1993

Transport and fate of dense non-aqueous phase liquids in an alluvial and karst/fractured aquifer Valley and Ridge Province mid-eastern United States

James Frederick Ford
The University of Montana

Let us know how access to this document benefits you.
Follow this and additional works at: https://scholarworks.umt.edu/etd

Recommended Citation
https://scholarworks.umt.edu/etd/9234

This Thesis is brought to you for free and open access by the Graduate School at ScholarWorks at University of Montana. It has been accepted for inclusion in Graduate Student Theses, Dissertations, & Professional Papers by an authorized administrator of ScholarWorks at University of Montana. For more information, please contact scholarworks@mso.umt.edu.
Permission is granted by the author to reproduce this material in its entirety, provided that this material is used for scholarly purposes and is properly cited in published works and reports.

** Please check “Yes” or “No” and provide signature**

Yes, I grant permission

Yes, I grant permission

No, I do not grant permission

Author’s Signature

Date: 11/15/93

Any copying for commercial purposes or financial gain may be undertaken only with the author’s explicit consent.
TRANSPORT AND FATE OF DENSE
NON-AQUEOUS PHASE LIQUIDS
IN AN ALLUVIAL AND
KARST/FRACTURED AQUIFER,
VALLEY AND RIDGE PROVINCE,
MID-EASTERN UNITED STATES

by

James Frederick Ford
B.S., East Carolina University

Presented in partial fulfillment of requirements
for the degree of Master of Science
University of Montana
October, 1993

Approved By:

[Signatures]
Chairperson, Board of Examiners
Dean, Graduate School

[Signature]
Date
Nov. 16, 1993
ABSTRACT

Ford, James Frederick, M.S., October, 1993           Geology

Transport and Fate of Dissolved Dense Non-Aqueous Phase Liquids in an Alluvial
and Karst/Fractured Aquifer, Valley and Ridge Province, Mid-Eastern United
States (202 pp.)

Director: Dr. William W. Woessner

A government-owned facility in West Virginia was selected to investigate the
transport and fate of selected DNAPL's in an alluvial and fractured/karst
environment. The facility was found to be primarily contaminated with TCE in the
dissolved and immiscible phases. The goal of this study was to identify the
contaminant sources and develop a conceptual hydrological model that explained the
physical and chemical behavior of the DNAPLs.

The conceptual model was developed based on interpretation of geologic mapping,
fracture trace analysis, in-situ aquifer testing, construction of potentiometric maps,
installation of seepage meters/mini-piezometers, and chemical analysis of ground-
water, surface water, sediment, and soil.

Study results show the presence of an unconfined, unconsolidated, alluvial,
floodplain aquifer and an underlying unconfined, bedrock aquifer at the site. The
alluvial and bedrock aquifers are hydraulically well connected. Hydraulic
conductivities range between 0.15 to 4.5 m/d for the alluvial aquifer while
transmissivities of the bedrock aquifer ranged from 25 to 77 m²/d. The North Branch
of the Potomac River appears to be the ultimate discharge point for the alluvial
aquifer and upper portion of the bedrock aquifer. Source areas of TCE are
solvent/acid disposal pits and burn area located adjacent to the site. The structure and
orientation of the bedrock geology underlying the site influences the location and
transport of the waste solvents that have penetrated the aquifer. The vertical attitude
of bedrock fractures and solution features has provided numerous pathways for
immiscible phase DNAPL to penetrate the bedrock aquifer. High dissolved
concentrations measured in both aquifers are used to infer the presence of immiscible
phase TCE. The dissolved TCE is also being transformed as it is transported in this
groundwater system.

Reductive dehalogenation caused by microbial degradation in the riverbed sediments
is implied by the presence of cis-1,2-dichloroethene and vinyl chloride in the river.
The bedrock ground-water system is inferred to be reduced, thus TCE has become
unstable and undergoes reduction.

Recommendations for site remediation plans include the excavation and treatment of
the unconsolidated alluvial material to remove immiscible phase contamination.
Remediation of the bedrock system appears infeasible at this time, thus a long-term
ground-water management plan is needed for this site.
ACKNOWLEDGEMENTS

I would like to thank Drs. William W. Woessner and Nancy Hinman whose direction, wisdom and knowledge helped focus my wandering thoughts. I also thank Greg Mott (CH2M HILL) without whose understanding and help this study could not have been possible and Dr. Caron Smith for his detailed review of this manuscript. Most of all I would like to acknowledge Laura, my family and friends for all their love, support and encouragement.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td><strong>CHAPTER I: INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>Statement of Problem</td>
<td>1</td>
</tr>
<tr>
<td>Project Goals</td>
<td>4</td>
</tr>
<tr>
<td>Study Site Setting</td>
<td>5</td>
</tr>
<tr>
<td>Thesis Organization</td>
<td>17</td>
</tr>
<tr>
<td><strong>CHAPTER II: DNAPL IN THE ENVIRONMENT</strong></td>
<td>18</td>
</tr>
<tr>
<td>Transport and Fate - A Conceptual Approach</td>
<td>18</td>
</tr>
<tr>
<td>Physical Behavior</td>
<td>19</td>
</tr>
<tr>
<td>Chemical Behavior</td>
<td>31</td>
</tr>
<tr>
<td>TCE-Transformations</td>
<td>36</td>
</tr>
<tr>
<td><strong>CHAPTER III: PREVIOUS INVESTIGATION OF THE FACILITY</strong></td>
<td>39</td>
</tr>
<tr>
<td><strong>CHAPTER IV: METHODOLOGY</strong></td>
<td>45</td>
</tr>
<tr>
<td>Conceptual Hydrogeological Model</td>
<td>45</td>
</tr>
<tr>
<td>Geology</td>
<td>45</td>
</tr>
<tr>
<td>Discharge Assessment</td>
<td>57</td>
</tr>
<tr>
<td>Defining Extent of Contamination</td>
<td>61</td>
</tr>
<tr>
<td>Identifying Potential Sources</td>
<td>61</td>
</tr>
<tr>
<td>Soil Investigation</td>
<td>61</td>
</tr>
<tr>
<td>Water Investigation</td>
<td>64</td>
</tr>
<tr>
<td>Surface Water and Sediment Investigation</td>
<td>64</td>
</tr>
<tr>
<td><strong>CHAPTER V: RESULTS</strong></td>
<td>67</td>
</tr>
<tr>
<td>Geology</td>
<td>67</td>
</tr>
<tr>
<td>Geologic Mapping</td>
<td>68</td>
</tr>
<tr>
<td>Groundwater Hydrology</td>
<td>86</td>
</tr>
<tr>
<td>Discharge Assessment</td>
<td>100</td>
</tr>
<tr>
<td>Extent of Contamination</td>
<td>102</td>
</tr>
<tr>
<td>Contaminant Fate and Transport</td>
<td>112</td>
</tr>
<tr>
<td>Chapter Title</td>
<td>Page</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>CHAPTER VI: POTENTIAL REMEDIAL APPROACHES</td>
<td>129</td>
</tr>
<tr>
<td>Conventional Approaches</td>
<td>129</td>
</tr>
<tr>
<td>Present Technology</td>
<td>130</td>
</tr>
<tr>
<td>Fractured Rock Technology</td>
<td>133</td>
</tr>
<tr>
<td>CHAPTER VII: CONCLUSIONS AND RECOMMENDATIONS</td>
<td>136</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>141</td>
</tr>
<tr>
<td>APPENDIX A: Identification of Potential Sources</td>
<td>A-148</td>
</tr>
<tr>
<td>APPENDIX B: Slug Tests</td>
<td>B-157</td>
</tr>
<tr>
<td>APPENDIX C: Well Logging &amp; Straddle-Packer Testing</td>
<td>C-162</td>
</tr>
<tr>
<td>APPENDIX D: Water-Level Measurements</td>
<td>D-168</td>
</tr>
<tr>
<td>APPENDIX E: Drilling &amp; Installing Monitoring Wells</td>
<td>E-171</td>
</tr>
<tr>
<td>APPENDIX F: Local Geology</td>
<td>F-177</td>
</tr>
<tr>
<td>APPENDIX G: Groundwater Sampling</td>
<td>G-182</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 1: A Comparison of Aqueous Solubilities to Maximum Contaminant Levels (MCLs) Allowed by the EPA for Nine Volatile Organic Compounds Most Commonly Found in Drinking Water ............................................................. 2

Table 2: Physical and Chemical Properties of Chemicals Detected at the Study Site ............................................................................................................................ 11

Table 3: Relative Critical Height for a Column of PCE before Penetration of Saturated Zone ........................................................................................................ 24

Table 4: Physical Properties of TCE .................................................................. 37

Table 5: Inorganic and Organic Compounds Analyzed ........................................ 63

Table 6: Bedrock Stratigraphic Units of the Wills Mountain Anticlinorium Surrounding the Study Site .................................................................................. 69

Table 7: Summary of Slug Test Results at Wells Screened in the Alluvium ....... 90

Table 8: Calculated Vertical Component of the Hydraulic Gradient at Paired Wells in the Alluvium and Bedrock ................................................................. 93

Table 9: Water Levels at Selected Alluvium and Bedrock Monitoring Wells Adjacent to the North Branch Potomac River .................................................. 96

Table 10: Seepage Meter Readings ..................................................................... 101

Table 11: Summary Statistics - Soils ................................................................. 106

Table 12: Summary Statistics - Groundwater .................................................... 107

Table 13: VOCs Detected in Surface Water and Sediment Samples ................114

Table 14: Total Mass Discharge of TCE/DCE/TCA From The Alluvial Aquifer Area Around Solvent Disposal Pits To The North Branch Potomac River . . 126

Table 15: Total Mass Discharge of TCE/DCE/TCA From The Bedrock Aquifer Area Around Solvent Disposal Pits To The North Branch Potomac River . . 127
LIST OF FIGURES

Figure 1: Area Map ................................................................. 6
Figure 2: Site Location ............................................................. 7
Figure 3: Study Site ................................................................. 8
Figure 4: Disposal Areas .......................................................... 10
Figure 5: Disposal Pits ............................................................. 12
Figure 6: Composite Cross-Section of Area Structure ............... 14
Figure 7: DNAPL Contact Angle (θ) .......................................... 22
Figure 8: DNAPL Pore Throat ................................................... 25
Figure 9: DNAPL Entry Pressure ............................................... 30
Figure 10: Reaction Pathway for TCE ........................................ 38
Figure 11: Old Monitoring and Production Wells Locations ........ 41
Figure 12: New Well Locations .................................................. 51
Figure 13: Locations of Slug Tested Wells ................................. 55
Figure 14: Seepage Meter Locations ......................................... 60
Figure 15: Surface-Water and Sediment Sampling Locations ....... 66
Figure 16: Geologic Map .......................................................... 70
Figure 17: Bedrock Surface Elevations ...................................... 77
Figure 18: Fracture Trace Map .................................................. 78
Figure 19: Geologic Cross-Section Alignments ......................... 81
Figure 20: Geologic Cross-Section A - A’ ................................. 82

vii
ABBREVIATIONS

1,1,1-TCA  1,1,1-trichloroethane
ASCs  Agriculture Stabilization Conservation Services
DNAPL  dense non-aqueous phase liquids
DRO  diesel-range organics
EM  electromagnetic terrain conductivity
EPA  U.S. Environmental Protection Agency
FTA  fracture trace analysis
GC  gas chromatograph
GM  geologic mapping
MEK  methyl ethyl ketone
msl  mean sea level
NC  nitrocellulose
NG  nitroglycerin
ppb  parts per billion
ppm  parts per million
SVOC  semivolatile organic compounds
TAC  target analyte list
TCDD  2,3,7,8-tetrachlorodibenzo-p-dioxin
TCE  trichloroethene
TCL  target compound list
TCLP  toxicity characteristic leaching procedure
TNT  2,4,6-trinitrotoluene
TPH  total petroleum hydrocarbons
USGS  United States Geological Survey
VOCs  volatile organic Compounds
VOA  volitile organic analysis
XRF  X-ray fluorescence
CHAPTER I: INTRODUCTION

Statement of Problem

Dense, non-aqueous phase liquids (DNAPLs) such as chlorinated solvents and hydrocarbons (e.g. trichloroethene \{TCE\}, 1,1,1-trichloroethane \{1,1,1-TCA\}, creosotes, PCB oils, and chloroform) are common causes of groundwater contamination in many industrialized areas (Feenstra and Cherry, 1988; Avon and Bredehoeft, 1989; Conner et al., 1989; Turney and Goerlitz, 1990; Keuper and McWhorter, 1990; Johnson and Pankow, 1992). Chlorinated hydrocarbons are relatively inexpensive to produce and have been widely used in industry as metal degreasers and dry cleaning compounds. As a result, releases of these compounds at production, use, and disposal sites have contaminated underlying groundwater resources (Keuper and McWhorter, 1990, Avon and Bredehoeft, 1989; Connor et al., 1989; Turney and Goerlitz, 1990; Johnson and Pankow, 1992). Approximately one quarter of the organic chemicals on the United States Environmental Protection Agency (EPA) List of Priority Pollutants are DNAPL compounds. These chemical compounds have densities greater than and viscosities that are less than water. They are non-polar molecules and hence immiscible with water (Mehran et al., 1987; Schwille, 1988; Feenstra and Cherry, 1988; Corapcioglu and Hossain, 1990; Keuper and McWhorter, 1990; Poulsen and Kueper, 1992).

When DNAPLs enter the subsurface environment they partition to DNAPL free product or immiscible phase, DNAPL vapor and dissolved phases. Though of limited
solubility, dissolved concentrations of DNAPL can exceed drinking water standards by orders of magnitude (Kueper and McWhorter, 1990; Johnson and Pankow, 1992; Table 1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility 20°C (mg/l)</th>
<th>W.H.O. Drinking Water Standard (mg/l)</th>
<th>US EPA Drinking Water Standard (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride</td>
<td>785</td>
<td>0.003</td>
<td>0.005</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>5500</td>
<td>0.0003</td>
<td>0.007</td>
</tr>
<tr>
<td>cis-1,2-Dichloroethene</td>
<td>800*</td>
<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>trans-1,2-dichloroethene</td>
<td>600</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tetrachloroethene (PER)</td>
<td>200</td>
<td>-</td>
<td>0.005</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane (1,1,1-TCA)</td>
<td>720*</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>Trichloroethene (TCE)</td>
<td>1100</td>
<td>0.03</td>
<td>0.005</td>
</tr>
<tr>
<td>Vinyl chloride (VC)</td>
<td>-</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Water</td>
<td>1.00</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>


Corapcioglu and Hossain, (1990) provide an excellent overview of DNAPL contamination and note that pools of chlorinated hydrocarbons may remain at an aquifer base and become a continuous source of contamination for extended periods of time. DNAPLs such as TCE and 1,1,1-TCA tend to remain a source of groundwater contamination.
contamination for many decades (Feenstra and Cherry, 1988; Connor et al., 1989; Turney and Goerlitz, 1990; Poulsen and Kueper, 1992).

Research into the behavior of DNAPLs in groundwater systems has intensified in the last decade as the ubiquitous nature of these compounds has been realized. Assessment of DNAPL behavior following a release into the subsurface has been restricted to controlled laboratory/field experiments (Schwille, 1988; Keuper et al., 1989; Poulsen and Keuper, 1992), and to accidental occurrences at spill sites (Spayd, 1986; McIelwain et al., 1989; Kueper et al., 1991). Most field studies have been focused on the behavior of DNAPL in shallow unconsolidated aquifers (Freeberg et al., 1987; Mehran et al., 1987; Feenstra and Cherry, 1988; Avon and Bredehoef, 1989; Connor et al., 1989; Corapcioglu and Hossain, 1990; Turney and Goerlitz, 1990; Poulsen and Keuper, 1992; Johnson and Pankow, 1992). Efforts have been expanded in recent years to develop numerical models to simulate DNAPL behavior in unconsolidated groundwater systems (Kaluarachchi and Parker, 1989; Kueper and Frind, 1991).

While laboratory studies can be effective in studying specific physical and chemical processes, they are hampered by an inability to recreate the heterogeneous nature of naturally occurring material (Poulsen and Kueper, 1992). Observations of DNAPL behavior at accidental spill sites and waste disposal sites usually are limited by poor source history data and an incomplete three-dimensional representation of the plume.

Published work on the behavior of DNAPL in hydrologically complex fractured and karst environments is limited (Kueper et al., 1991; Kueper and McWhorter, 1990; McIelwain and others, 1989; and Spayd, 1986). Obtaining a representative
groundwater sample is difficult enough in this type of hydrogeologic environment while attempting to describe groundwater flow and DNAPL transport is even more complex (White, 1988; Quinlan, 1988). Mature karst aquifers can have large solution cavities and integrated conduits, distinguishing them from other aquifer systems (White, 1988). This conduct porosity creates hydraulic conductivities orders of magnitude greater than unconsolidated materials. Unlike flow in most other aquifers, water in well developed karst aquifers flows in "pipelike" conduits and open cave stream channels as well as through fractures and pores.

**Project Goals**

I will evaluate a fractured and karst system contaminated with DNAPL and attempt to describe the factors controlling the transport and fate of the contaminants. I will also develop conceptual remediation approaches tailored to the field setting and recommend additional research if appropriate.

There are two major objectives to fulfill this goal. My first objective is to develop a conceptual hydrogeological model of the physical and hydrologic framework of a selected site. This conceptualization is based on: 1) the regional and local stratigraphy and geologic structure; 2) the dynamics of the groundwater flow systems; 3) aquifer properties; and 4) surface water-groundwater interactions.

My second objective is to characterize the source, transport and fate of selected DNAPL in accordance with the conceptual hydrogeologic model by: (1) determining the source or sources of groundwater contamination, (2) defining the extent and
concentration of contamination in the groundwater system, (3) determining the parameters controlling the transport processes, and (4) describing the fate of the DNAPL at the study site.

**Study Site Setting**

I selected a government-owned, contractor-operated facility in West Virginia to investigate the transport and fate of DNAPL in a fractured/karst environment (Figures 1 and 2). This facility was selected for study based on four distinct criteria: (1) regional hydrogeological setting, (2) evidence of the use and disposal of DNAPL at the site, (3) availability/accessibility of data generated by previous studies, and (4) permission to study the site.

The facility has been used primarily for research, development, testing, and production of solid propellant rocket motors for the Department of Defense (DOD) and the National Aeronautics and Space Administration (NASA). It consists of two plants occupying approximately 1,577 acres. The facility has been previously investigated to assess possible soil and groundwater contamination (Roy F. Weston, 1990). This study focuses on a 20-acre portion of the facility located in the floodplain of the North Branch Potomac River (Figure 3). This site contains several waste disposal areas including a burning ground for ordnance, a former storage area for drums containing hazardous waste, a landfill for incinerator ash, a burning ground for inert substances, and disposal pits for spent solvents and acids. The disposal pits for spent solvents and acids and the associated groundwater systems, are the primary focus of this work
Figure 1: Mid-Eastern Area Map
Figure 2: Facility/Site Location Map
Figure 3: Study Site Location
Possible Waste Types and Locations

The wastes found at the study site are principally related to the manufacturing of solid propellant rocket motors. Solvents are used for degreasing, mixing and cleaning. During this process, four general waste types are produced, (1) spent solvents, (2) reactive or ordnance materials, (3) inert (non-ordnance materials), and (4) solid waste.

The primary solvents in this processes include TCE, 1,1,1-TCA, acetone and methylene chloride. Each of these solvents have been used in varying and unspecified amounts over the years. Acetone was the primary solvent used from 1942 until 1959. Use continued after 1959 and it is still widely used today. TCE was also commonly used from 1959 until the late 1970’s. Reportedly, TCE was used in large volumes until the late 1970’s and its use was minimized in the late 1980’s. The use of 1,1,1-TCA replaced TCE beginning in the late 1980’s. Methylene chloride has been used since the late 1960s and is still used today (Table 2).

Previous geophysical work by Roy F. Weston (1990) revealed the presence of three backfilled disposal pits in the study area (Figure 5). The areal extent of the pits closely matched the visual observations of disturbed soil on the ground surface based on analysis of 1974 and 1983 aerial photographs (Appendix A). These pits were excavated in the floodplain sand and gravel, which ranged from
Figure 4: Disposal Areas
Table 2:
Physical and Chemical Properties of Chemicals Detected at the Study Site

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Molecular Weight (g/mole)</th>
<th>Absolute Viscosity (cp)</th>
<th>Vapor Pressure @ 25°C (torr)</th>
<th>Henry’s Law Constant atm·m³/mole</th>
<th>K&lt;sub&gt;x&lt;/sub&gt; (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volatile Organics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>99</td>
<td>0.50</td>
<td>2.34E+02</td>
<td>5.45E-03</td>
<td>3.02E+01</td>
</tr>
<tr>
<td>cis-1,2 Dichloroethene</td>
<td>97</td>
<td>0.48</td>
<td>2.00E+02</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>trans-1,2 Dichloroethene</td>
<td>97</td>
<td>0.40</td>
<td>2.65E+02</td>
<td>6.74E-03</td>
<td>5.89E+01</td>
</tr>
<tr>
<td>Tetrachloroethylene (PCE)</td>
<td>165.8</td>
<td>0.90</td>
<td>5.00E+02</td>
<td>1.31E-02</td>
<td>4.42E+01</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>85</td>
<td>0.44</td>
<td>4.35E+02</td>
<td>2.19E-03</td>
<td>2.80E+01</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane (1,1,1-TCA)</td>
<td>133</td>
<td>0.84</td>
<td>1.24E+02</td>
<td>1.72E-02</td>
<td>1.79E+02</td>
</tr>
<tr>
<td>Trichloroethene (TCE)</td>
<td>131</td>
<td>0.57</td>
<td>5.80E+01</td>
<td>1.03E-02</td>
<td>1.04E+02</td>
</tr>
<tr>
<td>Vinyl chloride (VC)</td>
<td>62.5</td>
<td>0.43</td>
<td>2.98E+03</td>
<td>2.70E-02</td>
<td>1.35E+02</td>
</tr>
</tbody>
</table>

Figure 5: Solvent Disposal Pits
three to five feet deep, five to 10 feet wide, and 15 to 40 feet long. Spent solvents and acids contaminated with reactive wastes were placed into the unlined pits and allowed to percolate into the ground. Pits would then be ignited to burn off any reactive filtrate. Large volumes of TCE were reported to be disposed of in these pits. Records of exact waste liquid chemical compositions and volumes were not maintained.

An asphalt drum storage pad is situated next to the open burn area and may be a secondary source of TCE contamination (Figure 4). Reportedly, the drum storage pad was operated from 1970 to 1981, and held 55-gallon drums containing spent solvent and bottom sludge from solvent-recovery stills. Spill containment berms or sumps are absent.

**Regional Geologic Framework**

The facility is located in the Valley and Ridge Physiographic Province of the mid-eastern United States near its western boundary with the Allegheny Plateau Province (Figure 1). The transition between these provinces is called the Allegheny Structural Front (Schultz, 1989). The Valley and Ridge Physiographic Province is underlain by sedimentary rocks folded and faulted during the late Paleozoic Era (Figure 6). The linear belts of ridges and valleys that characterize the province result from differential erosion of the various rock types. In general, more-resistant sandstones underlie ridges whereas less-resistant shales and soluble limestones underlie lowlands. Total relief is approximately 1,300 feet, from 655 feet
Figure 6: Composite Cross-Section of Regional Structure

Coal Bearing Rocks
Georges Creek Synclinal Axis
Allegheny Front

Appalachian Plateaus

Valley and Ridge

(site located 26 miles northeast of X, A - B' located on Figure 1)
Scale 1"=50 miles
on the North Branch Potomac River at the western edge of the Cresaptown quadrangle to 1,950 feet on Knobly Mountain. The study site lies below an altitude of 700 feet.

The most significant physiographic feature in the vicinity of the facility is Knobly Mountain, which flanks the study site to the south and east (Figure 3). The study site is located on the floodplain of the North Branch Potomac River at a point where the river has cut into the base of Knobly Mountain. This mountain is the surface expression of a portion of the Wills Mountain anticlinorium, the anticlinal axis of which trends approximately N30°E and plunges to the southwest (Eddy, 1964).

