

CRITICAL ANALYSIS OF THE FIELD-SCALE APPLICATION OF  
IN SITU CHEMICAL OXIDATION FOR THE REMEDIATION  
OF CONTAMINATED GROUNDWATER

by  
Friedrich J. Krembs

A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Environmental Science and Engineering).

Golden, Colorado

Date \_\_\_\_\_

Signed: \_\_\_\_\_  
Friedrich J. Krembs

Signed: \_\_\_\_\_  
Dr. Robert L. Siegrist  
Thesis Advisor

Golden, Colorado

Date \_\_\_\_\_

Signed: \_\_\_\_\_  
Dr. Robert L. Siegrist  
Division Director  
Environmental Science and Engineering

## ABSTRACT

In Situ Chemical Oxidation (ISCO) is a rapidly emerging technology that is used to treat organic contaminants during environmental remediation. To better understand the use and design of ISCO systems and the range of performance seen in the field, this critical analysis of case study data was performed to assess under what conditions ISCO has been successful and also what conditions it has not met the desired performance goals. This work began with the design of an ISCO Case Study Database (ISCO-DB1). ISCO-DB1 was designed to include as many potentially relevant parameters as possible regarding site conditions and remediation methods. Database design also included the development of data grouping categories (e.g. sites with similar geology) and performance metrics (e.g. calculation of percent contaminant reduction and rebound). The categories and metrics were developed to ensure that data was entered in a consistent manner to allow meaningful comparisons between sites. ISCO-DB1 was populated from case studies spanning a wide range of site types, contaminants, and ISCO designs. Sources of data included reports submitted to regulators as part of the site remediation process, science and engineering journals, conference proceedings, web-based databases, and technology vendor case study summaries. There are a total of 242 case studies included in ISCO-DB1. The data entered into ISCO-DB1 were subjected to quality assurance and quality control protocols, including an assessment of the reliability of the source data and an outlier analysis of the entered values.

ISCO-DB1 was then queried to examine under what site and contaminant conditions ISCO has been used, what various design techniques have been attempted, the range and frequency of use of various performance goals, and the frequency with which performance goals were met. An analysis of these results was performed to test hypotheses regarding ISCO best practices (e.g. that conducting pilot studies increases the likelihood of reaching desired performance goals) and to address common concerns related to the use of ISCO (e.g. ISCO will eliminate microbial populations that are needed for subsequent biological degradation of contaminants).

The results of the case study analysis show that ISCO has been applied at a wide variety of sites. ISCO has been used in permeable and impermeable unconsolidated

media, as well as in fractured bedrock. ISCO has been used to treat numerous contaminants, though chloroethenes and petroleum hydrocarbons are the two most commonly treated groups. ISCO has been used as part of a wide variety of coupling strategies, either on the front or toward the back of treatment trains. The median cost of the ISCO remediation projects in ISCO-DB1 is \$94/yd<sup>3</sup>.

ISCO has been successful in meeting a variety of goals, including six cases where maximum contaminant levels (MCLs) were achieved and maintained, a fact that was confirmed through correspondence with each site's regulatory official. However, attainment of MCLs has occurred at less than five percent of the sites reviewed. But other goals, such as risk-based standards and source zone depletion, have been met with more regularity, including at DNAPL sites. Over one fifth of the projects have attained site closure despite not attaining MCLs.

ISCO has been more successful at treating fuel related compounds (BTEX, MTBE, and TPH) than chlorinated compounds. However, reductions above 99%, alternative cleanup levels (ACLs), and site closure have been achieved when treating chlorinated compounds.

ISCO is more successful both in terms of meeting desired remediation endpoints achieving larger percent reductions in contaminant concentrations, and less likely to exhibit contaminant rebound when it is performed in homogeneous, permeable geologic material than heterogeneous material and bedrock. Pilot testing results in improved performance results in heterogeneous material.

Increases in chromium and manganese concentrations have persisted in the ISCO treatment zone, sometimes as long as three or more years. However, only two of 242 sites noted increases in metals concentrations off-site, and these abated once active ISCO remediation ceased. Microbial populations are not adversely impacted by ISCO. Permeability reductions may occur when using ISCO, but are relatively rare.

## TABLE OF CONTENTS

ABSTRACT.....	iii
LIST OF FIGURES.....	viii
LIST OF TABLES.....	ix
LIST OF ACRONYMS AND ABBREVIATIONS.....	xv
ACKNOWLEDGEMENTS.....	xviii
1.0 INTRODUCTION AND NEED FOR RESEARCH.....	1
1.1 Introduction to Subsurface Contamination.....	1
1.2 Introduction to In Situ Chemical Oxidation.....	2
1.3 Research Purpose and Scope.....	7
1.4 Thesis Organization.....	9
2.0 REVIEW OF RELEVANT LITERATURE.....	11
2.1 Summary of ISCO Literature.....	11
2.2 Summary of Previous Case Study Reviews.....	15
3.0 METHODS.....	25
3.1 Database Design.....	25
3.2 Data Collection.....	27
3.2.1 Sources of Data.....	27
3.2.2 Collaboration Efforts.....	34
3.2.3 Database Parameters.....	35
3.3 Data Treatment and Reduction.....	36
3.3.1 Grouping of Subsamples.....	36
3.3.2 ISCO Design Metrics.....	41
3.3.3 Performance Metrics.....	44
3.3.4 Rebound Metric.....	52
3.3.5 Geospatial Analysis.....	55
3.3.6 Normalization Methods.....	57
3.3.7 Subdividing Large Sites.....	60
3.4 Data Reliability, Thoroughness, and QA/QC Measures.....	61
3.4.1 Data Quality Class (DQC) System.....	62
3.4.2 Requests for Complete Information and Follow-up Correspondence.....	63
3.4.3 Outlier Analysis.....	63
3.5 Limitations of Methods.....	64
3.5.1 Data Collection Limitations.....	64
3.5.2 Data Reduction and Analysis Limitations.....	66

4.0	RESULTS .....	69
4.1	Overall Summary of ISCO Database.....	69
4.2	Results by COC Group .....	78
4.3	Results by Oxidant.....	81
4.4	Results by Geology Group.....	85
4.5	Results by NAPL Presence .....	89
4.6	Results of Impacts on Microbial Populations .....	92
4.7	Results of Impacts on Metals Mobility.....	93
4.8	Results of Impacts on Aquifer Permeability .....	95
5.0	STATISTICAL ANALYSIS OF RESULTS .....	97
5.1	Analysis of the Utility of Performance Metrics for Statistical Analysis .....	98
5.2	Analysis of the Impact of COC Group .....	101
5.2.1	<i>Comparison of Percent Reduction of Chlorinated and Fuel Related COCs</i> .....	101
5.2.2	<i>Comparison of Percent Reduction Among Chlorinated Compounds</i> .....	103
5.3	Analysis of Results by Oxidant .....	104
5.4	Analysis of the Impact of Geology.....	105
5.5	Analysis of the Impact of NAPL Presence .....	107
5.6	Analysis of Treatability and Pilot Testing .....	110
6.0	DISCUSSION .....	113
6.1	Discussion of the Impact of ISCO Goals on Success.....	113
6.2	Discussion of the Impact of COCs .....	114
6.3	Discussion of Impacts of Oxidant Used.....	115
6.4	Discussion of the Impact of Geology .....	117
6.5	Discussion of the Impact of DNAPL on ISCO Remediation.....	119
6.6	Discussion of the Impact of Bench and Pilot Testing.....	120
6.7	Discussion of the Impact of ISCO on Microbial Populations.....	121
6.8	Discussion of the Impact of ISCO on Metals Mobility .....	121
6.9	Discussion of the Impact of ISCO on Aquifer Permeability .....	122
7.0	CONCLUSIONS AND RECOMMENDED FUTURE WORK .....	125
7.1	Conclusions .....	125
7.2	Recommended Future Work .....	127
	REFERENCES.....	129
	APPENDIX A: GEOSPATIAL METHODS AND EXAMPLE OUTPUTS .....	137

APPENDIX B: COMPLETE DATA TABLES.....	143
B.1 Overall Summary of ISCO Database.....	143
<i>B.1.1 General Information – All Data</i> .....	144
<i>B.1.2 COCs – All Data</i> .....	146
<i>B.1.3 Subsurface Geology, Hydrology and Groundwater Chemistry – All Data</i>	148
<i>B.1.4 ISCO Design Parameters – All Data</i> .....	150
<i>B.1.5 ISCO Results – All Data</i> .....	154
B.2 Summary Statistics by Contaminant of Concern (COC).....	159
<i>B.2.1 General Information by COC Group</i> .....	160
<i>B.2.2 ISCO Design Parameters by COC Group</i> .....	162
<i>B.2.3 ISCO Results by COC Group</i> .....	168
B.3 Summary Statistics by Oxidant Type.....	171
<i>B.3.1 General Information by Oxidant Type</i> .....	172
<i>B.3.2 ISCO Design by Oxidant</i> .....	175
<i>B.3.3 ISCO Results by Oxidant</i> .....	181
B.4 Summary Statistics by Geologic Media.....	184
<i>B.4.1 General Information by Geology Group</i> .....	185
<i>B.4.2 ISCO Design by Geology Group</i> .....	188
<i>B.4.3 ISCO Results by Geology Group</i> .....	192
B.5 Summary Statistics by Presence of NAPL.....	195
<i>B.5.1 General Information by NAPL Presence</i> .....	196
<i>B.5.2 ISCO Design by NAPL Presence</i> .....	198
<i>B.5.3 ISCO Results by NAPL Presence</i> .....	202
APPENDIX C: DETAILS OF RANDOMIZATION TEST.....	207

## LIST OF FIGURES

Figure 3-1: Schematic Drawing of ISCO Injection.....	42
Figure 3-2: Schematic Contaminant Distributions.....	47
Figure 4-1: Distribution of Oxidants Used .....	70
Figure 4-2: Cumulative Frequency of Oxidants Used Over Time.....	71
Figure 4-3: Distribution of ISCO Delivery Methods .....	72
Figure 4-4: ISCO Delivery Methods Over Time .....	72
Figure 4-5: Distribution of Geology Groups .....	74
Figure 4-6: Geology Group Treated Over Time.....	75
Figure 5-1: Project Goals and Percent of Sites Meeting Goals - Full Scale ISCO Applications Only .....	99
Figure 5-2: Project Goals and Percent of Sites Meeting Goals - Pilot Scale ISCO Applications Only .....	99
Figure 5-3: Box Plot of Percent Reductions in Chlorinated and Fuel Related COCs.....	102
Figure A-1: Semi-Variogram Cloud and Experimental Semi-Variogram.....	138
Figure A-2: Fitted Semi-Variogram.....	140
Figure A-3: X Y Plot of Grids and Sample Locations Used in Kriging.....	141
Figure A-4: Contaminant Concentration Surface Estimated with Kriging .....	142
Figure C-1: Randomization Test Histograms .....	208



## LIST OF TABLES

Table 1-1: Summary of Oxidant Characteristics.....	3
Table 1-2: Summary of Reactive Species.....	4
Table 2-1: Summary of Previous Case Study Reviews.....	16
Table 3-1: Summary of Data Sources .....	28
Table 3-2: Examples of ISCO Case Study Papers in Science and Engineering Journals .	30
Table 3-3: Examples of ISCO Case Studies in Technical Bulletins and Guidance Documents.....	31
Table 3-4: Online Resources for ISCO Project Information .....	32
Table 3-5: Types of Treatability Studies .....	39
Table 3-6: Remediation Goals in ISCO-DB1 .....	40
Table 3-7: Quantitative Performance Metrics.....	45
Table 3-8: Qualitative Performance Metrics .....	50
Table 4-1: Goals of ISCO Remediation by COC Group.....	79
Table 4-2: Oxidant Used by COC Group .....	79
Table 4-3: ISCO Pre-Design Testing and Coupling by COC Group .....	80
Table 4-4: Selected Performance Results by COC Group .....	81
Table 4-5: Oxidant Concentration Injected .....	82
Table 4-6: Design Parameters by Oxidant Used.....	83
Table 4-7: Selected Performance Results by Oxidant.....	84
Table 4-8: Goals of ISCO Remediation by Geology Group.....	86
Table 4-9: Oxidant Used by Geology Group.....	87
Table 4-10: ISCO Pre-Treatment Testing by Geology Group.....	87
Table 4-11: Selected Performance Metrics at ISCO Sites by Geology Group.....	88
Table 4-12: Incidence of Rebound by at ISCO Sites Geology Group .....	88
Table 4-13: Oxidant Delivery Method by NAPL Presence.....	90
Table 4-14: Use of Pre-design Testing and Coupling at ISCO Sites Based on NAPL Presence .....	91
Table 4-15: Duration of Metals Increases After ISCO.....	94
Table 5-1: Results of Randomization Testing of COC Reductions .....	102
Table 5-2: Results of Randomization Testing of COC Reductions .....	104
Table B-1: Sites in Database by Nation.....	144

Table B-2: Sites in Database by U.S. State.....	144
Table B-3: Site Types in ISCO-DB1 .....	145
Table B-4: Summary of DQC Values .....	146
Table B-5: Summary of COCs.....	147
Table B-6: Indications of NAPL Presence .....	147
Table B-7: Use of COC Mass Flux as Baseline Site Assessment Criterion.....	147
Table B-8: Estimate of Baseline COC Mass (kg).....	148
Table B-9: Summary of Extents of Contamination.....	148
Table B-10: Summary of Geology Group Distribution.....	148
Table B-11: Summary of Hydrogeologic and Geochemical Data .....	149
Table B-12: Summary of Baseline Groundwater Chemistry.....	149
Table B-13: Summary of Goals of ISCO Remediation.....	149
Table B-14: Summary of Project Scale .....	150
Table B-15: Summary of Oxidant Used .....	150
Table B-16: Summary of Targeted Geologic Media.....	150
Table B-17: Summary of TTZ .....	151
Table B-18: Summary of Size of TTZ .....	151
Table B-19: Summary of Oxidant Delivery Method.....	151
Table B-20: Summary of ISCO Design Parameters.....	152
Table B-21: Summary of Use of Treatability Studies .....	152
Table B-22: Summary of Types of Treatability Studies Used.....	152
Table B-23: Summary of Use of Pilot Testing – Full Scale Applications Only.....	152
Table B-24: Summary of Program Modification.....	153
Table B-25: Summary of the Use of Coupling.....	153
Table B-26: Summary of Coupling Techniques .....	154
Table B-27: Summary of Qualitative Success Metrics .....	155
Table B-28: Summary of Project Goals vs. Percent Meeting those Goals – All Sites....	155
Table B-29: Summary of Project Goals vs. Percent Meeting those Goals – Full Scale Only .....	156
Table B-30: Summary of Project Goals vs. Percent Meeting those Goals – Pilot Scale Only .....	156
Table B-31: Summary Percent Reductions in Maximum COC Concentration – All Data .....	157

Table B-32: Summary Percent Reductions in Maximum COC Concentration – Only Sites with One Year Post-ISCO Data.....	158
Table B-33: Summary Rebound Testing and Occurrence.....	158
Table B-34: Summary of Project Costs.....	159
Table B-35: Site Type by COC Group.....	160
Table B-36: DQC by COC Group.....	160
Table B-37: Presence of NAPL by COC Group.....	161
Table B-38: Geology Group by COC Group.....	161
Table B-39: Goals of Remediation by COC Group .....	162
Table B-40: Oxidant Used by COC Group.....	162
Table B-41: TTZ by COC Group.....	163
Table B-42: Areal Extent of TTZ by COC Group .....	163
Table B-43: Volume of TTZ by COC Group .....	163
Table B-44: Number of Pore Volumes of Oxidant Solution Delivered by COC Group.	164
Table B-45: Number of Delivery Events by COC Group .....	164
Table B-46: Use of Treatability Studies by COC Group - Full and Pilot Scale .....	164
Table B-47: Type of Treatability Study Performed - All Sites.....	165
Table B-48: Use of Treatability Studies by COC Group - Full Scale Only .....	165
Table B-49: Use of Pilot Studies by COC Group - Full Scale Only.....	165
Table B-50: Use of Coupling by COC Group – Full and Pilot Scale Only.....	166
Table B-51: Coupling Techniques by COC Group.....	167
Table B-52: Percentage of Sites Attaining Closure by COC Group – Full Scale Only ..	168
Table B-53: Percentage of Sites Meeting Goals by COC Group.....	169
Table B-54: Percentage of Sites Attaining MCLs by COC Group.....	169
Table B-55: Percent Reduction in Maximum Groundwater VOC Concentrations by COC Group.....	170
Table B-56: Percentage of Sites with Rebound by COC Group.....	170
Table B-57: Total Project Cost by COC Group.....	171
Table B-58: Unit Cost by COC Group.....	171
Table B-59: Site Type by Oxidant .....	172
Table B-60: DQC by Oxidant.....	173
Table B-61: Presence of NAPL by Oxidant - Full and Pilot Scale Applications .....	173
Table B-62: COC Groups Present by Oxidant.....	174

Table B-63: Geology Group by Oxidant .....	174
Table B-64: Goals of Remediation by Oxidant .....	174
Table B-65: Delivery Method by Oxidant.....	175
Table B-66: TTZ by Oxidant .....	175
Table B-67: Areal Extent of TTZ by Oxidant .....	176
Table B-68: Volume of TTZ by Oxidant.....	176
Table B-69: Injected Oxidant Concentration by Oxidant.....	176
Table B-70: Oxidant Concentration after Mixing with Activator by Oxidant .....	177
Table B-71: Design Radius of Influence by Oxidant .....	177
Table B-72: Observed Radius of Influence by Oxidant .....	177
Table B-73: Oxidant Loading Rate by Oxidant.....	178
Table B-74: Number of Pore Volumes Delivered by Oxidant .....	178
Table B-75: Number of Delivery Events by Oxidant.....	178
Table B-76: Duration of Delivery Events by Oxidant .....	179
Table B-77: Use of Treatability Studies by Oxidant – Full and Pilot Scale Applications.....	179
Table B-78: Use of Treatability Studies by Oxidant - Full Scale Applications Only.....	179
Table B-79: Use of Pilot Studies by Oxidant - Full Scale Applications Only.....	179
Table B-80: Use of Coupling by Oxidant.....	180
Table B-81: Coupling Techniques by Oxidant .....	181
Table B-82: Percentage of Sites Attaining Closure by Oxidant – Full Scale Only .....	182
Table B-83: Percentage of Sites Meeting Goals by Oxidant .....	182
Table B-84: Percentage of Sites Attaining MCLs by Oxidant .....	183
Table B-85: Percent Reduction in Maximum Groundwater VOC Concentrations by Oxidant.....	183
Table B-86: Percentage of Sites with Rebound by Oxidant .....	183
Table B-87: Total Project Cost by Oxidant .....	184
Table B-88: Unit Costs by Oxidant.....	184
Table B-89: Site Type by Geology Group.....	185
Table B-90: Data Quality Classification Values by Geology Group.....	186
Table B-91: COCs Present by Geology Group.....	186
Table B-92: Presence of NAPL by Geology Group - Full and Pilot Scale Applications	187
Table B-93: Goals of Remediation by Geology Group.....	187

Table B-94: Oxidant Selected by Geology Group .....	188
Table B-95: Delivery Method by Geology Group .....	188
Table B-96: TTZ by Geology Group .....	189
Table B-97: Areal Extent of TTZ by Geology Group.....	189
Table B-98: Volume of TTZ by Geology Group.....	189
Table B-99: Use of Treatability Studies by Geology Group - Full and Pilot Scale Applications.....	190
Table B-100: Use of Treatability Studies by Geology Group - Full Scale Applications Only .....	190
Table B-101: Use of Pilot Studies by Geology Group - Full Scale Applications Only..	190
Table B-102: Use of Coupling by Geology Group.....	191
Table B-103: Coupling Techniques by Geology Group.....	192
Table B-104: Percentage of Sites Attaining Closure by Geology Group – Full Scale Only .....	193
Table B-105: Percentage of Sites Meeting Goals by Geology Group .....	193
Table B-106: Percentage of Sites Attaining MCLs by Geology Group.....	194
Table B-107: Percent Reduction in Maximum Groundwater VOC Concentrations by Geology Group .....	194
Table B-108: Percentage of Sites with Rebound by Geology Group .....	194
Table B-109: Total Project Cost by Geology Group.....	195
Table B-110: Unit Cost by Geology Group.....	195
Table B-111: Site Type by NAPL Presence .....	196
Table B-112: DQC by NAPL Presence.....	197
Table B-113: Geology Type by NAPL Presence.....	197
Table B-114: Goals of Remediation by NAPL Presence .....	198
Table B-115: Oxidant by NAPL Presence.....	198
Table B-116: Oxidant Delivery Method by NAPL Presence .....	199
Table B-117: TTZ by NAPL Presence .....	199
Table B-118: Areal Extent of TTZ by NAPL Presence .....	199
Table B-119: Volume of TTZ by NAPL Presence .....	200
Table B-120: Number of Pore Volumes Delivered by NAPL Presence .....	200
Table B-121: Number of Delivery Events by NAPL Presence .....	200
Table B-122: Use of Treatability Studies by NAPL Presence - Full and Pilot Scale Applications.....	200

Table B-123: Use of Treatability Studies by NAPL Presence - Full Scale Applications Only .....	201
Table B-124: Use of Pilot Studies by NAPL Presence - Full Scale Applications Only .	201
Table B-125: Incidence of Program Modification by NAPL Presence.....	201
Table B-126: Use of Coupling by NAPL Presence.....	201
Table B-127: Coupling Technology by NAPL Presence .....	202
Table B-128: Attainment of Site Closure by NAPL Presence – Full Scale Applications Only .....	203
Table B-129: Percentage of Sites Meeting Goals by NAPL Presence.....	203
Table B-130: Percentage of Sites Attaining MCLs by NAPL Presence .....	203
Table B-131: Percent Reduction in Maximum Groundwater VOC Concentrations by NAPL Presence .....	204
Table B-132: Percentage of Sites with Rebound by NAPL Presence.....	204
Table B-133: Total Project Cost by NAPL Presence .....	204
Table B-134: Unit Project Cost by NAPL Presence .....	205

## LIST OF ACRONYMS AND ABBREVIATIONS

ACLs	alternative (risk-based) cleanup levels
AFCEE	Air Force Center for Environmental Excellence
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and total xylenes
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
cf	cubic feet
CHP	catalyzed hydrogen peroxide
CLU-IN	USEPA Hazardous Waste Clean-Up Information
COCs	contaminants of concern
CVOCs	chlorinated volatile organic compounds
DCE	dichloroethene
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DOD	Department of Defense
DOE	Department of Energy
DPE	dual phase extraction
DQC	data quality class
DTSC	Department of Toxic Substances Control
EFR	enhanced fluid recovery
EISB	enhanced in situ bioremediation
EPA	Environmental Protection Agency
ERD	enhanced reductive dechlorination
ESTCP	Environmental Security Technology Certification Program
foc	fraction organic carbon
FOIA	Freedom of Information Act
FRTR	Federal Remediation Technologies Roundtable
FS	Feasibility Study
g/L	grams per liter
GAO	Government Accountability Office
GW	groundwater

HMX	high molecular weight RDX (cyclotetramethylene-tetranitramine)
ISCO	in situ chemical oxidation
ITRC	Interstate Technology & Regulatory Council
ITSRs	Innovative Technology Summary Reports
K	saturated hydraulic conductivity
L	length
LNAPL	light non-aqueous phase liquid
M	mass
MCL	maximum concentration limit
MDL	method detection limit
mg/L	milligrams per liter
mS/cm	millisiemens per centimeter
MNA	monitored natural attenuation
MnO <sub>4</sub> <sup>-</sup>	permanganate
MSDS	material safety data sheet
MTBE	methyl tertiary-butyl ether
n	porosity
n <sub>e</sub>	effective porosity
NOD	natural oxidant demand
NPL	National Priorities List
NTC	Naval Training Center
O&M	operations and maintenance
ODEQ	Oregon Department of Environmental Quality
ORP	oxidation reduction potential
ORT	Oxidative Reductive Technologies
P&T	pump and treat
PCBs	polychlorinated biphenyls
PCE	tetrachloroethene
peroxone	ozone catalyzed with hydrogen peroxide
QA/QC	quality assurance / quality control
RA	Remedial Action Report



RAOs	remedial action objectives
RCRA	Resource Conservation and Recovery Act
RD	Remedial Design Report
RDX	royal demolition explosive (cyclotrimethylenetrinitramine)
RI	Remedial Investigation Report
RMSE	root mean squared error
ROI	radius of influence
RPM	remedial project manager
S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	persulfate
SERDP	Strategic Environmental Research and Development Program
SOD	soil oxidant demand
SVE	soil vapor extraction
SWRCB	State Water Resources Control Board
TCA	trichloroethane
TCE	trichloroethene
TCEQ	Texas Commission on Environmental Quality
TOC	total organic carbon
TPM	Technology Practices Manual
TTZ	target treatment zone
ug/L	micrograms per liter
UMass	University of Massachusetts at Amherst
U.S.	United States
USEPA	United States Environmental Protection Agency
WDNR	Wisconsin Division of Natural Resources
VOCs	volatile organic compounds

## ACKNOWLEDGEMENTS

There are many people who were involved in this work and to whom I owe thanks for support received. First, I very much appreciate that my advisor, Dr. Robert Siegrist, invited me to work on this project, and also the support and faith in me that you showed during the execution of this work. I also owe Dr. Michelle Crimi a great deal for her help during the course of my involvement in this project. Dr. Reinhard Furrer made invaluable contributions to the statistical tools used in this work, and I am particularly grateful for his willingness to work with me. Tom Palaia of CH2M HILL also provided valuable feedback on issues as they arose during the data collection and analysis. Dr. John McCray provided insights into important hydrogeological issues.

I am also thankful for the United States Department of Defense's Environmental Security Technology Certification Program (ESTCP) funding this work (project ER-0623), and also the interest that individuals at that agency took in our project and my work as it progressed. The other members of our project team Tom Simpkin, Gene Ng (CH2M HILL), Mike Singletary and Nancy Ruiz (Navy) were most helpful in providing case study data and aiding with conceptual issues.

This work wouldn't have been possible without the help of all those individuals in various sectors of the environmental community who voluntarily provided me with case study data. While these people are too numerous to list here, I know who you are, and my heartfelt thanks goes out to all of you.

My experiences as an undergraduate and also in the working world have benefited my work as a Master's student. My thanks goes out to all of the people who taught me at Haverford and Bryn Mawr, in particular Drs. Weecha and Bill Crawford, Dr. Arlo Weil, Dr. Christopher Cairns, and Dr. Bruce Saunders. In consulting, I'd like to thank Fran Schultz and Tom Otto at GZA GeoEnvironmental for their mentorship, as well as Dennis Rubin for mentorship and for helping with my return to academia.

Finally, this wouldn't have been possible with the support of my family and friends, and in particular the love and support of Kristi Tarantola.

## 1.0 INTRODUCTION AND NEED FOR RESEARCH

### 1.1 Introduction to Subsurface Contamination

Contamination of subsurface soil and groundwater resulting from use and disposal of volatile organic compounds (VOCs) is a prevalent environmental problem in the United States. VOCs include components of many types of fuels, such as gasoline and diesel fuel, as well as various solvents, such as perchloroethene (PCE) and trichloroethene (TCE). While these chemicals have many valuable uses, they may also lead to adverse health effects in humans and other biota. The awareness of these health effects increased dramatically in the 1970s, with the release of Rachel Carson's Silent Spring, and environmental disasters such as Love Canal and Valley of the Drums. This era saw the passage of new legislation designed to protect the environment, including the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) and the Resource Conservation and Recovery Act (RCRA). These laws had the positive impact of improving common practices with respect to handling and disposal of chemicals. However, in many cases the damage had already been done. Prior to this time, chemical wastes were discharged directly to the ground or to surface water at many industrial sites. Some of these wastes, such as PCE and TCE, are very resistant to natural degradation and dissolution. This is especially true when the original release was of the pure phase chemical, or non-aqueous phase liquid (NAPL), a difficulty that is compounded further when the contaminants are dense non-aqueous phase liquids (DNAPLs). DNAPLs sink through the aquifer until they encounter a fine grained stratum on which they will form a pool of contaminant, leaving a trail of contamination as they sink. DNAPL source zones are difficult to locate in the subsurface, much less treat. For this reason, there are many sites in the United States at which contaminants that were discharged decades ago are still present at harmful concentrations in groundwater to this day.

The United States Environmental Protection Agency (EPA) reports that VOCs are present at 78% of CERCLA National Priorities List (NPL) sites, 67% percent of RCRA Corrective Action Sites, 64% of Department of Defense (DOD) sites, and 38% of

Department of Energy (DOE) sites (EPA 2004a). The EPA (2004a) reports that as of 2004, just under 300,000 sites will require environmental cleanup within the next 30 years under various federal or state regulatory programs at an estimated cost of 209 billion dollars. A recent United States Government Accountability Office (GAO) report identified nearly 6,000 DOD sites that have contamination to groundwater requiring environmental remediation (GAO 2005). In the years 1995 through 2005, the DOD spent over 20 billion dollars to begin remediating these sites (GAO 2005). In 2004, the United States federal government estimated its environmental liabilities to be 249 billion dollars (GAO 2006). Clearly the scope of this issue is quite broad, and will require a significant expenditure of time and dollars to address.

In the 1980s and 1990s, pump and treat (P&T) remediation systems were installed at many sites to mitigate risk and remediate VOCs in groundwater. The common thinking at that time was that groundwater quality would be restored to acceptable levels after a certain volume of fluid was flushed through the contaminated zone. However, such thinking initially neglected the consideration of NAPL. When present, NAPL is often the phase in which the vast majority of subsurface contaminant mass exists (Pankow and Cherry 1996). As the dissolution of NAPL to the aqueous phase is a kinetically limited process, P&T systems require a period of decades up to thousands of years to reach stringent cleanup goals such as maximum contaminant levels (MCLs) (Mackay and Cherry 1989, NRC 1994). Due to the large number of sites requiring remediation, and the inadequacy of P&T systems to meet project goals, additional remediation technologies to treat groundwater contamination have been developed. These technologies include in situ chemical oxidation (ISCO), as well as other in situ techniques such as enhanced biological remediation, thermal remediation, air sparging and others. Each of these technologies has its strengths and weakness. Choosing the proper technology for a contaminated site and employing it correctly will result in significant cost savings, both for the federal government and private sector site owners.

## **1.2 Introduction to In Situ Chemical Oxidation**

The use of chemical oxidants for the destruction of VOCs began in the wastewater treatment field, and was first applied as a remediation technology to treat

contaminants in situ in the early 1990s (e.g. Gates and Siegrist 1993, Gardner *et al.* 1996, Cline *et al.* 1997, Jerome *et al.* 1998). Initial efforts focused on the use of the oxidants permanganate, catalyzed hydrogen peroxide (CHP, also known as modified Fenton's reagent), and ozone. Persulfate, percarbonate, and ozone catalyzed with hydrogen peroxide (known as peroxone) have also been studied increasingly in recent years. The specifics of each of these oxidants are shown in Tables 1-1 and 1-2, and are discussed briefly below. A more thorough description of the reaction chemistry, delivery methods and contaminants amenable to degradation by these oxidants are given in a recent EPA guidance document (Huling and Pivetz 2006). Except where noted below, Huling and Pivetz (2006) is the source of the information contained in the following subsections. Additional information regarding specific oxidants may also be found in materials safety data sheets (MSDS) provided by the manufacturers of the chemical, many of which are available online (e.g. Carus Corporation 2007, FMC 2007, Regenesis 2007, U.S. Peroxide 2007).

Table 1-1: Summary of Oxidant Characteristics

Oxidant	Reactive Species	Commercial Form	Activator
Permanganate	$\text{MnO}_4^-$	powder or liquid	none
CHP	$\bullet\text{OH}$ , $\bullet\text{O}_2^-$ , $\bullet\text{HO}_2$ , $\text{HO}_2^-$	liquid	none, Fe(II)
Ozone	$\text{O}_3$ , $\bullet\text{OH}$	gas	none
Persulfate	$\text{SO}_4^{2-}$ , $\bullet\text{SO}_4^-$	powder	none, Fe(II), heat, hydrogen peroxide, or alkaline conditions
Peroxone	$\text{O}_3$ , $\bullet\text{OH}$	liquid and gas	hydrogen peroxide
Percarbonate	$\bullet\text{OH}$	powder	Fe(II)

Notes: Modified from Huling and Pivetz (2006) CHP = Catalyzed Hydrogen Peroxide (or modified Fenton's reagent). The activator Fe(II) used to activate CHP, persulfate, and percarbonate may be introduced before or during ISCO or may be naturally present in the subsurface at concentrations that are sufficient to activate the desired reactions. Data on Percarbonate from Regenesis (2007).

Table 1-2: Summary of Reactive Species

Formula	Name	Electrode Potential ( $E_h$ )
$MnO_4^-$	permanganate anion	1.7 V
$\bullet OH$	hydroxyl radical	2.8 V
$\bullet O_2^-$	superoxide radical	-2.4 V
$\bullet HO_2$	perhydroxyl radical	1.7 V
$HO_2^-$	hydroperoxide anion	-0.88 V
$O_3$	ozone	2.1 V
$SO_4^{2-}$	persulfate anion	2.1 V
$\bullet SO_4^-$	sulfate radical	2.6 V

Notes: Modified from Huling and Pivetz (2006)

Permanganate ( $MnO_4^-$ ) is available as both  $NaMnO_4$  and  $KMnO_4$ . The sodium form is distributed as a liquid available at 40% concentration by weight. Potassium permanganate is most commonly available in a crystalline form, and has a solubility of approximately 6% by weight in water at 20°C. While permanganate is most commonly delivered as an aqueous solution, it may also be mechanically mixed into soil or introduced via pneumatic or hydraulic fracturing. Permanganate dissociates to produce the permanganate anion, an oxidizing agent with an oxidation potential of 1.7 volts. The permanganate anion has an affinity for carbon-carbon double bonds (Wiberg and Saegerbarth 1957) and for this reason is most commonly applied to chloroethenes such as PCE and TCE. Chlorinated alkanes and chlorinated methanes are much less amenable to oxidation with permanganate. Depending on the subsurface conditions, there may be many naturally occurring materials (e.g. natural organic matter or reduced minerals) that may react with permanganate, referred to as natural oxidant demand (NOD). The presence of appreciable NOD reduces the efficiency with which permanganate reacts with the target contaminants of concern (COCs). This is also referred to as soil oxidant demand (SOD), though the term NOD is used in this document.

Catalyzed hydrogen peroxide (CHP, also known as modified Fenton's reagent), consists of an aqueous solution of hydrogen peroxide ( $H_2O_2$ ) catalyzed with ferrous iron, Fe(II). The hydrogen peroxide solution is available as a liquid at concentrations up to 50% by weight. The catalyst may be: added iron salts, such as ferrous sulfate; added chelated iron, such as an Fe-EDTA complex; or naturally-occurring reduced iron species in soil and aquifer sediments. CHP may be delivered to subsurface via direct push points or injection wells. The chemical reactions that occur during CHP remediation are relatively more rapid than the other oxidants, and for this reason it is less persistent in the subsurface during ISCO, precluding recirculation or other injection schemes that rely on long transport distances. Due to the number of highly reactive radical species that are generated by CHP, a relatively greater number of contaminants are amenable to degradation, including chloroethenes, chloroethanes (e.g. 1,1,2-trichloroethane and 1,1-dichloroethane), chlorobenzenes (dichlorobenzene isomers and monochlorobenzene), benzene, ethylbenzene, toluene, and xylenes (collectively BTEX), methyl tertiary-butyl ether (MTBE), energetics (RDX, HMX) and 1,4-dioxane. The reactions that occur during CHP use are highly exothermic and may also generate significant quantities of oxygen and carbon dioxide gases. Due to the highly reactive nature of hydrogen peroxide and the catalyst, nearly all applications of CHP mix the oxidant and the catalyst in situ. The reactive species formed during CHP reactions also react with non-target compounds in the subsurface, and also with hydrogen peroxide itself. The non-target depletion of CHP reactive species is referred to as scavenging because the reactions can occur both due to subsurface materials and the oxidant and catalyst themselves. Scavenging processes reduce the efficiency of ISCO applications using CHP producing an effect that is similar to NOD consuming permanganate. Several commercial vendors of CHP technology have patented hydrogen peroxide stabilizers that are designed to reduce the degree of scavenging and increase the in situ transport distance of CHP reagents from the injection point.

Ozone is a gaseous oxidant that is introduced through sparge points installed in the subsurface. Ozone is produced by an ozone generator and delivered to the subsurface through specialized sparge points, often in a rotating sequence of pulses. The ozone remediation systems require some degree of ongoing maintenance, and the sequence and

duration of delivery to each individual sparge point may be altered to modify the design as needed during remediation. The ozone molecule is an oxidizing agent itself, and also produces the more reactive hydroxyl radical (Table 1-2). Many of the same chemicals that are amenable to degradation by CHP are degraded by ozone as well. The solubility limit of ozone in water ranges between 11.1mg/L and 6.4mg/L between 5°C and 20°C, respectively. Ozone is considerably more stable in the gaseous phase than the aqueous phase, with typical half lives of three days and 20 minutes in these two media, respectively.

Sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) is a solid that is highly soluble in water, with a solubility limit of 73 g persulfate / 100 g water at 20°C. Persulfate is generally introduced in solution, though it can also be mechanically mixed into soil or theoretically introduced as a slurry during fracturing. The persulfate anion is an oxidizing agent, and may also be activated using heat, alkaline conditions, ferrous iron, or hydrogen peroxide to produce the more reactive sulfate radical ( $\bullet\text{SO}_4^-$ ). Persulfate is more persistent in the subsurface than ozone or CHP, yet generally less so than permanganate. However, it is reported that typical soils exhibit less of a natural oxidant demand for persulfate than for permanganate (Brown and Robinson 2004). As with the other radical-based oxidants (CHP and ozone), many organic contaminants are amenable to degradation by persulfate. However, contaminant degradation is dependent upon which method is used to activate the persulfate. Persulfate use in ISCO remediations has begun relatively more recently than permanganate, CHP, and ozone, with the first reported implementations in the late 1990's (e.g. Droste *et al.* 2002).

This oxidation system uses hydrogen peroxide to activate ozone, promoting the formation of hydroxyl radicals. The delivery method is similar to that of ozone systems as described above except that additional hydrogen peroxide delivery points are added near the ozone sparge point in the subsurface. The suite of contaminants that are amenable to degradation by peroxone is similar to that of ozone systems.

Percarbonate ( $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ ) is a crystalline solid that dissociates to form hydrogen peroxide in the subsurface, which may in turn be activated to form similar reactive species to those that are produced during CHP. Percarbonate is most commonly



introduced in solution, but may also be mechanically mixed into soil. Percarbonate is the most recently developed of the chemical oxidants used in ISCO applications.

### **1.3 Research Purpose and Scope**

The preceding paragraphs based on the scientific literature show that many contaminants are amenable to degradation with a number of oxidants. However, field-scale ISCO applications have not always produced the desired performance results. Commonly cited reasons for not meeting the desired performance goals include a lack of contact between the oxidants and COCs, back diffusion from low permeability materials, and NAPL mass transfer limitations. Another reason for a lack of success is that not all ISCO systems are designed properly.

There is precedent for performing case study reviews to evaluate remediation technologies. A case study review provides a broad-scale look at how a remediation technology has been applied, and presents a range of outcomes that may be expected in an unbiased fashion. In 1999, the Environmental Security Technology Certification Program (ESTCP) published “Technology Status Review: In Situ Oxidation,” an overview of ISCO technology and a review of 42 case studies (ESTCP 1999). This document provided case study examples of ISCO work performed and outcomes achieved, both positive and negative, and will be discussed further in Relevant Literature (Section 2.2). The fact that nearly half of the case studies reviewed in this publication did not meet the desired goals is an indication that at the time of its publication there was room to learn from past experiences. ISCO technology has advanced considerably since the writing of this ESTCP document, both in terms of the scientific understanding established through laboratory experimentation and also in terms of field-scale experience and regulatory acceptance of the technology. For this reason, another expanded research effort focusing on ISCO case studies is timely.

