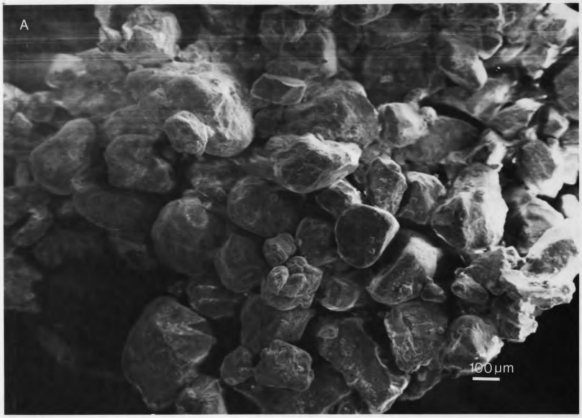


Figure 4-2

Figure 4-3. Photomicrographs of water wet soils; a) Croswell, and b) AuGres using cryo-SEM.



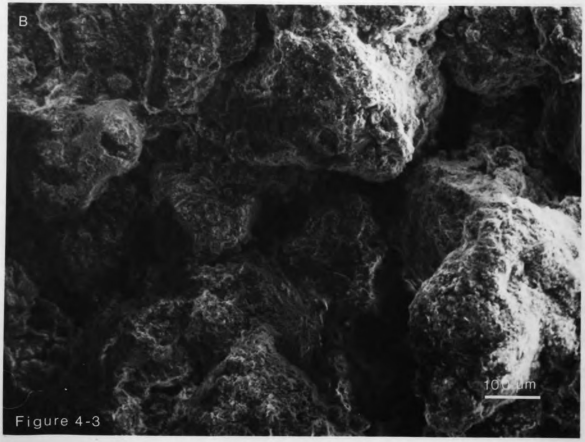


Figure 4-3

po
in

sa
The
sm
Cra
ele
se
in
4b.
is
to
con

sam
fil
4-5

with
that
corn
bias
up x
will
sampl
by a

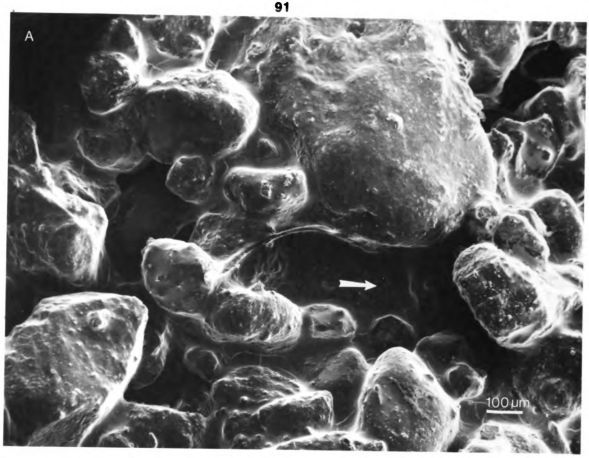
pore openings can readily be seen in the micrograph of the inorganic Croswell C soil (Figure 4-3a).

Croswell soil with residual water saturation and nearly saturated with iodobenzene in shown in Figure 4-4 (a and b). The iodobenzene is seen in the SEI photomicrograph as the smooth, cracking frozen liquid filling in the soil pores. Cracking is probably due to continued bombardment by the electron beam, as the cracking became progressively more severe as viewing time increased. An enlargement of a section in Figure 4-4a, indicated by the arrow, is shown in Figure 4-4b. At this level of saturation, it appears that all the NAPL is continuous. At higher magnifications, the NAPL can be seen to fill in the depressions on the sand grains but it is still connected to the bulk of the liquid in the pore.

Figure 4-5a shows a SEI photomicrograph of a similar sample at higher magnification. The pore spaces are still filled with the NAPL and exhibit complete continuity. Figure 4-5 (b-c) shows the dot maps for this same subject matter.

Figure 4-5b is the silica dot map and coincides nicely with the sand grains shown in Figure 4-5a. It should be noted that the x-ray detector would be located on the right lower corner of the subject matter, hence the dot maps are somewhat biased in the x-rays that they detect. The detector will pick up x-rays easily from certain portions of the sample and these will appear as bright areas on the photograph. Parts of the sample that are facing away from the detector or are blocked by a another portion of the sample may not be indicated on the

Figure 4-4. Photomicrographs of Croswell soil showing location of the DNAPL; a) 100 um, and b) 10 um scale.



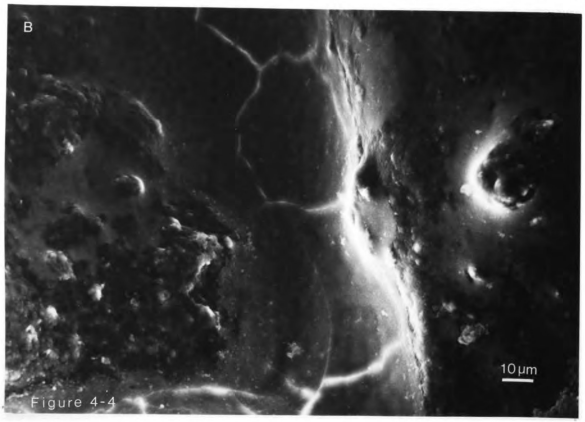


Figure 4-4

Figure 4-5. Cryo-SEM and x-ray analysis for Croswell soil; a) a) frozen DNAPL filled pores, b) x-ray dot map for silica, c) x-ray dot map for chlorine, and d) x-ray dot map for iodine.

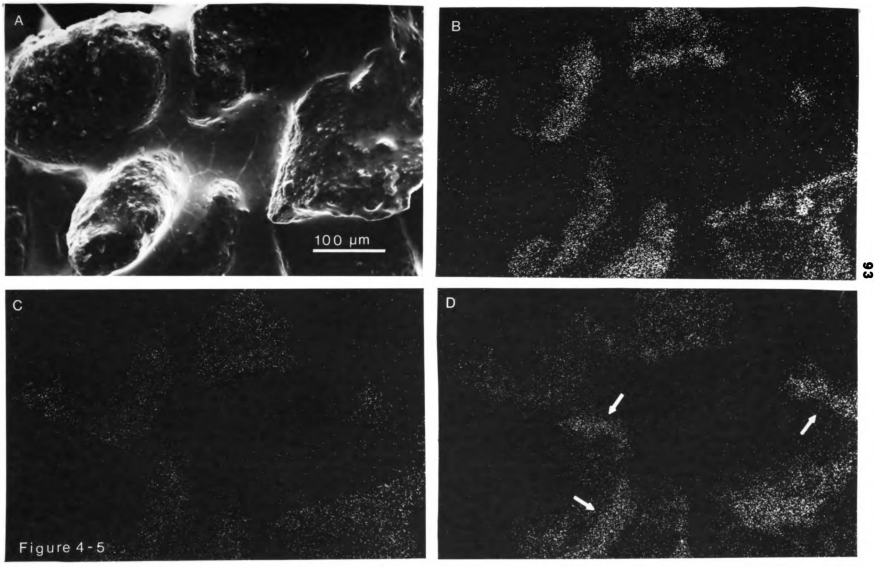


Figure 4-5

photographs or only marginally so.

Figure 4-5c is the chlorine dot map and indicates where the residual water is located. It is easily seen that the chlorine and silica dot maps coincide, which suggests that the water is coating the sand grains. This is in agreement with what is theorized about the location of the wetting fluid at residual saturations; that it is present in the form of thin films on or adsorbed to the soil grains.

Figure 4-5d is the dot map for iodine. Upon initial inspection, it may be difficult to see the difference in this dot map compared to the others, however, upon further scrutiny, it should be apparent that the dots indicative of iodine are generally found in the dark areas of the other two maps. The SEI photomicrograph, Figure 4-5a, also shows this clearly; that the iodobenzene is filling in the pore spaces between sand grains. However, certain areas containing NAPL as seen in Figure 4-5a, are not highlighted in Figure 4-5d. As previously noted, this is due to the location of the x-ray detector an its inability to detect subject material that is blocked or facing away from the detector.

After further drainage of the iodobenzene, Figure 4-6a, air begins to occupy the inner portion of the soil pores. The NAPL tends to retreat to the contact points between grains, however, still appears to be in a continuous form. The term pendular rings is used to describe the location of the NAPL at the soil grain contact points and is clearly evident in this photomicrograph. The dot maps, Figure 4-6 (c and d) indicate

Figure 4-6. Cryo-SEM with x-ray analysis for Croswell soil; a) frozen DNAPL and air filled pores, b) x-ray dot map for silica, c) x-ray dot map for chlorine, and d) x-ray dot map for iodine.

Figure 4-6

the location of the residual salt water and iodobenzene NAPL. The dot map of chlorine indicates that the salt water is coating the individual sand grains, while the NAPL has retreated to sand grain contact points and films on top of the water wet soil grains.

An example of an AuGres soil fracture with residual water and NAPL saturations is shown in Figure 4-7 (a and b). The presence of organic matter and the low liquid saturations of the sample resulted in significant charging of the sample. Overall poor SEI photomicrographs of the AuGres soil were obtained. The organic matter and lack of sufficient liquid contents may make it difficult to obtain a continuous coating of chromium on the sample. This noncontinuous coating is unable to conduct the negative charge of the incoming beam of electrons to the stub as it should. The sample, therefore, builds up negative charge and deflects both incoming and outgoing electrons from the sample. This results in distorted SEI photomicrographs, Figure 4-7 (a and b). Dot maps (Figure 4-7 c and d) can aid in interpreting the distorted SEI. Figure 4-7c shows the location of silica (sand grains) and the chlorine (residual water), however no characteristic iodine x-rays were obtained.

Drainage of the NAPL to residual saturation levels, is also seen in Figure 4-3 (a and b), no frozen liquid was observed in the SEI photomicrographs. X-ray analysis of samples with residual NAPL saturations resulted in virtually non-existent iodine peaks. At residual NAPL saturations, the

Figure 4-7. Cryo-SEM with x-ray analysis for AuGres soil; a) DNAPL at residual saturation (excessive charging), b) enlargement, c) x-ray dot map for silica, and d) x-ray dot map for chlorine.

100 µm
B
100 µm
D

NAPL is g

isolated

in small

a haysta

exhibited

to observ

4.6. SUMM

AuGr

saturatio

examined

analysis

NAPL, SE

for the C

in our a

soil sys

character

observed.

Seve

SEI photom

liquid sat

NAPL is generally believed to be in the form of thin films or isolated blobs in the porous media. Finding examples of these in small soil cores may be equivalent to finding a needle in a haystack. Samples at residual liquid saturations also exhibited considerable charging, making it even more difficult to observe any fluid present.

4.6. SUMMARY AND CONCLUSIONS

AuGres and Croswell soil cores with residual water saturations and various saturations of NAPL and air were examined using cryo-scanning electron microscopy and x-ray analysis. At residually saturated to near saturated levels of NAPL, SEI photomicrographs and x-ray dot maps were obtained for the Croswell soil. Photomicrographs such as these can aid in our ability to visualize the complexity of a three-phase soil system. At low residual NAPL saturations iodine characteristic x-rays were not detected in any of the samples observed.

Severe charging of AuGres samples resulted in distorted SEI photomicrographs. Charging was also a problem at residual liquid saturations in both AuGres and Croswell soil samples.

CHAPTER 5

MASS TRANSFER OF GASOLINE CONSTITUENTS TO AIR DURING SOIL VENTING

5.1. INTRODUCTION

Soil venting is gaining acceptance as an effective remediation technique for unsaturated soils contaminated with gasoline. Its success has been noted in field cases (Malot 1989 and Johnson et al. 1991) as well as laboratory studies (Thornton and Wootan 1982, Wootan and Voynick 1983, Marley and Hoag 1984, Brown et al. 1987 and Baehr et al. 1989).

Although soil venting is currently being used as a remediation technique for gasoline contaminated soils, some fundamental questions related to its effectiveness remain only partially answered. For example, the duration of soil venting as well as soil venting efficiency are intimately tied to the mass transfer of gasoline constituents to air from the gasoline residual NAPL in the soil, however, mass transfer of individual gasoline constituents to air has not been investigated. Anything that might limit the mass transfer of these constituents from the residual NAPL to air, may ultimately affect the efficiency of soil venting, hence the importance of

understanding this process. The multicomponent nature of gasoline further complicates the soil venting process and has been an impediment to the interpretation of field results.

Many specific constituents of gasoline are of particular concern. For example, the aromatic compounds, BTX, naphthalene and other benzene relatives are often regulated and monitored most closely because of their carcinogenicity or suspected carcinogenicity. Understanding the mass transfer of specific individual compounds to air during soil venting, therefore, is of the utmost importance. The majority of venting studies, however, have focused on total removal of gasoline and overall removal rates which may not reflect the removal of many of the specific constituents of concern. The fate and transport of individual gasoline constituents during soil venting needs to be studied.

Without a clear understanding of the fundamental processes, results from actual venting sites can be easily misinterpreted. Deviation from predicted local equilibrium behavior is typical at venting operations, but whether this is due to individual site characteristics and venting system layout, misinterpretation of field data or the characteristics and chemistry of the NAPL itself needs to be determined.

Another concern regarding the use of soil venting for gasoline contaminated sites deals with the removal from the soil of the less volatile fraction of gasoline. Gasoline contains numerous compounds that have low vapor pressures and are "slow" to vent from the soil. Many of these compounds are

related to benzene and are of environmental concern. Generally, the individual mass fractions of these less volatile components of gasoline are small, however, when they are summed, they do represent a sizable fraction of the gasoline. In other experimental studies on venting very few of the heavy gasoline constituents were identified or quantified. Determining the significance of these compounds during and after the venting process is important.

The research presented in the previous two chapters dealt with the physical and physical-chemical behavior of the residual NAPL in unsaturated soil and how the amount and location of residual may affect a remediation process such as soil venting. The focus of the research presented in the remainder of this dissertation deals with the chemical behavior of the residual gasoline, also from the standpoint of soil venting.

The objective of the work presented in this chapter was to investigate the mass transfer of various gasoline constituents to flowing air during simulated soil venting in laboratory experiments. Aromatic compounds, such as BTX and naphthalene were of particular interest.

5.2. BACKGROUND

Venting models have been developed to incorporate the mass transfer of individual compounds from the gasoline contaminated soil to the air (Marley and Hoag 1984 and Johnson et al. 1990). Both models employ the ideal gas law and

Raoult's law to determine air phase concentrations of individual components. The ideal gas law, simply stated, relates a compounds partial pressure to its air-phase concentration at a given temperature and is as follows:

$$C_{air} = P_i * MW/RT \qquad (5\text{-}1)$$

where C_{air} is the concentration of constituent i in the air phase (mg/l), P_i is the partial pressure of constituent i in the mixture (atm), MW is the molecular weight in g/mole, R is the universal gas constant, and T is the temperature (K).

Raoult's law relates the partial pressure of a compound in a mixture to its mole fraction in the mixture and its pure-phase vapor pressure. The equation is given below:

$$P_i = V_p * X_i \qquad (5\text{-}2)$$

where V_p is the vapor pressure of the pure compound, X_i is the mole fraction of constituent i in the mixture.

The model then calculates the change in mass over time by the following differential equation:

$$dM_i/dt = Q * V_{p,i} * X_{i(NAPL)} * MW_i/RT = Q * C_{air,i} \qquad (5\text{-}3)$$

where M_i is the mass of constituent i removed, t is the time, Q is the flow rate (ml/min).

To solve this differential equation numerical codes were developed by Marley and Hoag (1984) and Johnson et al. (1990). Changing mole fractions of individual components are recalculated as mass is continually removed from the soil during the course of venting. Local equilibrium is assumed for both models. The model by Johnson et al. (1990) also includes the option of adding more complex processes such as desorption

from soil and air-water exchange relationships. A comparison of experimental results to model predictions for individual gasoline components was not shown.

The assumptions made in the models of Marley and Hoag (1984) and Johnson et al. (1990), are that of local equilibrium and Raoult's law type partitioning between residual gasoline and air. Deviation from either local equilibrium or Raoult's law could mean that considerably longer venting times are necessary for a contaminated site to meet clean up requirements for soil and water. Baehr et al. (1989) used the model of Marley and Hoag (1984) to predict total hydrocarbon vapor transport during laboratory soil venting experiments for reasonably high flow rates. They found good agreement between total gasoline removed and that predicted by the model. The local equilibrium assumption, therefore, seems reasonable. However, mass transfer limitations for individual constituents may be possible when dealing with multicomponent NAPLs. The effect of soil properties, such as organic matter content on mass transfer during soil venting may also be important. Although, soil interactions were incorporated into the model by Johnson et al. (1990), they did not support this with experimental soil venting data.

5.3. OBJECTIVES

This study investigated the mass transfer of gasoline constituents from residual gasoline to air in two different soils. The specific research objectives were to:

1. Determine if gasoline/air partitioning behaves according to Raoult's Law.

2. Characterize the mass transfer from single and multi-component residual NAPL's in unsaturated moist soil to air during soil venting.

3. Compare the experimental soil venting air-phase data with simulated results obtained using a local equilibrium based model for soil venting.

4. Determine whether organic matter affects the mass transfer process of gasoline constituents from contaminated soil to air.

5.4. MATERIALS AND METHODS

5.4.1. Gasoline Characterization

Several gallons of gasoline were purchased and stored in glass containers (four liter size) in the spring of 1988. This provided a consistent gasoline source for subsequent experiments. When gasoline was required for experimentation, a four-liter container was divided into three (one liter) containers and approximately 50 (20 ml) headspace vials with crimp caps and Teflon^{R} lined septa. The one-liter and the 20 ml containers were stored in the refrigerator. The 20 ml vials were then used for experiments. Any excess gasoline that had been exposed to air during the experimental setup was properly discarded. The one-liter bottles were subdivided into 20 ml vials as needed. This method of storage was used to reduce losses of volatile gasoline constituents and insure

a consistent gasoline source.

Mass fraction determination for gasoline was conducted by preparing gasoline stock solutions in both tetrachloromethane and dichloromethane (as described for all stock preparation in Appendix A). Two different solvents were used because the solvent peak interfered with numerous gasoline peaks. Dichloro and tetrachloromethane elute at different times and it was possible to combine results from samples taken from both stocks to obtain a complete gasoline characterization. Two samples, one from dichloromethane and one from tetrachloromethane, provided a complete set of mass fraction data. Two complete sets of mass fraction data for each gasoline sample analyzed, were collected and the average was calculated.

Calibration data were determined for BTEX and N made up in both solvents. Because the responses for BTEX, N, dodecane and hexane, were very close, the calibrations data for o-xylene were used to determine the mass of other separable, but unknown, peaks in gasoline. The mass fraction for each separable peak was determined by dividing the calculated mass for each peak by the total amount of gasoline injected. The sum of mass fractions for all peaks should, therefore, equal 1.0.

Equilibrated air-phase concentrations for fresh gasoline were initially determined by drawing a known volume of gasoline headspace into a valved gastight syringe, closing the valve and immediately injecting the sample into the gas

chromatograph (GC). This preliminary method was deemed inappropriate because of the large pressure buildup within the vials. Attempts to relieve the pressure, resulted in considerable variation of results.

Another method was used to determine equilibrated air-phase concentrations for fresh gasoline. This was done by bubbling air through a vial of fresh unopened gasoline. A gastight syringe with a needle was inserted through the Teflon^{R} coated septum of the vial. Air was bubbled at the bottom of the vial through a 24 gauge stainless steel needle. The first flowing air sample through the syringe was then collected and immediately injected into the GC. This method allowed for pressure equalization between the air in the vial, air in the syringe and the atmosphere. The equilibrium of the air in the vial with gasoline was checked by using the same technique for pure toluene. The vapor phase concentration of toluene was within 10% of the known saturated vapor concentration at that temperature.

Equilibrated air-phase concentration determination for weathered gasoline (gasoline that had been collected from a column during the initial setup) was determined by taking the first flowing sample from the venting column from which the gasoline was taken, as well as the method outlined above.

5.4.2. Column design

The venting columns were made of borosilicate glass (5.44 cm in diameter, 4 cm or 10 cm in length), with stainless steel ends and fittings, Figure 5-1. The column design allowed for

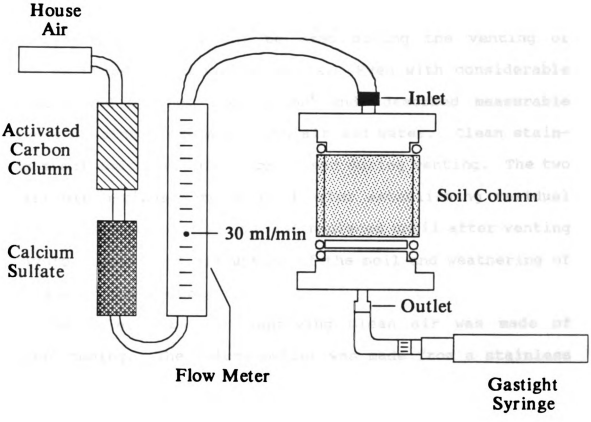


Figure 5-1. Experimental set up for soil venting.

easy assembly and disassembly. The length was adjusted by using either a 4 or 10 cm length glass tube. Three Teflon^{R} o-rings were used; one between the top end and the glass tube, one between the bottom end and plate and one between the plate and glass tube. Teflon^{R} ends were used to establish residual fluids. Because Teflon^{R} adsorbed considerable amounts of contaminant, it could not be used during the venting or leaching phases of the experiments. Even with considerable cleaning and baking, the Teflon^{R} ends desorbed measurable amounts of contaminants to both air and water. Clean stainless steel ends were, therefore, used during venting. The two accessible o-rings were changed after establishing residual fluids. The third o-ring was not replaced until after venting to avoid significant disruption of the soil and weathering of gasoline in the column.

The inlet tube for supplying clean air was made of Teflon^{R} tubing. The column outlet was made from a stainless steel 13 gauge hypodermic needle, with the tip ground smooth. This was connected to the bottom end cap with a stainless steel fitting and ferrule.

A sampling syringe was connected to the luer end of the hypodermic needle. The sampling syringe for the venting process was either a one or five millimeter gastight syringe, depending on the desired sample amount.

5.4.3. Experimental Setup

Two of the soils described earlier, Croswell C and AuGres, were used for venting experiments. Croswell C will be

referred to as Croswell for the rest of this dissertation. These were packed moist to pre-calculated bulk densities. A specified bulk density was achieved by gently tapping the bottom of the column while adding the soil. After all the soil was added, a metal cylinder was placed on top of the soil column and a weight was dropped on this several times. The average bulk density for all columns packed with Croswell was 1.57 g/cc, with a standard deviation of ±0.019 for 12 columns. The average bulk density for the columns packed with AuGres soil was 1.32, for 8 columns, with a standard deviation of ±0.017.

Residual saturations of water followed by gasoline were established using ceramic pressure plates (nominal air-water entry pressures of 1 bar), with edges sealed by epoxy paint. Water was slowly introduced from the bottom of the column over a period of several hours and was allowed to equilibrate overnight. A vacuum of 300 mbars was applied to the bottom of the column to drain excess water. Draining continued for three days, which was sufficient to obtain a water removal rate of virtually zero. The amount of residual water remaining was determined by removing the bottom end cap and pressure plate and weighing the soil column. To avoid back absorption of water from below the plate, a vacuum was maintained while the bottom assembly was removed.

A gasoline saturated plate was then placed in the bottom of the column and the bottom end cap was reattached. Fresh, 8°C gasoline, stored in crimp capped vials in the refrigera-

tor, was added to the top of the column in sufficient amounts to contaminate all the soil in the column. The column was quickly sealed and allowed to equilibrate overnight. A vacuum of 300 mbars was applied to the bottom of the column for approximately 24 hours, allowing gasoline drainage to cease. The column was then weighed to determine the residual gasoline saturation. The gasoline saturated plate was replaced by a clean stainless steel screen. Cleaned and baked stainless steel end caps were then substituted for the Teflon® ends. Two of the o-rings present during the initial setup were replaced with cleaned and baked o-rings that had never come in contact with pure gasoline.

Air used for venting was first passed through an activated carbon column, to remove any organic contaminants. The air then passed through a flowmeter and was finally bubbled through a column filled with acid washed glass beads and deionized water before entering the contaminated soil column. The air flow rate was maintained at 30 ml/min during the course of the venting experiment. Air flow from the bottom of the soil column was periodically monitored using a bubble meter to ensure there was no air leakage from the column system.

Air samples were collected using a 1 or 5 milliliter gastight syringe that was attached directly to the stainless steel outlet. The plunger was held near the end of the syringe for approximately 20 seconds before insertion. The syringe was then quickly detached from the column and a needle

was attached to the syringe. It was then directly injected into a GC.

Air samples were analyzed using a GC (DB-624 megabore column, 50m*0.53mm i.d., J&W Scientific, Inc.) and a flame ionization detector (FID). Calibration determination is described in Appendix A.

5.5. RESULTS AND DISCUSSION

The results and discussion section is divided into four main areas: 1) equilibrium air-phase partitioning of gasoline; 2) soil venting of a single component NAPL; 3) soil venting of a multicomponent NAPL; and 4) the effect of organic matter on soil venting.

5.5.1. Equilibrium air-phase partitioning of gasoline

To determine air-phase partitioning, it was first necessary to determine the mole fraction of the various gasoline constituents. Initially, however, the individual mass fractions needed to be determined. A typical chromatogram of a gasoline sample used to determine mass fractions is shown in Figure 5-2. The chromatograms of two samples (one made in tetrachloromethane and one made in dichloromethane), have been spliced together to qualitatively show a complete set of peaks. Peaks of various constituents of interest have been labeled. Over 100 peaks have been quantified and corresponding mass fractions have been calculated.

A summary of results for mass fraction data of n-butane, isopentane, n-pentane, BTEX, N and n-hexylbenzene is presented

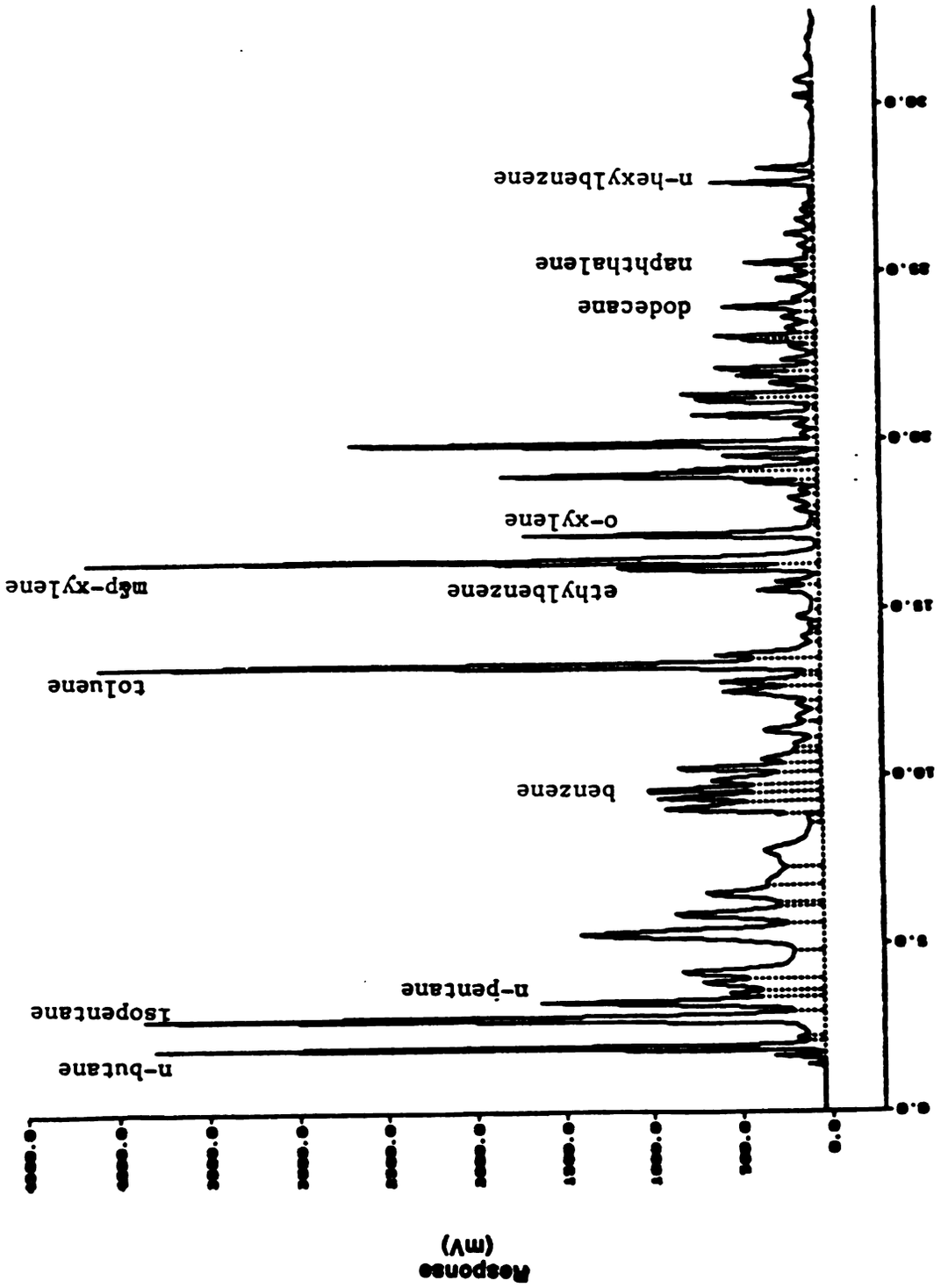


Figure 5-2. Gas chromatogram of gasoline.

in Figure 5-3. Identification of n-butane, isopentane and n-pentane was made by comparing gasoline chromatograms of this study with gasoline characterization studies from the literature (Sanders and Maynard 1968, Maynard and Sanders 1969, Johnson et al. 1990). A complete listing of mass fraction results for all 104 separable peaks is given in Appendix B. Many of the peaks have been identified by comparison as described above. BTEX and N were determined by using BTEX and N standards. n-Hexylbenzene was identified by using an ion trap detector and reference library (Perkin Elmer Corp.).

Mass fraction determination for fresh gasoline was determined on two separate occasions using two different vials containing gasoline. This was done to check the character of the stored gasoline. The vials had been filled from two different one-liter containers of gasoline, stored in the refrigerator. Each liter had been filled from the same four-liter container. One liter had been stored in the refrigerator for 100 days longer, before being subdivided. The fresh gasoline that had been stored in the refrigerator for an extra 100 days showed slight weathering which was evident for the highly volatile compounds. These minor changes may be attributed to weathering in the refrigerator or during the filling of the vials.

Gasoline that had been used to establish residual saturation for one of the venting columns shows signs of further weathering, especially for the highly volatile compounds. However, overall it appears that only minor

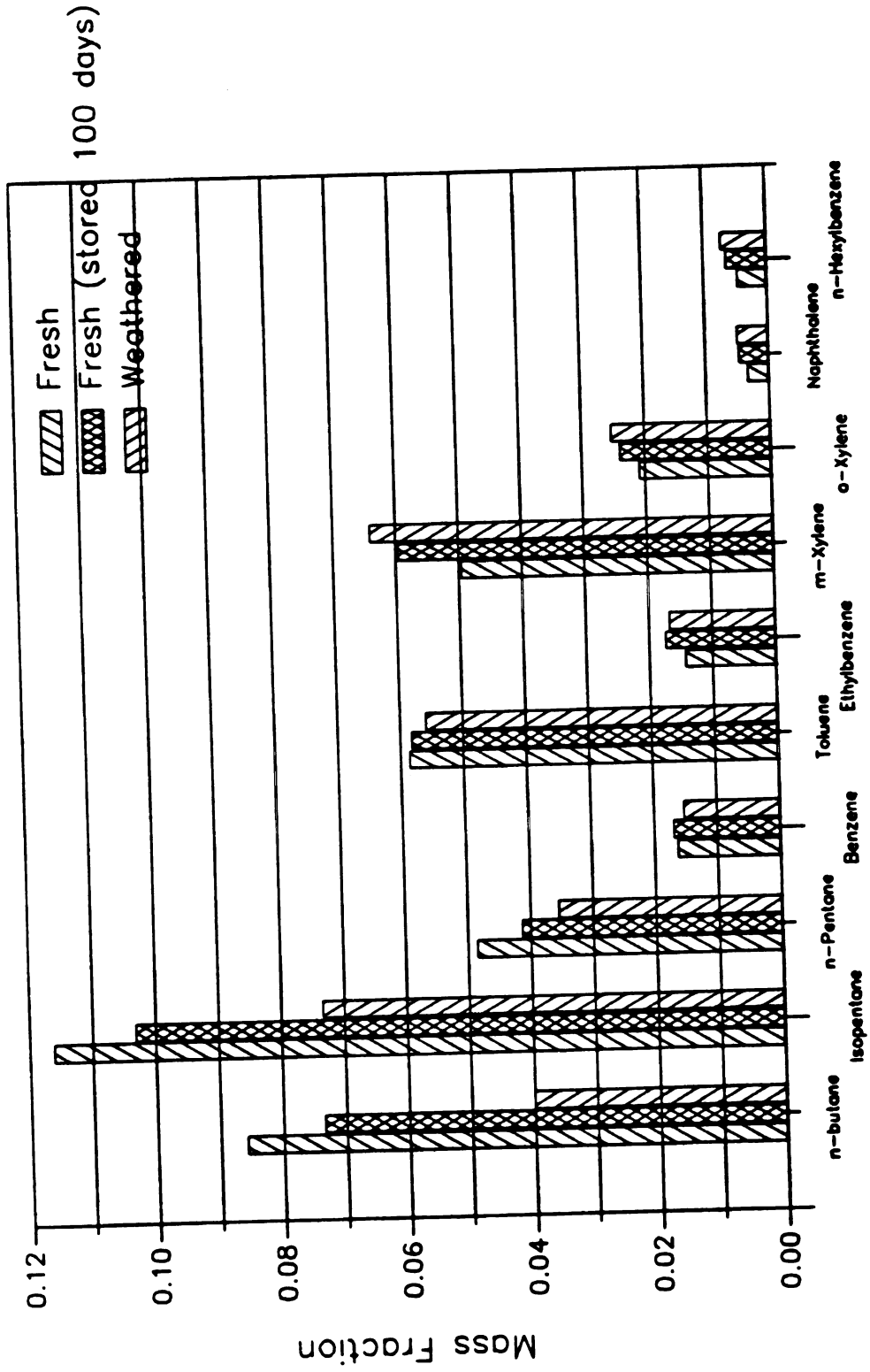


Figure 5-3. Mass fraction data for fresh, fresh & stored, and weathered gasoline.

changes in gasoline composition occurred during storage and the initial setup of venting and leaching columns.