Shales, limestones, and sandstones of Silurian and Devonian age underlie the portion of the Wills Mountain anticlinorium passing through the study site. Geological maps estimating the distribution of the various rock types in the region surrounding the study site have been prepared by Dyott (1956) and Eddy (1964).

The Wills Mountain anticlinorium is asymmetrical. To the southeast of the anticlinal axis, the strata dip relatively gently to the southeast at approximately 30 degrees (Dyott, 1956). The strata on the northwest limb of the anticline are generally vertical to slightly overturned (Schultz, 1989). Across the river to the north of the study site at Pinto, Maryland, outcrops reveal vertical to overturned strata containing numerous small-scale folding and faulting features (Schultz, 1989).

The western half of the facility is located on the vertical or overturned northwest limb of the anticlinorium; the dips of bedding planes underlying these portions of the study site are expected to be near vertical. Strata underlying the eastern half of the
facility is part of the southeast limb of the anticlinorium, and therefore, bedding planes
dip gently to the southeast.

Regional Hydrology

In this general area evapotranspiration (ET) consumes about 55 percent of the
average precipitation of 42 inches (Becher and Taylor, 1982).

The predominant hydrologic feature of the region is the North Branch Potomac
River, which borders the western and northern sides of the facility (Figure 4). The
elevation of the North Branch Potomac River, adjacent to the study site, ranges from
about 655 feet mean sea level (msl) at the eastern end of the facility to about 645 feet
msl to the south. The discharge of the river at the Pinto, Maryland gaging station,
2,000 feet upriver from the study site, averaged about 850 cubic feet per second
(according to U.S.G.S. records from 1938 through 1981).

The local topography is in an early mature stage of dissection, whereas the major
stream, the North Branch Potomac River, is in late youth or early maturity as shown by
the entrenched meanders. The North Branch Potomac River is the only consequent
stream in the study site. Its trellis drainage pattern is typical of the Valley and Ridge
Province.

The presence of groundwater in the region is strongly influenced by the geology.
The region's permeable rock formations are in a folded, faulted, and fractured sequence
of carbonate rock, over 14,000 feet thick, with alternating shales, about 3,000 feet
thick. Carbonate rock underlies 55 percent of the region, the remainder is shale (Eddy,
Generally, groundwater contributes 70-80 percent of the total surface water flow in the vicinity of the facility (Becher and Taylor, 1982). Regional carbonate rocks yield from 0.75 to 0.85 million gallons per day per square mile, and shale yields about 0.48 million gallons per day per square mile (Becher and Taylor, 1982).

The study site is underlain by 40 feet of floodplain sand, gravel and silts that overlay folded and faulted Silurian and Devonian rocks. Both alluvial deposits and underlying bedrock are used for municipal, industrial and domestic water supply.

**Thesis Organization**

The remainder of this thesis includes six chapters. Chapter Two discusses the previous environmental investigation. Chapter Three reviews the theoretical and observed behavior of DNAPL's in the environment, pertinent previous investigations of DNAPL contamination, and cites examples of contamination in fractured and karst environments. Chapter Four explains the methodology used in this investigation. Chapter Five is a discussion of the results, including the hydrogeologic framework, and potential DNAPL sources, their transport and fate at the study site. Chapter Six presents an overview of potential remediation techniques that could be applied to contain the plume of dissolved DNAPL's in this hydrogeologic environment. Chapter Seven presents the conceptual models and recommends additional potential data collection methods that could be used to better define the processes affecting the study site.
CHAPTER II: DNAPL IN THE ENVIRONMENT

This chapter is divided into two sections which provide background information on the behavior of DNAPL in the vadose zone and groundwater systems. The first section describes a conceptual approach for DNAPL transport and fate in a porous and fractured media. The second section discusses the specific physical and chemical factors controlling DNAPL contamination.

Transport and Fate - A Conceptual Approach

Transport and fate of DNAPL in the subsurface will be presented from the conceptual point of view. Along with the conceptual approach, detailed information will be presented explaining specific mechanisms, processes and variables which influence DNAPL fate and transport. An understanding of the pore-scale theory of multiphase contaminant flow is critical when examining the behavior of DNAPL in porous media. However, the behavior of DNAPL in a fractured environment is not well understood. This includes DNAPL characteristics, subsurface media properties, and saturated dependent parameters. For a more detailed description of movement in a unconsolidated porous media see Schwille, 1988.

In the vadose zone the transport of the contaminant can occur in three phases: (1) as a solute in water, (2) as vapor in air, and (3) as an unaltered immiscible constituent (Corapcioglu and Hossain, 1990). In the saturated zone, transport occurs only as a solute in water or as an immiscible phase. Movement in these environments is
controlled by density, viscosity, interfacial tensions of the liquids, hydrodynamic dispersion, adsorption, and chemical/biological degradation.

Physical Behavior

Because DNAPL's are immiscible with and denser than water, intuition suggests that any contamination of groundwater should occur by liquids infiltrating and migrating vertically through the vadose zone and saturated earth materials and collecting at the base of the aquifer or on a low permeability bed within the aquifer or vadose zone. However, the behavior of DNAPL is much more complex. The discussion below focuses on mobility of DNAPL in (1) the vadose zone, (2) the capillary fringe, (3) the saturated zone (with full and/or partial penetration by immiscible product), and (4) in a fractured bedrock environment.

Entry and Migration

In both the saturated and unsaturated zones, DNAPL's are primarily distributed as either an "immiscible product" or as a dissolved constituent (vapor or aqueous phase). In the aqueous phase, contaminant concentrations are determined largely by aqueous solubilities (Villaume et al., 1983, Keuper and McWhorter, 1991). In the immiscible product phase, the distribution of contaminant is controlled by a complex interplay among capillary pressure, gravitational, and viscous forces which are discussed in the following section.
Vadose Zone

Small, one time spills of DNAPL will most likely adhere to and remain within the vadose zone near the point of contamination. Immiscible DNAPL, held in residual saturation, will contaminate infiltrating water as it passes through the vadose zone (Anderson et al., 1992). Small quantities of DNAPL can contaminate large volumes of water (Table 1).

Once the DNAPL enters the vadose zone, a three-phase system evolves: DNAPL is present as a solute in water, vapor in air and as an unaltered immiscible constituent. The hydraulic gradient is the most important property influencing the downward migration of the liquid (Anderson et al., 1988). As the mass of DNAPL moves downward through the vadose zone under gravity, some part of the immiscible product will be trapped in the pore spaces due to capillary forces. Corapcioglu and Houssain (1990) referred to the product trapped in the vadose zone as the residual saturation ($S_r$). If the retention capacity $R$ is high enough ($R = \text{residual saturation} \times \text{porosity}$), no immiscible product will reach the water table.

When two or more immiscible fluids occupy the same soil space, the saturation of the given fluid is the fraction of void volume of the medium occupied by the fluid within that volume. For a saturated system, capillary pressure ($P$) is defined by the equation:
\[ p = \frac{(2\gamma) \cos \theta}{r} \]  

where \( \gamma \) is the interfacial tension between the two liquids, \( \theta \) is the wetting or contact angle formed by the contaminant phase against a solid surface in the presence of pore water, and \( r \) is the radius of the water filled pore which the contaminant must enter in order to move. The interfacial tension can be viewed, essentially, as a liquid-liquid interaction and the wetting angle as a liquid-solid interaction, although the wetting angle is actually defined in terms of interfacial tensions according to Young's Formula:

\[ \sigma_{gl} \cos \theta = (\sigma_{gs} - \sigma_{sl}) \]  

where \( \sigma \) is the interfacial tension between two substances denoted by subscripts where \( s \) is a solid, \( g \) is a gas, and \( l \) is a liquid. Angle \( \theta \) is the contact angle, and the product \( \sigma_{sl} \cos \theta \) is the adhesion tension which determines if a fluid will wet a solid (adhere to it). Figure 7 illustrates that when \( \theta < 90^\circ \), the fluid is said to wet the solid and is called the wetting fluid. When \( \theta > 90^\circ \), the fluid is called a nonwetting fluid (Kuepper et al., 1991).

Liquid-liquid interfacial tension is equal to the free surface energy at the interface formed between two immiscible or nearly immiscible liquids. The magnitude of the interfacial tension is always less than the larger of the surface tensions for the pure liquids due to the mutual attraction of unlike molecules at the interface (Keuper and Frind, 1988).

The final parameter in the capillary pressure equation is the porous radius, or pore structure. Unlike a single-phase system where permeability (hydraulic conductivity)
Figure 7: DNAPL Contact Angle
and porosity are adequate to describe fluid flow, pore structure is a critical parameter in characterizing the movement of fluids in a multi-phase system (Kueper and McWhorter, 1991). Pore size distributions are readily developed from moisture-tension curves, which are widely used by soil scientists to calibrate liquid-filled tensiometer gages for measuring in-place soil moisture. However, this is not the same as pore structure, which refers to the arrangement of interconnected pores to form passageways along which fluid movement can occur.

The DNAPL does not displace the water from the pore channel surfaces because water wets the solids. Instead, DNAPL can move from pore to pore once DNAPL saturation exceeds residual saturation (Domenico et al., 1990).

**Capillary Fringe**

The tension saturated zone or capillary fringe forms the base of the vadose zone through which the DNAPL must pass before entering the saturated zone. In order for the DNAPL to penetrate the capillary fringe, the water in the saturated pore spaces within the zone must be displaced (Kueper and Frind, 1988). The immiscible product will penetrate the water table when the pressure head of the DNAPL exceeds the capillary pressure barrier between the DNAPL and water (Anderson et al., 1988). The head required before penetration occurs depends upon the type of DNAPL and the grain-size distribution of the aquifer material. When the immiscible product on the capillary fringe reaches sufficient thickness (critical height) the capillary forces will be overcome and downward percolation will continue. Table 3
is an example of critical heights \((z_c)\) for a common DNAPL contaminant, perchloroethylene (PCE).

The following equation relates critical height \((z_c)\) of the contaminant required to overcome the capillary forces of water (Viloluame et al., 1983):

\[
z_c = \frac{2\sigma \cos \theta (1/r_i - 1/r_p)}{g(p_w - p_d)}
\]

\(z_c\) equals critical height of contaminant required to overcome the capillary forces of water, \(\sigma\) is the interfacial tension between water and DNAPL, \(\theta\) is the contact angle between the fluid boundary and the solid surface, \(r_i\).

<table>
<thead>
<tr>
<th>Porous Media</th>
<th>Grain Diameter (mm)</th>
<th>Critical Height (z_c) (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>coarse sand</td>
<td>1.0</td>
<td>13</td>
</tr>
<tr>
<td>fine sand</td>
<td>0.1</td>
<td>130</td>
</tr>
<tr>
<td>silt</td>
<td>0.01</td>
<td>1,300</td>
</tr>
<tr>
<td>clay</td>
<td>0.001</td>
<td>13,000</td>
</tr>
</tbody>
</table>

Values of \(z_c\) were calculated using \(\Delta \rho = 0.62 \text{g/cm}^3\), \(\gamma = 47.5 \text{dyne/cm}\), and \(\cos \theta = 1\) (perfect wetting).

is the radius of the pore throat, \(r_i\) is the radius of the pore, \(p_w\) is the density of water, and \(p_d\) is the density of the DNAPL (Figure 8). For a well-rounded, well-sorted
Figure 8: DNAPL Pore Throat
sediment of diameter \( d \) with rhombohedral packing, the pore-throat radius, \( r_n \), and the pore radius, \( r_p \), can be estimated from the following formulas (Avon et al., 1989):

\[
\begin{align*}
  r_p &= 0.212 \ d \\
  r_n &= 0.077 \ d
\end{align*}
\]

Once a path has been forged through the capillary fringe and into the saturated zone, transport will continue preferentially in these pore channels (Schwille, 1988, Keuper and McWhorter, 1990, Anderson et al., 1992).

**Saturated Zone**

After penetration of the capillary fringe and into the groundwater system, DNAPL must overcome residual DNAPL saturation in the water-filled pores before downward percolation will continue. Resisting this movement are the viscous forces within the DNAPL itself and the capillary pressure forces throughout the system.

As the DNAPL front moves downward, displacing water in the pore spaces, viscous "fingering" may occur (Anderson et al., 1988, Schwille, 1988). Rather than moving as a horizontal front, the DNAPL is split into vertical channels or "penetrating fingers". This fingering within the saturated zone may: (1) increase the infiltration rate, (2) increase depth of penetration, and (3) lessen the amount of DNAPL in contact with the flowing groundwater.

The literature clearly shows that soluble residual DNAPL is readily dissolved by groundwater in contact with the DNAPL. At typical velocities, groundwater attains DNAPL concentrations equal to their solubilities at the source areas (Hunt et al., 1988,
Schwille, 1988). However, typical concentrations of contaminants found in "field" situations, and at this study site, are often orders of magnitude lower than their solubilities. Anderson and others (1988) speculated that a possible cause may be the formation of narrow fingers of contaminant. Dissolved concentrations may be very high as a plume of contaminant emerges from a zone of contamination, but these narrow sources and the dispersion processes reduce contaminant concentrations measured in groundwater only slightly down gradient.

If sufficient volumes of contaminants are spilled, penetration below the water table may occur to the base of the aquifer or an inter-aquifer low-permeability unit. DNAPL accumulating on low-permeability unconsolidated units will move down-slope following topography (Corapcioglu and Houssain, 1990). Heterogeneities within the saturated zone may cause the DNAPL to spread laterally, depending on the attitude of the unit and its lateral extent. The DNAPL movement in many cases will be in a direction that is different than the groundwater movement. Spreading continues until one or any combination of three things happens: 1) the contaminant source is depleted, 2) the spill is at residual saturation, or 3) the contaminant collects in a depression or "pool area" (Schwille, 1988, Keuper and Frind, 1988). Groundwater in contact with the surface of these contaminant pools would become contaminated.
DNAPL Entry into Fractured Media

Solute transport in fractured rock media is an important process. Quantification of this process is difficult because such environments are complex and not easily described.

Berkowitz et al. (1988) suggested that solute transport in fractured media can be conceptualized at a number of different scales. A very-near-field scale isolates transport mechanisms in a single fracture. At a larger scale both the fracture network and the permeable rock mass would have separate, discernable impacts on flow. At a far-field scale, the entire domain can be considered as an equivalent porous medium.

For this discussion, the transport of DNAPL in a single fracture in contact with a porous rock mass, moving at a constant velocity will be assumed (Schwartz and Smith, 1988). The fractures themselves are, usually, not smooth channels and contain many dead-end passages that hold non-moving water into which solutes can defuze. Prior to DNAPL introduction the fracture is completely saturated with water. In order for DNAPL to enter this fracture, the capillary pressure, of the DNAPL, at the entrance of the fracture must exceed the fracture entry pressure (Kueper and McWhorter, 1991). The capillary pressure is defined as the difference between the pressure in the DNAPL phase at the point of entry into the fracture and the water pressure in the fracture at the DNAPL-water interface. Assuming hydrostatic equilibrium, the capillary pressure ($P_c$) equilibrium will be defined by the liquids heights according to (Bear, 1972):
where $P_{NW}$ is the pressure in the nonwetting fluid and $P_w$ is the pressure in the wetting fluid at the interface. Through consideration of a force balance in the DNAPL-water interface at the point of potential DNAPL entry into a smooth-walled fracture, the fracture entry pressure, $P_e$, may be expressed as (Kueper and McWhorter, 1991):

$$P_e = \frac{2\sigma \cos \theta}{r}$$  \hspace{1cm} (5)

where $\sigma$ is the DNAPL-water interfacial tension, $\theta$ is the contact angle, and $r$ is the local fracture aperture. Hence DNAPL will more readily enter the largest aperture regions of a water-saturated fracture, and DNAPL with lower entry pressures arise for cases of lower interfacial tensions will require lower entry pressures. In order for the DNAPL to enter an open fracture, the capillary pressure at the entrance to the fracture must exceed the entry pressure of the fracture such that the curvature of the DNAPL-water interface allows this interface to physically penetrate the fracture (Figure 9). The entry pressure of a fracture is a function of the geometry of the opening exposed to DNAPL (Kueper and McWhorter, 1991). As can be seen in Figure 9, the larger aperture regions of a fracture exhibit the lowest entry pressures to a DNAPL.

Capillary pressure immediately above the fracture may be expressed as a height of DNAPL pooled, assuming equilibrium. The height of pool required to bring about entry into the fracture is given by:
Figure 9: DNAPL Entry Pressure
\[ H_d = \frac{2\sigma}{\Delta \rho g} \]  \hfill (6)

where \( H_d \) is the height of DNAPL pooled [m], \( \Delta \rho \) is the density difference between the DNAPL and water [kg/m^3], and \( g \) is gravity [m/s^2].

Once the DNAPL has entered a fracture network it will migrate through the largest aperture pathways and only invade fractures if the capillary pressure of the DNAPL-water system exceeds the entry pressure (Kueper and McWhorter, 1991).

**Special Physical Problems**

Superimposed on the previous processes are the effects of hydrodynamic dispersion due to groundwater flow. From its position in a column through the saturated zone, the residual contaminant perpetually dissolves into the groundwater. It quickly reaches saturation near the source and spreads downgradient.

A complicating factor in determining the extent of contamination and the course of remediation is the presence of larger vertical conduits or of horizontal lenses of silt/clay. In this area, a well, boreholes or back-filled trenches, the critical height of DNAPL required before penetration is reduced drastically (Schwille, 1988).

**Chemical Behavior**

This section will review pertinent chemical factors which directly and indirectly affect DNAPL chemistry. This brief review should only be considered an overview; for a more detailed description see Miller et al., 1990, Pavlestatthi et al., 1991, Chiou et al., 1986, and Vogel et al., 1987.
Solubility

The solubility of DNAPL are usually low, generally ranging from 20 parts per million (ppm or mg/l) to 10,000 ppm (1%) (Table 1). It should be noted that these solubilities are orders of magnitude higher than maximum allowable concentration levels for drinking water standards in most industrialized nations (Table 1). DNAPL are halocarbons and nonpolar in nature (Miller et al., 1990). For this reason, they interact more strongly with solid and dissolved organic matter than with water. Natural dissolved organic matter (humic material) has both polar (generally containing oxygen, nitrogen and/or sulfur) and nonpolar functional groups (containing mainly carbon and hydrogen); the nonpolar groups remain in solution because they are attached to the polar functional groups which are soluble in water. Many studies have shown that the presence of dissolved organic matter can increase the solubility of halocarbons in water (Chiou et al., 1986 and Gschwend and Wa, 1985). Because the structure of humic materials varies with the source and solution chemistry, different systems are expected to exhibit different relationships between organic matter content and halocarbon solubility enhancement. As an example, the presence of soaps and detergents could serve to increase the solubility and hence transport.

Oxidation and Reduction

Generally, organic matter becomes oxidized in the environment. However, because of substitution by halogens, some DNAPLs are more likely to undergo reduction than
oxidation. If the groundwater system is oxygenated, halogenated hydrocarbons are extremely stable; if the system is reduced, halogenated hydrocarbons are not stable and undergo reduction (Vogel et al., 1987). Generally, the more highly substituted halogenated hydrocarbons are less susceptible to oxidation (Chiou et al., 1986).

Reactivity

The most rapid decomposition reactions are mediated by bacteria, provided that sufficient substrate and nutrients are present. However, abiotic reactions may also proceed at a sufficient rate to produce various substituted, oxidized and reduced products including trichloroethene, dichloroethenes, chloroethene, trichloroethanes, dichloroethanes and vinyl chloride (Vogel et al., 1987). The following discussion will focus first on substitution reactions, then dehydrohalogenation.

Substitution

Substitution occurs when water reacts with a halogenated compound to substitute an OH⁻ for an X⁻, creating an alcohol. This can occur in water without either inorganic or biological catalysts, but the reaction rates are slow. If the nucleophile is hydroxide, then the reaction is called hydrolysis; this is the most important substitution reaction (Vogel et al., 1987). The product of these reactions is an alcohol which can undergo further substitution if it is halogenated. Half-lives of these reactions are generally days to centuries (Vogel et al., 1987). Because the reaction involves the exchange of liquids, pH is an important factor in determining the rate of the reaction; high pH
values are expected to promote the abiotic reaction for ethenes (Vogel et al., 1987). An example of this would be the reaction of 1,1,2,2-tetrachloroethane → 1,2,2-trichloroethanol:

\[ \text{Cl}_2\text{HC-CHCl}_2 + \text{OH}^- = \text{Cl}_2\text{HC-CHClOH} + \text{Cl}^- \]

Chlorinated hydrocarbons are more stable to abiotic substitution reactions than other types of halogenated hydrocarbons. Monosubstituted hydrocarbons are more likely to undergo substitution than are polysubstituted hydrocarbons. Clay mineral content can promote the degradation of halogenated hydrocarbons (Chiou et al., 1986).

**Dehydrohalogenation**

Dehydrohalogenation is a reaction where an alkane loses a halide ion from one carbon atom and then a hydrogen ion from an adjacent carbon. The result is the formation of a double bond between carbon atoms, thus creating an alkene. Dehydrohalogenation can transform 1,1,1-trichloroethane to 1,1-dichloroethene:

\[ \text{CCl}_3 - \text{CH}_3 \rightarrow \text{Cl}_2 = \text{CH}_2 + \text{HCl} \]

The rate of dehydrohalogenation increases with increasing numbers of halogen ions; hence compounds that undergo substitution most slowly undergo dehydrohalogenation most rapidly. Bromine ions are more rapidly removed (up to six times faster) than chlorine ions in these abiotic reactions. The reaction of chlorinated hydrocarbons proceeds more rapidly at high or neutral pH than those with other halogens.
Microbial Mediation

Biological mediation by micro-organisms is extremely important in determining the rates and sequences of substitution, oxidation and reduction reactions (Chiou et al., 1986). Microorganisms, ubiquitous in the environment, can use a variety of electron donors and acceptors under different redox conditions. As each electron acceptor is consumed during the metabolism of organic carbon, the redox potential of the system is lowered (Pavlestatthis and Jaglal, 1991). In aerobic systems, oxygen is the electron acceptor. After oxygen is consumed, nitrate, sulfate, ferric iron, manganese (IV), and carbon dioxide may be used as electron acceptors depending on availability.

Oxidized groundwater can become anoxic or reducing very rapidly in the event of a release of organic-rich materials such as DNAPLs. If part of the aquifer becomes anoxic, or if the contaminants come in contact with reducing conditions, chemical reduction would be expected.

Kleopfer and others (1990) have shown that TCE is definitely dechlorinated in soil to 1,2-DCE. The TCE → DCE degradation appears to be "biological in nature, since soil samples which have been sterilized exhibited no such conversion". The possibility exists that DCE can be further biotransformed into vinyl chloride, a well known carcinogen, in soils (Parsons et al., 1984).

Special problems

A complicating factor in determining the mobility of DNAPLs is the importance of sorption processes. Sorption refers to absorption onto a surface as well as absorption
into the aquifer material. Under different circumstances, each process can be important. This point is extremely significant when discussing contamination of a fractured system.

Absorption refers to the transfer by diffusion of material from the pore spaces into the mineral matrix. The process of diffusion is slow and particularly so in solid phases. When the contaminant comes in contact with the aquifer material, some of the contaminant diffuses into the solid matrix. The amount of contaminant absorbed by the solid depends on the concentration of the contaminant, the physical properties of the contaminant/solid, and the amount of time the two phases are in contact (Pavlostathis et al., 1989). Higher concentrations in solution will promote greater diffusion into the solid. More microporous material will have more accessible pore spaces for diffusion. Longer periods of time will allow more contaminant to be retained in the solid phase. Absorption is, generally, a reversible process, when the dissolved or immiscible phase is removed from the environment, adsorbed contaminant will diffuse out of the solid matrix.

**TCE-Transformations**

TCE is highly oxidized compared to other alkenes and is therefore more stable in oxidizing environments (Table 4).

When reducing conditions are present, transition metals act as catalysts for reduction reactions of halogenated hydrocarbons in both abiotic and biotic systems.
(Vogel et al., 1987). With increased halogenation, reduction becomes more likely than does oxidation. For TCE the rate of oxidation is extremely slow, while the reduction rate is significant (Figure 10). The actual rate of the reaction is dependent upon the reductant and specific concentration conditions. Trichloroethene has a solubility of 1100 parts per million (ppm), while the EPA’s Maximum Contaminant Level (MCL) is
.005 ppm. TCE will quickly reach concentrations near saturation if sufficient immiscible product is available.