The purpose of this thesis research is to use information from past field-scale ISCO projects to examine when this remediation technique is most successful, identify inherent limitations of the technology, and determine what system designs seem to be most successful. This analysis considers the situations in which ISCO is performed, the methods through which it is implemented, and the results being achieved. This work has

been carried out in a systematic fashion to record the relevant data relating to each case study in a way that is consistent and allows meaningful comparison between case studies. The final goal of this work is to examine the case studies collectively and provide an unbiased assessment of what results ISCO can reasonably be expected to achieve depending on site conditions.

The scope of this work includes any field-scale ISCO remediation designed to remediate groundwater, with over 99% of these remediations being performed to treat VOCs. This includes situations in which ISCO reagents were injected into the saturated zone, and also some vadose zone applications provided that reductions in groundwater concentrations were a desired performance result. Case studies outside the scope of this work include all sites where soil sampling was the sole means of assessing performance. Also outside the scope of this work are remediations where oxidants were applied to stock-piled soils after excavation since this is not an in situ remediation.

In addition to measuring the success rate of ISCO under various scenarios, ISCO's side effects may also be evaluated through case study review. Examples of adverse impacts that may result from ISCO include reduction of microbial activity, reductions in aquifer permeability, mobilization of metals, and exceedances of secondary groundwater standards such as pH, chloride, or sulfate. Further discussion of the science relating to these issues and relevant citations will be presented in Section 2.1. They are mentioned now to reveal that a case study review can provide evidence regarding the frequency and duration that these impacts have been observed in the field. This evidence can allow the risks associated with these adverse secondary impacts to groundwater quality to be weighed against the expected benefits resulting from COC reductions achieved by ISCO.

The case study review and database completed in this thesis research supports the development of a guidance document that is currently in progress. Specifically, the Colorado School of Mines, CH2M HILL, and the Navy have been tasked by ESTCP to draft a Technology Practices Manual for In Situ Chemical Oxidation for Groundwater Remediation, ESTCP project number ER-0623 (ESTCP 2007a). This document will provide information on the current state of the science and practice with respect to ISCO, and will also provide decision support tools to aid those considering the use of ISCO at

their sites. The decision support tools will outline actions to be taken during ISCO screening or implementation based on site conditions. The case study experiences contained in ISCO-DB1 will be considered in addition to theoretical and laboratory experience in producing the decision support tools. Individual case studies will also be used to test the decision support tools to ensure that the predicted outcomes (or range of outcomes) are similar to those observed in the field. Finally, the case studies will be linked to the text and decision support tools contained within the Technology Practices Manual to provide real-world examples of the issues being discussed.

#### **1.4 Thesis Organization**

This thesis presents an introduction to the environmental contamination and remediation, relevant literature, the methods used in the case study review, the results of the case study data, analysis of results, discussion, and conclusions and recommended future work. The thesis consists of the following specific sections:

Section 1 – Introduction

Section 2 – Review of Relevant Literature

Section 3 – Methods

Section 4 – Results

Section 5 – Statistical Analysis of Results

Section 6 – Discussion

Section 7 – Conclusions and Recommended Future Work



## 2.0 REVIEW OF RELEVANT LITERATURE

This section presents a summary of literature relevant to this work. This literature falls into two general categories. The first is work pertaining to the science and engineering of ISCO systems. The second category consists of case study reviews, including those focused specifically on ISCO as well as those focusing on environmental remediation in general.

### 2.1 Summary of ISCO Literature

An overview of ISCO literature is presented in this section. Rather than being an exhaustive ISCO literature review, this section is intended to point the reader toward further background information on the topic. The introduction to general ISCO information sources is followed by several paragraphs presenting more detailed information on ISCO-specific secondary impacts that may occur during remediation. These secondary impacts are presented in more detail because they represent undesirable outcomes that may potentially result from the use of ISCO. This background information will also provide a frame of reference for the presentation and analysis of the occurrence of these side effects in Sections 4 through 6.

The chemistry of the destruction of organic compounds by chemical oxidants has been investigated for over a century (Wagner 1895, Fenton 1896). In the last twenty years, much research has been conducted specifically on the use of oxidants to destroy VOCs and other contaminants. That research has included exploration of contaminant-oxidant reaction pathways and kinetics, interactions of oxidants with soil matrices, the formation of reaction byproducts, the mobilization of metals, and impacts to microbial communities. The results of these studies are summarized in guidance documents and review papers such as Siegrist *et al.* (2001), Block *et al.* (2004), ITRC (2005), Watts and Teel (2005), and Huling and Pivetz (2006). The reader is referred to these documents for additional references on ISCO. The ESTCP ER-0623 project team has also included a thorough literature review as part of the preparation of the Technology Practices Manual previously referenced.

In addition to the guidance documents and reviews referenced in the previous paragraph, there is additional work that focuses on possible limitations or negative impacts that are associated with ISCO. These secondary impacts were introduced in Section 1.3, and include reductions in biological activity, increases in the mobility of metals, reductions in the permeability of the aquifer as a result of ISCO, and rapid oxidant depletion during subsurface delivery. This section is not meant to give the impression that there is not a sound scientific basis for ISCO technology, but rather is included to show how an analysis of case studies might provide further information to evaluate the frequency with which negative side effects occur.

One secondary impact of special interest that has been speculated to result from ISCO treatment is a reduction in aquifer microbial populations. There are many naturally occurring microbes that are capable of degrading hazardous contaminants to less hazardous or innocuous substances. This is one of the premises behind the use of monitored natural attenuation (MNA) as a remediation technology. Microbiological degradation can be enhanced through the addition of electron donors (biostimulation) or specialized microbiological cultures (bioaugmentation). These two remediation technologies are collectively referred to as enhanced in situ bioremediation (EISB) or sometimes enhanced reductive dechlorination (ERD). The changes in groundwater chemistry (e.g. pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), total organic carbon (TOC), formation of free radicals) that result from ISCO or direct reactions between oxidants and microbes could potentially harm microbial populations. Permanganate has been shown in laboratory studies to have mutagenic activity towards DNA (Bui and Cotton 2002). CHP and free radicals have been shown to be mutagenic (Imlay *et al.* 1988, Imlay and Linn 1988) and toxic (Buyuksonmez *et al.* 1999) to microbial populations as well. However, other studies of impacts to microbial communities conducted at the laboratory and field-scales referenced in Sahl and Munakata-Marr (2006) have shown that microbial populations are not permanently impacted by ISCO remediation. Specifically, microbial populations were found to: (1) rebound to levels similar to those pre-ISCO (Kastner *et al.* 2000, Hazen *et al.* 2000, Klens *et al.* 2001); (2) not be effected by ISCO (Gardner *et al.* 1996); or (3) increase immediately following ISCO (Droste *et al.* 2002, Azadpour-Keeley *et al.* 2004). The

conflicting conclusions of the laboratory studies and field-scale results regarding the impact of oxidants on microbial populations shows that additional field-scale evidence such as that which can be found in ISCO case studies may provide additional insights into what responses should be expected from microbial populations as a result of ISCO. In addition, documenting an appreciable number of situations in which EISB or MNA with a naturally-occurring biological component were used after ISCO would also provide evidence that ISCO does not do lasting harm to biological communities.

Another concern is that ISCO using permanganate may reduce the permeability of the aquifer due to the formation of insoluble byproducts. During the reaction with organic compounds, permanganate becomes reduced, and forms manganese dioxide ( $\text{MnO}_2$ ) solids (Perez-Bonito and Arias 1991, Yan and Schwartz 1999). The precipitation of manganese dioxide solids has been a concern in that it has been the cause of permeability reductions in treatment areas and in injection well filter packs at field sites (West *et al.* 1998, Lowe *et al.* 2000, Palaia *et al.* 2004) and simulated laboratory scale studies (Reistma and Marshall 2000, Lee *et al.* 2003). However, Siegrist *et al.* (2002) performed calculations showing that manganese dioxide would fill less than 1% of the pore space during permanganate degradation of TCE at concentrations up to 54 mg/L. Other authors have noted minimal reductions in permeability in field-scale tests, even in areas of intense manganese dioxide staining (Chambers *et al.* 2000, Mott-Smith *et al.* 2000, Nelson *et al.* 2001). While the reaction stoichiometry clearly shows that manganese dioxide solids will be formed during remediations using permanganate, the degree to which this will cause permeability reductions is unclear based on the inconclusive results presented above. ISCO case studies in addition to those cited above should provide further insights into the frequency of this issue and under what conditions it can be expected to occur.

A third potential concern associated with ISCO remediation is the mobilization of heavy metals due to changes in subsurface pH and/or ORP. Chromium is a particular concern, as it is more soluble and toxic in its oxidized hexavalent ( $\text{Cr(VI)}$ ) state (Rai *et al.* 1989, Saleh *et al.* 1989) and because the USEPA has set a MCL of 100 ug/L for total chromium (EPA 2007). Hexavalent chromium has been shown to be transported at the same speed as groundwater in column experiments using permanganate while lead,

molybdenum, nickel, and copper were not (Al *et al.* 2006). Chromium may also be present as a trace impurity in permanganate, though providers of permanganate have worked to reduce the amount of chromium present in permanganate (Crimi and Siegrist 2003). Manganese dioxide particles formed during oxidation of COCs by permanganate may serve as sorption sites that immobilize metals (Crimi and Siegrist 2003). Rock *et al.* (2001) assessed chromium mobilization during hydrogen peroxide oxidation in four diverse soils containing relatively high concentrations of chromium and showed that the results in terms of chromium mobility varied significantly depending on soil characteristics. Monahan *et al.* (2005) found that zinc, cadmium, copper and lead were desorbed from kaolinite during laboratory studies, though desorption did not occur at sufficiently low hydrogen peroxide concentrations. Other authors have noted changes in metals speciation and mobility resulting from treatment with ozone (Kim and Nriagu 2000, Lestan *et al.* 2005). These results collectively show that changes in subsurface geochemistry that occur during ISCO remediation projects have the potential to mobilize metals. But the degree to which this occurs at the field-scale, and the potential health or regulatory impacts that result, has not been evaluated.

A final concern related to ISCO implementation is that the very fast reaction rates of oxidants and activators may hinder subsurface distribution. This concern appears to be most prevalent with ozone and CHP, as these reactions produce hydroxyl radicals (as well as other reactive species) and these are very short lived. Chen *et al.* (2001) noted complete decomposition of a 10 g/L solution of hydrogen peroxide in 76 mm long columns packed with silica based sand. Baciocchi *et al.* (2004) found similar results in column studies using unstabilized hydrogen peroxide but found that the addition of a phosphate stabilizer increased transport dramatically. A recent CHP literature review by Petri (2007) noted a limited number of laboratory transport (column and tank) studies. However, CHP is a commonly applied oxidant, and many vendors of this technology have proprietary stabilizing agents. For this reason, evaluating effectiveness and transport of oxidants through a case study review should shed light on the issue of oxidant distribution in the subsurface.



## 2.2 Summary of Previous Case Study Reviews

Numerous case study reviews have been conducted on environmental remediation at field sites. The unifying purpose of these case study reviews is to examine what remediation technologies are being applied, how they are being applied, the results achieved, and the cost required to achieve these results. The case studies can be grouped into two general categories: demonstration studies and broad-scale overviews. The former are generally prepared for a remediation technology that is in an early stage of development. The phrase “demonstration” refers to demonstrating that a technology is capable of working at the field-scale, and to do this, this type of case study shows a limited number of specific examples of field-scale situations where the project has been successful. The demonstration case study reviews may point to general situations where the remediation technology might be generally applicable, but provide this guidance with the appropriate caveats as the sample size is relatively small. On the other hand, broad-scale overviews examine a relatively larger sample size, and provide more quantitative results. Broad-scale studies, of which this report is an example, are performed on relatively more mature remediation technologies that have proven to be successful in some situations, and address where and how the technology is being applied, and under what situations it is most (and least) successful.

Several previous case study reviews have focused on ISCO, or contained a significant number of ISCO case studies. Attempts were made to leverage these earlier works by including their findings within ISCO-DB1, and also following up with the site contacts when such information was available. The methods used in quantitative analyses and metrics developed by these case study authors were also examined, and incorporated to varying degrees within ISCO-DB1. These case study documents are summarized in Table 2-1 on the following page, and discussed in further detail in the text that follows.

Table 2-1: Summary of Previous Case Study Reviews

Name	Author	Year	# Sites	Type	Comments
In Situ Remediation Technology: In Situ Chemical Oxidation	USEPA	1998	14	D	Focused exclusively on ISCO case studies and showed examples of its use.
Technology Status Review: In Situ Oxidation	ESTCP	1999	42	BS	Focused exclusively on ISCO and included quantitative analysis, e.g. the percentage of sites that were successful vs. those that were not and total project costs.
Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater	ITRC	2001	8	D	Used case studies as supporting appendix to ISCO guidance document.
Assessing the Feasibility of DNAPL Source Zone Remediation: Review of Case Studies	Geo-Syntec for NAVFAC	2004	28	BS	Focused on DNAPL source zone remediation including ISCO and other technologies. Performed quantitative analyses of results.
DNAPL Remediation: Selected Projects Approaching Regulatory Closure	USEPA	2004	4	D	Examined selected case studies of DNAPL sites at or near regulatory closure, including what remediation technologies were used as well as regulatory framework.
Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater: 2 <sup>nd</sup> Ed.	ITRC	2005	14	D	Used case studies as supporting appendix to ISCO guidance document.
Analysis of DNAPL Source-Depletion Costs at 36 Sites	McDade <i>et al.</i>	2005	13	BS	Examined remediation cost data for 36 DNAPL sites, including ISCO as well as other technologies.
Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent Impacted Sites	McGuire <i>et al.</i>	2006	23	BS	Examined remediation performance at 59 DNAPL sites, including ISCO and other technologies. Developed numerical metrics to assess success and rebound. Companion paper to McDade <i>et al.</i> (2005)
Critical Evaluation of State-of-the-Art In Situ Thermal Treatment Technologies for DNAPL Source Zone Treatment	Johnson <i>et al.</i> for ESTCP	2007	0	BS	Performed case study review for the purpose of providing guidance on selection of thermal remediation technologies based on generic site scenarios.

Notes: # Sites refers to number of ISCO case studies in that source.

D = demonstration type case study review

BS = broad-scale type case study review

DNAPL = dense non-aqueous phase liquid

Other acronyms as defined within the text.

### In Situ Remediation Technology: In Situ Chemical Oxidation (EPA 1998)

This document briefly summarizes ISCO technology but focuses mainly on the presentation of case studies. This demonstration type study was the first of those completed to focus specifically on ISCO case studies. The project summaries include CHP, permanganate, and ozone applications dating back as far as 1995. The 14 case studies are presented in one to two page narrative descriptions, including references and site contact information when available. General trends are not reported in a quantitative way. Due to the time that has elapsed since this report was written, attempts by the author of this thesis to follow up with the site contacts listed for these projects were unsuccessful.

### Technology Status Review: In Situ Oxidation (ESTCP 1999)

The purpose of this report was to “capture the current state of the art for this very promising technology [which] is in a state of rapid development” (ESTCP 1999). In addition to presenting an overview of the technology, the authors reviewed the available literature and databases, and called site contacts to gather further information on ISCO case studies. This study relied on survey respondents or authors of case studies to determine the contaminant removal efficiency (percent reduction achieved or pounds of contaminant oxidized as a function of the quantity of oxidant introduced), as well as determine whether or not the remediation was successful (met project goals). This paper was the first to use a broad-scale overview approach and to present the results of ISCO case study review in a quantitative way.

Overall, 42 sites were included in the preliminary “Phase I” analysis, including sites where CHP, permanganate, and ozone were used as oxidants. The survey included a roughly even distribution of public (DOD n=14 and DOE n=3) and private sites (n=25). The information for 80% (20 of 25) of the private sites was supplied by technology vendors. Of these Phase I sites, 13 were selected for the more detailed “Phase II” analysis, including a survey of hydrology, groundwater chemistry, contaminants, ISCO design, and performance results.

The results of this case study review showed that ISCO had demonstrated success in meeting remedial action objectives (RAOs) at some sites, and had failed to meet goals at others. Nearly half (17 of 42, 40%) of the sites had not completed the performance

monitoring at the time that document was written, and were classified as having uncertain success. The Air Force Center for Environmental Excellence (AFCEE) is in the process of following up with some of these projects to assess the longer term results that were achieved after ISCO implementation (Becvar 2006).

Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater (ITRC 2001)

This Interstate Technology & Regulatory Council (ITRC) guidance document presented a summary of the state of the science and regulatory framework in which ISCO was being conducted. The report also included as an appendix eight previously unpublished case studies, including projects using CHP, permanganate, and ozone. The one to two page case studies were written by regulators or consultants who were involved in the projects. As with the ESTCP (1999) case study review, the results presented in the ITRC's case study review were mixed, with some sites meeting RAOs and some sites failing to achieve the desired performance. Success was determined by the survey respondent, and was not necessarily based upon a consistent metric from site to site.

Assessing the Feasibility of DNAPL Source Zone Remediation: Review of Case Studies (GeoSyntec Consultants 2004)

This broad-scale overview focused on case study results for sites suspected to contain DNAPL, and included a variety of remediation technologies, including ISCO. The authors of this study sent out requests to project managers and owners of DNAPL sites requesting that they complete a web-based survey. The survey form included information on contaminant characteristics, subsurface geology, hydrology, and geochemistry, remediation technology design, and performance results. The survey form was designed so that respondents would select from one of several options rather than enter a specific numerical value. The GeoSyntec (2004) project team included multiple metrics used to assess success of the remediation, including: respondent perception; DNAPL mass removal; decreases in mass flux; occurrence of rebound; ability to achieve RAOs; and impacts to secondary groundwater quality.

The authors received complete responses from 118 respondents, and also entered data from 21 published case study reviews. Of these, 28 case studies listed ISCO as the primary technology, including CHP, permanganate, and ozone applications.

Chloroethenes were the most commonly treated contaminants, with chloroethanes represented as well. The survey did not include any respondents who stated that MCLs or regulatory site closure had been achieved, either with ISCO or any of the other remediation technologies.

Despite the large scope of this effort, GeoSyntec stated that additional work was necessary in this area, and that “insufficient data were [provided by respondents] for much of the information requested, which can result in the results not being statistically significant” (2004). GeoSyntec also recommended using specific numerical values rather than ranges and obtaining case study information directly rather than relying on survey responses. Both of these measures were suggested by the authors as a means to increase the completeness of the data and to allow more quantitative statistical analysis.

#### DNAPL Remediation: Selected Projects Approaching Regulatory Closure (EPA 2004b)

The EPA produced this document to present examples of field sites at which DNAPL was known or believed to have been present that were treated with in situ remediation technologies and had met or were approaching regulatory closure requirements. At the time of this report’s publication, there was significant debate in the regulatory community about whether DNAPL source zones should be aggressively remediated, or if containment of the downgradient plume was more appropriate (e.g. Sale and McWhorter 2001, 2003, Rao and Jawitz 2003, EPA 2003, Stroo *et al.* 2003). While this debate has not been conclusively resolved, DNAPL source remediation has been increasingly implemented, in part due to documents such as this EPA (2004b) case study review that showed examples of sites at which regulatory closure had been or was anticipated to be achieved. None of the projects included in this report met and sustained MCLs at the time of its writing. However, site closure with institutional controls (e.g. deed restrictions, passive venting or monitoring requirements) represent the completion of active remediation, an important milestone in an environmental cleanup project. These facts highlighted the importance of clarifying what the goals of a particular remediation project were and showed that DNAPL remediation projects may be successful despite not attaining MCLs.

Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater: Second Edition (ITRC 2005)

This update to the previous ITRC guidance document expands on the previous version, including more description of reaction chemistry and ISCO design. Activated persulfate is included in addition to the other three oxidants previously referenced. Fourteen case studies are included as an appendix to this work. These case studies are summarized in one to several pages, and include figures and photographs in some cases. The authors state that “these case studies are presented for the sole reason to illustrate the effective in situ use of an oxidant at a particular site” (ITRC 2005). Given this statement, the ITRC 2005 case studies generally report good results. However, the performance data on which these results are based is unclear. Further, the methods used to verify the data contained within the case studies, if any, is not provided by ITRC. The attempts made by the author of this thesis to follow up with the site contacts did not lead to any further information. In the most extreme case, a regulatory contact in Indiana said that he had been contacted several times regarding a site in ITRC (2005) and that he had no knowledge of that site.

Analysis of DNAPL Source-Depletion Costs at 36 Field Sites (McDade *et al.*, 2005)

This project examined the costs of DNAPL remediation using ISCO, bioremediation, thermal treatment, and surfactant/cosolvent flushing. The authors of this study collected project files for the sites both from the available literature and from visits to regulatory file rooms. By acquiring raw project data such as contaminant concentrations over time at source area monitoring wells, the authors were able to evaluate performance using a consistent metric. The authors normalized the data on a volumetric basis, calculating the cost per cubic yard treated, as opposed to cost per pound of contaminants removed, as some studies have done (ESTCP 1999). ISCO had a median treatment cost of \$125/yd<sup>3</sup> (n=13), compared to \$29/yd<sup>3</sup> for bioremediation (n=11), \$88/yd<sup>3</sup> for thermal treatment (n=6), and \$385/yd<sup>3</sup> for surfactant/cosolvent treatment (n=6). No trends were observed between cost per cubic yard treated and percent reduction in contaminant concentrations for ISCO or the other three remediation technologies.

The information contained in the McDade *et al.* report is also available in the Strategic Environmental Research and Development Program (SERDP) Source Depletion Decision Support System, an interactive Microsoft Excel-based tool available at GSI's website (GSI 2007).

Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent-Impacted Sites (McGuire *et al.*, 2006)

This study focused on the remediation of sites contaminated with chlorinated solvent DNAPL, and included 23 sites where ISCO was used as a treatment technology. This work is a companion paper to the McDade *et al.* (2005) report, and uses many of the same sites. Case study data was compiled from the literature and file reviews as in McDade *et al.* (2005). The McGuire *et al.* (2006) study is of note because the authors developed several numerical metrics to assess the performance of the remediation in a quantitative way.

McGuire *et al.* (2006) calculated the percent contaminant reduction at a given site using the following algorithm:

- 1) Geometric mean groundwater concentrations over time at a monitoring well location were calculated for both the period before and period after remediation for up to four wells located in the treatment zone.
- 2) The percent change between the geometric means before and after were calculated for each monitoring well.
- 3) The median value among the percent changes calculated for each source area monitoring well location was defined to be the overall percent reduction in contaminants at that site.

McGuire *et al.* (2006) evaluated rebound for all monitoring wells with at least one year of post-treatment data. Geometric mean values of contaminant concentrations were evaluated for both the first half and second half of the monitoring period. In situations where the post-treatment monitoring data spanned two or more years, the geometric mean of the concentrations reported for the first year after remediation was compared to the geometric mean of the last year of monitoring. In either case, rebound was said to have occurred at a monitoring well location when the geometric mean of post-treatment concentrations increased by 25% or more.

The results of this study showed that ISCO resulted in a median contaminant reduction of 72% in source area monitoring wells. Rebound of contaminant concentrations was observed at a majority of the ISCO sites examined in this report. As with their companion report, the information contained in McGuire *et al.* (2006) is also available in the interactive SERDP Source Depletion Decision Support System (GSI 2007).

The data collection and analysis methods presented by McGuire *et al.* (2006) were helpful during the development of ISCO-DB1. While the GeoSyntec (2004) report highlighted the limitations of relying on survey responses, McGuire *et al.* showed the potential benefits of developing quantitative metrics to assess various aspects of remediation performance. This report also demonstrates the value of visiting the file rooms of regulatory agencies to acquire project files directly and then analyzing the raw data to ensure a consistent analysis. But due to the complexity of site remediation, extreme care must be taken when defining metrics so that they are applicable under a wide range of conditions. For example, consideration should be given to whether or not several remediation technologies were used together in a coupled approach. For example, if ISCO is applied to a site shortly after excavation of the contaminated vadose zone soils, it is difficult to separate the results achieved by ISCO versus those that would have occurred due to source removal alone. Also, pilot scale tests that only treat a portion of the contaminated area, and are not designed to be a permanent remedy, may be expected to exhibit contaminant rebound.

Critical Evaluation of State-of-the-Art of In Situ Thermal Treatment Technologies for DNAPL Source Zone Treatment (ER-0314) (ESTCP 2007b)

This ESTCP-funded project is assessing the performance of thermal remediation technologies employed to treat DNAPL source zones. A part of this work involves the examination of case studies. The purpose of the case study review component is to provide a basis for a guidance document that will allow practitioners to estimate performance expectations of a proposed thermal remediation based on a set of generalized site scenarios. These generalized scenarios will include site geology and contaminants present. The geologic media present at each case study site are being grouped into six categories based on permeability, heterogeneity, and consolidation of the



geologic media. This same categorization method is used in ISCO-DB1, and further description is given in Section 3.3.3.

While focusing on a different remediation technology, the goals of this thermal remediation project are similar to that of ISCO-DB1. For this reason, many of the methods of data collection and reduction follow after that project. ISCO-DB1 departs from the ER-0314 project methods in that change in mass flux as a result of remediation is not used as a primary performance metric in ISCO-DB1, for reasons to be discussed in the Performance Metrics Section 3.3.3.

### Conclusions Regarding Previous Case Studies

The case study documents described above were reviewed both to obtain information on case study data collection and analysis methods, and also as a means to populate ISCO-DB1 from existing ISCO case studies. This review provided insights into project parameters to consider, metrics to assess performance, and fruitful data collection avenues. Specifically, the broad-scale analyses (ESTCP 1999, GeoSyntec 2004, McDade *et al.* 2005, McGuire *et al.* 2006) showed the merits of attempting to gather a relatively large dataset and performing statistical analyses to examine trends. These case study reviews also demonstrated the need to develop meaningful metrics with which to assess the case studies and also the requirement that these be calculated or analyzed in a consistent way. For example, the GeoSyntec (2004) report left the definition of rebound up to the survey respondent, thereby losing the ability to ensure that this phenomenon is described consistently from site to site. The means through which the metrics used by others were borrowed or modified is described in detail in Section 3.3.

These previous case studies also showed the importance of gathering case study reports directly rather than relying upon survey respondents to fill out forms from which the database would be populated. Visits to regulatory file rooms and direct contact with site regulators both proved to be valuable data acquisition techniques during the population of ISCO-DB1. The case study reports (e.g. ESTCP 1999, GeoSyntec 2004, McDade *et al.* 2005, McGuire *et al.* 2006) themselves also proved to be a valuable source of information. To the degree possible, the data contained in these various case studies were entered into ISCO-DB1, and attempts were made to gather further information from site contacts. Further information on how these previous case study reviews were

leveraged to benefit this thesis project and how their techniques were borrowed and modified is included in the Methods section that follows.

### 3.0 METHODS

This section describes the methods used in the various stages of this project. Included are the conceptual design of ISCO-DB1, the data collection methods, the means of normalizing the data into a consistent format through treatment and reduction, and quality assurance and quality control measures. Finally, this section addresses the limitations of the methods and measures taken to mitigate these limitations.

#### 3.1 Database Design

This section describes the general procedures and theoretical considerations used during the design and development of ISCO-DB1, a process that began in the summer of 2006. The design effort considered both the theoretical considerations related to the engineering of an ISCO remediation and also general database design theory.

Existing case studies pertaining to ISCO and other remediation technologies were acquired and reviewed as discussed above (Section 2.2). In addition to being sources of field sites for this work, previous case study reviews were also examined with respect to how the authors analyzed their data. Of particular interest were what parameters were included in previous case studies, how different field sites were lumped together for analysis, and how performance results were calculated and normalized. When deemed appropriate, parameters were selected that were consistent with previous work, both to allow comparison to those previous works and also to keep with precedent. In certain situations, departures were made from previous work when theoretical or logistical considerations required. The specifics of these decisions are included in the following subsections.

A review of database design theory showed that the relational database was the most appropriate choice for this project. The three major database structures are the relational database, the hierarchical database, and the network database. The relational database is conceptually thought of as a table or group of tables. The hierarchical and network approaches are based on groupings of data in which major categories (called “parents”) are listed with their components (“children”), and the components are generally constrained to a single parent. The relational database is most appropriate to

ISCO applications because ISCO applications consist of various data that are in theory independent of one another. By way of comparison, the car model Taurus by definition constrains the make to be Ford Motor Company. In ISCO remediation, a site's geology and contaminant distribution do not by definition constrain the remediation methods or the likelihood of success, or any other parameters (though geology and contaminants can certainly make ISCO extremely difficult or unlikely to succeed). While this overall effort is designed to investigate possible relationships between site conditions, ISCO design, and result, statistical theory dictates that the starting hypothesis be that these parameters are all unrelated.

The initial stage of database design did not specifically consider the likelihood of attaining the desired data, but rather included as wide a range of parameters as was considered relevant for the analyses envisioned. Due to this effort towards inclusion of information, the list of parameters in the original database design included approximately 120 different parameters. This list grew during the data collection and entry process. However, it became apparent that data pertaining to all parameters would not be available in all reports. A comparison of the data that was most readily available as opposed to the larger list of desired data will be discussed with the Database Parameters (Section 3.2.3).

Each parameter was of one of three types of variables. The first, numerical values, could consist of any of a range of numbers. The range of values that this variable could assume depended on the parameter (e.g. COC concentrations greater than zero<sup>1</sup> and less than the solubility limit) and was entered in consistent units. The second type, categorical values, limited the parameter to taking on only one of a specific set of values. For example, the "oxidant" parameter was constrained to only be one of the six oxidants included in ISCO-DB1. The last category is binary variables, also known as dummy, Bernoulli, or bound variables, a variable constrained to take on a value of 0 or 1. Binary variables used in ISCO-DB1 are responses to questions such as "Were MCLs reached after ISCO?" and always take on a value of 1 when true and 0 when false.

---

<sup>1</sup> In samples in which a COC was analyzed for and not detected at the site, the field pertaining for this COCs concentration in ISCO-DB1 was left blank so that that particular site would be ignored when performing queries pertaining to that particular COC. In situations where a COC was detected at some locations and not others, non-detect (ND) values were entered as one tenth of the laboratory reported Method Detection Limit (MDL).

## 3.2 Data Collection

This section describes how the data were collected prior to being entered into ISCO-DB1. Discussion includes where the data were found, what type of information was examined, and specific collaborations made with other SERDP/ESTCP, DOD, and EPA projects. This aspect of the work represented a significant portion of the time expended during the work, and a great deal was learned regarding how best to access information as this effort progressed. The amount of data collection was needed to produce as large a sample size as possible prior to statistical analysis.

### 3.2.1 Sources of Data

The case studies used to populate ISCO-DB1 were collected from many different sources, including regulatory project files, peer-reviewed literature, technical bulletins and guidance documents, previous published case studies, online databases, conference proceedings and presentations, and case studies supplied by technology vendors. The thoroughness of the data generally contained in each of these sources and the degree to which it was considered as being reliable is described in the section on quality assurance (Section 3.4). The data sources are summarized in Table 3-1 on the following page, and discussed further in the text that follows.

Table 3-1: Summary of Data Sources

Type	Received From	Rel.	Thor.	Comments
Regulatory Project Files	Internal Project Team, State and Federal Regulators, Consultants, Project Owners	V. Good	Good to V. Good	These documents were the preferred source of information, and consist of reports submitted to regulators by environmental professionals. Thoroughness was sometimes less than desired if multiple consultants produced multiple reports and only one report could be obtained for review.
Science and Engineering Journals	Library Searches	V. Good	Good	These journal articles were a reliable source of information, but in many cases did not provide all the desired details because they represent a several page distillation of what would be reported to regulators in a more lengthy report.
Technical Bulletins and Guidance Documents	Online and Library Searches	V. Good to Fair	V. Good to Fair	Case studies were often included within these documents as supporting materials. In many cases the materials were less thorough than needed for this work. However, even brief case studies allowed for the collection of data on that site though other means, such as contacting site regulators. The authors' QA/QC measures taken during case study compilation were not always included in these reports.
Case Study Reviews	Online and Library Searches	V. Good	V. Good to Fair	These case study reviews included both demonstration and broad-scale type studies. The former's data is generally quite thorough regarding a limited number of sites. Broad-scale studies reported relatively few details on a larger number of projects. Both types of case study review were valuable in that they provided the names of sites so that further information could be gathered through other means.
Online Databases	Online Searches	V. Good to Fair	Good to Fair	There are several online databases devoted to remediation case studies, including ISCO sites. The content varies significantly among the case studies, and the QA/QC measures taken by the database managers to verify the data are unclear.
Conference Proceedings	Conference Host	Good	V. Good to Fair	Case study summaries of ISCO remediations reported in conference proceedings contain data of varying quality. This source provides limited ability to acquire further information as the project owner has often allowed only a limited amount of information be released and removed the site name and city from the reported material.
Technology Vendor Information	Vendor Webpages	Fair	Fair	Many technology vendors have brief case study summaries available on their websites. These are intended to provide an overview of the work rather than specific details.

Notes: Rel. = reliability of data, Thor. = thoroughness of data (see Section 3.4 for the distinction between these two terms).

### Regulatory Project Files

This group refers to reports that were prepared for submittal to regulatory agencies, most often by a consultant on behalf of the site owner, as required by the regulatory framework under which the site was being remediated. The titles of the reports vary depending on the regulatory context in which the remediation was being performed. For example, at sites being remediated under CERCLA, the Remedial Investigation (RI) Report would be reviewed to determine the nature and extent of contamination as well as the site characterization techniques used, the Remedial Action (RA) Report would be reviewed to determine how ISCO was designed and implemented, and reports documenting subsequent sampling would be used to determine what the results of ISCO were. In some cases, Feasibility Study (FS) and Remedial Design (RD) reports were reviewed as well. For sites remediated under RCRA or a state regulatory program, the names of the various reports differed from those described above. However, attempts were made to gather as much information as possible regarding each site, including as many project reports as were available. Also included within this group were the regulatory authority's responses to the results of the ISCO remediation, such as a No Further Action letter, NPL Deletion Report etc. In some situations, direct personal correspondence with the site regulator was used in lieu of receiving hard copies of the specific regulatory response documents.

Regulatory project files were collected with the following general methods. Many sites were received from internal project team sources such as the U.S. Navy and CH2M HILL. For some sites, information was requested through the Freedom of Information Act (FOIA) or a state's equivalent to that program, and received by mail or by visits to regulatory file rooms. Less formal requests to site regulators also proved to be a valuable means to getting project reports. Finally, full copies of the project reports were sometimes available online, such as at the state of California's Department of Toxic Substances Control (DTSC) Envirostor website, or the DOE's Office of Scientific and Technical Information's Information Bridge (URLs provided in the online sources section).

### Science and Engineering Journals

Some ISCO case studies are presented in science and engineering journals. When journal articles with ISCO case study data were found, the data was entered into ISCO-DB1 as in the journal article. A summary of the journals from which data were gathered is shown in Table 3-2 below.

Table 3-2: Examples of ISCO Case Study Papers in Science and Engineering Journals

<b>Journal Name</b>	<b>Example Citations</b>
Environmental Science & Technology	Nelson <i>et al.</i> 2001
Groundwater Monitoring & Remediation	Chapelle <i>et al.</i> 2005 McGuire <i>et al.</i> 2006
Remediation	Greenberg <i>et al.</i> 1998 McDade <i>et al.</i> 2005

Notes: This table is not meant to be an exhaustive list of journals that have published articles on ISCO case studies.

### Technical Bulletins and Guidance Documents

Several government agencies produce technical bulletins that contain information relevant to this project. These included bulletins related to ISCO that had supporting case study information in appendices and also bulletins prepared to report the result of a particular case study that used ISCO to remediate groundwater. These documents are generally available online at the publishing agency's website, and were found in citations of other authors or through internet search engines. Examples of such bulletins are shown in Table 3-3 on the following page.

### Previous Case Study Reviews

Several case study documents have been published, some focusing on ISCO exclusively, and others including ISCO case studies along with other remediation technologies. A listing of these case studies was provided in Table 2-1 (Section 2.2). These case studies were entered into ISCO-DB1 to the degree possible considering the breadth of the information provided. Attempts were also made to follow up with the site contacts to gain further information, which was sporadically available.



Table 3-3: Examples of ISCO Case Studies in Technical Bulletins and Guidance Documents

Source Name	Publisher	Internet URL	Example Citations
Innovative Technology Summary Reports (ITSRs)	DOE	<a href="http://www.osti.gov/bridge/basicsearch.jsp">http://www.osti.gov/bridge/basicsearch.jsp</a>	DOE 1999, DOE 2000
Remedial Action Operation Optimization Reports	NAVFAC	(see notes)	NAVFAC 2000a, NAVFAC 2000b
ESTCP Guidance Documents	ESTCP	<a href="http://www.serdp-estcp.org/ISCO.cfm">http://www.serdp-estcp.org/ISCO.cfm</a>	ESTCP 1999
EPA Guidance Documents and Bulletins	EPA	<a href="http://www.epa.gov/epahome/pubsearch.html">http://www.epa.gov/epahome/pubsearch.html</a>	EPA 1998, EPA 2004b
ITRC Guidance Documents	IRTC	<a href="http://www.itreweb.org/gd_ISCO.asp">http://www.itreweb.org/gd_ISCO.asp</a>	ITRC 2001, ITRC 2005

Notes: This table is not meant to be an exhaustive list of all technical bulletins that have reported on ISCO case studies. NAVFAC reports and ITSRs may be found through searches of general internet search engines.