Mole fractions were determined for individual gasoline constituents by estimating molecular weights. Molecular weight estimates were obtained by comparing gasoline chromatograms of this study with those of other studies (Sanders and Maynard 1968, Maynard and Sanders 1969, and Johnson et al. 1990). This worked quite well. For example, compounds with seven carbon atoms will have a molecular weight of 84 plus the number of hydrogen atoms in the compound. Most C-7 compounds will have a molecular weight of about 100 with the notable exception of toluene, which has a molecular weight of 92 g/mole. The complete set of mole fraction data is presented in Appendix B.

Table 5-1 shows experimentally determined pure-phase saturated air concentration, $C_{s,i}^*$, results for selected compounds found in gasoline, from both fresh and weathered gasoline samples. These were determined by combining Raoult's law and the ideal gas law as follows:

$$C_{air,i} * RT/MW = V_{p,i} * X_i \quad (5\text{-}4)$$

$$C_{air,i} = V_{p,i} * MW/RT * X_i \quad (5\text{-}5)$$

$$C_{air,i} = C_{s,i} * X_i \quad (5\text{-}6)$$

$$C_{air,i}/X_i = C_{s,i}^* = C_{s,i} \quad (5\text{-}7)$$

where $C_{s,i}$ is the saturated air concentration for the pure compound.

Overall, there is fairly good agreement between the predicted values and the experimentally determined values,

Table 5-1. Saturated vapor concentrations for pure phase compounds compared to experimentally determined partition coefficients for gasoline at 24° C, (mg/l).

Compound	Saturated vapor concentration for pure phase* (1)	Fresh gasoline (2)	Weathered gasoline	
			Vial (3)	Column (4)
n-butane	5775 (1)	3926	5580	2458
isopentane	2520 (1)	4127	4880	1908
n-pentane	1955 (1)	1981	1986	1950
benzene	385 (1)	432	466	448
toluene	140 (1)	145	214	155
ethylbenzene	51 (1)	54	104	55
m-xylene	45 (1)	50	87	46
o-xylene	37 (1)	44	74	37
naphthalene	1.6 (2)	18	3.4	4.1
n-hexylbenzene	1.5 (2)	18	15	2.9

* Intepolated for 24° C
(1) Vershueren 1983.
(2) Johnson et al. 1990.

indicating that Raoult's law and the ideal gas law are valid for gasoline-air partitioning. The experimental values do seem to be consistently higher than pure compound saturated vapor concentrations. One explanation for this could be that the method for determination of mass fractions resulted in estimations lower than the actual mass fractions of the gasoline constituents. However, mass fraction results from the two different times (calculated with different calibration standards and four different gasoline stocks as described in the methods section), show a reasonably good match.

The determination of equilibrated air-phase concentrations for individual constituents of gasoline could also be a source of error. Although the method of bubbling air through a vial of gasoline eliminated pressure differences between the sample in the syringe and the ambient pressure, other problems were encountered. Small sample amounts were used because of large area responses for high vapor pressure compounds. Larger samples would have caused the areas to be well out of the linear range for the calibration curve. The use of small sample volumes could have resulted in deviation from true values. The heavier compounds in gasoline also showed greater variability in concentration determination. This may be due to variable integration because of poor peak separability. The complete set of results for $C_{s,i}^*$ is presented in Appendix B.

The $C_{s,i}^*$ values determined from the initial flowing air sample from the soil column, (column 4 in Table 5-1), show

estimations closer to theoretical values for heavier compounds than those determined from bubbling air through a vial of gasoline. Some of the $C_{s,i}^*$ values for the very light compounds determined from this sample were less than $C_{s,i}$. This underestimation would occur if the actual mass fractions of these compounds in the residual gasoline in the column were less than those estimated from the weathered gasoline (gasoline that passed through the column). In other words, losses of lighter compounds in the residual gasoline may have occurred during continued drainage of the soil column.

To further explore the applicability of Raoult's law to gasoline-air partitioning, a mixture of hexane, BT, dodecane and naphthalene of known mass fractions was made up and pure phase saturated vapor concentrations were determined by the same technique outlined for gasoline. The results are presented in Table 5-2. The average $C_{s,i}^*$ value from three air samples is shown in column 4, with relative standard deviations shown in column 5. The percent errors for the experimental values and true values are shown in column 6 of Table 5-2. The mass fractions of each of the five constituents is also presented (column 1).

The $C_{s,i}^*$ values for n-hexane, B and T, show very good agreement with those predicted using Raoult's law from this mixture. There is, however, deviation from predicted values for the heavier compounds, dodecane and naphthalene. Problems of poor peak separation and quantification have been eliminated in the case of the mixture.

Table 5-2. Saturated vapor concentrations (C_s) for pure phase compounds compared to experimentally determined partition coefficents ($K_{air,i}$) from hydrocarbon mixture at 24°C, (mg/l),

Compound	Mass Fraction (1)	Mole Fraction (2)	C_s (3)	$K_{air,i}$ (4)	Relative % Deviation (5)	% Error (6)
n-hexane	0.380	0.405	688	682	2.9	0.87
benzene	0.166	0.195	385	412	6.1	7.00
toluene	0.337	0.336	140	143	8.2	2.14
n-dodecane	0.110	0.059	3.8	13.2	8.8	247
naphthalene	0.00673	0.00482	1.6	17.4	34.0	988

It is possible that the sampling method is causing some error, which results in an overestimation of air phase concentrations for heavier compounds. Overestimation of air phase concentrations would result in high $C_{s,i}^*$ values. The first flowing sample taken from the soil column seems to bear this out, suggesting that the overestimation of air phase concentration for many gasoline constituents may be an artifact of the method of determination rather than a true deviation from Raoult's law.

Some deviation from Raoult's law for gasoline may be expected because gasoline is a mixture of both aromatic and aliphatic hydrocarbons. However, compounds found in gasoline are non-polar hydrocarbons of similar chemical makeup, carbon and hydrogen, and when mixed may act in a near ideal manner. The data seem to indicate this as well. Although some deviation from Raoult's law was observed, and it varied for different constituents, from a practical standpoint, the use of Raoult's law in describing gasoline-air partitioning is probably valid.

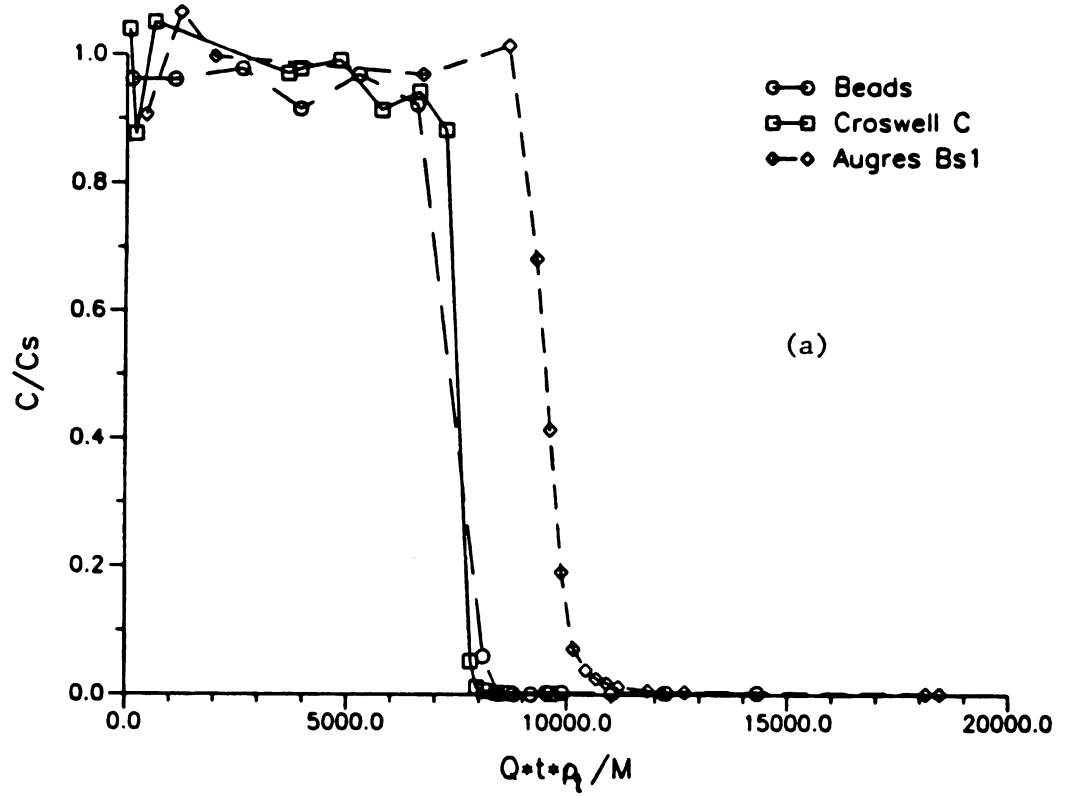
5.5.2. Soil venting of a single-component NAPL

Venting of a single component NAPL in soil was performed mainly to assess the local equilibrium assumption (LEA) and along with this, the presence of possible wall effects in the venting columns. If the system was operating under local equilibrium with few or no wall effects, then one would expect column effluent air levels to be at the saturated vapor

concentration for toluene throughout venting until such time when NAPL toluene was removed from the column. If wall effects were occurring, which means that most of the air was moving near the column walls, one would expect that effluent air levels to be at saturated vapor concentration for only a short period of time (while NAPL was still present near the walls). Perhaps then slowly decreasing over time, due to dilution of the contaminated air (from the center of the column) with clean air (from near the walls). If the system was not operating at local equilibrium, one would expect only the initial sample to be at saturated vapor levels, with a quick drop to some level determined by the rate coefficient.

The results presented in Figure 5-4a suggest the first scenario; that the system is operating under local equilibrium with little or no wall effects. The results shown in Figure 5-4a represent columns packed with Croswell C soil, AuGres soil and beads. The y-axis has been scaled using the saturated vapor concentration of toluene at the experimental temperature. Saturated vapor concentrations for the experimental temperature, were interpolated from data presented in Verschueren (1983). The time (x-axis) has been scaled based on the air flow rate, amount of residual toluene in the column and the density of toluene.

The results clearly indicate that the NAPL dominates the system as evidenced by similar results between beads and soil. The results also indicate that the local equilibrium assumption is valid and that wall effects are insignificant.



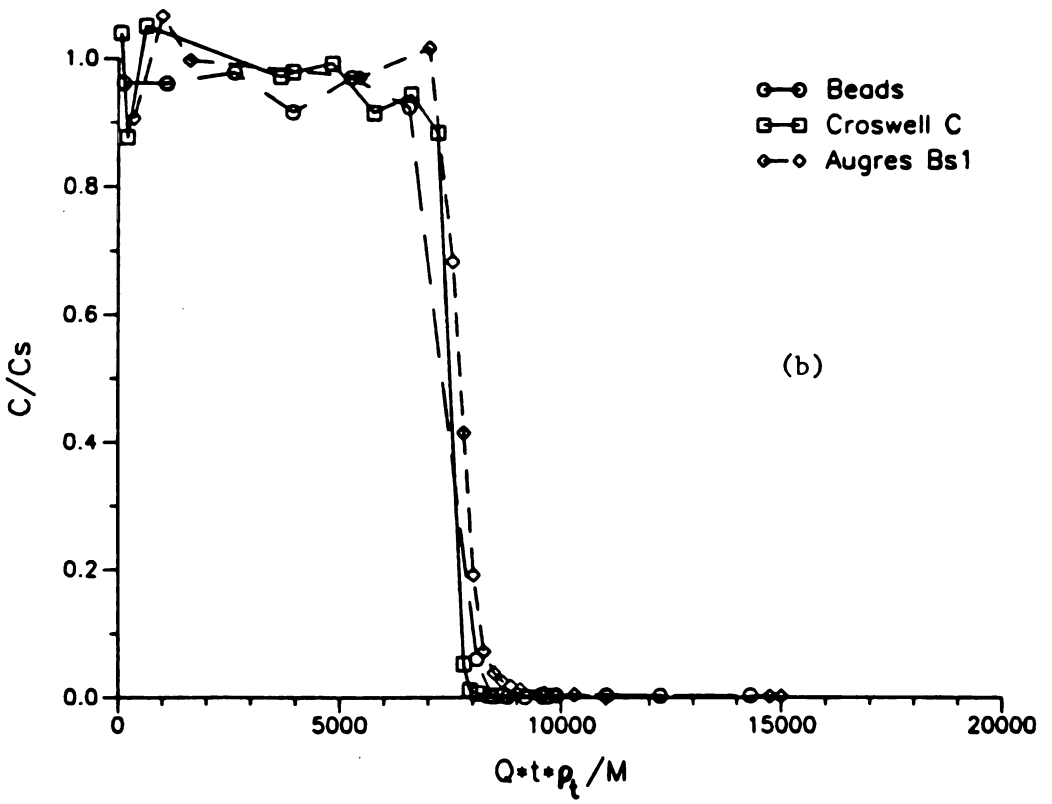


Figure 5-4. Scaled results from soil venting experiments using toluene as the residual NAPL. a) weighed mass and b) mass determined by integration.

This is evidenced by the saturated toluene levels in air samples during early venting times and a rapid decline when the NAPL has been depleted from the soil. Saturated vapor phase concentrations, temperature and air flow rates are presented in Table 5-3.

Table 5-4 summarizes the initial conditions of each column and the results of calculated initial mass based on integration of the area under each curve. The mass balances for the beads and Croswell C soil show excellent agreement. The results for the AuGres soil show about a 20 % difference. It is possible that some amount of experimental error may be responsible for the disparity in results, however, mass balances for the multiple component NAPL presented later also show a similar disagreement for the AuGres soil. Possible explanations for this will be discussed in that section.

If the calculated mass of toluene determined by integrating the area under the curve for the AuGres soil is used to scale time then the three plots all fall on top of each other (Figure 5-4b). This suggests that the soil type does not affect the mass transfer of toluene while NAPL is present in the soil; i.e. that the local equilibrium assumption is valid.

The local equilibrium assumption means that when all the NAPL has been depleted, the effluent concentrations should fall to zero. The air residence time in the column during venting is less than 1 minute. If air were moving equally through all pores and no other mechanisms were involved, it

Table 5-3. Experimental conditions for toluene contaminated soils and bead columns.

Column	Flow rate (ml/min)	Temperature (°C)	C_s * (mg/l)
Beads	(30-120)	21	117.4
Croswell	30	22	124.8
AuGres	30	22	124.8

* Interpolated from data presented in Verschueren (1984).

Table 5-4. Initial mass weighed and calculated for soil columns contaminated with toluene (g).

Column	Weighed Mass	Calculated Mass
Beads	2.22	2.21
Croswell C	1.85	1.96
Augres Bs1	1.00	1.23

should only take about a minute to flush the column out once the NAPL has been depleted and have clean air flowing out the bottom. This is not the case, which suggests that some pores or regions in the column are less accessible to the flowing air than others. There may also be other explanations such as desorption or water/air exchange rates that could result in an increased flushing time. The results shown for the AuGres soil indicate that it takes on the order of 30 minutes to flush the column to low levels. Although this suggests other mechanisms are involved, they only seem to be of significance after the NAPL has been depleted from the system. Processes that affect the mass transfer of contaminants at low levels may be important, however. It could mean that longer venting times are required to reduce soil contaminant levels to those required by government agencies regulating the cleanup of contaminated sites.

5.5.3. Soil venting of a multicomponent NAPL

Figure 5-5 shows two chromatograms of air samples taken during soil venting of gasoline contaminated soil. These chromatograms provide a visual illustration of the soil venting process for a multicomponent NAPL (gasoline) in soil. The top chromatogram represents an air sample taken two minutes after venting was initiated. Many large peaks can be seen at early retention times. These peaks represent compounds with high vapor pressures and many of these compounds constitute a large mass fraction of the gasoline.

A chromatogram of an air sample taken 150 minutes later

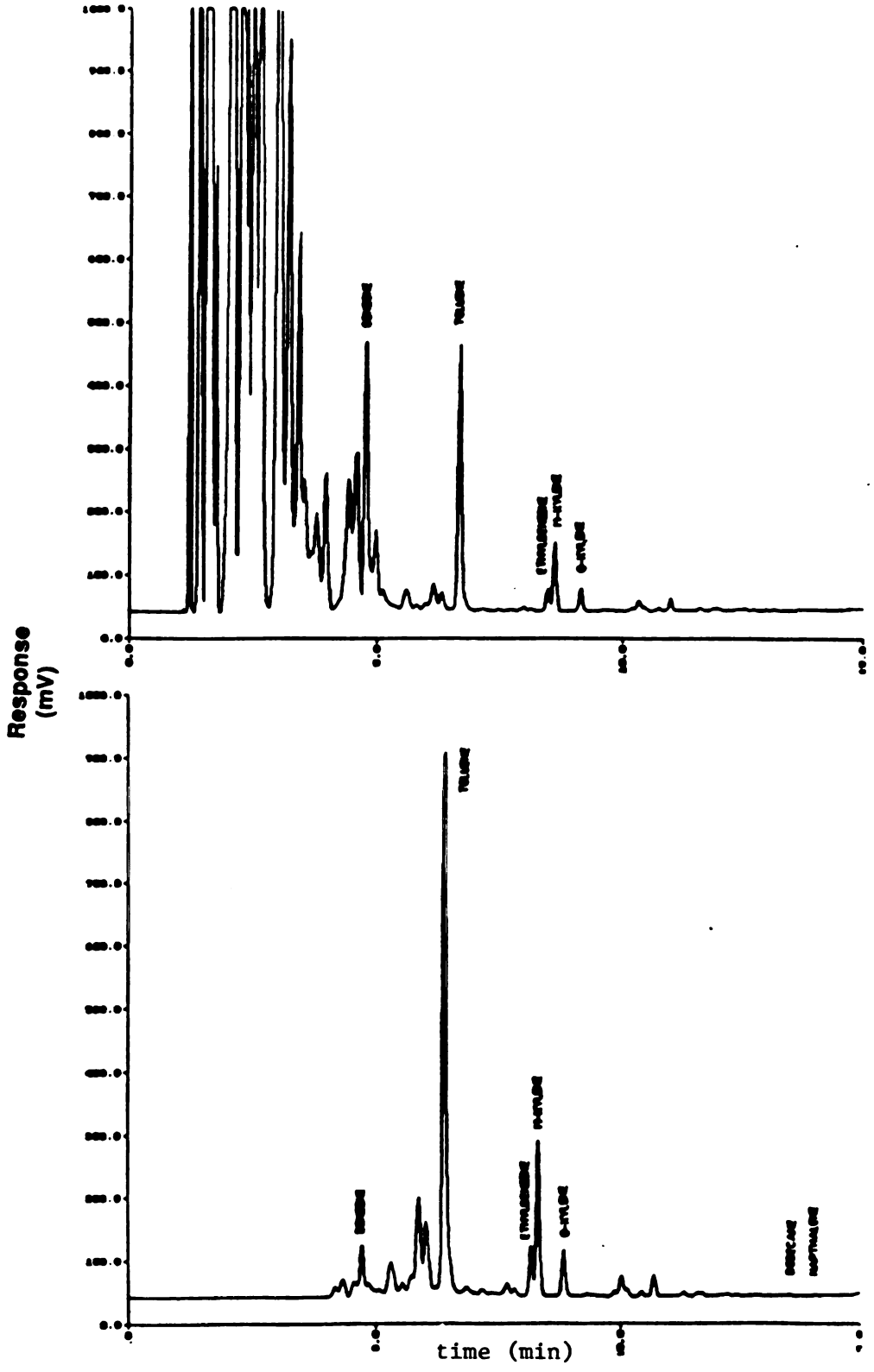


Figure 5- 5. Gas chromatograms of air samples taken during soil venting. a) two minutes after venting initiated, b) 50 minutes after venting initiated.

from the same soil column is also shown. The early peaks, representing the highly volatile compounds in gasoline, have virtually disappeared from the chromatogram. They have, therefore, been removed from the soil column as well. Other compounds, such as TEX, show an increase in FID response, corresponding to a higher concentration in the air sample.

The increase in response of toluene, for example, over the course of venting can be explained by Raoult's law and the ideal gas law. A change in mole fraction will result in a change in the air-phase concentration. The composition of the residual NAPL is constantly changing during the course of soil venting. The very volatile compounds of gasoline are quickly depleted at early venting times (Figure 5-5b). The residual NAPL thus becomes enriched in the other less volatile gasoline compounds. Their mole fractions increase because of this, which results in an increase in air phase concentration.

This increase in air-phase concentration for some compounds during venting may be disconcerting if one does not appreciate the changing composition of the gasoline throughout the venting process.

Figures 5-6 (a and b) show the dynamic nature of BTEX and N air concentrations during soil venting. Benzene, for example, has a higher vapor pressure than the other compounds shown in Figure 5-6a. It has a mole fraction of about 2 % in fresh gasoline. It is quickly depleted from the column when compared to the other compounds shown in Figure 5-6a. Toluene starts out at an air concentration of about 9 mg/l, but

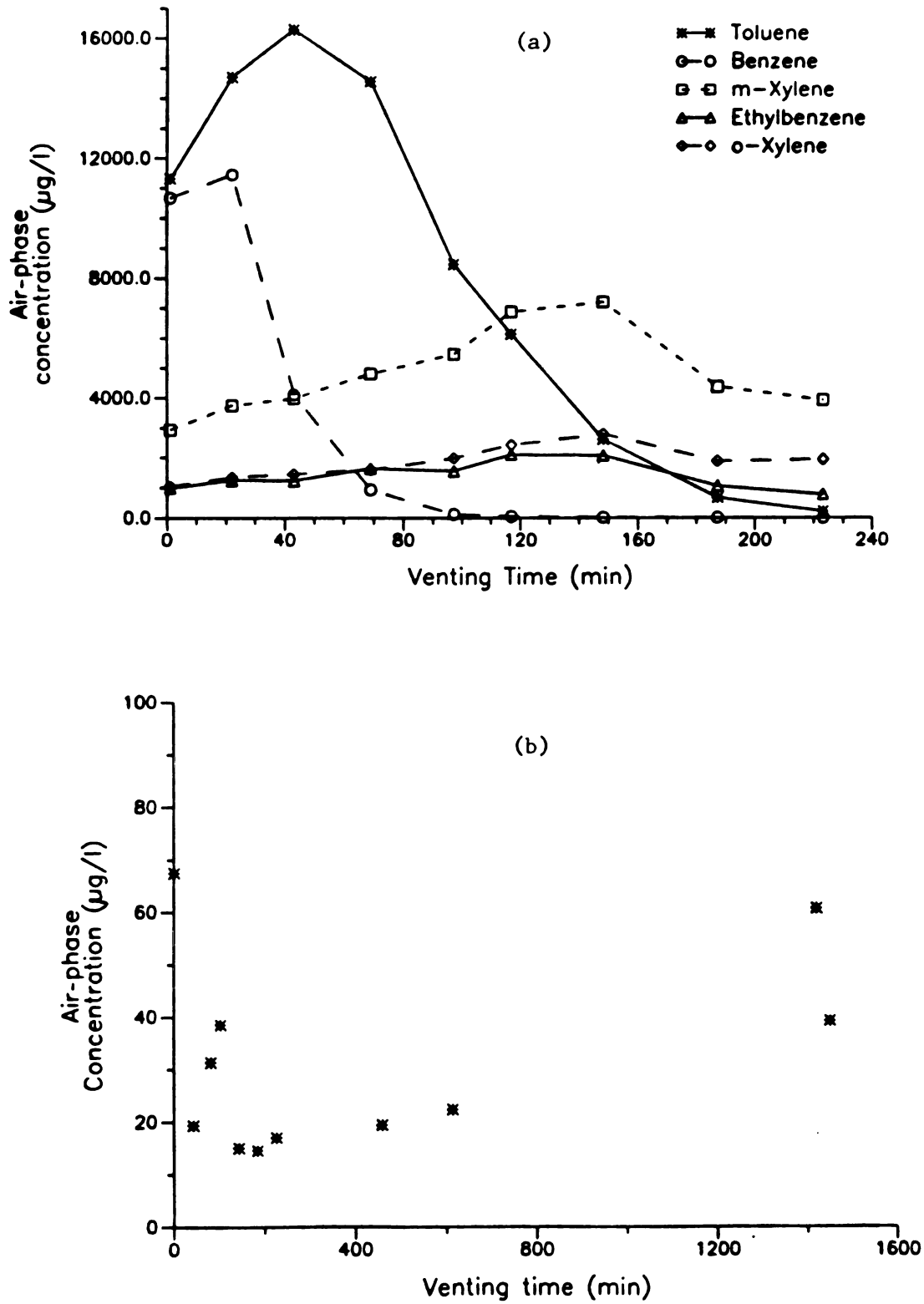


Figure 5-6. Venting results for residually held gasoline in AuGres soil: a) BTEX and b) naphthalene.

quickly increases to about 16 mg/l corresponding to the loss of highly volatile compounds. It then decreases to low levels, with some evidence of tailing. Naphthalene (Figure 5-6b), on the other hand, has a very low vapor pressure, as well as a low mole fraction. Both of these contribute to its low air concentration. The low vapor pressure contributes to its slow depletion from the NAPL.

Scaling the time axis for the data from these columns, in the same way that the time axis for the toluene data was scaled, allows a direct comparison of results from different columns. Figure 5-7 shows the scaled results for selected compounds from the AuGres and Croswell soil and a bead packed column. The overall trend is very similar and the toluene and o-xylene curves for the soils and beads agree quite closely. This suggests that the mass transfer process for a NAPL in the soil is dependant on the presence of the NAPL, itself, and not necessarily on soil type, as was previously stated for the single component NAPL.

In order to scale these data, the initial mass of gasoline in the column had to be known. However, discrepancies in the initial weights became evident when soil venting data showed significant amounts of gasoline in the columns even though initial weights of gasoline were close to zero. By integrating the area under the toluene curve, the initial gasoline mass could be determined. The amount of gasoline was back calculated based on the mass fractions of toluene in fresh gasoline (Table 5-5, column 1). Toluene was used be-

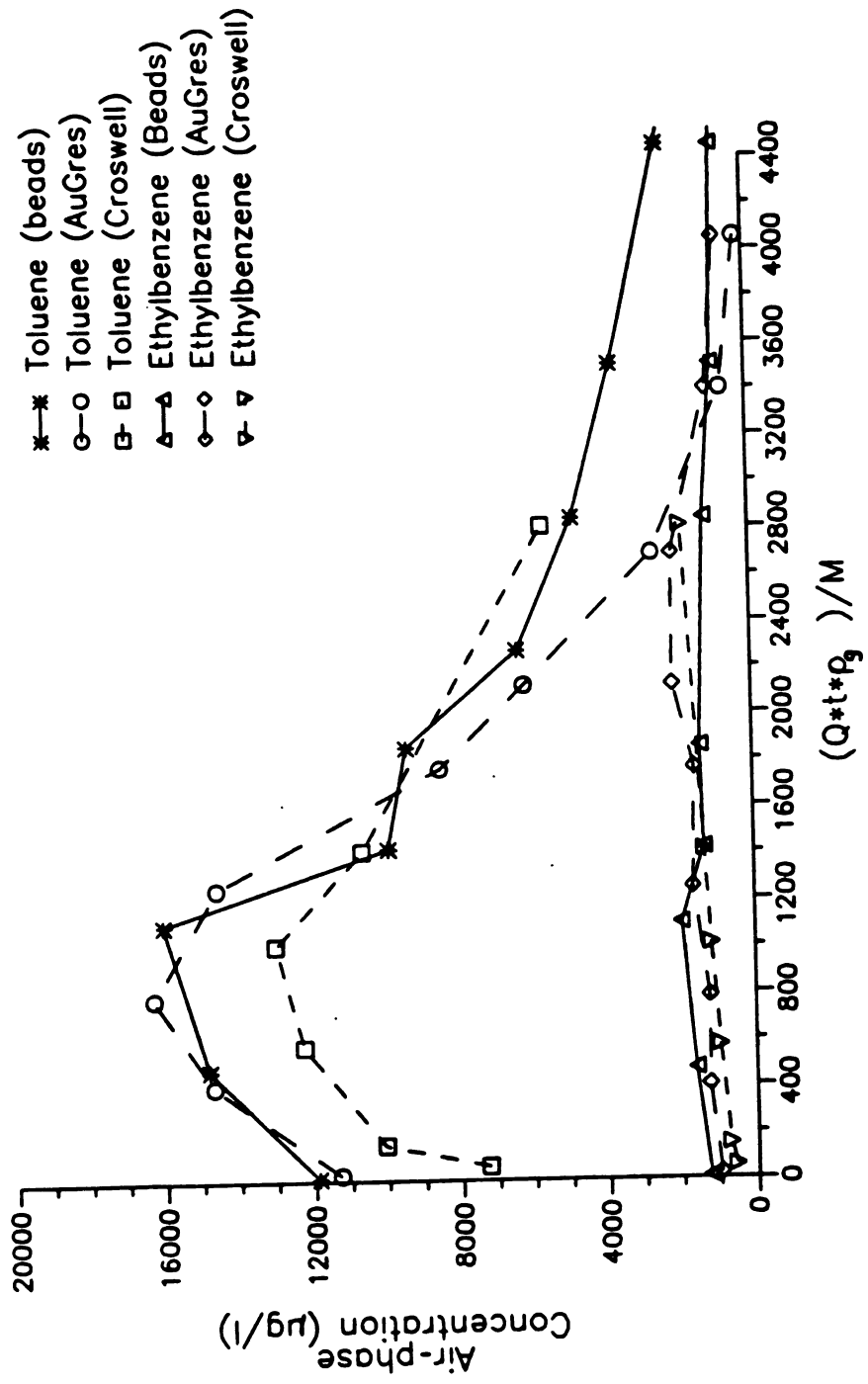


Figure 5-7. Scaled venting results for beads and soil columns.

Table 5-5. Mass balance for gasoline contaminated soils (g).

Column	Weight of Residual Gasoline (1)	Mass of Gasoline Calculated by Integrating Toluene Curve (2)
Croswell soil		
N14	0.63	1.13
N18	1.33	1.30
N21	0.45	1.11
N30	1.15	1.66
		average 1.30
AuGres soil		
N15	-0.2	1.15
N16	-0.9	1.54
N19	0.48	1.28
N31	0.61	1.29
		average 1.33

cause of the consistent, completeness of the data for various columns. No significant difference in residual gasoline saturations for the two different soils was found when using an F test and analysis of variance on the back calculated masses. The pressure cell results, presented, in Chapter 3 further substantiate the similar residual NAPL saturations between the two soil types.

The lack of the ability to balance the mass for the venting columns was very perplexing. A detailed investigation, led to the belief that the source of the mass balance problem was in the initial weight measurement of gasoline, not from other sources such as gas-phase measurement errors or "bleeding" from column parts. It became obvious, that there was more gasoline in the columns than was being weighed. Some mass was leaving the column during the time when gasoline was added (after establishing residual water saturations) to the time when the column was again weighed (after establishing residual gasoline saturations). Since negligible amounts of soil were leaving the system during this time, the only other possible explanation was that some water was being lost during the establishment of residual gasoline saturation.

Moisture content values, before adding the gasoline and after venting had occurred, indicate that some water may have left the column. Table 5-6 presents moisture content data for columns before adding gasoline and after venting. It is possible that some water, in vapor form may be leaving the column during the venting process. This, however, is generally

Table 5-6. Water mass balance for soil venting columns.