Figure 10:
Reaction Pathway for TCE
CHAPTER III: PREVIOUS INVESTIGATION OF THE FACILITY

The previous study of the facility (Roy F. Weston, 1990) indicated that possible groundwater contamination with volatile organics may be associated with several disposal sites including a burning ground for ordnance, three former disposal pits for spent solvents and waste acid disposal, a former storage pad for drums containing hazardous waste and a former landfill for incinerator ash (Figure 4). The behavior of these volatile organics (DNAPL) associated with the "three former disposal pits for spent solvents" will be the focus of this review.

Contaminant Reconnaissance

Disposal Pits

Analytical results, from soil-gas sampling at a depth of three to five feet, indicated high concentrations of TCE along the northern edge of the study site (Figure 3). TCE detected in the soil-gas samples probably originated from solvents disposed of in the pits and/or from solvents stored at the drum storage pad. Boring logs indicated a 15 foot silty-clay layer extends over most of the area sampled.

Drum Storage Pad

Analysis of soil samples collected around the drum storage pad indicated that the soil contained methylene chloride, methyl ethyl ketone (MEK), and trichloroethene
(TCE) at concentrations near or below the detection limits. The detection limit was not disclosed.

Incinerator Ash

The Weston study indicates disposal of incinerator ash and unburned residue occurred over the northern half of the study site. The ash was generated from open burning of municipal sanitary waste. Demolition debris, empty solvent drums, and rocket motor casings also were landfilled. Boring logs indicate that the average depth of the ash fill is approximately four feet.

Groundwater

A total of 25 groundwater monitoring wells were installed during the Weston study (Figure 11). Groundwater samples were collected and analyzed for VOCs, metals, xylenes, MEK, methyl isobutyl ketone (MIBK), 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), explosives, TNT breakdown products, and nitrates. Analytical data presented indicates that significant VOC contamination exists in groundwater under the study site. As many as three rounds of sampling were performed on wells with high VOC contamination. The first sampling round was performed in 1984, the second in 1985 and 1986, and the third in 1987. The analyses indicate that TCE occurs at the highest concentration and is the most widespread of all the contaminants of interest.

The highest levels of groundwater contamination and the widest variety of VOC contaminants have been detected in wells 1GW3 and 1GW9 (Figure 11), which are
Figure 11: Old Monitoring and Production Wells
located next to one another and screened across the alluvium-bedrock contact and in the bedrock, respectively. In addition, the soil-gas survey indicated that high levels of soil contamination occurs in the vicinity of these wells.

Well 1GW3 is considered to cross the alluvial/bedrock contact because the surface casing in the well does not reach bedrock.

Concentrations of TCE on the order of those detected in wells 1GW3 and 1GW9 (i.e., 130,000 µg/l and 110,000 µg/l, respectively) are approximately 10 percent of the solubility of TCE in water. Concentrations this high are often associated with the presence of immiscible phase DNAPL, which most likely were introduced into the subsurface during previous dumping of waste solvents into disposal pits at the study site.

During the Weston study, an Electromagnetic Terrain Conductivity (EM) survey was performed. The objectives of the EM survey were to determine the areal extent of a possible inorganic contaminant plume within the sand and gravel aquifer, and to define the topography of the underlying bedrock surface. The EM survey indicated that the saturated alluvium appears to generally thicken toward the east as the bedrock topographic surface lowers in elevation. No evidence of the presence of a contaminant plume in the alluvial aquifer was found in these data.

VOC contamination was also detected in production well PWA (Figure 11). Although this well is not located in the study site, information gathered at this location is applicable. Well PWA lies 2,200 feet south of the study site and more importantly it appears to lie down strike of the geologic structure and at a conjugate angle to the fold
axes (Figure 2). For these reasons there could be a possible connection between the contamination believed to be associated with the study site and well PWA. Because of these physical similarities between the sites and the detailed hydrologic and geologic data gathered at well PWA, well PWA will be discussed in detail throughout this thesis. It should be noted that well PWA has two adjacent monitoring wells PWA1 (bedrock, screened at a depth between 63 and 78 feet), and PWA2 (alluvium screened at a depth between 24-39).

Because 1,1,1-TCA was not detected in well PWA in September 1980 or March 1986, but appeared abruptly in July 1987, this may suggest that 1,1,1-TCA is migrating downward from a surface source. TCE also may be derived from a surface source, but one that is older (TCE was detected in well PWA as early as October 1984) and one whose surface concentration of contaminants has declined significantly.

According to the results of the pumping test conducted at well PWA the radius of influence, in both the alluvium and bedrock aquifers, may not reach the study site. This can be stipulated only if there is a detailed understanding of the bedrock and its joint/fracture pattern. It is the authors opinion that this geologic information was not available during the Weston study. It is possible that the study site is contributing to the VOC contamination in well PWA. DNAPL derived from the study site could be affecting the groundwater quality at well PWA because immiscible product DNAPL may have migrated along the top of the bedrock surface and through bedrock fractures and other openings to the vicinity of the production well. Alternatively, the
contamination in the production well may be coming from another source, perhaps nearer to the well.
The first two sections in this chapter describe the methodologies used to develop a conceptual hydrogeological model of the study site and to characterize the source and behavior of selected DNAPL in accordance with the physical conceptual model. Interpretations of the results are presented and discussed in Chapters V and VII.

**Conceptual Hydrogeological Model**

A primary objective of the study was to accurately characterize the physical environment for the purpose of developing a conceptual hydrogeological model of the study site. This section describes how geology was used to accomplish this goal.

**Geology**

Information on the geology of the study site was obtained during (in chronological order): (1) a thorough literature review of the area, (2) analysis of previous drilling logs, (3) photo-geologic interpretation, (4) geologic mapping/fracture trace analysis, and (5) boring logs developed during installation of monitoring wells. Borehole logs obtained by split-spoon sampling, and recorded during drilling, provided the lithologic characterization of the alluvium. Geologic information on the bedrock underlying the study site was obtained through a comprehensive literature review, an interpretation of regional geology and examination of samples of air rotary drill cuttings collected during bedrock drilling at nine locations. Additional geologic information was obtained by
interpreting the logs of 25 monitoring well borings completed during the previous investigation.

The bedrock characterization at the drill locations was based strictly on the examination of air-rotary drill cuttings; no rock-core samples were obtained. Unfortunately, drill cuttings do not preserve bedding relationships, aperture and structural features.

**Photogeologic Analysis**

Photogeologic analysis was performed to help define the geological framework on a site-specific and local scale. This analysis involved the identification of rock units through the use of aerial photographic resources. The photogeologic investigation supplied pre-field work (geologic mapping) information about rock types, outcrop locations, geologic contacts and relative resistance to weathering between units or beds. Identifications of rock units were based on drainage patterns, topography, and surficial textures and tones. All photogeologic mapping was confirmed with field checks.

The photo analysis was performed by viewing the photographs, backlit, on a light table. Light intensity was varied, but uniform, to enhance topographic features important in the identification of fracture trace features and geologic contacts. Geologic contacts and were marked directly on clear mylar overlays. Regional geological information also was transferred to an overlay.

Field identification of rock type, strike and dip measurements of bedding plains and fracture plains were taken at outcrops. Geological contacts identified by aerial photo-
graphic analysis, were checked. In this investigation, the locations, orientations and degree of weathering of both joint and fault surfaces were measured and recorded. In addition to fracture-plane orientation data, the degree of separation, alteration, mineralization and brecciation on the actual fault surfaces was recorded using similar field and photographic analysis. Photographic overlays were prepared and used to refine the initial analysis.

Geologic Mapping

The first report (Reger, 1924) includes history, physiography, geology, mineral resources, and paleontology of the respective counties but no geologic mapping was performed. General mapping was included in Woodward's (1949) report.

The mapped area is confined to the general facility area located in 7.5-minute Cresaptown topographic quadrangle, which incorporates parts of West Virginia and Maryland. The North Branch Potomac River separates West Virginia and Maryland. The Allegheny Front and Allegheny Plateau lies in the northwestern corner of the quadrangle, but the West Virginia part of the quadrangle lies entirely in the Valley and Ridge province. The geology was plotted on a topographic base map (scale 1:24,000) of the Cresaptown United States Geological Survey (U.S.G.S.) Quadrangle issued in 1949. Aerial photographs were used to accurately locate outcrop positions and to interpret structure and trace outcrops.
Information gathered during the "ground truthing" efforts described was compiled onto the 1947 photograph overlay. Photographic transparencies were further examined, refining the initial analysis based on field results.

Fracture Trace Analysis

This section describes the use of aerial photographic analysis in delineating fracture traces to identify potential contaminant migration pathways that exist in or around the study site.

Lattman (1958) described photogeologic fracture traces and lineaments as "linear trends of topographic features, soil tone, and vegetation, visible on aerial photographs". By convention, photogeologic fracture traces are continuously discernible on a photograph for less than one mile, whereas photogeologic lineaments are continuously expressed for at least one mile, and commonly are continuously or discontinuously expressed for many miles (Parizek, 1976).

Aerial photographic interpretation was incorporated into fracture trace lineation. Fracture trace analysis targets surface expressions of various features (e.g., contacts between rock types, faults, fractures, and bedding planes) that develop solution cavities or spaces and create conduits for groundwater flow.

Due to the nearly vertical attitude of the geologic beds in the study site, linear features believed to be surface expressions of solution activity along bedding planes or formation contacts were included in the fracture trace analysis. This modification was
made because of the hydrogeologic significance of solution channels forming along bedding or formation contacts as conduits to groundwater flow (Waltham, 1971).

A search of government and commercial photographic sources was undertaken to obtain the best quality photography available of the study site. A black and white, \( \approx 1:800 \) scale, 1947 aerial photograph was used to examine the study site conditions prior to the majority of construction at the site. Photogeologic information and fracture trace features were extracted from the following, 1:200 scale photographs. The two sources of photographs were the United States Geological Survey (U.S.G.S) and the Agricultural Stabilization and Conservation Service (A.S.C.S).

<table>
<thead>
<tr>
<th>Date</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>April 6,</td>
<td>1947</td>
</tr>
<tr>
<td>August 14,</td>
<td>1950</td>
</tr>
<tr>
<td>September 6,</td>
<td>1952</td>
</tr>
<tr>
<td>October 22,</td>
<td>1955</td>
</tr>
<tr>
<td>September 12,</td>
<td>1962</td>
</tr>
<tr>
<td>October 3,</td>
<td>1967</td>
</tr>
<tr>
<td>May 26,</td>
<td>1972</td>
</tr>
<tr>
<td>October 17,</td>
<td>1974</td>
</tr>
<tr>
<td>October 3,</td>
<td>1983</td>
</tr>
</tbody>
</table>

Great care was taken to exclude all linear features that are the result of humans activity (i.e., abandoned rock quarries, farm tiles) or biological activity such as game trails. To make the study as objective as possible, two hydrogeologists studied the photographs simultaneously.

Crude as it may sound, the best method used for plotting lineaments consisted of mounting the photographs on a wall and allowing two hydrogeologists to mark all the large linear features seen and periodically stand 10 to 20 feet away while viewing the
photographs with the naked eye and through an ordinary two or three-power reducing lens.

Some of the longer, more subtle tonal lineaments are not readily apparent when the line of sight is perpendicular to the photographs. These were best seen by mounting the photographs on a table and viewing with a line of sight at a low angle to the photograph surface. This low angle of view causes foreshortening of the lineament parallel to the line of sight, and emphasized subtle tonal alignments as well as vegetation, drainage and topographic alignments (Parizek, 1976). The connection of individual segments to form a single lineament was a matter of professional judgment.

Characterizing Groundwater Hydrology

Drilling and Installing of Monitoring Wells

A total of 14 monitoring wells were installed at nine locations around the facility (Figure 12). A monitoring well installed at each of the locations was screened in bedrock. At five of the nine locations, a second well, screened in the alluvium overlying bedrock, was installed. The procedures for drilling and installing the monitoring wells are described in detail in Appendix E as well as construction details for the new monitoring wells.

In general, monitoring wells were drilled and installed to:

- Characterize the lithology of the alluvial aquifer by analyzing soil samples collected during drilling.
Figure 12: New Well Locations
• Generally characterize the bedrock lithology by examining the drill cuttings generated during bedrock drilling.

• Estimate the directions and rates of groundwater flow in the alluvium and bedrock by measuring groundwater levels.

• Estimate the lateral and vertical extent of groundwater contamination by analyzing representative samples of groundwater.

• Assess the potential for the presence of DNAPL in the subsurface.

• Test the hydraulic characteristics of the alluvial aquifer.

Water-Level Measurements

Following the installation of the new monitoring wells during the study, all of the monitoring wells in the study site (including previously installed wells) were surveyed for vertical control. The ground-surface elevation adjacent to each well and the elevation of the top of the protective casing were determined to the nearest 0.01 foot above mean sea level. A control point also was surveyed at the edge of the North Branch Potomac River, from which the elevation of the river could be measured. Procedures used for measuring water level are described in detail in Appendix D.

The elevations of the monitoring wells were used to convert measurements of depth to water in each well into water-level elevations. Water-level measurements were recorded from all monitoring wells within a single 4.5-hour period, in order to develop a contemporaneous "snapshot" of water levels throughout the study site. These data
were necessary to assess the directions and rates of groundwater flow throughout the study site.

Water levels were also measured on several occasions at a cluster of wells on the northern perimeter of the study site adjacent to the North Branch Potomac River. The cluster included wells 1GW3, 1GW9, and 1GW13. The river elevation adjacent to the well cluster was measured during these events. These data were collected for an evaluation of vertical hydraulic-head gradients between the various screened intervals of the wells and the river.

In order to assess the degree of hydraulic connection between the river and the alluvial and bedrock aquifers, water-level monitoring was conducted at two monitoring wells adjacent to the river. The water-levels were measured and recorded simultaneously every 15 minutes at 1GW3 (screened in alluvium), 1GW9 (screened in bedrock), and the North Branch Potomac River, for a period of approximately five weeks. An electronic datalogger connected to pressure transducers was used to measure and digitally store the water-level data (Appendix D).

Well Testing

The well testing component of the study consisted of the slug testing of a number of wells screened in the alluvial aquifer, as well as the borehole geophysical logging, straddle-packer testing, and downhole video logging of production well PWA. The purpose of the well testing was to obtain additional information concerning the aquifer characteristics of both the alluvial and bedrock aquifers.
Slug Testing

Slug tests were performed in eight alluvial wells on the study site (Figure 13). Slug tests were performed by artificially depressing the water level in each well using a gas-displacement apparatus, and then monitoring and recording water level and time during the recovery of the water level to its original position. The slug test data were used to estimate the lateral hydraulic conductivity of the alluvial aquifer in the vicinity of the tested wells. Slug testing procedures and analytical methods are described in Appendix B.

Well Logging and Straddle-Packer Testing

A number of downhole procedures were performed in production well PWA, an approximately 200-foot-deep, eight-inch diameter well finished as an open borehole in bedrock. The downhole procedures included several types of geophysical logging, downhole video logging, and straddle-packer testing of selected borehole intervals. These activities were to determine the distribution and nature of fractures intersecting the well, characteristics controlling the directions and rates of groundwater flow and contaminant migration. In addition, groundwater samples were collected during the straddle-packer testing in order to assess the variability of groundwater quality with depth in the well. The procedures employed during well logging and straddle-packer testing activities at well PWA are detailed in Appendix C.
Figure 13: Slug Tested Monitoring Wells
The following types of geophysical logging were performed in the uncased portion of well PWA: caliper, temperature, fluid resistivity, self-potential, natural gamma, and single-point resistance. The geophysical logs provided valuable data about the location and size of fractures intersecting the borehole, possible zones of significant water contribution to the well, and changes in bedrock lithology with depth.

A downhole video survey was conducted in well PWA by slowly lowering a small-diameter television camera and spotlight down the length of the well. The video logging provided positive identification of fracture zones within the well and helped identify zones to be packer tested.

Straddle-packer testing was performed in well PWA to determine the variability of groundwater quality with depth, and to assess the degree of vertical interconnection between fracture zones intersecting the well borehole. An apparatus containing inflatable packers was used to isolate 30-foot-long intervals within the borehole. Five separate 30-foot intervals, as indicated by the geophysical and video logging, containing distinct fracture zones were isolated and tested.

The testing of each interval began with the inflation of the packers to prevent the interval from interacting with other water-bearing intervals via the well bore. Interconnection between intervals through the natural fracture and joint system was not affected. Following the isolation of the tested interval, water was pumped from inside the tested interval to determine the yield of the fracture zones within the interval. Water levels were monitored and recorded from above, within, and below the isolated interval during each test; these data were to be used to assess the natural
interconnection between the tested interval and the intervals above and below. Samples of groundwater also were collected from each tested interval in order to determine the variability of groundwater quality with depth (or a vertical profile of contamination).

**Discharge Assessment**

The objective of the groundwater discharge assessment was to quantify rates of groundwater discharge into the river. The basic elements of groundwater seepage are related to Darcy’s equation:

$$Q = -K\left(\frac{dh}{dl}\right)A$$

Where \(Q\) is the flux of groundwater expressed in volume per unit time, \(A\) is the area through which seepage occurs, \(dh/dl\) is the hydraulic gradient which is unitless and \(K\) is the hydraulic conductivity expressed in cm/sec. Components of the equation were determined by instrumenting the river bed with seepage meters and piezometers.

Mini-piezometers were used to assess groundwater gradients and hydraulic conductivities while seepage meters were used to determine seepage flux and velocity and groundwater quality. Documentation by numerous authors (Cherry and Lee, 1976; Lee, 1977; McBride and Pfannkunch, 1975 and Woessner and Sullivan, 1984) have indicated that these devices are reliable assessment instruments.

The mini-piezometers were constructed of %-inch diameter electrical conduit and installed by hand. The end of the electrical conduit was fitted with a bolt and driven
into the sediments until refusal at which point the piezometer was pulled-back three inches to remove the bolt.

Seepage flux between the groundwater and the overlying surface water was measured directly by covering an area of bottom sediment with an open-bottom container known as a seepage meter and measuring the time and change of water volume in a bag connected to the container (Woessner et al., 1984). Seepage meters were constructed by cutting a unused 55-gallon drum into two sections, to serve as collection pans. The top of one section was drilled with one small bore hole into which a tube adapter was welded as a port for a plastic water volume bag. The seepage meter was slowly pushed into the bottom sediments. It was important that the meter be imbedded at least three inches into the surface water bottom deposits to insure a good seal and thus a closed system, and that the entire measuring bag be submerged to maintain the same piezometric head in the seepage meter as in the surface water (Cherry and Lee, 1976).

Once the seepage meter was installed, the time was noted and an evacuated measuring bag (for measuring discharge) was connected. Approximately one hour later, the bag was removed and its volume measured in a graduated cylinder. In this discharge situation any water that seeps upward through the area of surface water bottom covered by the seepage meter will be trapped and diverted into the measuring bag.

The Darcy velocity, q, (volume per unit area per unit time) is calculated from the relation:

\[ q = \frac{S \cdot k \cdot h}{\mu} \]

where S is the hydraulic gradient, k is the hydraulic conductivity, h is the head, and \( \mu \) is the viscosity of the water.
\[ q = \frac{0.043V}{t} \]

where \( V \) is the volume of water (ml) entering the measuring bag, and \( t \) is the elapsed time in minutes. The factor 0.043 is a conversion factor (Lee and Cherry, 1978). The Darcy velocity is expressed as micrometers per second (1 um/s = 8.46 cm/day). The average hydraulic conductivity \( (K) \) is equal to the Darcy velocity \( (Q) \) divided by the porosity \( (n) \) of the sediment times the factor 0.0001 which converts the units of hydraulic conductivity into cm/sec.

**Installation Procedures for Mini-Piezometers and Seepage Meters**

A seepage meter was installed at different locations, in the bed of the North Branch Potomac River to allow measurement of groundwater discharge (i.e. seepage flux) and determination of the average volume of groundwater migrating through the contaminated section of the study site which is discharging into the river. Figure 14 identifies seepage meter sampling locations.

The seepage meter was pushed into the river sediment and allowed to fill with water. The meter was allowed to stabilize for 15 minutes before the start of the test. Mini-piezometers were installed near the seepage meter locations to allow measurement of vertical hydraulic gradients.

The bed of the North Branch Potomac River consists of one to two feet of organic deposits of medium to fine organic sand, and silt intermixed with gravels-cobbles near the bank and cobble to boulder-armored bed in the
thalweg (main channel). Because of the limited thickness of the unconsolidated bed material and the great variability in bed material size (silts to boulders), mini-piezometers could be installed adjacent to only some of seepage meters.

**Defining Extent of Contamination**

The first section is a review of the methods used to identify potential contamination sources prior to the start of field activities. Later sections are divided into three primary investigations used to define the extent of DNAPL contamination: soil, groundwater, and surface water/sediment.

**Identifying Potential Sources**

Preliminary study activities included reviewing aerial photographs and conducting a facility audit to identify potential sources of VOC. These activities were performed to gain critical information for focusing the study. Each of these preliminary investigation activities is discussed in Appendix A.

**Soil Investigation**

**Investigation of VOCs in Soil**

The soil was investigated to determine the approximate aerial and vertical extent of the VOC contamination. Analysis of the results of the soil-gas survey, which was performed during the previous study, indicated that TCE contamination at the study site
was widespread. Because TCE contamination was widespread, 113 new soil samples were collected at depths ranging from two to 13.5 feet below grade targeting each of the waste disposal areas.

Two methods were used for the field analyses of soil samples. An onsite mobile laboratory equipped with a gas chromatograph (GC) was used to analyze for VOCs and X-ray fluorescence (XRF) was used to screen for metals. Therefore, analytical results of previous samples were used to determine subsequent sample locations. In addition to the GC analyses performed on site, 21 split samples were collected and sent to an E.P.A. Certified Lab (CLP) in Montgomery, Alabama for VOC analysis. Analyses performed by the offsite laboratory include the target compound list (TCL) for VOCs and SVOCs; the Target Analyte List (TAL) for metals, dioxin, explosives, and the TCLP metal (Table 5).

Soil Investigation of Well PWA

Because VOCs, primarily TCE, have been detected in production well PWA, the objective of the soil investigation adjacent to well PWA, was to determine if local contaminated soils have caused the contamination in the well or if there is another possible source to VOC groundwater contamination.

The focused facility (Appendix A) audit determined that solvents are used or stored in nine buildings in the vicinity of well PWA. For this reason, soils adjacent to the solvent storage facilities were investigated. Samples ranged in depth from three to 12 feet below grade. No samples were collected below 12 feet because saturated soils
**Table 5:**
Inorganic and Organic Compounds Analyzed (TCL, TAL, and TCLP)

<table>
<thead>
<tr>
<th>Volatile Organic Compounds on Target Compound List (TCL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone, Benzene, Bromoform, Bromodichloromethane, Bromochloromethane, Bromomethane, 2-Butanone, Carbon Disulfide, Carbon Tetrachloride, Chlorobenzene, Chloroethane, Chloroform, Chloromethane, Dibromochloromethane, 1,2-Dibromo-3-Chloropropane, 1,2-Dibromoethane, cis 1,2-Dichloroethene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4 Dichlorobenzene, 1,1-Dichloroethane, 1,2-Dichloroethane, 1,1-Dichloroethene, 1,2-Dichloropropene, cis-1,3-Dichloropropene, Ethylbenzene, 2-Hexanone, 4-Methyl-2-Pentanone, Methylene Chloride, Styrene, 1,1,2,2-Tetrachloroethane Tetrachloroethene, Toluene, trans-1,2-Dichloroethene, trans-1,3-Dichloropropene, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, Trichloroethene, Vinyl Chloride, Xylenes (total)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Semivolatile Organic Compounds on</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-Dinitrophenol, 4-Nitrophenol, Dibenzo furan, 2,4-Dinitrotoluene, Diethylphthalate, 4-Chlorophenyl-phenylether, Fluorene, 4-Nitroaniline, 4,6-Dinitro-2-methylphenol, N-Nitrosodiphenylamine, 4-Bromophenyl-phenylether, Hexachlorobenzene, Pentachlorophenol, Phenanthrene, Anthracene, Di-n-butylphthalate, Fluoranthen, Pyrene, Butylbenzylphthalate, 3,3'-Dichlorobenzidine, Benzo(a)anthracene, Chrysene, bis-(2-Ethylhexyl)phthalate, Di-n-octylphthalate, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-c,d)pyrene, Dibenz(a,h)anthracene, Benzo(g,h,i)perylene</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metals on Target Analyte List (TAL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Cyanide, Iron, Lead, Magnesium, Manganese, Mercury, Nickel, Potassium, Selenium, Silver, Sodium, Thallium, Vanadium, Zinc</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TAL Explosives</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMX, RDX, Trinitrobenzene, Dinitrobenzene, Nitrobenzene, Tetryl, 2,4,6-Trinitrotoluene, 2,6-Dinitrotoluene, 2,4-Dinitrotoluene, 2-Nitrotoluene, 3-Nitrotoluene, 4-Nitrotoluene</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TCLP Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, Silver</td>
</tr>
</tbody>
</table>
were encountered between nine and 12 feet below grade. All samples were analyzed for VOCs by the mobile laboratory and six samples were split and analyzed for VOCs by the offsite laboratory.