### Online Databases

There are several online databases that contain information on environmental remediation case studies, including ISCO, shown on Table 3-4. These fall into two major categories. The first group is focused on environmental remediation case studies with the purpose of demonstrating how and under what circumstance a remediation was performed and what the results were. These include websites hosted by the State Coalition for the Remediation of Drycleaners, the EPA Technology Innovation Program's Hazardous Waste Clean-Up Information (CLU-IN) program, and the Federal Remediation Technology Roundtable (FRTR) case study database. These websites are similar in that the information may be queried by remediation technology or other parameters, and the query results are displayed as links to individual case studies. The amount of information contained in each of the case studies is highly variable. The two EPA CLU-IN sites and the State Coalition for the Remediation of Drycleaners both allow users to enter site profiles. The QA/QC procedures implemented once a new site is submitted are unknown. Once accessed online, the information contained at each page was entered into ISCO-DB1. When site contact information was provided with the case study this person was contacted to verify that the information available online was correct

Table 3-4: Online Resources for ISCO Project Information

Hosting Organization	Internet URL	Information Available
State Coalition for the Remediation of Drycleaners	<a href="http://www.drycleancoalition.org/profiles">http://www.drycleancoalition.org/profiles</a>	Webpage summaries with details of remediations performed at dry cleaners using ISCO and other technologies. Site summaries may be queried by remediation technology.
EPA CLU-IN (chemox)	<a href="http://www.clu-in.org/products/chemox">http://www.clu-in.org/products/chemox</a>	Webpage summaries of ISCO remediations. Summaries may be queried by remediation technology, impacted media, and other parameters.
EPA CLU-IN (fractured rock)	<a href="http://www.clu-in.org/fracrock/">http://www.clu-in.org/fracrock/</a>	Similar to above and pertaining to fractured rock sites only.
Federal Remediation Technology Roundtable (FRTR)	<a href="http://costperformance.org/search.cfm">http://costperformance.org/search.cfm</a>	Webpages summaries of remediation projects including cost data. Summaries may be queried by remediation technology, impacted media, and other parameters.
USEPA	<a href="http://www.epa.gov/superfund/sites/npl/npl.htm">http://www.epa.gov/superfund/sites/npl/npl.htm</a>	Contains information on CERCLA NPL sites, including reports such as Five-year Reviews, Records of Decision etc. Cannot be queried by remediation technology.
CalEPA State Water Resources Control Board (SWRCB)	<a href="http://www.geotracker.waterboards.ca.gov/search/">http://www.geotracker.waterboards.ca.gov/search/</a>	Contains site location, regulatory history, regulator contact information and ability to download project reports submitted to SWRCB in 2005 to the present. Cannot be queried by remediation technology.
California Department of Toxic Substances Control (DTSC)	<a href="http://www.envirostor.dtsc.ca.gov/public/">http://www.envirostor.dtsc.ca.gov/public/</a>	Contains site location, regulatory history, regulator contact information and ability to download certain project reports. Cannot be queried by remediation technology.
Colorado Department of Public Health and the Environment (CDPHE)	<a href="http://emaps.dphe.state.co.us/hmtrackreporter/VCRAFront.aspx">http://emaps.dphe.state.co.us/hmtrackreporter/VCRAFront.aspx</a>	Contains site location, regulatory status and regulator contact information. Cannot be queried by remediation technology.
Oregon Department of Environmental Quality (ODEQ)	<a href="http://www.deq.state.or.us/lq/ECSI/ecsi.htm">http://www.deq.state.or.us/lq/ECSI/ecsi.htm</a>	Contains site location, regulatory status, regulator contact information, and reports ODEQ has on file. Reports are available for selected sites. Cannot be queried by remediation technology.
Texas Commission of Environmental Quality (TCEQ)	<a href="http://www.tceq.state.tx.us/remediation/vcp/vcp.html#Database">http://www.tceq.state.tx.us/remediation/vcp/vcp.html#Database</a>	Contains links to tables with site location, regulatory status, regulator contact information, and comments field that may include remediation technology used for treatment.
Wisconsin Department of Natural Resources (WDNR)	<a href="http://botw.dnr.state.wi.us/botw/SetUpBasicSearchForm.do">http://botw.dnr.state.wi.us/botw/SetUpBasicSearchForm.do</a>	Contains site location, regulatory status, regulator contact information, and a list of reports WDNR has on file. Cannot be queried by remediation technology.

Notes: This table is not meant to be an exhaustive list of all state regulatory agencies that have online project databases, but rather examples that were used during the execution of this work. This table is current as of the date of this writing. CalEPA = California Environmental Protection Agency

and to request further information. Responses to such requests were received for approximately one fifth of the online sources included in ISCO-DB1. These websites are valuable when conducting a remediation technology-specific case study review such as this one because they may be queried by remediation technology. They were also valuable as a means of finding the names of ISCO sites that were previously unknown as well as contact information so that an attempt could be made to gather additional information such as complete project reports through other avenues.

The second type of online databases are those hosted by regulatory agencies presumably with the purpose of informing the public as to the location of contaminated sites, the contaminants present there, and what is being done to clean them up. These include the EPA's NPL website and those of the various state regulatory agencies shown on Table 3-4. These databases include information on the site locations, regulatory project number and status, and the regulator's contact information. In some cases project reports may be downloaded from these types of websites. These websites are generally queried by site name, location, or regulatory project number, not by remediation technology. They were used during data collection as a means to gain further information from sites whose name and/or location were already known to the project team but for which little information was available (e.g. sites reported in conference proceedings or at the case study websites discussed in the previous paragraph). If project reports were available online, they were downloaded and entered into ISCO-DB1. If project reports were not available, requests were made to obtain the information directly from the regulator or through FOIA.

### Conference Proceedings

The proceedings from remediation conferences were reviewed for case study information pertaining to ISCO projects. Conference proceedings examined covered the period 1998 to 2006 and included the Battelle International Conferences for the Remediation of Chlorinated and Recalcitrant Compounds, the Oxidation Reduction Technologies (ORT) International Conferences on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater, and the University of Massachusetts (UMass) Annual International Conference on Soils, Sediments and Water.

In situations when a full paper was included in conference proceedings, the data from this paper were entered into ISCO-DB1. Abstracts were entered as well, but only after attempting to get further information from the presenting authors.

#### Technology Vendor Information

Many providers of ISCO technology have case study information available on their websites which were found using internet search engines. These materials are provided by the vendors to aid in their marketing efforts by providing potential clients summary information regarding past implementations of their ISCO technology. This information was downloaded and reviewed, and if deemed useful entered into ISCO-DB1.

#### Summary of Sources of Data

Simply reviewing the project documents, published papers, reports, and website information did not produce data that was of a consistent reliability and thoroughness. When site name and location were provided in sources of lesser thoroughness (e.g. conference proceedings, online summaries, vendor information), attempts were made to gather further information by other means, such as contacting regulators or consultants to request further data, filing FOIA requests, or querying various online remediation databases. The methods used during data entry and analysis to address the lack of consistency with regard to thoroughness and reliability is discussed further in Section 3.4.1.

#### *3.2.2 Collaboration Efforts*

To increase efficiency, efforts were made to collaborate with other ongoing projects whenever possible. One example is a project funded by ESTCP titled Development of a Protocol and Screening Tool for Selection of DNAPL Source Area Remediation (ER-0424) (ESTCP 2007c).

Data was also shared with another project titled Post-ISCO Geochemical Impacts Associated with Permanganate Oxidation consisting of East Tennessee State University and the EPA's Kerr Laboratory in Ada, Oklahoma. This project is focusing on permanganate applications, and examining the post-ISCO impact of manganese on

groundwater quality. Numerous project files were exchanged between these two project teams, as were insights into how best to collect data regarding ISCO projects.

The ESTCP thermal remediation project team (ER-0314) previously referenced was also a valuable resource during the data collection effort (ESTCP 2007b). While this project team is examining a different remediation technique, it provided some important insights into fruitful data collection avenues based on their experience, such as engaging representatives of regulatory agencies whenever possible.

AFCEE is currently in the process of updating the ESTCP (1999) report to determine the status of the projects included in that report, especially those that were classified as having an uncertain outcome when the report was written (Becvar 2006). As of the date of this writing, the results of AFCEE's investigation have not yet been received by this author.

### *3.2.3 Database Parameters*

As initially designed, ISCO-DB1 contained over 120 parameters with a goal of including any parameter that could be relevant from a theoretical perspective. These parameters included attributes in the following general categories:

- General Site Information
- Contaminant Characteristics
- Geologic/Hydrologic/Geochemical Characteristics
- Site Characterization Techniques
- ISCO Design
- Remediation Results

These parameters may also be conceptually grouped into different categories when considered in the framework of the remediation design process. During selection of a remediation technology, certain constraints are dictated by the site conditions, decisions are made based upon these constraints, and finally, a result is achieved.

Given variables refer to those parameters that are independent of everything else, and over which the remedial project manager (RPM) and environmental design engineer have no control. Given variables include the site conditions and history, geology, hydrology, geochemistry, and the contaminants present and their distribution.

Results variables are the purely dependent variables, whose values are the result of the entire remediation process. Examples of results variables include whether or not the goals were achieved and the percent reduction in contaminants.

Decision variables include the site characterization methods and ISCO design. Decision variables are dependent or independent, depending on the context in which they are viewed. They are dependent variables relative to the given variables, because certain geologic media and contaminants are not amenable to all characterization and remediation technologies. The decision variables are independent variables relative to the results variables because the result of an ISCO remediation depends on the ISCO design, and conceivably on the site characterization methods used.

The combination of English and metric units used in ISCO-DB1 follow those most commonly used in the U.S.-based project reports, used in reporting by analytical laboratories, and promulgated in U.S. environmental regulations.

### **3.3 Data Treatment and Reduction**

This section describes the methods used to enter the data such that the input for each parameter was consistent across all sites and from the diverse group of data sources. The data reduction included means of grouping together sites that were similar with respect to a given parameter (e.g. subsurface geology) and also the development of metrics to quantify data in a consistent way.

#### *3.3.1 Grouping of Subsamples*

The ability of statistical techniques to explain phenomena in a meaningful way increases as the number of samples in a dataset increases. The number of case studies included in ISCO-DB1 is 242. These sites span a wide range of contaminants, oxidants, and geological conditions. However, when a specific subset of the sites is being examined, for example chlorinated benzene compounds, the sample size decreases, sometimes significantly. For this reason, it is necessary to lump together groups of similar sites whenever possible so that analyses could be performed on larger sample sizes. Sites were assigned to these groups with consideration of physical or chemical similarities and previous work, and are described below.

## Site Geology

Each site was assigned to a Geology Group denoted A through F based on the subsurface geology. This grouping system is taken from the ESTCP Critical Evaluation of State-of-the-Art In Situ Thermal Treatment for DNAPL Source Zone Treatment (ER-0314) lead by Dr. Paul Johnson of Arizona State University (ESTCP 2007b), which is in turn a modification of an NRC system (2004). The basis for the grouping is the permeability, heterogeneity, and consolidation of the geologic media. The boundary between permeable and impermeable unconsolidated media is reported as a saturated hydraulic conductivity (K) of greater than or less than  $10^{-5}$  cm/s (0.028 ft/day), respectively. For unconsolidated media, the boundary between heterogeneous and homogenous material is a range of hydraulic conductivity (maximum / minimum) of greater than or less than 1000, respectively. Note that the maximum and minimum hydraulic conductivity values used to assess heterogeneity are those that are present in a particular stratum, even if the stratum is too thin to have its hydraulic conductivity measured directly in the field. For example, a site underlain by sand with intermittent clay stringers would be considered heterogeneous even if the results of slug testing in wells with 10-foot screens did not differ by a factor of 1000. The consolidated (rock) material is subdivided based on the matrix porosity, which is inferred from the description of the rock type in project reports rather than a reported porosity value. A list of the six Geology Groups is shown below.

- Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )
- Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )
- Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )
- Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )
- Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)
- Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

In this project, sites were assigned to the above groupings based on the target treatment zone (TTZ) of the ISCO remediation. For example, a site underlain by a thick deposit of clay with a one-foot thick sand aquifer overlying bedrock would be assigned to Group C if the sand layer bounded by clay (above) and rock (below) was the zone to be treated during ISCO application. This site would not be assigned to Group A because of

the likely interaction between the permeable sand comprising the bulk of the TTZ and the less permeable materials above and below. It would not be assigned to Group D because the majority of the TTZ is permeable even though the bulk of the site's subsurface geologic media is not.

While this system arbitrarily imposes distinct groupings based on geologic properties that are in fact present on a continuum in the real world, it was a necessary step required to simplify the data analysis, and also followed precedent set by previous work (NRC 2004, ESTCP 2007b).

### Oxidants

The oxidants used during ISCO remediation projects were placed into six groups based on the oxidizing agent being used. These groups are:

- Permanganate ( $\text{MnO}_4^-$ ), including potassium and sodium forms
- CHP ( $\text{H}_2\text{O}_2$  w/  $\text{Fe}^{2+}$ ), also known as modified Fenton's reagent
- Ozone ( $\text{O}_3$ )
- Persulfate ( $\text{S}_2\text{O}_8^-$ )
- Percarbonate (e.g.  $[\text{Na}_2\text{CO}_3]_2 \cdot 3\text{H}_2\text{O}_2$ )
- Peroxone, ozone with hydrogen peroxide catalyst

### Treatability Studies

Laboratory-scale treatability studies conducted during design of an ISCO system were placed into two distinct groups. The first, batch studies, included vial-scale tests in which site soil and/or groundwater were placed in a small vial and allowed to react with the oxidant for a period of time. The second group, transport studies, included experiments in which a column or tank was packed with geologic media and contaminants, and oxidants were caused to flow through the experimental apparatus. Projects that were referred to as treatability studies but were conducted at the field-scale were classified as pilot studies, which were analyzed separately from laboratory treatability studies as defined above.

The type of information that a treatability study produced was also recorded in ISCO-DB1. The five groupings of treatability studies as well as brief descriptions are listed below in Table 3-5.



Table 3-5: Types of Treatability Studies

<b>Type of Treatability Study</b>	<b>Description</b>
Degradation	The study demonstrated that the site's COCs could be degraded by ISCO oxidant(s).
Optimization	The study examined multiple oxidant and/or activator concentrations to determine ideal ISCO chemistry conditions for field-scale application.
Secondary Groundwater Impacts	The study evaluated the potential for adverse impacts to secondary groundwater standards (e.g. mobilization of metals).
Natural Activators / Buffers	The study evaluated whether naturally occurring minerals (most commonly iron) could activate ISCO reagents without the addition of other activators. Also included in this group were studies that evaluated the presence of naturally occurring minerals (e.g. carbonates) that could hinder the ability to modify the subsurface pH during ISCO.
NOD / SOD	The study quantified the degree to which the subsurface media would consume oxidants. This group of studies included those performed on either contaminated or uncontaminated media, and also both kinetic studies in which the laboratory measured oxidant concentrations versus time and ultimate demand studies in which the laboratory measured the concentration of oxidant remaining after a predetermined amount of time.

Within ISCO-DB1, each of the five categories above existed as a dummy variable, taking a value of one when the treatability study gathered that type of information and zero when it did not. In many cases a treatability study would provide information that fit into more than one category, and in these cases that project's treatability study would be assigned a value of one for each of the applicable categories.

### Project Goals

ISCO has been used in an attempt to meet a wide variety of goals. Naturally, the level of effort required to meet the project goals and the likelihood of doing so depends on what those goals are. During the analysis of the case studies, five general categories of goals, or RAOs became clear. These five groups are listed in Table 3-6 and described briefly below.

Table 3-6: Remediation Goals in ISCO-DB1

Goal of Remediation	Description
Meet MCLs	The project team attempted to meet the most stringent regulatory groundwater criteria for COC concentrations.
Meet ACLs	The project team attempted to meet alternative cleanup levels (ACLs) in groundwater. ACLs are a numerical concentration to be met that are by definition higher than MCLs. Their use was often associated with a site-specific risk evaluation and/or a regulatory framework in which low-yield aquifers are not required to meet MCLs.
Reduce Mass/Concentration by Predetermined Percent	A set percent reduction in COC mass or concentration was targeted prior to remediation.
Reduce Mass/Concentration/Time to Cleanup	This goal differs from the above in that there was not a predetermined numerical percent reduction that was to be met, but rather the goal was just to generally reduce contaminant mass and/or concentration, thereby reducing the time to cleanup.
Evaluate Effectiveness or Optimize Future Work	This goal is most common in pilot studies, and includes a field-scale evaluation of effectiveness as well as remedial design analysis, such as well spacing, oxidant persistence, etc.

The last two types of goals in Table 3-6 merit further discussion. From a literal standpoint, if even one molecule of contaminant is oxidized during ISCO, then ISCO has resulted in a reduction in mass. However, such a strict interpretation would result in a metric that is achieved each time it is attempted, and is therefore not a useful metric for further analysis. To avoid this situation, sites in ISCO-DB1 that attempted to reduce mass would be considered to have failed to have done so if their sampling program did not demonstrate a reduction in contaminant mass as inferred through monitoring of contaminant concentrations in groundwater and sometimes soil after ISCO. An example of such a situation would be one in which groundwater concentrations remained constant or increased following ISCO, and no soil sampling for COCs was performed after ISCO.

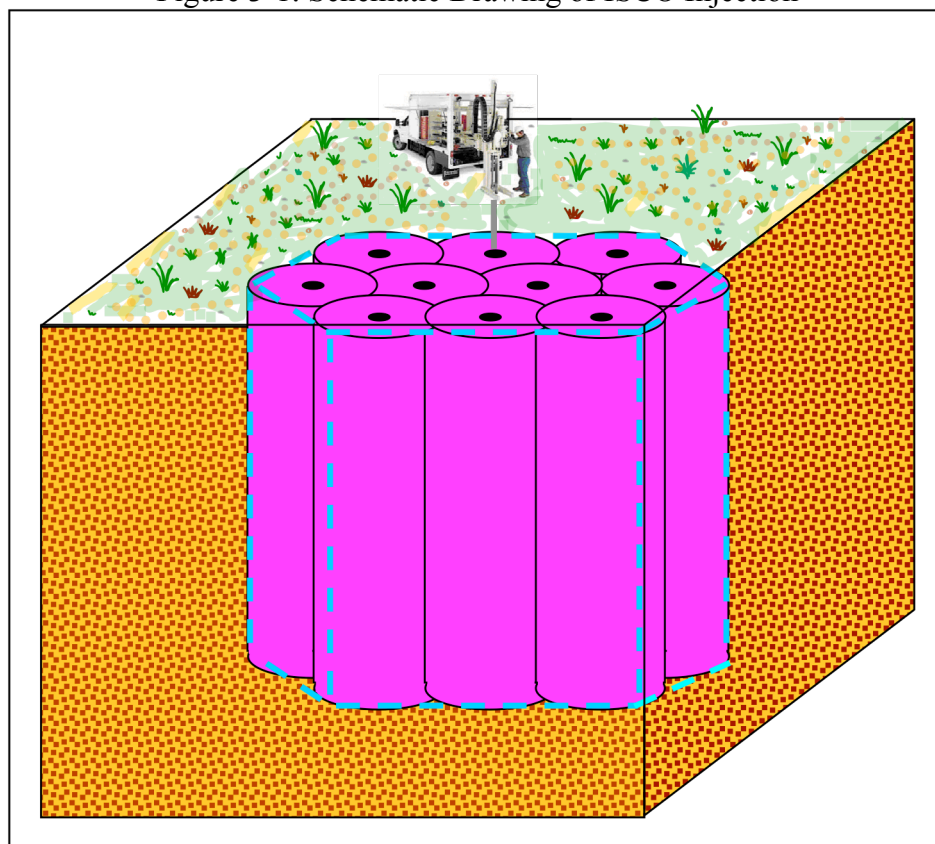
Failure to meet the goal of evaluating effectiveness (Table 3-6) was assigned as follows. Consideration was given to how the case study project team responsible for the case study project evaluated effectiveness through their performance monitoring program. This monitoring must have, at a minimum, evaluated the impact of ISCO on aqueous phase COCs and also the distribution of the oxidant throughout the treatment

zone. In situations where a project team did not do both of the above, they were considered to have deficient been in their attempt to evaluate the effectiveness of ISCO at their site, and hence did not meet the goal of effectiveness evaluation as defined in ISCO-DB1 (Table 3-6).

### 3.3.2 *ISCO Design Metrics*

ISCO-DB1 was designed to attempt to capture the complicated design of a remediation system that was tailored to site-specific conditions through the use of several parameters that would allow comparison between diverse ISCO projects. For this reason, metrics were defined to calculate the values of these parameters in a systematic, meaningful, and consistent way that would describe the data under a host of different circumstances. Explanations of these ISCO design metrics are listed in the paragraphs that follow. The metrics can be visualized using the schematic diagram presented in Figure 3-1 on the following page. This diagrams shows a direct push drill rig delivering reagents shown in purple to the subsurface below the site. The distance the oxidant has traveled from the injection point is the radius of influence (ROI). Each of the cylinders is the area of influence of one particular injection point. Collectively, these overlapping cylinders define the TTZ, shown with the dashed lines.

Figure 3-1: Schematic Drawing of ISCO Injection



Notes: The above schematic is an idealized representation of oxidant delivery. The oxidant is shown traveling an even distance in all horizontal directions from the injection point. Due to variations in subsurface geology, the distribution of oxidants is likely never this uniform in field applications. Geoprobe drawing from EPA's clu-in.org.

### Number of Pore Volumes Delivered

The term pore volume generally refers to a dimensionless number that relates the volume of solution introduced during remediation to a volume of pore space in a given volume of geologic media. In the case of ISCO-DB1, the ISCO design's number of pore volumes is calculated as

$$\# \text{ Pore Volumes } [-] = \frac{\text{Volume of Oxidant Injected } [L^3]}{\text{TTZ Volume } [L^3] * \text{porosity } [-]} \quad (3-1)$$

where the volume of oxidant injected includes only solutions that contain the oxidant, either with or without a catalyst. Catalysts and pH adjusters are not included in the calculation unless they are injected simultaneously with the oxidant. The TTZ, when not stated explicitly in the source document, is defined in areal extent as the outer edge of the injection location array with the design ROI considered in estimating the lateral extent of

the TTZ (the hexagonal shape surrounding the ten ovals in Figure 3-1 above). The TTZ volume is calculated from the TTZ aerial extent by multiplying the thickness of the interval over which oxidant is injected (vertical height of cylinders in Figure 3-1). The injection is assumed to proceed in a horizontal manner from the injection point due to hydraulic conductivity generally being considerably greater in the horizontal direction than the vertical direction (Freeze and Cherry 1979, Cleary 2004). When not given in the source text, the porosity is assumed to be 0.35. While an assumed porosity of 0.35 may not be correct in all cases, a total range of variation between 0.1 (glacial till) and 0.6 (clay) is the maximum reported for most unconsolidated media (Fetter 2001). The number of pore volumes calculated in ISCO-DB1 vary by over four orders of magnitude (Appendix B, Table B-20).

#### Oxidant Loading Rate

This parameter is a ratio of the mass of the oxidant injected to the total mass of geologic media in the TTZ, and is also referred to as the oxidant dosing or oxidant dose. This value is calculated by:

$$\text{Oxidant Loading Rate [g/kg]} = \frac{\text{Mass of Oxidant Injected [M]}}{\text{Volume TTZ [L}^3\text{] * Bulk Density [M/L}^3\text{]}} \quad (3-2)$$

The units for oxidant loading rate (g oxidant / kg bulk subsurface media) are based on industry standards, and also to allow easier comparison with total organic carbon (TOC) and NOD during design analysis. These units are M/M, and therefore consistent with the units on the right hand side of the above equation. The mass of total oxidant injected is generally reported explicitly. When it is not, it is calculated by multiplying the total volume of oxidant solution delivered by the weighted average oxidant solution concentration. When not reported explicitly, the formation dry bulk density for unconsolidated sediments is assumed to be 110 lbs/ft<sup>3</sup> (50 kg/ft<sup>3</sup> or 1.76 g/cm<sup>3</sup>) (Freeze and Cherry 1979). While it is admitted that there may be errors associated with assuming a dry bulk density when none is provided, this likely varies within plus or minus 20% of this amount (90 to 130 lbs/ft<sup>3</sup>), while the range of oxidant loading rates in ISCO-DB1 vary by over a factor of 5,000 (Appendix B, Table B-20).

When permanganate was used as the oxidant, the oxidant loading rate is calculated based on the mass of permanganate anion introduced. The weight of the

cation (K or Na) is subtracted to allow consistent calculation regardless of which permanganate form was used. No corrections were made to account for impurities based on the grade of permanganate used. The oxidant loading rate for persulfate was reported as the persulfate anion, and no corrections were made for oxidant purity.

### 3.3.3 *Performance Metrics*

Several metrics were developed to evaluate the success of each project in ISCO-DB1. These included quantitative metrics that assigned a numerical value to the results of ISCO (e.g. percent reduction, total cost). Also included were qualitative metrics, which assigned a binary variable based on whether or not a particular result was achieved after implementation of ISCO (e.g. site closure, meeting MCLs). The specific quantitative metrics are described in the subsections below, followed by the qualitative metrics.

#### Quantitative Performance Metrics

When analyzing time series data (e.g. groundwater concentrations in a monitoring well as sampled quarterly for a period of years) it is common to perform some type of calculation to derive a quantitative measure of how that quantity has changed over time. A simple example is the percent change of a value between before and after data. In the case of the ISCO data to be analyzed in this effort, percent change is not a simple calculation. Several measures were considered during the ISCO-DB1 design, as shown in Table 3-7 on the following page and described further in the text that follows.

Table 3-7: Quantitative Performance Metrics

Performance Metric	Method of Calculation	Comments
Percent Change in Maximum Values	$(\text{Max Before} - \text{Max After}) / \text{Max Before}$	Max Before and After refer to the single highest sampling concentration before and after ISCO, respectively. A limitation of this metric is its reliance on one sampling location (or two locations in the event of two different locations in the TTZ having the maximum concentration before and after).
Percent Change in Arithmetic Mean of Concentrations	$(\text{Mean Before} - \text{Mean After}) / \text{Mean Before}$	A limitation of this metric is that it does not consider spatial locations of samples.
Percent Change in Mass Flux	$(\text{Flux Before} - \text{Flux After}) / \text{Flux Before}$	Mass flux calculations are extremely rare in the materials reviewed, and few provide the inputs necessary to perform such calculations.
Percent Change in Spatially-weighted Mean Concentrations	$(\text{Mean Before} - \text{Mean After}) / \text{Mean Before}$	Mean refers to a weighted mean calculated by interpolating between known sample locations. A limitation of this method is that it requires a somewhat larger number of samples and site-specific statistical analysis.

Notes: The arithmetic mean calculation consists of summing all reported sample concentrations collected within the TTZ prior to ISCO and dividing by the number of samples. The spatially-weighted mean is calculated using a geostatistical kriging approach, described further in the text that follows. Both of these calculations of the mean use the same well locations before and after ISCO.

#### Percent Change in Maximum Values

Other authors have calculated the percent change in the maximum value before and after remediation (GeoSyntec, 2004). This approach was used in ISCO-DB1 as well to keep with precedent. Percent change is calculated in ISCO-DB1 (for this and other metrics) as:

$$\text{Percent Change [-]} = \frac{\text{Max. Conc. Before [M/L}^3] - \text{Max. Conc. After [M/L}^3]}{\text{Max. Conc. Before [M/L}^3]} \quad (3-3)$$

The percent change in maximum values was calculated based upon data collected within the TTZ before the start of ISCO compared to data collected within the TTZ collected within a period of one year after the end of last oxidant injection during ISCO implementation. The post-ISCO period of one year was selected to allow the oxidant to become depleted and the subsurface contaminant phase distribution to re-equilibrate. Therefore the metric was designed so that the percent change calculations should include the opportunity to observe rebound if any occurred. The post-ISCO monitoring period was also kept short to avoid influences of any non-ISCO processes, such as other remediation technologies being used at the site. This calculation may be based on the

same single location before and after ISCO (e.g. a persistent hot spot) or on two different sampling locations (e.g. the highest reported concentration after ISCO was not at the same location as before ISCO). A negative change refers to an increase in concentration, and a change of 100% refers to a 100% decrease.

Based on the data available in the case studies reviewed, groundwater is by far the most common media that is monitored when assessing ISCO performance, as opposed to soil samples. Though both percent change in maximum soil and groundwater concentrations were calculated, the latter is the more commonly available data, and thus the more commonly calculated metric. This performance metric has the benefit of being easy to calculate, regardless of the spatial or temporal sampling frequency. Another benefit of this method is that if a specific concentration in groundwater (e.g. MCLs) at all locations is the goal of ISCO, then the remediation must achieve a certain reduction in maximum concentrations to achieve this goal. However, using only maximum values as a performance metric suffers the limitation of only considering a very limited portion of the TTZ and does not evaluate changes in risk to receptors. The limitations of the data collection and analysis methods are discussed in greater detail in Section 3.6.

#### Percent Change in Arithmetic Mean Concentrations

This metric is calculated by comparing the arithmetic mean of all measured concentrations in the TTZ for the period within one year prior to ISCO, and also for the period within one year after the completion of the last ISCO injection event. The percent change in these two means is then calculated as shown above (following Equation 3-3 but using arithmetic mean values). This metric has the advantage of considering more locations within the TTZ than just the locations with the highest contaminant concentrations. This metric suffers the limitation of not accounting for the spacing of individual sampling locations. The importance of spatial sampling locations is shown on Figure 3-2 on the following page. This figure is schematic, and is drawn to illustrate the importance of sampling locations rather than presented to be a faithful representation of how sampling grids are oriented at field sites. The sites shown in both panels have the same size plume (as defined by the location of non-detect values), the same reported sample concentrations, and hence the same arithmetic mean of these concentrations. But



clearly the panel on the left (Site A) likely has a higher mass in the aqueous phase, as there is a larger spatial area between high sample concentrations.

Figure 3-2: Schematic Contaminant Distributions

Site A		Site B	
ND 100		ND	ND
	1,000	100	100
		1,000	
		100	100
100 ND		ND	ND

Notes: The above figure is a plan view schematic though the two sites are intended to be to-scale. Numbers indicate groundwater sampling concentrations collected at that location. ND = non-detect.

Other authors (e.g. McGuire *et al.* 2006) have chosen to use geometric mean of concentrations rather than the arithmetic mean. The reasons cited for this choice are: 1) that environmental data is commonly log-normally distributed, and 2) that the industry standard is to use geometric means (because the data is assumed to be log-normally distributed). However, a geometric mean, calculated by multiplying all of the  $n$  number of sample concentrations together, then raising that product to the  $1/n$  power, is biased low, and therefore is not as sensitive to the highest values in a dataset (Parkhurst 1998). But the highest concentrations reported during groundwater sampling, such as those from the source zone, are of critical importance when the purpose of ISCO is to reduce contaminant concentrations to an acceptable level.

In addition to the above theoretical considerations, computer-based simulations have shown that the arithmetic mean is a less biased estimate of the population mean than the geometric mean, even for log-normally distributed data. Parkhurst (1998) constructed normal, mildly skewed log-normal, highly skewed log-normal, and several other skewed datasets. Parkhurst then randomly selected subsamples of varying sizes ( $n=5, 10, 20, 50$

and 100), and calculated the arithmetic mean, geometric mean, naive bias-corrected geometric mean, and Finney bias-corrected geometric mean. This random sampling of each population was repeated 25,000 times for each of the five sample sizes (5 to 100) and the bias (estimated sample mean minus population mean) and root-mean-squared-error (RMSE) (a measure of variability of samples from the estimated mean) calculated for each repetition. The arithmetic mean of each sample size's bias and RMSE was calculated for each of the five sample sizes. The result of this analysis showed that the arithmetic mean had less bias (i.e. more accurately predicted the population mean) as well as a lower RMSE than the other means. The one exception to this statement is that the geometric mean did have a lower RMSE for the highly skewed log-normal dataset for sample sizes of five.

#### Percent Change in Mass Flux

Change in mass flux is a performance metric that has been used by others in academic research studies (ESTCP 2007b) and by a limited number of ISCO practitioners in reports submitted to regulators during the remediation process. A recent expert panel convened by the EPA cited mass flux as a promising new metric that is currently in the development stage, but has yet to gain regulatory acceptance (EPA 2003). This metric was considered as a potential performance metric for use in ISCO-DB1. However, given the uncertainty in hydrogeologic parameters (groundwater velocity, porosity, and flow direction), the frequent concurrent use of other remediation technologies in addition to ISCO, the lack of transect-style monitoring data, and the possibility of a rate-limited re-equilibration period, mass flux was not calculated for any of the sites, but was entered only when included explicitly in project reports.

#### Percent Change in Spatially-weighted Average Concentrations

This metric calculates the percent change in groundwater concentrations that occurred at a site as a result of ISCO while taking into account the spatial sampling locations, which is essentially equivalent to calculating the percent change in aqueous phase mass. This approach requires knowing the spatial relationship between sampling locations, which is straightforward when to-scale site plans are provided. The sampled concentrations and their spatial locations are then used together to estimate the

concentration between these sampling locations. This latter issue requires using a spatial interpolation routine such as kriging for geospatial analysis, and is discussed in detail in Section 3.3.5 below.

Note that this metric can use groundwater concentrations as a proxy for total mass. Calculation of the total mass of contaminants present in the subsurface requires detailed sampling and many assumptions regarding the distribution of contaminants in the subsurface, the presence and amount of NAPL being of particular importance (Pankow and Cherry 1996). Given that soil sampling is conducted considerably less frequently than groundwater sampling during performance monitoring, total mass was not calculated directly in this thesis study. Further discussion of this issue will be presented along with other limitations in Section 3.6.

#### Total Cost and Unit Cost

The cost of ISCO remediation is also important when evaluating its field-scale performance. Total project cost is reported in ISCO-DB1 when the information is provided in the sources. When the volume of the TTZ is also provided, or may be calculated from the available data, the project unit cost (in  $\$/\text{yd}^3$  treated) is also calculated. These data provide general guidance as to what the expected range of costs for an ISCO remediation might be under various circumstances.

Other authors have calculated the cost per mass of contaminant treated (e.g. ESTCP 1999). Due to the intensive data requirements and many assumptions that must be made to calculate the total contaminant mass at a site, those calculations are not performed here. For this reason, unit costs in terms of cost per mass removed are not included here.

#### Qualitative Performance Metrics

ISCO is performed by a group of site owners and remediation practitioners as a method to restore the subsurface to a condition that satisfies the regulatory agency's need that COCs be managed in a way that is protective to human health and the environment. From a practical standpoint, the ability of a remediation effort to meet the project objectives and help reach site closure is of more importance than knowing in a quantitative way exactly how much contaminant mass was oxidized. Given their

relevance from a practical perspective, and the relative ease with which they may be assigned, several qualitative metrics were included in ISCO-DB1. The simplest of these metrics is whether or not ISCO met the RAOs specified before its implementation. The response to this question may be entered as a dummy (or binary) variable, assuming a value of one when the answer is yes and zero when it is not. These types of variables may also be examined with statistical tools. The qualitative metrics used in ISCO-DB1 are shown in Table 3-8 and defined in the text that follows.

Table 3-8: Qualitative Performance Metrics

<b>Performance Metric</b>	<b>Comments</b>
Did ISCO Meet Performance Goals?	The likelihood of meeting this metric depends on what the goals were. Confirmation was not required from project regulators to confirm that goals were met.
Did need for active remediation cease after ISCO?	This metric represents a transition from active remediation to long term monitoring. Confirmation from regulators was not required to enter this metric in the affirmative.
Was Site Closure Attained?	This metric did not require confirmation from project regulators though attempts were made to confirm site closure through project documentation, online regulatory databases or correspondence with regulators.
Were MCLs Met After ISCO?	This metric was not entered in the affirmative unless confirmed with the project regulator.
Were Risk-Based Concentrations (ACLs) Met After ISCO?	This metric represents a means to reach site closure without attaining MCLs.

Notes: All of the above are entered into ISCO-DB1 as 1 when true and 0 when false.

#### Did ISCO Meet Performance Goals?

The question of whether ISCO met the desired performance goals is an important one, and the likelihood of meeting the desired goals depends on what those goals were. Because of this relationship between the goals of ISCO remediation and the likelihood of meeting them, there is a group of five performance metrics relating whether or not ISCO met the five general groups of goals (MCLs, ACLs, reduction of mass by predetermined percent, general reduction in mass or time to clean up, and evaluation of ISCO's effectiveness, see Table 3-6 for definitions). For example, project documents may state that the goals of a particular ISCO remediation were to meet MCLs and also reduce the mass of contaminants present. Should project documents indicate that MCLs were not

met, but that mass was reduced, this site would be entered with a 0 in the MCLs field indicating that the goal of MCLs was not met, and with a 1 in the mass reduction field indicating that the mass reduction goal was met. The remaining three fields in this group of metrics would be left blank because the remaining three groups (ACLs, a percentage mass reduction, and technology evaluation) were not goals of this particular ISCO project. The use of these metrics helps to clarify what goals are currently being met with regularity versus those that have proven to be elusive.

#### Did need for active remediation cease after ISCO?

The transition from active remediation to long term monitoring is an important milestone during the remediation of a contaminated site. If ISCO is unable to meet MCLs, but has reduced groundwater concentrations to levels that may be treated with MNA, this may represent a successful outcome. For this reason, this qualitative metric has been included in ISCO-DB1. This is not necessarily to say that the transition to MNA will lead to the attainment of MCLs in the near future, as this is difficult to predict and impossible to prove based on documents written shortly after the completion of ISCO. Rather, what this metric means is that the project's environmental engineer or regulator, in their professional judgment, considered the site's concentrations to be amenable to treatment with MNA after ISCO in a situation where they were not prior to ISCO implementation.

#### Was site closure achieved?

Site closure as defined in ISCO-DB1 is the attainment of whatever standards are required by the site regulators, and is the goal of most remediation applications. Closure may be achieved by reaching MCLs, or through the use of risk-based standards, institutional, and/or engineering controls. Each of these situations represents a positive outcome for the project owner, and the incidence with which it occurs is recorded in ISCO-DB1. Attempts were made to verify that site closure was achieved from the site regulator and also to find out what conditions were required, if any. However, in situations in which the site was reportedly closed and the regulator could not be contacted, the project sources were trusted to be correct and this metric was entered in the affirmative.

### Were MCLs met after ISCO?

This metric answers an important fundamental question regarding the potential benefit of using ISCO as a remediation technology for treating groundwater, as MCLs represent the final remediation goal that must be met at many sites to gain regulatory closure. As this is such an important metric, and because of the rarity with which it occurs as a result of source zone remediations (EPA 2003), this metric was not entered in the affirmative until it was confirmed through correspondence with the site regulator that MCLs had been attained at the site.

### Were ACLs met after ISCO?

This metric represents another remediation endpoint for projects being performed in a regulatory framework where ACL (risk-based) goals (which are by definition higher than MCLs) have been deemed protective of human health and the environment. Evaluating the occurrence of meeting this type of goal provides insights into the utility of using ISCO at sites with ACLs.

#### *3.3.4 Rebound Metric*

The issue of contaminant rebound has been a perceived performance deficiency associated with the use of ISCO to remediate groundwater. Rebound in the colloquial sense is any increase in groundwater concentrations that is observed at a given location after ISCO implementation has been completed. A more precise definition has been used in this thesis project. Rebound as it is defined here is an increase in aqueous phase COC concentrations that occurs after ISCO following an initial reduction in concentration that resulted from the ISCO application. This phenomenon can occur when oxidants degrade the COCs that are present in the aqueous phase, but do not entirely degrade contaminants that are present in the sorbed and NAPL phases. Once the oxidant is depleted, any remaining sorbed or NAPL phase COCs can re-equilibrate with the groundwater, resulting in an increase in aqueous phase contamination observed during the post-ISCO monitoring period. Another potential mechanism for contaminant rebound is back-diffusion from low permeability materials that were not completely treated during ISCO implementation. The purpose of evaluating rebound in this report is to evaluate its prevalence in ISCO field applications.

Incidence of rebound should not be equated with failure of an ISCO remediation, and thus was not included with the performance metrics listed above. Rebound has the positive attributes of marking the transfer of contaminants to the more treatable aqueous phase and can also help locate previously unknown areas of NAPL or high sorbed-phase concentrations. Rebound is included in ISCO-DB1 to allow those considering ISCO to have a fair assessment of the likelihood that contaminant concentrations in groundwater within the TTZ may increase to a degree during the post-ISCO monitoring period.

Increases in contaminant concentrations may also occur as the result of an influx of contaminated groundwater from untreated upgradient locations at the site. This type of concentration increase could happen with any in situ remediation technology if it is not successfully applied to the entire contaminated area. For this reason, groundwater increases as a result of contaminated groundwater influx will not be considered rebound as used in this project, as the purpose is to examine the ISCO-specific incidence of rebound.

The influx of contaminated groundwater may be determined by several of the following techniques. First, if a pilot study intentionally targets only a portion of the contaminated area, then contaminated groundwater often can be expected to return. Secondly, a project report may specifically call out that a previously unknown area of contamination was discovered upgradient of the ISCO TTZ. Finally, increases in COC concentration may first be observed in the upgradient portion of the ISCO TTZ followed later by downgradient portions. In this situation, the timing of these increases are compared to the reported groundwater flow velocity. If any of the three indications listed show that contaminated groundwater flowed into the TTZ and caused an increase in COC concentrations at monitoring locations, rebound was not evaluated at that site.