Column	Residual Water Saturation (% by Weight) (1)	Moisture Content After Venting (% by Weight) (2)	Difference (1)-(2) (g of Water) (3)	Maximum Water Removed Venting (g of Water) (4)	Unaccounted Water (g) (5)
Croswer Soil					
N14	2.40	1.46	1.44	0.88	0.56
N18	2.29	1.89	0.64	0.89	0
N21	1.89	1.64	0.40	0.94	0
N30	2.09	1.70	0.64	0.98	0
AuGres Soil					
N15	16.99	14.40	3.03	0.88	2.15
N16	16.87	13.00	4.91	0.88	3.97
N19	16.31	14.58	1.42	1.08	0.34
N31	16.53	14.65	2.49	0.99	1.50

not sufficient to account for the missing mass from the system. The maximum amount of water that could have left in the air phase during venting was calculated based on 100% relative humidity in the outflowing air and assuming 0% in the incoming air. These values are shown in column (Table 5-6). This is the maximum amount that could leave during venting, and it is likely that much less water was leaving the columns this way. This is because the incoming air was bubbled through water prior to entering the column. The air may not have been at maximum saturation for that temperature, but was probably much higher than 0% relative humidity. The water unaccounted for (column 5, Table 5-6), is generally much higher in the AuGres soil, than the Croswell soil. Possible explanations for this are given below.

It is unlikely that immiscible water was exiting the column through the pressure plate during gasoline drainage. This is because the pressure plate acts as an impermeable barrier for water at the experimental pressure used. No immiscible water was ever observed in the collection vials during gasoline drainage, either. This was looked for specifically. The possibility that water was leaving the column dissolved in the gasoline was also checked using an Aquametry Apparatus (Lab Industries, Inc.) and a Karl Fischer titration. The average moisture content for gasoline samples that had been passed through the soil columns was 0.28% with one standard deviation of 0.05%. A fresh gasoline sample had a moisture content of 0.32%. There is no indication that

appreciable amounts of water were leaving the column dissolved in gasoline.

The possibility exists that during water drainage, some water accumulated near the bottom, inner o-ring and soil. This part of the column may have been slower to drain because the epoxy sealed edges of the plate did not allow for a direct path vertically for the draining water. Water accumulating here would be weighed as residual water. During the addition of gasoline and gasoline drainage, this water may have exited the system, resulting in errors in weights of residual gasoline.

To test this possibility, two columns were setup with approximately 10 ml of water and sealed. In one of the columns, a small amount of water leaked out the side initially, resulting in a 1.1 gram loss from the system. The column was tipped again but no more water could be seen leaking from the column. Twenty four hours later, both columns were again weighed and an additional 0.3 g were lost from the first column and 0.36 g from the second. Twenty four hours later, only a loss of 0.06 g was recorded for each column. This suggests that it may be possible for an some amount of water (near the bottom o-ring) to leave the columns even when it appears as though the columns are well sealed. The addition of a large amount of gasoline to the residually water saturated soil may result in some mobilization of the residual water, due to capillary forces or possible dehydration of surfaces because of the large amount of solvent added.

This mobilized water may make its way to the lower part of the column where it could possibly exit. The AuGres soil may be affected to a greater extent because of its higher water content than Croswell soil at residual water saturations. This explanation seems plausible. The discrepancy between the initial gasoline weight and the amount calculated to leave the column during venting was never proved even after considerable effort.

Two, 10 cm columns, with Croswell soil, were also used for venting experiments. This was done, in part, to address the mass-balance problems encountered with the 4 cm columns and also to obtain a more complete picture of the venting process. In the 10 cm columns, the calculated mass of gasoline compared to the weighed mass differed by only 7 and 12 %, respectively. The amount of gasoline retained in these columns is approximately 2 to 3 times the amount retained in the small columns. If losses of water are about the same as in the small columns packed with Croswell soil, this would result in a much lower percent difference between weighed and calculated gasoline masses.

The other reason for using the longer columns was that they retained more gasoline and thus took a longer time to vent. This allowed for more time to collect samples with less dramatic changes in air concentration between samples.

Figure 5-8 compares the scaled results from a 10 cm column and a 4 cm column, both containing Croswell soil. The fact that when the data are scaled, they are very similar

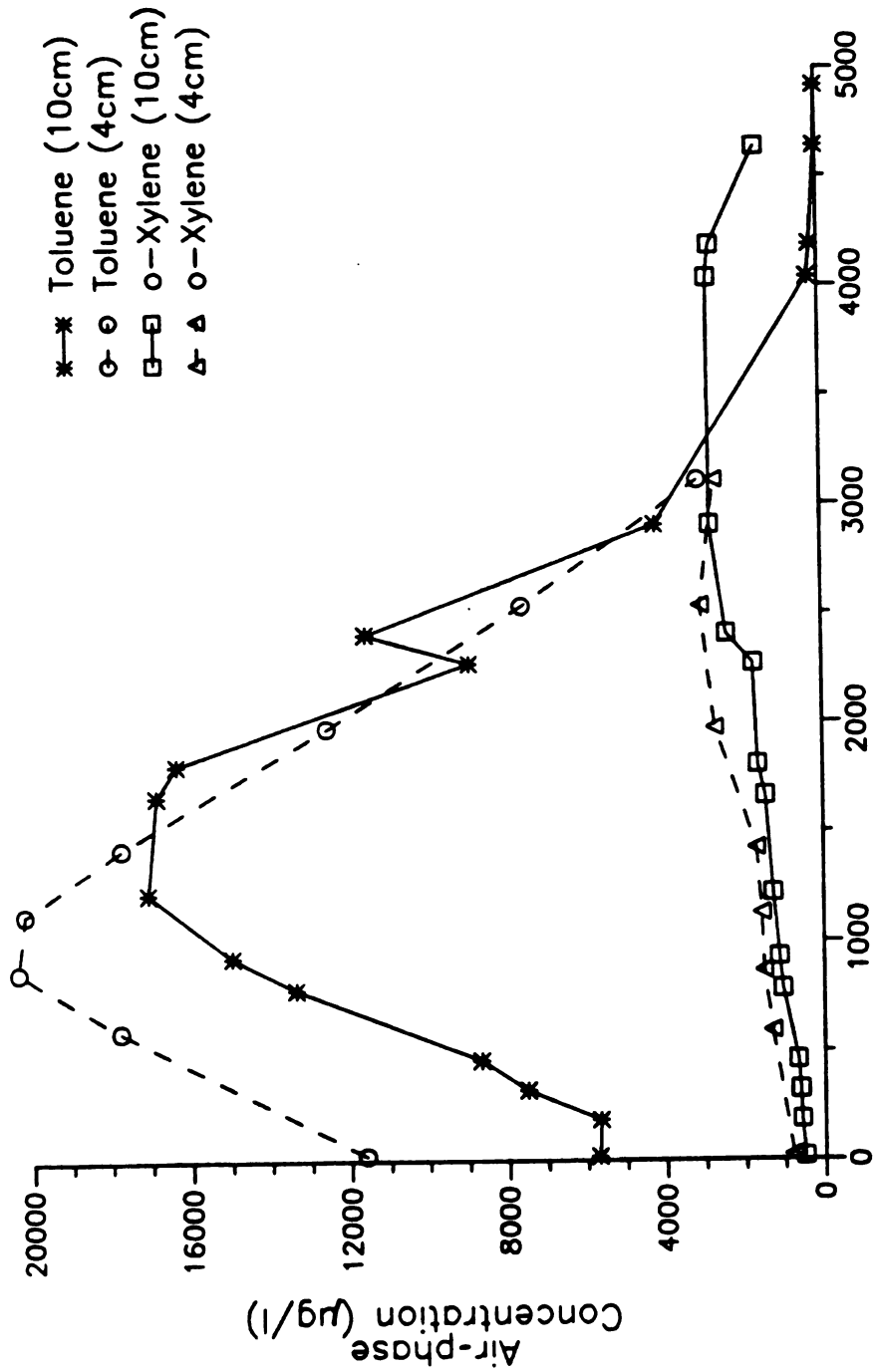


Figure 5- 8. Scaled venting results from 10cm and 4cm columns packed with Croswell soil.

between columns lends credence to the idea that the venting process is operating under local equilibrium.

Johnson et al. (1990) have calculated that a path length of less than 0.2 cm is sufficient for air to reach equilibrium in soil containing gasoline. The air then has sufficient time to equilibrate in the four or ten centimeter columns used in my study. Other mechanisms may influence mass transfer, however.

Pfannkuch (1984) suggested that as compounds are depleted from the surface of the NAPL, further removal may be hindered by the diffusion of compounds through the NAPL. This was suggested for a pool of gasoline at the water table and not necessarily for residual gasoline of the vadose zone but it is an interesting possibility. If this skinning effect exists, in that the rate of mass transfer of a compound from gasoline is determined by its rate of diffusion through the NAPL, then this would cause a deviation from local equilibrium and require longer venting times to achieve the same level of cleanup. This is important from a practical standpoint because longer venting times may be more costly. It might also be important from a site management standpoint. Once the system has become rate limited, lower flow rates could be used to remove the same amount of contaminant at lower costs.

Two methods were employed to determine if the local equilibrium assumption is valid for mass transfer of gasoline constituents to air during soil venting of laboratory columns. The first technique involved the use of a local equilibrium

based model (modified from Marley and Hoag, 1984), compared to venting results for a number of soil columns.

The second method for assessing the local equilibrium assumption involved various experimental techniques such as flow rate interruption, flow rate reduction and discrete soil sampling from different locations in the column.

Local Equilibrium Model

The model used was adapted from that of Marley and Hoag (1984) and was discussed in the background section. It incorporates the ideal gas law and Raoult's law (Equations 5-1 and 5-2). The change in mass due to venting is calculated using Equation 5-3. The numerical code for the model is presented in Appendix C.

Figure 5-9a shows soil venting results for a gasoline contaminated Croswell soil column (10 cm) with the model simulation. Input parameters for the model include: air-flow rate; the initial mass of gasoline in the column; the initial mole fractions of the gasoline constituents; and the pure-phase saturated air concentrations. Mole fraction data from fresh gasoline were used in the input file. Pure-phase saturated air concentrations, $C_{s,i}$, were determined for known compounds and estimated for the unknowns for this gasoline by comparing it to those from the literature (Mackay and Shiu 1981, Verschueren 1983, Johnson et al. 1990). The mass of gasoline weighed during the initial setup was used in the input file.

Overall, the model predicts the dynamic behavior of

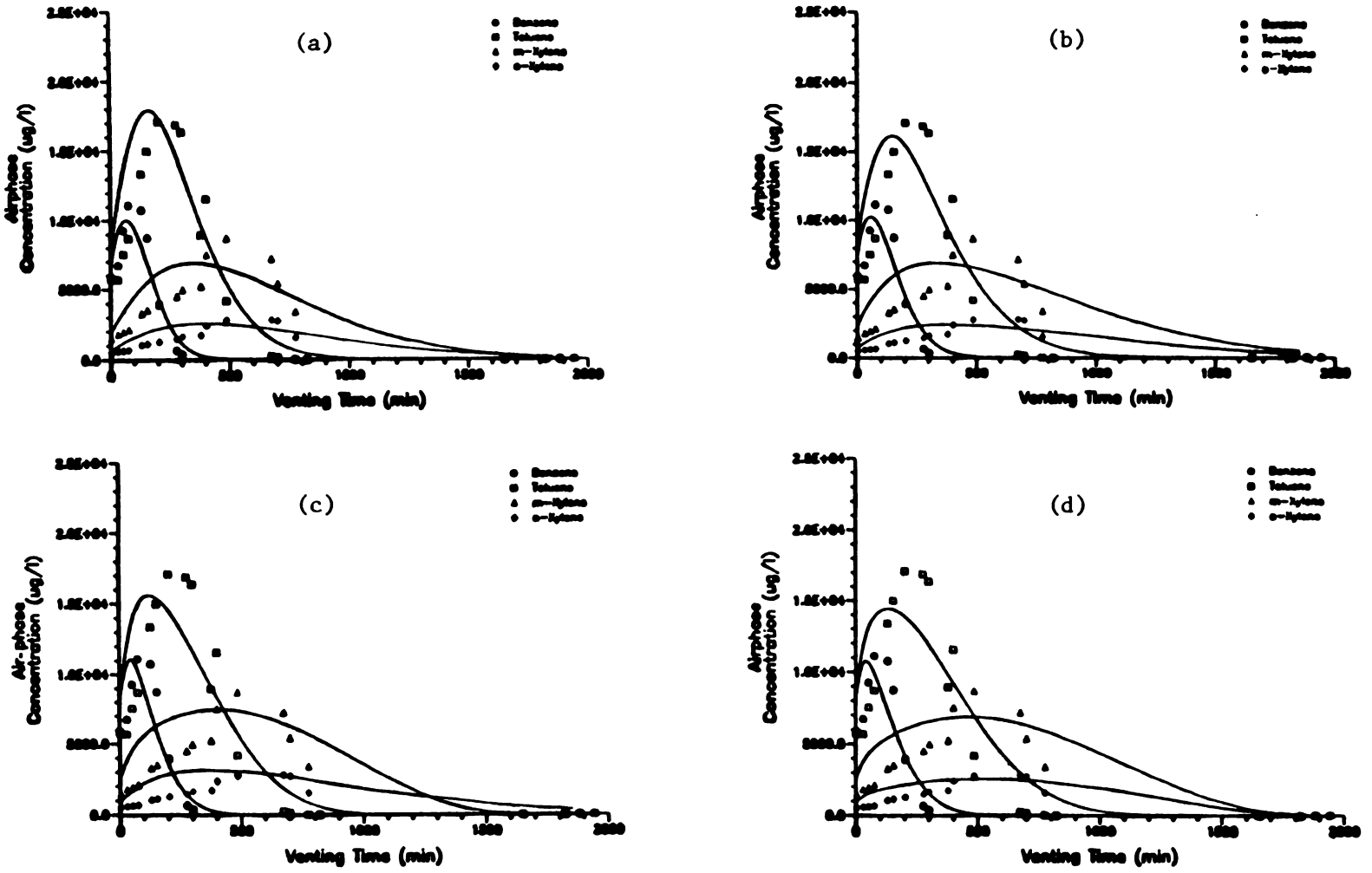


Figure 5-9. Model simulation of soil venting of Croswell soil; with input file: a) fresh gasoline characterization and $C_{s,i}$ from literature; b) fresh and stored gasoline characterization and $C_{s,i}$ from literature; c) isopentane adjustment; and d) experimentally determined $C_{s,i}$.

individual constituents well, however, three noticeable differences emerge. One of the differences is that the model does not predict as high a maximum air concentration as that of the data. The second difference is that the model predicts the maximum value earlier than the data show. In other words, the model appears to be offset from the data. The other noticeable difference between the model and the data is that the model results for m-xylene do not simulate the shape of the m-xylene data.

A sensitivity analysis was performed to determine the effect of various input parameters on the air-phase concentration estimates of the model. The two major parameters affecting peak air-phase concentration for a given constituent are its mole fraction, X_i, and $C_{s,i}$. If either of these are increased, the result is an increase in the maximum air concentration achieved over the course of simulated venting for that constituent. An increase in a constituent's mole fraction can be achieved in two ways; by increasing its own mass fraction or by decreasing the mass fractions of other compounds in the gasoline. Mass fraction determinations were similar for the different gasoline samples used and differences measured were not enough to change the predication made by the model. Figure 5-9b shows the results of the model with input values for mass fractions taken from the fresh and stored gasoline. Very little difference is seen in the model's output for this gasoline sample compared to the one used to generate the curves in Figure 5-9a. There is,

however, a slightly lower maximum concentration for toluene and longer tailing for m-xylene.

Lower mole fractions for high vapor pressure compounds can also affect the maximum air concentration of BTX. Increasing the mole fraction of isopentane for example, a high vapor pressure compound, results in model predictions of maximum air concentrations approaching that of the data for benzene but slightly lower for toluene (Figure 5-9c). A slight increase in the model's maximum air phase concentration for m-xylene and o-xylene was also observed. The mole fraction of isopentane was increased from 0.13 to 0.20. Slight decreases in mole fractions of other gasoline constituents occurred, however, the rapid removal of a large percentage of the gasoline, caused a quick net increase in the mass fraction of benzene. Overall, however, this did not dramatically affect the model simulation.

Increasing the percentage of low vapor pressure compounds does little to affect the model prediction of BTX. It does, as expected, dramatically affect other low vapor pressure compounds, such as naphthalene.

Increasing model input parameters such as air flow rate or initial gasoline mass in the column do not affect maximum air concentration predicted by the model. The air flow rate reduces or expands the curve along the time axis, while increasing the initial mass increases the tailing of the curve predicted by the model.

As is quickly evident, when modeling a multicomponent

NAPL, such as gasoline, correct characterization of the gasoline is important, but not essential. The results suggest that the model is not that sensitive to minor adjustments in constituent mass fractions. The other major factor affecting a constituents air-phase concentration determined by the model is the $C_{s,i}$. Since slight deviations from ideality may occur in a complex mixture such as gasoline, values of $C_{s,i}^*$ were also used in the model simulation. Figure 5-9d presents the results of fresh and stored gasoline with the corresponding $C_{s,i}^*$ values determined for this gasoline sample. This did not result in a significant increase in air-phase concentrations of BTX as was expected. It was expected because $C_{s,i}^*$ for these compounds were higher than $C_{s,i}$. The fact that the simulated air-phase concentrations of BTX did not increase was probably due to the considerable overestimations of $C_{s,i}^*$ for the heavy compounds using the flow through vial technique. This overestimation resulted in an inadequate prediction of air-phase concentrations for heavier compounds, i.e. naphthalene (Figure 5-10). Model simulation using partition coefficients determined from the first flowing air sample from a venting column are also shown in Figure 5-10. These provide a better estimation of actual data but still overestimate the results. The model simulations using $C_{s,i}$ values show very good agreement with the data.

The offset of the model and data evident in Figures 5-9 (a and b) could be due to differing gasoline composition over the length of the column. The assumption used in the model is

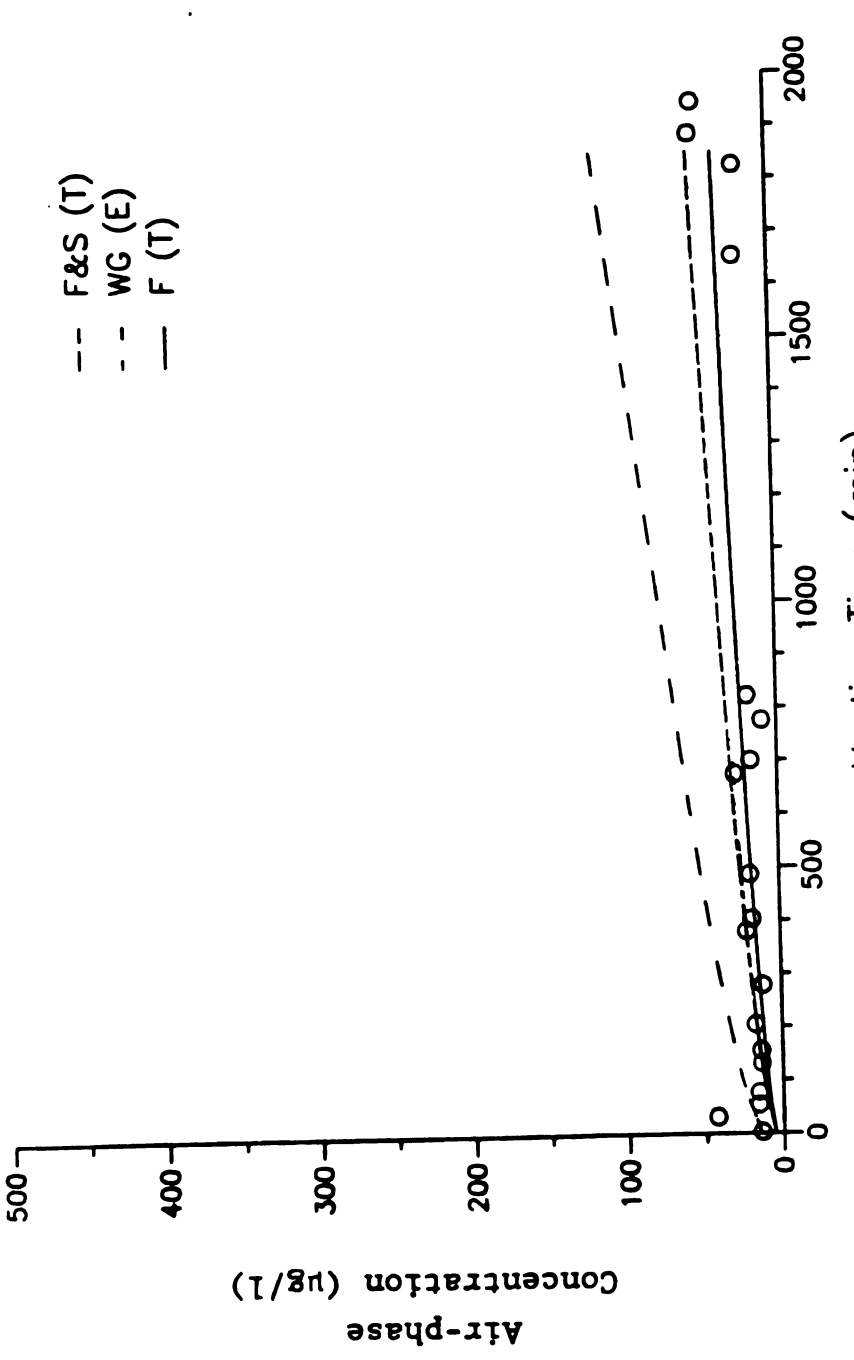


Figure 5-10. Model simulation of soil venting showing naphthalene concentration for Croswell soil.

that the composition of gasoline in the column is the same throughout the column. The model does not attempt to descritize the column, but assumes that the air is in equilibrium with all of the gasoline in the column. Johnson et al. (1990) estimates that a path length of about 20 mm is needed for the air to come into equilibrium with the NAPL. In reality then, the air flowing out the bottom of the column would be at equilibrium with the NAPL at the bottom of the column. This could result in a slower increase in air phase concentration in the actual data, than the model would predict. NAPL constituents would be depleted first from the top of the column, only to re-equilibrate with the NAPL at the bottom as the air passes through this region. This phenomenon of differences in gasoline composition over the length of the column may produce greater deviations in the xylenes because they are depleted at a slower rate from the column.

Figures 5-11 (a and b) show results from soil venting experiments using 4 cm soil columns. The model does a better job at predicting the data in terms of the time scale. Part of this may be explained by the shorter column length. The shorter the column length, the more representative the column is of a single point, which the model assumes. The model, however, still underestimates the maximum air concentration of benzene, in particular, and to a lesser extent toluene. The initial mass input into the model for the 4 cm columns was the calculated value determined by integrating the area under the toluene curve and back calculating to determine initial

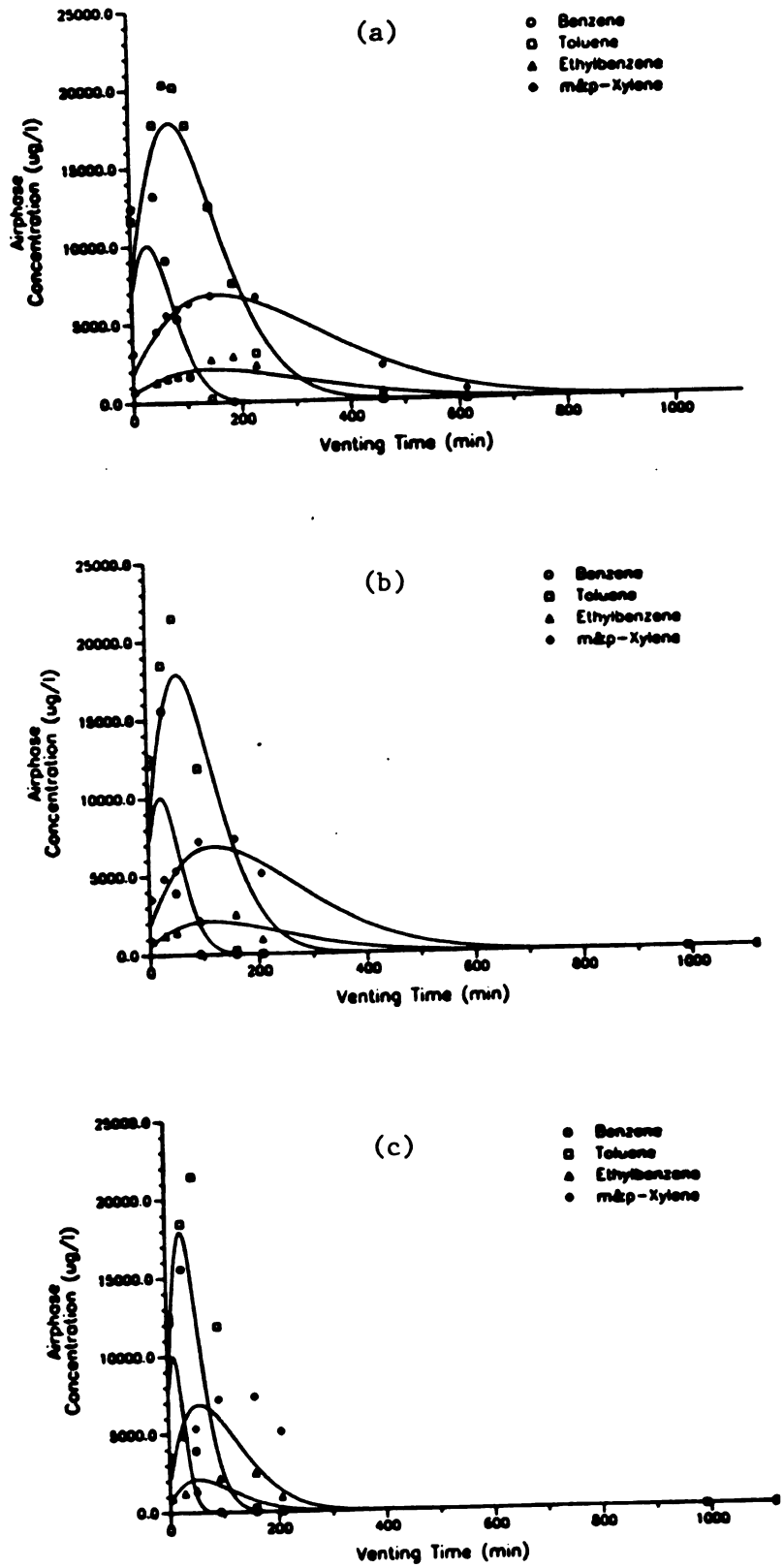


Figure 5-11. Model simulation of soil venting (4 cm columns) a) Croswell soil, b) AuGres soil, and c) AuGres soil using weighed mass as input.

gasoline mass. As previously discussed in the section on scaling multicomponent NAPL's, the amount of residual weighed may not be an accurate method to determine initial mass for soil in the short soil columns. The model results support this conclusion.

Figure 5-11c shows the model simulation for data shown in Figure 5-11b using the initial mass input value to be the amount weighed during the column setup. Clearly, the weighed mass is incorrect.

The model strongly supports the assumption of local equilibrium for venting residual multicomponent NAPLs, such as gasoline, from soil.

Mass Transfer Limitations

At much later venting times, when the model predicts air phase concentrations of zero, small amounts of toluene and xylenes can still be measured in the flowing air. This suggests that the local equilibrium assumption is no longer valid and that at some time, mass transfer becomes rate limited.

Various experimental techniques were used to further investigate the local equilibrium assumption and possible rate-limiting behavior in the soil columns at later venting times. The experimental techniques employed were flow rate reduction, flow interruption and discrete soil sampling with subsequent static headspace measurements.

Flow rate reduction was performed on a 10 cm soil column packed with Croswell soil. Figure 5-12 shows the results for

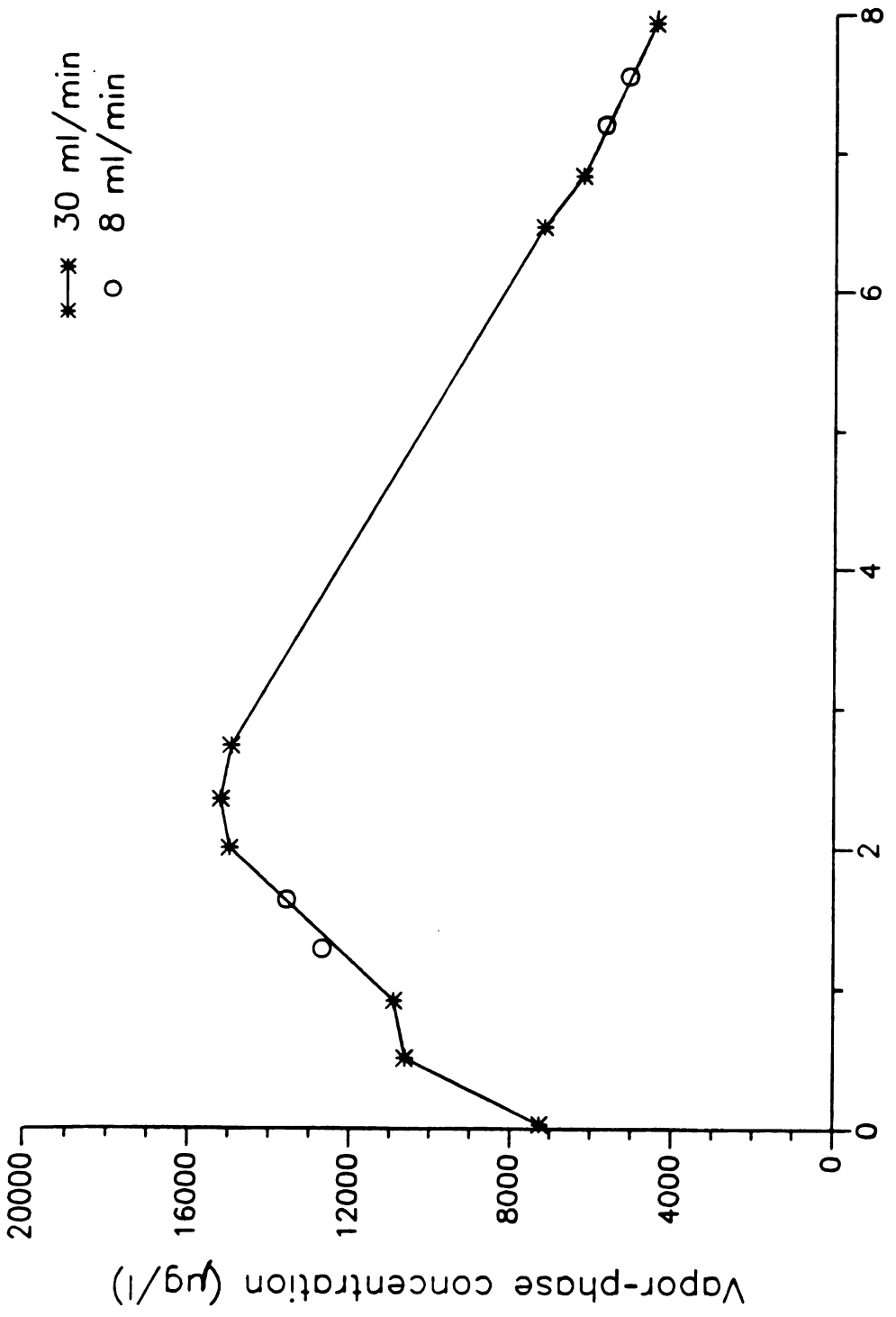


Figure 5-12. Changing benzene concentration during soil venting with flow rate reduction.

benzene. On two separate occasions, during the first eight hours of venting, the flow rate was reduced from 30 ml/min to 8 ml/min. These changes are indicated by the open circles. There does not seem to be any deviation from the expected curve, when either the flow rate is reduced to 8 ml/min or increased to 30 ml/min. If rate limiting behavior was occurring, then clearly when the flow rate was reduced, one would expect to see an increase in the air phase concentration. When the flow rate was increased to 30 ml/min, the air phase concentration would be decreased. This is not exhibited in these data. This further supports the claim that at high contaminant levels, the local equilibrium assumption is valid.

At later venting times (approximately 23 hours later), for the same column, the flow rate was again reduced to 8 ml/min. The results for isopentane and benzene are shown in Table 5-7. When the flow rate was reduced, there was about a four fold increase in the air concentration for both compounds. This is to be expected if the mass transfer to air for these compounds is rate limited. When the flow rate was increased, the concentrations decreased, again as to be expected. It should be noted that the air-phase concentrations are less than 1 ug/l, while at early venting times, concentrations as high as 15,000 ug/l in the flowing air were measured.

Air-phase concentrations for m-xylene are also presented. The concentrations are still very high and as such it does not appear to be operating with mass transfer limitations. The

Table 5-7. Results of flow rate reduction during soil venting.

Time (h)	Flow rate (ml/min)	C_{air} isopentane (ug/l)	C_{air} benzene (ug/l)	C_{air} m-xylene (ug/l)
23.1	30	0.28	ND(<0.1)	5318
23.5	8	0.92	0.40	5364
23.8	8	1.0	0.41	5841
24.2	30	1.1	0.51	5476
24.6	30	0.30	0.30	5371
25.2	30	0.20	0.15	4971
25.5	8	0.31	ND	4703
25.9	8	1.0	0.45	4707

data suggest that rate limiting behavior is only significant and important when the individual constituent levels are quite low in the remaining NAPL.

Flow interruption was another technique used to investigate mass transfer limitations during soil venting. Figure 5-13 shows the results for BTX during the flow interruption experiment. The data points (indicated by the arrows on the x axis) were measured in the first flowing air sample taken after the flow had been stopped and the column had been sealed for 6-10 hours. The first set of points at 1 hour venting time show an increase in TX concentration after venting was resumed, from the point immediately prior to stopping the flow. Benzene, however, shows a sharp decline initially. The concentration for B appears to go back to expected values after about an hour.