**Water Investigation**

The general groundwater sampling procedure at most monitoring wells consisted of:

1) Purging of the well by pumping, with simultaneous measurement of pH, conductivity (μmho/cm), and temperature (°C) of purged water.

2) Collection of sample.

3) Cleaning of those parts of the measurement and sampling equipment that had come in contact with well water.

Water levels and well depths were measured at each well prior to sampling to determine the volume of water inside the well, therefore the amount needed to purge three well volumes. The majority of the wells were purged and sampled with a portable Well Wizard® pump manufactured by Q.E.D. Environmental Systems, Inc.

**Surface Water and Sediment Investigation**

Four surface-water samples and one sediment sample were collected from the North Branch Potomac River during the study. Surface-water samples were collected at four locations into 40-ml VOA vials at approximately one foot from the bank; (1) upstream of the study site (SW-1); (2) in the vicinity of the study site (SW-2), adjacent to well cluster 1GW3, 1GW9 and 1GW13, with the highest concentrations of contaminates; (3) downstream of the study site but upstream of (SW-3); and (4) downstream of the
study site (SW-4). A single sediment sample (SD-1) was collected in the same location as SW-2, adjacent to the area of greatest known groundwater contamination at the study site at three inches below the river bed and placed directly into the eight-ounce sample jar. The surface-water and sediment sampling locations are depicted in Figure 15. The surface-water and sediment samples were analyzed for TCL VOCs and TAL metals (the samples were not field-filtered).
Figure 15: Surface Water and Sediment Sampling Locations
CHAPTER V: RESULTS

This chapter is divided into four sections that describe the results of data analysis described in Chapter IV. The first two sections, geology and groundwater hydrology, are used to develop the conceptual hydrogeological model of the study site. The third and fourth sections, extent of contamination, and contaminant fate and transport, define and characterize the source and behavior of selected DNAPLs in accordance with the physical conceptual model. Overall interpretations of the results are presented and discussed in Chapter VII.

Geology

The most significant physiographic feature in the vicinity of the study site is Knobly Mountain, which flanks the study site to the south and east, an asymmetric anticlinorium (Figure 2). Shales, limestones, and sandstones of Silurian and Devonian age underlie the portion of the Wills Mountain anticlinorium passing through the study site. The strata on the northwest limb of the anticline are generally vertical to slightly overturned (Schultz, 1989). The mountain derives its name from the series of knobs which were left as resistant remnants after solution of the limestone present in the Tonoloway Formation and the Helderberg Group (Woodward, 1941). The water responsible for the solution flowed underground passing through joints in the Helderberg chert and the Oriskany Sandstone to emerge at the surface at the east base of the mountain. Subsequent collapse of the overlying chert and sandstone formed
narrow, steep-walled valleys in the chert and sandstone which cut the mountain into a series of knobs (Woodward, 1941).

Geologic Mapping

This section will first develop the bedrock geology which directly underlies the study site. Other geologic units mapped will be discussed in greater detail in Appendix F: Geology. The unconsolidated geology of the site will be developed in the last part of this section.

Stratigraphy

The region surrounding the site has eleven mappable units which total approximately 5,200 feet of sedimentary rock containing shale and siltstone (69%), limestone (26%), and sandstone (5%). These stratigraphic units range from the Rose Hill Member of the Clinton Group of lower Silurian age to the Marcellus Formation of Upper Devonian age (Table 6).

Silurian System

The study site is entirely underlain by the Silurian section discussed here (Figure 16).

Clinton Group

The Clinton Group is composed of, in ascending order, the Rose Hill Member
<table>
<thead>
<tr>
<th>System</th>
<th>Formation</th>
<th>Description</th>
<th>Approximate Thickness (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Devonian</td>
<td>Marcellus Shale</td>
<td>Shale, thinly laminated to fissile, black or grayish black, pyritic.</td>
<td>250&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Needmore Shale</td>
<td>Shale, usually calcareous, non fissile, medium dark gray.</td>
<td>100&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Oriskany Group:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ridgeley Member</td>
<td>Sandstone, calcareous and cherty at bottom, siliceous at top, coarse-grained, bluish.</td>
<td>180 to 200&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Helderberg Group:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Keyser Member</td>
<td>Limestone, medium to dark gray, with interbeds of crystalline. Basal unit called the Keyser For. massive, knobby limestone.</td>
<td>450&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Silurian</td>
<td>Tonoloway Formation</td>
<td>Argillaceous dolomitic limestone with interbedded calcareous shale, dark gray.</td>
<td>608&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Wills Creek Formation</td>
<td>Calcareous shale and interbedded argillaceous limestone, medium to dark gray. Williamsport Sandstone Formation at base (21 feet thick), consisting of an upper and lower sandstone unit separated by shale or limestone.</td>
<td>428&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Clinton Group:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>McKenzie Member</td>
<td>Shale, calcareous, medium gray, and interbedded argillaceous limestone. Shale, fissile, medium to dark gray, interbedded with fossiliferous limestone. Sandstone, fine-grained, dark gray, overlain by a thin seam of oolitic hematite. Shale interbedded with lesser amounts of sandstone; a few beds of highly fossiliferous dolomitic limestone at the top of the formation. Greenish-gray to moderate brown.</td>
<td>241.5&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Rochester Member</td>
<td></td>
<td>27&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Keefer Member</td>
<td></td>
<td>7.5&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Rose Hill Member</td>
<td></td>
<td>55&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Sources: ¹Woodward (1941) ²Eddy (1964), ³Dyott (1956).
Source: USGS 7.5 minute Cresaptown, WV-MD quadrangle map.

Figure 16: Geologic Map of Area
Shale), Keefer Member (sandstone), the Rochester Member (shale), and the McKenzie Member (shale). The Clinton Group, the oldest unit in the study site, is poorly exposed in the region, most likely because of its large percentage of shale.

The Rose Hill Member is a 55 foot sequence of greenish gray and moderate brown shales, interbedded with thin layers of sandstone. A few thin layers of fossiliferous limestone occur mainly in the upper part of the unit. Overlying the Rose Hill Member is the Keefer Member which is a fine-grained, medium gray (N5) sandstone averaging 7.5 feet thick. Some of the upper sandstone beds are calcareous.

At the top of the Keefer Member is a 0.5 to 1.0 foot thick oolitic hematitic zone known as the Roberts Iron Ore (Swartz, 1923). This zone was encountered in boring GGW-6 (Figure 12). This contains up to 37 percent iron at nearby Cumberland (Singwald, 1911). Overlying the Keefer Member is the Rochester Member which is the 27-foot thick assemblage of thin bedded, fissile or platy, gray to dark gray shale weathering to a pale yellowish brown, interbedded with thin, dense, highly fossiliferous, blue-gray limestones (Dyott, 1956).

The McKenzie Member, considered to be the uppermost formation of the Clinton Group by most writers, consists of approximately 241 feet of interbedded shales and limestones (Dyott, 1956). Shales are calcareous (i.e. contains calcite as a noteworthy minor constituent), platy and medium gray (N6) weathering to greenish gray. Limestones are bluish gray weather to light olive gray are present. Because of it was difficult to differentiate the Rochester Member with the McKenzie Member they were
mapped as one unit. The upper part of the formation is composed of greenish and yellowish sandstone which grades into the Williamsport Sandstone of the Wills Creek Formation.

Wills Creek Formation

In the mapped area the Williamsport Sandstone is approximately 21 feet thick. Eight feet above the base of the formation is an 8-foot thick calcareous member called the Cedar Cliff Limestone (Woodward, 1941). The upper and lower beds of the Williamsport Sandstone consist of non-marine red and greenish shales with thin interbedded sandstones. These red beds are probably a westward extension of the Bloomsburg facies (Woodward, 1941). Although the Williamsport Sandstone is a distinctive bed and makes a sharp contact with an overlying Wills Creek Formation, it is too thin to be mapped by itself; therefore, it has been included with the Wills Creek Formation.

The Wills Creek Formation is a poorly exposed uniform sequence of thin interbedded calcareous shales and argillaceous limestones. The medium gray fresh rock weathers to yellowish gray, however, some beds weather to a greenish hue. Woodward (1941) reports a thickness of 428 feet for the Wills Creek Formation at Pinto, Maryland.

The upper contact is marked by a change between the thin bedded argillaceous limestones and shales of the Wills Creek Formation and the interbedded massive and
laminated limestones of the Tonoloway Limestone. The Tonoloway weathers to an orange-red soil which contrasts with the gray soil of the Wills Creek.

**Tonoloway Formation**

The Tonoloway Limestone is an interbedded sequence of massive and dolomitic laminated limestones, argillaceous limestones, and calcareous shales. The laminated beds weather into flat platy fragments which are common in the soil that develops on the formation. Woodward (1941) gives a thickness of 608 feet for the Tonoloway Limestone at Pinto, Maryland. Reger (1924) measured a total thickness of 463 feet for the Tonoloway Limestone in the cliff on Knobly Mountain which overlooks the study site. Reger chose a hard, gray limestone as the uppermost bed in the Wills Creek Formation. In accordance with Woodward’s description (1941), at least part of this limestone unit should be included in the Tonoloway, this would make Reger’s thickness more closely agree with Woodward’s for the Tonoloway thickness.

**Helderberg Group**

The Helderberg Group is 450 feet thick (Dyott, 1956). Of this group only the Keyser Limestone could be positively identified in the general area of study. The Keyser Limestone is the oldest formation in the Helderberg Group and has a thickness of 280 feet (Dyott, 1956). The lower boundary is a massive, Knobly limestone. Diversity of limestone lithologies is more pronounced in the Keyser than in any other formation in the area. The massive Knobly beds of the lower Keyser were easily
recognized in the field. Much of the formation is a gray, massive argillaceous limestone.

Site Drilling in Bedrock

A correlation of the surrounding geologic mapping with the drill cuttings to delineate the geologic units that underlie the study site was attempted.

The elevation of the top of the bedrock surface at the study site generally ranges from about 654 feet msl to a low of about 635 feet msl, averaging about 640 feet msl. Figure 17 presents a map of bedrock surface elevations across the study site, and provides interpretive contours at 5-foot intervals. Both the bedrock surface contour map in Figure 17, and cross sections in Figures 20, 21 and 22, are based on less accurate data from the previous investigation and on logging performed as part of this study. The reported depths to bedrock for wells PWA2, 2GW5, and 2GW6 may be miscalculated. The Weston investigation relied exclusively on the interpretation of air-rotary drill cuttings to determine lithologic contacts, a method that can be very unreliable. The boring logs for wells PWA2 and 2GW5, indicate that the wells were drilled to elevations of approximately 634 and 629 feet msl, respectively, without encountering bedrock. This suggests the presence of a bedrock valley or depression. However, at production well PWA, approximately 30 feet away from well PWA2, a downhole television survey made during the study indicated that in the vicinity of well PWA bedrock occurs at an elevation of approximately 645 feet msl. In addition, the
borehole log for well 2GW5 indicates the presence of "rock fragments" in cuttings from near the bottom of the hole. These rock fragments might indicate that the borehole had entered bedrock after all, and at an elevation consistent with data collected during this study. These data offer no evidence of a bedrock valley or depression beneath the study site. Additional data could establish the presence of such significant features. In addition, the reported depth to bedrock at well 2GW6, which would indicate a bedrock surface at about 627 feet msl, was not used for purposes of contouring the bedrock surface in Figure 16.

Bedrock drilling during the study at nine locations revealed that shale is the most prevalent bedrock type beneath the site, particularly beneath the eastern half, which is most likely the Clinton Group. During drilling, no sandstone was encountered at the study site. However, the shale was noticeably siliceous in some beds. Limestone was not encountered east of well 1GW10, except for some traces of argillaceous (clayey) limestone seen at well 1GW14 (Figure 17). The bedrock at wells 1GW10, 1GW12, and GGW4 consists of calcareous shale and argillaceous limestone which is most likely the Wills Creek Formation; the limestone and shale are interbedded at wells GGW4 and 1GW10. At the location of the westernmost bedrock well, well GGW2, bedrock consists of a calcite-veined limestone interbedded with a highly weathered shale. The bedrock encountered at the westernmost monitoring well at the study site, well GGW2, is most likely the limestone and shale of the Keyser Member of the Helderberg Group of Upper Silurian Lower Devonian age (Table 6 and Figure 17).
The shales and occasional limestones of the Wills Creek Formation and the McKenzie and Rose Hill Members of the Clinton Group probably constitute the bedrock beneath the remaining majority of the study site. The boreholes for monitoring wells GGW6 definitely intersect the top of the Keefer Member of the Clinton Group, as shown by distinctive red-colored oolitic hematite encountered during drilling.

Fracture Trace Analysis

Figure 18 is a fracture trace map. The resulting average fracture concentration orientations in descending order of density are as follows:

<table>
<thead>
<tr>
<th>Fracture Set</th>
<th>Strike</th>
<th>Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One</td>
<td>N26°E</td>
<td>44</td>
</tr>
<tr>
<td>Two</td>
<td>N39°W</td>
<td>29</td>
</tr>
</tbody>
</table>

Fracture Set One, trending N26°E is the most abundant fracture pattern in the region surrounding the study site. This pervasive set was prevalent in most lithologies and is parallel to the Appalachian Structural Trend. Set Two, trending N39°W, oblique to the central Appalachian folds of the region. A dip angle was difficult to determine on most measured traces, but generally varied around 90° (+ or - 15°).

In the general area, transverse faults are common to incompetent strata. Most are high-angle reverse faults with less than 10 feet of stratigraphic displacement with obvious sets of well developed slickensides on some fracture surfaces. In addition to slicke
Figure 17: Bedrock Surface Elevations
Source: USGS 7.5 minute Ceretown, WV-MD quadrangle map

Figure 18: Fracture Trace Analysis Map
nsides, quartz and calcite mineralization and clay alteration were noted on several of these surfaces indicating that these fractures have indeed transmitted water. The fractures on which these features were observed are similar in location and orientation to both fracture sets One and Two.

Results from the photo analysis, used in conjunction with data gathered during the field work in the study site, yielded:

(1) Limestone dissolution was identified in the vertical to overturned Tonoloway Formation along the contact between it and the Wills Creek Formation (Figure 16). Generally, karst development occurs in the solution valleys and to a lesser extent, on the steeply inclined northwest limb of the structure. Groundwater seems to be retarded by the Wills Creek Formation (aquitard) allowing springs to form at each contact. These springs are easily identified on the cliffs to the east of the site. In the Tonoloway, which is well suited for solution development, most sinkhole development is restricted to the Tonoloway-Wills Creek boundary (Dyott, 1956).

(2) Two important fracture trace lineaments were identified in the Tonoloway Limestone. These high angle, eastward dipping, longitudinal faults are parallel to the structural trend. Stratigraphic displacement appears to be less than eight feet. These faults have the ability to facilitate solutional development in carbonates and can be seen at the outcrop along the railroad bypass directly across from the study site in Pinto, Maryland.

(3) The McKenzie Formation appears to be shattered due to fracturing and cross-fau-

lting.
(4) The Rose Hill Formation of the Clinton Group appears to be fairly competent and consistent throughout the study site. The Clinton Group encompasses the majority of the central and eastern half of the site.

Soil Borings

In several instances where monitoring wells were drilled adjacent to wells from the previous investigation, borehole logs from the new wells showed significant differences in such features as depth to bedrock and depth to top of the alluvial layer. For example, it was reported by Weston (1990) that bedrock was not encountered above a depth of 40 feet at well 1GW5. However, during the study, bedrock was encountered at a depth of approximately 25 feet in well 1GW14, which is located only about 20 feet from well 1GW5, and at nearly the same surface elevation.

Three interpretative cross-sections of the materials underlying the study site have been prepared to assist in formulating the conceptual model. Figure 19 shows the locations of the cross section alignments. Figures 20, 21 and 22 present the cross sections.

Alluvium and Floodplain Deposits

The cross sections illustrate that the unconsolidated deposits overlying bedrock in the study site consist of two basic hydrostratographic layers. In descending order, they are:
Figure 19:
Geologic Cross-Section Alignments
Figure 20: Geologic Cross-Section A - A'
Figure 21: Geologic Cross-Section B - B'
Figure 22: Geologic Cross-Section C - C’
- A silty clay layer, considered flood deposits from the North Branch Potomac River.
- A sand and gravel layer containing pebbles and cobbles, with variable but typically significant amounts of clay and silt. This layer is presumably alluvium deposited by the North Branch Potomac River.

The natural surficial material at the study site is a silty clay layer. However, at some locations, particularly along the northern perimeter of the study site adjacent to the river, up to several feet of fill material is located at the surface. The silty clay is typically light to dark brown. Towards the lower portions of the layer it contains traces of fine-grained sand. The thickness of the silty clay layer has a range from about eight to 25 feet in the majority of the study site, averaging approximately 14 feet. The silty clay layer appears to thicken where the surface topography rises toward the base of Knobly Mountain, in the southern portion of the site. This is supported by a silty clay layer thickness of 33 feet at well 1GW7.

Samples from the bottom of the silty clay layer were typically moist to wet. The elevation of the bottom of the silty clay layer ranges from about 645 to 661 feet msl, averaging approximately 652 feet msl. By comparison, the river surface elevation adjacent to the study site is estimated on the basis of measurements recorded during the study, to average 648 feet msl.

This alluvial layer of generally poorly sorted gravel, sand, pebbles, and cobbles with variable, but typically significant amounts of clay and silt underlies the silty clay layer. Pebbles and cobbles generally were well-rounded and composed of sandstone or
quartzite, but occasionally were composed of limestone and shale. This layer is heterogeneous. The study site alluvium varies in thickness from about six to 24 feet. Typical thicknesses are approximately 15 feet. The alluvium generally is saturated through its entire thickness, except near the river. The average elevation of the bottom of the alluvium is about 640 feet msl.

Groundwater Hydrology

The geological information obtained during the study indicates that the alluvium, which generally consists of clayey gravel, pebbles, and sand, is saturated and constitutes the shallow aquifer beneath the study site. The fractured bedrock underlying the alluvium constitutes a second, deeper aquifer that is hydraulically connected with the alluvium. Because of the lithologic differences between the alluvium and bedrock, the two units will be considered as separate hydrogeologic units. For the purposes of this thesis the upper unconsolidated aquifer will be described as the alluvial aquifer and the fractured bedrock underlying the alluvial aquifer will be described as the bedrock aquifer.

Alluvial Aquifer

Slug tests were conducted at eight monitoring wells open to the alluvium during the study to provide estimates of its hydraulic conductivity (Figure 13 and Table 7)(see appendix C for details of methods and analytical procedures for the slug tests). The observed hydraulic conductivities range from $1 \times 10^4$, to $5 \times 10^3$ cm/sec with a median
of approximately $6 \times 10^4$ cm/sec. The large range in hydraulic conductivities reflects the heterogeneity of the alluvium. At locations where the alluvium had a high clay content (wells GGW5, GGW7, 1GW11, and 3GW3), hydraulic conductivities were in the range of $10^3$ to $10^4$ cm/sec. Where the alluvium was relatively free of clay (wells GGW3, 1GW8, and PWA2), hydraulic conductivities were on the order of $10^3$ cm/sec. They wells were used to produce an interpretive contour map of the water levels (piezometric surface) in the alluvial aquifer (Figure 23). The facility alluvial piezometric-surface map indicates that, on the scale of the study site, the groundwater flow is toward the river. The potentiometric surface appears to slope relatively uniformly toward the river along the northern study site perimeter, but the gradient is noticeably smaller in the south-central portion of the study site.

The geology section states that the top and bottom elevations of the alluvium are approximately 652 and 640 feet msl, respectively. During average flow conditions in the vicinity of well 1GW13, the river level was measured twice at approximately 648 feet msl. The elevation of the river and the nearby water table suggest that the river is the ultimate discharge zone for groundwater flowing through the alluvium.

At some locations in the study site, a monitoring well screened in the alluvium is located within about 20 feet of a well screened in bedrock. Water-level measurements from these paired wells were compared in order to determine the direction and magnitude of the vertical component of the hydraulic gradient (Figure 24). The results, presented in Table 9, indicate that the calculated vertical components of flow between the alluvium and bedrock were downward at all locations. The alluvial and bedrock
Figure 23: Piezometric Surface of the Alluvial Aquifer
Figure 24: Vertical Gradients
aquifers are most likely well connected at locations where the vertical hydraulic gradient is small.

The horizontal hydraulic gradients at the facility within the alluvial aquifer range from a low of approximately 0.002 feet per horizontal foot between the 662 feet msl contour and well GGW5 in the south central portion of the facility, to a high of approximately 0.015 between wells 1GW11 and 1GW3 near the northern perimeter of

<table>
<thead>
<tr>
<th>Well</th>
<th>Date of Test</th>
<th>Nature of Alluvium in the Screened Zone</th>
<th>Test Number</th>
<th>Computed Hydraulic Conductivity (cm/s)</th>
<th>Computed Hydraulic Conductivity (ft/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGW3</td>
<td>7-30-92</td>
<td>Sand and gravel</td>
<td>1, 2</td>
<td>$4 \times 10^3$, $4 \times 10^3$</td>
<td>12, 12</td>
</tr>
<tr>
<td>GGW5</td>
<td>7-29-92</td>
<td>Clayey gravel</td>
<td>1, 2</td>
<td>$7 \times 10^5$, $9 \times 10^5$</td>
<td>0.2, 0.3</td>
</tr>
<tr>
<td>GGW7</td>
<td>7-30-92</td>
<td>Clayey gravel</td>
<td>1, 2</td>
<td>$1 \times 10^4$, $1 \times 10^4$</td>
<td>0.3, 0.04</td>
</tr>
<tr>
<td>1GW8</td>
<td>8-12-92</td>
<td>Sand and gravel</td>
<td>1, 2</td>
<td>$2 \times 10^3$, $2 \times 10^3$</td>
<td>5, 5</td>
</tr>
<tr>
<td>1GW11</td>
<td>8-13-92</td>
<td>Clayey sand and gravel</td>
<td>1, 2</td>
<td>$2 \times 10^4$, $3 \times 10^4$</td>
<td>0.7, 0.7</td>
</tr>
<tr>
<td>2GW4</td>
<td>7-30-92</td>
<td>Sand and gravel, trace clay</td>
<td>1, 2</td>
<td>$9 \times 10^4$, $1 \times 10^3$</td>
<td>2, 3</td>
</tr>
<tr>
<td>3GW3</td>
<td>8-12-92</td>
<td>Clayey gravel</td>
<td>1, 2</td>
<td>$2 \times 10^5$, $2 \times 10^5$</td>
<td>0.05, 0.05</td>
</tr>
<tr>
<td>PWA2</td>
<td>7-28-92</td>
<td>Sand and gravel</td>
<td>1, 2</td>
<td>$5 \times 10^3$, $5 \times 10^3$</td>
<td>15, 13</td>
</tr>
</tbody>
</table>
Groundwater velocities were estimated based on hydraulic gradients and conductivity (k) measurements (Table 7). Adjacent to the river and study site (1GW3 and 1GW9), where a hydraulic gradient is 0.052, hydraulic conductivity is $2.5 \times 10^4$ (1GW11) and porosity (n) is assumed to be 20%, the estimated average linear velocity ranges from approximately 1 to 400 feet per year (ft/yr), with a median linear velocity of approximately 47 ft/yr. In the south-central portion of the facility where the hydraulic gradient is 0.0018 (PWA1 and PWA2) is measured, hydraulic conductivity is $5 \times 10^{-4}$ (PWA2) and n is assumed to be 20%, the estimated average linear velocity ranges from 0.1 to 52 ft/yr, with a median linear velocity of approximately 6 ft/yr. The large range of average linear velocities reflects the wide range of alluvial hydraulic conductivities.