Now that rebound as it is used in this context has been defined, the metric through which it is evaluated can be described. An increase in post-ISCO COC concentrations must be placed in the appropriate context when considering its importance. For example, a post-ISCO increase from 0.5 to 5.5 ug/L is 1000% increase during that period. However, the relative importance of this increase will vary depending on what the MCL is and also if the initial concentrations were 10 or 1,000 ug/L. For this reason, the rebound metric used in this study will compare post-ISCO increases to pre-ISCO baseline

values. Note that this is a departure from previous case study works. GeoSyntec (2004) left the definition of rebound up to those who responded to their survey. McGuire *et al.* (2006) only examined concentration changes in the post-remediation monitoring period, and stated that rebound occurred when there was an increase of 25% or more in the second half of the post-treatment monitoring period relative to the first half regardless of pretreatment concentrations. In this study, rebound is said to occur at a monitoring location if post-ISCO concentrations increase greater than 25% relative to baseline values, or if the inequality below holds:

$$\frac{\text{Most Recent Post ISCO} - \text{Lowest Post ISCO}}{\text{Baseline}} \geq 0.25 \quad (3-4)$$

“Most Recent Post ISCO” is the most recent (closest to present day) analytical result collected within one year after the completion of oxidant delivery. “Lowest Post ISCO” is the lowest recorded value in the post-ISCO monitoring period. In the event that concentrations continually decline at a monitoring location after ISCO, then rebound clearly did not occur, and the most recent and lowest concentration will be the same, and the above inequality will not hold. “Baseline” values are ideally an arithmetic mean of all sampling results at that location collected within the year prior to ISCO’s application. However, in many cases only one round of COC sampling data collected just prior to ISCO implementation are presented, and in this case that baseline value will be used for the rebound calculation. In the case when a series of pre-ISCO concentrations appeared to show a continued decrease over three or more sampling rounds collected within one year prior to ISCO’s implementation, these data were evaluated using the non-parametric Mann Kendall test. When using this test, a p-value of 0.167 or less was used to disprove the null hypothesis that no trend existed in the data. This p-value is that reported for the Mann Kendall S statistic when a series of three samples showed a continued decrease over time, or when a series of four sample shows that five of the six possible combinations of these samples shows a decreasing trend (Helsel and Hirsch 1991). In the event that a downward trend existed in the data, the most recent sampling event prior to ISCO implementation was used as the baseline value (as opposed to the mean of all pre-ISCO samples).

In order to perform an evaluation of rebound using the above technique, at least one year of post-ISCO performance monitoring data collected in three or more sampling



events is required. This amount of time is necessary to allow the oxidant to be depleted in the TTZ and for the subsurface to re-equilibrate. In situations in which the oxidant is particularly persistent (e.g. purple color is observed in wells over one year after a permanganate application) then the monitoring period on which the rebound metric will be based will be extended to include the next two sampling events after oxidant depletion.

In situations in which contaminant concentrations increase to levels above baseline values immediately after ISCO, rebound was not evaluated because rebound is not relevant in this context. The incidence of this occurrence will be quantified in ISCO-DB1 during the calculation of the percent change of aqueous phase concentrations as described in Section 3.3.3.

Once again, the above rebound calculation was performed at each well in the TTZ. The percentage of well locations in the TTZ experiencing rebound as defined above were also calculated and recorded. This is a second metric that provides information on the site-wide prevalence of rebound at a given field site.

The rebound calculations were performed on total COCs that were the target of the ISCO remediation. This is another departure from the methods of McGuire *et al.* (2006), as those authors examined only parent chlorinated compounds (e.g. what was assumed to be the chemical originally released, and not including degradation products). This change in methodology reduced the number of calculations required and simplified the analysis.

### 3.3.5 Geospatial Analysis

An optimal metric for determining the site-wide percent change in groundwater concentrations that occurred as a result of ISCO is a spatially-weighted average. This requires the use of a geospatial technique to interpolate between the available data points. The use of a kriging technique is the most mathematically robust method of spatial interpolation as it is unbiased (mean estimation error of zero) and minimizes the variance of the estimation errors as well. This section briefly describes the processes and tools used during the kriging analysis of the data in ISCO-DB1. More details regarding mathematical equations and computer scripts are provided in Appendix A.

The use of any geospatial technique requires knowing the spatial locations where the samples were collected. This was determined from to-scale site plans, which were provided with nearly all project reports and many conference proceedings as well. The spatial analysis also requires data on the variable to be estimated, in this case groundwater concentrations at a given sample location. Though the number of sampling locations required for analysis varies depending on how the samples are distributed with respect to concentration and spatial location, ten or more sampling locations were generally sufficient to perform these analyses. This determination was made by the author of this thesis on a case-by-case basis. The data was considered to be insufficient when an upward sloping experimental variogram could not be generated from the data (see Appendix A for an explanation of the experimental variogram).

The statistical software package R (v. 2.6.1) was used for the geospatial analyses. This is a statistical and graphics environment that is free for public use. The add-on packages *mvtnorm* (v. 0.8-1), *sp* (v. 0.9-19), *geoR* (v. 1.6-20), *fields* (v. 4.1), *spam* (v. 0.13-2), and *splancs* (v. 2.01-23) were used in the various analyses as well. R also has many graphics capabilities that can be used to create concentration maps, variograms, and estimated data plots shown in Appendix A. The R base package and add-ons are available at <http://cran.r-project.org>.

Ordinary kriging was the method selected for the geospatial analysis. In some situations the data was detrended so that the data used satisfied the required assumption that the expected value of sample concentration be independent of location. After detrending (if any was needed) an experimental variogram was generated from the spatial contaminant concentration data. A model variogram was then fitted to the experimental variogram using an isotropic spherical structure and a nugget effect. Ordinary kriging was performed to estimate the contaminant concentration at several hundred equally spaced locations within the TTZ based on the sampled concentrations at known locations. The mean of these equally spaced estimates was calculated and used as the spatially-weighted average. This kriging technique was performed on both baseline and post-ISCO samples, and the difference between the spatially-weighted average before vs. after is considered to be the percent change in the average groundwater concentration at that site using an equation of the form of Equation 3-3 (substituting spatially-weighted

values). The geospatial data analysis is not complete at this time, and therefore no results of this metric are included in this thesis.

### 3.3.6 Normalization Methods

The case study data were converted into consistent units prior to entry into ISCO-DB1. The units selected followed what is most commonly reported, and are therefore a mix of metric and imperial units. Nearly all units were converted using standard conversion tables that will not be detailed here. The conversion of oxidant concentrations is more complicated, and is discussed in the subsection below. Also discussed below are methods used to normalize cost data and groundwater flow velocity.

#### Oxidant Concentration

The unit of oxidant concentration used in ISCO-DB1 is grams of oxidant per liter of solution (g/L). This unit was selected to be consistent across multiple oxidants and to allow easier calculation of mass loading rates. However, hydrogen peroxide and permanganate concentrations are typically reported in terms of solution weight percent. The calculations used to convert between hydrogen peroxide weight percent and g/L are based upon a table of weight percent and molarity from U.S. Peroxide (2007). The molarity was multiplied by the molecular weight of hydrogen peroxide (34.016 grams per mole) to produce a table of weight percents and concentrations in g/L that were compared graphically on a scatter plot. The maximum weight percent used in this calculation was 50%, as this is the highest concentration of hydrogen peroxide that was encountered in the case study review. The resulting curve was non-linear due to changes in solution density, and was fit by the polynomial equation:

$$\text{concentration (g/L)} = 0.0409 * \text{wt}\%^2 + 9.8594 * \text{wt}\% \quad R^2 = 1.0000 \quad (3-5)$$

This equation was used to compute the concentration of a hydrogen peroxide solution in g/L when the concentration was given in terms of weight percent.

The above analysis is predicated on the assumption that concentrations reported as weight percent for diluted hydrogen peroxide solutions did in fact reflect the change in solution density that results from dilution, or in other words, that they were not simply volumetric dilutions.

A similar approach was used to convert weight percent concentration of permanganate to concentrations in g/L using weight percent and specific gravity information from the Carus Chemical Corporation (2007). The derived polynomial equations for sodium and potassium permanganate are shown below, respectively:

$$\text{concentration (g/L)} = 0.1080 \cdot \text{wt}\%^2 + 9.3469 \cdot \text{wt}\% \quad R^2 = 1.0000 \quad (3-6)$$

$$\text{concentration (g/L)} = 0.0713 \cdot \text{wt}\%^2 + 9.9860 \cdot \text{wt}\% \quad R^2 = 1.0000 \quad (3-7)$$

Note that the above concentrations include the weight of the cation. Also note that the non-linearity of the potassium permanganate solutions is essentially negligible, as the specific gravity of a nearly saturated solution is only 4% greater than that of water.

The permanganate concentrations as calculated above were normalized to g/L as  $\text{MnO}_4^-$ . The purpose of this calculation was to allow consistent comparison of oxidant concentrations and loading rates between the two permanganate forms. The cation's contribution was also omitted for persulfate, in this case because more project documents report the mass or concentration as persulfate than as sodium persulfate. Persulfate concentrations in the source documents were reported in the units g/L or mg/L as persulfate or as sodium persulfate. For this reason, no polynomial expression relating concentration in the units g/L and weight percent was developed.

### Cost Data

Cost data is not always presented in a consistent way among the various files reviewed as in some cases certain items such as well installation or professional fees are explicitly omitted, and in other ancillary items such as site assessments were included. A means of normalizing the project costs was implemented so that the total project cost and unit cost (total cost /  $\text{yd}^3$  treated) were as consistent as possible between sites.

First, the default assumption when itemized cost details were not provided was that a total cost included in a source describing an ISCO remediation included the design, implementation (including injection well installation), project management, reporting and sampling necessary to evaluate the effectiveness of the remediation. The cost associated with site assessments performed to delineate the general nature and extent of contamination was assumed to be omitted unless stated otherwise. When included as a line item, the cost of the site assessment was deleted from the normalized total cost.

When the source data described the total cost for a remediation consisting of ISCO coupled with another technology, the cost of the other technology's implementation was deleted from the total cost. When operations and maintenance (O&M) costs were reported for a coupled remedy, it was assumed that the O&M costs associated with ISCO were \$10,000 per year. This assumed amount is comparable with other sites for which O&M was itemized for non-coupled ISCO projects. It is also reasonable assuming that four quarterly sampling events are required and accounting for sampling, laboratory and reporting costs. It is admitted that this is a general assumption. However, this assumption is an improvement over including the O&M costs as reported for coupled projects, especially those coupling ISCO with technologies such as P&T and SVE, both of which require operating pumps and other equipment in addition to environmental sampling. This general assumption is also an improvement over omitting the O&M costs entirely.

Other reports that provided itemized total costs stated that some items were omitted, specifically well installation and professional fees. Professional fees are assumed to include engineering design and project management services. To account for the cost of excluded professional fees, the set of complete cost breakdowns was assessed. The manner in which each of the various sources itemized their total cost was inconsistent. However, of those that did explicitly include professional fees as a line item, the average percentage of the total project cost was approximately 30%, after eliminating outliers. The normalized total cost of projects that explicitly excluded professional fees was calculated by multiplying the reported total cost by 1.43 ( $100\% / [100\% - 30\%]$ ). This calculation was performed to produce a normalized total cost for five projects that explicitly omitted professional fees.

One project that involved both ISCO and extensive excavation included a single line item for project management. The project management line item was reduced by half by this author, the proportion of ISCO to total number of technologies implemented. While project management costs are unlikely to be linearly related to the number of remediation technologies implemented, this assumption is an improvement over leaving the reported cost as-is or deleting it entirely. The professional fees associated with this

project after this modification accounted for 34% of the total cost, which is comparable to the ratio found for other sites as described in the preceding paragraph.

Two sites explicitly omitted well installation costs. A cost-estimating tool that was developed for the TPM by the environmental consulting company CH2M HILL was used to estimate the well installation costs at these sites based upon the number and depth of wells installed and their completion details. This calculation was performed on the total cost data for two sites. A third site excluded the cost of a horizontal well installation in some sources, but included the cost for that item in another. In this case the cost of the well installation was added to the costs associated with the remainder of the ISCO implementation to calculate the normalized total cost.

The normalized total costs as modified using the above methods were used in the analysis when comparing total cost and total unit cost to the other parameters in ISCO-DB1.

#### Groundwater Flow Velocity

The groundwater flow velocity is the average speed at which groundwater flows through the subsurface measured along a straight line, and is also called groundwater velocity or average linear velocity. When not explicitly stated in source documents, the groundwater flow velocity was calculated by the equation:

$$V_x = \frac{K * i}{n_e} \quad (3-8)$$

where  $V_x$  is the groundwater flow velocity,  $K$  is the saturated hydraulic conductivity,  $i$  is the horizontal hydraulic gradient, and  $n_e$  is the effective porosity. This is not the same as the Darcy velocity or specific discharge, which is equal to the volumetric flux divided by the full cross-sectional area of interest, or alternatively as  $K*i$ . Groundwater flow velocity is not calculated in the absence of hydraulic conductivity or gradient data. When effective porosity is not provided, it is assumed to be 0.3.

#### *3.3.7 Subdividing Large Sites*

In some situations, ISCO was performed at multiple but separate locations at a single large site. In these cases, when design and performance details were sufficiently thorough to demonstrate that the remediation practitioner designed ISCO systems that

were tailored to the separate portions of the site, then the entire site was subdivided so as to have separate TTZ's, each of which were entered as distinct sites in ISCO-DB1. For example, project reports that detailed three phases of ISCO performed in separate locations at the Eastland Woolen Mill in Corrina, ME were reviewed. Each phase targeted a specific portion of that site, with data presented for each phase on contaminants present, subsurface geology, ISCO design, and performance result. The larger Eastland Woolen Mill project is therefore divided into three sites in ISCO-DB1. Subdivision of large sites with multiple treatment zones was performed both to increase the overall sample size, and more importantly because each treatment zone of such sites was sufficiently different that lumping them together would have misrepresented the data.

### **3.4 Data Reliability, Thoroughness, and QA/QC Measures**

This section discusses the various issues associated with the reliability, thoroughness and quality of the data contained in ISCO-DB1, including the definition of these terms as they are used here and means taken to address them during data entry and analysis. Reliability as used in this context refers to the degree to which a fact stated in a information source reviewed during data collection is an accurate, truthful account of what actually happened in the field. A lack of accuracy in source data may be the result of clerical error, laboratory error, or other sources. The likelihood that these types of errors exist in a document decreases with increasing amounts of peer review completed during preparation of the case study source documents. The degree of reliability of the source data will be communicated to the users of ISCO-DB1 through assignment of a Data Quality Class (DQC) as discussed below in Section 3.4.1.

Thoroughness in this context is used to describe the level of detail present in a case history source, and is not necessarily the same as the reliability of the data. For example, a journal article that omits certain data regarding the site investigation and groundwater chemistry may still be considered reliable despite that information being omitted. The degree of thoroughness cannot be corrected for during data entry or analysis. Sites with incomplete data will have certain blank cells, and for this reason will be ignored when conducting analyses of parameters for which the case study document authors omitted those data.

The previous issues pertain to recording an assessment in ISCO-DB1 of how faithfully the data contained in the source material is to what actually occurred in the field. Another, separate issue is how accurately the particular entries in ISCO-DB1 represent the information contained in the source material. To ensure the accuracy of the data entered, quality assurance (QA) and quality control (QC) measures were implemented as part of this project. QA is generally defined as a series of measures taken during the “production” stages to ensure that the output of a process will be of the desired quality, while QC are methods implemented after production is complete to verify that the product meets the required quality specifications. One QA measure was that the same person, the author of this thesis, entered all the data into ISCO-DB1. This measure was taken to eliminate the possibility that multiple data entry operators would not enter data in a consistent fashion. The specific measures taken to deal with reliability and QA/QC are described in the subsections that follow.

#### *3.4.1 Data Quality Class (DQC) System*

During data entry, each site is assigned an integer value of 1 to 3 based on the DQC system described in this section. The data are screened according to the source from which they were received as well as other factors. Each of the three DQCs are generally populated from the following sources:

- Class 1: Project reports submitted to regulators, articles in science and engineering journals
- Class 2: Conference proceedings, online databases
- Class 3: Promotional materials (e.g. vendor-supplied case studies).

The classification system is flexible to allow for modifications of the above criteria for some sites based on the breadth of information provided. For example, an ISCO application reported in a conference proceeding might be assigned to Class 1 if the information is well supported with additional data. When project data was obtained from more than one type of source (e.g. project reports and a conference proceedings paper) the site was assigned to the higher reliability DQC (in this example Class 1). The author of this thesis assigned all DQC's, and assignments were made in a consistent fashion.

The purpose of assigning DQCs is to subdivide the data into groups based on confidence in the reliability of that data. The proposed system is not a “weighting”



system, i.e. if an analysis were being performed on Classes 1 & 2, a site from Class 1 would not be weighted any more than a site from Class 2. The DQCs will communicate the relative assessed reliability of the data for each site to end users of ISCO-DB1.

### *3.4.2 Requests for Complete Information and Follow-up Correspondence*

To the degree possible, ISCO-DB1 is populated from project reports and/or science and engineering journals (Class 1 sources). This serves as a QA measure as it works to ensure that data entry is based on as reliable data as possible, as both are peer-reviewed. A second QA measure is to attempt to correspond with site contacts. This correspondence consisted of brief telephone conversations or emails to confirm the basic project descriptions and clarify certain details. Conversations, especially with regulators, were also valuable in that they can give an overall impression of the success of a project, and contacts familiar with the site may point out subtle details that were not included in reports or whose true importance may not have been apparent.

Gathering as much information as possible and speaking with site contacts is also a good way of avoiding duplication of sites. For example, conference proceedings may report a site with a generic name, while the same data may be available under the specific project name at the USEPA's website of NPL sites.

### *3.4.3 Outlier Analysis*

After populating ISCO-DB1, an outlier analysis was conducted as a QC measure designed to detect data entry errors. The analysis consisted of examining the minimum and maximum values of the numerical parameters. The purpose of such an analysis is to reveal anomalous, and likely incorrect values, such as aqueous phase concentrations above the solubility limit of a compound. Such an analysis also catches data entry errors in dummy variables, which can only take on a value of zero or one.

In the event that this analysis discovered errors, the errors were corrected by consulting the original source to verify the information. Note that some values that seemingly appear to be outliers may still be correct values, even if the information appears impossible. For example,  $\text{KMnO}_4$  can be delivered at concentrations well above its solubility limit in a slurry delivered via fracturing.

### 3.5 Limitations of Methods

The methods described in the previous subsections have certain limitations. These limitations do not reduce the validity of this effort, which is to collect past experiences, provide the necessary data reduction to ensure that they are tabulated in a consistent fashion, and finally to share these experiences in reports such as this thesis. These limitations arose because the methods used in this work are a compromise between two conflicting philosophies. The first is using only ideal methods and data sources, and not making any calculations or assumptions beyond what is provided. If carried to its extreme, this pursuit of perfection would preclude the use of all but the most well-documented case studies. This would result in an exceedingly small sample size that could not be analyzed statistically, and would therefore be contrary to the purpose of this work. The second extreme is a verbatim transcription of data from all reported sources, omitting all critical analysis of the case studies during data entry. This work attempted to strike a balance between perfection and inclusion that would faithfully represent the data in a consistent way but retain enough information so that a large number of experiences could be shared. This compromise included certain limitations relating to data collection and reduction, and these are discussed below along with the efforts taken to mitigate them.

#### 3.5.1 *Data Collection Limitations*

The data collection methods employed during this work suffered from certain inherent limitations. Namely, these were (1) a potentially biased sampling of ISCO case studies, and (2) an inability to get complete information.

There were several potential sources of bias that may limit how representative the sampling of ISCO sites contained in ISCO-DB1 are to the larger population of all field-scale ISCO sites. These stem from how the data were collected. First, an effort was made to collect as much data as possible, and for this reason data were gathered from existing, easily-accessible sources. These existing sources may not be representative of ISCO as a whole. For example, the State Coalition for the Remediation of Drycleaners has an online database of thorough case studies, many of which pertain to sites where ISCO was used. For this reason, dry cleaners may be an over-represented facility type in

ISCO-DB1, and chloroethenes may be an over-represented contaminant group. That said, experiences at dry cleaners remediated with ISCO are applicable to other sites contaminated with similar contaminants. Federal facilities may have dry cleaners onsite, such as the Naval Training Center (NTC) in Orlando, which had a chlorinated solvent plume as a result of dry cleaning operations that was remediated using ISCO.

A second example is a bias towards successful studies. As stated previously, conference proceedings and promotional literature were both sources of data. Given that a site owner, project engineer, and/or technology vendor is voluntarily sharing information on a case study, they may consider it to be in their best interest to choose case studies that were successful. This is particularly true when the individual reporting the case study has a financial incentive in the form of future work to portray their past work in as favorable a light as possible. However, if such a bias towards good sites does in fact exist, it would have a positive aspect as well. One of the purposes of this work is to examine under what sets of conditions ISCO is successful, so having as many successful sites as possible will help serve this purpose of the work.

The second class of limitations was the difficulty encountered in gathering information. Based on informal personal correspondence with several ISCO practitioners, a rough estimate of the total number of sites where ISCO has been applied at the field-scale is between 1,000 and 1,500. Of all these sites, 242 are represented in ISCO-DB1, and 111 are within the most reliable DQC. The difference between the estimated number of total sites and those in ISCO-DB1 is not due to a lack of sampling or reporting: regulatory agency requirements dictate that nearly all of these 1,000 or more sites be sampled for COCs somehow, and the results documented in reports. The relatively smaller sample size in ISCO-DB1 is the result of difficulty in accessing more of the ISCO project data due to several sources. The first of these is that consultants and technology vendors must receive permission from the site owner prior to releasing data to a study such as this. If a site owner views any discussion of environmental impacts to their property as a potential liability, and sees no benefit to releasing the information, they will often keep it to themselves. Another data access limitation, which stems from the confidentiality issue above, is not knowing what to ask/search for when querying various online resources. FOIA requests and queries of regulatory agency search engines

require knowing the site name and location, so simply asking for any sites where ISCO has been conducted is impossible. However, reviewing 242 ISCO projects which represent at least 10% or more of all purported ISCO projects is a significant amount.

### *3.5.2 Data Reduction and Analysis Limitations*

There are also limitations to the methods used to reduce and analyze the data. First, the sites were placed into six groups based on geology. Unconsolidated materials were divided into four groups based on permeability and heterogeneity. In reality, the degree of permeability and heterogeneity of unconsolidated media exist on a continuum, so dividing them based upon cutoffs at average saturated hydraulic conductivities of  $10^{-5}$  cm/s and a factor of 1,000 variation in hydraulic conductivity is somewhat arbitrary. Fractured rock sites were split into two groups based on an assessment of matrix porosity, which also exists on a continuum in reality. While imperfect, this site classification method follows after previous work and has proven to be useful in this effort as well (NRC 2004, ESTCP 2007b). Also, the assessment of the degree of heterogeneity is also a somewhat subjective. Data from multiple field hydraulic conductivity tests (slug or pump tests) is rarely available for a particular site. And even when it is, it may underestimate the degree of heterogeneity. For example, at a site underlain by coarse sand with thin silt beds, the literature and much previous lab testing indicates that the hydraulic conductivity in the sand is almost certainly at least 1,000 times greater than that of the silt (Freeze and Cherry 1979). However, if the silt beds were sufficiently thin, and also horizontally extensive, hydraulic conductivity testing in fully-screened monitoring wells would not show nearly such a wide variation in hydraulic conductivity. For that reason, the degree of heterogeneity must be estimated from descriptions of soil lithology and boring logs, and literature values for hydraulic conductivity of the strata described. A measure taken to mitigate this limitation is that the same person, the thesis author, assigned all sites to one of the Geology Groups, and did so using the same criteria in each case.

The calculation of ISCO design parameters such as oxidant dose applied (g oxidant / kg of media treated) and number of pore volumes of oxidant solution delivered (volume oxidant solution / volume of pore space in TTZ) often required several

assumptions regarding the porosity and dry bulk density of the materials, as outlined in Section 3.3.2. These assumptions included using a standard porosity of 0.35 and bulk density of 110 pounds per square foot when no other data were provided. While these assumptions may not have been correct in all cases, the range with which they vary is small relative to the variation in calculated ranges of oxidant dose and number of pore volumes delivered (Appendix B, Table B-20). Also, when the volume of the TTZ was not explicitly stated, it was estimated from available information whenever possible. In sites using direct push or well injection, the stated ROI or delivery location spacing was used to define the horizontal extent of the TTZ. The thickness was calculated based on the range of depths that were treated, and the area and thickness used to calculate the volume. The above assumptions may not have been correct in all cases, but were based upon the best available data and were necessary to keep the sample size relatively large.

The degree of oxidant persistence in the subsurface has significant impacts on the cost and success of an ISCO remediation. However, in the reports reviewed there were many different means through which practitioners measured the persistence of the oxidant at their sites. For more persistent oxidants, the duration for which oxidant persisted before being consumed was generally determined to an accuracy on the order of months (e.g. report language such as “the oxidant persisted for five months in the TTZ and was not present during the site visit conducted eight months after ISCO was completed”). Due to these constraints, it was not possible to input data on oxidant persistence into ISCO-DB1.

Oxidant persistence during permanganate applications is largely dependent on NOD, as well as other factors. However, in the reports reviewed, there are many ways in which practitioners have determined the NOD through bench scale testing. The main variations are the amounts of oxidant and site soil used in the test, and also how frequently and over what duration of time the oxidant concentrations were measured. Due to this wide variation in testing protocols, the data cannot be compared in a consistent way, thus the case studies offer little guidance with respect to ranges of NOD at permanganate sites.

The use of groundwater concentrations as proxy for contaminant concentrations in other phases (sorbed and NAPL) has certain limitations. Groundwater COC

concentrations are reported on a far more frequent basis than soil sample concentrations in the reports reviewed. A major reason for this is that groundwater is nearly always the regulatory driver for the projects included in ISCO-DB1.<sup>2</sup> However, at sites with NAPL or significant sorbed phase concentrations of COCs, only a small percentage of the total contaminant mass is present in the aqueous phase. In addition, the manner in which the COCs partition between the aqueous phase and other phases may change after ISCO, as naturally occurring organic matter which can serve as a sorption site for COCs may be destroyed during ISCO (Siegrist and Satijn 2002, Siegrist *et al.* 2003). Despite these limitations, groundwater data must be used as the predominant media when assessing performance or else the number of sites available for analysis would shrink dramatically.

The limitations caused by the reliance on groundwater data are mitigated by several factors. First, groundwater samples may be collected from the same sampling location repeatedly over time. Soil samples cannot, as soil sampling requires disruption of the subsurface and the destruction of the entire area previously sampled. Contaminant concentrations in soils can vary widely over a very small area, especially in the presence of geologic heterogeneities (Pankow and Cherry 1996). Thus, sampling soils very near the location of previous samples does not necessarily provide representative contaminant time series data. A second positive aspect of groundwater sampling relative to soil sampling is that it is representative of a larger area of the subsurface. During the purging of wells prior to sample collection, water enters the well radially, resulting in a sample that is essentially a composite sample over that screened interval and representative of liters of material (this fact is less true for wells screened in heterogeneous material or when low flow sample collection techniques are used). By comparison, soil samples are generally collected from discrete intervals and represent approximately 10 mL, and due to the variation in contaminant concentrations in soil previously described, may not be representative of concentrations at nearby locations.

---

<sup>2</sup> Sites where ISCO was used to treat soils with no consideration of mitigating groundwater impacts are deemed to be outside the scope of project ER-0623, and are therefore not included in ISCO-DB1.

## 4.0 RESULTS

This section presents the summary statistics of the data contained in ISCO-DB1. This section begins with an overview of the data, followed by selected tables and figures showing interesting trends. A statistical analysis of the results is presented in Section 5, and discussion of the results is included Section 6. Supporting tables are included in Appendix B, which presents detailed summary statistics of the following categories: site and contaminant conditions, ISCO goals and design, and performance results. The summaries of the data in each of these categories are shown for all sites in ISCO-DB1 as well as smaller subsets based on contaminants, oxidant used in remediation, Geology Group, and the presence of NAPL.

The breadth of data varies widely among the case study sources. This resulted in many parameters remaining blank during data entry due to a lack of data. For this reason, the number of sites in each analysis fluctuates greatly, as shown by the n values associated with each analysis. The n values reported are the number of sites in ISCO-DB1 that have data for all of the parameters being analyzed (i.e. the fields for all parameters in the analysis are non-blank).

### 4.1 Overall Summary of ISCO Database

This section presents data of selected parameters for all the case studies in ISCO-DB1. Unless otherwise noted, these statistics describe all scales of remediation (full scale and pilot tests). The reader is referred to Appendix B, Section B.1 for the complete set of tables on which this text is based.

ISCO-DB1 contains 242 sites from seven nations and 42 states in the U.S.. There are 19 different site types represented. The bulk of sites are Federal, manufacturing/industrial, and dry cleaning facilities. An appreciable number of chemical production, former manufactured gas plants (MGP), service stations, waste disposal, and wood treatment sites are included as well. Nearly half of the data sources were from the most reliable type (DQC 1) while less than fifteen percent were from the least reliable.

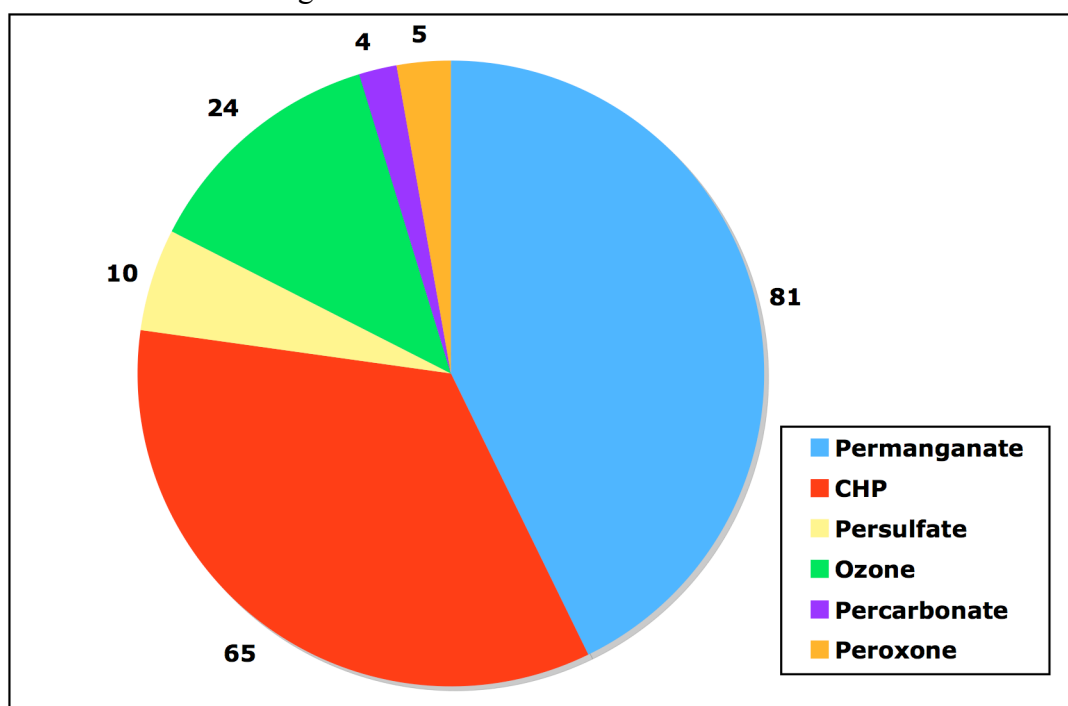
A wide range of contaminants have been treated at the field-scale using ISCO. However, a bulk of the sites were contaminated with chloroethenes (70%), while BTEX

(18%), TPH (11%), chloroethanes (8%), MTBE (7%), SVOCs (7%), and chlorobenzenes (5%) were present as well. Other contaminants were present at less than 3% of the sites (Appendix B, Table B-5). Approximately half of the sites were contaminated with DNAPL, and approximately one tenth were contaminated with LNAPL.

The scope of this work is an analysis of the use of ISCO to treat contaminated groundwater, and for this reason, only sites where the project team reportedly sampled groundwater are included. Approximately one quarter of sites also used measured or estimated (from aqueous concentrations and TOC data in soil) COC concentrations in soil to supplement their site conceptual model and ISCO performance analysis. Total contaminant mass and mass flux were estimated at only 6% and 2% of the sites, respectively.

Six oxidants were included in ISCO-DB-1. The overall frequency of their use and the cumulative frequency over time are shown in Figures 4-1 and 4-2, respectively.

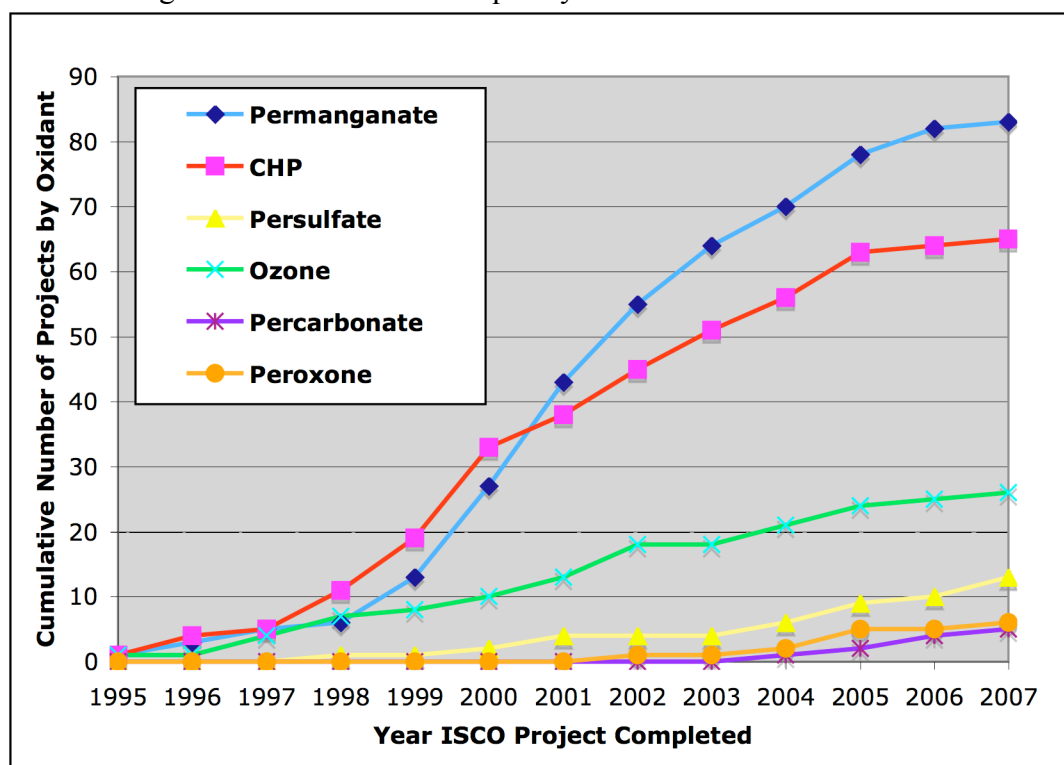
Figure 4-1: Distribution of Oxidants Used



Notes: n=189. The printed value is the number of sites using that particular oxidant in ISCO-DB1.



Figure 4-2: Cumulative Frequency of Oxidants Used Over Time

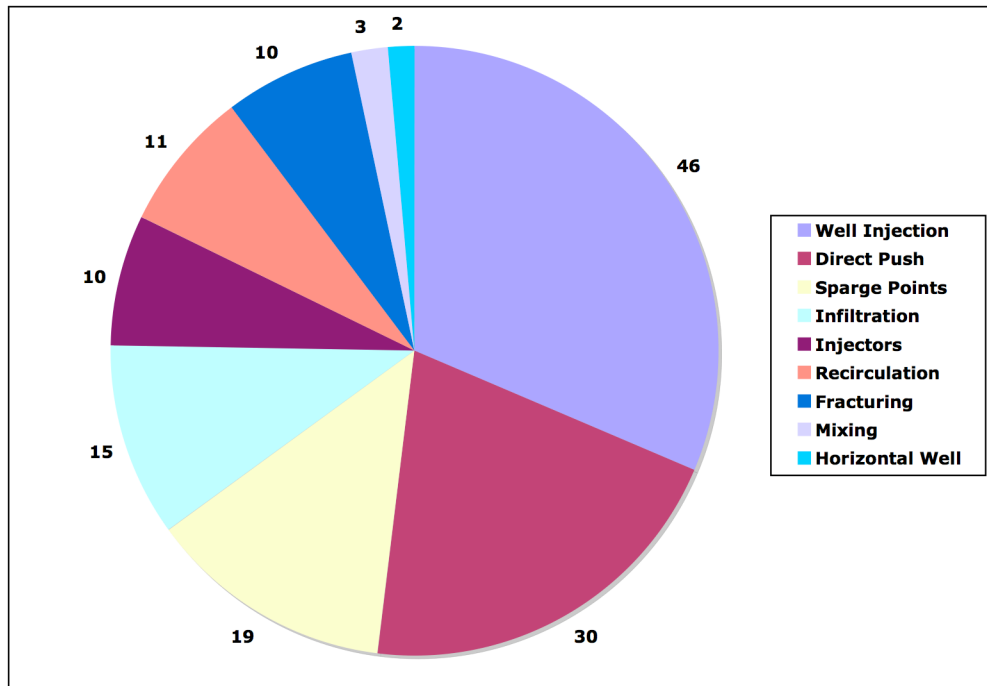


Notes: n=182. The apparent decline in the frequency of the use of ISCO (the slope of the above curves) is an artifact of the fact that there is a lag time between when a project is finished and when the results are made available to the public. Thus the decrease in slope of the curves in this and other similar charts near the year 2007 should not be interpreted as a decline in the use of ISCO as a remediation technology.

The trend over time shows that permanganate and CHP are the most commonly applied, followed by ozone, and that sodium persulfate, peroxone, and percarbonate are the more recently developed of the oxidants. The overall trends in field-scale oxidant use over time are similar to the results of a similar analysis from a literature review of laboratory studies of ISCO oxidants conducted by Petri (2007) in that permanganate and CHP are the most commonly used/studied, though ozone and persulfate are prevalent as well.

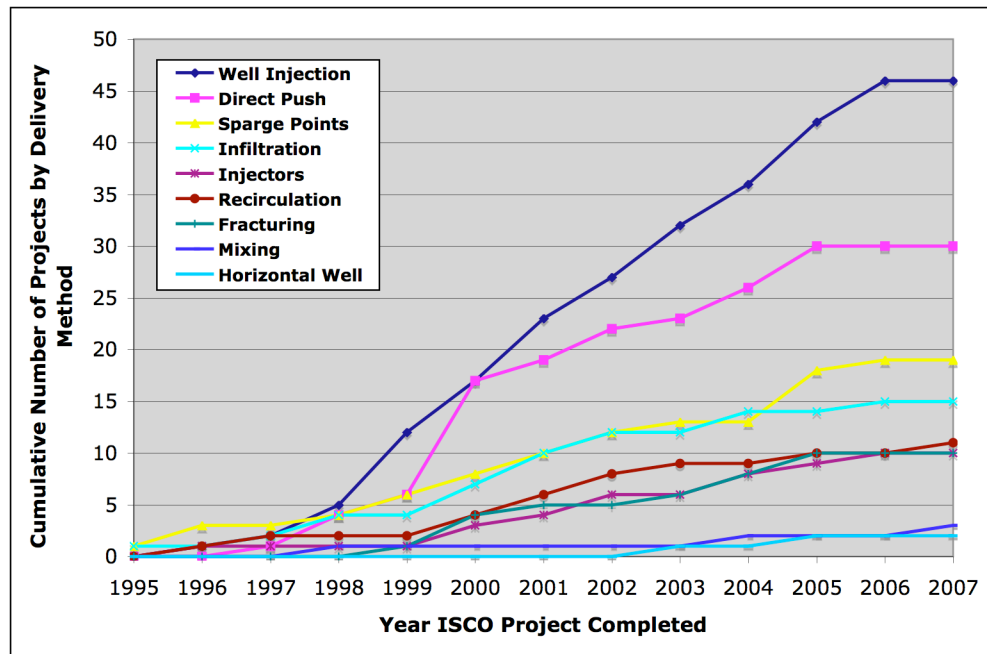
ISCO reagents have been delivered using many techniques. However, well injections, direct push points, and sparge points (applicable only to ozone and peroxone) are the most commonly used (Figures 4-3 and 4-4 on following page).