Flow interruption after three hours, shows a similar trend, except that now the toluene shows a sharp decline, while m- and o-xylene show an increase. The reason for the drop in concentration is not clear. It does not seem to stem from mass transfer limitations, otherwise all compounds would show an increase in concentration. A likely explanation may be the variation in gasoline constituent makeup at different depths in the column, suggested earlier. During the time when the flow had been turned off, the air in the column would equilibrate with all the gasoline in the column, perhaps further altering the constituent makeup of the residual gasoline. Toluene that volatilized from the lower portion of

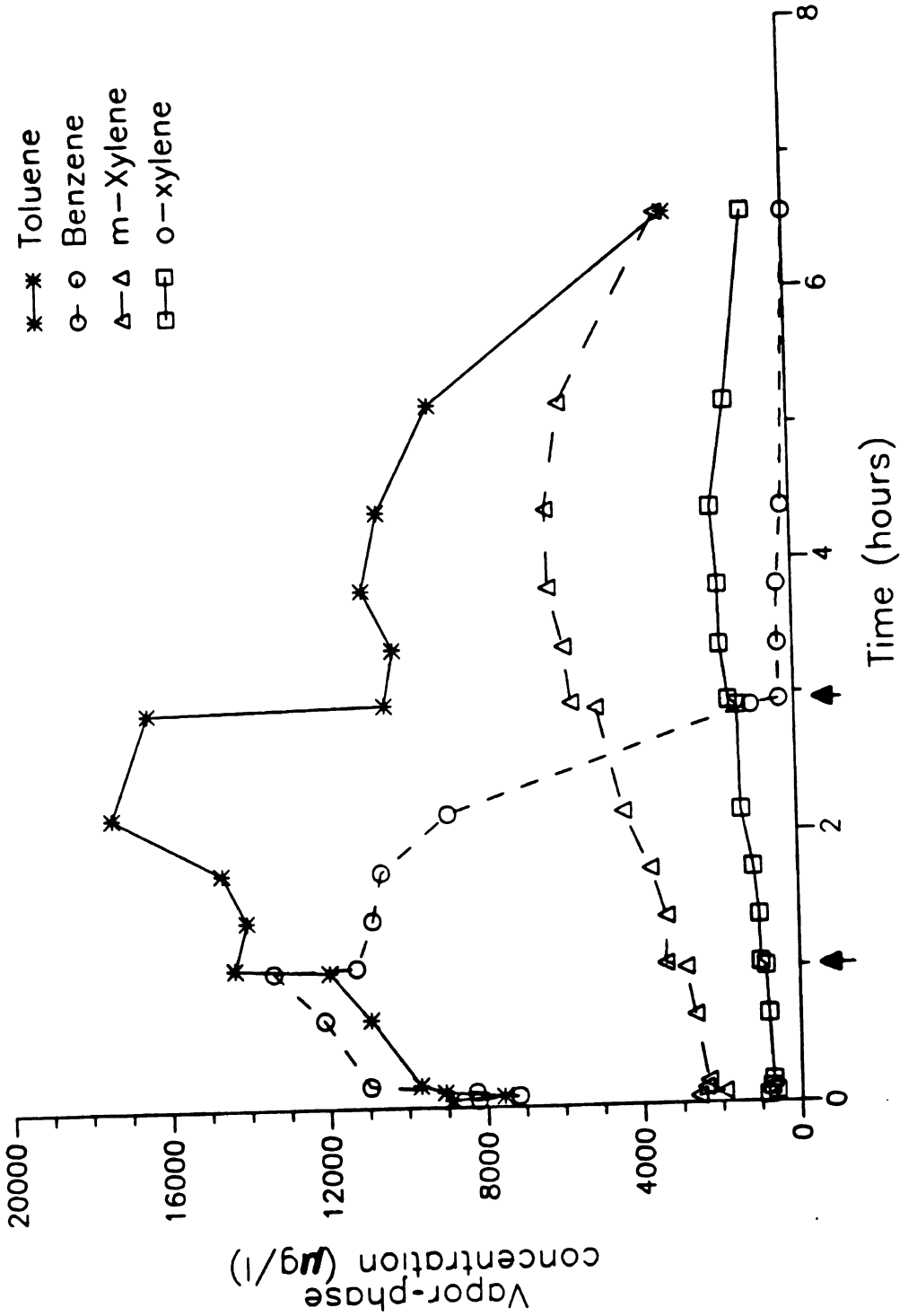


Figure 5-13. Flow interruption during soil venting.

the column may condense or adsorb in the upper portion of the column while the column is sealed. Once flow is resumed, the concentration of toluene in the outflowing air from the column would be at chemical equilibrium with the gasoline in the lower portion of the column. This gasoline would now have a lower mole fraction of toluene because of redistribution of compounds during the time when the column was sealed. This would explain why there was a decrease in the toluene air concentration. This may also explain why it took a long time for the toluene data to return to expected values.

The last technique used to study mass transfer limitations was discrete soil sampling and subsequent static headspace measurements of the soil samples. Table 5-8 shows static headspace results for soil samples taken 400 minutes after venting started, in a 10 cm soil column packed with Croswell soil, and then at 3100 minutes after the start of venting from the same column. Soil samples were taken from the top of the column.

There is an increase in benzene concentration in the static air sample over that of the flowing air sample taken from the bottom of the column, 400 minutes after venting was initiated. The benzene in the flowing sample is at non-detectable levels (<5 ug/l), while toluene and m&p-xylene have very high flowing concentrations (>8000 ug/l). The static air concentration levels for BTX are all measurable, in the 20-50 ug/l range. The concentration of benzene in the static air samples are higher than in the flowing air samples. This

Table 5-8. Flowing and static headspace air samples for early and later venting times (ug/l).

	Early Venting, Scaled Time (2990) (400 min)		Later Venting, Scaled Time (23200) (3100 min)	
Compound	Flowing	Static	Flowing	Static
benzene	ND (<5)	20.5	0.65	4.7
toluene	11,540	22.4	0.75	6.6
m-xylene	8,526	56.7	0.36	3.5
naphthalene	18.2	49.7	61.1	7.7

indicates that benzene has been depleted in the NAPL throughout the length of the column. The higher concentration in static air samples over flowing samples would occur if the mass transfer of benzene was rate limited. The static levels for toluene and m&p-xylene are 2-3 orders of magnitude lower than flowing levels. This suggests that these compounds have been significantly depleted from the top of the column (where the static soil samples were taken).

Naphthalene has flowing air concentration of 18.2 ug/l and a static air concentration of 49.7 ug/l. For this constituent which has a low vapor pressure, rate limiting behavior is probably not the explanation. What is more likely is that naphthalene has been enriched in the residual NAPL of the upper layers of the column. This is due to the depletion of high vapor pressure compounds evidenced by the low concentrations of TX in the static soil samples. The air samples taken from the outlet of the column reflect the NAPL at the bottom of the column. The mass fractions of toluene and xylene in the NAPL at the bottom of the column are still high enough to provide high concentrations of toluene and m-xylene in the flowing air. Because TX and many other compounds are still present in the NAPL, the mass fraction of naphthalene is lower in the NAPL at the bottom of the column than at the top of the column. The flowing air concentration of naphthalene is, therefore, reduced. This could only occur if naphthalene was condensing down the length of the column.

At later venting times (3100 min), BTX are all showing

signs of rate limiting behavior, as evidenced by higher static air concentration compared to flowing air concentrations. Naphthalene now has become enriched in the remaining residual at the bottom of the column and high naphthalene concentrations in the flowing air samples are the result. Static headspace measurements from soil samples taken from the top of the column for naphthalene are quite low. This indicates that longer venting times will eventually reduce naphthalene contaminant levels in the soil. This point was not reached for the residual gasoline at the bottom of the column for this experiment.

Soil samples were also taken from four soil columns, 4 cm in length, that had been vented for 25 hours. Soil samples were taken from both the top and bottom of the columns. The average concentrations for BTX and naphthalene for both flowing and static air samples are shown in Table 5-9. The data suggest that the mass transfer of BTX is rate limited, as evidenced by the order of magnitude increase in concentration of the static air sample over the flowing air sample. The results also suggest that there is little difference between BTX levels from samples taken at the top or bottom of the column.

Results for naphthalene suggest that flowing air is in equilibrium with the bottom of the column and that its mass transfer can still be described by local equilibrium. The fact that naphthalene and other heavy compounds are still present in the soil after BTX levels have been drastically

Table 5-9. Average final flowing and static headspace air results taken from four soil columns vented for 25 hours (scaled time = 24000), in ug/l, standard deviations shown in parentheses.

Compound	Final Flowing	Static Headspace From Top	Static Headspace From Bottom
benzene	0.203 (0.17)	31.2 (8.63)	34.7 (15.6)
toluene	0.773 (0.12)	34.8 (11.4)	36.8 (13.9)
m-xylene	1.54 (0.78)	15.4 (4.99)	19.4 (8.44)
o-xylene	0.808 (0.68)	6.46 (1.61)	9.27 (3.11)
naphthalene	63.21 (16.8)	17.6 (21.1)	72.8 (16.2)

reduced is important. The net mass fraction of the heavy compounds has been increased and they may pose a significant threat to groundwater. Cleanup criteria should emphasize removal of certain heavy constituents to ensure that these do not pose a further health risk.

5.5.4. The effect of organic matter on soil venting

It is often difficult to compare venting results from different soils and different columns because of small differences in the initial and operating conditions of each column. Scaling (Figures 5-7 and 5-8) discussed earlier in this Chapter) allows comparisons to be made between different columns and different soils.

Scaled data (Figure 5-7) suggest that at early venting times, there is no difference in the mass transfer of gasoline constituents to air between the Croswell (inorganic) or AuGres (organic) soil contaminated with gasoline. The presence of NAPL dictates that air is at equilibrium with the residual gasoline. Figures 5-11 (a and b), which represent Croswell (without organic matter) and AuGres (with organic matter), further substantiate this claim. The initial conditions for both columns are presented in Table 5-10. It should be noted that the AuGres soil has approximately 10 times the organic matter content and a correspondingly much higher moisture content than the Croswell soil. Neither of these factors, however, affected the mass transfer process during the early stages of venting. This is in agreement with the results of the single-component venting experiments, as well.

Table 5-10. Initial conditions for AuGres and Croswell soil columns shown in Figures 5-1 3.

Column	% Organic Matter (by Weight)	% Residual Water (by Volume)	Residual Gasoline (g)
AuGres	3.0	21.53	1.26
Croswell	0.20	3.40	1.60

Table 5-11. Final flowing air concentrations for BTX and naphthalene from eight soil venting columns (ug/l), scaled time = 24000.

Treatment	Compound	Replicates			
		(1)	(2)	(3)	(4)
AuGres soil (organic)	benzene	0.42	0.76	0.81	0.77
	toluene	0.93	1.16	1.44	1.55
	m-xylene	1.06	0.53	1.08	2.30
	naphthalene	69.3	69.6	62.4	33.4
Croswell soil (inorganic)	benzene	<DL*	<DL*	<DL*	<DL*
	toluene	0.55	0.82	1.04	<DL*
	m-xylene	0.89	1.30	1.02	1.85
	naphthalene	60.7	53.7	29.6	48.5

* A value of 0.40 was used for determination of statistical significance.

DL less than 0.40 ug/l.

At later venting times when the NAPL had been depleted, there are some differences observed in flowing air concentrations for benzene and toluene in soils with and without organic matter. Table 5-11 summarizes the results from paired vented columns packed with either AuGres (organic) or Croswell (inorganic) soil. The statistical difference for the means of the flowing air concentration of BTX and naphthalene for each soil was tested by the F ratio and an analysis of variance. The difference in means for benzene was significant at the $p = 0.02$ level. The difference in means for toluene was significant at the $p = 0.04$ level. There was no significant difference in the mean concentrations for m&p-xylene and naphthalene between the two soils.

Two possible explanations for the difference in BT concentration means are: 1) there was a greater residual in the AuGres soil than in the Croswell soil; and/or 2) there were differences in mass transfer of BT for the two different soils. Results presented earlier for these soil columns indicated there was no statistical difference in the initial retained gasoline. However, at later times, the soil with the high organic matter content may have a greater contaminant mass content due to gasoline constituents that have partitioned into the organic matter. This may be very important.

At later venting times there is evidence of rate limited transfer, therefore, differences in the rate at which air is moving through the soil pores could be important. The average number of pore volumes of air moved through 4 columns each of

AuGres and Croswell soil is shown in Table 5-12. Although the same air flow rate was used, differences in porosity resulted in a greater number of pore volumes for the AuGres soil, for the same volume of air. If the system is always at local equilibrium, then only the total volume of air would be important, however, when mass transfer becomes rate limited then air moving through the soil faster will pick up less contaminants than slower moving air. This is the opposite of what was observed, since the AuGres soil had a greater number of pore volumes but also has higher flowing air concentrations than the Croswell soil.

These data suggest that partitioned contaminants into the organic matter becomes significant at later venting times, resulting in higher mass retained in the soil after depletion of the NAPL. It should be emphasized, however, that final flowing air concentrations after venting were around 1 or 2 ug/l for BTX, and from a practical sense, differences due to organic matter can probably be ignored.

Overall the presence of organic matter does not affect the venting process. This is because during the bulk of gasoline removal, the properties of the NAPL, not the soil, govern the mass transfer process.

5.6. SUMMARY AND CONCLUSIONS

Pure-phase saturated vapor concentrations were determined for two multicomponent NAPLs at ambient conditions using experimentally determined air phase concentration, mole

Table 5-12. Average pore volume determination for 4 Croswell and 4 AuGres post-vented soil columns.

Soil	Porosity	Effective Porosity	Volume Air Through Soil (L)	Pore Volumes
Croswell	0.403	0.365	47.7	1310
AuGres	0.502	0.284	46.9	1650

fractions and Raoult's law/ideal gas law calculations. The two hydrocarbon NAPLs used were gasoline and a 5 compound mixture made in the laboratory. Predicted pure-phase saturated vapor concentrations were compared to literature values determined for pure compounds. Although the two multicomponent NAPLs contained significant fractions of aromatic and aliphatic hydrocarbon compounds, of various volatilities, their partitioning behavior to air was adequately described by Raoult's law and the ideal gas law.

The local equilibrium assumption for describing mass transfer from NAPL (in soil) to air was evaluated in three ways: a) venting a single component NAPL in soils and beads; b) comparing soil venting data from gasoline contaminated soils to a local equilibrium based model simulation of the experiments; and c) through experimental techniques including flow rate reduction, flow rate interruption and discrete soil sampling.

Soil venting a single component residually held NAPL showed that there was no difference between soils or beads. In all cases, the concentration of toluene in the air from venting columns was at saturated levels until the NAPL was depleted. Mass transfer was operating at local equilibrium.

The use of the local equilibrium model also supported the claim that mass transfer of constituents from a multicomponent NAPL to air is operating at equilibrium. The local equilibrium assumption is generally valid for venting gasoline contaminated soil.

Experimental techniques revealed that mass transfer limitations exist after significant depletion of a constituent from the gasoline has occurred. At times of high constituent concentration in the residual NAPL, local equilibrium was observed.

This is an important conclusion from a practical standpoint. It suggests that as long as air can reach the NAPL, the air will become saturated based on near ideal (Raoult's Law) partitioning. Apparent rate limiting behavior often exhibited at field sites may be due to: 1) air bypassing caused by soil or liquid heterogeneities at the site; or 2) the venting system layout and design, which results in poor control of the air flow path in three dimensions. In any case, the result is that less contaminated air is mixed with highly contaminated air and the outflowing air becomes diluted, resulting in lower contaminant air concentrations than predicted. When the system is turned off and allowed to equilibrate, all air will become contaminated and the initial concentrations once venting is started again are high. They may not be as high as when venting first started because some removal will have taken place. The air concentrations will then fall back relatively quickly to lower levels because of dilution with less contaminated air.

The presence of the NAPL dominates the mass-transfer process, such that differences in mass transfer would not be expected based on organic matter content of the soil. Two different soils, with similar properties but different organic

matter contents, were used in venting experiments to test this hypothesis. Organic matter does not affect the mass transfer of gasoline constituents to air at early venting times. It does show an affect at later venting times.

CHAPTER 6

LEACHATE CHARACTERISTICS OF GASOLINE CONTAMINATED SOIL PRE- AND POST-VENTING

6.1. INTRODUCTION

Leaks and spills of gasoline into the soil threaten groundwater because gasoline can be a long-term source of soluble gasoline constituents such as; benzene, toluene, and xylenes (BTX). Remediation techniques, such as soil vapor extraction, are designed to remove contaminants from soil thereby eliminating their potential for contaminating groundwater.

Cleanup assessment for a vented site is often based on individual contaminant concentrations remaining in the soil and groundwater. Contaminants remaining in the soil after soil venting can threaten groundwater because they can be a source of further contamination. Monitoring groundwater contaminant concentrations at a field site are meant to be an indicator of contamination potential but can be misleading. Significant volumes of clean water from uncontaminated areas may enter the well resulting in sample dilution. Intensive soil sampling is generally performed before and after venting

a gasoline contaminated site, but problems with sampling procedure, storage, handling, measurement and interpretation may lead to erroneous conclusions about the contamination potential of the site. A better understanding of leaching behavior of a multicomponent NAPL in vadose zone soil may aid in predicting site contamination potential as well as field data interpretation.

The effectiveness of soil venting for removing low vapor-pressure constituents from the residual NAPL is not clear. These constituents may persist in the soil after venting has ceased posing a threat to groundwater. There is increasing concern about the heavier constituents of gasoline, naphthalene and other multiple benzene ring compounds, because of their suspected carcinogenicity and possible persistence.

The focus of study presented in this chapter was to determine the efficacy of soil venting for reducing groundwater contamination. This was performed by investigating leachate characteristics from gasoline contaminated soil columns before and after laboratory venting.

6.2. BACKGROUND

Understanding the NAPL-water mass transfer process in porous media has been of interest as it relates to groundwater contamination and contaminant transport. Past studies have shown that contaminants leach from residual NAPL in porous media based on their equilibrium partition coefficients (van der Waarden et al. 1971, Pfannkuch 1984, Anderson et al. 1987,

Hunt et al. 1988, and Miller et al. 1990). Zalidis et al. (1991) specifically looked at leaching of BTX from residually held gasoline in soil columns with unsaturated flow conditions. They found that BTX concentrations in leachate remained at equilibrium levels during the course of their experiments.

Equilibrium partitioning of BTX and naphthalene from gasoline and other solvents to water was investigated by Cline et al. (1991). They determined distribution coefficients based on the following equation:

$$K_{d,i} = C_{oil,i}/C_{w,i} \qquad (6\text{-}1)$$

where $C_{oil,i}$ and $C_{w,i}$ are solute concentration (mol/l) in the organic and aqueous phases. They reported that fuel-water partition coefficients could be estimated based on reported solubilities and Raoult's law:

$$C_{w,i} = X_i S_{w,i} \qquad (6\text{-}2)$$

where X_i is the mole fraction of constituent i in the gasoline and $S_{w,i}$ is the pure phase solubility of constituent i. Assuming the organic phase to be an ideal mixture of liquids, Equations 6-1 and 6-2 were combined and restated as follows:

$$K_{d,i} = C_{oil,i}/X_i S_{w,i} \qquad (6\text{-}3)$$

$$C_{oil,i}/X_i = (Mol_i/V_{oil})/(Mol_i/Mol_T) \qquad (6\text{-}4)$$

$$C_{oil,i}/X_i = (Mol_T/V_{oil}) = p/MW \qquad (6\text{-}5)$$

$$K_{d,i} = [10^3(p/MW)]/S_{w,i} \qquad (6\text{-}6)$$

where Mol is moles, V_{oil} is the volume of oil, p is the density and MW is the weighted average molecular weight of gasoline. They found that for many of the aromatic compounds

found in gasoline some deviations from Raoult's law existed. The deviations tended to result in somewhat higher aqueous phase concentrations than those predicted based on Raoult's law (Cline et al. 1991). The implications of this are that slightly higher concentrations of BTX may leach from a gasoline spill site than would be predicted based on Raoult's law. The fact that deviations from Raoult's law may exist could be important for predicting the transport of individual constituents from the contaminated site. Understanding the partitioning process from a NAPL to water is also important for proper data interpretation at contaminated sites.

The partitioning behavior of complex organic mixtures to water has been investigated by others (Coleman et al. 1984, Banerjee 1984 and Al-Sahhaf 1989). These studies did not utilize porous media. Banerjee (1984) found mixtures containing chemically similar hydrophobic liquids exhibited near ideal behavior, i.e. activity coefficients in the organic phase were equal to 1, therefore Equation 6-2 could be employed. Deviations from ideality in hydrophobic mixtures were generally attributed to variations in activity coefficients in the organic phase and not the aqueous phase.

Very few studies have investigated aqueous-phase gasoline contaminant concentrations for gasoline contaminated porous media. Some notable exceptions include Wootan and Voynick (1983), Borden and Kao (1989) and Zalidis et al. (1991). Borden and Kao (1989) investigated water flushing of trapped residual gasoline in a water saturated soil column. The

dissolution of BTX exhibited an early equilibrium period, a period where BTX effluent concentrations decreased rapidly and a period when BTX effluent concentrations slowly decreased. Zalidis et al. (1991) studied dissolution of residual gasoline with unsaturated flow conditions and found BTX concentrations remained at equilibrium levels.

Wootan and Voynick (1983) investigated aqueous-phase gasoline concentrations during a simulated venting process. They measured groundwater concentrations of "light" and "heavy" gasoline constituents in an aquifer model that had a pool of gasoline on the water table. They noticed that there was a shift in constituent type in the water, from "lighter" to "heavier" compounds during venting. This shift would be expected as high vapor-pressure compounds are removed quickly from the NAPL, resulting in an increase in mole fractions of low vapor-pressure constituents. Increases in mole fractions would result in increases in aqueous phase concentration.

A study related to hydrocarbon venting was performed by Burris and MacIntyre (1986). They allowed a hydrocarbon mixture to float on pure water while the headspace above the hydrocarbon mixture was continually purged with clean N_2. They measured hydrocarbon concentrations in the water and in the hydrocarbon mixture as a function of time. They observed that the higher vapor-pressure compounds were the first to show a decrease in aqueous-phase concentration in response to their decreasing mole fraction in the hydrocarbon mixture. The hydrocarbon phase composition, they concluded to be one of

the important controlling factors for aqueous-phase concentrations.

Baehr (1987) developed a mathematical model which predicted gasoline constituent partitioning into unsaturated zone water as a function of time. The simulated results showed the changing concentration of constituents in the aqueous-phase due to selective removal of individual constituents. Experimental data, however, was not presented.

6.3. OBJECTIVES

The specific research objectives have been to:

1. Characterize gasoline-water partitioning behavior for the gasoline used in this study.

2. Determine the effect of organic matter on effluent concentrations of various aromatic constituents of gasoline for contaminated soils before and after soil venting.

3. Determine the efficacy of soil venting for reducing aqueous-phase concentrations of gasoline contaminated soil.

6.4. MATERIALS AND METHODS

6.4.1. Gasoline-water partitioning

Gasoline-water partition coefficients were determined on fresh and weathered gasoline samples. The procedure used was modified from API (1985). Approximately five milliliters of gasoline sample was transferred to a 20 ml headspace vial containing 15 ml of DI water. This left virtually no headspace in the vial. The vials were mixed for two hours using an end

over end mixer and centrifuged (480 x g) upside down so that the water would be in contact with the teflon septum. Five milliliters of sample were withdrawn using a 5 ml gastight syringe, put in headspace vials and crimp capped.

The samples were heated to 80^{0}C in a headspace auto-sampler and analyzed using gas chromatography (DB-624 megabore column 50m*0.53mm i.d., J&W Scientific) with a flame ionization detector. Calibration determination is described in Appendix B.

6.4.2. Experimental setup

The same packed soil columns used in the laboratory venting experiments were used in the leaching experiments. Upon completion of the venting experiment, the stainless steel screen was replaced with a stainless steel pressure plate. All o-rings were replaced with newly washed and oven dried o-rings that had not been in contact with gasoline. The stainless steel end parts were replaced with clean oven dried ends.

The soil was saturated with 0.001 M $CaSO_4$ deaired distilled water by allowing it to slowly infiltrate from the bottom of the column. This was allowed to equilibrate overnight.

Unsaturated leaching was initiated by first taking several equilibrated water samples. A sample was taken with a glass syringe connected to the outlet by a stainless steel tube and fitting. The syringe was housed in a vacuum flask with a 80 mbar vacuum. The near frictionless glass syringe

allowed the vacuum to be transferred to the bottom of the pressure plate (Figure 6-1).

Water flow at 2 ml/min was initiated using a syringe pump (model 22, Harvard Apparatus, Inc. S. Natick, MA) when excess water from the soil had been drained. Water samples were generally collected daily. When sampling, more than 5 ml of leachate were collected. The excess liquid was discarded and exactly 5.0 ml were injected into a clean dry headspace vial. This was crimp capped and stored in the refrigerator until analysis, typically within 3 days. This method for collecting water samples insured minimal exposure of the sample to air.

6.5. RESULTS AND DISCUSSION

6.5.1. Gasoline-water partitioning

Estimated pure-phase solubilities, $S_{w,i}^*$, based on Raoult's law (Equation 6-2), aqueous-phase concentrations from the batch study and mole fractions for the gasoline used in this study were compared to pure-phase solubilities, $S_{w,i}$, from the literature (Mackay and Shiu 1981) for various aromatic and aliphatic constituents (Table 6-1). The estimated values in most cases are higher than the literature values. This may be expected because gasoline is a complex mixture of aliphatic and aromatic compounds and, therefore, may not behave in a truly ideal manner. A complete list of experimentally determined pure phase solubilities is presented in Appendix B.

Distribution coefficients were determined experimentally using Equation 6-1, calculated using Equation 6-3 for gasoline

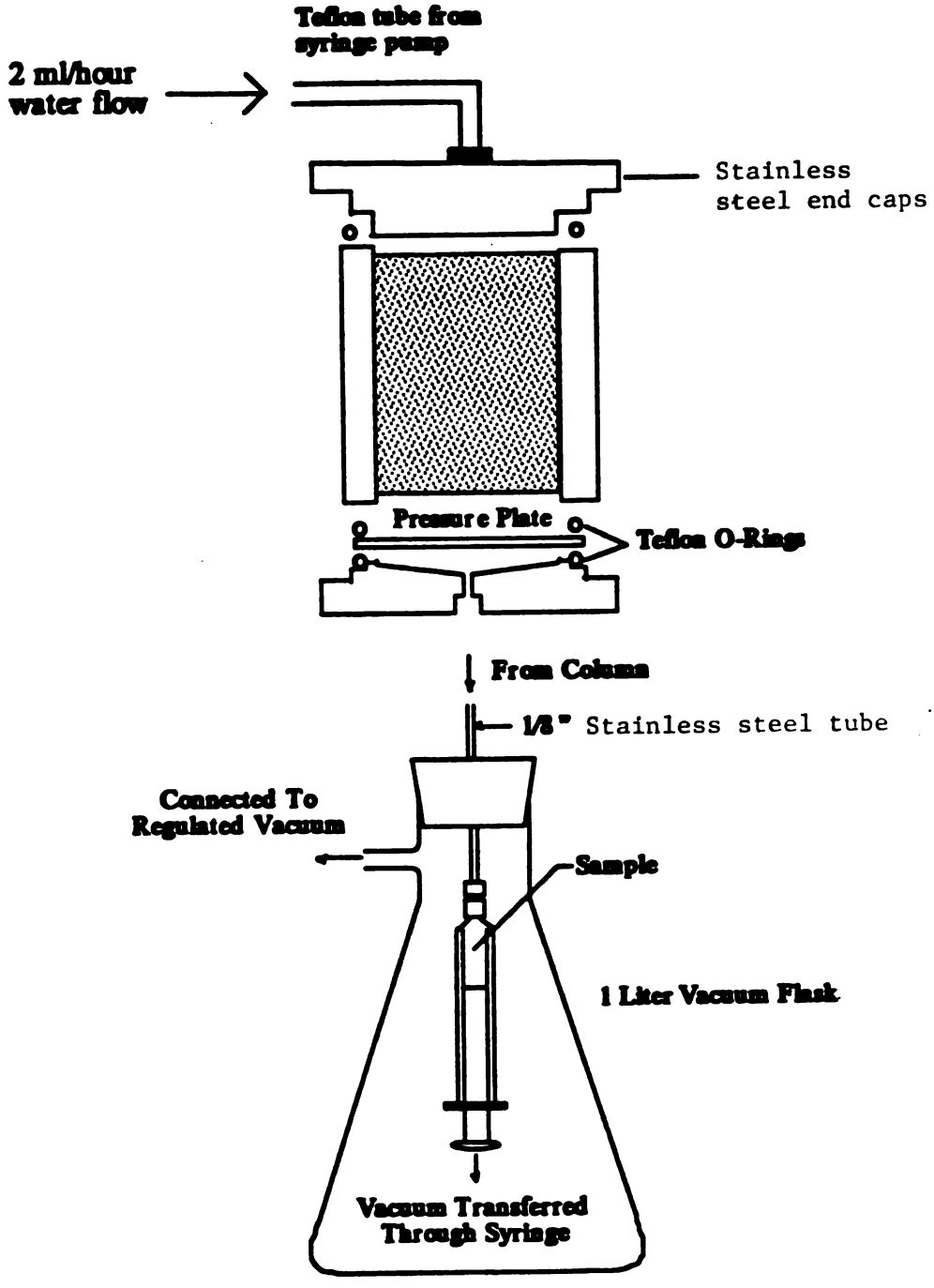


Figure 6-1. Unsaturated flow column setup.

Table 6-1. Experimentally determined pure phase solubilities, S_w^*, for compounds in a mixture based on Raoult's Law, compared to S_w from the literature, mg/l.

Compound	S_w(25°C)[1]	S_w^*(24°C)
Benzene	1760	2580
Toluene	542	698
Ethylbenzene	165	193
m&p-Xylene	174	175
o-Xylene	221	216
Naphthalene	24.0[2]	108
n-Hexylbenzene	1.02	14.7
1-Methylnaphthalene	28.0	20.2

[1] Yaws and Yang (1990).
[2] Chiou (1989) for supercooled liquid.

used in this study and compared to experimentally determined coefficients from Cline et al. (1991). These are presented in Table 6-2. Octanol-water partition coefficients (Chiou 1989) are also shown. Although there is some deviation from Raoult's law predictions, it does not appear to be extreme with the exception of naphthalene. The predicted $K_{d,N}^{*}$ for naphthalene, is more than four times the measured value from this study and 25 times the $K_{d,f}$ determined by Cline et al. (1991). For the other compounds, the predicted distribution coefficients using Raoult's law are generally higher than calculated values. They are about 40 % higher for benzene and toluene; 20 % higher for ethylbenzene; and within 5 % for the xylenes. This would result in lower predictions of aqueous-phase concentrations than would be actually be measured. The use of measured coefficients especially for benzene, toluene and naphthalene, therefore, is recommended. Characterization of the true residual NAPL may be sufficiently difficult and introduce considerable error such that deviations in predictions based on Raoult's Law may be less significant.

There is also good agreement in measured distribution coefficients between this study and the work by Cline et al. (1991), with the exception of naphthalene.

Measured distribution coefficients for gasoline-water are all considerably higher than octanol-water partition coefficients indicating that a hydrophobic compound in gasoline behaves more ideally than in octanol. This would be expected, since the constituents of gasoline are more hydrophobic than

Table 6-2. Measured and predicted gasoline-water distribution coefficients, $K_{d,i}$, and $K_{d,i}^*$, and octanol-water partition coefficients, K_{ow} for selected compounds.

Compound	$K_{d,i}$	$K_{d,i}$[1]	$K_{d,i}^*$	K_{ow}[2]
benzene	279	217	372	135
toluene	1030	687	1430	490
ethylbenzene	3730	4470	5390	1410
m&p-xylene	4120	4370	5110	1490
o-xylene	3320	3630	4030	1490
naphthalene	6680	1510	44800	2290

[1] Cline et al. (1991) BTN; C^{14} method, EX; GC/FID method.
[2] Leo et al. (1971)

octanol.

Overall, it appears that Raoult's law is generally applicable for predicting aqueous phase concentrations from complex mixtures such as gasoline and could be easily applied for predictive purposes at field sites. The use of experimentally determined distribution coefficients is recommended when available since these would result in more conservative estimates.