**Bedrock Aquifer**

Unlike the alluvial aquifer, lateral groundwater flow in the bedrock aquifer is confined to fractures and solution channels. The directions and rates of groundwater movement in fractured bedrock are controlled by the size, frequency, and orientation of fractures and by the hydraulic gradient. Because of the significant number of compositionally and structurally varied bedrock stratigraphic units underlying the study area the hydraulic characteristics of the bedrock aquifer are likely to vary greatly across the site.

One estimate of the hydraulic properties of a portion of the bedrock aquifer was calculated during the previous investigation (Chapter III). An 8-hour pumping test
conducted in production well PWA produced an estimate of the transmissivity of the bedrock on the order of 2,000 to 6,300 gallons per day per foot in the vicinity of the well. The results of the pumping test also indicated a hydraulic connection between the alluvial and bedrock aquifers.

Water-level measurements from five wells screened across the alluvium/bedrock contact also were used (Table 8). Although the majority of the screened zone in these wells is in the alluvium, the water-level measurements from these wells are questionable because of the positioning of their screens across the alluvium/bedrock boundary. An interpretive contour map of the potentiometric surface for the bedrock aquifer is derived from the water-level elevations in monitoring wells screened entirely in bedrock (Figure 25). It should be noted that groundwater flow in a fractured, jointed bedrock environment has flow patterns distinctly different from flow patterns of an unconsolidated porous media. Contouring of groundwater elevations in this complex bedrock infers the system is composed of well connected fractures and solution features, which may not be the case.

The potentiometric surface indicates that the horizontal flow patterns in the bedrock are similar to those in the overlying alluvium. The horizontal hydraulic gradients are similar also, ranging from approximately 0.003 in the south-central portion of the facility between the 662 feet msl contour and well GGW6, to 0.016 between wells 1GW11 and 1GW3 near the northern perimeter of the study site.

Because fracture set one is roughly parallel to the strike of bedding planes in the Wills Mountain anticlinorium and fracture set two is oblique to the general structural
## Table 8:
Calculated Vertical Component of the Hydraulic Gradient at Paired Wells in the Alluvium and Bedrock

<table>
<thead>
<tr>
<th>Well Pair*</th>
<th>Measured Difference in Water Level Elevations (ft)</th>
<th>Distance Between Well Screens* (ft—max/min)</th>
<th>Vertical Component of Hydraulic Gradient (max/min)</th>
<th>Direction of Vertical Component of Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGW1/GG W2</td>
<td>-0.12</td>
<td>62/47</td>
<td>0.0026/0.0019</td>
<td>Down</td>
</tr>
<tr>
<td>GGW3/GG W4</td>
<td>1.07</td>
<td>68/48</td>
<td>0.022/0.016</td>
<td>Down</td>
</tr>
<tr>
<td>GGW5/GG W6</td>
<td>-0.42</td>
<td>64/44</td>
<td>0.0095/0.0066</td>
<td>Down</td>
</tr>
<tr>
<td>GGW7/GG W8</td>
<td>-2.22</td>
<td>67/47</td>
<td>0.047/0.033</td>
<td>Down</td>
</tr>
<tr>
<td>1GW11/1G W10</td>
<td>-0.71</td>
<td>69/52</td>
<td>0.014/0.010</td>
<td>Down</td>
</tr>
<tr>
<td>1GW3/1G W9'</td>
<td>-1.31</td>
<td>70/25</td>
<td>0.052/0.019</td>
<td>Down</td>
</tr>
<tr>
<td>1GW5/1G W14</td>
<td>-0.52</td>
<td>72/32</td>
<td>0.016/0.0072</td>
<td>Down</td>
</tr>
<tr>
<td>PWA2/PW A1</td>
<td>-0.05</td>
<td>58/28</td>
<td>0.0018/0.00086</td>
<td>Down</td>
</tr>
</tbody>
</table>

**NOTES:** *Alluvial well/bedrock well. *Max = Top of screen for alluvial well minus bottom of screen for bedrock well. Min = Bottom of Screen for alluvial well minus top of screen for bedrock well. 1GW3 is screened across the alluvium/bedrock contact, while 1GW9 is screened entirely in bedrock.

The trend (Figure 18), fracture orientations similar to either of these sets in the bedrock beneath the study site would facilitate the movement of groundwater toward the North Branch Potomac River. The water-level contour map of bedrock indicates that the
Figure 25: Piezometric Surface of the Bedrock Aquifer
general direction of the groundwater flow beneath the eastern two-thirds of the facility is roughly parallel to the strike of fracture set two. The general direction of groundwater flow beneath the western one-third of the facility is roughly parallel to the strike of fracture set one.

Solution-widened fractures in limestone and dolomite bedrock of the Tonoloway and Wills Creek Formations may facilitate rapid migration of groundwater. The drilling did not reveal large solution channels except at well GGW2, the westernmost bedrock well in the study site finished in the Keyser Formation of the Helderberg Group. Bedrock drilling east of well GGW2 during the study revealed predominantly shale bedrock without voids or large solution cavities. However, because of the relatively few bedrock drilling locations and the lack of bedrock "core", solution channels may be present at other locations within the study site.

The results of the packer tests on well PWA indicated that the yield of well PWA was highly variable over the length of the borehole. The yields of the intervals were, in gallons per minute (gpm): interval one, 2.3 gpm; interval two, 24 gpm; interval three, 13 gpm; interval four, greater than 26 gpm (the maximum flow rate of the pump at this depth); and interval five, 7 gpm. On the basis of these results, intervals two and four appear to provide the majority of the total yield of well PWA.

During the packer testing of interval four, pumping produced piezometric responses in intervals three and five, indicating some degree of hydraulic interconnection between the intervals. The pumping of the other intervals did not produce responses outside of the tested interval.
The variability of yields and interconnections between the tested intervals at well PWA demonstrates that the bedrock aquifer is hydrogeologically complex. Because of this complexity, extrapolating the properties or distribution of specific fracture zones any great distance from site PWA is tentative.

Surface Water/Groundwater Interactions

Simultaneous water-level measurements were recorded for two periods in well cluster 1GW13, 1GW9, and 1GW3, adjacent to the North Branch Potomac River and of the river stage (Table 9). The measured wells included well 1GW3 (screened across the alluvium/bedrock contact, from 24 to 40 feet below ground), well 1GW9

<table>
<thead>
<tr>
<th>Location</th>
<th>Screened Unit</th>
<th>Screen Depth Interval (ft)</th>
<th>Water Level (ft. MSL) 8-31-92</th>
<th>Water Level (ft. MSL) 9-16-92</th>
</tr>
</thead>
<tbody>
<tr>
<td>1GW3</td>
<td>A,B</td>
<td>24-40</td>
<td>649.20</td>
<td>648.75</td>
</tr>
<tr>
<td>1GW9</td>
<td>B</td>
<td>65-80</td>
<td>648.30</td>
<td>648.06</td>
</tr>
<tr>
<td>1GW13</td>
<td>B</td>
<td>111-121</td>
<td>650.35</td>
<td>650.17</td>
</tr>
<tr>
<td>River</td>
<td></td>
<td></td>
<td>648.07</td>
<td>647.98</td>
</tr>
</tbody>
</table>

**NOTES:** Screened Unit: A = Alluvium; B = Bedrock; A,B = Well screened across the alluvium/bedrock contact. Effective screen zone. Although the well screen extends from 10-40 ft., a steel surface casing extends from the surface to a depth of 24 ft (screened in bedrock from 65 to 80 feet below ground), and well 1GW13 (screened in bedrock from 111 to 121 feet below ground). These measurements permitted a
comparison of groundwater response to river water level changes. They also permit evaluation of the vertical component of the hydraulic gradient between the alluvium and shallow bedrock, and between the shallow and deep bedrock.

The results of the comparisons indicate a downward vertical component of groundwater flow at this location between the alluvium/shallow bedrock and moderately deep bedrock. However, vertical groundwater flow between moderately deep bedrock and deeper bedrock was upward. The magnitude and direction of the gradients were consistent between measurement periods. Moreover, the water level in the moderately deep bedrock well (well 1GW9) was slightly higher than the river level. Relative to the other wells, well 1GW9 was closest to the river level. On the basis of these results, the bedrock aquifer appears to be hydraulically connected to the river at this location. Because the top-of-bedrock surface adjacent to the river at this location was about eight feet below the river level, the bedrock groundwater flow system and the river are believed to be connected. A hydraulic connection between the bedrock and the river does not eliminate the possibility that some portion of bedrock groundwater flow crosses beneath the river. However, without measurements of groundwater levels north of the river and a better definition of the bedrock groundwater flow system, the potential for this flow cannot be evaluated.

Simultaneous water-level measurements also were recorded continuously (i.e., at 15-minute intervals using pressure transducers and a datalogger) at wells 1GW3 and 1GW9 and the river for a period of approximately five weeks. Long-term water-level monitoring helped to determine the degree of hydraulic interconnection between the
river and the alluvial and bedrock aquifers. Figure 26 is a plot of the observed river and water-level changes; in order to avoid a large vertical scale, the data are plotted as deviations from their means. The water-level changes in the bedrock well (well 1GW9) correspond very closely in time and magnitude to changes in river level. This indicates a strong hydraulic connection between the bedrock aquifer and the river. However, the water-level changes in the well screened across the alluvium/bedrock contact (well 1GW3) show only occasional very subdued responses to river-level changes, which would indicate an unexpectedly poor hydraulic connection with the river.

Well construction may explain the poor response of well 1GW3 to the changes in the river level. Installed during a previous investigation, this well has a screened zone extending from 10 to 40 feet below ground. However, a steel surface casing extends from the ground surface to 24 feet below ground, reducing the effective screen zone to the interval from 24 to 40 feet below ground. During the installation of well 1GW13, adjacent to well 1GW3, bedrock was encountered at 26.5 feet below ground surface, and water-bearing fractures in bedrock were not encountered until a depth of approximately 62 feet. This means that well 1GW3 is screened approximately 2.5 feet in alluvium and 13.5 feet in bedrock that is possibly devoid of fractures. Moreover, the alluvium at the 24 to 26.5 foot depth at this location was characterized during the study as a clayey gravel, which generally has relatively low permeabilities. The limited exposure of well 1GW3 to the alluvium, combined with the relatively low permeability of the alluvium at the location, may explain the poor
Figure 26: Observed River and Water-Level Changes
response of well 1GW3 to the changes in river level. These results are probably not indicative of the general degree of hydraulic connection between the alluvium and the river. Therefore, it is still extremely likely that a hydraulic connection exists.

Discharge Assessment

Interpretation of the hydrologic data gathered during the study indicated that the alluvial groundwater migrating through the site discharges to the North Branch Potomac River. This interpretation was based upon the lateral direction of groundwater flow from the site towards the river and the distribution of vertical upward gradients observed in multi-level bedrock wells installed adjacent to the river and mini-piezometers installed in the river. In order to quantify the volume of groundwater which migrates through the site and discharges to the river, a round of discharge measurements from the seepage meters and head measurements from the wells and piezometers were taken to specifically assess the interconnection of the surface water and groundwater (Figure 14).

Discharge measurements from the seepage meters indicated seepage fluxes ranging from 0.0003 to 0.001 gallons/minute/feet² (gal/min/ft²). This range of values is in agreement with the flow rate range of 1 to 15 gallons/minute (gpm) (Table 10) moving through the study site which is 11,240ft². It should be noted that the results of this discharge assessment are representative of discharge conditions only at this particular time of this year. Measurements from mini-piezometers confirmed, by their higher head, that significant discharging conditions are present into the river.
<table>
<thead>
<tr>
<th>Distance (ft)</th>
<th>Water Depth (ft)</th>
<th>Total Time (min)</th>
<th>Vol. (ml)</th>
<th>Seating</th>
<th>Seepage Flux (cc/m²/sec)</th>
<th>Map Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.6</td>
<td>90</td>
<td>513</td>
<td>Good</td>
<td>0.25</td>
<td>1</td>
</tr>
<tr>
<td>2.4</td>
<td>1.4</td>
<td>60</td>
<td>763</td>
<td>P/G</td>
<td>0.55</td>
<td>2</td>
</tr>
<tr>
<td>15.0</td>
<td>3.0</td>
<td>90</td>
<td>1206</td>
<td>V.Poor</td>
<td>0.58</td>
<td>3</td>
</tr>
<tr>
<td>2.0</td>
<td>1.2</td>
<td>60</td>
<td>1091</td>
<td>P/G</td>
<td>0.78</td>
<td>4</td>
</tr>
<tr>
<td>1.0</td>
<td>1.3</td>
<td>60</td>
<td>267</td>
<td>Good</td>
<td>0.19</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>60</td>
<td>136</td>
<td>Good</td>
<td>0.10</td>
<td>0.14</td>
</tr>
<tr>
<td>2.0</td>
<td>2.2</td>
<td>73</td>
<td>368</td>
<td>V.Good</td>
<td>0.22</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>70</td>
<td>480</td>
<td></td>
<td>V.Good</td>
<td>0.29</td>
<td>0.26</td>
</tr>
<tr>
<td>1.1</td>
<td>0.9</td>
<td>75</td>
<td>467</td>
<td>Excel.</td>
<td>0.27</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>75</td>
<td>292</td>
<td>Excel.</td>
<td>0.17</td>
<td>0.22</td>
</tr>
<tr>
<td>4.0</td>
<td>1.4</td>
<td>60</td>
<td>768</td>
<td>Excel.</td>
<td>0.55</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>60</td>
<td>813</td>
<td>Excel.</td>
<td>0.58</td>
<td>0.57</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>60</td>
<td>455</td>
<td>Excel.</td>
<td>0.33</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>60</td>
<td>320</td>
<td>Excel.</td>
<td>0.23</td>
<td>0.28</td>
</tr>
<tr>
<td>2.0</td>
<td>1.3</td>
<td>60</td>
<td>308</td>
<td>Excel.</td>
<td>0.22</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>60</td>
<td>1095</td>
<td>Excel.</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>433</td>
<td></td>
<td>Excel.</td>
<td>0.28</td>
<td>0.43</td>
</tr>
<tr>
<td>4.2</td>
<td>3.1</td>
<td>66</td>
<td>488</td>
<td>Excel.</td>
<td>0.32</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>66</td>
<td>507</td>
<td>Excel.</td>
<td>0.33</td>
<td>0.32</td>
</tr>
<tr>
<td>3.0</td>
<td>2.7</td>
<td>60</td>
<td>686</td>
<td>Excel.</td>
<td>0.49</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>35</td>
<td>455</td>
<td>Excel.</td>
<td>0.56</td>
<td>0.53</td>
</tr>
</tbody>
</table>

1 - Distance is measured from the River Bank
2 - see Figure 13
Note: The greater volume of discharge adjacent to IGW-13 may be due to the steeper ground-surface slope.
Extent of Contamination

This section presents and discusses chemical analytical data for the vadose and groundwater at the study site. Results of the soil, groundwater, surface-water and sediment analysis for the North Branch Potomac River are also presented and discussed.

Source Identification

Chemical analysis of the soils at the study site were performed for VOCs, SVOCs, metals and explosives, and ash was evaluated for metals and dioxins. All groundwater samples were analyzed for Target Compound List (TCL) Volatile Organic Compounds (VOCs). Groundwater samples collected from the study site monitoring wells and PWA were also analyzed for Target Analyte List (TAL) metals (i.e. total metals, samples were not field-filtered). Groundwater samples collected from the study site and PWA were also analyzed for the Explosive Compounds List. Because of some floating "oil" product in well PWA, it was also analyzed for Total Petroleum Hydrocarbons (TPH), Gasoline-Range Organics (GRO), and Diesel-Range Organics (DRO).

TCE was the most prevalent compound found in the site soil, having been detected in 95 of the 111 samples analyzed or 86 percent of the samples. The concentration of TCE detected in soil samples ranged from 5 to 16,000 \( \mu \)g/kg. A value equal to one-half the EPA Contract Lab Program (CLP) detection limit was entered for all non-detects. The arithmetic mean of TCE detected in the 111 samples is roughly 500
The standard deviation for TCE is almost four times the arithmetic mean, however indicating a wide range of TCE concentrations.

Both 1,1,1-TCA and cis-1,2-DCE were detected in approximately 15 percent of the samples. 1,1,1-TCA concentrations ranged from 5 μg/kg to 215 μg/kg. In addition, 15 of the 17 samples in which 1,1,1-TCA was detected contained considerably higher concentrations of TCE.

Review of the analytical data for VOC-contaminated soil clearly indicates that TCE is the VOC contaminant most prevalent and at the highest concentrations in soils at the study site. In addition, other VOCs detected generally are found in sampling locations containing high concentrations of TCE (e.g., solvent disposal pits). Hence, the approximate extent of TCE soil contamination is a good indicator for the approximate extent of VOC-contaminated soil at the study site. Figure 27 shows the location and TCE concentrations for all soil samples collected at the study site. For soil samples analyzed by both laboratories, the higher reported concentration is included in the figure.

Some areas of the study site contain low concentrations of TCE. Little or no TCE contamination was detected in soil samples collected at all depths from the drum storage pad area. This is consistent with results of the soil sampling conducted during the previous study. Samples collected at any depth immediately south of all three disposal pits contained little or no TCE above detection limits. Little or no TCE was detected southwest or southeast of the ordnance burning ground and low levels were detected in
Figure 27: TCE Detected in Soil Samples
the southeast portion of the ordnance burning ground. This is consistent with soil-gassampling reported in the previous study.

**VOCs Detected in Soils at Well PWA**

A total of 28 soil samples were also collected from various depths in the vicinity of well PWA and the VOC analyses performed were identical to those performed at the study site (Table 11). TCE was only detected near two of the buildings targeted as a result of the focused facility audit.

**Groundwater Contamination**

The results of the analyses of all groundwater samples collected during the study are presented and discussed below.

**VOCs Detected in Groundwater**

The VOC summary statistical analysis for the study site wells is presented in Table 12. Sample duplicates, sample reruns, and the analytical data from samples collected during straddle-packer testing were not used in the statistical analysis. Two VOCs, carbon tetrachloride and 2-butanone, were only detected in groundwater samples from straddle-packer testing, and therefore, are not included in the statistical analysis presented in Table 12. Fourteen VOCs were detected in the groundwater beneath the study area:

- 1,1,1-TCA
- 1,1-DCA
### Table 11
Summary Statistics - Soils (ug/kg)

<table>
<thead>
<tr>
<th></th>
<th>Maximum Conc.</th>
<th>Minimum Conc.</th>
<th>Std. Dev.</th>
<th>Arithmetic Mean</th>
<th>Upper 95% Conf.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DIOXINS &amp; PURANS (ug/kg)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL-HEXACHLORODIBENZO-p-DIOXIN</td>
<td>1.8</td>
<td>1.1</td>
<td>0.495</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td><strong>EXPLOSIVES (mg/kg)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMX</td>
<td>14</td>
<td>1.1</td>
<td>4.934</td>
<td>5.825</td>
<td>23.8148</td>
</tr>
<tr>
<td>RDX</td>
<td>34</td>
<td>2.1</td>
<td>10.723</td>
<td>7.9125</td>
<td>22.8612</td>
</tr>
<tr>
<td><strong>INORGANICS (mg/kg)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ARSENIC</td>
<td>14.4</td>
<td>4.5</td>
<td>3.394</td>
<td>10.325</td>
<td>13.0176</td>
</tr>
<tr>
<td>CADMIUM</td>
<td>154</td>
<td>0.5</td>
<td>44.439</td>
<td>27.9975</td>
<td>965.1161</td>
</tr>
<tr>
<td>CHROMIUM</td>
<td>110</td>
<td>10</td>
<td>38.618</td>
<td>53.983333</td>
<td>114.3909</td>
</tr>
<tr>
<td>COPPER</td>
<td>2150</td>
<td>28.8</td>
<td>747.67</td>
<td>716.6</td>
<td>5030.645</td>
</tr>
<tr>
<td>LEAD</td>
<td>12100</td>
<td>6.5</td>
<td>3748</td>
<td>2341.1417</td>
<td>176494.7</td>
</tr>
<tr>
<td>MERCURY</td>
<td>16.8</td>
<td>0.23</td>
<td>4.575</td>
<td>2.946667</td>
<td>12.4135</td>
</tr>
<tr>
<td>SILVER</td>
<td>121</td>
<td>0.42</td>
<td>46.936</td>
<td>44.485</td>
<td>1041.218</td>
</tr>
<tr>
<td><strong>SEMIVOLATILE ORGANICS (ug/kg)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-METHYLNAPHTHALENE</td>
<td>350</td>
<td>40</td>
<td>74.299</td>
<td>158.16667</td>
<td>232.5479</td>
</tr>
<tr>
<td>2-NITROANILINE</td>
<td>13000</td>
<td>94</td>
<td>3533.9</td>
<td>1799.5</td>
<td>4067.811</td>
</tr>
<tr>
<td>ACENAPHTHENE</td>
<td>165</td>
<td>67</td>
<td>28.29</td>
<td>156.83333</td>
<td>183.6771</td>
</tr>
<tr>
<td>ANTHRACENE</td>
<td>730</td>
<td>165</td>
<td>162.6</td>
<td>214.16667</td>
<td>270.0683</td>
</tr>
<tr>
<td>BENZO(A)ANTHRACENE</td>
<td>1700</td>
<td>95</td>
<td>458.66</td>
<td>331.66667</td>
<td>548.9772</td>
</tr>
<tr>
<td>BENZO(A)PYRENE</td>
<td>1400</td>
<td>83</td>
<td>378.15</td>
<td>304.83333</td>
<td>499.5704</td>
</tr>
<tr>
<td>BENZO(B)FLUORANTHENE</td>
<td>1500</td>
<td>100</td>
<td>407.33</td>
<td>317.91667</td>
<td>518.4715</td>
</tr>
<tr>
<td>BENZO(G,H,I)PERYLENE</td>
<td>910</td>
<td>84</td>
<td>226.38</td>
<td>243.25</td>
<td>353.5466</td>
</tr>
<tr>
<td>BENZO(K)FLUORANTHENE</td>
<td>1100</td>
<td>130</td>
<td>286.61</td>
<td>274.58333</td>
<td>405.4746</td>
</tr>
<tr>
<td>BIS(2-ETHYLHEXYL)PHTHALATE</td>
<td>1600</td>
<td>41</td>
<td>523.92</td>
<td>393.58333</td>
<td>970.4405</td>
</tr>
<tr>
<td>CHRYSENE</td>
<td>1600</td>
<td>160</td>
<td>444.81</td>
<td>342.91667</td>
<td>560.7703</td>
</tr>
<tr>
<td>DI-N-BUTYLPHthalate</td>
<td>5100</td>
<td>64</td>
<td>1438.5</td>
<td>535.66667</td>
<td>1010.34</td>
</tr>
<tr>
<td>DIBENZ(A,H)ANTHRACENE</td>
<td>230</td>
<td>165</td>
<td>18.764</td>
<td>170.41667</td>
<td>179.8533</td>
</tr>
<tr>
<td>FLUORANTHENE</td>
<td>2900</td>
<td>42</td>
<td>822.31</td>
<td>471.83333</td>
<td>1100.064</td>
</tr>
<tr>
<td>FLUORENE</td>
<td>410</td>
<td>81</td>
<td>76.824</td>
<td>178.41667</td>
<td>219.2925</td>
</tr>
<tr>
<td>INDENO(1,2,3-CD)PYRENE</td>
<td>790</td>
<td>60</td>
<td>192.12</td>
<td>227.08333</td>
<td>338.9613</td>
</tr>
<tr>
<td>N-MITROSODIPHENYLAMINE (1)</td>
<td>3000</td>
<td>64</td>
<td>821.56</td>
<td>392.83333</td>
<td>616.3386</td>
</tr>
<tr>
<td>NAPHTHALENE</td>
<td>250</td>
<td>76</td>
<td>37.105</td>
<td>164.66667</td>
<td>192.6642</td>
</tr>
<tr>
<td>PHENANTHRENE</td>
<td>2300</td>
<td>165</td>
<td>622.07</td>
<td>390.41667</td>
<td>640.5581</td>
</tr>
<tr>
<td>PYRENE</td>
<td>2300</td>
<td>165</td>
<td>638.43</td>
<td>410.41667</td>
<td>715.0223</td>
</tr>
<tr>
<td><strong>VOLATILE ORGANICS (ug/kg)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-TRICHLOROETHANE</td>
<td>410</td>
<td>5</td>
<td>49.943</td>
<td>16.856061</td>
<td>12.0936</td>
</tr>
<tr>
<td>1,2-DICHLOROETHANE (TOTAL)</td>
<td>27000</td>
<td>5</td>
<td>5887.7</td>
<td>1304.9524</td>
<td>592.5041</td>
</tr>
<tr>
<td>ACETONE</td>
<td>820</td>
<td>5</td>
<td>196.42</td>
<td>64.047619</td>
<td>62.7112</td>
</tr>
<tr>
<td>CARBON DISULFIDE</td>
<td>6</td>
<td>2</td>
<td>1.017</td>
<td>4.666667</td>
<td>5.3206</td>
</tr>
<tr>
<td>TETRACHLOROETHENE</td>
<td>1400</td>
<td>3</td>
<td>309.03</td>
<td>87.142857</td>
<td>77.4811</td>
</tr>
<tr>
<td>TRICHLOROETHENE</td>
<td>94000</td>
<td>1</td>
<td>11309</td>
<td>2316.4227</td>
<td>2135.28</td>
</tr>
<tr>
<td>XYLENES (TOTAL)</td>
<td>290</td>
<td>2</td>
<td>72.66</td>
<td>26.714286</td>
<td>31.4179</td>
</tr>
</tbody>
</table>