Figure 4-3: Distribution of ISCO Delivery Methods



Notes: n = 146.

Figure 4-4: ISCO Delivery Methods Over Time



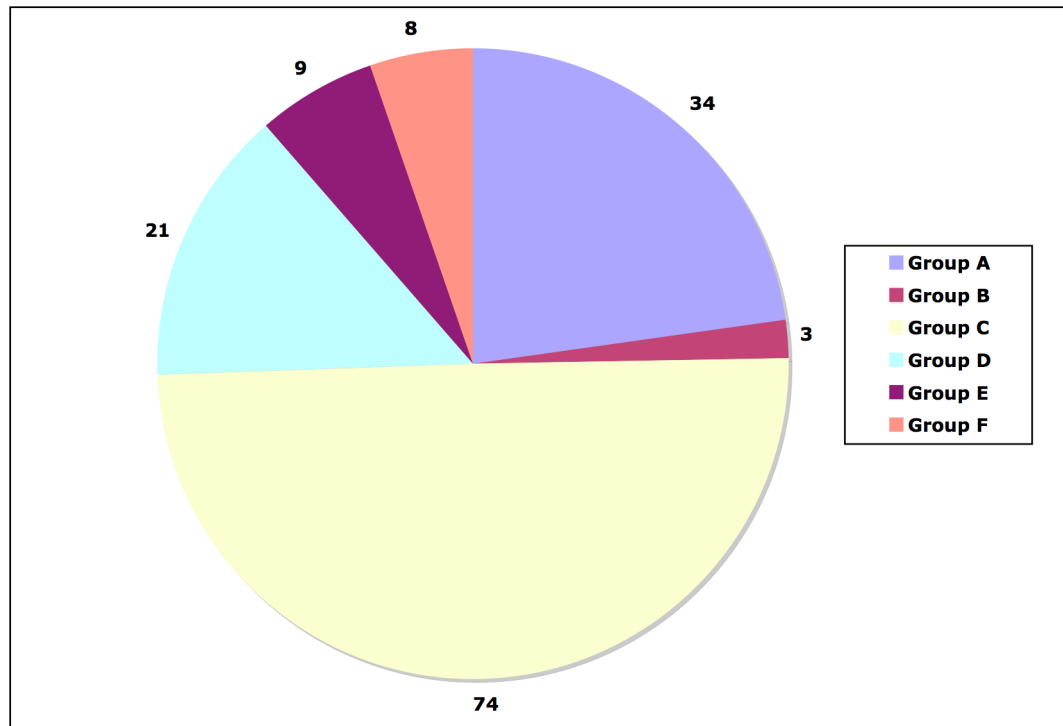
Notes: n=146

ISCO has been used in a wide variety of geologic media, including unconsolidated sediments and fractured bedrock. The average saturated hydraulic

conductivities reported among sites varied between  $10^{-4}$  (a silty clay) to 2400 (a karst system) ft/day, with a median of 4.5 ft/day (n=87). The depth to water varied between 1 to 150 ft bgs with a median of 10 ft bgs (n=124). The range of reported and calculated (using Darcy's law and assuming an effective porosity of 0.3 if none provided) groundwater flow velocity was 0.002 to 5 ft/day, with a median of 0.2 ft/day (n=58). The TOC in soil ranged between 0.0013 to 280 g/kg, with a median of 4.1 g/kg (n=23) (Appendix B, Tables B-11 and B-12 for more information on these and other hydrogeologic parameters). The degree of heterogeneity in unconsolidated soils varied considerably, with descriptions ranging from "homogeneous fine sand, trace silt" to "highly heterogeneous sand, gravel, and silt." The ratio between the maximum to minimum hydraulic conductivity values recorded at a single site (another measure of heterogeneity) ranged between 1.25 to nearly 4000 (n=12).

To put this wide range in geological characteristics into an organized system that could be analyzed, the geology grouping system described in the methods section was used. ISCO was most commonly applied to permeable, heterogeneous systems (Group C), followed by permeable, homogeneous systems (Group A). There are appreciable, but less frequent applications to impermeable materials and fractured rock. The overall distribution of geology groups in ISCO-DB1 is shown in Figure 4-5 on the following page, and trends over time in Figure 4-6.

Figure 4-5: Distribution of Geology Groups



Notes: n=149

Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

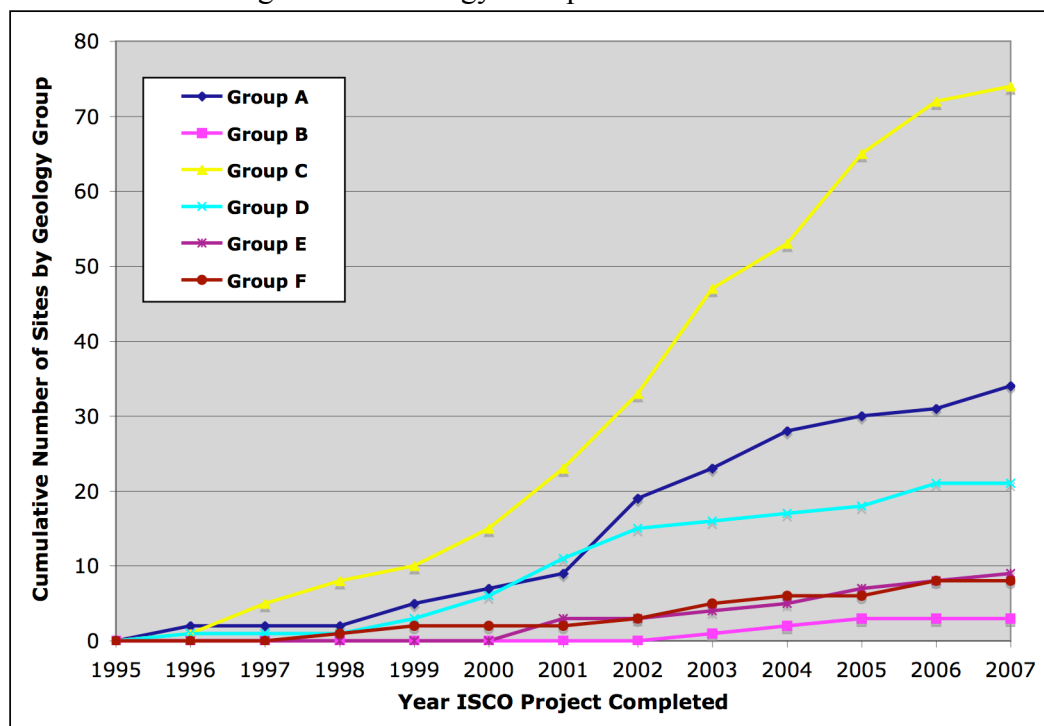
Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)

Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

Figure 4-6: Geology Group Treated Over Time



Notes: n=149

Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)

Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

The RAOs of an ISCO remediation vary between a desire to reduce COC concentrations to below MCLs to evaluating the effectiveness of the remediation technology at the field-scale. As described in the methods section, the goals of an ISCO remediation were placed into five categories, and some projects had multiple goals for the remediation technology. MCLs were the most common goal (37%), followed by general mass or time to cleanup reduction (31%), technology evaluation or optimization (27%), ACLs (25%), and lastly mass reduction by a predetermined percentage (9%) (n=112) (Appendix B, Table B-13). However, the goals of remediation appeared to be dependent upon a multitude of factors. Sites contaminated with fuel related compounds had a much higher frequency of attempting to meet MCLs (75% MTBE, 66% TPH, 48% BTEX) than

chlorinated compounds (28% chloroethenes and 16% chloroethanes) (Appendix B, Table B-39).

The ISCO designs within the case studies reviewed were predominantly full scale applications (65%) with a lesser amount of pilot tests (35%). Over half (52%) of ISCO designs targeted both sorbed and aqueous phase contaminants, slightly less than half (45%) targeted aqueous phase contaminants only, and a few sites (2%) treated both aqueous phase contamination and that trapped within the bedrock matrix (n=164) (Appendix B, Table B-16). [The distinction between aqueous only and the other categories was based upon the text description of the site conceptual models and also the TOC content of the soil if reported. The latter category does not mean that sorbed phase contamination did not exist, just that it was considered negligible relative to the aqueous phase contamination.] Most designs (52%) targeted the source zone only, while 19% targeted both the source and the plume, 14% targeted the plume only, and 14% were pilot tests and only targeted a smaller portion of the source or plume (n=170) (Appendix B, Table B-17). The areal extent of the target treatment zone ranged from 80 to 260,000 sf with a median of 8,100 sf (n=110). The volume of the TTZ ranged from 200 to 9,100,000 cf with a median of 135,000 cf (n=110) (Appendix B, Table B-18). Oxidant loading rates (mass oxidant / mass soil treated) varied between 0.004 g/kg and 60 g/kg with a median of 1.1 g/kg (n=68). The number of pore volumes varied between 0.004 and 56 with a median of 0.12 (n=65). The number of delivery events varied between one and ten with a median of two (n=159) (Appendix B, Table B-20).

A majority of sites (78%) performed a treatability study (n=121) (Appendix B, Table B-21). However, this may be an overestimate because it was difficult to ascertain that a treatability study was not performed in many cases simply because no mention was made of treatability studies in project documents. When treatability studies were not mentioned, no assumption was made (i.e. the field was left blank, and would not be included in analyses such as the calculation of the 78% frequency above). Note that this is not the same as assuming that no treatability study was performed. Treatability studies were determined not to have been performed by correspondence with the site contacts and from report language indicating that a treatability study was deemed unnecessary, and were entered as a 0 in ISCO-DB1. A majority of full scale sites (60%) performed a

pilot test (n=87) (Appendix B, Table B-23). The ISCO program was modified during field implementation at 58% of the sites (n=78) (Appendix B, Table B-24). Program modification was tracked to evaluate the frequency with which practitioners are using the Observational Approach. This theory of environmental remediation has recently been adapted from geotechnical engineering (Peck 1969) and follows the philosophy that uncertainty may be acceptable during the initial implementation but that performance results should be continually monitored and the site conceptual model and ISCO system design updated based upon observations made during implementation. Most sites were coupled (76%), with 60% using a pre-ISCO couple, 22% coupling during ISCO implementation, and 30% coupling post-ISCO (n=135) (Appendix B, Table B-25). Coupling includes other remediation technologies implemented in the exact same location as ISCO and those that were implemented directly adjacent to ISCO (e.g. SVE in vadose zone). The frequency of post-ISCO coupling is likely an underestimate because many of the documents that were reviewed were written shortly after ISCO was completed, and post-ISCO coupling may have been initiated after the writing of those documents. Excavation was the most common pre-ISCO couple (50%), followed by SVE (18%). P&T (11%) and SVE (9%) were used most frequently during ISCO, while MNA (19%) and EISB (17%) were the most common post-ISCO couples (Appendix B, Table B-26).

The performance results achieved by ISCO varied as widely as any of the parameters listed above. At some sites ISCO achieved greater than 99.99% reductions in maximum COC concentrations in groundwater. Six sites have met and maintained MCLs, including two chlorinated solvent sites (DNAPL did not appear to be present prior to ISCO at either of these two sites). One site with a known DNAPL release reduced concentrations of TCE from near its solubility limit to risk-based levels (300 ug/L) using ISCO (Sun Belt Precision Products, reported by B.L. Parker in EPA 2003 and ITRC 2005). However, other sites have shown negligible changes, or even increases, in groundwater COC concentrations following ISCO. While there are many confounding factors that impact the percent reductions noted in ISCO-DB1, non-chlorinated compounds generally showed greater decreases than chlorinated compounds. The six sites that met MCLs represent 15% of the sites in ISCO-DB1 that attempted to meet

MCLs (n=39). ACLs were met by 39% of projects attempting to do so (n=28), while 46% successfully reduced mass or concentration by the targeted percentage (n=11). Site closure was attained at 24% of the full scale sites (n=74). Site closure as defined here means that the project met whatever regulatory criteria were required (e.g. MCLs, ACLs, implementation of institutional controls) such that remediation and monitoring were no longer required. The median total project cost was \$220,000 (n=55) and the median unit cost was \$94/yd<sup>3</sup> (n=33) (see Appendix B, Table B-28 through B-34 for detailed performance tabulation).

Overall, rebound occurred at over half (62%) of sites in ISCO-DB1 (n=71). Among those sites that experienced rebound, it occurred at nearly half (49%) of the monitoring wells within the TTZ (n=26). Rebound occurred less frequently at sites with fuel related contaminants than at sites contaminated with chlorinated VOCs. In addition, when rebound did occur at sites with fuel related contaminants, it did so at a lower percentage of monitoring locations than chlorinated VOC sites.

#### **4.2 Results by COC Group**

The use of ISCO is variable depending on the COCs present at a site. This section will focus on differences between treatment of chloroethenes and fuel-related compounds. Other chlorinated compounds and SVOCs are omitted in this section because of the relatively smaller number of case studies for these compounds. The data for chloroethanes and chlorinated benzene compounds are more similar to chloroethenes than it is to fuel-related compounds. Refer to Appendix B, Section B.2 for more detailed data on these omitted contaminant groups as well as tabulation of parameters not presented here subdivided by COC group.

First, more practitioners attempted to meet MCLs at BTEX, TPH, and MTBE contaminated sites than they are at sites contaminated with chloroethenes (Table 4-1 on following page).



Table 4-1: Goals of ISCO Remediation by COC Group

Goals of Remediation	Percent of Sites			
	Chloroethenes	BTEX	TPH	MTBE
Meet MCLs	28	48	67	75
Meet ACLs	28	19	13	8
Reduce Mass by a Given %	10	5	0	0
Reduce Mass and/or Time to Cleanup	34	33	20	17
Evaluate Effectiveness / Optimize	32	5	7	0
<i>n</i>	<i>110</i>	<i>21</i>	<i>15</i>	<i>12</i>

Notes: Horizontal summation does not yield the total number of sites with each goal, as multiple contaminant groups may have been present at a given site. The *n* value given at the base of the table may be less than the sum of the above cells because some sites had more than one of the above goals.

The selection of oxidant also varies by COC group. Permanganate was the most commonly selected oxidant for the chloroethenes, whereas CHP and ozone were the more commonly selected for the fuel related compounds (Table 4-2). The other COC groups have also been included in this table for reference. Note that the COC groups are not mutually exclusive, and that the high percentage of chloroethane sites treated with permanganate may have been situations in which the chloroethane was a co-contaminant and the primary goal of the remediation was to treat chloroethenes.

Table 4-2: Oxidant Used by COC Group

Oxidant Used	Percent of Sites						
	Chloroethenes	Chloroethanes	Chlorobenzenes	BTEX	TPH	MTBE	SVOCs
Permanganate	58	50	18	8	13	7	15
CHP	31	33	64	50	46	20	45
Persulfate	6	28	27	13	8	13	5
Ozone	8	6	9	21	25	53	40
Peroxone	1	6	0	3	4	13	5
Percarbonate	1	6	0	11	8	0	5
<i>n</i>	<i>154</i>	<i>18</i>	<i>11</i>	<i>38</i>	<i>24</i>	<i>15</i>	<i>20</i>

Notes: Horizontal summation does not yield the total number of sites with each oxidant, as multiple contaminant groups may have been present at a given site.

The approach in the remediation design with respect to pre-design testing and use of coupled approaches varied between the chloroethenes and the fuel related compounds, particularly MTBE. All three groups of fuel related sites used a coupled approach more frequently. MTBE sites used treatability studies less and pilot scale studies more often than the other groups. These results are shown in Table 4-3 on the following page.

Table 4-3: ISCO Pre-Design Testing and Coupling by COC Group

	<b>Chloro-ethenes</b>	<b>BTEX</b>	<b>TPH</b>	<b>MTBE</b>
<b>Percent Using Treatability Study</b>	67	70	56	33
<i>n</i>	51	10	9	3
<b>Percent Using Pilot Study – Full Scale Sites Only</b>	58	67	55	83
<i>n</i>	60	12	11	6
<b>Percent of Sites Using Coupling</b>	71	94	93	92
<b>Percent Coupled Before ISCO</b>	53	83	64	83
<b>Percent Coupled During ISCO</b>	19	33	21	33
<b>Percent Coupled After ISCO</b>	33	17	43	8
<i>n</i>	95	18	14	12

The results of ISCO remediation were different between the sites contaminated by chloroethenes versus those contaminated by fuel related compounds. Sites contaminated with chloroethenes did not show on average results that were as positive as ISCO implementations conducted at sites contaminated with fuel related compounds. These results are shown in Table 4-4 on the following page.

The low incidence (0%) of meeting MCLs at BTEX sites may be confounded by the stringent data collection methods. This metric was not entered in the affirmative unless the fact that MCLs were met and maintained could be confirmed by contacting the regulatory official responsible for the project. Such confirmation was attempted but unsuccessful for the BTEX sites. The result in the table should not be interpreted as meaning that no ISCO remediation has ever reduced BTEX concentrations to MCLs. It

only means that the regulatory officials could not be contacted during the course of this case study review to confirm that MCLs had been met.

Table 4-4: Selected Performance Results by COC Group

	<b>Chloroethenes</b>	<b>BTEX</b>	<b>TPH</b>	<b>MTBE</b>
<b>Percent Attaining Closure</b>	20	43	38	63
<i>mean DQC</i>	1.4	2.0	1.4	1.5
<i>n</i>	50	7	8	8
<b>Percent Attaining MCLs</b>	3	0*	25	60
<i>mean DQC</i>	1.4	2.1	1.6	1.2
<i>n</i>	105	12	12	5
<b>Percent of Sites with Rebound</b>	72	38	43	29
<i>n</i>	54	8	7	7
<b>For Rebound Sites, Percentage of MWs w/ Rebound</b>	50	29	25	29
<i>n</i>	22	2	1	2

Notes: \* = The incidence of meeting MCLs was only entered in the affirmative if after attempting to discuss the case with the regulatory official (see Section 3.3.3). This percentage shown should not be interpreted to mean that ISCO has never reached MCLs at a BTEX site. Site closure is defined as the completion of active remediation and monitoring, and includes the attainment of MCLs, risk-based standards, and may include requirements of institutional and engineering controls. The percentage attaining MCLs is based on those samples, including those who stated that their goals for the remediation were another outcome besides meeting MCLs.

### 4.3 Results by Oxidant

There are differences in the results when the entire dataset is subdivided by oxidant, a selection of which is detailed in this section. A more detailed set of summary statistics of the ISCO-DB1 data subdivided by oxidant are provided in Appendix B, Section B.3.

Among the projects contained in ISCO-DB1, permanganate was used to treat predominantly chloroethenes, with this group of COCs being present at 95% of the sites at which permanganate was applied (n=87). Among sites at which CHP was applied, chloroethenes were present at 61%, while BTEX, TPH, and SVOCs were present at 26%,

15%, and 11% of the sites, respectively (n=72). Note that the percentages of this and other analyses in which COC groups are analyzed may exceed 100% because multiple contaminant groups were present at some sites. Among ozone sites, chloroethenes were present at 44%, BTEX at 30%, TPH at 22%, MTBE at 30%, and SVOCs present at 26% (n=27) (Appendix B, Table B-62).

The goals of remediation varied somewhat by oxidant. Among ozone sites, 71% attempted to meet MCLs (n=21), and 50% of peroxone sites attempted MCLs (n=4). The other four oxidants attempted to meet MCLs between 20 and 33% of the time (Appendix B, Table B-64).

The design of ISCO systems varies between the different oxidants. Ozone and peroxone were used to treat only the contaminant plume (as opposed to the source zone) at 35% (n=20) and 50% (n=4) of the sites at which those two technologies were applied, respectively. The other oxidants only targeted the plume at between 0 and 13% of sites (Appendix B, Table B-66). Ozone and peroxone systems generally targeted larger TTZ areas and volumes than the other four oxidants (Appendix B, Tables B-67 and B-68). The oxidant concentration was lower for permanganate than for CHP and persulfate, both as injected and after in situ mixing with activators and injected water (Table 4-5).

Table 4-5: Oxidant Concentration Injected

	<b>Permanganate</b>	<b>CHP</b>	<b>Persulfate</b>
<b>Median Injected Oxidant Concentration (g/L)</b>	24	190	160
<b><i>n</i></b>	59	37	8
<b>Median Oxidant Concentration After in situ Mixing (g/L)</b>	23	90	100
<b><i>n</i></b>	40	23	5

Notes: See Appendix B, Tables B-69 and B-70 for further details including data on other oxidants. The second measure of concentration above was calculated for each site by reducing the injected oxidant concentration to account for the injection of activator and/or water, assuming complete mixing in situ. Permanganate and persulfate concentrations are for those anions only, while CHP is the concentration of hydrogen peroxide.

Other design parameters also differ between the oxidants, including ROI, the number of pore volumes delivered, the number of delivery events, and the duration of those delivery events (Table 4-6). The design ROI, as determined from project reports' text descriptions

or injection spacing, is consistent between the aqueous phase oxidants (permanganate, CHP, and persulfate) and greater for ozone. The observed ROI, as determined from project documents' results of injection monitoring, showed that CHP generally attained the design ROI, while permanganate, persulfate, and ozone observed greater oxidant distribution than that for which the project was designed. Permanganate was delivered at a lower oxidant loading rate (g oxidant / kg media treated) and higher number of pore volumes than CHP, while persulfate was introduced at a higher median dose and number of pore volumes. The number of delivery events and their duration was similar for the aqueous phase oxidants, and the duration of delivery events much longer for ozone.

Table 4-6: Design Parameters by Oxidant Used

	<b>Permanganate</b>	<b>CHP</b>	<b>Persulfate</b>	<b>Ozone</b>
<b>Median Design ROI (ft)</b>	14	15	13	25
<i>n</i>	29	30	6	5
<b>Median Observed ROI (ft)</b>	25	15	20	38
<i>n</i>	11	6	3	2
<b>Median Oxidant Dose (g/kg)</b>	0.4	1.2	5.1	0.1
<i>n</i>	36	19	6	4
<b>Median Number of Pore Volumes Delivered</b>	0.16	0.073	0.57	no data
<i>n</i>	32	26	6	
<b>Median Number of Delivery Events</b>	2	2	1	1
<i>n</i>	65	57	10	15
<b>Median Duration of Delivery Events (days)</b>	4	6	4	210
<i>n</i>	45	42	7	15

Notes: Refer to Appendix B, Tables B-71 through B-76 for additional data on these parameters.

Treatability studies were used for 78% of permanganate sites (n=50), 78% of CHP sites (n=45), 100% of persulfate sites (n=8), 100% of percarbonate sites (n=2), 43% of ozone sites (n=7), and 33% of peroxone sites (n=3) (Appendix B, Tables B-77 and B-78). The frequency of pilot testing among full scale applications ranged between 50 and

65% for permanganate, CHP, ozone, and peroxone, while 100% of persulfate sites used a pilot test (n=4) and 0% of percarbonate sites used a pilot test (n=1) (Appendix B, Table B-79).

The performance achieved by ISCO varied within ISCO-DB1 depending on the oxidant used (Table 4-7). This table includes all contaminants and sites with and without NAPL, and also does not consider the cost of the remediation. These confounding factors have not been accounted for in this table, and therefore this table should not be interpreted to mean that one oxidant is universally preferable over another.

Table 4-7: Selected Performance Results by Oxidant

	Permanganate	CHP	Ozone	Persulfate	Peroxone
<b>Percent of Sites Attaining Closure</b>	16	27	50	0	50
<i>mean DQC</i>	1.4	1.5	1.6	1.3	1.3
<i>n</i>	32	22	12	4	2
<b>Percent of Sites Attaining MCLs</b>	0	2	31	0	50
<i>mean DQC</i>	1.4	1.5	1.5	1.3	1.0
<i>n</i>	55	45	13	8	2
<b>Median Percent total COC Reduction</b>	51	56	96	24	no data
<i>n</i>	27	26	5	5	
<b>Median Total Cost (1000s U.S. \$)</b>	240	270	160	15	270
<i>n</i>	25	14	10	1	3
<b>Median Unit Cost (\$/yd<sup>3</sup>)</b>	130	130	44	no data	32
<i>n</i>	17	10	2		2
<b>Percent of Sites with Rebound Observed</b>	78	57	27	50	0
<i>n</i>	32	21	11	2	1
<b>For Rebound Sites, Percentage of MWs w/ Rebound</b>	48	53	28	no data	na
<i>n</i>	11	10	3		

Notes: na = not applicable. This table includes all contaminants, Geology Groups, and sites with and without NAPL. See Appendix B, Tables B-82 through B-88 for additional data. The percentage of sites listed in the Attaining MCLs category includes all sites irrespective of their remediation goals.

#### 4.4 Results by Geology Group

This section presents selected statistics based on the six geology groups into which the sites were placed. See Appendix B, Section B.4 for the complete set of tables based upon Geology Group. The classification system used to group the sites based on geologic media is repeated below and described thoroughly in Section 3.3.1 above.

- Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )
- Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )
- Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )
- Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )
- Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)
- Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

Geology Groups A and C collectively comprise 69% of the case studies in ISCO-DB1. The three Groups B, E, and F comprise another 17% collectively. These latter three groups are actually similar physically in that they are dominated by flow through fractures that are interconnected to varying degrees, but also have an interaction between the generally immobile matrix porosity and the more mobile fracture zones. For this reason they are lumped together in the tables that follow. The lumping of these three groups is based upon the assumption that the homogeneous, impermeable sites comprising Group B are in fact fractured. Fractures in clay materials were reported at many clay sites in ISCO-DB1. The presence of contamination within clay materials, including concentrations of COCs indicative of DNAPL, is further evidence that these systems are fractured, because the contamination must have gotten through the clay somehow. These two lines of evidence support the lumping of Geology Groups B, E, and F, termed Group BEF, together for analysis.

There are some differences between the ways in which practitioners approach sites based upon the geologic media to be treated. Group A is that for which projects attempt to meet the most stringent remediation goal of meeting MCLs most often, as shown in Table 4-8 on the following page.

Table 4-8: Goals of ISCO Remediation by Geology Group

Goal of Remediation	Percent of Sites			
	Group A	Group C	Group D	Group BEF
Meet MCLs	43	35	31	29
Meet ACLs	27	22	56	10
Reduce Mass by X%	3	12	6	10
Reduce Mass and/or Time to Cleanup	20	37	13	43
Evaluate Effectiveness / Optimize	20	31	13	38
<i>n</i>	30	78	16	21

Notes: Group BEF is the aggregate of Groups B, E and F. Vertical summation of the columns may yield greater than 100% because some sites had multiple treatment goals.

Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{max}/K_{min} < 1000$ )

Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{max}/K_{min} < 1000$ )

Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{max}/K_{min} > 1000$ )

Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{max}/K_{min} > 1000$ )

Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)

Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

ISCO system design varied with respect to the geologic media treated.

Permanganate is the selected oxidant relatively more frequently in the lower permeability Groups D and BEF, whereas CHP is selected relatively less frequently at these types of sites (Table 4-9). Group A sites performed treatability and pilot studies less frequently than the other Geology Groups (Table 4-10). However, the difference in the use of coupling was not nearly as marked, as 77% of both Group A ( $n=30$ ) and C ( $n=66$ ) sites used a coupled approach, while 57% of Group D sites coupled ISCO with another technology ( $n=14$ ) and 94% of Group BEF sites coupled ( $n=16$ ). These trends are similar when considering whether the coupled technology was implemented before, during, or after ISCO (Appendix B, Tables B-102 and B-103).



Table 4-9: Oxidant Used by Geology Group

Oxidant	Percent of Sites			
	Group A	Group C	Group D	Group BEF
Permanganate	33	38	68	50
CHP	41	40	32	29
Persulfate	5	6	0	7
Ozone	12	17	3	14
Peroxone	7	2	0	0
Percarbonate	5	3	0	0
<i>n</i>	42	98	31	14

Table 4-10: ISCO Pre-Treatment Testing by Geology Group

Type of Pre-Treatment Test	Group A	Group C	Group D	Group BEF
Percent Using Treatability Study – All Scales	55	83	80	75
<i>n</i>	20	64	15	16
Percent Using Treatability Study – Full Scale Only	25	40	70	75
<i>n</i>	12	75	10	8
Percent Using Pilot Study – Full Scale Only	29	59	85	78
<i>n</i>	17	44	13	9

Notes: Group BEF is the aggregate of Groups B, E and F. Vertical summation of the columns may yield greater than 100% because some sites had multiple treatment goals.

Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)

Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

The results of ISCO remediation also vary with the type of geologic media treated. Using the attainment of site closure as the performance metric, Group A sites were closed 47% of the time ( $n=15$ ), whereas 13% of Group C sites attained closure ( $n=38$ ) (Appendix B, Table B-104). Using the attainment of MCLs as the performance metric, among sites that attempted to meet this goal, 33% of Group A sites were successful ( $n=24$ ) as opposed to 13% of Group C sites ( $n=38$ ) (Table 4-11). No (0%) of sites in other categories attained MCLs. When examining percent reduction of maximum total COC concentrations, Group A sites had a median percent reduction of 77% ( $n=11$ ),

compared to 58% for Group C (n=39), 43% for Group D (n=9), and 43% for Group BEF (Appendix B, Table B-107). Rebound occurred least frequently at Group A sites, and most frequently in Group BEF sites (Table 4-12). The number of wells experiencing rebound at sites where rebound did occur shows the opposite trend, with rebound occurring over a larger percentage of the site's monitoring wells at Group A sites, and less at Group BEF sites (Table 4-12).

Table 4-11: Selected Performance Metrics at ISCO Sites by Geology Group

Performance Result	Group A	Group C
<b>Percent Attaining Closure – Full Scale Only</b>	47	13
<i>n</i>	15	38
<b>Percent Meeting MCLs</b>	33	11
<i>n</i>	9	19
<b>Percent Meeting ACLs</b>	29	50
<i>n</i>	7	12

Notes: The percentages for sites meeting MCLs and ACLs are only from the subset of those who stated that that particular standard was a goal of their remediation. The mean DQC values for Group A are 1.4, 1.4, and 1.4 from top to bottom, and for Group C are 1.5, 1.2, and 1.3. See Appendix B, Tables B-102 and B-103 for details on omitted Geology Groups.

Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Table 4-12: Incidence of Rebound by at ISCO Sites Geology Group

	Group A	Group C	Group D	Group BEF
<b>Percent of Sites with Rebound</b>	35	65	75	89
<i>n</i>	17	34	8	9
<b>For Rebound Sites, Percentage of MWs w/ Rebound</b>	56	49	52	36
<i>n</i>	3	15	4	3

Notes: Group BEF is the aggregate of Groups B, E and F.

Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)

Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

See Appendix B, Tables B-104 through B-110 for further details on performance results by Geology Group.

#### 4.5 Results by NAPL Presence

The presence of NAPL impacted the design and results of ISCO remediation, selected examples of which are presented in this section. Refer to Appendix B, Section B.5 for the complete tabulation of results with respect to NAPL presence.

There were three metrics used to assess the presence of NAPL. The first two are whether or not the project reports and documents stated that DNAPL or LNAPL were present, and are termed “LNAPL Reported” and “DNAPL Reported” in the tables that follow. These groups include both situations in which NAPL was observed directly (e.g. in monitoring wells or with ribbon samplers) or situations in which it was assumed to be present based on aqueous or solid phase sampling concentrations. The third metric is whether or not groundwater concentrations were measured above 1% of that compound’s solubility limit, labeled “>1% of Solubility”. This metric is based off of EPA’s guidance, and was applied only to chlorinated compounds (EPA 1992, EPA 1993). None of these three metrics are mutually exclusive. Some sites reported that both LNAPL and DNAPL were present. And the DNAPL Reported and >1% of Solubility metrics have considerable overlap, as would be expected.

The groups based on these three NAPL metrics are compared to sites at which NAPL was not present. This fourth group is all sites that do not fall into any the three categories above. In the case of chlorinated solvents, projects that reported concentrations exceeding the 1% of solubility criterion were not included in the “No NAPL” category even if project documents made no mention of the possibility of DNAPL.

As with the other parameters, the presence of NAPL appears to impact the goals that project teams select for ISCO remediation. Sites without NAPL attempted to meet MCLs at 51% of sites (n=120), while 40% of LNAPL sites (n=10), 19% of DNAPL sites (n=57) and 21% of >1% of Solubility sites (n=68) attempted this most stringent of the goals (Appendix B, Table B-114).

Oxidant selection varied with NAPL presence and type, with permanganate selected relatively more often at DNAPL sites, and ozone, peroxone, and percarbonate selected relatively more often at LNAPL sites and sites without NAPL. The selection of CHP and persulfate as the oxidants did not vary as much with respect to the presence of

NAPL (Appendix B, Table B-115). The oxidant delivery method also varied with respect to the four NAPL indicators (Table 4-13). Note that recirculation, fracturing, and mechanical mixing were used almost exclusively at DNAPL sites, while sparge points were used almost exclusively at LNAPL and no NAPL sites.

Table 4-13: Oxidant Delivery Method by NAPL Presence

Delivery Method	Percent of Sites			
	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
Well Injection	8	43	45	36
Direct Push	33	22	25	20
Sparge Points	42	2	3	19
Infiltration Trench/Gallery	8	5	11	10
Injectors	8	13	8	4
Recirculation	0	15	13	4
Fracturing	0	10	8	4
Mixing	0	2	3	2
Horizontal Well Injection	8	0	0	1
<i>n</i>	12	60	76	94

Notes: Injectors refer to injection wells fitted with a mixer designed to mix injected oxidant and activator solutions at the well screen.

Source zone treatment was relatively more common at DNAPL sites, at 70% for DNAPL Reported (n=59) and 64% for >1% of Solubility (n=75), versus 54% of LNAPL sites (n=13), and 37% of sites without NAPL (n=82). Plume treatment was selected at 29% of sites without NAPL, 8% of LNAPL sites, and 0% and 1% for the two groups of DNAPL sites (n values same as previous analysis). Treatment of the source and plume ranged between 17% and 23% for these four NAPL metrics (n values same as preceding analyses, see Appendix B, Table B-117). The median number of pore volumes delivered ranges between 0.11 for sites without NAPL to 0.13 for sites with DNAPL reported. LNAPL sites are an outlier with respect to this metric, with a median number of pore volumes of 0.37 (n=2) (Appendix B, Table B-120). The median number of delivery events for DNAPL sites was two (2) compared to one (1) for LNAPL and no NAPL sites (Appendix B, Table B-121).

Use of pre-treatment testing (treatability and pilot studies) and coupling varied with respect to NAPL presence. Treatability studies were used less frequently at LNAPL sites than other sites. Pre-treatment testing and coupling were used with consistent frequency at DNAPL sites and sites without NAPL (Table 4-14). Conversely, pilot studies were conducted less frequently at DNAPL sites compared to LNAPL sites and sites without NAPL. The incidence of program modification was relatively constant between the various NAPL indicators. Coupling was used most frequently at LNAPL sites and least frequently no NAPL sites. However, post-ISCO coupling was used more commonly used at DNAPL sites (Appendix B, Table B-122 through B-126).

Table 4-14: Use of Pre-design Testing and Coupling at ISCO Sites Based on NAPL Presence

	<b>LNAPL Reported</b>	<b>DNAPL Reported</b>	<b>&gt;1% of Solubility</b>	<b>No NAPL</b>
<b>Percent Using Treatability Study</b>	67	77	76	79
<i>n</i>	6	47	53	58
<b>Percent Using Pilot Study – Full Scale Only</b>	67	59	54	63
<i>n</i>	6	34	41	38
<b>Percent Modified During Implementation</b>	60	66	58	56
<i>n</i>	5	29	38	36
<b>Percent of Sites Using Coupling</b>	90	80	76	73
<b>Percent Coupling Before ISCO</b>	70	57	58	61
<b>Percent Coupling During ISCO</b>	20	25	22	22
<b>Percent Coupling After ISCO</b>	10	45	41	22
<i>n</i>	10	49	59	64

The results of ISCO remediation vary with respect to whether NAPL is present and whether that NAPL is a DNAPL or LNAPL. 10% of sites without NAPL attained MCLs (n=59) while none of the sites indicating NAPL met MCLs (Appendix B, Table B-130). The preceding statistic includes all sites, not just the sites that stated that meeting MCLs was the goal of their remediation. The same caveat applied to the fuel related

compounds in Section 4.2 applies here: the data entry requirement for entering that a site had met MCLs in the affirmative was confirmation with the regulatory official. This is not to state that no LNAPL site has ever met MCLs, simply that none of these situations could be confirmed with regulatory officials by the author of this thesis during this project. Site closure was attained with less frequency at DNAPL sites (9% DNAPL Reported sites (n=32) and 13% of >1% of Solubility sites (n=40)), compared to 37% of No NAPL sites (n=30) and 60% of LNAPL Reported sites (n=5) (Appendix B, Table B-128). The median maximum total COC reduction at sites without NAPL was 68% (n=28), compared to 48% (n=33) and 50% (n=44) for the DNAPL Reported and >1% of Solubility metrics, respectively (Appendix B, Table B-131). Rebound occurred with greater frequency at DNAPL sites (71% DNAPL Reported sites (n=28) and 78% of >1% of Solubility sites (n=36)), compared to 56% of No NAPL sites (n=34) and 0% of LNAPL Reported sites (n=5) (Appendix B, Table B-132). Both median total cost and unit costs were greater for DNAPL sites than for LNAPL sites and sites without NAPL (Appendix B, Tables B-133 and B-134).

#### **4.6 Results of Impacts on Microbial Populations**

Fifteen case studies examined microbial communities before and after ISCO. As microbiology has experienced a rapid technological evolution, the methods used to assess the microbial communities at ISCO sites were quite variable (plate counts measuring biomass to various molecular techniques). Despite these varying techniques, none of the case studies reviewed showed a lasting decrease in microbial biomass. Some studies showed an initial decrease immediately after ISCO implementation, however the microbial biomass rebounded to baseline levels in all situations.

EISB was used as a post-ISCO coupled technology at 19 sites in ISCO-DB1. MNA was explicitly used post-ISCO at 20 sites in ISCO-DB1. The use of MNA after ISCO is likely underestimated because: 1) it was only entered as a post-ISCO couple when project documents explicitly stated it was to be used, and 2) because many of the project documents reviewed were written shortly after ISCO and the need for and selection of a post-ISCO technology had not been assessed at that time.

#### **4.7 Results of Impacts on Metals Mobility**

Metals concentrations in groundwater were examined to evaluate the incidence and severity of changes in metals mobility as a result of ISCO. Metals concentrations may increase because: 1) ISCO changes the aquifer redox state, 2) ISCO may change the aquifer pH, and 3) because metals are a trace impurity in some oxidants (e.g. permanganate). Ten of 23 sites (43%) of sites that tested for metals reported that metals concentrations remained within background ranges during and after ISCO. The remaining 13 sites reported metals concentrations during and after ISCO that were elevated relative to baseline concentrations.

However, the degree to which metals mobilization constitutes a risk is highly site-specific, depending on nearby receptors and regulatory standards. For these and other reasons, the means through which project teams assessed metals mobilization were highly variable. These issues made assigning a yes/no answer to the question of whether or not metals were mobilized impractical. The results were recorded as described in the project reports, and are shown in Table 4-15 below. Except when otherwise noted (the two ozone sites), the metals impacts described below were restricted to the TTZ. The two ozone sites warrant further explanation, which is shown on Table 4-15 on the following page.