6.5.2. The effect of organic matter on effluent concentrations for pre- and post-vented soils

Two soil columns packed with Croswell and two packed with AuGres soil were brought to residual gasoline saturations and leached without being vented (pre-vented). Leachate concentrations for BTEX are shown in Figure 6-2 for one pair of soil columns. Overall, there is no discernable difference in leaching behavior between AuGres (organic) and Croswell (inorganic) soil, indicating that partitioning behavior at high concentrations is dominated by the presence of the NAPL and not the presence of organic matter in the soil. This would be expected based on partition coefficient results. For example, organic matter-water partition coefficients are generally one tenth octanol-water partition coefficients (Boyd and Sun 1990). Gasoline-water partition coefficients for BTX are generally higher than octanol-water partition coefficients (Table 6-2). Therefore, at residual saturations when a given constituent's mole fraction is large, for example benzene in pre-vented gasoline contaminated soil, the effect of organic

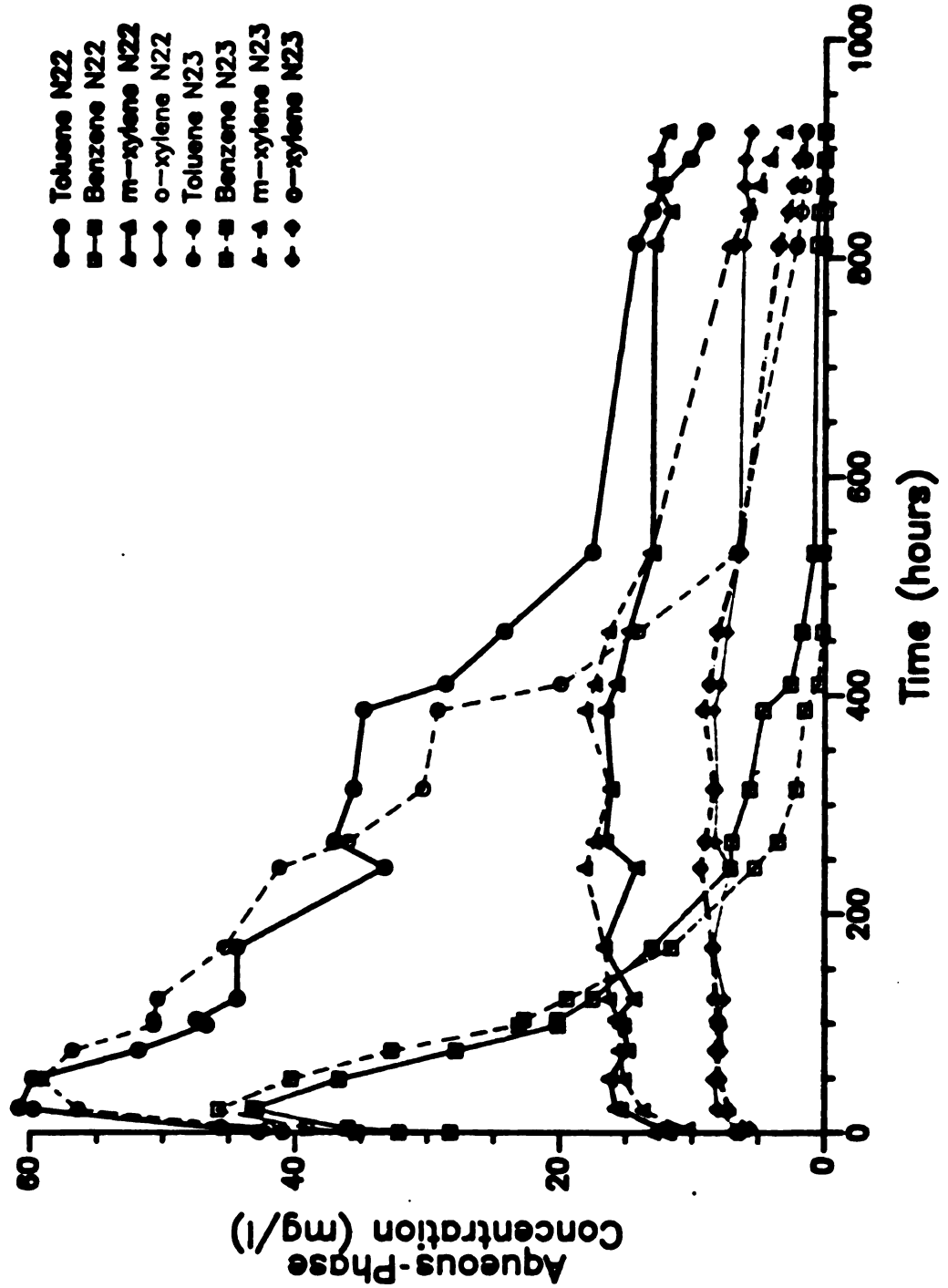


Figure 6-2. Comparison of leachate concentrations in pre-vented columns for AuGres and Croswell soil.

matter-water partitioning would generally be overshadowed by the effect of gasoline-water partitioning.

The data suggest an initial start up period in the leaching experiments; effluent concentrations start out low and then increase. This is probably caused by: sample dilution from uncontaminated water initially below the plate; or insufficient equilibration time for the water and NAPL of these early samples. It should be mentioned again that the column was initially saturated from the bottom, with an equilibration time of 24 hours. Several static samples were taken in quick succession when the vacuum was first applied. The first sample was discarded to take into account the presence of the uncontaminated water below the plate, however, insufficient removal of this water from below the plate could have accounted for the lower initial aqueous-phase concentrations. Insufficient time for all of the water to chemically equilibrate within the column is another possible explanation. No matter what the reason, this start up period was generally less than 24 hours and not believed to affect later results.

Average initial concentrations, after the start up period, for two columns are compared to equilibrated aqueous-phase concentrations from batch studies (Table 6-3). Average aqueous-phase concentrations of BTEX and naphthalene from two different gasoline samples analyzed six weeks apart (using different calibration curves) are presented in Table 6-3, columns 2 and 3. The results in column 2 are the average of two equilibrated aqueous samples. The results in column 3 are

Table 6-3. Average measured concentrations from initial column effluent samples, $C_{w,i}^{c}$, compared to batch samples, $C_{w,i}^{B}$ (mg/l).

Compound	$C_{w,i}^{c}$ (average of 2)	$C_{w,i}^{B1}$ (average of 2)	$C_{w,i}^{B2}$ (SD) (average of 4)
Benzene	40.3	41.9	40.5 (1.08)
Toluene	57.6	43.5	39.7 (2.59)
Ethylbenzene	4.50	3.99	3.16 (.202)
m&p-Xylene	14.0	12.6	9.53 (.798)
o-Xylene	6.75	5.99	4.55 (.390)
Naphthalene	0.710	0.546	0.328 (.068)

$C_{w,i}^{B1}$ gasoline sample referred to as fresh (Chapter 5).

$C_{w,i}^{B2}$ gasoline sample referred to as fresh & stored (Chapter 5).

the average of four equilibrated aqueous samples, and the standard deviation about the mean is presented in column 4. Concentrations of all the constituents of interest except benzene were higher in the column effluent than concentrations determined from batch experiments. Benzene is about the same. Zalidis et al. (1991) attributed their discrepancies in concentration to weathering of gasoline in the column. This seems a plausible explanation. Smaller columns were used in the experiments presented here and it seems possible that weathering was more severe and therefore had a greater impact on leachate concentrations. Differences in concentration results between batch experiments is probably also due to weathering of the gasoline used for the experiment. Herein, lies one of the greatest difficulties in working with and studying a multicomponent mixture such as gasoline; the likelihood of it changing chemical composition from mild to slight exposure to air. This results in alterations in partitioning behavior.

The local equilibrium based model, presented in Chapter 5, was used to describe the leaching process. However, the removal of gasoline constituents in these simulations occurred only as a result of partitioning into the water, i.e. there was no air flow. The change of mass over time in the column (Equation 5-3) was a result of equilibrium partitioning into the aqueous phase. It was necessary to input the water flow rate (instead of air) and the gasoline-water partition coefficients (instead of gasoline-air) described in this

chapters background section.

Predicted BTEX concentrations from the model compared to leaching data for two pre-vented columns are presented in Figures 6-3 and 6-4. Because the initial column effluent concentrations suggested that weathering of the gasoline had occurred, new mole fractions were determined for the constituents of interest based on the effluent concentrations, $C_{w,i}^{c}$, and the distributions coefficients. These values were used for the model input. Experimentally determined pure-phase solubilities were also used. This method was an attempt to account for the weathering of the residual gasoline in the column prior to leaching.

The model does a reasonably good job in predicting the overall trend of the data indicating that local equilibrium for the aqueous-phase is also a good assumption. However, aqueous-phase concentrations are higher than model predictions even with adjustments to the mole fractions. This suggests that the NAPL characterization of the residual gasoline may still be slightly inaccurate or that distribution coefficients for fresh gasoline may be different than distribution coefficients for residual gasoline. Cline et al. (1991) found variations in constituent distribution coefficients of 30% for different gasoline samples. It would therefore not be surprising to expect that residual gasoline (slightly weathered) would exhibit slightly different distribution coefficients than fresh gasoline. This implies that distribution coefficients may continually be changing over the course of

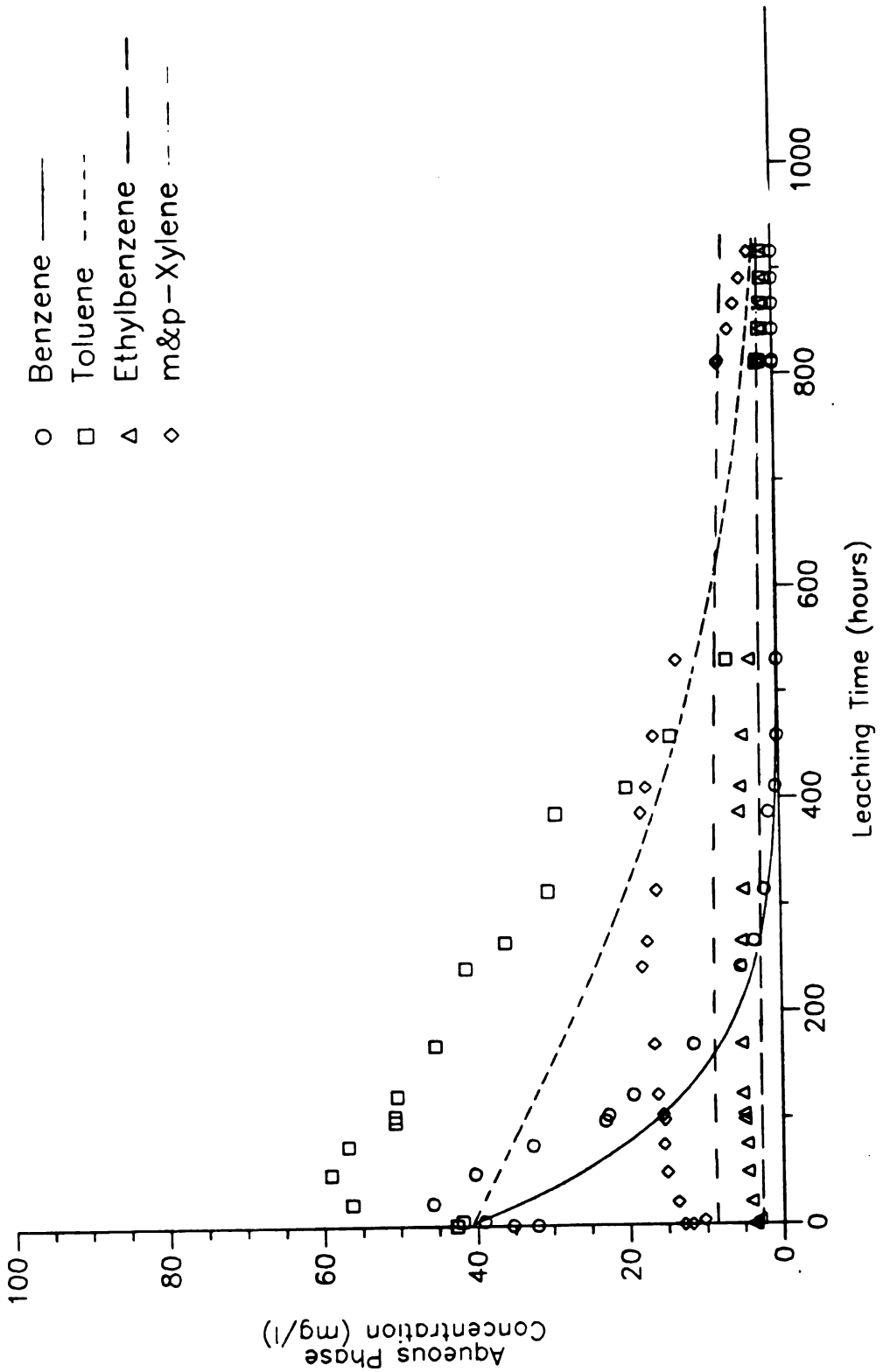


Figure 6-3. Model simulation of leaching for pre-vented Croswell soil.

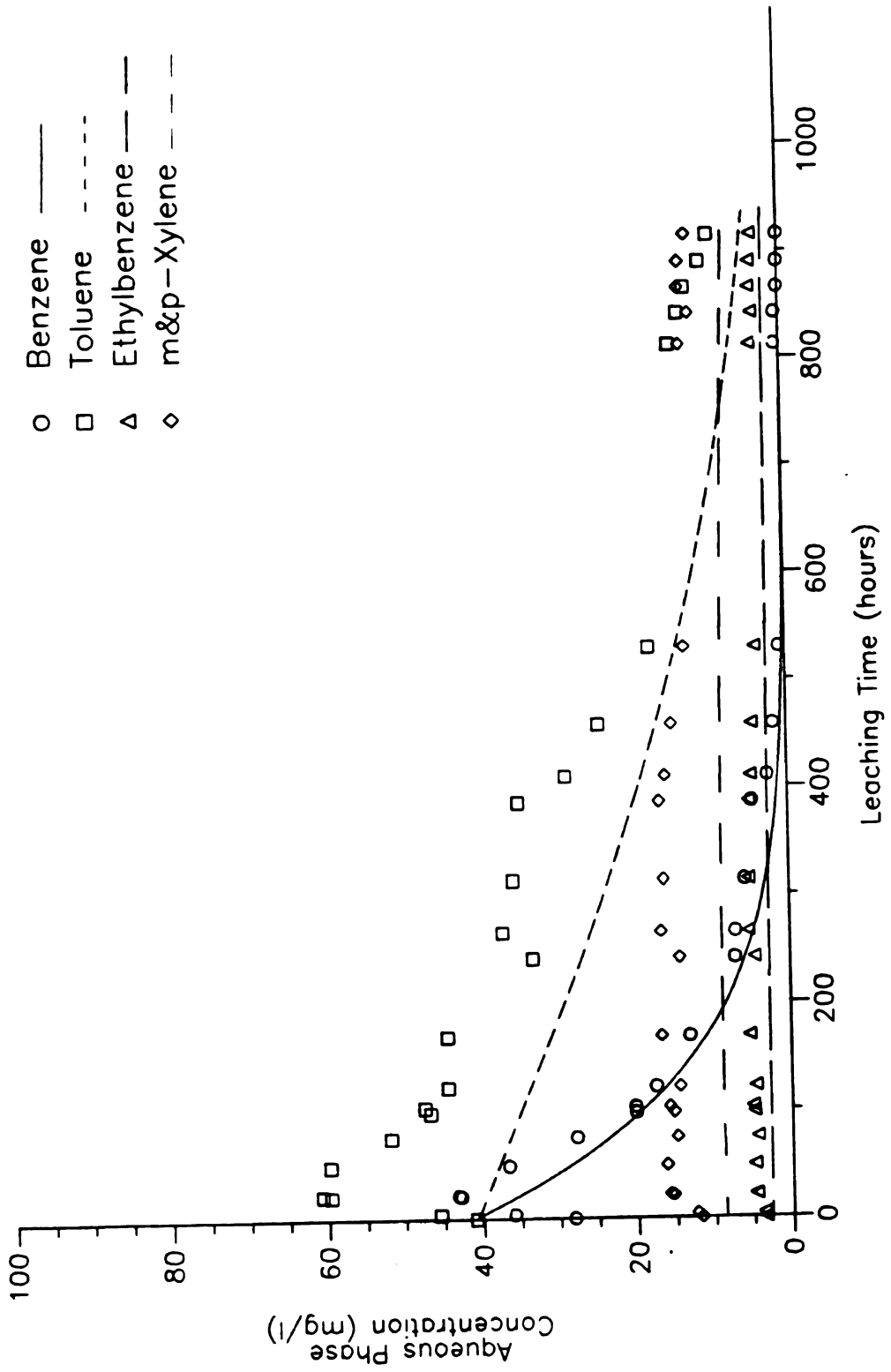


Figure 6-4. Model simulation of leaching for pre-vented Augres soil.

leaching. It is more probable that the greatest source of error is in the characterization of the residual. Characterization of fresh gasoline is only an approximation of the residual gasoline that is located in the soil columns, since changes to the gasoline can occur during the initial setup and over the course of the experiment.

For predictive purposes, however, the model may be adequate. It does tend to underestimate aqueous-phase concentrations. Using pure-phase solubilities from the literature (Mackay and Shiu 1981) in the model input file instead of experimentally determined values gave poor predictions of the data (Figure 6-5). Mole fraction data from fresh gasoline was used as the input file, and part of the poor fit may be due to differences in residual gasoline compared to the fresh gasoline. The poor fit may also be due in part to the use of pure phase solubilities, since these are generally lower than those determined experimentally. If this method were to be applied at a field site for predictive purposes, characterization of weathered samples of gasoline such as those pumped from the water table and experimentally determined distribution coefficients should be used.

After a venting operation, other methods may be necessary to predict aqueous-phase concentrations emanating from the spill site since directly characterizing the residual at that time would not be feasible.

Venting proved to be very effective in reducing BTEX leachate concentrations. Benzene effluent concentrations for

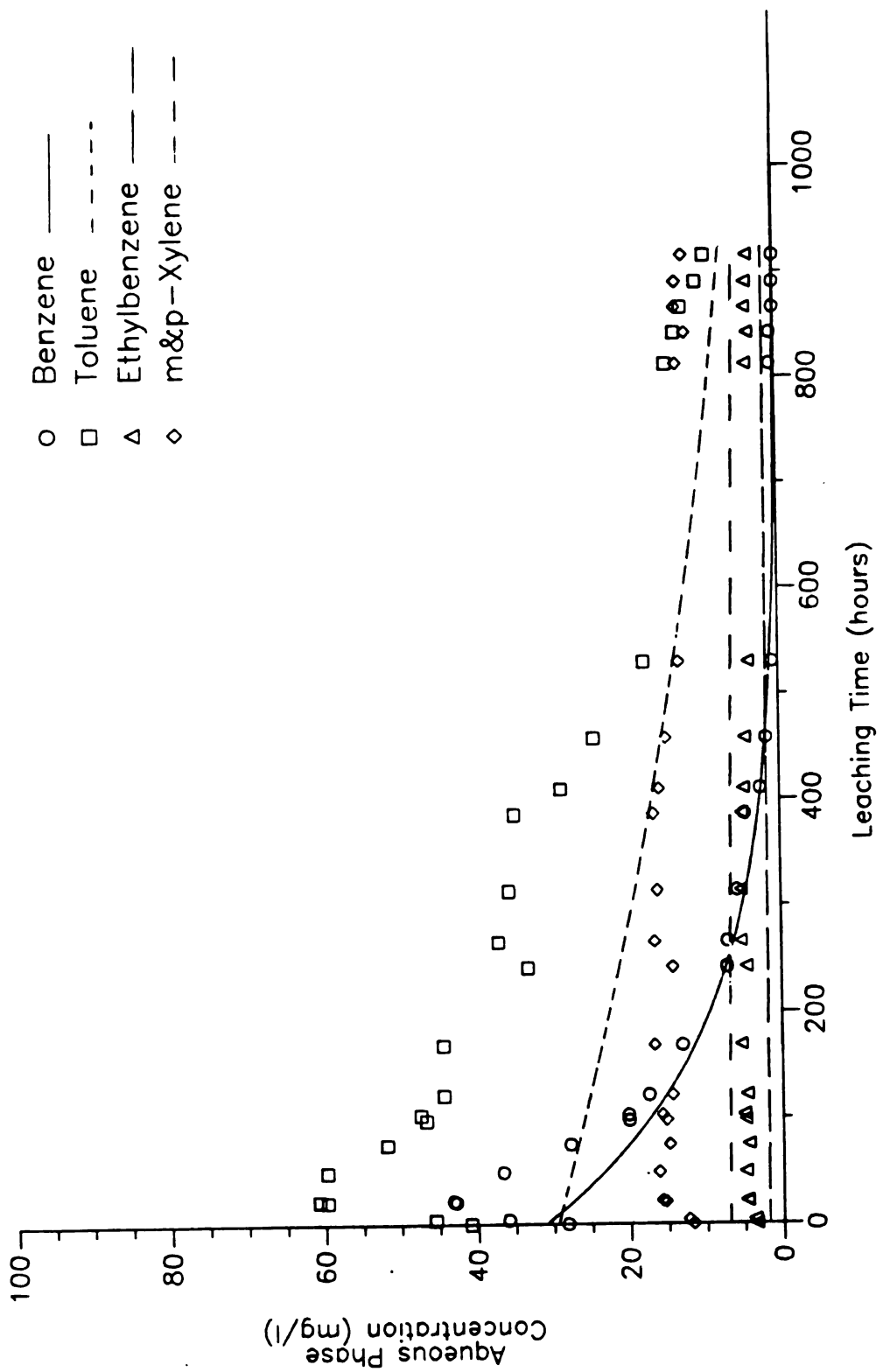


Figure 6-5. Model simulation of leaching for pre-vented Croswell soil.

pre- and post-vented soil columns (vented for 25 hours) are shown in Figure 6-6. There is a three order of magnitude decrease in benzene aqueous phase concentrations in vented column leachate compared to initial pre-vented leachate concentrations. Benzene concentrations after leaching for 35 days (not shown in figure) show a similar three order of magnitude decrease. Other constituents, such as ethylbenzene and xylenes, also exhibited similar decreases in leachate concentration for post-vented soils columns, however, for these constituents effluent concentrations from pre-vented columns during 35 days of leaching showed little decrease from initial levels. Figure 6-7 shows the effluent concentrations from pre-vented and post-vented columns for m&p-xylene. Much longer flushing times would be required to reduce the concentration of this constituent to post-venting levels as was the case with benzene.

Mass-transfer limitations in the aqueous-phase were not considered to be even partly responsible for the three order magnitude differences in pre- and post-vented leachate results. Annable (1991) described in detail leaching behavior from post-vented gasoline contaminated columns and showed that even at low aqueous-phase concentrations leaching behavior can still be described by a local equilibrium assumption.

For heavier constituents of gasoline such as naphthalene, aqueous-phase concentrations in column effluent increased in post-vented soils compared to pre-vented soils (Figure 6-8). Naphthalene concentrations show an increase. This is because

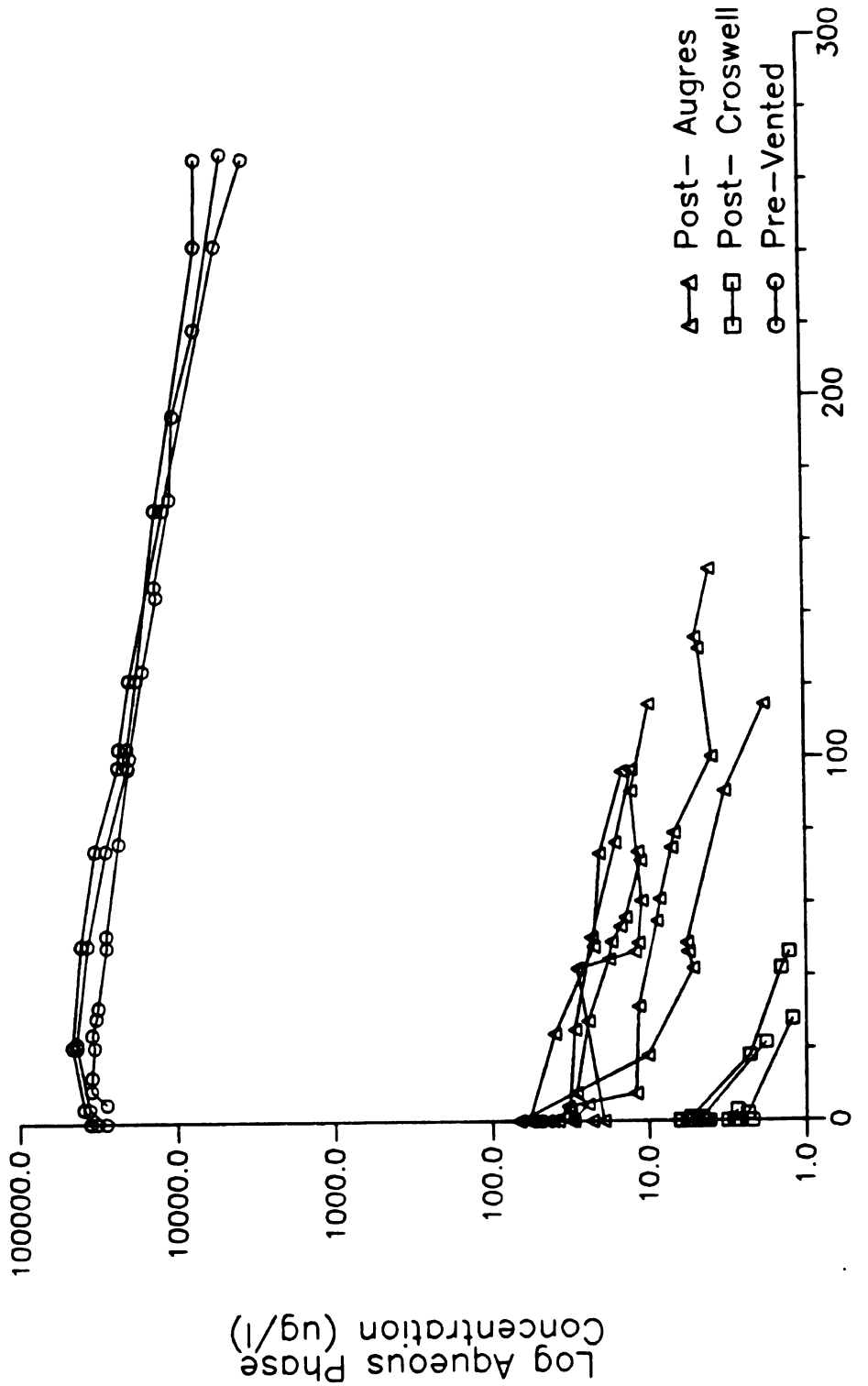


Figure 6-6. Benzene leachate concentrations for pre- and post-vented soil columns.

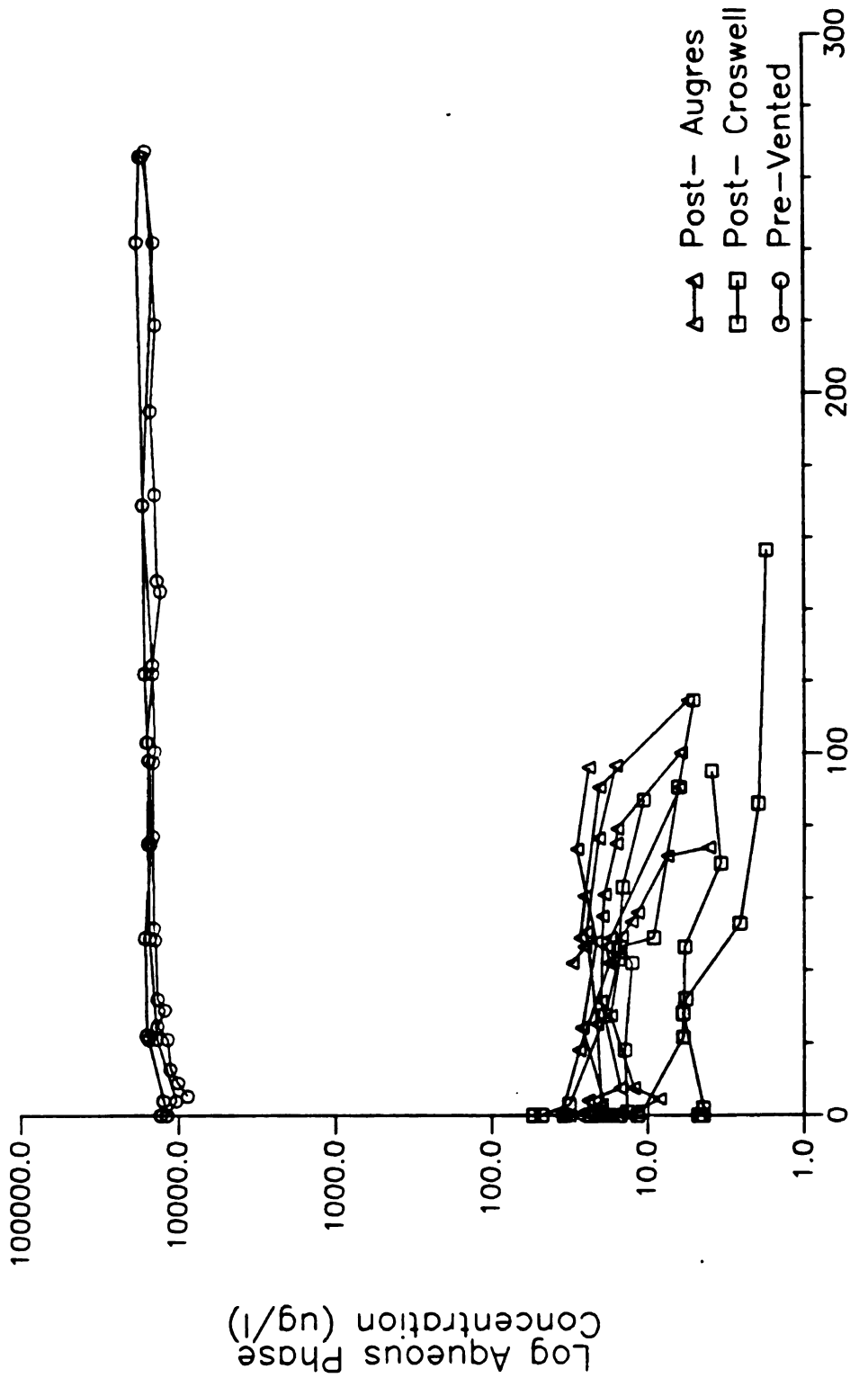


Figure 6- 7. m&p-xylene leachate concentrations for pre- and post- vented soil columns.

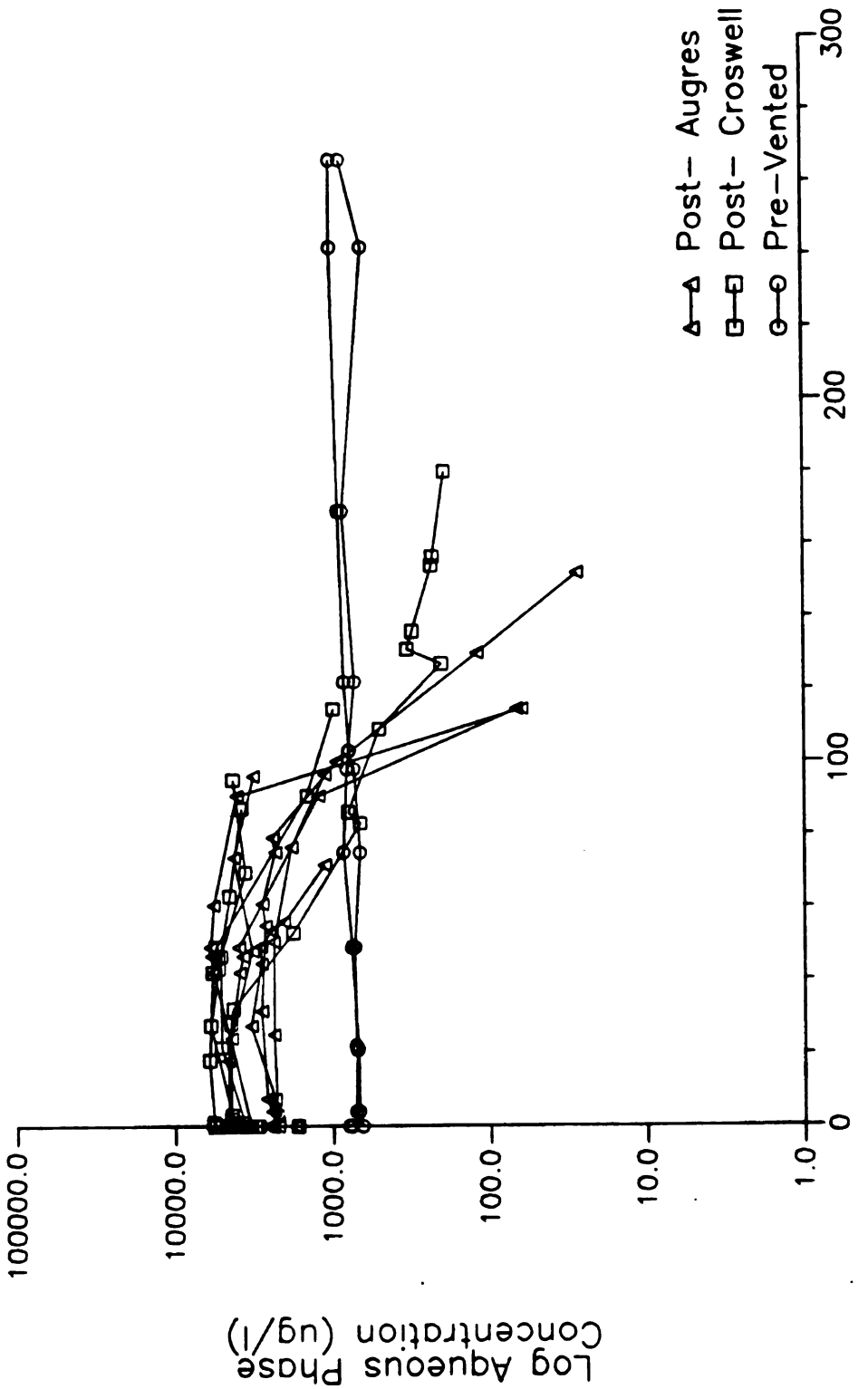


Figure 6-8. Naphthalene leachate concentrations for pre- and post- vented soil columns.

after 25 hours of venting, the naphthalene represents a higher percentage of the remaining residual gasoline. Soil venting selectively removed the high vapor-pressure constituents of gasoline, causing a net increase in the mole fraction of heavy less volatile components, such as naphthalene.