**NOTE:**
Total Count = Number of Samples
Detected Count = Number of Contaminated Samples
Table 12
Summary Statistics- Groundwater
(ug/l or ppb)

<table>
<thead>
<tr>
<th></th>
<th>Detected Count</th>
<th>Total Count</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INORGANICS (UG/L)</strong></td>
<td>Frequency</td>
<td></td>
</tr>
<tr>
<td>ARSENIC</td>
<td>0.92</td>
<td>35</td>
</tr>
<tr>
<td>CADMIUM</td>
<td>0.03</td>
<td>1</td>
</tr>
<tr>
<td>CHROMIUM</td>
<td>0.76</td>
<td>29</td>
</tr>
<tr>
<td>COPPER</td>
<td>0.76</td>
<td>29</td>
</tr>
<tr>
<td>LEAD</td>
<td>0.87</td>
<td>33</td>
</tr>
<tr>
<td>MERCURY</td>
<td>0.11</td>
<td>4</td>
</tr>
<tr>
<td>SILVER</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td><strong>VOLATILE ORGANICS (UG/L)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-TRICHLOROETHANE</td>
<td>0.15</td>
<td>7</td>
</tr>
<tr>
<td>1,1-DICHLOROETHANE</td>
<td>0.06</td>
<td>3</td>
</tr>
<tr>
<td>1,2-DICHLOROETHENE (TOTAL)</td>
<td>0.38</td>
<td>18</td>
</tr>
<tr>
<td>ACETONE</td>
<td>0.23</td>
<td>11</td>
</tr>
<tr>
<td>CARBON DISULFIDE</td>
<td>0.06</td>
<td>3</td>
</tr>
<tr>
<td>METHYLENE CHLORIDE</td>
<td>0.62</td>
<td>29</td>
</tr>
<tr>
<td>TETRACHLOROETHENE</td>
<td>0.13</td>
<td>6</td>
</tr>
<tr>
<td>TRICHLOROETHENE</td>
<td>0.70</td>
<td>33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Maximum Conc.</th>
<th>Minimum Conc.</th>
<th>Standard Deviation</th>
<th>Arithmetic Mean</th>
<th>Upper 95% Confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INORGANICS (UG/L)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ARSENIC</td>
<td>140</td>
<td>1.3</td>
<td>33.281</td>
<td>16.85</td>
<td>23.6816</td>
</tr>
<tr>
<td>CADMIUM</td>
<td>2.8</td>
<td>2.5</td>
<td>0.049</td>
<td>2.507895</td>
<td>2.5912</td>
</tr>
<tr>
<td>CHROMIUM</td>
<td>451</td>
<td>2.3</td>
<td>98.404</td>
<td>46.3</td>
<td>69.1451</td>
</tr>
<tr>
<td>COPPER</td>
<td>667</td>
<td>4.9</td>
<td>123.116</td>
<td>68.942105</td>
<td>93.6122</td>
</tr>
<tr>
<td>LEAD</td>
<td>212</td>
<td>1</td>
<td>40.707</td>
<td>25.557895</td>
<td>53.083</td>
</tr>
<tr>
<td>MERCURY</td>
<td>0.92</td>
<td>0.1</td>
<td>0.144</td>
<td>0.135789</td>
<td>0.1449</td>
</tr>
<tr>
<td>SILVER</td>
<td>5</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>5.1671</td>
</tr>
<tr>
<td><strong>VOLATILE ORGANICS (UG/L)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-TRICHLOROETHANE</td>
<td>2400</td>
<td>1</td>
<td>407.749</td>
<td>87.93617</td>
<td>23.3776</td>
</tr>
<tr>
<td>1,1-DICHLOROETHANE</td>
<td>920</td>
<td>1</td>
<td>133.45</td>
<td>24.851064</td>
<td>10.3385</td>
</tr>
<tr>
<td>1,2-DICHLOROETHENE (TOTAL)</td>
<td>12000</td>
<td>1</td>
<td>2446.287</td>
<td>535.6383</td>
<td>118.7152</td>
</tr>
<tr>
<td>ACETONE</td>
<td>78</td>
<td>5</td>
<td>10.65</td>
<td>7.042553</td>
<td>7.0371</td>
</tr>
<tr>
<td>CARBON DISULFIDE</td>
<td>5</td>
<td>1</td>
<td>0.77</td>
<td>4.808511</td>
<td>5.2292</td>
</tr>
<tr>
<td>METHYLENE CHLORIDE</td>
<td>4000</td>
<td>1</td>
<td>600.759</td>
<td>115</td>
<td>34.6773</td>
</tr>
<tr>
<td>TETRACHLOROETHENE</td>
<td>78</td>
<td>1</td>
<td>11.09</td>
<td>7.382979</td>
<td>7.7464</td>
</tr>
<tr>
<td>TRICHLOROETHENE</td>
<td>98000</td>
<td>1</td>
<td>17456.75</td>
<td>3659.2979</td>
<td>1069.7027</td>
</tr>
</tbody>
</table>

**NOTE:**
Total Count = Number of Samples
Detected Count = Number of Contaminated Samples
The six most prevalent VOCs (detected in six or more samples), in order of frequency of detection were: TCE, methylene chloride, 1,2-DCE, acetone, PCE, and 1,1,1-TCA. The locations and concentrations of these six VOCs in the alluvial and bedrock aquifers beneath the study site are shown in Figures 28 and 29, respectively. Each of the remaining eight detected VOCs were found in three or fewer samples.

Surface-Water and Sediment Contamination

Surface-water samples were collected from four locations along the North Branch Potomac River, adjacent to the study site (Figure 15). The samples (except SW-2) were analyzed for VOCs and metals.

The surface-water sample collected upstream of the study site (SW-1) contained no detectable VOCs. The surface-water sample collected downgradient from the well cluster 1GW3, 1GW9, 1GW13 (SW-2) contained 9 μg/l of TCE and 4 μg/l of 1,2-DCE (Figure 30). The surface-water sample collected downstream of the study site but upstream of SW-3
Figure 28: Selected VOC Concentrations in the Alluvial Aquifer
Figure 29: Selected VOC Concentrations in the Bedrock Aquifer
Figure 30: Selected VOC Concentrations in the Surface Water
contained TCE (6 µg/l), 1,2-DCE (10 µg/l), and methylene chloride (1 µg/l). The surface-water sample collected near the downstream end of the study site contained TCE at a concentration of 2 µg/l, 1,2-DCE at a concentration of 4 µg/l, and methylene chloride at a concentration of 2 µg/l.

The only sediment sample collected, was taken near the location of SW-2 (SD-1) contained TCE, vinyl chloride, and 1,2-DCE at concentrations of 460 µg/l, 1,700 µg/l, and 12,000 µg/l, respectively. Further investigation of sediments in the river are needed to better define the extent of sediment contamination in the river.

Contaminant Fate and Transport

The nature and extent of contamination, hydrogeology, and geology at the study site, is necessary for developing an overall conceptual site model. The fate and transport of VOCs through the media at the site in which they were detected is qualitatively discussed. Media of concern include soil, groundwater, surface water, and sediment.

Fate and Transport of VOCs

VOCs were detected at the study site in all media of concern. Of the VOCs, TCE was the most prevalent and occurred at the highest concentrations in all media. The transport of VOCs within and between each media for VOC contamination, with special attention to TCE, is discussed below.
Soil Contaminant Transport of VOCs

Soil sampling has identified contamination, mainly by TCE on the site at shallow depths (two to four feet) and at greater depths (10 to 13 feet). The highest concentrations were detected at the study site along the river and in the former solvent disposal pits.

TCE and other VOC contaminants occur primarily as adsorbents on soil particles. Despite the VOCs in the soil having been subject to volatilization, degradation, and other processes that reduce their concentrations, they still occur at significant levels at the study site. The soil contamination potentially serves as a source of contamination for groundwater by infiltration.

While they are being transported, VOCs are subject to several processes that may reduce their concentrations. Volatilization and degradation also may occur concurrently to reduce the VOC concentrations. This distribution will be distorted by the variability of the transport properties in the soil.

Data from the analysis of samples from the solvent disposal pits show differing trends in VOC migration. At pit Three the highest concentration of TCE in soil was detected in the shallow soil and the lowest concentration was detected in the deepest soil (Figure 5). This suggests that some mass of the contaminate is still in the shallow material and the leading edge of the contaminant mass has just reached the water table. At pit one the highest concentration of TCE was detected at the water table and the lowest was detected in the shallow soil, indicating that the some mass of the contaminant at this location is now entering the water table. It is always possible, of
Table 13
VOCs Detected in Surface Water and Sediment Samples

<table>
<thead>
<tr>
<th>VOLATILE ORGANICS</th>
<th>SW-1 (UG/L)</th>
<th>SW-2 (UG/L)</th>
<th>SW-3 (UG/L)</th>
<th>SW-4 (UG/L)</th>
<th>SD-1 (UG/KG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1,1-TRICHLOROETHANE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>1,1,2,2-TETRACHLOROETHANE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>1,1,2-TRICHLOROETHANE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>1,1-DICHLOROETHANE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>1,2-DICHLOROETHANE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>1,2-DICHLOROETHENE (TOTAL)</td>
<td>5 U</td>
<td>4 J</td>
<td>10 J</td>
<td>4 J</td>
<td>12000 U</td>
</tr>
<tr>
<td>1,2-DICHLOROPROPANE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>2-BUTANONE</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>2100 U</td>
</tr>
<tr>
<td>2-HEXANONE</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>2100 U</td>
</tr>
<tr>
<td>4-METHYL-2-PENTANONE</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>2100 U</td>
</tr>
<tr>
<td>ACETONE</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>2100 U</td>
</tr>
<tr>
<td>BENZENE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>BROMODICHLOROMETHANE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>BROMOFORM</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>BROMOMETHANE</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>2100 UJC</td>
</tr>
<tr>
<td>CARBON DISULFIDE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>CARBON TETRACHLORIDE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 UJC</td>
</tr>
<tr>
<td>CHLOROBENZENE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>CHLOROETHANE</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>2100 U</td>
</tr>
<tr>
<td>CHLOROFORM</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>CHLOROMETHANE</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>2100 U</td>
</tr>
<tr>
<td>CIS-1,3-DICHLOROPROPENE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>DIBROMOCHLOROMETHANE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 UJC</td>
</tr>
<tr>
<td>ETHYL BENZENE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>METHYLENE CHLORIDE</td>
<td>5 U</td>
<td>1 U</td>
<td>1 J</td>
<td>2 J</td>
<td>2100 UBJ</td>
</tr>
<tr>
<td>STYRENE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>TETRACHLOROETHENE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>TOLUENE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
<tr>
<td>TRANS-1,3-DICHLOROPROPENE</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 UJC</td>
</tr>
<tr>
<td>TRICHLOROETHENE</td>
<td>5 U</td>
<td>9 J</td>
<td>6 J</td>
<td>2 J</td>
<td>460 J</td>
</tr>
<tr>
<td>VINYL ACETATE</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>2100 U</td>
</tr>
<tr>
<td>VINYL CHLORIDE</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>10 U</td>
<td>1700 J</td>
</tr>
<tr>
<td>XYLENES (TOTAL)</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>5 U</td>
<td>1100 U</td>
</tr>
</tbody>
</table>
course, that the contamination in wells 1GW3, 1GW9, and 1GW13 was caused by another source. However, TCE contamination detected in soil samples collected from the pits suggests that the pits continue as a source of contamination to groundwater.

The TCE contamination detected in wells 1GW3, 1GW9, and 1GW13 probably originated from these pits, because little or no TCE was detected in soil samples taken at various depths south or hydrogeologically upgradient of the pits and no TCE was detected in wells 1GW10 and 1GW11, south and hydrogeologically upgradient of the pits.

Contaminant Transport of VOCs in the Groundwater System

Disposal of TCE and other DNAPL contaminants was reported in the solvent disposal pits during the late 1970s and early 1980s but volumes are unknown. Migration of DNAPL to the groundwater is a function of several factors, including, but not necessarily limited to:

• infiltration rate of water through the source materials
• distribution and continuity of lithological units in the subsurface, particularly those that retard groundwater flow, such as clay and silt layers
• ability of soils, particularly clays and silts, to adsorb DNAPL
• physical and chemical properties of the DNAPL
• dispersion of the DNAPLs as they are transported by water
• possible "short-circuiting" effect of improperly installed wells
Once VOCs have reached groundwater they may migrate in a variety of ways, depending upon whether the DNAPL is dissolved in water or is in an immiscible phase.

The dissolved phase DNAPLs will migrate generally in the direction of groundwater flow. The migration of the dissolved DNAPLs occurs from the solvent disposal pits, towards the North Branch Potomac River, which forms the northern perimeter of the study site. As shown in Figures 22 and 24, groundwater in both the alluvial aquifer and the bedrock aquifer generally flows toward the river from the high topographic area to the south of the facility. Because of heterogeneities in the geologic materials composing the alluvial aquifer, groundwater flow is presumably not exactly at right angles to the potentiometric contours shown in Figures 22, but the absence of anomalous water levels suggests that groundwater flow is generally in this direction. Dissolved DNAPLs also will migrate downward through the alluvial aquifer toward the bedrock aquifer, because the bedrock has a lower potentiometric surface elevation and the potential for downward flow, therefore, exists. While the contaminants are being transported by the groundwater they are undergoing sorption, advection, dispersion, dissolution, degradation, volatilization, and other processes that reduce their concentrations. Figure 31 is a schematic drawing illustrating the measured and likely physical, chemical, and biologic processes that are most likely affecting the transport and fate of the chlorinated solvents at the study site. The highest concentrations of dissolved TCE were detected in alluvial and bedrock monitoring wells located immediately, hydraulically downgradient of the former solvent disposal pits and along the river.
Figure 31: Schematic Drawing Showing the Conceptual Physical, Chemical, and Biologic Processes that May be Affecting the Transport and Fate of the Chlorinated Solvents at the Study Site
Immiscible phase DNAPLs will not move under the influence of groundwater flow but rather will migrate downward under gravity and provide a continuous source of contaminants to the groundwater. Upon reaching the bedrock surface, immiscible DNAPL masses will travel down any existing slope in the surface. If the mass reaches a depression in the bedrock it may pool there and become immobile. Immiscible DNAPLs that encounter fractures in the bedrock will continue to travel downward, if the fracture separation is of sufficient width. This is probably the case in the vicinity of the solvent disposal pits. In this area, DNAPLs presumably reached the bedrock and possible moved both along the top of the bedrock surface to contaminate well 1GW3 and also may have moved down into the bedrock to contaminate well 1GW9. As discussed earlier, indirect methods for assessing the presence of immiscible DNAPLs in the subsurface rely on comparing measured chemical concentrations to the effective solubility limits for groundwater. When present as an immiscible phase, DNAPL compounds are generally detected at <10% of their aqueous solubility limit (Feenstra and Cherry 1988, Hunt et al., 1988). Immiscible DNAPLs are not detected in the soils, but the dissolved concentrations detected in alluvial groundwater wells 1GW3 and 1GW9 (>70,000 ppb TCE) suggest that residual and possible "pools" of immiscible DNAPL are present, though the exact locations are not known. The concentration of TCE in groundwater at well 1GW3 is almost ten percent of the solubility limit of TCE. The presence of immiscible DNAPLs is also suggested by the high soil concentrations of TCE measured in the solvent disposal pits (i.e., up to 160 mg/kg). Given measured soil and alluvial groundwater concentrations, it is highly probable that immiscible
DNAPLs are still present in the vicinity of the disposal pit's alluvium. I believe that it is likely that immiscible DNAPL have reached the bottom of the alluvium and has penetrated the fractured/karst bedrock aquifer.

It is not currently possible to say with certainty where any such DNAPL mass is in the vicinity of wells 1GW3, 1GW9, and 1GW13. Because well 1GW13 (the deeper well at the cluster) has a greatly reduced concentration of TCE, >13,000 ppb TCE (1.3 mg/l), compared to well 1GW9 (the intermediate depth well at the cluster), >70,000 ppb TCE (71 mg/l), the mass probably has not migrated deeper at this location but instead may have moved laterally. The mass has probably moved along the bedding planes that are generally oriented northeast-southwest and dipping southwest, or along fractures that are oriented generally northwest-southeast and northeast-southwest.

Two conceptual models of the transport and fate of the chlorinated solvents have been developed (Figures 32 and 33). These models incorporate the important factors discussed throughout this thesis which control the transport and fate of the contaminants at this site.

Model I stresses the possibility that contamination of production well PWA and the solvent pit source area is unrelated. An important component of this model is the "fingering" of the immiscible phase DNAPL in the saturated zone. This fingering would tend to follow preferential physical pathways on its vertical migration. As can be seen from this model, fracture orientation, aperture, infilling, etc. is the utmost importance.
Figure 32: Schematic Drawing Showing Conceptual Model I of the Fate and Transport of Chlorinated Solvents in the Groundwater System at the Study Site
Figure 33: Schematic Drawing Showing Conceptual Model II of the Fate and Transport of Chlorinated Solvents in the Groundwater System at the Study Site
Model II was developed under the hypothesis that the disposal pits and production well PWA contamination are inter-related. This relationship can be theorized by the understanding of the local geologic structure, geologic contact alignment, flow system, contaminant location and its physical/chemical properties.

Production well PWA had drawn its water from the uncased portion of the bedrock aquifer which changed the flow system. This would tend to induce the contaminant migration, towards the well, in the upgradient direction of the fractured/karst bedrock. It was determined in the fracture trace analysis (FTA) that one of the two principal fracture orientations was measured at N39°W which is oblique to the general structural trend and generally aligns the solvent disposal pits and well PWA. Packer testing of five intervals in well PWA indicated some degree of hydraulic interconnection between the packered intervals which indicates vertical pathways for downward migration of a contaminant, adjacent to well PWA.

Contaminated groundwater at the study site is contributing contamination, TCE and its degradation products, to surface-water and sediments in the North Branch Potomac River. Although TCE concentrations decreased in surface water samples collected down river, 1,2-DCE (total) and vinyl chloride (VC) concentrations increased. Further investigation is required to determine the approximate extent of contamination in the river.

Analytical data for surface-water samples and the sediment sample indicate that significant degradation of VOCs is occurring. VC and 1,2-DCE were detected at concentrations of 1,700 and 12,000 μg/kg in the sediment sample, respectively, and
TCE was detected at a concentration of 460 μg/kg. VC and 1,2-DCE are typical by-products of the degradation of TCE. VC was not detected in the study site's soil or surface-water. This not only suggests that little degradation of TCE in soils is occurring at the study site, but also indicates that VC was not likely disposed at the study site and that the VC detected in the sediment sample has resulted from the breakdown of TCE in discharging to surface-water. These conditions suggest that the TCE source is close to the river at this location.

Surface-water samples collected downstream of the study site show a decrease in TCE and an increase in 1,2-DCE as sampling sites farther away from the site are assessed. The decreases in TCE and the increases in 1,2-DCE and VC suggest that degradation of TCE is occurring. This process, if it is occurring, is most likely due to reductive dehalogenation caused by microbial degradation in the riverbed sediments. Vogel (1985, 1987) has shown that substitution by halogens are much more likely to undergo reduction in the environment under reducing conditions than under oxidizing conditions (Figure 34). Thus, if a system is oxygenated, TCE would be extremely stable; if the system is reduced TCE is not stable and would be expected to undergo reduction to 1,2-DCE and VC. Groundwater at the site would be expected to contain fewer nutrients and be a more anaerobic environment. The groundwater system below the site is believed to be reducing. As stated earlier, TCE can be reduced to 1,2-DCE by abiotic reactions and then transformed by biotic reactions to VC and then transformed abiotically by hydrolysis to ethanol (Pavlestatthis et al., 1991).
Figure 34: Schematic Drawing Showing A Conceptual Model of Possible Biological Reductive Dechlorination of Trichloroethylene (TCE)
Greater biological activity would be expected in a riverbed than in groundwater, though no samples were collected for biologic analysis. This biological activity would be enhanced by the increase in oxygen and humic material of the river bed. A shallow, organic rich river such as the North Branch Potomac River is typically an aerobic environment where many nutrients are available for biological growth. Figure 34 shows a conceptual model of possible reductive dechlorination pathways of TCE.

The degradation of TCE in the river is probably biodegradation for the most part. Given these conditions, it is theorized that the organic sediments in the river are effectively attenuating and degrading discharging contaminants and significant dilution of contamination is taking place in the river.

Around the solvent pits the annual mass contaminant loading, from the alluvial aquifer, to the North Branch Potomac river can be calculated from the average seepage flux and the contaminant concentrations. Using the variables in Table 14, the total annual mass discharge of TCE/DCE/TCA would be 3 lbs/yr or 0.24 gal of immiscible product.

Around the solvent pits from the average seepage flux and the contaminant concentrations. Using the variables in Table 15, a concentration of 84,500 ug/l in 1GW9 and the other assumptions used for the bedrock aquifer the annual mass contaminant loading, from the bedrock aquifer was calculated. The total annual mass discharge of
Table 14: Total Mass Discharge of TCE/DCE/TCA From The Alluvial Aquifer Area Around Solvent Disposal Pits To The North Branch Potomac River

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Flux</td>
<td>0.0002 gal/min/ft²</td>
</tr>
<tr>
<td>Total TCE/DCE/TCA Concentrations at 1GW3</td>
<td>112,400 ug/l, ppb</td>
</tr>
<tr>
<td>Discharge Area</td>
<td>1,800 ft²</td>
</tr>
<tr>
<td>Porosity</td>
<td>20.0 %</td>
</tr>
<tr>
<td>Contaminant Density</td>
<td>1.46 g/cm³</td>
</tr>
<tr>
<td>Annual Contaminant Mass Discharge</td>
<td>3.0 lbs/yr</td>
</tr>
<tr>
<td>Annual Equivalent Contaminant Volume Discharge</td>
<td>0.24 gal</td>
</tr>
</tbody>
</table>

TCE/DCE/TCA would be 2.85 lbs/yr or 0.23 gal of immiscible product.