Table 4-15: Duration of Metals Increases After ISCO

Metal	Oxidant Used			
	Permanganate	Persulfate	Ozone / Peroxone	Percarbonate
<b>Arsenic</b>	>1 month <5 months >18 months in single TTZ location			>1 month
<b>Chromium</b>	<12 months >5 months >18 months	<3 months	Increase at off-site location (two projects)	
<b>Manganese</b>	>24 months >36 months			
<b>Nickel</b>	>1 month <5 months			

Notes: Each duration refers to a specific project. 10 sites reported no changes in metals concentration. < refers to a duration of elevated metals concentration that lasted less than this amount of time. > refers to a duration that lasted at least this long, and is the most recent sampling event whose data was available for review.

For the two ozone/peroxone sites shown in Table 4-15, both had off-site exceedances of the MCL for chromium that occurred during system operation. The off-site monitoring locations were located less than 100 feet from where the treatment system was operating. Chromium levels dropped below non-detect in both situations within one month after the ozone system was shut down. In one case, the MTBE contamination being treated by the ozone system had been reduced below the regulatory standard by that time, and the system remained shut down because it was no longer needed. In the other, the ozone and hydrogen peroxide loading rates were decreased so that this peroxone sparge curtain could continue to operate and successfully degrade the MTBE flowing through it, but so that aqueous chromium remained below the MCL.

The arsenic impacts are also unexpected, because arsenic is generally less soluble under more highly oxidizing conditions (Smedley and Kinniburgh 2002). However, arsenic is removed from some sorption sites on mineral surfaces with increasing pH, especially when pH rises above approximately 8.5 standard units (Smedley and Kinniburgh 2002). The case study in which arsenic concentrations increased for at least one month was a percarbonate application that used an alkaline activator. The situation



with the single localized increase of arsenic for at least 18 months was a CHP application to a karst aquifer. One possible explanation for the lasting arsenic increase is that the CHP reagents dissolved the karst, liberating arsenic that had been present in the rock matrix.

#### **4.8 Results of Impacts on Aquifer Permeability**

Overall, reductions in permeability were reported at 17% (n=36) of sites. Among CHP sites, permeability reductions were noted at 9% (n=11). This was a situation in which gas generation in low permeability materials resulted in higher injection pressures than desired. This situation was remedied by changing from a pressurized injection system to a gravity feed injection system (Lisiecki and Colvin 2004). Among permanganate sites, 26% reported permeability reductions (n=19). The maximum concentration of permanganate injected among these five sites that experienced permeability reductions was 19 g/L as permanganate. The incidence of permeability reduction reported above may overstate the frequency with which this occurs, because a lack of permeability reduction was only entered when the project documents specifically stated that it did not occur. Also of note in this analysis is that one of the permanganate case studies reporting a permeability reduction was a demonstration study in which the authors were attempting to demonstrate that permanganate remediation could serve the dual purpose of both oxidizing contaminants (in this case creosote) and encapsulating the unoxidized residual COCs in manganese dioxide (Lamarche *et al.* 2002). So in this particular application reductions in permeability are a success, not a negative side effect. Several projects reported measures taken to improve injection well performance after it had shown decreases in permeability after permanganate injection. These included surging and redevelopment and also addition of acids and dilute hydrogen peroxide. In some situations well performance improved, while in others it did not.



## 5.0 STATISTICAL ANALYSIS OF RESULTS

This section presents the statistical analysis of the results presented in Section 4. The analyses will evaluate the statistical significance of selected results, and will attempt to remove confounding factors to the degree possible. The purpose of these analyses is to attempt to verify that ISCO design conditions and performance results depend on various parameters such as geology or NAPL presence as theory and process understanding predict they should. The analyses are presented in the order in which they were performed because the first sets of analyses are used as justification of the steps taken in later analyses.

The non-parametric randomization test was used as a one directional test to assess the statistical significance of differences between groups of samples. This test was chosen over the Wilcoxon Rank Sum test because it can be applied to both binary and continuous data, and because it does not require assumptions about the shape and size of the probability density functions of the two samples being analyzed (Navidi 2006). Because it is not a commonly reported test, it will be explained briefly here. See Appendix C for further details on the randomization test theory and its implementation.

The randomization test is predicated upon using repeated random sampling to evaluate the probability that the observed differences between the two groups arose by chance (Navidi 2006). For continuous numerical parameters, the statistic compared was the trimmed arithmetic mean of the two groups being tested. The mean was trimmed by removing the upper and lower 10% of the data prior to calculation. The trimmed mean was selected because it is a more robust statistic than the untrimmed mean, yet considers more data than the median. For binary parameters, the statistic tested was the untrimmed mean value because outliers do not occur in parameters that can only take a value of 0 or 1. The p-value reported has the same meaning as a one-sided p-value for other more commonly used statistical tests (e.g. a p-value  $< 0.05$  is statistically significant at the 95% confidence level). The n value reported in the tables and parenthesis in the text that follow are the number of samples used in the randomization test.

Unless otherwise noted, the randomization test performed on a particular subsample is a comparison of that subsample to all the other samples. For example, a

statement such as “ozone was less likely to perform a treatability study than the other oxidants (p-value=0.013, n=98)” means that a randomization test was performed comparing the use of treatability studies among ozone sites to the incidence among all sites that were not ozone sites, and that there was a total of 98 such sites between both the ozone and not ozone sites.

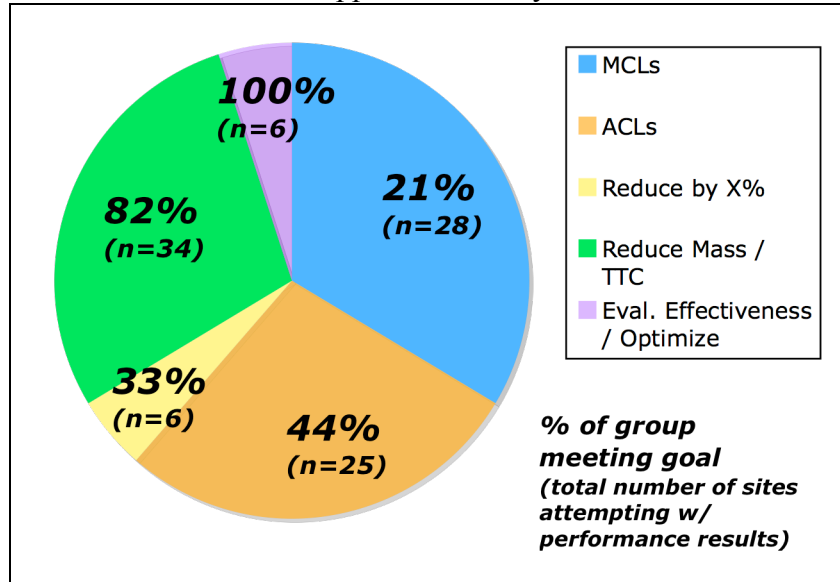
### **5.1 Analysis of the Utility of Performance Metrics for Statistical Analysis**

This section presents the various qualitative performance metrics that could be analyzed, including the attainment of MCLs and ACLs, and of reaching site closure. The purpose of this section is to justify why quantitative performance metrics are used in the subsequent statistical analysis.

As presented in the results section, the percentage of sites that achieve a given goal depends on the difficulty of the goal attempted, with MCLs being the most difficult goal to achieve, and general evaluation of the remediation technology the easiest. This is shown in the following two figures, which show both the relative frequency of the goals attempted (the size of the pies) and the percentage of sites (printed text) in that category that met that particular goal (Figures 5-1 and 5-2 on the following page). Also note the differences in goals attempted between full scale applications (Figure 5-1) and pilot scale applications (Figure 5-2).

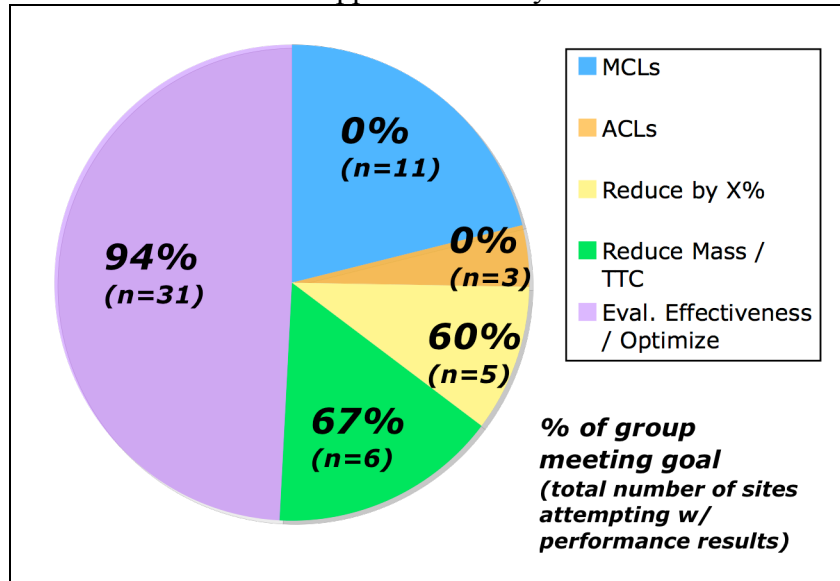
MCLs were met and maintained at six sites in ISCO-DB1. Due to this very small sample size, no analysis is presented to examine if these sites are different with respect to any qualities from a standpoint of statistical significance. A brief description of these sites will be provided here. Three sites that met MCLs were contaminated with MTBE and treated with ozone or peroxone. These systems were installed as sparge curtains to treat the plume of MTBE emanating from the source, which in these three cases were previously excavated underground storage tanks. Of these three MTBE sites, one had data on oxidant delivery duration, and that system operated for six months. Two sites that met MCLs were contaminated with PCE, one at a concentration of 48 ug/L and treated with an ozone sparge curtain and another at 3.5 ug/L treated with CHP. Rebound did not occur at either of these sites. The sixth site that met MCLs was contaminated with TCE at a maximum concentration of 70 ug/L. An existing horizontal air sparging

Figure 5-1: Project Goals and Percent of Sites Meeting Goals - Full Scale ISCO Applications Only



Notes: The percentages of the sites attempting each goal is represented by the size of the pie, the percentage of sites attaining that goal is shown as the printed percentage, and the number of sites attempting each goal with performance results on which the percentage attaining is based is shown with printed n values.

Figure 5-2: Project Goals and Percent of Sites Meeting Goals - Pilot Scale ISCO Applications Only



Notes: The percentages of the sites attempting each goal is represented by the size of the pie, the percentage of sites attaining that goal is shown as the printed percentage, and the number of sites attempting each goal with performance results on which the percentage attaining is based is shown with printed n values.

system was retrofitted as an ozone injection system, which operated for a year and a half. MCLs were maintained, rebound did not occur, and the site was deleted from the NPL.<sup>3</sup>

ACLs were met at 11 sites in ISCO-DB1. ACLs as defined in this study are the attainment of a specific contaminant concentration as required by the regulatory framework under which the project is being conducted. However, each state has its own way of assigning ACLs. For example, both Texas and Florida have formal contaminant criteria that are 100 times the MCL that can be met to be granted site closure in certain situations (e.g. lack of receptors, low yield aquifers etc.). However, other states allow practitioners to demonstrate that a plume is stable or contracting and does not pose any harm to receptors without requiring that groundwater concentrations be reduced below a certain numerical standard. Therefore, despite similarities in some situations, the ACLs included in ISCO-DB1 are too diverse to allow statistical comparison between them.

The attainment of site closure is even more dependent upon the regulatory context. Some regulatory programs allow “treatment to the extent practicable” or site-specific risk assessment, whereas others require attainment of specific concentrations.

A small number of sites attempted to meet the goal of reducing mass or concentrations by a predetermined percentage. Also, the desired percentage reduction varied between these sites, making statistical analysis impractical. The last two goals, general reduction in mass and evaluation or optimization of the technology, were met in most cases. Conceptually, these goals should be met with a 100% success rate. As stated in the Methods section, failure to meet these goals was assigned when performance monitoring did not characterize a mass reduction or oxidant distribution. These failures are therefore failures of the monitoring program, though not necessarily failures of the implementation itself. Because of the high frequency with which these goals were met and because of the failure to meet these goals is related to monitoring practices, these goals are not analyzed statistically.

As opposed to the above qualitative metrics, quantitative metrics can be compared between different sites and are independent of regulatory context. Percent reduction in

---

<sup>3</sup> The individual who provided the information on this site did so with the understanding that it would be kept confidential and identified with the generic name “South Carolina Superfund Site.”

maximum contaminant concentrations in groundwater is the most prevalent quantitative metric, primarily because it can be calculated with a modest amount of data. As stated in the Methods section, this metric was calculated as the percent change in the highest concentration of a COC (or group of COCs) in the TTZ before ISCO versus after ISCO. This performance metric allows useful comparison for those considering using ISCO to meet a numerical remediation endpoint (i.e. MCLs or ACLs) because their remediation will need to reduce the maximum concentration within their TTZ by a certain percentage to meet that performance goal.

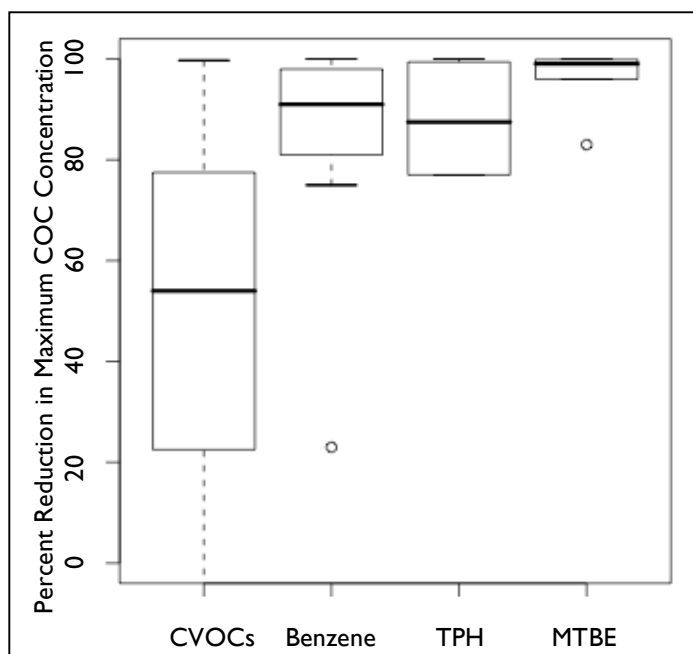
## **5.2 Analysis of the Impact of COC Group**

This section presents an analysis of the percent reductions revealed among the various COCs included in ISCO-DB1. The reaction kinetics between oxidants and contaminants is highly variable. Contaminants also differ in the ways in which they migrate through the subsurface and sorb to soil, which in turn affect their availability to be treated during ISCO. For these reasons, it would be expected that performance results would differ among the various COCs present in ISCO-DB1.

### *5.2.1 Comparison of Percent Reduction of Chlorinated and Fuel Related COCs*

The data presented in Section 4.2 showed that the results in terms of percent reduction of the maximum groundwater concentration appeared to be quite different when comparing chlorinated VOCs (CVOCs) to fuel related compounds. A figure showing box plots of the percent reductions in maximum groundwater concentrations of four selected contaminants (total CVOCs, benzene, TPH, and MTBE) is shown in Figure 5-3 on the following page. The results of randomization tests showed that both MTBE and benzene had reductions that were greater than those of CVOCs at the 95% confidence level (Table 5-1 on following page). The differences between the three fuel related compounds were not significant at the 95% confidence level (Table 5-1 on following page).

Figure 5-3: Box Plot of Percent Reductions in Chlorinated and Fuel Related COCs



Notes: The n values are 55, 10, 6 and 6 from left to right.

Table 5-1: Results of Randomization Testing of COC Reductions

<b>COCs Compared</b>	<b>Difference in Trimmed Mean % Reduction.</b>	<b>p-value</b>	<b>n</b>
<b>MTBE – CVOCs</b>	45*	0.001	<b>61</b>
<b>Benzene – CVOCs</b>	37*	0.001	<b>65</b>
<b>TPH – CVOCs</b>	16	0.134	<b>51</b>
<b>MTBE – TPH</b>	29	0.054	<b>12</b>
<b>MTBE - Benzene</b>	6	0.085	<b>16</b>
<b>Benzene – TPH</b>	23	0.741	<b>16</b>

Notes: \* = result that is significant at the 95% confidence level. The entries in the differences columns are the amount by which the trimmed mean percent reduction of the first contaminant was greater than the second contaminant listed at the far left. The n value is the total number of reported maximum reduction values between the two groups of contaminants being compared. The p-value is that resulting from the randomization test.

The total project cost was impacted by the COCs present. The results of the randomization tests performed on cost parameters by COC group are presented below for results that were statistically significant. Note that the n value refers to the number of sites used to calculate the trimmed mean of that COC group's total cost. Chloroethene sites (n=40) had a trimmed mean total cost that was \$188,000 higher (p-value=0.011, n=45) than sites at which chloroethenes were not present (n=15). BTEX sites (n=8) had a



trimmed mean total cost that was \$161,000 lower (p-value=0.035, n=47) than sites at which BTEX was not present (n=47). The TPH sites (n=7) had a trimmed mean total cost that was \$159,000 lower (p-value=0.047, n=47) than sites at which TPH was not present (n=48). MTBE sites also had a lower total cost, but the difference was not statistically significant (p-value=0.152, n=45). Note that the mean DQC values for chloroethene, BTEX, and TPH sites that reported total costs were 1.4, 2.1, and 2.1, respectively. No statistically significant differences were found between unit costs (\$/yd<sup>3</sup> treated), the areal extent or the volume of the TTZ among the COC groups. This lack of significance of the unit cost test is likely due to the fact that aside from chloroethene sites, the maximum number of sites in any of the other COC groups for which unit costs could be calculated was three.

The above analysis shows that the performance results with respect to maximum contaminant concentration reductions differ when comparing chlorinated and fuel related compounds. The sample size for the various fuel related compounds is much smaller than that of chlorinated compounds. For this reason, the remainder of the analysis will focus on chlorinated compounds.

### *5.2.2 Comparison of Percent Reduction Among Chlorinated Compounds*

Based on randomization test results, the difference in the trimmed mean of percent reductions between various CVOCs (PCE, TCE, 1,1,1-TCA, and total chlorobenzenes) were not significant at the 95% confidence level. The lowest p-value of any of these analyses was 0.066, which indicated that this particular analysis between PCE and total chlorobenzenes was significant at the 90% confidence level (Table 5-2 on the following page).

Table 5-2: Results of Randomization Testing of COC Reductions

<b>COCs Compared</b>	<b>Difference in Trimmed Mean % Reduction.</b>	<b>p-value</b>	<b><i>n</i></b>
<b>PCE - TCE</b>	-2	0.576	69
<b>PCE - total CBs</b>	33	0.066	31
<b>TCE - total CBs</b>	34	0.195	48
<b>PCE - 1,1,1-TCA</b>	-8	0.715	30
<b>TCE - 1,1,1-TCA</b>	-7	0.689	47
<b>PCE - 1,2-DCB</b>	26	0.167	30
<b>PCE - 1,4-DCB</b>	13	0.310	30
<b>PCE - CB</b>	21	0.181	31
<b>PCE - TCE</b>	-2	0.576	69

Notes: A negative difference in trimmed means shows that the second compound listed had a greater percent reduction than the first. The p-value is that resulting from the randomization test.

However, based on the considerations of the reaction kinetics between oxidants and the various groups of chlorinated compounds, they should not be lumped together for analysis. Given that the bulk of sites in ISCO-DB1 are PCE and TCE sites, the specific analyses into the impacts of subsurface geology, oxidant, and presence of NAPL that are in the subsections that follow this one are focused on these two compounds.

### 5.3 Analysis of Results by Oxidant

As shown in the Results Section 4.3, there are differences in the way that practitioners design the remediation system depending on what oxidant is selected. The trimmed mean number of pore volumes delivered during CHP applications was 0.15 (n=27), a number that is significantly lower (p-value=0.006, n=56) than the trimmed mean of 0.47 pore volumes used with other oxidants (n=39). Note that the number of pore volumes delivered was calculated using the injected volume of oxidant and did not include separately injected activators. Permanganate had a trimmed mean number of pore volumes delivered of 0.42 (n=26), an amount that was statistically greater at the 90% confidence level (p-value=0.087, n=54) than the other oxidants. CHP was delivered with a greater number of delivery events than the other oxidants (p-value=0.003, n=132), and permanganate appeared to be as well (p-value=0.056, n=130), while ozone and persulfate were delivered with significantly fewer delivery events (p-value=0.001, n=131 and p-value=0.035, n=130, respectively). Ozone and peroxone systems were designed

with a significantly greater ROI (trimmed mean of 24 feet, n=9) when compared to the other oxidants (p-value=0.025, n=69). No significant differences were observed between the design ROI of the other oxidants. The differences between design ROI and observed ROI were not statistically significant for any of the oxidants.

The use of pre-design testing varied among the oxidants. When using ozone practitioners performed a treatability study at 43% of sites (n=7), an amount significantly lower than the other oxidants (p-value=0.013, n=121). Persulfate practitioners performed treatability studies at 100% of sites (n=8), an amount significantly greater than the other oxidants (p-value=0.045, n=121). The remaining oxidants did not show statistically significant variation with respect to the frequency of treatability testing. However, the apparent differences in the use of pilot testing prior to full scale applications were not significant among the various oxidants (minimum p-value 0.117). Among full scale sites, coupling was used at lower frequency (86%, n=57) for permanganate sites (p-value=0.039, n=90), though the difference in the mean percentage of sites that were coupled was only 9% less than for the other oxidants. None of the other oxidants showed statistically significant differences in the frequency with which they were coupled at full scale projects.

The difference in percent reduction of maximum PCE and TCE concentrations in groundwater were not statistically different for permanganate and CHP sites, the only two oxidants that had enough data for randomization testing. The total and unit cost of ISCO remediations was also not statistically different between these two oxidants. The statistical significance of the impact of the oxidant use on the frequency of attaining qualitative performance metrics was not investigated due to the confounding factors related to that varying amenability of various COCs to oxidation and the variation in regulatory context under which success is defined as outlined above.

#### **5.4 Analysis of the Impact of Geology**

This section presents a statistical analysis of the significance of the differences observed in ISCO design and performance depending on the geologic media being treated. As in Section 4.4, the Geology Groups B, E, and F have been aggregated to form

Geology Group BEF. This aggregated group is presented along with Groups A, C, and D. The definitions of the Geology Groups are shown in the list that follows.

- Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )
- Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )
- Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )
- Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )
- Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)
- Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

There are no statistically significant differences with which sites within the Geology Groups attempt to meet MCLs. However, 56% of Group D sites attempted to meet ACLs ( $p=0.004$ ,  $n=145$ ) versus 21% of the remaining Geology Groups. Group BEF sites attempted to meet this standard 10% of the time, a frequency significantly less ( $p$ -value=0.015,  $n=145$ ) than the other Geology Groups. Groups A and D are less likely ( $p$ -value=0.024,  $n=145$  and  $p$ -value=0.019,  $n=145$ , respectively) to attempt to generally reduce the mass of contaminants or the time to cleanup, choosing this performance goal at 20% and 13% of sites in ISCO-DB1, respectively.

The use of pre-design treatability testing varies with geology as well, with projects treating Group A geologic materials performing this test at 55% of sites, statistically lower ( $p$ -value 0.002,  $n=115$ ) than the frequency of 81% among the other groups. This difference is even more marked when considering only full scale applications, with projects treating Group A geologic materials performing treatability tests at 25% sites compared to 74% for the other Geology Groups ( $p$ -value=0.001,  $n=70$ ). Pilot tests were conducted less frequently at full scale Group A sites (29%) than at other sites (66%) ( $p$ -value 0.025,  $n=125$ ). ISCO performed in Group D materials were less likely to use a coupled approach ( $p$ -value=0.008,  $n=86$ ) whereas the other groups were not statistically different with respect to the frequency with which they coupled ISCO with other technologies. Group BEF sites were more likely to couple at a 90% confidence level ( $p$ -value 0.073,  $n=125$ ).

Site closure was significantly more likely to occur at Group A full scale sites (47%,  $n=15$ ) than the others (16%,  $n=55$ ) ( $p$ -value=0.024,  $n=70$ ). The attainment of site

closure was less likely to occur at full scale sites treating Group C geologic materials (13%, n=38) than other groups (34%, n=32) (p-value=0.008, n=70). Rebound occurred at 35% of Group A sites (n=13), while the remaining groups had a range in incidence of rebound between 65% and 89%. This difference between Group A and the others is significant at the 95% confidence level (p-value=0.001, n=50). The trimmed mean total VOC concentration reduction in groundwater is greater for Group A sites (p-value=0.048, n=55) while no statistical significance in trimmed mean total VOC reduction was noted between the other Geology Groups. However, as shown in Section 5.2, the types of contaminants that are present at a site play a significant role in the percent reductions that are achieved. When considering PCE and TCE concentration reductions, the difference in trimmed mean is not statistically different at Group A sites compared to others (p-value=0.207, n=28 for PCE, p-value=0.219, n=43 for TCE). The trimmed mean of the total project cost is \$155,000 lower for Group A sites compared to the others (p-value=0.038, n=44) while the trimmed mean total cost appears to be \$150,000 higher for Group C sites compared to the others (p-value=0.056, n=44). However, when examining only chloroethene sites, there is no statistically significant difference between the total cost of Group A and Group C sites. There is no statistically significant difference between the trimmed mean unit cost (\$/yd<sup>3</sup> treated) of the Group A and C sites, while the remaining groups collectively had three unit costs reported, and were therefore omitted from the analysis.

## **5.5 Analysis of the Impact of NAPL Presence**

There are differences with respect to the goals, design, and results of ISCO remediation depending on whether NAPL is present at a site, and this section examines the statistical significance of these differences. Because LNAPL was present at only 17 sites in ISCO-DB1, this analysis focuses primarily on DNAPL compounds unless there are notable differences between the results in LNAPL and sites and sites at which no type of NAPL was present. The primary metric used to assess DNAPL presence relative to ISCO design is whether or not project documents reported that DNAPL was present. The purpose of the analysis of design parameters is to evaluate the differences between how practitioners treat sites depending on DNAPL presence, and their statements as to

DNAPL's presence or absence are the most direct means of considering what type of problem they were attempting to treat. The primary metric used to assess the impact DNAPL presence on ISCO performance is the >1% of Solubility metric described in Section 4.5. This metric is selected because it could be entered based on COC concentrations, whereas the DNAPL Reported metric relied on statements made in project reports, some of which were incomplete. This metric may also include sites at which DNAPL was present yet the remediation designer did not know or consider this in the remediation design. These cases are more appropriate to consider as DNAPL sites when evaluating performance results rather than considering them not to be DNAPL sites or omitting them from the analysis. When significant differences between the >1% of Solubility and DNAPL Reported metrics exist, they are highlighted in the paragraphs that follow. In most cases the results between the two are consistent.

Sites at which project documents stated that DNAPL was present were less likely to attempt to meet MCLs (19%, n=57) as a performance goal (p-value=0.001, n=126), a result that is true for both full scale and pilot scale remediations. None of the oxidants were used more commonly at DNAPL sites relative to their frequency of use at other sites (LNAPL and sites without NAPL). Ozone was used less frequently at DNAPL sites (p-value=0.002, n=148) than at other sites. However, this is likely because ozone was used at a higher frequency at LNAPL sites (p-value=0.029, n=148) relative to other sites.

The trimmed mean volume of the TTZ was 115,000 cubic feet (n=40) at DNAPL sites, an amount significantly lower than the trimmed mean volume of 232,000 cubic feet (n=48) for sites without DNAPL (p-value=0.047, n=72). The areal extent of the TTZ was not significantly different between DNAPL sites and sites without DNAPL. The trimmed mean number of pore volumes delivered to sites where DNAPL was reported to be present was not significantly higher than the other sites (p-value=0.130, n=49). When recirculation sites are omitted from the analysis, the trimmed mean number of pore volumes delivered appears to be 0.2 pore volumes higher at DNAPL sites (0.4 pore volumes delivered, n=32) than at other sites (0.2 pore volumes delivered, n=27) (p-value=0.081, n=45) based on significance at the 90% confidence level. The trimmed mean number of delivery events was one event greater for DNAPL sites (2.6 events, n=50) compared to other sites (1.6 events, n=73) (p=0.001, n=99). The trimmed mean

duration of delivery events was 9.0 days (n=36) at DNAPL sites, an amount significantly greater than the 5.5 day (n=42) trimmed mean duration at sites without DNAPL (p-value=0.095, n=64). This analysis does not include ozone and peroxone, which confound analysis of treatment duration because they are applied continuously and were shown above to be more prevalent at LNAPL sites. Sparge points were used less frequently at DNAPL sites (p-value=0.001, n=134) while recirculation systems were used more frequently at DNAPL sites (p-value=0.012, n=134). The use of other delivery approaches was not statistically different between DNAPL sites and other sites. The use of treatability testing was not more frequent at DNAPL sites. The use of pilot testing was not more frequent at full scale sites where DNAPL was reported to be present. However, pilot testing was performed at a *lower* percentage of sites where contaminant concentrations exceeded 1% of solubility (54%, n=41) than at sites where concentrations did not exceed this metric (77%, n=22) (p-value=0.017, n=63). DNAPL sites were not more likely to be modified during implementation than other sites. However, DNAPL sites were more likely to be coupled with other technologies (p-value=0.029, n=85). In particular, they were more likely to be coupled with a post-ISCO technology, doing so at 45% of sites (n=49) (p-value=0.001, n=84).

DNAPL sites also show significant differences in performance results achieved relative to other sites. DNAPL sites are significantly less likely to meet MCLs (0%, n=69) or attain site closure (13%, n=40) (p-value=0.001, n=110 and p-value=0.001, n=93, respectively), and appear to be less likely to meet a predefined percent reduction in mass or concentration as well (p-value=0.060, n=11). However, DNAPL sites achieved ACLs at 39% of sites (n=18), a frequency that is not significantly less than the 50% frequency with which other sites (n=8) met this goal (p-value=0.385, n=26). There were no statistically significant results of randomization tests of maximum PCE and TCE reductions with respect to DNAPL presence (p-values between 0.221 and 0.373). However, the coefficients on the differences in trimmed mean percent reduction were of a different sign depending on which metric was used to assess DNAPL presence. When using project reports' statements, sites that reported DNAPL to be present appeared to show a greater percentage decrease in maximum PCE and TCE concentrations relative to sites without DNAPL. However, when using the >1% of solubility metric, DNAPL sites

appeared to have a lower percent reduction in maximum PCE and TCE concentrations. DNAPL projects had a trimmed mean total cost that was \$285,000 higher (\$526,000, n=20) than sites without DNAPL (\$241,000, n=18) when using the >1% of solubility metric (p-value=0.016, n=32). The difference in trimmed mean total cost is \$407,000 when using the DNAPL reported metric (p-value=0.001, n=40). The trimmed mean total cost of LNAPL remediations was \$165,000 (n=6), an amount significantly lower than the \$342,000 trimmed mean cost of other sites (n=40) (p-value=0.046, n=38). Note that the mean DQC value among LNAPL sites reporting a total cost is 1.9 versus a mean DQC of 1.4 for sites at which LNAPL was not reported to be present. The differences in unit costs (\$/yd<sup>3</sup> treated) were not statistically significant for DNAPL or LNAPL sites.

The differences with respect rebound between DNAPL sites and other sites were not statistically significant, but still show some interesting results. Project documents that stated DNAPL was present had rebound at 71% of sites versus 56% of sites whose project documents stated DNAPL was not present (p-value=0.181, n=60). However, sites that reported concentrations >1% of solubility had rebound at 78% of sites versus 55% of sites with concentrations below the 1% solubility criterion (p-value=0.067, n=56). While not significant at the 95% confidence level, these data indicate that in situations when DNAPL is present and the practitioners do not know or account for it when implementing their design, that rebound is more likely to occur.

## **5.6 Analysis of Treatability and Pilot Testing**

The commonly held belief is that both treatability and pilot testing aid in the design of full scale ISCO remediation projects and the performance achieved. To evaluate the hypothesis that these studies are beneficial, randomization tests were conducted on several performance indicators to examine if the mean or trimmed mean values were different between those groups that performed pre-design tests versus those that did not, all else equal. In an effort to avoid confounding factors, the presence of DNAPL and the type of geologic material were held constant.

The use of pilot testing appears to have a positive impact on the results of ISCO remediation in some situations, and no statistically significant impact in others. At full scale sites with permeable, heterogeneous materials (Group C) seemingly contaminated



with DNAPL (indicated by COC concentrations above the 1% solubility criterion) the mean percent reduction in maximum PCE concentration was greater ( $p$ -value=0.015,  $n=10$ ) among sites that performed pilot tests versus those that did not, with mean percent reductions in these two groups of 79% ( $n=7$ ) and 9% ( $n=6$ ), respectively. The remaining Geology Groups had at most three full scale sites that had data on percent reduction of maximum PCE concentration, and therefore these sample sizes were too small to analyze the impact of pilot testing on the performance of ISCO remediations conducted at sites with those Geology Groups.

No significant differences were noted with respect to reductions in maximum PCE concentrations at full scale projects not contaminated with DNAPL based on pilot testing. However, there were only two sites in this category.

Statistical analyses similar to those described in the preceding paragraphs were performed on mean percent reduction in maximum TCE concentrations, again holding DNAPL and geologic media being treated constant. No statistically significant results were found that indicated that performing a pilot test at a TCE-contaminated site impacted the percent reduction of maximum TCE concentration.

Randomization testing was performed on several performance criteria to assess whether the use of treatability testing resulted in a higher incidence of positive outcomes at a statistically significant level. The performance criteria tested included reaching ACLs, attaining site closure, and percent reduction in maximum total chlorinated VOCs, PCE, and TCE. DNAPL presence and Geology Group were examined separately and also lumped together. None of the statistical tests produced significant results, which indicates that treatability testing does not have an impact on the performance seen at the field-scale. One very important caveat with respect to the evaluation of the impacts of treatability studies is that this analysis does not include projects that performed treatability studies and did not continue to the field-scale because the results were unfavorable. These situations almost certainly would have seen poor results at the field-scale if the laboratory scale results were not good. In these instances, use of a treatability study resulted in cost savings by preventing a field-scale implementation of a remediation that would be unlikely to succeed.



## 6.0 DISCUSSION

This section presents discussion of the results and statistical analyses presented in Sections 4 and 5. The organization of this section follows after those of the previous sections, first discussing goals of remediation, followed by the impacts of COCs being treated, oxidant used in ISCO, geologic materials present in the TTZ, the presence of DNAPL, and the impact of pre-design testing.

### 6.1 Discussion of the Impact of ISCO Goals on Success

As revealed in Section 5.1, the frequency with which projects meet particular goals is inversely proportional to the stringency of those goals. The most stringent goal, MCLs, was met at 21% of full scale projects that attempted this goal, while ACLs were met at 44% of projects. The goals of general mass reduction and technology evaluation were met at 82% and 100% of full scale sites, respectively.

Among the six sites in ISCO-DB1 that met MCLs, the following similarities exist. Half of the sites treated MTBE using ozone or peroxone sparge systems. The other half treated dissolved plumes of chlorinated solvents. While a sample size six precluded statistical testing, these data collectively indicate that MCLs can be reached in these two situations.

Because ISCO is used primarily to treat chlorinated solvents, and because there has not yet been a reported case where a chlorinated solvent DNAPL site has met MCLs, confirmation from the site regulator was required prior to entering in the affirmative that MCLs had been achieved. Attempts to reach regulators associated with BTEX and TPH sites were unsuccessful. This stringent quality control measure should be kept in mind when considering the statement that none of the sites contaminated with BTEX and TPH in ISCO-DB1 were successful in meeting MCLs.

ACLs were met at 11 full scale sites in ISCO-DB1, or 44% of sites that attempted to meet this goal (n=25). Site closure was attained at 24% of full scale sites (n=74). These results are expected, because there are regulatory frameworks under which ISCO may be implemented other than the requirement to meet MCLs throughout the entire site. However, the ability to meet these other regulatory requirements is very much dependent

on what the regulatory requirements are. Several examples are provided to illustrate this point. One project was performed at a drycleaner, and the state regulatory agency required that soil concentrations of PCE be reduced below hazardous waste levels, and that the aqueous PCE plume be stabilized. ISCO was successful in reducing the soil concentrations below the state's requirement, the plume stabilized with a maximum PCE concentration of approximately 70,000 ug/L, and the site was granted closure. In other states closure would not have been granted with a groundwater concentration this high in the source zone. Several case studies in ISCO-DB1 performed at chlorinated solvent suspected DNAPL sites demonstrated reductions in maximum COC concentrations of two or more orders of magnitude. Some of these sites are closed because the regulatory agency had framework in place for risk-based closure while others remain open because such a framework was not in place. These examples are provided to highlight that: 1) risk-based ACLs can be achieved with ISCO, even when DNAPL is present; and 2) that the regulatory context of an ISCO remediation has an important bearing on the remediation's success.

## **6.2 Discussion of the Impact of COCs**

Based on the case studies in ISCO-DB1, ISCO remediation achieves a larger percent reduction in maximum contaminant concentration when fuel related compounds are being treated relative to chlorinated compounds. The reason for this is likely not due to the reaction kinetics between oxidants and these two groups of COCs. Huling and Pivetz (2006) document that kinetic rates between oxidants and chloroethenes and chlorobenzenes are as fast as those between oxidants and petroleum hydrocarbons, BTEX, and MTBE. Since oxidation kinetics are not the reason for this difference in performance, this difference likely arises due to how these various COCs migrate through the subsurface. MTBE is more soluble than these other COCs, and is therefore more available to be oxidized during ISCO treatment. The solubility and sorption characteristics as predicted by the octanol-water partitioning coefficient ( $K_{ow}$ ) are not greatly different for chloroethenes and selected fuel components (benzene, ethylbenzene, and toluene) (Hemond and Fechner-Levy 2000). Therefore, it is likely that this difference in behavior is due to the fact that DNAPL releases will sink below the water

table, whereas releases of fuels will remain at the groundwater surface (Pankow and Cherry 1996).

Based on the data in ISCO-DB1, there are no apparent differences between the performance in terms of percent reduction of maximum groundwater concentrations among the various CVOCs. Based on the reaction kinetics, it should be expected that chloroethanes would generally not achieve percent reductions as great as other CVOCs (Huling and Pivetz 2006). However, the mean reduction in maximum 1,1,1-TCA concentration in ISCO-DB1 is 65% (n=4), which is greater than the mean of other CVOCs. It is postulated that this unexpected result is due to the relatively smaller sample size of the 1,1,1-TCA sites. However, based on the four sites that are available, ISCO appears to be able to achieve reduction of this COC in some situations.

The total cost of ISCO projects performed to treat fuel related COCs is also lower than those treating CVOCs. This difference does not appear to be an issue of project size, as unit costs, areal extent and volume of the TTZ did not differ significantly between fuel related and CVOC sites. One possibility for this difference in cost is that fuel related compounds are more accessible for treatment due to their migration characteristics.

### **6.3 Discussion of Impacts of Oxidant Used**

There are several ways in which ISCO remediation designs differ depending on what oxidant is being applied. This is expected due to the differences in reactivity and persistence among the various oxidants. This may also arise due to issues of personal preference, as many practitioners specialize in applications of one type of oxidant, and they may have developed their own specialized techniques based on experience gained in the field.