This is important from a practical standpoint since it is common practice to regulate remediation of a spill site based on measured BTX concentrations in groundwater samples. Concentrations of naphthalene and other heavy constituents may have increased to unacceptable levels. Annable (1991) showed that naphthalene could be reduced in the aqueous-phase after much longer venting times. A compound such as naphthalene, therefore, would provide a better indication of overall site remediation than other gasoline constituents, such as BTEX. Naphthalene measurements after venting should be a requirement for clean up assessment.

Organic matter seems to have an effect on leachate concentrations from post-vented soils. Figure 6-9 shows the results of post-vented soil column effluent concentrations for toluene. Soil type is indicated in the legend. To determine if this effect was statistically significant, an F test and analysis of variance were performed for post-vented leaching concentrations on paired Croswell and AuGres soil columns. Because the initial effluent samples may be subject to dilution or equilibration errors, a later time was used for the comparison. Effluent concentrations taken between 20 and 30 hours of leaching were compared. Table 6-4 presents

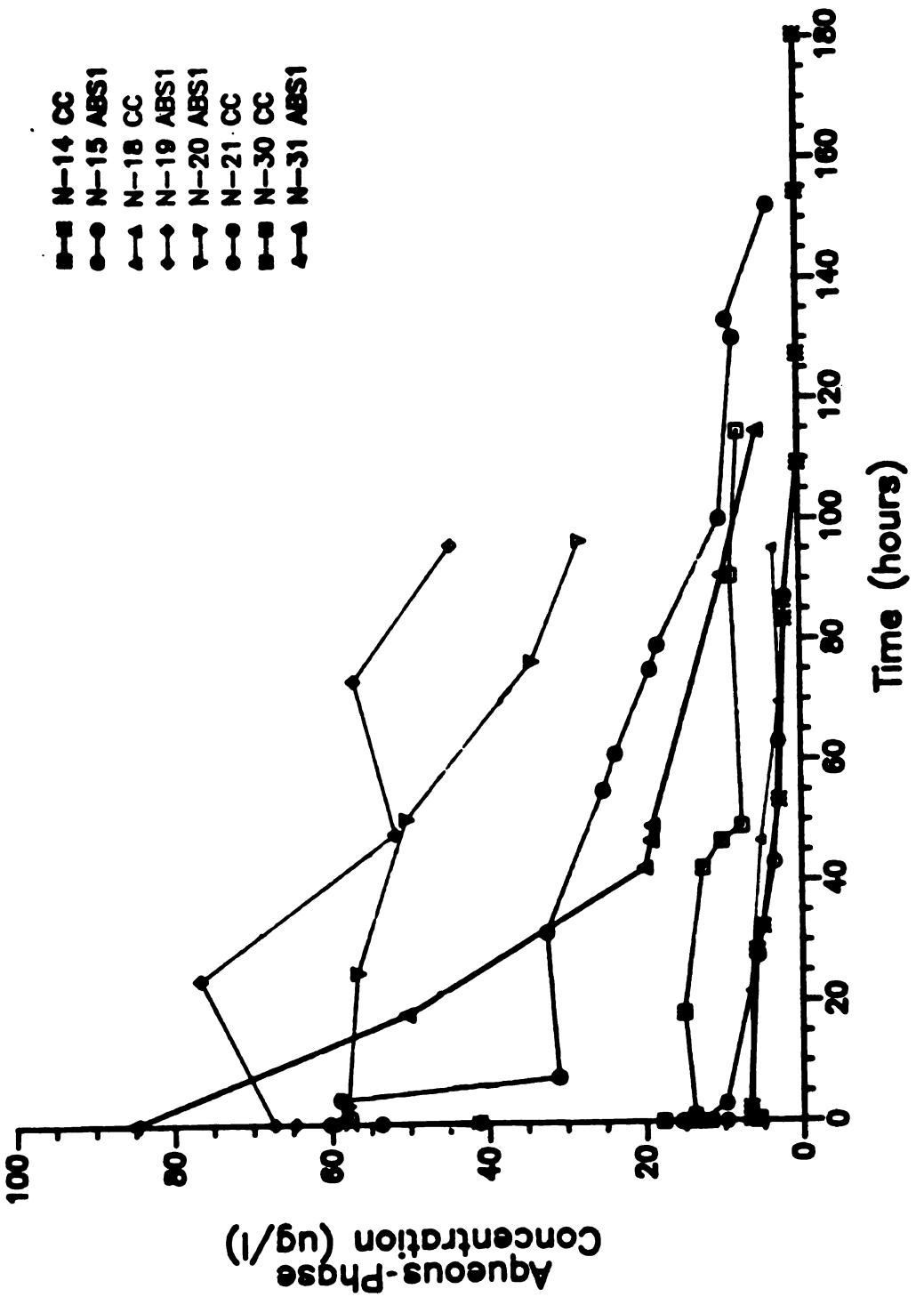


Figure 6-9. Toluene leachate concentrations from post-vented Croswell and AuGres soil.

Table 6-4. Comparison of measured post-vented column leachate concentrations taken between 20 and 30 hours leaching, from organic and inorganic paired columns (ug/l).

Treatment		B	T	E	m-X	o-X	N
AuGres	1)	10.1	50.3	7.23	27.4	15.9	4610
	2)	29.7	56.5	6.27	21.0	11.1	2370
	3)	39.8	76.5	7.96	26.1	14.7	4400
	4)	24.3	47.5	4.72	17.3	15.2	3320
	average	26.0	57.7	6.55	23.0	14.2	3670
Croswell	1)	2.28	15.0	3.20	14.0	7.59	6030
	2)	<1.0	5.55	4.36	18.8	12.3	5941
	3)	1.80	6.44	1.47	5.89	3.59	5084
	4)	1.22	5.70	2.37	5.92	3.08	4436
	average	1.57	8.18	2.85	11.1	6.65	5373

measured leachate concentrations from AuGres and Croswell soil columns. An analysis of variance and F test revealed that for all constituents of interest, the difference in the average leachate concentrations was statistically significant at the $p = 0.05$ level. For naphthalene, the difference was significant at the $p = 0.07$ level.

Two possible explanations for the concentration differences observed between soils are: 1) there was a greater residual in the AuGres (organic) soil than in the Croswell (inorganic) soil; and/or 2) there were differences in gas mass transfer of BTEX for the two different soils. A third possible explanation is that the organic matter acted as a sink for contaminants during the initial stages of venting. Partitioning into the organic matter may have affected its mass transfer to air during the remaining venting period.

Results previously presented for these same soil columns indicated that there was no statistical difference in retained gasoline. The differences in the naphthalene averages suggest that the columns may be at a different stage of the venting process. Higher concentrations in the Croswell soil indicate there is a higher mole fraction of naphthalene in the remaining residual NAPL. If the mass transfer process is at equilibrium throughout the venting process, then these results would only be possible if different masses of residual gasoline were present in the columns initially.

The appearance that the columns are at different stages in the venting process may also result from rate limited

behavior during the venting process. As shown in Table 5-12, a greater number of pore volumes of air passed through the AuGres soil than the Croswell soil, although the same total volume of air passed through both. This would result in more contaminants being removed in the Croswell soil if mass transfer were rate limited, thus giving the appearance that this column was at a later stage in the venting process.

Partitioning into organic matter (in the AuGres soil) may be another reason for the difference in leachate results between the two soil types. The gasoline constituents that have partitioned into the organic matter may be slower to "vent out" of the soil, due either to a reduction in their vapor pressure or mass transfer limitations. If this were true, then after significant venting the soil with the higher organic matter content would have a higher mass of partitioned gasoline constituents. These constituents would then contribute substantially to aqueous-phase concentrations during leaching.

From a practical standpoint, however, the organic matter causes significant but only moderate increases in aqueous-phase concentrations. The aqueous-phase concentrations were reduced almost three orders of magnitude for BTX compounds in both soils. Initially AuGres leachate concentrations may be higher than those of the Croswell soil but these are further reduced during leaching.

6.6. SUMMARY AND CONCLUSIONS

Gasoline-water partitioning was characterized for the gasoline used in this study. Deviation from Raoult's law predictions for BTX was evident but not severe. Naphthalene showed significant deviation. Gasoline-water distribution coefficients are higher than octanol-water partition coefficients for these compounds.

Venting for 25 hours resulted in a three order of magnitude decrease in aqueous concentrations of BTEX in column leachate compared to pre-vented column effluent concentrations. Naphthalene concentrations increased 5-10 times which indicates that longer venting times are required to reduce this compound from the residual NAPL and thus from the aqueous-phase.

The effect of organic matter on leachate concentrations was investigated for both pre- and post-vented soil columns. In pre-vented columns, no discernable difference was observed. A local equilibrium model adequately predicted aqueous-phase concentrations when experimentally determined pure-phase solubilities were used and the residual gasoline was corrected for weathering. For post-vented columns, there was a significant difference in aqueous-phase concentrations means between organic and inorganic treatments. The presence of organic matter resulted in an increase in aqueous-phase concentrations for BTEX and a decrease in naphthalene. A probable explanation for this that of partitioning into the organic fraction of the soil and subsequent change in vapor pressure of the

partitioned constituents. Rate limited behavior during venting is also possible.

CHAPTER 7

AIR-PHASE CONCENTRATION MEASUREMENTS AS PREDICTORS OF LEACHATE CONTAMINATION

7.1. INTRODUCTION

Assessing the level of remediation achieved by soil venting at gasoline contaminated sites involves numerous soil and groundwater samples. Soil sampling is initially performed to delineate the type and extent of soil contamination and after remediation to determine if the site has been properly cleaned up. Monitoring groundwater and vented air samples are also routinely performed to evaluate remediation progress.

Contaminant concentrations determined in flowing air and pumped water, however, may lead to incorrect conclusions regarding the level of remediation achieved. For example, dilution of the sample may occur as clean fluid mixes with the contaminated fluid. For this reason, static air concentration measurements are often performed. This involves turning off the system for a fixed time and then sampling the first flowing air when venting in resumed. It is typically found that air concentrations increase after the shut down period only to again fall as venting resumes. This is often inter-

preted as a mass transfer problem, i.e. that the mass transfer of gasoline constituents to air is rate limited. As shown in chapter 5, mass transfer limitations from NAPL to air only occur at low constituent concentrations.

In the field, the rate limited behavior is probably related to dilution and bulk mass transport problems due to: 1) the heterogeneous distribution of NAPL in the spill site which results in air moving through "clean" soil and mixing with air containing contaminants; 2) poor system layout which also results in large volumes of cleaner air being mixed with contaminated air; and 3) soil heterogeneities resulting in preferential flow paths of air. This results in certain portions of the site getting "cleaned out" faster than others. For these reasons, an air sample at equilibrium should be obtained to determine the level of remediation achieved thus far. This would avoid concluding remediation success only to determine, after performing costly soil sampling, that further venting is needed.

Air concentration measurements may also be useful in predicting the aqueous-phase contamination potential of the spill site. Estimating rainfall and infiltration rates would allow a prediction of groundwater contamination potential to be made from the site.

The focus of the work presented in this chapter has been to utilize the results obtained in chapter 5 to predict leachate concentrations. Predicted leachate concentrations were compared to measured leachate values determined in

chapter 6. Predictions were made based on Henry's Law and Henry's Law constants obtained from the literature.

7.2. BACKGROUND

The use of soil-gas measurements for detection of contamination by volatile organic compounds (VOCs) in the subsurface environment has recently been of interest (Kerfoot 1987, Morgan and Klingler 1987, Marks and Selby 1989, Marrin 1989 and Schroedl and Kerfoot 1989). Most of this work has been performed by environmental consulting firms in an effort to develop quick and easy screening techniques to ascertain groundwater and soil contamination. Although this technique is useful as a qualitative technique for groundwater contamination, as a quantitative tool it has been limited. This is largely to be expected based on sampling procedure and the fact that it is a single point measurement.

Air-phase concentration measurements would provide a strong basis for predicting groundwater concentration measurements based on Henry's Law provided the air-phase samples were at equilibrium with the aqueous-phase and the sampling procedure was sound and not biased. The problem with correlating gas measurements to groundwater concentrations encountered is probably due to the long time for equilibrium to occur given the complexities and ongoing processes occurring within the subsurface soil environment. Relating soil-gas concentrations to percolating water moving through the spill site is probably a more realistic goal. In the context of

soil venting it may be possible to predict potential leachate concentrations based on air-phase concentration measurements obtained from the vapor extraction well using Henry's Law.

Henry's Law is applicable to dilute ideal solutions and very generally it states that at equilibrium the partial pressure of a solute in the vapor phase (P_i) is proportional to its mole fraction in the liquid phase (X_i):

$$P_i = X_i K_H \qquad (7\text{-}1)$$

where K_H is the Henry's Law constant. Henry's Law constants have been determined for various compounds of environmental interest for dilute aqueous systems and are generally expressed as the ratio of the partial pressure of the compound in the air to its partial pressure in the liquid. It is also commonly expressed as a ratio of concentrations. Mackay and Shiu (1981) present a compilation of Henry's Law constants for various compounds. Most of these constants have been calculated based on vapor pressure and solubility data measured independently. The chemical composition of the aqueous phase, however, may affect the Henry's Law constant (Yurteri et al. 1987). It is possible that Henry's Law constants determined from complex aqueous solutions may be different than calculated values based on solubility in pure water.

7.3. RESULTS AND DISCUSSION

The experimental data utilized to generate the predictive results presented in this chapter were obtained in chapter 5 and chapter 6. A detailed section on materials and methods

was omitted from this chapter since column packing, setup, and sampling for the data have been previously described. The reader is directed to sections 5.4. and 6.4 for review of these procedures.

The average initial air-phase concentration measurements taken during the venting experiments were used to predict the average initial aqueous-phase concentrations for pre-vented soils columns using the Henry's Law constants from the literature (Mackay and Shiu 1981) and Equation 7-1. The results are presented in Table 7-1, column 3. The average effluent concentrations for various compounds measured from two soil columns are presented in column 4 of Table 7-1. Effluent concentrations are generally higher than the predicted concentrations using Henry's Law constants. The exception is naphthalene which is much lower.

A possible explanation for differences in predicted versus actual results may be related to weathering of the residual gasoline in the columns. The leaching columns were saturated with water and allowed to equilibrate for 24 hours prior to the start of leaching. This meant that the leached columns sat for 24 hours longer than the columns that were vented first. The introduction of the water may also have subjected the residual NAPL in the leaching columns to additional exposure to air. Weathering of the residual gasoline may have been the result.

A comparison between predicted concentrations and aqueous phase concentrations determined in the batch study are also

Table 7-1. Predicted aqueous phase concentrations, $C_{w,i}^*$ based on Henry's Law constants compared to measured concentrations from batch, $C_{w,i}^B$, and pre-vented soil columns, $C_{w,i}^C$ (mg/l).

Compound	$K_{H,i}$[1] (1)	$C_{air,i}$ (2)	$C_{w,i}^*$ (3)	$C_{w,i}^C$ (4)	$C_{w,i}^B$ (5)
benzene	0.227	9.39	41.3	40.3	40.5
toluene	0.276	9.48	34.3	57.6	39.7
ethyl-benzene	0.329	0.801	2.43	4.50	3.16
m&p-xylene	0.287	2.65	9.23	14.0	9.53
o-xylene	0.206	0.830	4.03	6.75	4.55
naphtha-lene	0.0178	0.0575	3.23	0.710	0.328

[1] Mackay and Shiu (1981).

shown (Table 7-1, column 5). Overall, there is better agreement between the predicted concentrations and those determined in the batch study. This suggests that deviations in predicted concentrations compared to effluent concentrations of the columns are largely due to weathering of the residual gasoline.

The predicted naphthalene concentration was an order of magnitude greater than the naphthalene concentration measured in the batch study. This may be due to sampling and quantitative problems for this compound since it has a low vapor pressure and low concentration in the residual NAPL. However, it is also quite different than the other constituents investigated because naphthalene is a solid at room temperature in the pure state. It has often behaved in a manner different than predicted.

Most deviations appear to be largely due to weathering of the residual gasoline, however some deviations from ideality may exist because of the complex nature of the aqueous phase. Henry's Law constants are typically determined in deionized water systems. It is assumed that the activity of the solute in the dilute aqueous solution is unity, so that concentrations can be used. However, the presence of other constituents in the water may result in deviation from ideal dilute solution behavior and Henry's Law constants from the literature may result in poor estimations for some constituents.

Henry's Law constants were determined for post-vented soils, and compared to literature values (Table 7-2), however,

Table 7-2. Henry's Law constants, $K_{H,i}^{1}$, compared to predicted values, $K_{H,i}^{*}$, based on measured concentrations in air and water for three columns.

Compound	$K_{H,i}$	$K_{H,i}^{*}$
benzene	0.227	1.68
toluene	0.276	0.690
m&p-xylene	0.287	0.683
naphthalene	0.0178	0.0176

in post-vented columns, the static air measurements were used because these are assumed to represent the equilibrium air phase levels. Henry's Law constants represent ratio of equilibrium concentrations in air and water. The calculated constants, K_H^* are higher in all cases except for naphthalene. The reason for this may be an artifact of the way the measurements were made. Static air concentration measurements were taken from discrete soil samples before saturating the column with water. Aqueous-phase samples were taken after the column had equilibrated with water at soil water saturations near 100 %. It seems possible that if air concentrations were measured in the column while the soil was water saturated lower values would be obtained, in the cases of constituents at low concentrations. This is because at low mass concentrations in the soil, removing air during saturation may have removed a significant mass of BTX from the columns. This would have resulted in lower aqueous-phase concentrations. The mass of naphthalene removed in the air from the column was low because of the low vapor pressure of naphthalene. The percentage of naphthalene remaining in the NAPL at this time was still quite high, thus the mass removed in the air during water saturation may have been insignificant.

Overall, air phase concentration measurements may give an adequate estimate of aqueous phase concentrations but they tend to overestimate aqueous concentrations, in some cases severely. Problems of insufficient equilibration time and dilution of contaminated air with clean air at a field venting

site, may also result in inaccurate estimates.

7.4. SUMMARY AND CONCLUSIONS

Measured air-phase concentrations used with Henry's Law constants underestimate aqueous-phase concentrations in prevented soils and overestimate aqueous concentrations in post-vented soils. Coupled with other concentration measurements in field situations, however, they may be useful indicators of leachate contamination.

CHAPTER 8

PREDICTION OF LEACHATE CONCENTRATIONS IN GASOLINE CONTAMINATED SOILS

8.1. INTRODUCTION

Post-remediation cleanup assessment for gasoline contaminated sites is often based on contaminant levels measured in soil and groundwater samples. Measurement of benzene, toluene and xylenes (BTX) in gasoline contaminated soils and groundwater is a requirement in most states to determine if cleanup standards have been met. Determination of the total petroleum hydrocarbon (TPH) content or analysis of other specific compounds may also be required. In Michigan, for example, regulations have recently been adopted which require measurement of a series of polynuclear aromatic hydrocarbons (PAH's) as well as BTX in soil and groundwater samples (State of Michigan, Public Act 307).

Numerous problems are encountered when attempting to determine contaminant levels in soils and groundwater. Sampling groundwater from wells may not be representative of actual aqueous-phase concentrations emanating from a contaminated site. Factors such as well location, pumping rate and dilution may lead to the appearance of a clean site

when in reality leachate levels may result in unacceptable groundwater contamination.

Soil concentration measurements are performed to determine the potential of the soil for contaminating groundwater. Contaminant levels measured directly from soil samples, however, may not be indicative of the contamination that is transferred to percolating water. This is because the relationship between the contaminant concentrations in the soil and in the leachate is not fully understood. Although the best method for determining a soil's potential contribution to groundwater contamination would be to perform leachate tests under closely simulated field conditions, this is not always practical. A reliable means for predicting leachate levels from soil concentration measurements would improve our ability to establish remediation standards that reflect the potential environmental impact of the contamination remaining after remediation.

The focus of this study has been to determine if measured soil concentrations of toluene, m&p-xylene and naphthalene from gasoline contaminated soils can be used with either Raoult's Law or the method of Boyd and Sun (1990), to predict concentrations in the aqueous-phase. Predicted aqueous-phase concentrations were compared to measured leachate concentrations for soil columns from which soil samples were collected and analyzed.

8.2. BACKGROUND

It has been shown that BTX leaches from soil containing residual saturation levels of gasoline at concentrations predicted by equilibrium partitioning of the BTX between gasoline and water (Zalidis et al. 1991). Equilibrium partitioning of BTX into water from gasoline was determined to follow near ideal behavior and could be described by Raoult's Law (Cline et al. 1991). This relationship says that the concentration of a gasoline constituent in the aqueous phase (C_i) is equal to the mole fraction of constituent i in the gasoline (X_i) multiplied by the aqueous solubility of the pure constituent (S_i):

$$C_i = X_i S_i \quad . \qquad (8\text{-}1)$$

The amount of constituent that partitions into water is thus dependent on its mole fraction in the nonaqueous phase liquid (NAPL) and not on the amount of NAPL present in the soil. A greater amount of NAPL present, however, would result in a higher measured value of the constituent in the soil. This means that for a soil sample with an initial gasoline saturation of 5%, five times the amount of toluene would be measured compared to a soil sample with an initial gasoline saturation of 1%. Leachate concentrations would be the same in both cases, however.

Raoult's Law is generally applicable to mixtures of structurally related hydrocarbon liquids such as those found in gasoline (Cline et al. 1991). When a mixture contains compounds with different chemical structures, concentrations

in an equilibrated aqueous solution may deviate from those predicted by Raoult's Law (Atkins 1986). For example, in the case of a two component system of dissimilar liquids, A and B, Raoult's Law is generally valid for compound B only as the mole fraction of B (X_B) approaches 1. However, as X_A approaches zero, compound A, now considered the solute, may exhibit considerable deviation from Raoult's Law.

Soil venting of gasoline contaminated sites dramatically alters the chemical composition of the residual NAPL by preferentially removing the more volatile constituents. The residual becomes enriched in heavier, low vapor-pressure compounds. A compound such as toluene, with a high vapor pressure, may now deviate significantly from Raoult's Law.

Chiou and Schmedding (1982) have shown that the partitioning of organic solutes in solvent(octanol)/water systems deviates significantly from that calculated based on the assumption of Raoult's Law. This deviation results in aqueous-phase concentrations higher than those predicted by Raoult's Law. This was attributed to octanol-solute incompatibility, and to a lesser degree, the effects of dissolved octanol on solute-water solubility.

Slightly water-soluble organic compounds are believed to partition into the organic fraction of the soil in soil/water systems much in the same way they would in a solvent(octanol)/water system (Chiou 1989). The concentration of an organic contaminant in soil (Q_i) at equilibrium is directly related to its concentration in the water (C_i) by a

distribution coefficient ($K_{d,i}$). This describes a situation when only the natural organic matter is present in the soil, i.e. there is no residual oil. The relationship is summarized in the following linear equation:

$$Q_i = K_{d,i} * C_i \quad . \qquad (8\text{-}2)$$

The distribution coefficient divided by the fractional organic matter content (f_{om}) of the soil defines a new constant $K_{om,i}$ which has been found to be essentially independent of the soil used (Lambert, 1968). $K_{om,i}$ has been shown to be primarily determined by the properties of the partitioning solute (Briggs, 1969). As an approximation, $K_{om,i}$, is typically one-tenth the value of the octanol-water partition coefficient, $K_{ow,i}$. A linear relationship between $K_{om,i}$ and ($K_{ow,i}$) has been found for a wide range of organic compounds.

Boyd and Sun (1990) extended the theory of organic matter-water partitioning to account for situations when a residual oil phase is present in the soil. The developed a distribution coefficient that includes terms for both the natural organic matter and the residual petroleum oil in the soil:

$$K_{d,i} = f_{om}K_{om,i} + f_{oil}K_{oil,i} \qquad (8\text{-}3)$$

where f_{oil} is the fraction of residual oil in the soil, and $K_{oil,i}$ is the residual oil/water partition coefficient for constituent i. The residual petroleum phase was found to be more effective as a partitioning medium than the natural organic matter phase of the soil. The distribution coefficient for soil containing both residual oil and natural

organic matter, determined from sorption isotherms matched quite well to predicted values using Equation 8-3. It was assumed in their study that $K_{oil,i}$ could be approximated by $K_{ow,i}$. In a later study, however, they found that for residual polychlorobiphenyl (PCB) oil in soils, the PCB oil was 3.5 times more effective than octanol as a partitioning medium for 2-chlorobiphenyl (Sun and Boyd 1991). This suggests that $K_{oil,i}$ is a function of both the partitioning solute and the residual oil and experimentally determined values should be used whenever possible.

8.3. MATERIALS AND METHODS

8.3.1. Experimental setup

The soil columns were made of borosilicate glass (5.44 cm in diameter, 4 cm long), with stainless steel ends and fittings. Teflon o-rings were used between the ends and the glass tube. The inlet tube was made of Teflon^R, a stainless steel needle with a luer fitting was used on the outlet. Glass syringes were attached directly to column outlet for collection of leachate samples.

Soils were packed moist to a known bulk density by tapping the column as soil was added then dropping a weight on the soil surface after all the soil was added. Two sandy soils, Croswell and AuGres, with similar grain size distributions and pH were utilized. The Croswell soil had an organic matter content of 0.20%, AuGres had an organic matter content of 3.2%.

Residual saturations of water and gasoline were established using ceramic pressure plates (air-water entry pressure of 1 bar), with edges sealed using epoxy paint. Residual saturations for each fluid were established by using a water or gasoline saturated plate and applying a vacuum of 300 mbars to the bottom of the column. Drainage continued for a predetermined length of time sufficient to reduce the outflow rate to virtually zero. All soil columns were allowed to drain for the same length of time.

Soil venting was simulated by passing clean moist air at 30 ml/min through the column. Air flow rates were monitored before entering and upon leaving the soil column to ensure that there was no leakage.

After venting, soil columns were saturated with deionized, 0.001M $CaSO_4$ water, and allowed to equilibrate for 24 hours. A glass syringe was attached to the outlet and a vacuum of 80 mbars was applied to the bottom of the column. Several samples of equilibrated water were collected immediately. The inflow line was then attached to the top of the column and a water flow of 2 ml/h was established. Samples were collected periodically for the next 4-7 days. The regulated vacuum applied to the bottom of the column ensured that unsaturated conditions were maintained in the soil column. This procedure is described in detail elsewhere (Zalidis et al. 1991).

8.3.2. Soil sampling and measurement

Soil samples were collected from the bottom of the

columns following venting and again after leaching. Freon and methanol extractions were performed and the moisture content was determined on all soil samples. A summary of the sampling schedule is presented in Figure 8-1.

Methanol extractions were performed on soil samples by placing approximately 4 g (oven dry weight) of soil into pre-weighed vials containing 10 ml of methanol. These were immediately crimp capped. They were sonicated at 50°C for 15 minutes and then centrifuged at 480 x g for 10 minutes to enhance separation of soil and methanol. The methanol extraction method is modified from EPA method SW 8240 (Voice and Ryan 1991). One milliliter of methanol was then placed in a headspace vial with 9 ml of NaCl saturated water, sonicated and measured using a headspace sampler and gas chromatograph (GC) with a flame ionization detector.

Freon extractions were carried out on soil samples by placing approximately 4 g of soil in a pre-weighed vial, adding 10 ml of water and lowering the pH to 3. The samples were crimp capped and shaken. Five milliliters of freon were injected through the septum, the contents were shaken on a reciprocating shaker for 20 minutes and then centrifuged 480 x g for 10 minutes (modified from American Petroleum Institute 1987). Several microliters of freon were directly injected into the GC. Vials not immediately sampled were stored in the refrigerator after exchanging the pierced septum for a new one and were analyzed within 3 days.

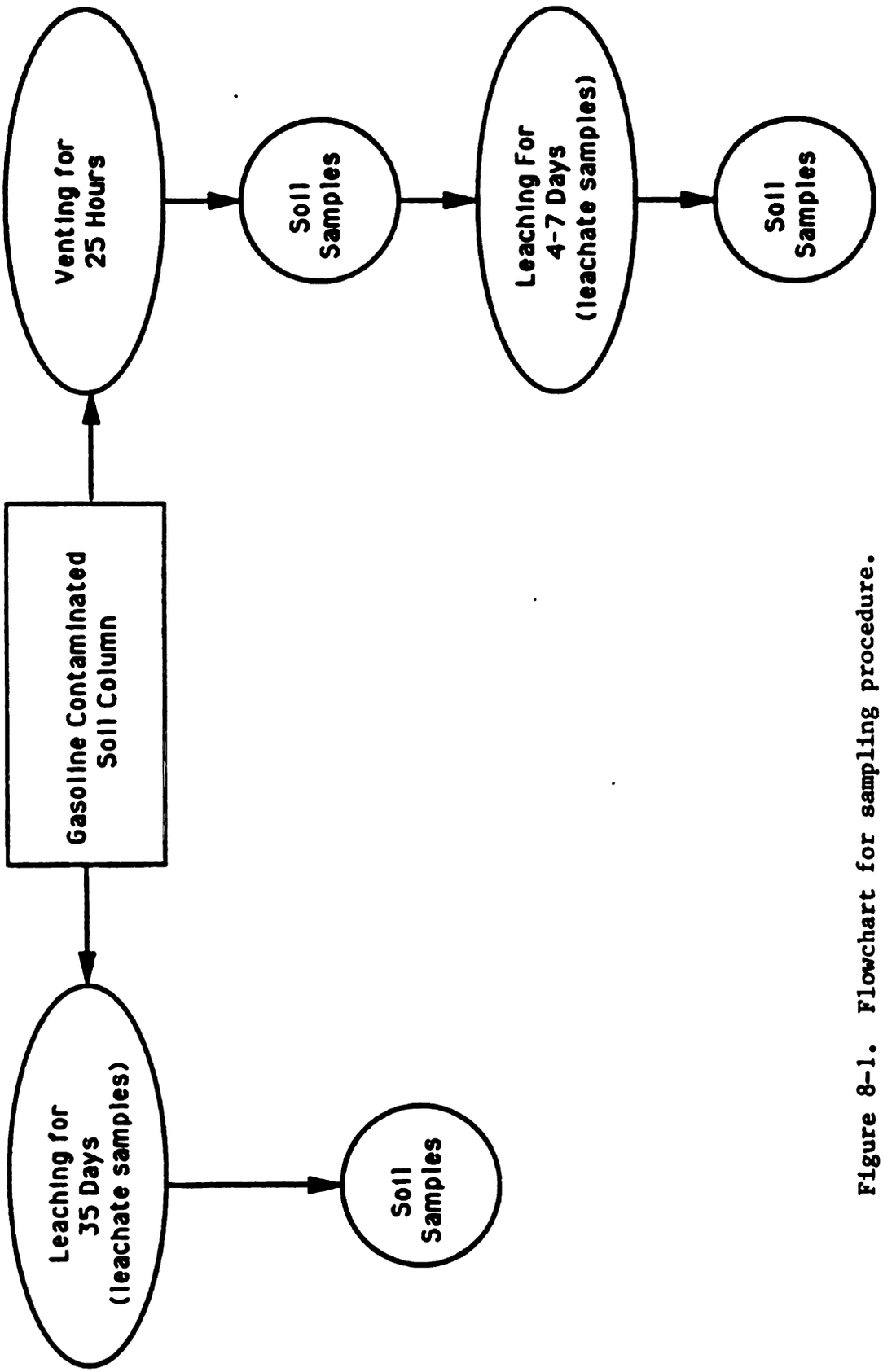


Figure 8-1. Flowchart for sampling procedure.

8.4. RESULTS AND DISCUSSION

Two soil columns packed with Croswell and AuGres soils and contaminated with gasoline were leached for 35 days. Soil samples were collected to determine if aqueous-phase concentrations could be predicted using soil concentration measurements with Raoult's Law (Equation 8-1). In order to determine the aqueous concentration of a constituent, C_i, according to Raoult's Law, the mole fraction, X_i, of the constituent in the hydrocarbon mixture must be known or estimated. Mole fractions were determined analytically for a sample of the original gasoline introduced into the column. However, after 35 days of leaching, the composition of the residaul gasoline has been altered. A similar situation would occur at a contaminated field site. A gasoline sample taken from the bottom of the leaking tank or from the gasoline accumulated at the water table may not be representative of the residual NAPL in the soil. Weathering or remediation could make this initial characterization highly inaccurate.

In this study, mass fractions, X_i^*, of toluene, m&p-xylene and naphthalene in the residual gasoline for soil columns that had been vented or leached were calculated and used as an estimate of mole fraction. Mass fractions were determined by dividing the measured soil concentration of the compound by the total petroleum hydrocarbon concentration determined from the same sample. Benzene concentrations in most of the soil and water samples were nondetectable. Therefore, this compound was eliminated from further study.