**Surface Water and Sediment**

Analytical results of surface-water samples indicate that VOCs detected in groundwater and soil at the study site are contaminating surface water in the North Branch Potomac River (Figure 14). TCE was detected at a concentration of 9 µg/l in the surface water sample collected downgradient from the cluster of wells including 1GW3, 1GW9, and 1GW13. Analysis of the two surface-water samples collected downstream from the study site indicate TCE concentrations decrease with samples collected further downstream.
Table 15:
Total Mass Discharge of TCE/DCE/TCA From The Bedrock Aquifer Area Around Solvent Disposal Pits To The North Branch Potomac River

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Flux</td>
<td>0.0002 gal/min/ft²</td>
</tr>
<tr>
<td>Total TCE/DCE/TCA Concentrations at 1GW3</td>
<td>84,500 ug/l, ppb</td>
</tr>
<tr>
<td>Discharge Area</td>
<td>1,800 ft²</td>
</tr>
<tr>
<td>Porosity</td>
<td>20.0 %</td>
</tr>
<tr>
<td>Contaminant Density</td>
<td>1.46 g/cm³</td>
</tr>
<tr>
<td>Annual Contaminant Mass Discharge</td>
<td>3.0 lbs/yr</td>
</tr>
<tr>
<td>Annual Equivalent Contaminant Volume Discharge</td>
<td>0.23 gal</td>
</tr>
</tbody>
</table>

VOC contamination detected in the North Branch Potomac River is probably a result of the influx of VOC-contaminated groundwater. VOC contamination was detected at the highest concentrations in groundwater in wells 1GW3, 1GW9, and 1GW13. The surface-water sample containing the highest concentration of VOCs was a slick emanating from the river bank immediately downgradient of these wells and no VOC contamination was detected in the surface-water sample collected upstream of the study site. As discussed earlier, the river and the bedrock aquifer show a strong hydraulic connection. The data presented do not indicate a strong hydraulic connection between the alluvial aquifer and the river. However, as discussed, this may result from the construction of the alluvial well tested and is probable that a strong hydraulic
connection exists. In addition, volatilization of VOCs would be minimal or eliminated with a direct flow of groundwater into the river, where significant volatilization of VOCs transported by runoff would be expected. For these reasons, VOC-contaminated groundwater at the study site is the likely source of VOCs detected in the river. Similarly, contaminated groundwater is also the probable source of VOC contamination detected in the sediment sample collected from the river bottom downgradient of wells 1GW3, 1GW9, and 1GW13.
CHAPTER VI: POTENTIAL REMEDIAL APPROACHES

In an editorial Allan Freeze and John Cherry state "There is now little doubt that at sites where DNAPLs are the problem, the local ground-water zone has terminal cancer. A cure, in the form of returning aquifer quality to drinking-water standards, is unachievable at almost any cost. At DNAPL sites, costs are going up and aquifers are not much improved" (Ground Water, 1989). With that in mind this chapter will concentrate on immiscible phase DNAPL removal. Present techniques of containing and removal of the dissolved phase contaminants usually prevent contaminant migration, but do little at reducing the volume of immiscible phase source. Following immiscible phase removal, a combination of purge wells, slurry walls and collector trenches could be used to remove the dissolved phase DNAPL from the groundwater, which could then be treated by hydrogen peroxide, ozone oxidation or air stripping.

Conventional Approaches

If the immiscible phase DNAPL source is not removed or contained, any scheme to remediate the site through the control of the dissolved phase DNAPL would only contain the movement of the dissolved phase DNAPL and not remove, on any appreciable timetable, the problem. In porous materials where pools or zones of immiscible phase DNAPL have been located in the subsurface, it is found that only a small portion of the DNAPL can be removed with recovery wells or collector trenches (Ferry et al., 1986, and McIelwain et al., 1989).
Conventional methods for removal of contaminated groundwater, pump and treat, at this site, may not be effective for the removal of immiscible phase DNAPL source because the movement of immiscible phase DNAPL is not controlled by the groundwater flow pattern. The immiscible phase DNAPL in the vadose zone is immobile except under extremely high hydraulic gradients (i.e. one to ten or more) which can seldom be achieved in near-surface groundwater environments (Poulsen, 1991 and Kueper, 1991).

**Present Technology**

At the present time, excavation and removal of the contaminated soil is the only method that has been demonstrated to be an effective means of fully remediating immiscible phase DNAPLs in an unconsolidated media. Excavation is a well recognized remedial measure because of its simplicity and its ability to remove the source completely (Poulsen, 1991). Therefore, it would be prudent to excavate all unconsolidated materials beneath and around the solvent disposal pits.

Because of the geological setting at this site, the only practical options for remediation of the bedrock are in situ removal techniques. They include:

**Chemically-Enhanced Displacement**

Chemically-enhanced displacement methods are used in the petroleum industry for secondary and enhanced recovery of oil from oil fields. Chemically-enhanced displacement involves the injection of surfactants or other chemical agents into the
formation to reduce the interfacial tensions between the non-aqueous phase and the groundwater. This allows the non-aqueous phase to be more readily displaced by the flowing groundwater (Hunt et al., 1988). The addition of surfactants can reduce interfacial tensions by a factor of 1,000 times or more and increase the potential mobility of the non-aqueous phase by the same order of magnitude (Latil, 1980).

This method would have to be greatly modified to be of any use in subsurface remediation. Many surfactant chemicals considered for such a scheme could pose a serious inherent environmental threat when injected into shallow (<100m) groundwater environments. In addition, subsurface pressures used by the petroleum industry are many orders of magnitude higher than could be used in near surface groundwater environments.

**Chemically-Enhanced Dissolution**

The injection of surfactants or other chemical agents may also act to increase the solubility of the DNAPLs in the groundwater. If the solubility of the DNAPL can be increased sufficiently, it may be possible to remove the DNAPLs from the subsurface by focusing groundwater flow through the DNAPL zones.

Chemically-enhanced dissolution, although potentially feasible, has not been demonstrated on a field scale. The considerations discussed for chemically-enhanced displacement are also applicable to enhanced dissolution. In both these systems the recovered groundwater would have very high concentrations of dissolved or emulsified
chemicals. This highly contaminated water must then be contained within a recovery system.

In Situ Biodegradation

In situ biodegradation methods have been successfully applied to treatment of LNAPLs but have not been used in remediation of DNAPLs. This method involves the injection of oxygen and other nutrients into the groundwater to stimulate growth and activity of naturally occurring aerobic bacteria which can degrade the organic compounds. However, most DNAPL chemicals are halogenated compounds which degrade better under anaerobic conditions or are entirely resistant to degradation. Degradation of many DNAPL chemicals, when it does occur, does not generally produce innocuous compounds, rather transformations to other equally undesirable chemical compounds usually occur (Chiou et al., 1986).

Studies with enrichment cultures of TCE-degrading microorganisms provided evidence that, under methanogenic conditions, mixed cultures are able to completely dechlorinate TCE to ethylene, a product which is environmentally acceptable. The rate limiting step appears to be in the pathway of the conversion of vinyl chloride to ethylene. To sustain reductive dechlorination of TCE, it would be necessary to supply an electron donor, such as methanol or hydrogen. This might be the best method for bedrock remediation.
Fractured Rock Technology

Generally, most fractured rock aquifers in this region are highly permeable primarily because of the interconnected fractures and solution cavities rather than the rock matrix, which is relatively impervious. The effective fracture porosity of a fractured-rock aquifer is generally in the range of 0.001-0.1%, which is much smaller than the porosities of a typical granular aquifer (20-40%). For example, a rock mass with one fracture per linear meter with a fracture aperture of 500 µm would be very permeable but at saturation would have a small storage volume of mobile groundwater (only about one-half liter per cubic meter of rock); (Kueper, 1991).

When DNAPL enter these fracture dominated aquifers, flow is mainly through the interconnected fractures and the immiscible phase DNAPL settles out in dead-end segments of the fracture system. Relatively small volumes of immiscible phase DNAPL can move deep and long distances into the rock because the retention capacity offered by the dead-end fractures and the immobile filaments and globules in the larger fractures are so small, much less than the percentage given above for water in saturated fractured rock. Cohen and others (1985) have shown that dissolved phase DNAPL contamination, at the Hyde Park Landfill in Niagara Falls, New York, can vary 1,000s of feet in the vertical and horizontal direction from the landfill site. Although the rock matrix typically has a relatively small intergranular porosity, it is commonly large enough to allow dissolved contaminants from the fractures to enter the matrix by diffusion and be stored there by adsorption, as shown in Figure 35.
The prognoses for cleanup of DNAPL in fractured rock aquifers is worse than unconsolidated aquifers. Even if the location of the spill is known exactly, the location of the immiscible phase DNAPL is typically difficult or impossible to determine from site investigations. This is because DNAPL pathways through the fracture system are exceptionally complex and result in the distribution of the immiscible phase DNAPL into many small and scattered amounts. When attempts are made to clean such fractured rock aquifers by pumping, major improvements in water quality are exceedingly slow because little or no water flushes through dead-end fracture segments or through the porous but impervious rock matrix, both of which are likely to retain the bulk of the contaminated mass. Such has been the experience at an organic liquids disposal site in Ville Mercier, Quebec, where the effectiveness of pump-and-treat remediation of the large plume has been severely hampered by the penetration of the DNAPL into the fractured bedrock (Martel, 1988).
DNAPL RELEASE

FRACTURED POROUS ROCK

Ground Surface

Vapor
Plume

VADOSE ZONE

TOP OF CAPILLARY FRINGE

DISSOLVED
PHASE

GROUNDWATER
FLOW

DNAPL

Diffusion
into
Matrix

DIFFUSION INTO ROCK MATRIX

Figure 35: Diffusion into Rock Matrix
CHAPTER VII: CONCLUSIONS AND RECOMMENDATIONS

Conclusions

I have shown that the hydrogeology of the study site and facility is extremely complex. A conceptual model of the physical system was developed from all sources of data collected.

There are three primary hydrologic units; 1) silty clay floodplain deposits, 2) alluvium, and 3) fractured/karst bedrock. The alluvium consists of clayey gravel, pebbles, and sand, and averages 15 to 20 feet in thickness while the fractured bedrock consists of shales and limestones. The alluvium and fractured bedrock constitute the principal hydrostratigraphic units underlying the study site. Geologic mapping of the surrounding area indicates that the bedrock units underlying the site have a high degree of dip (>75°), strike NE-SW, and possible karstic features.

Groundwater flow in both the alluvium and fractured bedrock is towards the river and has a slight downward vertical gradient. Fracture trace analysis indicates that groundwater flow in the bedrock aquifer may be much more complicated than presented and is probably confined to formation contacts, fractures, bedding planes and solution channels. Continuous water level monitoring of the river and wells indicated a strong hydraulic connection between the bedrock aquifer and the river. Hydraulic connection between the alluvial aquifer and the river was observed and quantified with seepage meters. Although a hydraulic connection between the bedrock aquifer and the river
was observed, it is not clear whether the river acts as a hydraulic barrier for migration of contaminated groundwater.

VOCs were the most widespread contaminants detected at the study site. TCE was detected most often and at the highest concentrations in soil and groundwater of both the alluvial and bedrock aquifers. Figures 31 - 34, represent the physical framework of the site conceptual model. The bedrock, located at approximately 650 feet above mean sea level (msl), is primarily composed of shale/siltstone with 25 percent limestone. The high angle of dip and gentle slope of the bedrock were delineated by the combination of drilling and geologic mapping. Although there was no rock core, it was determined during geologic mapping and fracture trace analysis (FTA) that geologic unit contacts of many limestones and shales/siltstones have been extenuated by groundwater solubilization. This would create large vertical conduits which would tend to extenuate penetration of DNAPL. The fracture orientation was superimposed, from the FTA and geologic mapping, onto these figures. It should be noted that the figure's vertical scale is exaggerated.

Recommendations

Despite the comprehensive nature of the study conducted at this site, several unresolved critical issues and/or data needs were identified.

1. A major unresolved issue is the potential for contaminant loading to the North Branch Potomac River via groundwater discharge. This is a critical issue as it has been determined during the study that some part of the contaminated groundwater from the
site discharges into the river. The future work should determine the relative ability for
organic riverbed deposits to cause a decrease in levels of contaminants discharging into
the river by identifying those factors which cause a decrease in contaminant levels
detected in groundwater and in surface water in the river. Using techniques described
in the discharge assessment section, a more detailed analysis of the quantity and quality
of groundwater discharging through the inorganic and organic sediments into the river
should be performed. An effort should also be made to locate seepage meters in the
center as well as on both edges of the plume. Once the seepage meters are installed,
they should be allowed to stabilize for at least two days prior to sampling to insure that
potentially contaminated sediments which would be disturbed during installation
processes were allowed to settle and that the collected sample represented discharge
water which did not contain suspended sediment. Additionally, the seepage meters
should be allowed to vent discharge water into the river to insure that the water
collected was groundwater discharge and not a combination of surface and
groundwater. The analytical data for samples derived from the seepage meters would
represent the quality of groundwater discharge from the inorganic sediments underlying
the river bottom through the organic sediments. The analytical data derived from the
installation of additional mini-piezometers, installed to depths of five to seven feet,
would indicate the quality of groundwater discharge in only the inorganic sediments.

Given site conditions, it could be hypothesized that the organic sediments in the
river are effectively attenuating and degrading discharging contaminants and significant
dilution of contamination is taking place. Vogel (1988) has shown that reduction of
chlorinated volatiles (as well as base neutrals and acid extractibles) can be attributed to volatilization as they enter through surface water, dilution and biological degradation of the compounds by aerobic bacteria as they discharge through the organic sediments. A more comprehensive discharge assessment should confirm the role which organic sediments provide in the transport of TCE and other DNAPLs.

2. Determine if contaminants are being transported under the North Branch Potomac River. A portion of the hydrologic flow field should be delineated on the opposite side of the river. In limited terms, this could be accomplished with measuring and sampling a combination of alluvial monitoring wells and in-place bedrock residential wells. One set of nested monitoring wells with screens at varying depths would be needed to determine the vertical gradient at a location directly across from the southern end of the disposal pits. Measurements of the potentiometric surface from a variety of wells would give the horizontal gradients. These measurements combined with results of water quality samples and the discharge assessment would help determine if groundwater is passing beneath the river at the area studied.

3. Wells that were installed during the previous study with screens that straddle the alluvium-bedrock interface may be allowing contamination from the alluvial aquifer to migrate downward into the bedrock at the locations of these wells. This cross-contamination may give an improper representation of the true distribution of contaminants in the bedrock. It seems clear that these monitoring wells should be properly abandoned following strict protocols and new monitoring wells properly installed if the well locations are necessary for monitoring.
4. A better delineation of the fracture distribution is needed. Without samples of continuous wire-line rock core during drilling, the bedrock cannot be accurately delineated for: (a) geologic formation, (b) formation attitude, and (c) fracture locations, orientations, aperture and roughness. Geologic coring is needed to further delineate the hydrogeologic environment of the bedrock. Fracture trace features and their influence on groundwater flow, identified during this simple fracture trace analysis, could also be investigated further through additional: 1.) fracture trace analysis, 2.) monitoring well placement, 3.) aquifer testing, and 4.) geophysical surveying. This evaluation would determine if additional fracture trace work will facilitate characterization of the bedrock.
REFERENCES


APPENDIX A: Identification of Potential Sources
Preliminary study activities included reviewing aerial photographs and conducting a focused facility audit. These activities were performed to gain critical information for focusing the study and to help determine soil-sampling locations. Aerial photographs also were used to perform a fracture trace analysis. Each of these preliminary activities is discussed below.

**Review of Aerial Photographs**

The aerial photographs were reviewed primarily to determine the identity and location of waste disposal units at the study site. Nine aerial photographs of the study site were reviewed. The year and source of each is listed below:

- 1947, United States Geologic Survey
- 1950, Agriculture Stabilization Conservation Services (ASCS)
- 1952, ASCS
- 1955, ASCS
- 1962, ASCS
- 1967, ASCS
- 1972, ASCS
- 1974, ASCS
- 1983, ASCS

The approximate scale of all aerial photographs is 1":200', with the exception of the aerial photograph taken in 1947. This aerial photograph has an approximate scale of 1":800'. Information gained from reviewing the aerial photographs is outlined below in the chronological order of the photographs.

**1947, USGS**

This photograph was taken on April 6. Although no buildings are shown in the photograph, the disturbed area appears to be close to the southeast corner of where
Building 361 stands today. The area is an estimated 20 to 50 feet in diameter. The study site appears to be well vegetated and no activity is indicated. However, roads providing access to these sites exist. Well PWA is shown but well PWC does not appear in the photograph.

1950, ASCS

This photograph was taken on August 14. In general, little change from the 1947 photograph can be seen. The only difference noted is that the western end, roughly one-third, of the study site appears to be covered with small garden plots.

1952, ASCS

This photograph was taken on September 6. A dirt road leading to two unvegetated, disturbed areas can be seen. Each area appears to be approximately 50 to 100 feet across. A dark patch is shown in the center of each area. Each area appears to be similar to the burn pads currently existing at the study site. Although the only buildings existing in the vicinity are Buildings 108 and 109, each of the disturbed areas appear to be located on either side of the southern end of where Building 362 exists today.

The study site shows little change from the 1950 photograph. The disturbed area seen in earlier photographs is still visible and the western third of the study site is covered with small garden plots. However, two small disturbed, unvegetated areas can be seen in the center of the study site. They appear to be approximately 10 feet in diameter. Well PWC can be seen in this photograph.

1955, ASCS
This photograph was taken on October 22. In addition to the two disturbed areas in the 1952 photograph, four parallel linear features 50- to 75-feet long can be seen in the center of the site. The linear features appear to be at the same location where Building 362 stands today. The photograph shows that Building 151 had been constructed since 1952.

The study site shows very little change. The disturbed area noted earlier had overgrown and can barely be seen. A number of small structures, possibly trailers, can be seen to the west. The garden plots appear to be covering more than half of the study site and the two small disturbed, unvegetated areas in the 1952 photograph have overgrown and cannot be seen.

1962, ASCS

This photograph was taken on September 12. Dramatic changes can be seen at the study site. The ordnance burning ground appears to be in full operation with all eight burn pads shown within the fenced area. No garden plots can be seen and unvegetated, disturbed soil appears along the river east and west of the ordnance burning ground. These areas likely represent the open burn area landfill to the west and the inert burn area to the east. The fence surrounding the open burn area immediately north of the drum pad can be seen.

Buildings 257 and 178 had been constructed since 1955. The two disturbed areas and four linear features in the 1955 photograph cannot be seen and the entire area is covered with patchy vegetation.

1967, ASCS
This photograph was taken on October 3. The study site appears to be in full operation. A large disturbed area along the river, covering the distance between the ordnance burning ground and open burn area to the west can be seen. This area likely represents the open burn area landfill. Much of the wooded area along the river had been cleared. What appears to be debris had been scattered on the ground immediately west of the ordnance burning ground.

1972, ASCS

This photograph was taken on May 26. The study area appears to be in full operation. Little has changed since 1967. The inert burn area east of the ordnance burning ground appears more disturbed and less vegetated than in 1967. In addition, a small triangular fenced-in area can be seen at this location.

1974, ASCS

This photograph was taken on October 17. The study site appears to be more vegetated overall. The burn pads in the ordnance burning ground appear smaller. The large disturbed area along the river (the open burn area landfill) had re-vegetated. The inert burn area east of the ordnance burning ground also had re-vegetated. The scattered debris noted in previous photographs to the west of the ordnance burning ground had been removed.

1983, ASCS

This photograph was taken on October 3. Some significant changes can be seen at the study site. The inert burn area had been moved within the fence surrounding the ordnance burning ground. The inert burn area had been located just inside the west
gate, where it remains today. Two of the three reported solvent disposal pits can be seen at the southern side of the ordnance burning ground. The old inert burn area and open burn area located near the drum pad had re-vegetated and appear to be inactive.

**Focused Facility Audit**

The focused facility audit was conducted on June 24 and 25, 1992. The objectives of the focused facility audit were to (1) determine potential sources of VOC contamination detected in well PWA and (2) investigate the study site in an effort to determine the type and location of waste disposal units at each site. The approach used to meet these objectives included the following activities:

- Interviewing plant personnel with knowledge of plant operations specific to the handling of solvents containing VOCs and investigating current and historical plant operations and solvent disposal practices
- Interviewing plant personnel with knowledge of waste disposal practices at the site
- Identifying and inspecting areas where solvents and organic waste are stored, disposed of, or used in plant processes, and where they might be contributing to possible contamination detected at the sites
- Conducting site walkovers, inspecting evidence of past and current disposal practices at the sites

No pertinent records indicating quantities or types of wastes generated or disposed of were found. Consequently, all information was obtained primarily through interviews and site inspection. Information gathered during the focused facility audit is
discussed in the following paragraphs. The overall plant processes and the wastes generated are described briefly and wastes handled or disposed of at each of the sites are discussed.

Individual Sites

No pertinent records were found documenting waste types and volumes disposed of at the site. However, through interviews with past and present Hercules employees and conducting site walkovers, much information was gained.

Reportedly, the study site included a number of disposal units handling a variety of waste types. Figure 4 identifies the many different disposal units comprising the study site.

The study site contained three solvent- and acid-disposal pits. The pits ranged from three to five feet deep, five to 10 feet wide, and 15 to 40 feet long. Which pits were used for waste acid or spent solvents is unknown. The pits have been backfilled but were reportedly operated during the late 1970s until the early 1980s. This also is indicated by the 1974 and 1983 aerial photographs. Spent solvents and acids contaminated with reactive wastes were placed into the unlined pits and allowed to percolate into the ground. The pit then was ignited to burn off any reactive filtrate. Reportedly, TCE was used heavily during the late 1970s and spent TCE was primarily placed in the pits.

Two burn areas existed at the study site: the inert burn area and the open burn area (referred to as the incinerator in the Interim the study report). The inert burn area was located along the river east of the ordnance burning ground. Inert wastes, which may
or may not have been contaminated with reactive materials, were burned here. Reportedly, all ash and residue then was spread along the river downstream from the inert burn area. The open burn area was located west of the ordnance burning ground along the river. The open burn area was enclosed in a chain-link fence and solid wastes were burned and spread along the riverside. In addition, much demolition debris, concrete rubble, and rocket casings were disposed of along with the ash generated from the open burn area. The inert burn area and the open burn area reportedly operated during the 1960s. Since that time the inert waste material has been burned within the southwest corner of the ordnance burning ground and solid wastes disposed of at the inert landfill. Today, all solid wastes are disposed of off site. Although both the open burn area and the inert burn area are revegetated, ash and debris were observed during the site walkover.

The drum storage pad is situated next to the open burn area. Reportedly the drum storage pad operated from 1970 to 1981, storing 55-gallon drums containing spent solvent and bottom sludge from solvent-recovery stills. The asphalt pad has no berms or sumps for containment and circular impressions are visible where drums were once stored.

No disposal units were near Well PWA. However, buildings where solvents currently are handled and those where solvents were reportedly handled in the past were identified and inspected. These buildings include:

- Building 2, Machine Shop
- Building 3, Sheet Metal Shop
- Building 7, Auto Vehicle Maintenance Shop
- Building 9, Chemistry Laboratory Building
• Building 9A, General Warehouse
• Building 16, Physical Analysis Laboratory
• Building 100, Ingredient Preparation Building
• Building 145, Maintenance Facility
• Building 151, Disassembly Mold Wash Building
• Building 157, General Warehouse
• Building 255, Sensitivity Test Building
• Building 256, Shipping and Receiving
APPENDIX B: Slug Tests
This appendix describes the procedures and analytical methods used to perform slug tests at the site. Slug tests were conducted between July 28 and August 13, 1992, in eight monitoring wells screened in the alluvial aquifer. The purpose of the tests was to estimated the hydraulic conductivity of the aquifer material in which the wells are screened. At least two tests were performed at each well in order to check the reproducibility of the results. Plots of the test data are presented at the conclusion of this appendix.

Test Methods

The slug tests conducted at the facility were "rising-head" tests; i.e., the water level in the tested well was artificially lowered, followed by the collection of data during the subsequent recovery of the water level. Data from all slug tests were collected in digital form using a Campbell Scientific, Inc. Model 21X datalogger linked to Druck pressure transducers. All of the tested wells are two inches in diameter.