CHP practitioners appear to use a higher concentration, lower injection volume, and a greater number of delivery events approach relative to permanganate practitioners. These differences should be expected given that permanganate is a more persistent oxidant than CHP. It is this author's opinion that this result also arises because many CHP practitioners routinely plan on delivering oxidants during multiple treatment events. The differences in the total number of pore volumes delivered between CHP and permanganate applications may also be due to the means through which this calculation

was performed at CHP sites, in which only the hydrogen peroxide volume and not the separately added activator solution was included in the calculation. The ROI achieved by the various oxidants was also similar, with the exception of ozone, which achieved a greater ROI. There was no significant difference between the design or observed ROI between CHP and permanganate, the two oxidants for which there is the most data. This result is surprising, as permanganate is more persistent than CHP in the subsurface. One possible explanation for this is that CHP was more commonly applied to permeable materials (Geology Groups A and C) relative to permanganate, and less commonly applied to impermeable materials (Geology Groups B and D) relative to permanganate (Appendix B, Table B-63). Another explanation is that the proprietary hydrogen peroxide stabilizers used by many CHP vendors are successful in stabilizing the reagents so that they may be delivered a greater distance through the subsurface than would be predicted by the transport studies reported in Section 2.1. When considering the ROI for all oxidants, it is important to note that observing the oxidant to be present in a monitoring well location a certain distance away from an injection point does not mean that the entire screened thickness of the monitoring well or injection point was contacted by the oxidant, because coarse grained strata can be preferential conduits for injected oxidants.

Use of pre-design testing (pilot or treatability studies) also varied among the various oxidants. Half of ozone projects performed treatability studies as a pre-design test, and amount significantly lower than project at which the other oxidants were used, while all of persulfate projects performed a treatability study, an amount significantly greater than projects using the other oxidants. Treatability studies were used as a pre-design test at approximately 80% of CHP and permanganate. The fact that treatability studies were performed for all persulfate sites is expected, because there are multiple activation methods that may be used with this oxidant. The fact that CHP and permanganate were similar is somewhat surprising, as CHP requires activators of some sort (naturally occurring or injected) while permanganate does not. However, the degree of permanganate consumption due to NOD is an important design consideration, and 71% of permanganate sites for which there was sufficient data to determine what type of treatability study was performed (n=39) used a treatability study to determine the NOD.

The use of pilot scale testing did not vary depending on the oxidant selected for ISCO remediation. This result is not surprising, because pilot testing evaluates oxidant distribution and delivery issues (as well as other issues), and these issues are more dependent upon subsurface geology than oxidant characteristics. An exception to this statement might be the gaseous oxidants ozone and peroxone. However, pilot studies that consisted of installing a single delivery point and monitoring the distribution were frequently used with these oxidants. The purpose of these tests were generally to optimize full scale well spacing and also to evaluate the impact of these continuous oxidation systems on aqueous metals concentrations.

There was no difference noted in terms of mean reductions in maximum PCE or TCE concentrations depending on what oxidant was selected. These are the only two contaminants on which there was enough data to perform statistical testing. This result is not surprising: given that some of these oxidants have been used in ISCO for over 10 years, if one oxidant were definitively better (or worse) than the others, practitioners would use it more exclusively (or not use it at all). No differences were noted between total cost and unit cost of ISCO remediations depending on the oxidant selected.

#### **6.4 Discussion of the Impact of Geology**

The type of geologic material being treated has important impacts on both the design of ISCO systems and the results achieved. Conventional thinking is that permeable materials are more amenable to ISCO treatment, as are homogeneous materials. This thinking is supported by the data in ISCO-DB1, as homogeneous and permeable sites (Group A) achieved better performance with respect to many indicators, such as attainment of site closure and incidence of rebound. However, there was not a significantly greater reduction in the maximum PCE or TCE concentration achieved at Group A sites relative to other geologic media.

The Group A sites also performed treatability and pilot studies less frequently than other Geology Groups, yet still achieved good results. The result with respect to pilot studies is expected, as this type of pre-design test is primarily aimed at gathering information on oxidant deliverability issues, and oxidant delivery is less problematic in homogeneous, permeable materials relative to other geologic media.

When considering the attainment of ACLs at the performance metric, the conventional wisdom is contradicted by the results of ISCO-DB1. ACLs were met more frequently at Group C (permeable and heterogeneous) than at Group A sites. This result is significant at the 90% confidence level for all sites, and at the 95% confidence level when considering only chloroethene sites that had concentrations present greater than the 1% solubility criterion. One possible explanation for this seemingly anomalous result is variations in regulatory context.

There were also no statistically significant differences noted between Group A and Group C (the two groups for which there was the most data) with respect to the percent reduction in maximum PCE or TCE concentrations. These statistical tests were conducted both with and without accounting for the presence of DNAPL. This analysis examines consistent contaminants and a metric whose result is independent of regulatory context. This result is contrary to the conventional wisdom that homogeneous sites are more amenable to ISCO than heterogeneous ones. One possible explanation for this is that ISCO remediation designers are compensating for the increased challenges posed by heterogeneous sites and are therefore able to achieve good results in heterogeneous, permeable materials (Group C). This theory was evaluated by examining the number of pore volumes, number of delivery events, and duration of delivery events between Group A and Group C sites contaminated with chloroethenes above the 1% of solubility criterion. This analysis did not note significant differences in these three parameters between these two Geology Groups holding oxidant and DNAPL presence constant. When considering the oxidant dose (g oxidant applied / kg media treated), there are differences between the designs of both CHP and permanganate remediations performed at chloroethene sites depending on whether Group A or Group C materials are being treated. In the case of both oxidants, the oxidant dose was greater for Group C materials. Though these results were not statistically significant (p-value=0.155, n=9 for CHP and p-value=0.222, n=12 for permanganate), the lack of significance is postulated to be due to the small sample size for these two analyses.



## 6.5 Discussion of the Impact of DNAPL on ISCO Remediation

The presence of free phase (NAPL) contamination has important implications for environmental remediation. As shown in the preceding sections, DNAPL sites are treated using ISCO with considerably more regularity relative to LNAPL sites. While ISCO can achieve good results at LNAPL sites, this section will focus on the impact of DNAPL to ISCO remediation because this is the more prevalent and challenging of the two types of NAPLs.

The presence of DNAPL impacts ISCO goals, design, and performance results. When DNAPL is present, practitioners are less likely to attempt to meet MCLs immediately after ISCO. ISCO remediations at DNAPL sites also targeted a smaller volume TTZ than sites without DNAPL. ISCO systems were designed to deliver a greater number of pore volumes of reagents and a higher oxidant dose at sites where DNAPL was present relative to sites where DNAPL was not present. The average duration of delivery events was also higher for DNAPL sites.

The use of pre-design treatability testing did not differ between DNAPL sites and sites without DNAPL. For full scale sites where DNAPL was reported to be present, pilot testing was not used with greater frequency relative to sites without DNAPL. However, when using the 1% of solubility metric to assess DNAPL, pilot testing was performed at a lower percentage of DNAPL sites relative to sites without DNAPL. This result is unexpected as it runs contrary to conventional thinking.

DNAPL sites were no more likely to be modified during implementation than sites without DNAPL. However, DNAPL sites were more likely to couple ISCO with other technologies, especially post-ISCO technologies such as EISB and MNA.

DNAPL sites also differ with respect their performance results, being significantly less likely to meet MCLs or attain site closure relative to sites without DNAPL. However, they are no less likely to meet ACLs. Returning to the issue of goals of ISCO remediation, these last statistics point to the importance of setting realistic expectations for ISCO applications treating DNAPL. If possible, ACLs should be negotiated for the site. If MCLs are an absolute requirement, a post-ISCO coupled technology will likely be required. Several sites in ISCO-DB1 used computer models to estimate the duration of time required after ISCO was completed to reach MCLs based on

site-specific estimates of natural biodegradation of contaminants (Chapelle and Bradley 1998, Chapelle *et al.* 2005). These estimates were predicated upon ISCO achieving a reduction to a specified concentration, and also that natural biodegradation rates will return to baseline levels sometime after ISCO is completed. This first assumption depends on proper ISCO design and implementation, and is similar to sites that have a regulatory ACL framework in place because ISCO must meet a specific groundwater concentration that is higher than MCLs. The latter assumption is reasonable because none of the case studies in ISCO-DB1 noted lasting reductions in microbial populations and because EISB and MNA were frequently used after ISCO, especially at DNAPL sites (see Sections 4.6 and 6.7).

DNAPL sites had a higher total cost of treatment relative to other sites. This is expected given that DNAPL sites are generally considered to be more difficult to remediate, and also that DNAPL sites used a greater duration of delivery events, greater number of pore volumes of reagents and a greater amount of oxidant as shown above.

## **6.6 Discussion of the Impact of Bench and Pilot Testing**

Pilot scale testing lead to improved performance of full scale ISCO projects that were implemented in permeable, heterogeneous materials (Group C) but did not seem to improve performance in permeable, homogeneous materials (Group A). One of the primary reasons that practitioners perform pilot tests is to assess issues related to oxidant delivery. The frequency of success of Group A sites that did not perform pilot tests indicates that oxidant delivery may be predicted with an acceptable level of certainty based upon data available after general site characterization (e.g. grain size, extent of contamination etc.). Conversely, the level of uncertainty regarding oxidant distribution in permeable and heterogeneous materials (Group C) appears to be great enough that pilot testing is of particular importance when treating this type of material.

Based on the statistical tests that were performed, treatability studies do not appear to increase the success of ISCO remediations (Section 5.6). However, as stated earlier, there are caveats to this statement. First, because ISCO-DB1 is based upon field-scale ISCO projects, it does not include treatability studies that showed unfavorable results that caused the project designer to select another remediation method. These

types of situations highlight the value of treatability studies, because if the results of laboratory scale work are not promising, the likelihood of success at the field-scale is low. Unsuccessful laboratory studies are considerably less costly than unsuccessful field-scale ISCO implementations. A second caveat is that it was difficult to determine that a treatability study was not performed based upon the materials reviewed. If no mention of treatability studies was made in project documents, this field was left blank unless it could be confirmed that a treatability study was not performed. This may result in an overestimate of the frequency of treatability study use.

### **6.7 Discussion of the Impact of ISCO on Microbial Populations**

The data in ISCO-DB1 indicate that ISCO does not cause lasting adverse impacts to microbial populations. All (100%) of the 15 studies that examined microbial populations before and after ISCO found that the populations returned to baseline levels sometime after ISCO. Some of these studies noted no impacts, others noted temporary reductions followed by rebound to baseline levels, while still others noted increases in microbial activities after ISCO (e.g. due to increased oxygen or sulfate concentrations in the subsurface). In addition to these case studies that examined microbial populations directly, EISB was used after ISCO in 19 case studies, and MNA in at least 20 case studies. This provides further evidence that ISCO does not cause lasting impacts to the TTZ with respect to the ability of the subsurface to support microbial life. Taken collectively, these data indicate that ISCO does not have a lasting impact on microbiological populations, and in some cases has no impact at all, or may even benefit microbial life.

### **6.8 Discussion of the Impact of ISCO on Metals Mobility**

ISCO may cause increases in aqueous phase metals concentrations due to changes in aquifer geochemistry and/or impurities in the oxidants delivered (Section 4.7). Among the 23 case studies that measured metals concentrations, slightly over half reported increases above background levels for some metals. The duration and magnitude of increase in metals concentrations is highly site-specific, and depends upon the geochemical properties of the oxidant and the subsurface media being treated. The

relative severity of the metals increase is also site-specific, and depends on the regulatory context and proximity of the ISCO TTZ to receptors. Only two case studies reported metals concentrations exceeding regulatory standards outside the treatment zone, and these exceedances abated once ISCO activities ceased. Metals mobility is something that should be considered when implementing ISCO, but based upon the data available is not an issue that should preclude the use of ISCO in most situations.

Some projects in ISCO-DB1 used batch (vial scale) treatability studies to evaluate the impact that ISCO would have on metals mobility. While potentially valuable, such tests should be used with caution. These tests evaluate what the impact to metals concentrations will be within the core of the TTZ if there is complete contact between the oxidant and media being treated. If such tests do not result in increased metals concentrations, this is a favorable outcome from a designer's perspective. However, if metals concentrations increase during these tests, this result can only be extrapolated to the specific portion of the TTZ where there is significant contact between the oxidant and media being treated, and does not address how metals concentrations will be impacted once the oxidant is depleted, or as groundwater flows outside the treatment zone after ISCO into areas with ambient (less oxidizing) geochemical conditions. This is not a favorable outcome from a designer's perspective, because it will likely result in a reluctance to use ISCO on the part of the site owner or regulator, but has also not evaluated how metals concentrations will be impacted except within the core of the TTZ in a worst case scenario. Another way to address metals mobility through pre-design testing are column scale studies assuming a portion of the column can remain in a less oxidizing state that is representative of ambient conditions that will be present outside the TTZ in field-scale applications. Finally, pilot scale studies can also evaluate impacts on metals concentrations both inside and outside the ISCO TTZ.

## **6.9 Discussion of the Impact of ISCO on Aquifer Permeability**

Permeability reductions were noted at a small percentage of sites. For permanganate applications these reductions were in some cases permanent and problematic. The reaction of permanganate with contaminants produces solid manganese dioxide (Section 2.1). However, these solids may remain in a colloidal form and be

transported some distance away from the treatment zone or they may sorbed to mineral surfaces. The occurrence of permeability reductions at permanganate sites appeared to be highly site-specific, and did not appear correlated with aquifer geochemical properties (e.g. TOC, pH etc.). In some cases the project teams were successful in improving injection well performance that had been hampered by manganese dioxide formation through well redevelopment or addition of acids or hydrogen peroxide. The single CHP site that noted a permeability reduction due to gas generation reported that this was a transient phenomenon, and also that it was prevented at future injections at this site by using a gravity feed system rather than pressurized injections. In short, permeability reductions should be considered when designing an ISCO system, but their occurrence is the exception rather than the rule.



## 7.0 CONCLUSIONS AND RECOMMENDED FUTURE WORK

### 7.1 Conclusions

This section highlights the key findings and presents conclusions drawn from the analysis of the 242 case studies contained in ISCO-DB1.

- ISCO has been applied across most of the United States and at a significant number of countries abroad. ISCO has been used extensively at federal sites, dry cleaners, and manufacturing facilities as well as historically recalcitrant sites such as former MGPs and wood treatment facilities.
- ISCO has been used to treat a wide variety of organic compounds, though a majority of case studies targeted PCE and TCE.
- ISCO has been used most frequently in permeable soils, though an appreciable number of sites with impermeable soils or fractured rock have been treated as well.
- ISCO has been used to treat sites contaminated with DNAPL and sites without NAPL with approximately equal frequency. LNAPL sites have been treated with ISCO reagents as well, though with relatively less frequency.
- Six sites in ISCO-DB1 met MCLs, a fact that was confirmed with regulatory officials in all cases. Three of these sites used ozone or peroxone sparge curtains to treat MTBE. The other three sites treated PCE or TCE at concentrations ranging between 5 and 70 ug/L, and used ozone or CHP.
- Multiple sites met ACLs and were granted site closure, including sites with known DNAPL spills or suspected DNAPL based upon contaminant concentrations.
- Mass reduction and technology evaluation are also goals of ISCO remediations, and these goals are met relatively more frequently than specific concentration standards such as MCLs or ACLs. Soil sampling before and after ISCO is an important means through which practitioners verify contaminant mass reduction when attempting such goals.

- Rebound occurred in at least one monitoring location at 62% of sites. In those situations when rebound did occur, it occurred in approximately half of monitoring wells within the treatment zone.
- The median total cost of ISCO remediations is \$220,000, and the median unit cost is \$94/yd<sup>3</sup> treated.
- ISCO has achieved a significantly better performance for treatment of fuel related compounds, particularly MTBE, relative to chlorinated compounds. In particular, ozone and peroxone sparging systems have demonstrated a high success rate at MTBE and other fuel related sites both in terms of the frequency with which they meet MCLs and also consistently high percentage decreases in maximum contaminant concentrations.
- ISCO has achieved up to 99.9% reductions in maximum chlorinated compound concentrations. However, the performance of ISCO with respect to this metric is more variable at sites contaminated with chlorinated compounds, particularly at sites with significant sorbed or DNAPL phase contaminants.
- The degree of heterogeneity in permeable soils impacts both the success of remediation and the incidence of rebound. Homogeneous and permeable sites (Group A) are more likely to meet MCLs and attain site closure, have a higher mean percent reduction in maximum contaminant concentrations, and are less likely to experience rebound relative to permeable, heterogeneous sites (Group C). However, ACLs are met with consistent frequency after ISCO remediations conducted in permeable soils independent of the amount of heterogeneity. Practitioners use a higher oxidant dose when treating heterogeneous materials.
- The use of pilot testing improves performance results in heterogeneous, permeable materials (Group C), but does not have an impact on performance in homogenous, permeable materials (Group A).
- The presence of DNAPL is a challenge to ISCO as it is to other remediation technologies. No DNAPL sites in ISCO-DB1 attained MCLs. However, ACLs and site closure were attained for some DNAPL sites. ISCO practitioners use longer delivery events, greater injection volumes, and a higher oxidant dose for DNAPL sites. DNAPL sites are more likely to use a coupled post-ISCO



technology, particularly EISB and MNA. Rebound is more prevalent at DNAPL sites.

- Microbial populations are not permanently reduced due to ISCO, and may be unaffected by ISCO or even flourish after ISCO treatment. ISCO is not incompatible with EISB and MNA when these two technologies are used after ISCO.
- Approximately half of the case studies that monitored metals concentrations noted transient increases as a result of ISCO. The duration and severity of increases is highly site-specific. Two projects noted increases in chromium concentrations downgradient of the ISCO treatment zone. These were both ozone/peroxone applications, and chromium concentrations abated within one month of system shutdown. In one case the system design was modified so that it could continue to operate without creating chromium exceedances. In the other the system remained shut down because it was no longer needed.
- Permeability reductions were noted in approximately one fifth of case studies, and one quarter of permanganate case studies. These numbers may overstate the incidence of these issues because some project documents did not discuss permeability changes, most likely because they did not occur. The causes of permeability reduction are highly site-specific, and could not be correlated with any of the data in ISCO-DB1. In some cases well performance was improved by redevelopment or addition of acids or hydrogen peroxide.

## **7.2 Recommended Future Work**

The geospatial interpolation technique that has been developed should be applied to those sites that have sufficient data in order to calculate a spatially-weighted average contaminant reductions. The results of this calculation of percentage contaminant reduction should be analyzed and the results compared to those reported for percent reduction in maximum contaminant concentration. The results should also be compared to the percent change in arithmetic mean values before and after ISCO. The purpose of both these analyses would be to examine if the more time-intensive spatial weighting procedure does in fact produce different results than the other techniques.

The data contained in ISCO-DB1 may be made available to the general public as an online or spreadsheet-based database. This would allow interested members of the environmental community to conduct their own analyses similar to those performed here.

## REFERENCES

- Al, T.A., V. Banks, D. Loomer, B.L. Parker, and K.U. Mayer (2006). Metal Mobility during In Situ Chemical Oxidation of TCE by  $\text{KMnO}_4$ . *Journal of Contaminant Hydrology* 88: 137-152.
- Azadpour-Keeley, A., L.A. Wood, T.R. Lee, and S.C. Mravik (2004). Microbial Responses to In Situ Chemical Oxidation, Six-Phase Heating, and Steam Injection Remediation Technologies in Groundwater. *Remediation* 14(4): 5-17.
- Bacocchi, R., M.R. Boni, and L. D'Aprile (2004). Application of  $\text{H}_2\text{O}_2$  Lifetime as an Indicator of TCE Fenton-like Oxidation in Soils. *Journal of Hazardous Materials B107*: 97-102.
- Becvar, E.S. (2006). AFCEE/TDE, Brooks Military Base, Texas. Personal Communication via email received December 5.
- Block, P.A., R.A. Brown, and D. Robinson (2004). Novel Activation Technologies for Sodium Persulfate In Situ Chemical Oxidation. *Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, ed. A.R. Gavaskar and A.S.C. Chen, Battelle Press, Columbus, Ohio.
- Brown, R.A. and D. Robinson (2004). Response to Naturally Occurring Organic Material: Permanganate Versus Persulfate. in *Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, ed. A.R. Gavaskar and A.S.C. Chen, Battelle Press, Columbus, Ohio.
- Bui, C.T. and R.G.H. Cotton (2002). Comparative Study of Permanganate Oxidation Reactions of Nucleotide Bases by Spectroscopy. *Bioorganic Chemistry* 30: 133-137.
- Buyuksonmez, F., T.F. Hess, R.L. Crawford, A. Paszczyński, and R.J. Watts (1999). Optimization of Simultaneous Chemical and Biological Mineralization of Perchloroethylene. *Applied and Environmental Microbiology* 65: 2784-2788.
- Carus Chemical Corporation (2007). CAIROX Potassium and Sodium Permanganate Fact Sheets. <http://www.caruscorporation.com/>, accessed July 23.
- Chambers, J., A. Leavitt, C. Walti, C.G. Schreier, and J. Melby (2000). Treatability Study: Fate of Chromium during Oxidation of Chlorinated Solvents. in Chemical Oxidation and Reactive Barriers, ed. G.B. Wickramanayake, A.R. Gavaskar, and A.S.C. Chen, Battelle Press, Columbus, Ohio.
- Chapelle, F.H. and P.M. Bradley (1998). Selecting Remediation Goals by Assessing the Natural Attenuation Capacity of Groundwater Systems. *Bioremediation Journal* 2 (3-4): 227-238.

Chapelle, F.H., P.M. Bradley, and C.C. Casey (2005). Behavior of a Chlorinated Ethene Plume following Source-Area Treatment with Fenton's Reagent. *Ground Water Monitoring and Remediation*. 25 (2): 131-141.

Chen, G., G.E. Hoag, P. Chedda, F. Nadim, B.A. Woody, and G.M. Dobbs (2001). The Mechanism and Applicability of in situ Chemical Oxidation of Trichloroethylene with Fenton's Reagent. *Journal of Hazardous Materials* B87: 171-186.

Cleary, R.W. (2004). Fundamental and Advanced Concepts in Groundwater Hydrology in Manual of The Groundwater Pollution and Hydrology Course, Princeton Groundwater, Princeton, New Jersey, 503pp.

Cressie, N.A.C. (1991). Statistics for Spatial Data. John Wiley & Sons, Inc. New York, New York, 900pp.

Crimi, M.L. and R.L. Siegrist (2003). Geochemical Effects on Metals Following Permanganate Oxidation of DNAPLs. *Ground Water* 41(4): 458-469.

DOE (1999a). Innovative Technology Summary Report: Fenton's Reagent (Savannah River Site). Office of Environmental Management / Office of Science and Technology Subsurface Contaminants Focus Area. DOE/EM-0484, OST/TMS ID 2161, October.

DOE (1999b). Innovative Technology Summary Report: In Situ Chemical Oxidation Using Potassium Permanganate (Portsmouth Gaseous Diffusion Plant). Office of Environmental Management / Office of Science and Technology Subsurface Contaminants Focus Area. DOE/EM-0496, OST/TMS ID 167, September.

DOE (2000). Innovative Technology Summary Report: Remediation of DNAPLs in Low Permeability Soils (Portsmouth Gaseous Diffusion Plant). Office of Environmental Management / Office of Science and Technology Subsurface Contaminants Focus Area. DOE/EM-0550, OST/TMS ID 163, September.

Droste, E.X., M.C. Marley, J.M. Parikh, A.M. Lee, P.M. Dinardo, B.A. Woody, G.E. Hoag, and P.V. Chheda (2002). Observed Enhanced Reductive Dechlorination After In Situ Chemical Oxidation Pilot Test. in *Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, ed. A.R. Gavaskar and A.S.C. Chen, Battelle Press, Columbus, Ohio.

EPA (1992). Estimating the Potential for Occurrence of DNAPL at Superfund Sites. Office of Solid Waste and Emergency Response, 9355.4-07FS, January.

EPA (1993). Evaluation of the Likelihood of DNAPL Presence at NPL Sites: National Results. Office of Solid Waste and Emergency Response, 540-R-93-073, September.

EPA (1998). In Situ Remediation Technology: In Situ Chemical Oxidation. Office of Solid Waste and Emergency Response, 542-R-98-008, September.

- EPA (2003). The DNAPL Remediation Challenge: Is There a Case for Source Depletion?. Office of Research and Development, 600-R-03-143, December.
- EPA (2004a). Cleaning Up the Nation's Waste Sites: Markets and Technology Trends (2004 Edition). Office of Solid Waste and Emergency Response, 542-R-04-015, September.
- EPA (2004b). DNAPL Remediation: Selected Projects Approaching Regulatory Closure. Office of Solid Waste and Emergency Response, 542-R-04-016, December.
- EPA (2007). List of Contaminants and their MCLs.  
<http://www.epa.gov/safewater/contaminants/index.html>, accessed October 28.
- ESTCP (1999). Technology Status Review: In Situ Oxidation. November.
- ESTCP (2007a). In Situ Chemical Oxidation for the Remediation of Groundwater (ER-0623) Project Fact Sheet. <http://www.estcp.org/Technology/ER-0623-FS.cfm>, accessed August 28.
- ESTCP (2007b). "Critical Evaluation of State-of-the-Art In Situ Thermal Treatment Technologies for DNAPL Source Zone Treatment (ER-0314)" Project Fact Sheet. <http://www.estcp.org/Technology/ER-0314-FS.cfm>, accessed August 29.
- ESTCP (2007c). "Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation (ER-0424)" Project Fact Sheet. <http://www.estcp.org/Technology/ER-0424-FS.cfm>, accessed October 23.
- Fenton, H.J.H. (1894). The Oxidation of Tartaric Acid in the Presence of Iron. *Journal of Chemistry Society Proceedings* 10: 157-158.
- Fetter, C.W. (2001). Applied Hydrogeology: 4<sup>th</sup> Ed. Prentice-Hall, Inc. Upper Saddle River, New Jersey, 598pp.
- Freeze, R.A. and J.A. Cherry (1979). Groundwater. Prentice-Hall, Inc. Upper Saddle River, New Jersey, 604pp.
- Gardner, F. G., N. Korte, J. Strong-Gunderson, R.L. Siegrist, O.R. West, S.R. Cline, and J.L. Baker (1996). Implementation of Deep Soil Mixing at the Kansas City Plant, Oak Ridge National Laboratory. ORNL/TM-13532, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Gates, D.D. and R.L. Siegrist (1993). X-231B Technology Demonstration for In Situ Treatment of Contaminated Soil: Laboratory Evaluation of Chemical Oxidation Using Hydrogen Peroxide. Oak Ridge National Laboratory for DOE, ORNL/TM-12259, Environmental Sciences Division Publication No. 4106, September.

GeoSyntec Consultants, Inc. (2004). Assessing the Feasibility of DNAPL Source Zone Remediation: Review of Case Studies. Contract Report CR-04-002-ENV for NAVFAC, May.

Greenberg, R.S., T. Andrews, P.K.C. Kakarla, and R.J. Watts (1998). In-Situ Fenton-like Oxidation of Volatile Organics: Laboratory, Pilot, and Full-Scale Demonstrations. *Remediation* 8(2): 29-43.

GSI (2007). SERDP Source Depletion Decision Support System. [http://www.gsi-net.com/Software/serdp\\_dss.asp](http://www.gsi-net.com/Software/serdp_dss.asp), accessed August 15.

Hazen, T.C., G. Sewell, and A.R. Gavaskar (2000). The Effect of Source Remediation Methods on the Presence and Activity of Indigenous Subsurface Bacteria at Launch Complex 34, Cape Canaveral Air Station, Florida. in Chemical Oxidation and Reactive Barriers, ed. G.B. Wickramanayake, A.R. Gavaskar, and A.S.C. Chen, Battelle Press, Columbus, Ohio.

Helsel, D.R. and R.M. Hirsch (1991). Statistical Methods in Water Resources, Book 4: Hydrologic Analysis and Interpretation (Chapter A3). United States Geological Survey, Reston, Virginia.

Hemond, H.F. and E.J. Fechner-Levy (2000). Chemical Fate and Transport in the Environment: 2<sup>nd</sup> Ed. Academic Press, San Diego, California. 433pp.

Huling, S.G and B.E. Pivetz (2006). Engineering Issue: In-Situ Chemical Oxidation. United States Environmental Protection Agency, 600-R-06-702.

Imlay, J.A., S.M. Chin, and S. Linn (1988). Toxic DNA Damage by Hydrogen Peroxide Through the Fenton Reaction in Vivo and in Vitro. *Science* 240: 640-642.

Imlay, J.A. and S. Linn (1988). DNA Damage and Oxygen Radical Toxicity. *Science* 240: 1302-1309.

Isaaks, E.H. and R.M. Srivastava (1989). Applied Geostatistics. Oxford University Press, New York, New York. 561pp.

ITRC (2001). Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater. [http://www.itrcweb.org/gd\\_ISCO.asp](http://www.itrcweb.org/gd_ISCO.asp), accessed October 23.

ITRC (2005). Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater: Second Edition. [http://www.itrcweb.org/gd\\_ISCO.asp](http://www.itrcweb.org/gd_ISCO.asp), accessed October 23.

ITRC (2007). In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones: Case Studies. [http://www.itrcweb.org/gd\\_BioDNAPL.asp](http://www.itrcweb.org/gd_BioDNAPL.asp), accessed August 21.

Kastner, J.R., J. Santo Domingo, M. Denham, M. Molina, and R. Brigmon (2000). Effect of Chemical Oxidation on Subsurface Microbiology and Trichloroethene Biodegradation. *Bioremediation Journal* 4: 219-236.

Kim, M.J. and J. Nriagu (2000). Oxidation of Arsenite in Groundwater Using Ozone and Oxygen. *Science of the Total Environment* 247: 71-79.

Lamarche, C., N.R. Thomson, and S. Forsey (2002). ISCO of a Creosote Source Zone by Permanganate. in *Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Battelle Press, Columbus, Ohio.

Lestan, D., A. Hanc, and N. Finzgar (2005). Influence of Ozonation on Extractability of Pb and Zn from Contaminated Soil. *Chemosphere* 61: 1012-1019.

Li, X.D. and F.W. Schwartz (2000). Efficiency Problems Related to Permanganate Oxidation Schemes. in Chemical Oxidation and Reactive Barriers, ed. G.B. Wickramanayake, A.R. Gavaskar, and A.S.C. Chen, Battelle Press, Columbus, Ohio.

Lisiecki, J.B. and M.D. Colvin (2004). Assessment and Remediation of TCE DNAPL and Adjacent Plume. in *Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, ed. A.R. Gavaskar and A.S.C. Chen, Battelle Press, Columbus, Ohio.

Lowe, K.S., F.G. Gardner, and R.L. Siegrist (2002). Field Evaluation of in situ Chemical Oxidation through Vertical Well-to-Well Recirculation of NaMnO<sub>4</sub>. *Groundwater Monitoring & Remediation* 22 (1): 106-115.

Lowe, K.S., F.G. Gardner, R.L. Siegrist, and T.C. Houk (2000). Field Pilot Test of In Situ Chemical Oxidation through Recirculation Using Vertical Wells at the Portsmouth Gaseous Diffusion Plant. in *Proceedings of the Abiotic In Situ Technologies for Groundwater Remediation Conference*, Dallas, Texas. EPA/625/R-99/012.

Lunneborg, C.E. (2000). Data Analysis by Resampling: Concepts and Applications Duxbury Press, Pacific Grove, California, 568pp.

Mackay, D.M. and J.A. Cherry (1989). Groundwater Remediation: Pump-and-Treat Remediation. *Environmental Science & Technology* 23 (6): 630-636.

McDade, J. M., T. M. McGuire, and C.J. Newell (2005). Analysis of DNAPL Source-Depletion Costs at 36 Field Sites. *Remediation* 15(2): 9-18.

McGuire, T. M., J. M. McDade, and C.J. Newell (2006). "Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent-Impacted Sites." *Ground Water Monitoring & Remediation* 26(1): 73-84.

Monahan, M.J., A.L. Teel, and R.J. Watts (2005). Displacement of Five Metals Sorbed on Kaolinite during Treatment with Modified Fenton's Reagent. *Water Research* 39: 2955-2963.

Mott-Smith, E., W.C. Leonard, R. Lewis, W.S. Clayton, J. Ramirez, and R. Brown (2000). In situ Oxidation of DNAPL using Permanganate: IDC Cape Canaveral Demonstration. in Chemical Oxidation and Reactive Barriers ed. Wickramanayake, G.B., A.R. Gavaskar, and A.S.C. Chen. Battelle Press, Columbus, Ohio.

NAVFAC (2000a). Optimization of Remedial Action Operation to Treat Chlorinated Hydrocarbons in Groundwater: NAS Pensacola, FL. Remedial Action Operation Optimization Summary Report.

NAVFAC (2000b). Site 11, Old Camden County Landfill Remedial Action Operation: NSB Kings Bay, GA. Remedial Action Operation Optimization Summary Report.

NRC (1994). Alternatives for Ground Water Cleanup. National Academy Press, Washington, D.C, 315pp.

NRC (2004). Contaminants in the Subsurface: Source Zone Assessment and Remediation. The National Academies Press, Washington, D.C, 372pp.

Nelson, M.D., B.L. Parker, T.A. Al, J.A. Cherry, and D. Loomer (2001). Geochemical Reactions Resulting from In Situ Oxidation of PCE-DNAPL by KMnO<sub>4</sub> in a Sandy Aquifer. *Environmental Science & Technology* 35 (6): 1266-1275.

Palaia, T.A., S.N. Tsangaris, M.A. Singletary, and B.R. Nwokike (2004). Optimization of a Groundwater Circulation System for In Situ Chemical Oxidation Treatment in *Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Battelle Press, Columbus, Ohio.

Pankow, J.F. and J.A. Cherry (1996). Dense Chlorinated Solvents and Other DNAPLs in Groundwater: History, Behavior, and Remediation. Waterloo Press, Portland, Oregon, 522pp.

Parkhurst, D.F. (1998). Arithmetic Versus Geometric Means for Environmental Concentration Data. *Environmental Science & Technology* 32(3): 92A-98A.

Peck, R.B. (1969). Advantages and Limitations of the Observation Method in Applied Soil Mechanics. *Geotechnique* 19(2): 171-187.

Perez-Bonito, J. F. and C. Arias (1991). Occurrence of Colloidal Manganese Dioxide in Permanganate Reactions. *Journal of Colloid and Interface Science* 152: 70-84.



Petri, B.G., R.L. Siegrist, and M.L. Crimi (2007). The State of ISCO Science: A Critical Review of the Literature. in *Proceedings of the Fifth International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater (ORTs-5)*, Niagara Falls, New York.

Rai, D., L. E. Eary, and J. M. Zachara (1989). Environmental Chemistry of Chromium” *Science of the Total Environment* 86 (1-2): 15-23.

Rao, P.S.C. and J.W. Jawitz (2003). Comment on “Steady State Mass Transfer from Single-component Dense Nonaqueous Phase Liquid” by Sale, T.C. and D.B. McWhorter.” *Water Resource Research* 39 (3): 1068-1070.

Regenesis (2007). RegenOx™ product information.  
<http://www.regenesis.com/products/chemOx/regenOx/> accessed October 22.

Rock, M.L., B.R. James, and G.R. Helz (2001). Hydrogen Peroxide Effects on Chromium Oxidation State and Solubility in Four Diverse, Chromium Enriched Soils. *Environmental Science & Technology* 35: 4054-4059.

Sahl, J. and J. Munakata-Marr (2006). The Effects of In Situ Chemical Oxidation on Microbial Processes: A Review. *Remediation* 16 (3): 57-70.

Sale, T.C. and D.B. McWhorter (2001). Steady State Mass Transfer from Single-component Dense Nonaqueous Phase Liquid. *Water Resources Research* 37 (2): 393-404.

Saleh, F.Y., T.F. Parkerton, R.V. Lewis, J.H. Huang, and K.L. Dickson (1989). Kinetics of Chromium Transformation in the Environment.” *Science of the Total Environment* 86 (1-2): 25-41.

Siegrist, R.L., K.S. Lowe, M.L. Crimi, and M.A. Urynowicz. Quantifying PCE and TCE in DNAPL Source Zones: Effects of Sampling Methods Used for Intact Cores at Varied Contaminant Levels and Media Temperatures. *Ground Water Monitoring & Remediation* 26(2): 114-124.

Siegrist, R.L. and B. Satijn. Performance Verification of in situ Remediation Technologies. Report from the 2001 Special Session of the NATO/CCMS Pilot Study on Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater. EPA 542-R-02-002.

Siegrist, R. L., M.A. Urynowicz, M.L. Crimi, and K.S. Lowe (2002). Genesis and Effects of Particles Produced During In Situ Chemical Oxidation Using Permanganate. *Journal of Environmental Engineering* 128(11): 1068-1079.

Siegrist, R. L., M.A. Urynowicz, O.R. West, M.L. Crimi, and K.S. Lowe (2001). Principles and Practices of In Situ Chemical Oxidation Using Permanganate. Battelle Press, Columbus, Ohio, 348pp.

Smedley, P.L. and D.G. Kinniburgh (2002). A Review of the Source, Behavior and Distribution of Arsenic in Natural Waters. *Applied Geochemistry* 17: 517-568.

Sperry, K.L., M.C. Marley, C.J. Bruell, C. Liang, and J. Hochreiter (2002). Iron Catalyzed Persulfate Oxidation of Chlorinated Solvents. in *Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, ed. A.R. Gavaskar and A.S.C. Chen, Battelle Press.

Stroo, H.F., M. Unger, C.H. Ward, M.C. Kavanaugh, C. Vogel, A. Leeson, J.A. Marqusee, and B.P. Smith (2003). Remediating Chlorinated Solvent Source Zones. *Environmental Science & Technology* 37: 224A-231A.

United States Government Accountability Office (GAO) (2005). Groundwater Contamination: DOD Uses and Develops a Range of Remediation Technologies to Clean Up Military Sites. GAO-05-666, June.

United States Government Accountability Office (GAO) (2006). Environmental Liabilities: Long-term Fiscal Planning Hampered by Control Weaknesses and Uncertainty in the Federal Government's Estimates. GAO-06-427, March.

U.S. Peroxide (2007). <http://www.h2o2.com/intro/properties/physical.html#2>, accessed July 24.

Wagner, G (1895). *Journal of Russ. Physical Chemistry Society* 27: 219.

Watts, R.J. and A.M. Teel (2005). Chemistry of Modified Fenton's Reagent (Catalyzed H<sub>2</sub>O<sub>2</sub> Propagations-CHP) for In Situ Soil and Groundwater Remediation. *Journal of Environmental Engineering* 131 (4): 612-622.

West, O.R., S.R. Cline, W.L. Holden, F.G. Gardner, B.M Schlosser, J.E. Thate, D.A. Pickering, and T.C. Houk (1998). A Full-scale Demonstration of In Situ Chemical Oxidation Through Recirculation at the X-701B Site. ORNL/TM-13556, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Wiberg, K. B. and K.A. Saegebarth (1957). The Mechanisms of Permanganate Oxidation: IV. Hydroxylation of Olefins and Related Reactions. *Journal of the American Chemical Society* 79: 2822-2824.

Yan, Y. E. and F.W. Schwartz (1999). Oxidative Degradation and Kinetics of Chlorinated Ethylenes by Potassium Permanganate. *Journal of Contaminant Hydrology* 37: 343-365.

## APPENDIX A: GEOSPATIAL METHODS AND EXAMPLE OUTPUTS

This appendix describes in greater detail the theory of the geospatial analysis introduced in Section 3.3.5 as well as the specific computing and mathematical techniques used. The reader is referred to the supporting references for further details on this subject (Cressie 1991, Isaaks and Srivastava 1989).