Mass fractions, X_i^*, provide a good estimation of X_i for toluene, m&p-xylene and naphthalene when the molecular weight of a constituent is close to the weighted average molecular weight of the mixture. For gasoline, the weighted average molecular weight is about 100 g/mole, with molecular weights of 92 g/mole for toluene, 106 g/mole for m&p-xylene and 128 g/mole for naphthalene. Therefore, mole fractions for these compounds can be reasonably predicted using mass fractions if the weathering process has not dramatically altered the weighted average molecular weight.

Final leachate concentrations, C_i, divided by X_i^*, determined from soil measurements, were used to estimate pure-phase solubility, S_i^*, using Raoult's Law (Equation 8-1) for two gasoline contaminated columns that had been leached for 35 days. The calculated values are compared to the reported pure-phase solubilities, S_i, (Verschueren 1983) in Table 8-1. Calculations based on X_i^* determined from both freon and methanol extracted samples are shown.

Overall, there is reasonably good agreement between S_i and S_i^*. This implies that aqueous-phase concentrations can be estimated using soil concentration measurements and Raoult's Law for NAPLs that have not been highly weathered. The predicted leachate concentration, C_i^*, using soil concentration measurements from the methanol extraction and literature values for pure-phase solubility are compared with the measured values, C_i, in Table 8-2. Estimations based on methanol extracted samples were lower than literature values

Table 8-1. Comparison of reported pure-phase solubility, S_i, to predictions, S_i^*, based on Raoult's Law and experimentally determined mass fractions and leachate values prior to venting, at 24°C, (mg/l).

Compound	S_i[1]	S_i^* from freon data	S_i^* from methanol data
toluene	542	403 674	261 254
m&p-xylene	174	141 173	167 162
naphthalene	24.5[2]	44.2 23.9	32.9 7.95

[1] Verschueren, 1983.
[2] supercooled liquid

Table 8-2. Measured leachate concentrations, C_i, compared to predicted concentrations, C_i^*, using Raoult's Law and soil concentration measurements (methanol extraction) from two soil columns prior to venting, at 24°C, (mg/l).

Compound	Column	C_i	C_i^*
toluene	1	9.07	18.9
	2	1.43	2.77
m&p-xylene	1	11.9	12.5
	2	3.10	2.31
naphthalene	1	0.790	0.587
	2	0.380	1.17

and would, therefore, produce conservative estimates of aqueous-phase concentrations. This may be preferable.

The same approach was used for aqueous samples taken after soil columns had been vented with air for 25 hours. Twenty-five hours was sufficient time to remove in excess of 95% of the gasoline mass. Calculated pure-phase solubilities for toluene and m&p-xylene were significantly lower than S_i (Table 8-3). The toluene average S_i^* for six different columns, two containing Croswell soil and four containing AuGres soil, was almost five times lower than the literature value. The m&p-xylene average for six soil columns was almost nine times lower than the literature value. This means that aqueous phase concentrations estimated from the soil concentration measurements would be overestimated by that same amount. This suggests that the approach is unacceptable for highly weathered residual.

The mass fractions of toluene and m&p-xylene calculated from soil data were 2-3 orders of magnitude lower for vented soils than soils that had not been vented. The soil venting process removes higher vapor pressure compounds from the residual NAPL. Because the removal is constituent selective, the composition of the remaining residual will be dramatically different than the original NAPL. Partitioning of toluene and m&p-xylene, now at low concentrations, may deviate from Raoult's Law. The altered composition of the residual NAPL after venting may also result in actual mole fractions very different from estimated mole fractions, mainly due to the

Table 8-3. Comparison of reported pure-phase solubility, S_i, to the average predicted value, S_i^*, based on Raoult's Law and methanol soil data from vented soil columns at 24°C, (mg/l).

Compound	S_i[1]	S_i^*
toluene	542	115
m&p-xylene	174	22.4
naphthalene	24.5[2]	18.4

[1] Verschueren, 1983.
[2] supercooled liquid.

change in the weighted average molecular weight of the residual gasoline.

In contrast to toluene and m&p-xylene, mass fraction data for naphthalene show almost an order of magnitude increase after venting compared to those calculated from columns that had not been vented. The naphthalene occupies between 10 and 15 % of the remaining residual NAPL. Estimating mole fractions from mass fraction data may still be appropriate. The residual NAPL may also be chemically similar to naphthalene, so that Raoult's Law would still be valid. In either case, the naphthalene data supports the use of Raoult's Law for predicting aqueous-phase concentrations (Table 8-3). Soil and leachate samples taken from six vented soil columns show good agreement with the literature value, S_i. The solubility of naphthalene determined from the methanol extraction soil data produces a more conservative prediction of C_i and may, therefore, be preferable.

A methanol extraction procedure (EPA 1986) is currently the accepted method for determining volatile organic contaminant concentrations in soils with concentrations greater than 1 mg/kg. The use of soil concentration measurements and Raoult's Law to predict aqueous phase concentrations, therefore, could easily be implemented in field investigations. While an additional measurement, TPH, is required, this analysis could be perforemed on the same samples used to measure BTX concentrations.

After soil remediation, when contaminant concentrations

may be very low, predictions based on Raoult's Law may severely overestimate aqueous-phase concentrations. This may be due to the reasons stated earlier, that poor mole fraction estimates result mass fraction data, as well as deviations from Raoult's Law. Another important consideration may be that at low constituent concentration in the soil, the effect of the soil-contaminant interactions needs to be incorporated into the estimation procedure.

A better approach for low compound concentrations in the NAPL may be the one taken by Boyd and Sun (1990). This was evaluated for its predictive capabilities to determine aqueous-phase concentrations of toluene and m&p-xylene after soil venting in this study. The distribution coefficient, $K_{d,i}$, was determined from Equation 8-2. In this study, Q_i was considered to be the amount of constituent in the soil as determined by the soil concentration from the methanol extraction for toluene and m&p-xylene. The C_i is the corresponding measured concentration in the leachate. The $K_{d,i}$ determined from Equation 8-2 was compared to the $K_{d,i}^*$ predicted by Equation 8-3. TPH concentration was used to estimate the oil fraction, f_{oil}, in the soil. The octanol-water partition coefficient, $K_{ow,i}$, from the literature, (Chiou 1989) was used as an approximation of the oil-water partition coefficient, $K_{oil,i}$. Boyd and Sun (1990) found this to be a good assumption for residual petroleum oils. The experimentally determined fuel-water partition coefficient, $K_{fw,i}$ for toluene and m&p-xylene for the gasoline used in this

study were also used. Values for $K_{om,i}$, $K_{ow,i}$ and $K_{fw,i}$ are shown in Table 8-4. The fraction of organic matter, f_{om}, was measured on samples of uncontaminated soil. The partition coefficient for organic matter, $K_{om,i}$, was found in the literature (Chiou 1989) and as previously stated is relatively constant for a given compound and not strongly dependent on organic matter type.

Toluene and m&p-xylene results for different columns are presented in Tables 8-5 and 8-6. Only results using samples from the methanol extraction are presented because toluene and m&p-xylene concentrations in the freon were often below detection limits. The measured K_d values determined from soil and leachate values (Equation 8-2) are generally about 2-3 times higher for toluene and 3-4 times higher for m&p-xylene, except in two of the nine samples, than those determined from Equation 8-3. Using the $K_{d,t}^*$ determined from Equation 8-3 for predictive purposes results in toluene aqueous phase concentrations that are within a factor of 2 to measured concentrations in over half of the samples (Table 8-7). Overall this approach gave better predictions than Raoult's Law.

Predictions for m&p-xylene aqueous concentrations resulted in higher than measured values (Table 8-8). This approach, overall, resulted in better estimates that those using Raoult's Law.

After venting the total residual NAPL, f_{oil}, was about 10 times lower than the f_{om} for the Croswell soil. The

Table 8-4. Partition coefficient values.

Compound	K_{om}	K_{ow}	K_{fw}
toluene	44.7	489	1030
m&p-xylene	128	1490	4360
naphthalene	210	2290	8550

Table 8-5. Comparison of K_d and K_d^* for toluene. (b) soil samples taken before leaching and (a) soil samples taken after leaching (methanol extraction).

Column	f_{oil}	K_d	K_d^{*ow}	K_d^{*f}
3 (a)	0.013	0.945	0.152	0.220
3 (b)	0.028	7.24	0.225	0.375
4 (a)	0.0079	17.3	1.25	1.62
4 (b)	0.018	3.37	1.46	1.51
5 (a)	0.023	1.33	1.54	1.66
5 (b)	0.0025	2.07	1.44	1.46
6 (a)	0.017	3.43	1.51	1.60
7 (a)	0.097	1.71	0.564	1.09
8 (a)	0.042	3.20	1.64	1.86

f_{oil} = TPH (GC method)
K_d^{*ow} $K_{oil} = K_{ow}$
K_d^{*f} $K_{oil} = K_{fw}$

Table 8-6. Comparison of K_d and K_d^* for m&p-xylene. (b) soil samples taken before leaching and (a) soil samples taken after leaching (methanol extraction).

Column	f_{oil}	K_d	K_d^{*ow}	K_d^{*f}
3 (a)	0.013	11.6	0.634	1.36
3 (b)	0.028	4.08	0.411	0.745
4 (a)	0.0079	24.5	4.52	5.00
4 (b)	0.018	7.11	4.36	4.57
5 (a)	0.023	14.1	4.29	4.35
5 (b)	0.0025	20.6	4.59	5.18
6 (a)	0.017	10.5	4.49	4.93
7 (a)	0.097	13.7	1.67	4.22
8 (a)	0.042	13.3	4.87	5.98

---

f_{oil} = TPH (GC method)
K_d^{*ow} $K_{oil} = K_{ow}$
K_d^{*f} $K_{oil} = K_{fw}$

Table 8-7. Measured toluene leachate concentrations, C_t, compared to predicted concentrations, C_t^*, in ug/l.

Column	C_t	C_t^{*1}	C_t^{*2}	C_t^{*2}
3 (a)	7.64	31.8	46.3	31.7
3 (b)	15.0	85.5	182	109
4 (a)	5.33	657	125	117
4 (b)	93.6	605	60.9	59.1
5 (a)	22.0	72.4	18.3	17.0
5 (b)	72.5	2670	79.9	79.1
6 (a)	21.8	252	47.9	45.2
7 (a)	31.8	7.21	21.5	11.1
8 (a)	7.3	136	60.2	53.0

[1] Raoult's Law
[2] Boyd and Sun (1990), $K_{ow} = K_{oil}$
[3] Boyd and Sun (1990), $K_{rw} = K_{oil}$

Table 8-8. Measured m&p-xylene leachate concentrations, C_x, compared to predicted concentrations, C_x^*, in ug/l.

Column	C_x	C_x^{*1}	C_x^{*2}	C_x^{*2}
3 (a)	5.07	80.6	92.6	43.2
3 (b)	14.0	51.5	200	110
4 (a)	3.40	184	18.4	16.7
4 (b)	27.5	231	55.3	52.7
5 (a)	5.50	59.6	18.0	17.8
5 (b)	30.1	1270	39.9	25.4
6 (a)	6.82	74.8	15.9	14.5
7 (a)	9.84	24.0	80.8	32.0
8 (a)	18.5	102	50.2	41.0

[1] Raoult's Law
[2] Boyd and Sun (1990), $K_{ow} = K_{oil}$
[3] Boyd and Sun (1990), $K_{fw} = K_{oil}$

contribution of the oil as a partitioning medium would be at least equal to that of the natural organic matter, since K_{oil} is more than 10 times greater that K_{om}. Because the oil fraction was of equal importance to the organic matter in the Croswell soil, using K_{fw} values resulted in significantly lower estimates of C_i^*. The f_{om} in the AuGres soil is more than 100 times that of f_{oil}, however. The result is that the organic matter is more important than the oil phase as a partitioning medium. Therefore, using K_{ow} or K_{fw} to estimate K_{oil}, resulted in very little difference in C_i^*. Partitioning into the organic matter is an important consideration at low constituent concentrations for either soil.

A possible explanation for the underestimation of $K_{d,i}^*$ (Table 8-5) may be due to the TPH measurement. Although the intent of this study was not a critical evaluation of soil concentration measurement methods, invariably the results need to be discussed in light of the measurement methods. Recoveries for benzene and xylene spiked soil samples were low for the methanol extraction procedure, less than fifty percent in some soils (Voice and Ryan 1991). In all likelihood, percent recoveries for heavier, more hydrophobic compounds of gasoline may also be low. TPH values determined for soil samples from columns that had only been leached, indicated that the TPH values were about 5 times lower than expected based on initial gasoline content and accounting for removal of soluble components by leaching. If the same extraction efficiency was assumed for the vented soil samples, this would

account for much of the discrepancy. Predicted aqueous-phase concentrations based on mole fraction estimates may be less susceptible to the effects of underestimated TPH concentrations because a ratio of two soil concentration measurements was used.

For the freon extractions, soil samples spiked with dodecane showed an average percent recovery of about 85 % for both soils. However, TPH values determined from the freon extraction were generally lower than those determined from the methanol extractions. Thus, it may be that recovery efficiencies based on spiked samples are not representative of recoveries of actual samples.

Boyd and Sun (1990) used a soxhlet extraction technique with gravimetric determination for oil and grease to determine the amount of residual petroleum oil. This technique is probably more efficient in extracting petroleum compounds from soils, however, it is not applicable for soils contaminated with gasoline or light fuels. At very low contaminant concentrations in the soil, such as after venting, it may also not be appropriate. A method of determinations other than gravimetric, such as GC/FID, may extend its detection limit.

An increase in the TPH value would also affect the results based on Raoult's Law. It would result in a decrease in mole fraction, causing a decrease in the aqueous-phase concentration prediction. This may result in overall better predictions for compounds at low concentration using Raoult's Law, as well.

8.5. CONCLUSIONS

Mass fractions of toluene, m&p-xylene and naphthalene were determined based on their measured concentration and total petroleum hydrocarbon concentration in a NAPL contaminated soil. Aqueous-phase concentrations were estimated from measured mass fractions and pure-phase solubilities using Raoult's Law. Reasonably good agreement between measured and predicted aqueous-phase concentrations was obtained when these compounds were present at high mole fractions in the residual NAPL, that is in samples that had not been vented. Aqueous-phase concentrations for all three compounds were predicted reasonably well. For vented soils, only naphthalene showed reasonable agreement; aqueous-phase concentrations for toluene and m&p-xylene could no longer be adequately predicted by Raoult's Law.

Aqueous-phase concentrations predicted using a soil distribution coefficient that accounted for both the natural organic matter and residual NAPL in the soil were also higher than measured values at low constituent concentrations. Low estimates of f_{oil} may be partly responsible. Overall, however, this method resulted in better estimates of leachate concentration than Raoult's Law for vented soils. This suggests that the effect of organic matter at low contaminant concentrations needs to be considered.

CHAPTER 9

SUMMARY AND RECOMMENDATIONS

9.1. SUMMARY

The purpose of this research was to develop a better understanding of soil vapor extraction as a remediation technique for gasoline contaminated soil. Our ultimate concern in venting gasoline contaminated soil is to significantly reduce the threat of human exposure to harmful gasoline constituents. Exposure can occur through gasoline vapors and contaminated groundwater emanating from a spill site, therefore, the efficacy of venting in reducing vapor-phase concentrations and aqueous-phase contamination was the primary goal. To achieve this goal, an understanding of the: 1) retention of gasoline in unsaturated soil; and 2) mass transfer of gasoline constituents from residual gasoline to air during venting and water during leaching was required.

The amount, location and character of the residual gasoline are all important from a soil venting standpoint. For that reason, the study dealing with gasoline retention in unsaturated soils was presented first. Capillary pressure-saturation relations were determined for gasoline in two

different soils; one with and one without significant organic matter content at two different moisture contents; air dry and with residual water saturation. Retention for air-dry conditions increased in soils with increasing organic matter contents. However, when residual water saturations were established in the columns, no discernable difference in gasoline retention was observed between soils with and without appreciable organic matter. Residual gasoline contents were generally 4-10 times lower when water was present in the soil than when it was air dried.

Scaling pressure-saturation relationships using surface tension and residual saturations resulted in the three air-liquid curves collapsing into one curve. Even the air-gasoline curve determined when residual water was present, fell in line with the other curves.

Microscopic observation of a NAPL in soil was performed by taking soil cores at residual water saturation and greater than residual NAPL saturations and viewing them using a cryo-scanning electron microscope with x-ray analysis. Photomicrographs revealed that NAPL on water-wet soil does behave as an intermediate wetting liquid. Observation of pendular rings and v-shaped wedges was made. No photomicrographs could be obtained at residual NAPL saturations because of the inability to locate NAPL blobs or films as well as charging problems due to inadequate conductance of the sample.

To better understand the venting process, mass transfer of gasoline constituents to air during soil venting was

studied. It was first necessary to characterize the gasoline as well as air-gasoline partitioning behavior. Overall, Raoult's law was determined to be valid for air-gasoline partitioning, although some deviations were evident.

Mass transfer from a single component NAPL to air acted according to the local equilibrium assumption. To determine if mass transfer from the multicomponent NAPL gasoline, could be described by the local equilibrium assumption, a local equilibrium based model was employed to simulate the venting process. Simulations were compared to soil venting data and overall the model did a good job at a predicting the data. Experimental techniques such as flow rate reduction, interruption and measurement of static air concentration were also used to evaluate the mass transfer process. The data indicate that at early venting times the local equilibrium assumption is valid. After significant depletion of a constituent from the NAPL, mass transfer became rate limited. BTX vapor-phase concentrations were reduced three orders of magnitude from initial air-phase concentrations. Soils with and without organic matter showed little differences in mass transfer behavior during venting.

Mass transfer of gasoline constituents to water was also investigated. The partitioning process from gasoline to water could adequately be described by Raoult's Law. Some significant deviations were observed, however, suggesting that when available experimental distribution coefficients should be used.

Effluent concentrations from pre-vented soil columns were predicted using the local equilibrium based model. Estimates were generally lower than actual data. Leachate concentrations for BTX were three orders of magnitude lower for post-vented soil columns than columns that had not been vented.

Soil venting is very effective in reducing aqueous-phase contaminant concentrations from gasoline contaminated soil. The relationship between air-phase concentrations, soil-phase concentrations and aqueous contamination was investigated for its possible practical application to contaminated field sites. Leachate concentrations could be adequately predicted using either soil or air concentration measurements.

9.2. RECOMMENDATIONS FOR FURTHER STUDY

Future research on NAPL retention in the unsaturated zone is still required for further optimization of remediation strategies as well as predicting environmental impact of contaminants in soils. Research in this area should include:

1) Investigation of mechanisms responsible for retention of NAPL in a soil with residual water saturations. This is of fundamental importance for determining the amount and microscale location of NAPLs in unsaturated soil.

2) An understanding of residual saturation at a field site from the standpoint of time of drainage. This is intimately associated with the first recommendation because invariable the amount retained will need to be considered for a given time frame. Understanding the drainage behavior when

free product is pumped from the water table during the initial stages of remediation would be beneficial for determining an optimal point to begin vadose zone remediation.

3) The importance of heterogeneities in affecting residual NAPL saturation. This is critical for successful application of remediation technologies to field settings and correct interpretation of field results. Mass transfer limitations observed in the field are invariably linked to heterogeneities of the soil which may affect air flow paths and NAPL distribution.

Further study in the area of mass transfer from a multicomponent NAPL in the soil to either air or water should consider:

1) Multicomponent partitioning and factors which may cause deviation from ideal behavior. This is important for predicting contaminant transport and interpreting results from remediated sites.

2) The effect of soil characteristics on mass transfer, especially as they relate to field situations. This would be beneficial for optimizing remediation techniques.

3) Developing relationships between air, soil and water concentration measurements that can be used to better assess site cleanup by accurately predicting aqueous contamination emanating from a site. Coupled with this should be further investigation of sampling, storage and analytical techniques for organic contaminants in various matrices.

APPENDICES

APPENDIX A

ANALYTICAL PROCEDURES

A.1. STOCK SOLUTIONS

All stock and stock standard solutions were prepared in a manner similar to that described in the EPA 602 Method. Stock standard solutions for water analysis were made by placing about 9.8 ml of methyl alcohol into a 10 ml ground glass stoppered volumetric flask. Naphthalene was added first and the weight was recorded. The xylene, ethylbenzene, toluene and benzene were subsequently added, with the weight recorded after each addition. The compounds of interest were added using separate syringes to avoid contamination and the drops were added directly to the alcohol to avoid any contact with the neck of the flask. After the final compound was added, methyl alcohol was added to the 10 ml mark. The flask was then inverted several times to insure mixing. All chemicals used were 99% purity or higher.

Stock standard solutions for gasoline analysis were made in the same manner, however, dichloromethane or tetrachloromethane were used instead of methyl alcohol. In these cases, however, considerable care was taken to reduce the

effect of evaporative losses of the solvent during addition of compounds of interest. The 10 ml volumetric flask remained stoppered until the last possible moment when the selected compound was added. The stopper was inserted and twisted tightly which reduced losses of the solvent during weighing periods. High concentration stock solutions were prepared which reduced the effect of minor evaporative losses of the solvent on concentration determination. Gasoline stock solutions were made in the same way.

The stock and stock standard solutions were transferred to Teflon^{R}-sealed crimp-cap vials with minimal headspace, covered and stored at 4°C. The stock solution was allowed to warm to room temperature before secondary stock solutions were made. These were made by taking a sample of the stock solution (obtained by piercing the septum) and injecting into a 10 ml flask partially filled with the same solvent as the stock solution. Secondary stock standards were transferred to Teflon^{R}-sealed crimp-cap vials and stored as previously described for the stock standard solutions. Septa were changed daily if they had been pierced. Using and storing standard solutions in this manner maximized the replacement time. Typically the replacement time for stock and standard solutions was 2-3 months. However, the maximum replacement time was never fully realized.

Calibration and check standards were made by placing 2 g of salt (NaCl) in a headspace vial and adding 5 ml of deionized water. A known volume of stock or secondary solution was

added to the salt solution using a microliter syringe. The vial was quickly capped and crimped. Stock standard septa were changed daily if they had been pierced as previously described.

Stock standard solutions for vapor analysis were made with dichloromethane and verified using a BTEX specialty mix of known concentration (Scott Gas, Inc.). Sampling of the gas was performed using gastight syringes of various sizes. However, problems with reproducibility using the larger syringes, calibration range limitations and lack of naphthalene in the mix were the main reasons the specialty gas was not used for day to day calibration when analyzing vapor samples.

Stock standard solutions for soil analysis were made according to the EPA 602 Method with either methyl alcohol or freon in the same way as previously described.

A.2. CALIBRATION CURVES

Calibrations curves consisted of a minimum of 5 points, with a three-point minimum over the linear range of interest. Calibration data were obtained using at least two different secondary standard solutions. Checking new stock and secondary standard solutions with old solutions was routinely performed when new stock solutions were made. Stock solutions made by different laboratory personnel were always checked against those made by the laboratory technician.

Calibration curves for water analysis or other analyses

involving automatic samplers were performed daily. Check standards were analyzed after every 10 samples and after the last sample of the day, with at least one check standard per linear range analyzed daily. A daily water blank was also routinely analyzed. The percent error was determined for each check standard and if it was above 10%, those samples were not considered. This very rarely occurred.

Calibration data for manual injection analysis also contained a minimum of 5 points, with at least a three-point curve over the linear range, however, new calibration curves were not generated daily. New calibration curves were only generated if daily check standards were not within 10% for all compounds of interest. Check standards were typically within 5% for most compounds. Check standards were analyzed daily and at a maximum of every tenth sample. Syringe and instrument blanks were analyzed daily. Air blanks were run when gas samples were analyzed.

A.3. SAMPLE ANALYSIS

All samples were analyzed using a gas chromatograph with a flame ionization detector using external standards. Water samples were analyzed using automated headspace analysis. This involved heating the aqueous sample to 80°C in a headspace vial with a Teflon^{R}-lined septum and a crimp cap. Septa and caps from various manufacturers were checked for leaks in a 80°C water bath but none were found. As long as the caps were properly crimped no leaks were detected. The crimper was

of high quality (West Co.). Samples were heated for one hour. This proved to be optimal for obtaining the greatest quantity of contaminant from the sample as determined by detector response. An aliquot of headspace was taken as determined by the type of hardware used and transferred directly to the GC.

Two different headspace analyzers were employed, the Hewlett Packard 19359A and the Perkin Elmer HS-101. The HP uses a sample loop (Figure A-1), while the HS-101 utilizes a pressurization technique to send the desired aliquot of sample to the GC (Figure A-2). Relative response of benzene and o-xylene for the two different instruments is shown in Figure A-3 for different aqueous matrices. Each bar represents the average of six replicates. Overall, the HS-101 system gives a higher relative response for these types of aqueous samples. Because of this, all leachate samples were analyzed using the PE HS-101 system.

Because most of the samples analyzed could not be duplicated, in the sense that column experiments were continuous, extra samples were taken whenever possible. This provided a level of check on precision of the analytical method. Samples were also analyzed in a random order, typically within three days of collection.

Limits of quantification were determined for each compound based on whether multiple check standards could be quantified and maintained within 10%. The limits of quantification were clearly above the limits of detection.

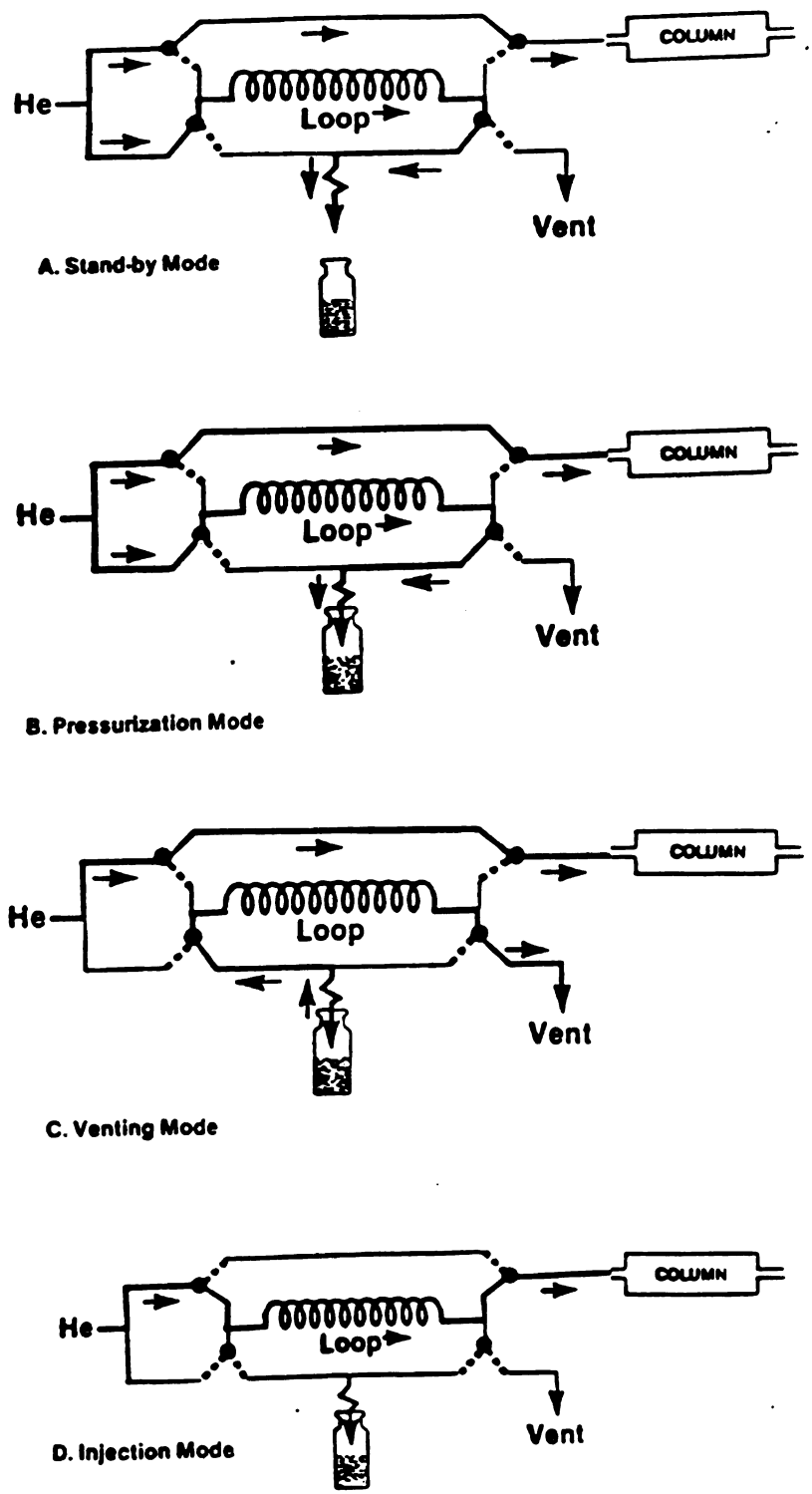


Figure A-1. Hewlett Packard headspace autosampler sampling method.

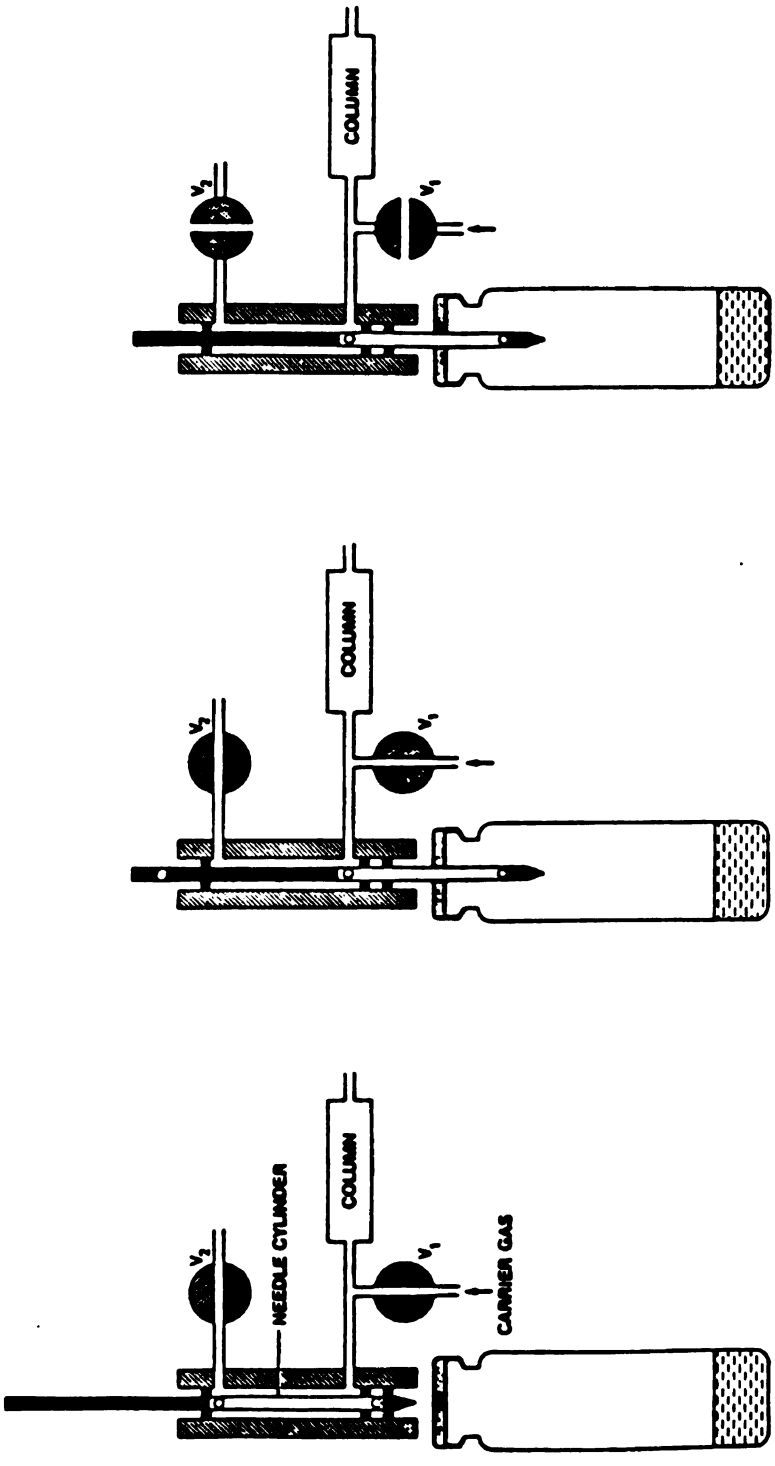


Figure A-2. Perkin Elmer headspace autosampler sampling method.