The artificial lowering of the water level in each well was accomplished with a specially developed air-displacement apparatus. The air-displacement apparatus consisted of a packer assembly, fittings to accommodate transducers and air pressurization, and a pressure-release valve. The packer was lowered into the upper portion of the monitoring well, secured in place and inflated, providing a seal between the apparatus and the inside of the well. Two fittings were provided for inserting transducers; one transducer was fed through the inside of the device and positioned below the water surface (generally three-four feet), and the other was inserted to measure the artificially induced air pressurization. A third fitting allowed air to be
introduced to pressure the well. High-pressure air was supplied from a compressed air
tank, then fed through regulators and into the apparatus. The pressure could be
released quickly through a ball valve to start each test.

Each test was conducted as follows. After the test apparatus was installed in the
well, the packer was inflated. The datalogger was programmed to display the
artificially induced air pressure (in units head), the pressure head measured by the
submerged transducer, and the difference between the two, which equates to the height
of the water column above the transducer. After recording the equilibrium height of
water above the submerged transducer in a field notebook, air pressure equal to
between three and seven feet of head was applied to the apparatus and held at a
constant level. The amount of air pressure head applied was always less than the static
height of water above the top of the screened zone.

Responding to the increased air pressure inside the well, the water level declined by
an amount approximately equal to the number of feet of air pressure head applied.
Tests were begun only after allowing time for equilibration of the water level at the
artificially depressed level. The length of time required for equilibration was highly
variable between the wells. This would be expected in the heterogeneous nature of the
alluvial material of the study site.

Each test was started by releasing the air pressure inside the well by opening the
ball valve and shutting off the pressurized air supply. The release of air pressure
allowed to artificially depressed water level to begin recovery. When the datalogger
perceived a change in water level above the submerged transducer greater than a preset
trigger amount (generally 0.1 feet), it automatically began to record the elapsed time and water level. Readings were taken at intervals of 0.5, 5, 60, or 300 seconds, and were controlled by the test operator according to the rate of recovery of the water level in each well. Each test was terminated after the water level recovered to at least 90 percent of the original equilibrium level before pressurization.

Data Analysis

Each set of test data was analyzed using methods developed by Bouwer and Rice (1976). The analysis were performed with the software package AQTESOLV (Version 1.1), marketed by Geraghty & Miller, Inc.

The AQTESOLV software generates a plot of the logarithm of drawdown versus time for each data set. The slope of the best-fitting line through the data points is then used in the following equation to calculate the hydraulic conductivity (K):

\[
K = \frac{r_c^2 \ln \left( \frac{R_e / r_w}{L_e} \right)}{2L_e} \cdot \frac{1}{t} \ln \frac{y_o}{y_t}
\]

where: \( r_c \) is the radius of the well casing [L], \( \ln(R_e/r_w) \) is an empirical "shape factor" determined from tables provided in Bouwer and Rice (1976), \( L_e \) is length of well screen [L], \( y_o \) is the initial drawdown in a well due to instantaneous removal of water from a well [L], \( y_t \) is drawdown in a well at time \( t \) [L], and \( t \) is equal to elapsed time.

The initial calculation of hydraulic conductivity was based on the linear regression, best-fit line for the entire data set. However, in some instances a straight line was
matched to the portion of the data curve interpreted by the most representative of the water-level recovery in the surrounding aquifer.
This appendix describes the downhole well logging and strattle-packer testing performed at production well PWA. PWA is an 8-inch diameter, approximately 200-food deep well that is finished as an open borehole in bedrock. An 8-inch ID steel casing seated in bedrock extends to a depth of approximately 28 feet below ground surface. No drilling log for PWA was available prior to the well logging activities conducted during the study.

Three types of downhole procedures were performed in PWA. Borehole geophysical logging was performed on August 4, 1992. Downhole television logging took place on August 11, 1992. Strattle-packer testing commenced on August 11 and concluded on August 13, 1992.

**Borehole Geophysical Logging**

Six types of borehole geophysical logging were performed in PWA, including caliper, temperature, fluid resistivity, self-potential, natural gamma, and single point resistance. A copy of the logs are provided in a pocket at the end of this appendix.

**Downhole Television Logging**

A downhole television survey was conducted in PWA by lowering a small diameter television camera down the length of the well, with a spotlight providing illumination. One run was performed, which included the videotaping of both the decent and the ascent of the camera assembly. The depth below the top of the surface casing in PWA,
which sticks up 1 foot, 1 inch above ground surface (floor of the pumphouse), appears on the video image to provide depth correction.

In the open borehole beneath the surface casing, bedding plains were vertical to near vertical where visible. A number of fracture zones were visible throughout the borehole. The majority of the visible fractures appeared to intersect the borehole at angles between 70 and 90 degrees from horizontal. The fracture zones that appeared to have the greatest water-baring potential were visible at the following depths:

- 59-61 feet - Fractures at approximately 80 degrees
- 85-89 feet - Fractures at 75 degrees to near vertical
- 111-113 feet - Large fracture at approximately 75 degrees
- 124-126 feet - Large fracture at approximately 80 degrees
- 132-134 feet - Fractures at approximately 80 degrees

The television survey did not reveal any significant solution cavities or voids. However, the borehole walls widened in several places where small blocks of bedrock had apparently broken away during the drilling of the well. The video survey revealed conclusively that the steel casing in PWA extends to a depth of approximately 28 feet below the ground surface.

The video survey also revealed that a cylindrical object is located at the bottom of the borehole, beginning at a depth of approximately 183 feet. The object blocked the downward movement of the television camera below a depth of approximately 184 feet. The identity and origin of the object is unknown, but it appears to be a length of pipe that is approximately 3 inches in diameter (possibly a drilling rod). Because of the
obstruction, the exact depth of PWA could not be determined with the camera. Estimates provided indicate the well is approximately 200 feet deep.

**Straddle-Packer Testing**

Five intervals of the PWA well bore were selected for straddle-packer testing. The interval selection was based primarily on the results of the down hole video and caliper logs. These logs provided the most information concerning the location of significant fractures intersecting the borehole. The primary criterion used in selection of the test intervals was the desire to isolate significant fracture zones in the borehole. A second criterion was the necessity of locating interval boundaries in smooth-walled sections of the borehole; this allowed the packers to form a tight seal and effectively isolate each packed interval. The five test intervals were selected as follows:

- Interval 1 - 0 to 40 feet
- Interval 2 - 40 to 70 feet
- Interval 3 - 72 to 102 feet
- Interval 4 - 108 to 138 feet
- Interval 5 - 138 to approx. 200 feet (bottom of well)

The straddle-packer assembly consisted of two 6-inch diameter (uninflated) packers attached to 1¼-inch-diameter galvanized steel pipe, positioned such that the distance between the bottom of the top packer and the top of the bottom packer (i.e., the length of the packed interval) was exactly 30 feet. A Grundfos® submersible pump was positioned inside the packed interval. An in-line flowmeter was attached to the
discharge line. Pressure transducers were ported above, within, and below the packed interval to monitor hydraulic head in these three zones; the transducer cables extended to the surface and were connected to a datalogger. A personal computer was connected to the data logger, allowing the monitoring of the transducer pressure readings in real time. When inflated, the packers isolated the test interval from the remainder of the borehole, provided that an adequate seal between the packers and the borehole wall had been attained.

The testing of each interval proceeded as follows. After the packer assembly (uninflated) was positioned at the desired depth interval, the three transducers were all calibrated to read the depth to the static water level in PWA, which was measured at 6.65 feet below ground before the packer assembly was lowered into the borehole. The recording by the datalogger of the transducer readings, at 15 second intervals, began following calibration. To conduct the tests of Intervals 2, 3, and 4, both packers were inflated to isolate the test interval. When testing Interval 1, it was necessary to inflate the bottom packer (positioned at 40 feet below ground) to isolate the interval. When testing Interval 5, only the top packer (positioned at 138 feet below ground) was inflated to isolate the interval.

After the transducer readings had stabilized following packer inflation, the pump was turned on. The pumping rate was adjusted as closely as possible to the maximum rate which could be attained without serious risk of pump damage. In all but one of the tested intervals (Interval 4), this pumping rate was below the capacity of the pump, and an estimated yield of the test interval could be determined. The response to pumping
observed in the transducer readings from above and below the test interval, if any, provided some indication of the degree of interconnection between fractures intersecting the borehole inside the test interval and fractures intersecting the borehole above and below the test interval. Pumping continued until a volume of water greater than three times the volume of the test interval had been discharged. Groundwater samples were then collected from each tested interval. Typically, the drawdown inside the test interval had approached steady-state or had leveled off considerably by the time the samples were collected. Following sampling, the pump was turned off, and the recording of transducer readings continued until hydraulic head in the test interval had recovered to approximately 90 percent of the pre-pumping equilibrium level. The test was then concluded and the packers were deflated; the packer assembly was either moved into position for the next test, or removed from the well at the conclusion of the final test.

The estimated yields for each test interval determined during the straddle-packer testing are as follows:

- Interval 1 - 2.3 gallons per minute (gpm)
- Interval 2 - 24 gpm
- Interval 3 - 13 gpm
- Interval 4 - greater than 26 gpm
- Interval 5 - 7 gpm
APPENDIX D: Water-Level Measurements
Water-level measurement activities at the study are consisted of two events: 1) the collection of synoptic water-level measurements from all monitoring wells at the facility, and 2) long-term water-level monitoring of alluvium and bedrock wells adjacent to the North Branch Potomac River.

**Water Level Measurements in Monitoring Wells**

Water levels were measured, in all monitoring wells at the facility, with an electronic water level indicator. Each measurement consisted of the distance (in feet, to the nearest 0.01) between the water level in the well and top of the protected casing. The measurements were taken by sighting across the top of the protective casing adjacent to the padlock tabs; this portion of the lip of the casing was surveyed. In order to determine elevation of the water level at each well, each water level measurement was subtracted from the surveyed elevation of the protective casing at the appropriate well. The water level data were used to produce piezometric contour maps of the alluvial and bedrock aquifers.

**Long-Term Water-Level Monitoring**

Long-term water-level monitoring was performed at two monitoring wells located side-by-side and adjacent to the North Branch Potomac River. The river level adjacent to the monitoring wells was also monitored. The purpose of the long-term water-level monitoring event was to assess the degree of hydraulic interconnection between the
North Branch Potomac River and the alluvial and bedrock aquifers underlying the study site.

The two monitoring wells, 1GW3 and 1GW9, are located along the northern perimeter of the study site and the facility. Well 1GW3 is screened across the contact between the alluvial and bedrock aquifers, and has a screen interval from 24 to 40 feet below the ground surface. Well 1GW9 is screened in bedrock from 65 to 80 feet below the ground surface.

Pressure transducers were installed in the two monitoring wells and in the river. The transducer in the river was secured to a heavy cylinder block placed in the river bottom near the river bank. In order to secure the transducer from movement caused by storm flow in the river, the cylinder block was positioned between two metal stakes driven into the river bottom. The transducers were wired to a Model 21X datalogger manufactured by Campbell Scientific, Inc. The datalogger recorded water-level data at 15-second intervals for the duration of the five week monitoring event.
APPENDIX E: Drilling & Installing Monitoring Wells
This appendix describes drilling and monitoring well installation performed during the summer of 1992. Fourteen monitoring wells were installed in and around the study site, including five wells installed into the alluvial aquifer (GGW1, GGW3, GGW5, GGW7, and 1GW11), and nine wells installed into the bedrock (GGW2, GGW4, GGW6, GGW8, 1GW10, 1GW12, 1GW13, 1GW14, and 2GW7). There is also numerous other monitoring wells installed during the previous investigation.

During drilling activities for well installation, ten soil borings in unconsolidated sediments were sampled and lithologically characterized; soil boring logs are included in the end of this appendix.

Drilling and Installation of Monitoring Wells

This appendix describes drilling and monitoring well installation performed at the study site during July - September, 1992. Five wells were installed in the alluvial aquifer (GGW1, GGW3, GGW5, GGW7, and 1GW11) and nine were installed in the bedrock (GGW2, GGW4, GGW6, GGW8, 1GW10, 1GW12, 1GW13, 1GW14, 2GW7).

During drilling activities for well installation, ten soil borings in unconsolidated sediments were sampled and lithologically characterized; soil boring logs are included in the subsection at the end of this appendix. Descriptions of the drill cuttings generated during bedrock drilling are also included to provide some insight into the nature of bedrock lithology at each bedrock well location.
**Drilling and Soil Sampling**

Monitoring well installation at each location was generally performed in four stages: 1) A pilot hole was drilled with hollow stem augers to auger refusal, with split-spoon samples collected at intervals to provide lithologic characterization of the shallow alluvial aquifer. 2) The pilot hole was reamed out to approximately 11 inches in diameter and extended at least five feet into competent bedrock using mud rotary or cable tool drilling methods; a 6-inch inside diameter (ID) steel surface casing was installed and grouted into the borehole, extending from the surface to a minimum of five feet into the bedrock. 3) At the locations where shallow alluvial wells were to be installed, a borehole was drilled to auger refusal with hollow stem augers, and a 2-inch ID monitoring well was installed. 4) Where 6-inch ID steel surface casings were installed, the borehole was extended from the bottom of the surface casing into bedrock using 6-inch air rotary drilling techniques; a 2-inch ID monitoring well was installed in each bedrock borehole.

**Monitoring Wells Installed**

The numbering of the wells continued the numbering scheme established from the previous study. The first new monitoring well is numbered as 1GW10 to follow the last well (1GW9) installed during the previous study.

**Monitoring Wells**

- **1GW10 and 1GW11.** This pair of adjacent wells consists of a shallow well screened in the alluvial aquifer (1GW11) and an 80-foot-deep well screened in bedrock (1GW10). The wells are located just south of the study site. The wells provide data
on the water level and groundwater quality in the alluvium and bedrock immediately upgradient of the study site.

- **1GW12 and 1GW14.** These 80-foot-deep bedrock wells are located along the northern perimeter of the study site near the North Branch Potomac River. The wells have screen zones in relatively deep bedrock, and were installed adjacent to previously installed wells that have screen zones extending only into shallow bedrock. The wells were intended for assessing the depth of contamination adjacent to the river, the determining the local vertical hydraulic-head gradient, and evaluating the potential for contaminant migration into the river.

- **1GW13.** This 121-foot-deep bedrock well was installed along the northern perimeter of the study site, adjacent to previously installed wells 1GW3 (screened in alluvium) and 1GW9 (screened from 65 to 80 feet in bedrock). The well was to be used to assess the vertical hydraulic-head gradient adjacent to the river and downgradient of the study site, and to determine the distribution of contamination with bedrock depth in an area where the presence of DNAPL is suspected.

- **2GW7.** This 81-foot-deep bedrock well is located along the northern perimeter of the study site near the North Branch Potomac River. The well was intended to be used to provide data on the water level and water quality in bedrock.

**General Area Monitoring Wells**

Four well pairs, each consisting of a shallow well screened in the alluvial aquifer and an 80-foot-deep well screened in bedrock. Therefore, the well numbers begin with the letter “G” indicating a general area of the study site. Each of the well pairs was to provide data for assessing the directions and rates of groundwater flow, for determining the local vertical hydraulic-head gradient, and for assessing water quality in the alluvial and bedrock aquifers in areas where no previously existing data were available.

- **GGW1 and GGW2-These wells are located on the northwest perimeter of the plant near the North Branch Potomac River.**

- **GGW3 and GGW4-These wells are located upgradient of the study site.**
- **GGW5 and GGW6**—These wells are located to the south of the study site.

- **GGW7 and GGW8**—These wells were installed upgradient of the study site, towards the southeastern corner of the study site.

  Boring logs and well completion diagrams of monitoring wells installed during the study as well as of those installed during previous investigations were interpreted. Also interpreted were the slug tests (Appendix B) conducted during the study to assess the hydraulic properties of the alluvial aquifer underlying the study site and the straddle-packer tests (Appendix C) conducted at production well PWA to evaluate the yields of isolated fracture intervals within the borehole, and to assess the degree of vertical interconnection between these intervals. The water-level measurements (Appendix D) recorded at all monitoring wells on the study site to evaluate the directions and rates of flow in the alluvial and bedrock aquifers beneath the study site and the long-term water-level monitoring of the North Branch Potomac River and adjacent alluvial and bedrock wells to assess the degree of hydraulic interconnection between the aquifers and the river were interpreted.

  During the study, some apparent errors were discovered in the data from the previous study concerning the screened units of monitoring wells. The errors that affect the development of a conceptual hydrogeologic model of the site are discussed briefly below.

  On the basis of a review of the information from the report of the previous investigation, monitoring wells 1GW2, 1GW4, 1GW6, 2GW1, and 3GW1 were determined to have been assigned to the wrong hydrogeological units. Wells that reportedly were screened across the alluvium/bedrock contact because of very long
screen zones (wells 1GW2, 1GW4, and 1GW6), have been reinterpreted as being screened only in bedrock because their steel casings are reported to extend from the surface into the bedrock, presumably eliminating contact of the screens with the alluvium. Also, wells 2GW1 and 3GW1, which were reported in a previous investigation as being screened only in the bedrock, have been reinterpreted as being screened across the alluvium/bedrock contact because the reported depths of the steel surface casings do not reach the reported depths of the bedrock surface.
APPENDIX F: Local Geology
STRUCTURAL SETTING

Deformation in this region is dominated by close folding, which generated a series of axially extensive folds of considerable amplitude and small wavelength. Regionally, three distinct types of faults, some tens of kilometers long with thousands of meters of displacement, were generated at different times during the Alleghenian deformation of the Cambro-Ordovician rocks (Mumpower, 1976). The fault pattern set by these deformations is important to understand as it greatly influences the groundwater flow pattern of the regions bedrock aquifers. Three types of faults acted as parts of a continuum in the process of horizontal shortening of the area and are:

(1) Cross faults that were subvertical strike-slip faults normal to structural grain with horizontal shortening on one side independent of that of the other;

(2) East-dipping steep thrusts parallel to the structural grain and usually in the west-facing subvertical to overturned anticlinal limbs; and

(3) West-dipping steep thrusts parallel to the structural grain and also in west-facing subvertical to overturned anticlinal limbs (Root, 1973).

The general structure of the Central Appalachians in the study site is illustrated in Figure 6. The Valley and Ridge province lies between the Blue Ridge province to the southeast and the Allegheny Plateau province to the northwest (Figure 1). The study site is located within the western half of the Valley and Ridge structural and physiography province. The area is characterized by long parallel anticlines and synclines trending approximately NNE-SSW with wavelengths of several miles. Most folds are asymmetric and overturned toward the northwest. Southeastern limbs dip
gently, generally less then 30 degrees. Low angle Thrust faults intersecting the surface are common throughout the Valley and Ridge Province. These thrust faults are a consequence of the thin-skinned deformatinal style that predominated during the orogenesis of the Appalachian mobile belt (Mumpower, 1976). Most major structures plunge to the southwest. The distinct topographic and structural boundary between the Allegheny Plateau and the Valley and Ridge is the Allegheny Structural Front. The rocks of the Allegheny Structural Front form broad open folds with little surface evidence of faulting. The large amplitude in the surface folds forming along the Allegheny Structural Front is a result of longitudinal ramping. The Knobbly Mountain anticlinorium (anticline) formed over a decollement thrust stepped-up (i.e. longitudinal ramp) from the lower Cambrian Waynesboro Formation to the Ordovician Martinsburg and Juniata Formations. The genetic relationship between surface anticlines and subsurface longitudinal ramps is an important concept in the structural evolution within the study site and throughout the Appalachian region.

Faulting appears to be of minor importance at the surface, but local drilling near the study site shows that faulting is a major structural feature in the subsurface (Mumpower, 1976). The formations were probably folded and faulted during the Appalachian Orogeny near the close of the Paleozoic Era.

Folds

Knobbly Mountain, in the southwest corner of the Cresaptown quadrangle, is the surface expression of the Wills Mountain anticline. Reager (1924) considered the Wills
Mountain anticline to be a continuous structure from Bedford County, Pennsylvania, to Bath County, Virginia, a total of 162 miles. Southwest of the Cresaptown quadrangle in the Keyser quadrangle, Dennison (1955) suggested that the Wills Mountain anticline ends and the Noswad anticline continues to the southwest.

Faults

While mapping, major thrust faults were not located at the surface, but deep drilling in the area by Shell Oil Company in 1964 showed the presents of deep thrust faults. Mumpower (1976) wrote a Masters Thesis on "Regional Fracture Investigation of the Brallier Formation and its Transient Fracture Morphology" in counties to the south of the study site. The regional field investigation of fractures in the Brallier Formation in a local anticlinorium and synclinorium reviled six fracture sets, of which four were pervasive on either the regional or local scale (Mumpower, 1976). Fracture morphology indicated all sets were caused by tensile stresses. The relative fracture chronology among sets was determined. Two northwest trending fracture sets developed prior to folding while bedding was still horizontal. A north-northeast trending fracture set had two distinct periods of fracture inception. A limited number of fractures in this set formed during early stages of fold growth of the major structures in the area. The majority of the fractures in this set, however, developed after Alleghenian folding. An east-west trending fracture set probably formed in response to east to northeast trending compressive stresses probably associated with Triassic plate spreading along the Mid-Atlantic Ridge. The dominant regional trend for fracture
origin points within lower stratum levels supports the theory that fractures are propagated upward through the sedimentary column.

Joints and Cleavage

Cleavage is generally restricted to the Marcellus and Needmore Shales. Axial plane cleavage is well developed in the Marcellus Shale but is found in the Needmore Shale only where they are intensely folded. The jointing structure of the region is important because it creates the basic pattern for groundwater flow.

Oriskany Group

The Oriskany Group is limited to one formation in the study site, the Ridgeley Sandstone. The Ridgeley Sandstone is 180-200 feet thick near Keyser, West Virginia and may thin slightly towards Cumberland (Eddy, 1964). The Ridgeley is divided into two units: 1) a lower unit, 80 feet thick, is gray calcareous sandstone, and 2) an upper unit, approximately 100 feet thick, is a gray, course-grained, massive calcareous sandstone which can resemble sections of the Tonoloway and Keyser (Dyott, 1956). This unit is extremely resistant to erosion and is quite easy to map.
APPENDIX G: Groundwater Sampling
The objectives of the groundwater investigation were to define the hydrogeology of the study site and to determine the approximate extent of groundwater contamination. The Well Wizard® pump is a positive-displacement bladder pump operated by pressurized air, designed so that there is no contact between the air and the water being pumped. The pump itself is composed of a stainless steel body with Teflon® bladder, valves, and end fittings. The pump is operated through a control box which regulates pressurized air supplied by a compressor, which is powered by a built-in gasoline-powered generator. The discharge tubing for the pump is constructed of Teflon®-lined polyethylene. At some locations, sampling was accomplished with reusable Teflon® or disposable polyethylene bailers due to inadequate recharge rates or insufficient height of water column for pump operation.

Samples were collected from the Teflon®-lined discharge tube of the sampling pump directly into the sampling container. The sampling containers were supplier-cleaned to laboratory standards and certified. Samples for TCL volatiles were collected in three 40-ml clear glass vials containing hydrochloric acid as preservative. Samples for explosives were collected in two 40-ml amber glass vials containing no preservative. TAL metal samples were collected in a 1-liter polyethylene bottle containing nitric acid as a preservative. Gasoline-Range Organics/Total Petroleum Hydrocarbons (GRO/TPH) samples were collected in three 40-ml clear glass vials containing hydrochloric acid as a preservative. Samples for Diesel Range Organics (DRO) analysis were collected in a 2-liter amber bottle containing no preservative.
Each sample was placed in an ice cooler after collection. At the end of each day, the samples were carefully packed in iced coolers with vermiculite as packing material, and shipped via overnight carrier to the appropriate laboratory.

At wells purged and sampled with portable Well Wizard® pumps, the pumping system was decontaminated prior to initial use and immediately after each sampling event. As the pump was withdrawn from a well after sampling, the air supply and discharge tubing were sprayed off with a 20-percent methanol solution followed by a deionized water rinse, and wound onto a reel assembly. The pump was the inserted into an upright, six-foot long, two-inch inner diameter PVC tube with a PVC end-cap fitted at the bottom. One gallon of Alconox® detergent solution, one gallon of 20-percent methanol solution, and one gallon of deionized water were successively poured from dedicated bottles into the PVC tube and pumped through the full length of the discharge tubing. On completion of pump and tubing decontamination, the tubing was disconnected from the pump. The pump was left in the PVC tube and transported to the next well.