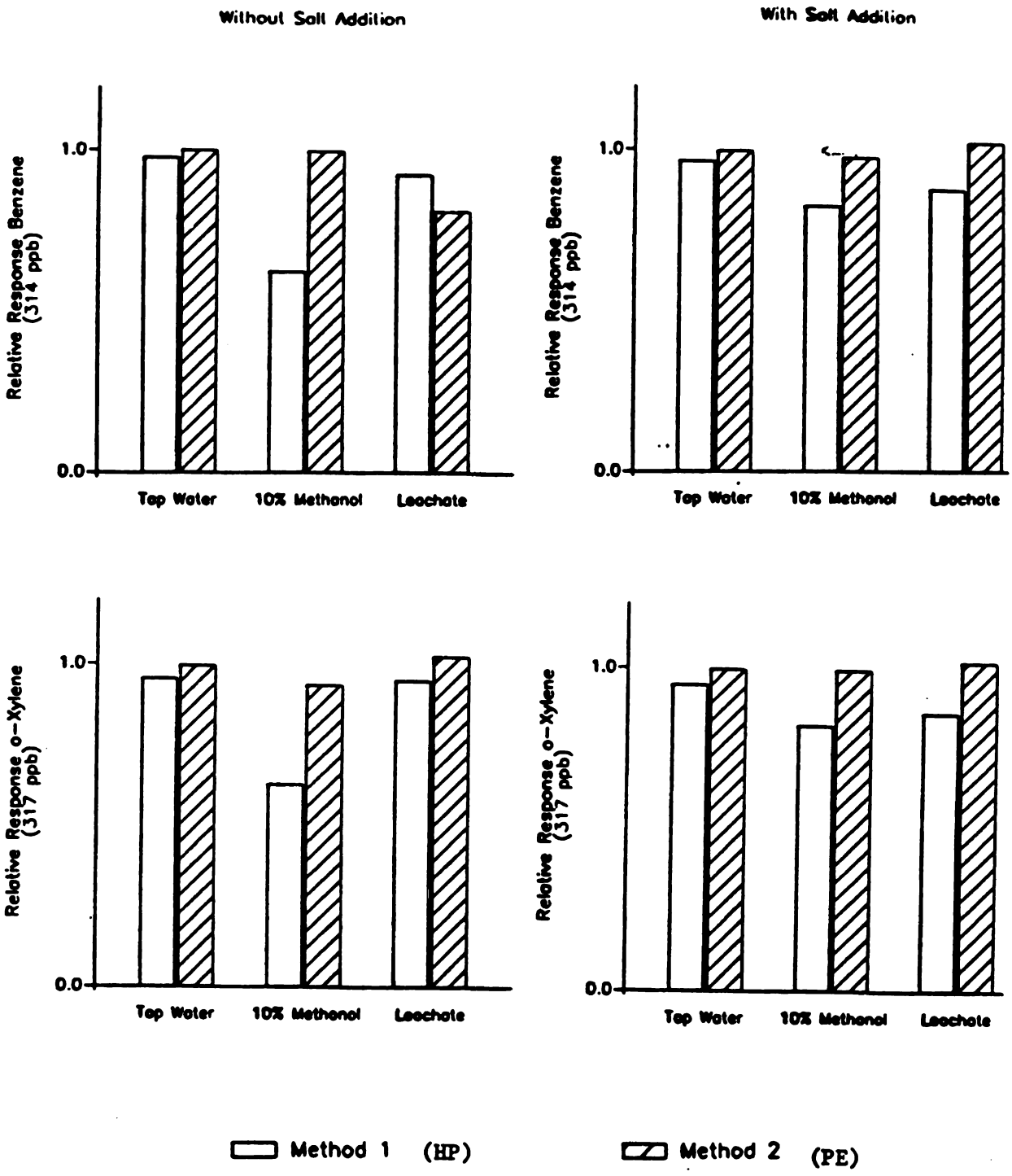


Figure A-3. Relative response for benzene and xylene from various aqueous solutions.

APPENDIX B

COMPLETE CHARACTERIZATION FOR FRESH GASOLINE SAMPLE

Name	Mole Fraction	$C_{s,i}^*$	$S_{w,i}^*$	MW	Mass Fraction
	0.000022	122927.7	85253.07	44	0.00001
propane	0.004448	17527.46	4363.905	58	0.00258
isobutane	0.011672	9333.113	553.389	58	0.00677
n-butane	0.147724	3926.912	523.278	58	0.08568
butene	0.003885	6349.915	2807.429	70	0.00272
isopentane	0.165328	4126.882	135.401	70	0.11573
n-pentane	0.067333	1980.896	174.139	72	0.04848
2-methyl-2-butane	0.014805	2132.773	296.782	72	0.01066
3,3-dimethyl-1,2-butadiene	0.032777	1884.3	336.452	72	0.0236
3-methyl-1-pentane	0.036267	1443.036	32.638	86	0.03119
2,3-dimethyl-pentane	0.080639	1169.031	1.468	86	0.06935
2-methyl-pentane	0.036534	935.392	28.287	86	0.03142
3-methyl-pentane	0.003976	1052.101	150.476	86	0.00342
2-methyl-2-pentene	0.028848	733.269	3.778	86	0.02481
	0.015435	818.551	51.9	78	0.01204
hexene	0.004538	815.777	854.295	78	0.00354
	0.009023	755.45	33.296	86	0.00776
n-hexane	0.015441	678.149	31.974	86	0.01328
trans-2-hexane	0.007654	487.44	17.222	84	0.00643
3,3-dimethyl pentane	0.038083	359.139	7.465	84	0.03199
2,2-dimethyl pentane	0.02486	293.403	0	100	0.02486
benzene	0.020589	432.837	2576.882	78	0.01606
2,4-dimethyl pentane	0.0188	234.565	13.113	100	0.0188

1-methylcyclo pentene	0.01922	216.539	0	100	0.01922
	0.00712	225.691	49.768	100	0.00712
cyclohexane	0.00169	132.565	0	100	0.00169
2-methyl hexane	0.00288	221.181	28.591	100	0.00288
n-heptane	0.01168	159.272	54.666	100	0.01168
	0.00264	216.619	0	100	0.00264
	0.00276	204.264	0	100	0.00276
dimethyl- pentane	0.02049	94.141	0	100	0.02049
trimethyl- pentane	0.012464	70.048	0	114	0.01421
	0.00186	56.542	0	100	0.00186
toluene	0.063532	145.402	698.284	92	0.05845
2,3,4-trimethyl- pentane	0.011289	65.869	5.985	114	0.01287
2,3-dimethyl- hexane	0.002464	43.149	28.699	114	0.00281
2-methyl- heptane	0.000561	12	0	114	0.00064
4-methyl- heptane	0.000815	12.198	0	114	0.00093
3,4-dimethyl- hexane	0.002508	22.326	0	114	0.00286
	0.001008	20	535.397	114	0.00115
3-methyl- heptane	0.004578	18.002	0	128	0.00586
n-octane	0.002414	19.221	0	128	0.00309
ethyl- benzene	0.013254	53.844	193.233	106	0.01405
m&p-xylene	0.046792	50.32	175.096	106	0.0496
trimethyl- hexane	0.000164	35	0	128	0.00021
o-xylene	0.019613	44.028	216.754	106	0.02079
	0.000507	2.367	0	140	0.00071
	0.0005	2	0	140	0.0007
	0.0011	2	90.335	140	0.00154
	0.002085	1.658	0	140	0.00292
	0.000907	3.05	0	140	0.00127
	0.002828	13.303	45.656	140	0.00396
trimethyl- benzene	0.02045	10.866	62.516	120	0.02454
	0.006542	8.135	35.28	140	0.00916
	0.003864	10.133	123.164	140	0.00541
	0.021728	7.622	56.392	140	0.03042
	0.001028	5	0	140	0.00144
	0.001221	2.744	0	140	0.00171
	0.004971	5.213	110.298	140	0.00696
	0.000407	5	0	140	0.00057

	0.0048	4.271	29.906	140	0.00672
	0.0052	3.494	15.413	140	0.00728
	0.002092	1.559	17.061	140	0.00293
	0.00395	2.182	27.217	140	0.00553
	0.003692	2.07	21.412	140	0.00517
	0.00155	2.358	26.379	140	0.00217
	0.001221	0.301	31.916	140	0.00171
	0.002364	1.796	0	140	0.00331
	0.003664	1.153	33.23	140	0.00513
dodecane	0.002114	1.5	0	170	0.00296
	0.001611	2.48	18.577	140	0.00274
	0.004126	1.508	18.346	150	0.00619
	0.001193	5.025	0	150	0.00179
	0.00032	28.924	0	150	0.00048
	0.002053	3.33	0	150	0.00308
	0.000866	4.307	0	150	0.0013
naphtha-lene	0.002523	18.154	107.797	128	0.00323
	0.00048	0	0	150	0.00072
	0.000713	0	0	150	0.00107
	0.000193	43.819	0	150	0.00029
	0.001206	1.74	0	150	0.00181
	0.000286	7.042	0	150	0.00043
	0.000813	0	0	150	0.00122
	0.000513	0	0	150	0.00077
	0.00044	0	0	150	0.00066
	0.001006	0	0	150	0.00151
n-hexyl-benzene	0.002864	17.726	14.74	162	0.00464
methylnaph-thalene	0.002232	0.942	20.146	142	0.00317
	0.00014	0	0	150	0.00021
	0.00004	0	0	150	0.00006
	0.000033	0	0	150	0.00005
	0.000113	3039.661	0	150	0.00017
	0.000386	123.091	0	150	0.00058
	0.00072	2.686	0	150	0.00108
	0.001193	0	0	150	0.00179
	0.000313	6.233	0	150	0.00047
	0.000126	317.891	0	150	0.00019
	0.00028	274.162	0	150	0.00042
	0.000046	1435.247	0	150	0.00007
	0.000033	0	0	150	0.00005
	0.000026	399.027	0	150	0.00004
	0.000026	0	0	150	0.00004
	0.000006	7247.95	0	150	0.00001

APPENDIX C

VENTING MODEL

```
$LARGE
      REAL X(200),XMAS(200),XML(200),XAQU(200),XM(200)
      REAL XMLR(200),KW(200),KAIR(200),XMOL(200)
      REAL NCI(200),TOTMAS,TOTMOL
      INTEGER PEAK(200),CMW(200)
      TEMP=294.25
      R=82.04
      V=1000.00
C     INPUT FLOW RATE AIR,WATER,GAS (BOTH ML/MIN), MG
      READ(8,*) Q,QWATER,TOTMAS
      WRITE(*,*) Q,QWATER,TOTMAS
C
C     READ NUMBER OF COMPOUNDS AND THOSE OF INTEREST
C     NC,NI,NCI(I)
      READ (8,*) NC,NI,(NCI(I),I=1,NI)
C
C     READ IN TOLERANCE  MAX ITERATION  NSKIP FOR WRITE
      READ (8,*) TOL,MAXIT,NSKIP
C     READ FOUR TIME STEPS
      READ (8,*) DELT1,DELT2,DELT3,DELT4
C
      J=1
5     READ (8,*) (PEAK(I),XM(I),KAIR(I),KW(I),CMW(I),
     +X(I),I=1,NC)
      WRITE (*,10) (PEAK(I),XM(I),KAIR(I),KW(I),CMW(I),
     +X(I),I=1,NC)
10    FORMAT (I5,5X,F8.6,5X,F10.3,5X,F10.3,5X,I5,5X,F8.6)
C     TMR=TOTAL MASS REMOVED (MG)
C     TOT=TOTAL MASS REMOVED (MG)
      TIME=0.0
      TOT=0.0
C     CALC MASS OF EACH COMPOUND
      DO 12 I=1,NC
      XMAS(I)=TOTMAS*X(I)
12    CONTINUE
```

```
C
      DO 600 J=1,MAXIT,1
      TMR=0.0
      TOTMOL=0.0
      MASRT=0.0
      IF (TIME.LT.10.0) DELT=DELT1
15    IF (TIME.GE.10.0) DELT=DELT2
      IF (TIME.GE.60.0) DELT=DELT3
      IF (TIME.GE.300.0) DELT=DELT4
      TIME=TIME+DELT
      DO 100 I=1,NC,1
C     CALCULATE XMLR=MASSLOSS RATE OF COMP IN DELTA T
C     CALCULATE XML=MASSLOSS OF COMP IN TIME DELTA T
      XML(I)=Q*DELT*XM(I)*KAIR(I)/1000
      XAQU(I)=QWATER*DELT*XM(I)*KW(I)/1000
      TMR=TMR+XML(I)+XAQU(I)

C
      XMAS(I)=XMAS(I)-XML(I)-XAQU(I)
      IF(XMAS(I).LE.0.0) XMAS(I)=0.00000000
      XMOL(I)=XMAS(I)/CMW(I)
      TOTMAS=TOTMAS-XML(I)-XAQU(I)
      TOTMOL=TOTMOL+XMOL(I)
100   CONTINUE
C
C     CALCULATE NEW MOLE FRACTION


      DO 200 I=1,NC,1
       IF (TOTMOL.EQ.0.0) X(I)=0.0
C       WRITE(*,*) TOTMOL
       IF (TOTMOL.EQ.0.0) GO TO 900
       XM(I)=XMOL(I)/TOTMOL
200   CONTINUE
C
      IF(TMR.LE.TOL) GO TO 900
      TOT=TOT+TMR
      IF (MOD(J,NSKIP).EQ.0.0) THEN
      WRITE(7,300) TIME,(XM(NCI(I)),I=1,NI),TOTMAS
      ENDIF
300   FORMAT(3X,F8.1,5X,7F12.9,5X,F12.3)
600   CONTINUE
900   CONTINUE
      STOP
      END
```

LIST OF REFERENCES

Abriola, L.M. and G.F. Pinder, 1985. A multiphase approach to the modeling of porous media contamination by organic compounds. 1. Equation development. Water Res. Res. 21(1):11-18.

Al-Sahhaf, T.A. 1989. Prediction of the solubility of hydrocarbons in water using UNIFAC. J. Envir. Sci. and Health 24:49-56.

Adamson, A.W. 1990. Physical Chemistry of Surfaces, 5th edition. Wiley and Sons, Inc. New York, NY.

Ambwani, D.S. and Fort, T. Jr. 1979. Pendant drop technique for measuring liquid boundary tentions. Surface and Colloid Science. 2:93-119.

API. 1985. Laboratory study on solubilities of petroleum hydrocarbons in groundwater. API Publication # 4395.

American Petroleum Institute. 1987. Manual of Sampling and Analytical Methods for Petroleum Hydrocarbons in Groundwater and Soil. API Publication # 4449:167-170.

Anderson, M.R., R.L. Johnson and J.L. Pankow. 1987. The dissolution of residual DNAPL from a saturated porous medium. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Dectection and Restoration. 409-428.

Anderson, S.H.; Gantzer, C.J.; Boone, J.M. and Tully, R.J. 1988. Rapid nondestructive bulk density and soil-water determination by computed tomography. Soil Sci. Soc. of Am. J. 52:35-40.

Anderson, W.G. 1987. Wettability literature survey - Part 4. Effects of wettability on capillary pressure. J. Pet. Technology 1283-1300.

Annable, M.D. 1991. Aqueous-phase transport in soils contaminated with a multicomponent liquid hydrocarbon and subjected to vapor flow. Ph.D. Dissertation, Michigan State

University.

ASTM. 1990. Annual Book of ASTM Standards. American Society of Testing Materials, Philadelphia, PA.

Atkins, P.W. 1986. Physical Chemistry. 3rd edition. W.H. Freeman and Company, New York, NY pp 166-169.

Baehr, A.L. 1987. Selective transport of hydrocarbons in the unsaturated zone due to aqueous and vapor phase partitioning. Water Res. Res. 23:1926-1938.

Baehr, A.L. and M.Y. Corapcioglu. 1987. A compositional multiphase model for groundwater contamination by petroleum products 2. numerical solution. Water Res. Res. 23:201-213.

Baehr, A.L., G.E. Hoag and M. Marley. 1989. Removing volatile contaminants from the unsaturated zone by inducing advective air-phase transport. J. of Contaminant Hydrology 4:1-26.

Batchelder, G.V., W.A. Panzeri and H.T. Phillips. 1987. Soil ventilation for the removal of adsorbed liquid hydrocarbons in the subsurface. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, 678-691.

Banerjee, S. 1984. Solubility of organic mixtures in water. Environmental Science and Technology. 18:587-591.

Bisdom, E.B.A. and Theil, F. 1981. Submicroscopy of Soil and Weathered Rocks. Bisdom, E.B.A., Ed.; 1st workshop of the International Working-Group on submicroscopy of undisturbed soil materials (IWGSUSM), 1980, Wageningen, the Netherlands. pp 191-206.

Borden, R.C. and Kao, C.M. 1989. Water flushing of trapped residual hydrocarbon: mathematical model development and laboratory validation. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration.

Bourchard, D.C., C.G. Enfield and M.D. Piwoni. 1989. Transport processes involving organic chemicals. In: Reactions and Movement of Organic Chemicals in Soils. Sawhney, B.L., Brown K. Eds. SSSA Special Publication 22:349-372.

Bowles, J.E. 1896. Enginnering Properties of Soils and Their Measurement. 3rd. Ed.; Verma, K. Ed. Mcgraw-Hill, Inc.

Boyd, S.A. and Sun, S. 1990. Residual petroleum and polychlorobiphenyl oils as sorptive phases for organic contaminants in soils. Environ. Sci. Technol. 24:142-144.

Boyd, S.A. 1991. Personal communication.

Briggs, G.G. 1969. Molecular structure of herbicides and their sorption by soil. Nature 233:1288.

Brooks, R.H. and Corey, A.T. 1964. Hydraulic properties of porous media. Hydrology Paper no.3, Colorado State University, Fort Collins, CO, 27pp.

Brown, R.A.; Hoag, G.E. and Norris, R.D. 1987. The remediation game: pump, dig, or treat. Water Pollution Control Federation.

Brusseau, M.L., P.S.C. Rao, R.E. Jessup and J.M. Davidson. 1989. Flow interruption: a method for investigating sorption nonequilibrium. J. Contaminant Hydrology 4:223-240.

Burris and MacIntyre. 1986. Solution of hydrocarbons in a hydrocarbon-water system with changing phase composition due to evaporation. Environ. Sci. Tech. 20:296-299.

Chatzis, I., and F.A.L. Dullien. 1983. Dynamic immiscible displacement mechanisms in pore doublets: theory vs. experimentation. J. Colloid and Interface Science 91:199-222.

Chatzis, I., N.R. Morrow and H.T. Lim. 1983. Magnitude and detailed structure of residual oil saturation. SPE Journal 23:311-325.

Chiou, C.T. and Schmedding, D.W. 1982. Partitioning of organic compounds in octanol-water systems. Environ. Sci. Technol. 16:4-10.

Chiou, C.T., P.E. Porter and D.W. Schmedding. 1983. Partition equilibria of nonionic organic compounds between soil organic matter and water. Environ. Sci. Technol. 17:227-231.

Chiou, C.T. 1989. Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. In: Reactions and Movement of Organic Chemicals in Soils. Sawhney, B.L., Brown, K. Eds.) Special Pub. # 22:1-29.

Cline, P.V., Delfino, J.J. and Rao, P.S. 1991. Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures. Environ. Sci. Technol. 25:914-920.

Coleman, W.E., J.W. Munch, R.P. Streicher, H.P. Ringhand and F.C. Kopfler. 1984. The identification and measurement of components in gasoline, kerosene, and number 2 fuel oil that partition into the aqueous phase after mixing. Arch. Environ. Contam. Toxicology 13:171-178.

Conrad, S.H., E.F. Hagan and J.L. Wilson. 1985. Why are residual satuations of organic liquids different above and below the water table. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration.

Convery, M.P. 1979. The behavior and movement of petroleum products in unconsolidated surficial deposits. M.S. Thesis, University of Minnesota.

Corapcioglu, M.Y. and A.L. Baehr. 1987. Acompositional multiphase model for groundwater contamination by petroleum products 1. theoretical considerations. Water Res. Res. 23:191-200.

Corey, A.T. 1986. Mechanics of Immiscible Fluid in Porous Media, 2nd ed. Water Resources Publ., Fort Collin, CO.

Crow, W.L.; Anderson, E.P. and Minugh, E.W. 1987. Subsurface venting of vapors emanating from hydrocarbon product on ground water. Ground Water Review. 4:51-56.

Demond, A.H. 1988. Capillarity in two-phase liquid flow of organic contaminants in groundwater. Ph.D. Dissertation, Stanford University. 221pp.

EPA. 1988. Must for USTs, a summary of the new regulations for underground storage tanks, EPA/600/M-86/020.

EPA, Method 8240. 1986. Gas chromatography/mass spectrometry for volatile organic contaminatns. In: Test Methods for Evaluating Solid Waste. Vol. 1B: Laboratory Manual Physical/Chemical Methods.

Faust, C.R. 1984. Transport of immiscible fluids within and below the unsaturated zone-a numerical model. GeoTrans Technical Report #84-01.

Faust, C.R., J.H. Guswa and J.W. Mercer. 1989. Simulation of three-dimensional flow of immiscible fluids within and below the unsaturated zone. Water Res. Res. 25:2449-2464.

Ferrand, L.A.; Milly, P.C.D. and Pinder, G.F. 1989. Experimental determination of three-fluid saturation profiles in porous media. J. of Contaminant Hydrology. 4:373-395.

Gannon, K., P.J. Wilson, A.N. Clarke, R.D. Mutch, Jr. and J.H. Clark. 1989. Soil cleanup by in situ aeration. II Effects of impermeable caps, soil impermeability and evaporative cooling. Separation Sci. and Tech. 24:831-862.

Hayden, N.J. 1987. Sulfate Retention and Release in Six Eastern Soils. MS Thesis, Michigan State University.

Heilman, M.D., Carter, D.L. and Gonzalez, C.L. 1965. The ethylene glycol monoethyl ether (EGME) technique for determining soil-surface area. Soil Science 100:409-413.

Hern, S.C. and S.M. Melancon (eds) 1986. Vadose zone modeling of organic pollutants. Lewis Pub., Inc. 295 pp.

Hinchee, R.E., D.G. Downey and E.J. Coleman. 1987. Enhanced bioreclamation, soil venting and groundwater extraction: a cost effectiveness and feasibility comparison. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Protection, Detection and Restoration. 147-164.

Hoag, G.E. and B. Cliff. The use of the soil venting technique for the remediation of petroleum contaminated soils.

Hoag, G.E. and M.C. Marley. 1986. Gasoline residual saturation in unsaturated uniform aquifer materials. J. Environ. Eng. 112:586-603.

Hunt, J.R.; Sitar, N. and Udell, K.S. 1988. Nonaqueous phase liquid transport and cleanup I. Analysis of mechanisms. II. Experimental studies. Water Research. 24:1247-1269.

Hutzler, N.J., J.S. Gierke and B.E.Murphy. 1990. Vaporizing VOC's. Civil Engineering. 57-60.

Hutzler, N.J., Gierke, J.S. and Krause, L.C. 1989. Movement of volatile organic chemicals in soils. Soil Science Society of America Society of Agronomy. pp 373-403.

Hutzler, N.J. and J.S. Gierke. 1989. State of Technology Review Soil Vapor Extraction Systems. EPA Report. 600/2-89/024. 87 pp.

Jenssen, P.D. and Heyerdahl, P.H. 1988. Soil column descriptions from X-ray computed tomography density images. Soil Science. 146:102-107.

Johnson, R.L., C.D. Palmer and J.F. Keely. 1987. Mass transfer of organics between soil, water and vapor phases: implications for monitorying, biodegradation and remediation. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration. 498-507.

Johnson, R.L., K.A. McCarthy and M. Perrott. 1989. Direct comparison of vapor-, free-product-and aqueous-phase monitoring for gasoline leaks from underground storage systems. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration. 605-616.

Johnson, P.C., Kemblowski, M.W., Colhart, J.D., Byers, D.L. and Stanley, C.C. 1989. A practical approach to the design, operation, and monitoring of in-situ venting systems. Proceeding of USEPA Soil Vapor Extraction Technology Workshop. 38pp.

Johnson, P.C.; Kembloski, M.W. and Colthart, J.D. 1990. Quantitative analysis for the cleanup of hydrocarbon-contaminated soil by in-situ soil venting. Ground Water 28:413-429.

Johnson, P.C., C.C. Stanley, D.L. Byers, D.A. Benson, and M.A. Acton. 1991. Soil venting at a california site: field data reconciled with theory. Schell Development, Westhollow Research Center, Houston, TX.

Kaluarachchi, J.J. and J.C. Parker. 1989. An efficient finite element method for modeling multiphase flow. Water Res. Res. 25:43-54.

Kaluarachchi, J.J. and J.C. Parker. 1990. Modeling multicomponent organic chemical transport in three-fluid-phase porous media. J. Contam. Hydrology 5:349-374.

Kerfoot, H.B. 1987. Soil-gas measurement for detection of groundwater contamination by volatile organic contaminants. Environ. Sci. Technol. 21:1022-1024.

Lambert, S.M. 1968. Omega (Ω): a useful index of soil sorption equilibria. J. Agric. Fd. Chem. 16:340-343.

Lenhard, R.J. and J.C. Parker. 1987. Measurement and prediction of saturation-pressure relationships in three-phase porous media systems. J. Contam. Hydrology. 1:407-424.

Leverett, M.C. 1941. Capillary behavior in porous solids. Trans. AIME 142:152-169.

Mackay, D. and Shiu. W.Y. 1981. A critical review of Henry's Law constants for chemicals of environmental interest. J. Phys. Chem. Ref. Data 10:1175-1198.

Marley, M.C. and Hoag, G.E. 1984. Induced soil venting for recovery/restoration of gasoline hydrocarbons in the vadose zone. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Restoration. pp 474-503.

Marks, B.J., D.A. Selby, R.E. Hinchee and G. Davitt. 1989. Soil gas and groundwater levels of benzene and toluene-qualitative and quantitative relationships. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Restoration. 71-85.

Marrin, D.L. 1989. Detection of non-volatile hydrocarbons using a modified approach to soil-gas surveying. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Restoration. 357-366.

Massman, J.W. 1989. Applying groundwater flow models in vapor extraction system design. J. of Environmental Engineering. 115:129-149.

Maynard, J.B. and Sanders, W.N. 1969. Determination of the detailed hydrocarbon composition and potential atmospheric reactivity of full-range motor gasoline. J. of the Air Pollution Control Association. 19:505-510.

McKee, J.E., F.B. Laverty, and R.H. Hertel. 1972. Gasoline in groundwater. J. WPCF. 44:293-302.

Miller, C.T. and Mayer, A.S. 1990. Groundwater: A review of the 1989 literature. Journal WPCF. 62:700-737.

Miller, C.T., M.M. Poirier-McNeill, and A.S. Mayer. 1990. Dissolution of trapped nonaqueous phase liquids; mass transfer characteristics. Water Res. Res. 26:2783-2796.

Morgan, C. and C. Klingler. 1987. The soil gas survey as a preliminary investigative tool for hydrocarbon release. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration 347-355.

Morrow, N.R. and B. Songkran. 1981. Effect of trapping and buoyancy forces on nonwetting phase trapping in porous media. In: Surface Phenomena in Enhanced Oil Recovery. D.O. Shah Ed. Plenum Publ. Corp.

Paetzold, R.F.; De Los Santos, A. and Matzkanin, G.A. 1987. Pulsed nuclear magnetic resonance instrument for soil-water content measurement: sensor configurations. Soil Sci. Soc. of Am. J. 51:287-290.

Parker, J.C. 1989. Multiphase flow and transport in porous media. Review of Geophysics 27:311-328.

Parker, J.C. and R.J. Lenhard. 1987. Amodel for hysteretic constitutive relations governing multiphase flow, 1. saturation-pressure relations. Water Res. Res. 23:2187-2196.

Parker, J.C., R.J. Lenhard and T. Kuppusamy. 1987. A parametric model for constitutive properties governing multiphase flow in porous media. Water Res. Res. 23:618-624.

Petrovic, A.M.; Siebert, J.E. and Reike, P.E. 1982. Soil

bulk density analysis in three dimensions by computed tomographic scanning. Sol. Sci. Soc. of Am. J. 46:445-450.

Phannkuch, H.O. 1984. Determination of the contaminant source strength from mass exchange processes at the petroleum-groundwater interface in shallow aquifer systems. Proc. NWWA/API Conf. Pet. Hydrocarbons and Organic Chem. in Ground Water Prevention, Detection and Restoration.

Protz, R.; Shipitalo, M.J.; Mermut, A.R. and Fox, C.A. 1987. Image analysis of soils - present and future. Geoderma. 40:115-125.

Raymond, R.L.; Jamison, V.W. and Hudson, J.O. 1975. Final report on beneficial stimulation of bacterial activity in ground waters contaning petroleum products. American Petroleum Institute.

Rhoades, J.D. 1982. Cation exchange capacity. Method of Soil Analysis; Part 1: Physical Mineralogical Methods.

Riddick, J.A., W.B. Bunger, and T.K. Sakano. 1986. Techniques of Chemistry, Vol. II. Organic Solvents. Physical Properties and Methods of Purification, 4th ed. Wiley, NY.

Robbins, G.A. 1987. Influence of pore air/water exchange on the diffusion of volatile organic vapors in soil. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration. 509-520.

Sanders, W.N. and Maynard, J.B. 1968. Cappillary gas chromatographic method for determining tha C3-C hydrocarbons in full-range motor gasoline. Analytical Chemistry. 40:527-535.

Schroedl, S.R. and H.B. Kerfoot. 1989. Long-term soil-gas monitoring of underground storage tanks. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration. 617-626.

Schwille, F. 1988. Dense Chlorinated Solvents in Porous and Fractured Media. Lewis Pub. Chelsea, MI. 146pp.

Schiegg, H.O. 1984. Considerations on water, oil and air in porous media. Wat. Sci. Tech. 17:467-476.

Schiegg, H.O. nad McBride, J.F. 1987. Laboratory setup to study two-dimensional multiphase flow in porous media. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration. pp 371-395.

Senn, R.B. and M.S. Johnson. 1985. Interpretation of gas chromatography data as a tool in subsurface hydrocarbon investigations. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration.

Sleep, B.E. and J.F. Sykes. 1989. Modeling the transport of volatile organics in variably saturated media. Water Res. Res. 25:81-92.

Stevenson, F.J. 1982. Humus Chemistry. Wiley and Sons. 444p.

Sun, S. and Boyd, S.A. 1991. Sorption of polychlorobiphenyl (PCB) congeners by residual PCB-oil phases in soils. J. Environ. Qual. 20:557-561.

Sutanto, E.; Davis, H.T. and Scriven, L.E. 1990. Liquid distributions in porous rock examined by cryo-scanning electron microscopy. Presented at the 1990 SPE Annual Technical Conference and Exhibition. pp 3-9.

Sutanto, E. 1988. Cryo-sem of liquid-bearing rock. Bailey, G.W., Ed., Proceeding of the 46th Annual Meeting of the Electron Microscopy Society of America: San Francico Press, Inc.:104-105.

Thomas, J.M.; Lee, M.D.; Bedient, P.B.; Borden, R.C.; Canter, L.W. and Ward, C.H. 1987. Leaking underground storage tanks: Remediation with emphasis in in-situ biorestoration. USEPA Research and Development.

Thornton, J. and Wootan, L.W. 1982. Venting for the removal of hydrocarbon vapors from gasoline contaminated soil. J. Env. Sci. Health. A17:31-44.

Tucker, W.A.; Kemblowski, M.W. and Draney, D.E. 1989. Technological limits of groundwater remediation: a statistical evaluation method. Proc. of NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Restoration. pp 249-263.

van der Waarden, M., Bridie, A.L.A.M. and Groenewood, W.M. 1971. Transport of mineral oil components to groundwater. Water Research. 5:213-226.

Verschueren, K. 1983. Handbook of Environmental Data on Organic Chemicals. VanNostrand Reinhold Company, Inc. 1310 pp.

Voice, T.C. and Ryan J.F. 1991. Comparison of alternative methods for analysis of VOCs in environmental matrices. Presented at the 7th Annual Waste Testing and Quality Assurance Symposium, Washington, D.C.

Warner, G.S., Nieber, J.L., Moore, I.D. and Geise, R.A. 1989. Division S1-soil physics: Characterizing macropores in soil by computed tomography. Soil Sci. Soc. of Am. J. 53:653-660.

Wilson, J.L. and S.H. Conrad. 1984. Is physical displacement of residual hydrocarbons a realistic possibility in aquifer restoration? in Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, pp274-298.

Wilson, J.L. 1988. The role of wetting in environmental problems. in Proc. of Conf. on Fundamental Research Needs in Environmental Eng., Assoc. Environ. Engr. Professors, Washington, D.C.

Wilson, J.L., S.H. Conrad, W.R. Mason, W. Peplinski and E. Hagan. 1990. Laboratory investigation of residual liquid organics from spill, leaks, and the disposal of hazardous wastes in groundwater. EPA report 600/6-90/004.

Wilson, J.T., Leach, L.E., Henson, M. and Jone, J.N. 1986. In-situ biorestoration as a ground water remediaton. Ground Water Monitoring Review. 3:56-64.

Wilson, D.J., Clarke, A.N. and Clarke, J.H. 1988. Soil cleanup by in-situ aereation I. Mathematical modeling. Separation Science and Technology. 23:991-1037.

Wootan, W.L. and Voynick, T. 1983. Forced venting to remove gasoline vapor from a large-scale model aquifer. Texas Research Institute, Inc. Report submitted to API. 61pp.

Yaws, C. L. and Yang, H.C. 1990. Water solubility data for organic compounds. Pollution Eng. 70-75.

Yurteri, C., Ryan, D.F., Callow, J.J. and Gurol, M.D. 1987. The effect of chemical composition of water on Henry's Law constant. Journal WPCF 59:950-956.

Zalidis, G.C., Annable, M.D., Wallace, R.B., Hayden, N.J. and Voice, T.C. 1991. A laboratory mehtod for studying the aqueous phase transport of dissolved constituents from residually held NAPL in unsaturated soil columns. J. Cont. Hydrology 8:143-156.

Zalidis, G.C., Wallace, R.B. and Voice, T.C. (unpublished). Influence of initial water saturation on the residual saturation of a spreading organic liquid in the vadose zone.