The statistical software package R (v. 2.6.1) was used for the geospatial analyses. This is a statistical and graphics environment that is free for public use. The add-on packages *mvtnorm* (v. 0.8-1), *sp* (v. 0.9-19), *geoR* (v. 1.6-20), *fields* (v. 4.1), *spam* (v. 0.13-2), and *splancs* (v. 2.01-23) were used in the various analyses as well. R also has many graphics capabilities that can be used to create concentration maps, semi-variograms, and estimated data plots shown in this appendix. The R base package and add-ons are available at <http://cran.r-project.org>. R scripts may be obtained from the author of this thesis at [fkrembs@hotmail.com](mailto:fkrembs@hotmail.com).

Ordinary kriging was the geospatial analysis technique used to estimate a spatially-weighted average. This technique requires that the data satisfy the stationarity assumption, which is that the mean and variance of the data are independent of location. Isotropic models were also used, which assume that the spatial variability in sampling concentration is only a function of the distance between points, and not a function of direction. In cases where the data revealed trends in concentration with respect to location or were clearly more variable in one direction than another for a given separation distance, these assumptions did not hold. In these cases, the raw data were detrended. Detrending the large-scale variation in a dataset is a common practice in geostatistics and is necessary when the stationarity assumption is violated (Cressie 1991, Isaaks and Srivastava 1989). The detrending technique used in this study involved creating an anisotropic Gaussian spatial function, and fitting the parameters for this function to the raw data using a least sum of squares method. The transformed data were calculated by subtracting the value of the fitted Gaussian function from the raw data at each of the sampled locations. The detrended data were then used to perform the kriging as described below.

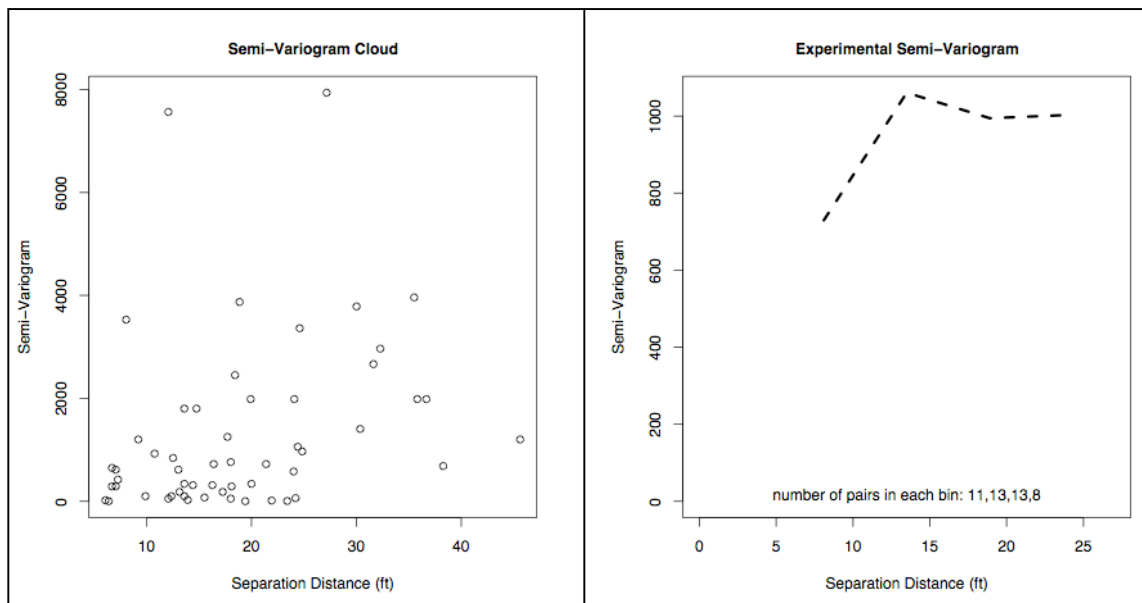
The first step in the kriging process is to create a contaminant concentration map showing the reported groundwater sample concentration at the spatial location where the sample was collected. Each of these maps is examined to: 1) verify that the spatial data was entered correctly, and 2) to consider whether the data violated the assumptions of constant mean and isotropy.

The next step is to create an experimental variogram using the raw or detrended data. In geostatistics, the variogram is a representation of the squared difference between concentrations as a function of separation distance calculated using the formula

$$\gamma(h) = (Z(o) + Z(o + h))^2 \quad (\text{A-1})$$

where  $\gamma(h)$  is the variogram value for a pair of points separated by a distance  $h$  and the  $Z$  values are the sampled concentrations at those two points. This calculation is performed for all pairs of points, and the results may be plotted versus separation distance to create a variogram cloud, shown below in Figure A-1 (left panel). This figure contains many points, and making sense of them is difficult when the data are presented in this way. This is overcome by creation of the experimental variogram plot, which groups together the data based on ranges of separation distances and calculates the mean variogram value for all points within these bins of separation distance, producing the result shown in Figure A-1 (right panel), where each bend in the line is the mean value for that bin.

Figure A-1: Semi-Variogram Cloud and Experimental Semi-Variogram



Conceptually, the variogram of a stationary process must continually increase up to some point after which it remains constant. This is the case because generally speaking concentration data should be more similar to points that are nearby relative to those that are farther away. But beyond a certain distance from a given point, the data reach a peak of dissimilarity. The distance at which the data reaches its maximum dissimilarity is called the “range”, and no further increase in separation distance beyond this amount impacts the variation any further. The variogram value at which this occurs is referred to as the “total sill”. The process of creating a good experimental variogram requires manipulating the maximum separation distance that will be considered and also how the points within that distance are allocated between the bins. These are both done in an effort to make an experimental variogram that is initially increasing and eventually plateaus.

Once an acceptable experimental variogram has been created from the raw data, it must be fitted with a model variogram. This is done by specifying a set of functions that approximate the experimental variogram. Two types of functions were used to fit the variograms in this study: a nugget effect and a spherical structure.

The nugget effect models discontinuity at the origin. The term nugget is from geostatistics’ mining roots, and was initially used to describe a physical process (presence or absence of a nugget of metal) that was not spatially continuous. It is also used in geostatistics to incorporate measurement error. Even though groundwater concentrations are theoretically spatially continuous (NAPL being defined as a phase different than groundwater), there is measurement error associated with groundwater data. To estimate the measurement error associated with the samples in ISCO-DB1, a random selection of 100 duplicate samples were taken from the case study data. Of these 100 samples, the arithmetic mean of the error between duplicates (calculated by the difference between the duplicates divided by the average of the two) was 20.8%. For this reason, the nugget effect was defined to be 20% of the total sill.

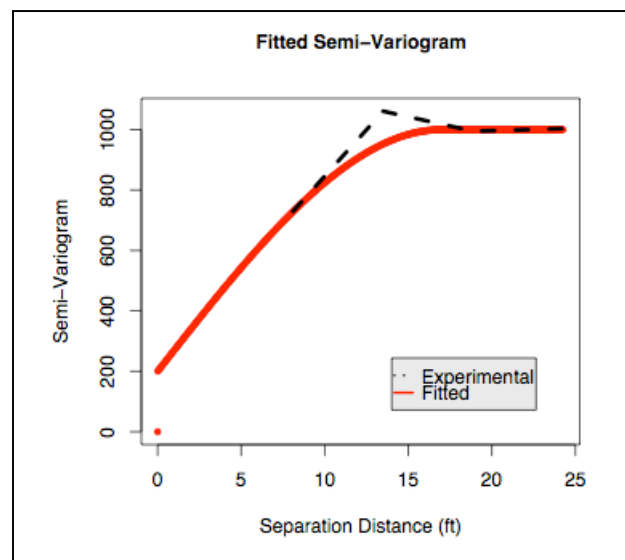
A spherical structure produces a concave down function that increases until it reaches the range, at which point it stays constant. The spherical structure is calculated with the formulas in Equation A-2 shown below.

$$\begin{aligned}
 Spherical(h) &= Sill * \left[ 1.5 \left( \frac{h}{range} \right) - 0.5 \left( \frac{h}{range} \right)^3 \right] && \text{for } h < range \\
 Spherical(h) &= Sill && \text{for } h \geq range
 \end{aligned}
 \tag{A-2}$$

$h$  is the separation distance, sill refers to the sill of the spherical structure, and range is the range of the spherical structure. The sill of the spherical structure was defined to be 80% of the total sill.

When this structure is added to the nugget effect described in the previous paragraph, the result is a set of nested functions that are discontinuous at the origin, and gradually increase until they reach the total sill at a separation distance equal to the range. When the proper range and sill are selected, the result is the fitted variogram shown in red in Figure A-2, which in this case has been fitted to the experimental variogram.

Figure A-2: Fitted Semi-Variogram

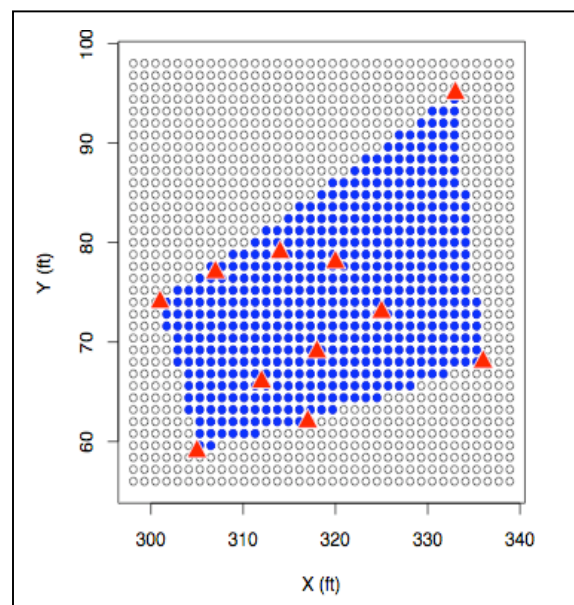


The fitted variogram is the basis for estimating the unknown points using kriging. The conceptual process of kriging is described in this paragraph. First, the fitted function is used to generate the square covariance matrix (“C matrix”) that contains the covariances between known sampled locations based on their known separation distances. Next, the spatial location of an unknown coordinate whose value will be estimated is selected. The “D matrix” is a  $n \times 1$  matrix that contains the correlation between the unknown point being estimated and the known points based on the separation distance between the known point and the unknown points calculated from a mathematical model relating the covariance to the separation distance derived from the

fitted variogram. The matrix of weights (“w matrix”) to be used in kriging is calculated by multiplying the inverse of the C matrix by the D matrix. The result is a  $n \times l$  matrix containing the weights to be associated with the known sampling locations. Finally, the known sampled concentrations are multiplied by their respective weight in the w matrix, and the sum of these weighted values is the concentration estimated at the unknown location calculated with Ordinary Kriging.

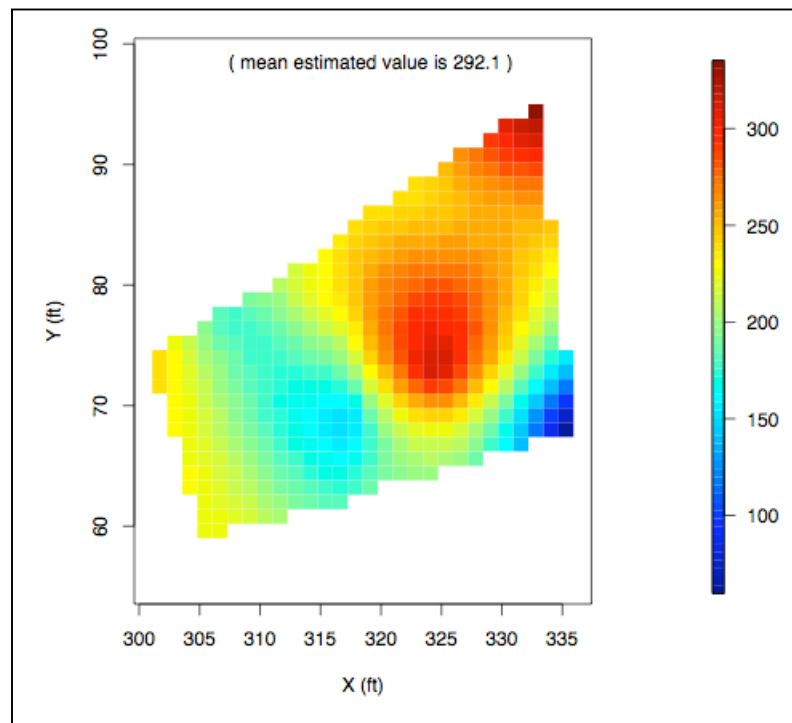
The previous paragraph described how to estimate the concentration at a single unknown point. In the analysis of ISCO-DB1, R was used to automate this process so that the estimated value at evenly spaced locations within the TTZ was calculated with a single series of computer scripts. The first step in this process consisted of generating a square grid of approximately 1000 equally spaced points spanning slightly beyond the entire range of X and Y in the sampled region (the actual number of points estimated varied depending on the ratio of the range in X to range in Y values, and is at least 900 points when the ranges are equal). Next, the grid points lying outside the sampled region were deleted and those inside were retained. Inside in this case is defined as those grid points that were on or within the convex hull polygon defined by the outermost sampled locations. The entire square grid and the retained portion are shown as open and blue closed circles, respectively, in the Figure A-3 below. Sampled locations are shown by red triangles.

Figure A-3: X Y Plot of Grids and Sample Locations Used in Kriging



The value estimated by the kriging functions was calculated at each grid node within the convex hull (in this example all blue points above). This was performed in R using matrix algebra to calculate the C matrix, an expanded D matrix with the columns comprised of D matrices, one for each grid node being estimated, and an expanded w matrix with each of the columns consisting of the weights associated with each grid node being estimated. A matrix of estimated values at each grid node was calculated using the weights and the known sampled locations. A plot of the estimated values is shown on Figure 3-6 below. The arithmetic mean of the grid node estimates was calculated as the spatially-weighted average groundwater concentration.

Figure A-4: Contaminant Concentration Surface Estimated with Kriging



Notes: The above plot shows estimated contaminant concentrations in groundwater, with the units ug/L.

This entire process is performed on both baseline and post-ISCO samples, and the difference between the spatially-weighted average before versus after is considered to be the percent change in the average groundwater concentration at that site (after form of Equation 3-3 substituting spatially-weighted values).



## **APPENDIX B: COMPLETE DATA TABLES**

This appendix provides the detailed tables supporting the Results and Analysis of Results sections in the body of the text. A brief text description introducing the tables is included here, while the bulk of the appendix consists of tables and explanatory notes. This appendix shows summary statistics of the ISCO sites contained in ISCO-DB1, first including all sites (Section B.1), followed by sections formed by dividing the entire dataset along the parameters COCs treated (Section B.2), oxidant used in remediation (Section B.3), Geology Group (Section B.4) and the presence of NAPL (Section B.5). Each of these sections is subdivided further into general information/site conditions, ISCO design, and performance results.

Some explanation is required prior to presenting the results. First, the breadth of data varies greatly from site to site, and for that reason the sample size changes dramatically depending on the statistics being presented. Secondly, when an analysis is performed on multiple parameters, all the parameters in the analysis must be non-blank, or else the site is dropped from the analysis. This fact causes a further decrease in the sample size.

In addition, some grouping parameters are not mutually exclusive, and for this reason the sum of percentages in a given column may be greater than 100. An example of this situation is the type of information generated by a treatability study, which in some cases included both verifying contaminant degradation and also optimization of oxidant and activator chemistry. These situations are highlighted in the notes of the table.

This is an appendix designed primarily to provide support to the bulk of the text rather than be read continuously from start to end. For this reason, explanatory notes associated with similar tables are repetitive.

### **B.1 Overall Summary of ISCO Database**

This section shows summary statistics of all of the sites contained in ISCO-DB1. Unless otherwise noted, these tables include all scales of remediation (i.e. full-scale, pilot scale).

B.1.1 General Information – All Data

Table B-1: Sites in Database by Nation

Nation	# of sites	Nation	# of sites
USA	230	Italy	1
Australia	2	Netherlands	3
Brazil	2	Norway	1
Canada	3	<b>Total</b>	<b>242</b>

Table B-2: Sites in Database by U.S. State

State	# of sites	State	# of sites	State	# of sites
AK	1	MA	10	OR	5
AL	5	MD	1	PA	8
AR	2	ME	7	RI	1
AZ	2	MI	3	SC	10
CA	40	MN	2	TN	5
CO	9	MO	3	TX	13
CT	1	MT	2	UT	1
DE	1	NC	3	VA	2
FL	21	NE	1	VT	1
GA	10	NH	1	WI	4
IA	1	NJ	19	WV	2
IL	2	NM	1	WY	5
IN	2	NY	9		
KS	5	OH	5		
LA	1	OK	2	<b>Total</b>	<b>215</b>

Notes: The total in this table is less than that reported for the USA in Table B-1 because 15 sites did not report the state in which the remediation occurred. These 15 sites are generally from conference proceedings or vendor materials, and presumably the state was intentionally omitted because of confidentiality issues.

Table B-3: Site Types in ISCO-DB1

Site Type	Percent of Sites
<b>Federal</b>	20.5
<i>Air Force / ANG</i>	6.3
<i>Army</i>	0.4
<i>general DOD</i>	7.6
<i>DOE</i>	3.1
<i>miscellaneous</i>	0.4
<i>NASA</i>	1.8
<i>Navy</i>	5.8
<b>Manufacturing/Industrial</b>	20.1
<b>Dry Cleaner</b>	20.1
<b>Service Station</b>	11.2
<b>Chemical Production/Handling</b>	5.4
<b>Former MGPs</b>	4.9
<b>Landfill / Lagoon / Waste Storage</b>	2.2
<b>Wood Treatment</b>	1.8
<b>Auto Sales/Repair</b>	1.3
<b>Equipment Repair</b>	1.3
<b>Fuel Distribution</b>	1.3
<b>Farm Supply Dealer</b>	0.4
<b>Field Demonstration</b>	0.4
<b>Mine Tailings</b>	0.4
<b>News Publisher</b>	0.4
<b>Quarry</b>	0.4
<b>Residence</b>	0.4
<b>Utility Authority</b>	0.4
<b>Warehouse</b>	0.4
<i>n</i>	224

Notes: The category “general DOD” includes sites that were provided with the understanding that the site and its sector within the DOD complex would remain confidential and also project summaries that did not report the DOD sector in which the work was performed. “miscellaneous” is a federal facility that wanted its government sector to remain confidential.

Of note in the above table are the former MGP sites and wood treatment facilities, both of which are generally considered to be recalcitrant sites due to the frequent presence of low volatility NAPLs at these sites. These types of sites show a progression from the types of sites that ISCO was used to treat in its earlier stages of development, which were predominantly those contaminated with chloroethenes and BTEX.

The distribution of data reliability, ranked by DQC, is shown in Table B-4. There are 111 sites that have an assumed data reliability that is high. Keep in mind that reliability and thoroughness are not necessarily correlated.

Table B-4: Summary of DQC Values

<b>DQC</b>	<b>Percent of Sites</b>
<b>Class 1</b>	46
<b>Class 2</b>	40
<b>Class 3</b>	14
<b><i>n</i></b>	<b><i>241</i></b>

Notes: Class 1 (most reliable) = project reports and journal articles, Class 2 = conference proceedings, online resources, Class 3 = vendor information

### *B.1.2 COCs – All Data*

The next several tables show data on various aspects of the contaminants represented in ISCO-DB1. Notes with respect to how the parameters are defined are included after each table when the definition is not evident from the table itself.

Table B-5: Summary of COCs

<b>COCs Present</b>	<b>Percent of Sites</b>
<b>chloroethenes</b>	70
<b>BTEX</b>	18
<b>TPH/GRO/DRO</b>	11
<b>chloroethanes</b>	8
<b>MTBE</b>	7
<b>PAHs</b>	7
<b>chlorobenzenes</b>	5
<b>methylene chloride</b>	3
<b>chloroform</b>	2
<b>carbon tetrachloride</b>	1
<b>pentachlorophenol</b>	1
<b>arsenic</b>	1
<b>cyanide</b>	1
<b>herbicides/ pesticides</b>	1
<b>methyl isobutyl ketone</b>	1
<b>TAME</b>	1
<b><i>n</i></b>	<b>223</b>

Notes: Percentages sum to greater than 100% because multiple COC groups are present at some sites. "TAME" is the fuel oxygenate tertiary-amyl-methyl-ether. The following COCs were present at only one site each (0.5%): 1,4-dioxane, and dicyclopentadiene (DCPD).

Table B-6: Indications of NAPL Presence

<b>Type of Indication</b>	<b>yes (%)</b>	<b>no (%)</b>	<b><i>n</i></b>
<b>Project Reports Stated that DNAPL is Present</b>	44	56	149
<b>Project Reports Stated that LNAPL is Present</b>	11	89	149
<b>COC Concentrations Reported Above 1% of Aqueous Solubility</b>	66	34	127

Notes: The first two metrics presented in this table are independent of the last. The first two refer to whether the project reports reviewed stated that NAPL was present. The second parameter refers to whether maximum concentrations exceeded 1% of the solubility limit, and was applied only to chlorinated solvent sites.

Table B-7: Use of COC Mass Flux as Baseline Site Assessment Criterion

	<b>yes (%)</b>	<b>no (%)</b>	<b><i>n</i></b>
<b>Project Reports Estimated Baseline Mass Flux</b>	2	98	231

Table B-8: Estimate of Baseline COC Mass (kg)

Minimum	Maximum	Median	<i>n</i>
0.0004	44,579	270	15

Table B-9: Summary of Extents of Contamination

Parameter (units)	Minimum	Maximum	Median	<i>n</i>
<b>Plume Areal Extent (1,000s sf)</b>	0.1	1,900	55	57
<b>Plume Volume (1,000s cf)</b>	3.5	124,000	1,800	37
<b>Source Areal Extent (1,000s sf)</b>	0	150	3	38
<b>Source Volume (1,000s cf)</b>	0	4,500	63	32

Notes: Plume refers to aqueous phase concentrations of a COC higher than that COC's MCL. Source zone refers to areas with observed NAPL or aqueous phase concentrations greater than 1% of the solubility limit for that COC. Sites without NAPL or significant sorbed phase contamination were considered to have no saturated zone source (area and volume equal to 0).

### B.1.3 Subsurface Geology, Hydrology and Groundwater Chemistry – All Data

The tables that follow (Tables B-10 through B-12) describe various aspects of the subsurface geology present. Again, notes are included to clarify definitions of parameters.

Table B-10: Summary of Geology Group Distribution

Geology Groups	Percent of Sites
<b>Group A</b>	21
<b>Group B</b>	3
<b>Group C</b>	47
<b>Group D</b>	15
<b>Group E</b>	7
<b>Group F</b>	7
<b><i>n</i></b>	<b>209</b>

Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)

Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

Table B-11: Summary of Hydrogeologic and Geochemical Data

Parameter (units)	Minimum	Maximum	Median	<i>n</i>
Depth to Water (ft bgs)	1	150	10	124
Hydraulic Conductivity (ft/day)	0.0001	2400	4.5	86
Groundwater Flow Velocity (ft/day)	.002	5	.19	58
Total Organic Carbon (g/kg)	0.0013	280	4.1	23

Notes: Groundwater velocity, when not reported, was calculated using the formula, velocity = hydraulic conductivity\*gradient / effective porosity. Effective porosity was assumed to be 0.3 when not explicitly stated. This parameter is also called the pore velocity, and is not the same as the Darcy velocity. Fraction organic carbon (foc) data entered as TOC by converting units to g/kg.

Table B-12: Summary of Baseline Groundwater Chemistry

Parameter (units)	Minimum	Maximum	Median	<i>n</i>
pH (SU)	3.9	8.5	6.7	45
ORP (mV)	-135	560	64.5	32
DO (mg/L)	0	9.3	1.115	34
Temperature (°C)	11.5	28	19.35	26
Total Organic Carbon (mg/L)	1.17	148	5.4	17
Alkalinity (meq/L)	0.5	17	3.9	11
Turbidity (NTU)	1.6	407	71.1	6
Conductivity (mS/cm)	0.275	100	0.806	13

Table B-13: Summary of Goals of ISCO Remediation

Goal of Remediation	Percent of Sites
Meet MCLs	37
Meet ACLs (Risk-Based)	25
Reduce Mass by Certain %	9
Reduce Mass and/or Time to Cleanup	31
Evaluate Effectiveness and Optimize Future Injections	27
<i>n</i>	112

Note: Sites may have had more than one of the above goals, and for this reason the percentages sum to greater than 100%.

#### B.1.4 ISCO Design Parameters – All Data

Tables B-14 through B-26 summarize ISCO design parameters. Except where noted, these tables include both full scale applications and ISCO pilot tests. All tables include all DQC groups.

Table B-14: Summary of Project Scale

<b>Maximum Project Scale</b>	<b>Percent of Sites</b>
<b>Full</b>	65
<b>Pilot only</b>	35
<b><i>n</i></b>	<b>217</b>

Table B-15: Summary of Oxidant Used

<b>Oxidant</b>	<b>Percent of Sites</b>
<b>Permanganate</b>	44
<b>CHP</b>	37
<b>Persulfate</b>	7
<b>Ozone</b>	12
<b>Percarbonate</b>	3
<b>Peroxone</b>	2
<b><i>n</i></b>	<b>218</b>

Notes: Multiple oxidants used at six sites. Peroxone refers to the use of hydrogen peroxide as an activator during ozone sparging.

Table B-16: Summary of Targeted Geologic Media

<b>Targeted Media</b>	<b>Percent of Sites</b>
<b>Groundwater</b>	45
<b>Groundwater and Soil</b>	52
<b>Groundwater and Rock Matrix</b>	2
<b><i>n</i></b>	<b>164</b>

Notes: Projects designed to remediate soils only without consideration of mitigating impacted groundwater were outside the scope of this project. Projects were assigned to the “Groundwater” category when project reports did not state that non-aqueous phase contaminants were to be targeted by ISCO. This should not be interpreted to mean that COCs were only present in the aqueous phase in these situations.



Table B-17: Summary of TTZ

<b>ISCO TTZ</b>	<b>Percent of Sites</b>
<b>Source</b>	52
<b>Source and Plume</b>	19
<b>Plume</b>	14
<b>Other (pilot test)</b>	14
<b><i>n</i></b>	<b><i>170</i></b>

Table B-18: Summary of Size of TTZ

<b>Parameter (units)</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Median</b>	<b><i>n</i></b>
<b>TTZ Areal Extent (1,000s sf)</b>	0.08	260	8.1	<i>120</i>
<b>TTZ Volume (1,000 cf)</b>	0.2	9,100	135	<i>110</i>

Table B-19: Summary of Oxidant Delivery Method

<b>Delivery Method</b>	<b>Percent of Sites</b>
<b>Injection Wells</b>	40
<b>Direct Push</b>	23
<b>Sparge Points</b>	14
<b>Infiltration</b>	10
<b>Injectors</b>	7
<b>Recirculation</b>	7
<b>Fracturing</b>	6
<b>Mechanical Mixing</b>	2
<b>Horizontal Wells</b>	1
<b><i>n</i></b>	<b><i>181</i></b>

Note: n=181. Percentages sum to greater than 100% because multiple delivery techniques were used at some sites. "Injectors" refers to permanent wellpoints that are designed to mix activators and oxidants at the wellpoint so that they may be delivered simultaneously. "Infiltration" refers to trenches, galleries, or vertical wellpoints installed in the vadose zone so that the oxidant will migrate vertically through the treatment zone.

Table B-20: Summary of ISCO Design Parameters

Parameter (units)	Minimum	Maximum	Median	<i>n</i>
<b>Design ROI (ft)</b>	2	55	15	83
<b>Oxidant Mass Loading Rate (g oxidant / kg media)</b>	0.004	60	1.05	68
<b>Number of Pore Volumes Delivered ( - )</b>	0.004	56	0.12	65
<b>Number of Delivery Events ( - )</b>	1	10	2	159

Notes: ROI = radius of influence.

Table B-21: Summary of Use of Treatability Studies

	yes (%)	no (%)	<i>n</i>
<b>Project Performed a Treatability Test</b>	78	22	121

Notes: It was difficult to assume the absence of the use of treatability studies from many of the project reports, therefore the field was left blank if no mention was made of a treatability study and it could not be confirmed with project contacts that a treatability study was not performed.

Table B-22: Summary of Types of Treatability Studies Used

Type of Treatability Study	Percent of Sites
<b>Demonstrate COC Degradation</b>	53
<b>Optimize Oxidant/Soil/Activator Ratios</b>	37
<b>Evaluate Secondary Groundwater Impacts</b>	9
<b>Evaluate Soils for Buffering or Activating Attributes</b>	8
<b>Measure NOD/SOD</b>	48
<b><i>n</i></b>	75

Notes: Percentages sum to greater than 100% because some projects used treatability studies that would provide data to fit multiple categories.

Table B-23: Summary of Use of Pilot Testing – Full Scale Applications Only

	yes (%)	no (%)	<i>n</i>
<b>Project Performed a Pilot Test</b>	60	40	87

Notes: This analysis is presented for full scale applications only because performing a pilot test is only a relevant design tool for full scale applications.

Table B-24: Summary of Program Modification

	<b>yes (%)</b>	<b>no (%)</b>	<b><i>n</i></b>
<b>Program Was Modified During Field Implementation</b>	58	42	78

Table B-25: Summary of the Use of Coupling

	<b>All Scales</b>	<b>Full Scale Only</b>	<b>Pilot Scale Only</b>
<b>Percent of Sites Using Coupling</b>	76	89	44
<b>Percent Coupled Before ISCO</b>	60	68	36
<b>Percent Coupled During ISCO</b>	22	30	3
<b>Percent Coupled After ISCO</b>	30	38	15
<b><i>n</i></b>	<i>135</i>	<i>90</i>	<i>39</i>

Notes: Coupling as defined in this table includes both situations in which ISCO designers planned on a coupled approach prior to ISCO implementation or where ISCO was implemented after another treatment method had been attempted in the same area. The sum of the percentages of the bottom three rows may exceed the top row if coupling techniques were used before and after ISCO. MNA was only included as a coupled technique when project documents specifically stated that it would be used after ISCO. For this reason, the percentage of sites using coupling after ISCO is likely underestimated.

Table B-26: Summary of Coupling Techniques

Type of Coupling	Percent of Sites
<i>Coupling Technique Used Before ISCO</i>	
<b>Excavation</b>	50
<b>Air Sparging</b>	8
<b>SVE</b>	18
<b>Bioventing</b>	1
<b>P&amp;T</b>	22
<b>EFR</b>	2
<b>DPE</b>	1
<b>EISB</b>	3
<i>Coupling Technique Used Concurrently With ISCO</i>	
<b>Excavation</b>	4
<b>Air Sparging</b>	3
<b>SVE</b>	9
<b>P&amp;T</b>	11
<b>DPE</b>	2
<b>Surfactant/Cosolvent</b>	3
<b>EISB</b>	2
<i>Coupling Technique Used After ISCO</i>	
<b>Excavation</b>	8
<b>P&amp;T</b>	8
<b>Air Sparging</b>	1
<b>Biosparging</b>	1
<b>SVE</b>	4
<b>DPE</b>	2
<b>EISB</b>	17
<b>MNA</b>	19
<b><i>n</i></b>	<b><i>103</i></b>

Note: DPE = dual phase extraction. EFR = enhanced fluid recovery. SVE = soil vapor extraction. Percentages sum to greater than 100% because multiple coupling techniques were used at some sites. MNA was only entered as a coupling technique after ISCO when the project files specifically called out that it was used after ISCO. Due to this fact, it is likely that the use of MNA after ISCO is underestimated.

#### B.1.5 ISCO Results – All Data

The last tables within this subsection show a brief overview of various success indicators as well as cost. Note that these data includes all contaminants, oxidants, and types of geologic media. The sites that are listed as having met MCLs include only those

where the regulatory official was listed in the project reports and the regulators could be reached by email or telephone to verify that the site had reached and maintained MCLs.

Table B-27: Summary of Qualitative Success Metrics

<b>Success Indicator</b>	<b>yes (%)</b>	<b>no (%)</b>	<b><i>n</i></b>
<b>Goals Were Achieved</b>	52	48	121
<b>MCLs Were Attained</b>	5	96	132
<b>Site Closure Was Attained (Full Scale Only)</b>	24	76	74

Notes: First row refers to sites where all the project's goals were met. This required that project documents clearly what the goals were and state whether or not those goals were met with supporting evidence. The second row refers to whether or not MCLs were met and maintained *irrespective of the project's goals*. The fact that MCLs were met and maintained was confirmed with regulatory officials in all cases. The last row refers to situations where site closure was achieved, either by meeting MCLs or some other regulatory standard, and possibly including requirements for engineering and institutional controls. This metric was only applied to full scale sites because pilot tests are generally not expected to lead to site closure.

Table B-28: Summary of Project Goals vs. Percent Meeting those Goals – All Sites

<b>Project Goals</b>	<b>Percent Meeting Goals</b>		
	<b>yes (%)</b>	<b>no (%)</b>	<b><i>n</i></b>
<b>MCLs</b>	15	85	39
<b>ACLs (Risk-Based)</b>	39	61	28
<b>Reduce Mass by Certain %</b>	46	55	11
<b>Reduce Mass and/or Time to Cleanup</b>	80	20	40
<b>Evaluate Effectiveness and Optimize Future Injections</b>	95	5	37

Notes: A site was considered to have failed to reduce mass if concentrations of the media sampled after ISCO (groundwater and/or soil) showed no concentration reductions. This occurred most often when no soil samples were collected. Further explanation of this metric is included in the Methods section. The percentage of sites meeting MCLs in the table above differs from the previous table because this table considers only sites that set MCLs as the goal of their remediation. Mean DQC values are 1.3, 1.4, 1.2, 1.5, and 1.5 from top to bottom.

Table B-29: Summary of Project Goals vs. Percent Meeting those Goals – Full Scale Only

Project Goals	Percent Meeting Goals		
	yes (%)	no (%)	<i>n</i>
<b>MCLs</b>	21	79	28
<b>ACLs (Risk-Based)</b>	44	56	25
<b>Reduce Mass by Certain %</b>	33	67	6
<b>Reduce Mass and/or Time to Cleanup</b>	82	18	34
<b>Evaluate Effectiveness and Optimize Future Injections</b>	100	0	6

Notes: A site was considered to have failed to reduce mass if concentrations of the media sampled after ISCO (groundwater and/or soil) showed no concentration reductions. This occurred most often when no soil samples were collected. Further explanation of this metric is included in the Methods section. The percentage of sites meeting MCLs in the table above differs from the previous table because this table considers only sites that set MCLs as the goal of their remediation.

Table B-30: Summary of Project Goals vs. Percent Meeting those Goals – Pilot Scale Only

Project Goals	Percent Meeting Goals		
	yes (%)	no (%)	<i>n</i>
<b>MCLs</b>	0	100	11
<b>ACLs (Risk-Based)</b>	0	100	3
<b>Reduce Mass by Certain %</b>	60	40	5
<b>Reduce Mass and/or Time to Cleanup</b>	67	33	6
<b>Evaluate Effectiveness and Optimize Future Injections</b>	94	6	31

Notes: A site was considered to have failed to reduce mass if concentrations of the media sampled after ISCO (groundwater and/or soil) showed no concentration reductions. This occurred most often when no soil samples were collected. Further explanation of this metric is included in the Methods section. The percentage of sites meeting MCLs in the table above differs from the previous table because this table considers only sites that set MCLs as the goal of their remediation.

Table B-31: Summary Percent Reductions in Maximum COC Concentration – All Data

<b>Parameter (units)</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Median</b>	<b>Mean</b>	<b><i>n</i></b>
<b>Percent Reduction in Mass</b>	73	94	84	82	9
<b>Percent Reduction in Max. Total VOCs in GW</b>	-146	99.99	75	64	67
<b>Percent Reduction in Max. Total Chlorinated VOCs in GW</b>	-146	99.7	54	47	55
<b>Percent Reduction in Max. PCE in GW</b>	-72	99.9	61	52	32
<b>Percent Reduction in Max. TCE in GW</b>	-590	99.99	66	38	53
<b>Percent Reduction in Max. cis-1,2DCE in GW</b>	-8900	96	33	-295	28
<b>Percent Reduction in Max. VC in GW</b>	-380	96	25	3	12
<b>Percent Reduction in Max. 1,1,1-TCA in GW</b>	6	98	77	65	4
<b>Percent Reduction in Max. total Chlorinated Benzenes in GW</b>	-15	80	16	23	5
<b>Percent Reduction in Max. Benzene in GW</b>	23	99.99	91	84	10
<b>Percent Reduction in Max. MTBE in GW</b>	83	99.99	99	96	6

Notes: GW = groundwater. Max. = maximum. Percent reduction as defined in methods section. Contaminant acronyms as in list of acronyms.

Table B-32: Summary Percent Reductions in Maximum COC Concentration – Only Sites with One Year Post-ISCO Data

<b>Parameter (units)</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Median</b>	<b>Mean</b>	<b><i>n</i></b>
<b>Percent Reduction in Mass</b>	84	94	86	88	4
<b>Percent Reduction in Max. Total VOCs in GW</b>	-146	99.99	57	48	34
<b>Percent Reduction in Max. Total Chlorinated VOCs in GW</b>	-146	99.7	53	45	28
<b>Percent Reduction in Max. PCE in GW</b>	-72	99.9	49	50	20
<b>Percent Reduction in Max. TCE in GW</b>	-588	99.99	77	38	28
<b>Percent Reduction in Max. cis-1,2DCE in GW</b>	-8900	96	21	-552	16
<b>Percent Reduction in Max. VC in GW</b>	68	68	68	68	1
<b>Percent Reduction in Max. 1,1,1-TCA in GW</b>	84	94	86	88	4
<b>Percent Reduction in Max. total Chlorinated Benzenes in GW</b>	-15	12	-1	-1	2
<b>Percent Reduction in Max. Benzene in GW</b>	88	99.99	94	94	3
<b>Percent Reduction in Max. MTBE in GW</b>	96	99.99	99	98	3

Notes: This table is identical to the preceding table except that it includes only projects that had data available for review from a post-ISCO monitoring period of at least one year. GW = groundwater. Percent reduction as defined in methods section. Contaminant acronyms as in list of acronyms.

Table B-33: Summary Rebound Testing and Occurrence

	<b>Percent</b>	<b><i>n</i></b>
<b>Was Rebounded Tested For (% yes)</b>	64	116
<b>Did Rebound Occur (% yes)</b>	62	71
<b>Percentage of Wells With Rebound</b>	49	26

Notes: At least one year of monitoring after the end of ISCO injections was required to state that a project tested for rebound. An entry of no rebound testing indicates that such data was not available for review. Rebound was said to occur if one or more wells in the treatment zone showed rebound as defined by a 25% increase in total COC concentrations relative to baseline values. See Methods section for further details.



Table B-34: Summary of Project Costs

Parameter (units)	Minimum	Maximum	Median	Mean	<i>n</i>
<b>Total Project Cost (1000s U.S. \$)</b>	15	1,670	222	360	55
<b>Total Cost per Cubic Yard Treated (U.S. \$ / yd<sup>3</sup>)</b>	2	4,720	94	380	33

Notes: Total cost per cubic yard is defined as the total cost divided by the volume of the TTZ. Total costs include project management, reporting, O&M, and performance sampling, and do not include initial site assessment costs. See Section 3.3.6. for specific details on how costs were determined.

## B.2 Summary Statistics by Contaminant of Concern (COC)

This section presents summary data similar to that presented above on the subgroups of ISCO-DB1 divided by COC groups. A contaminant was only considered a COC if it was explicitly targeted by the ISCO remediation. For example, a site contaminated with TCE at 20,000 ug/L and 1,1,1-TCA at 100 ug/L would not be considered a chloroethane site unless the project documents specifically stated that ISCO targeted both compounds. COCs that are represented by only a few sites are omitted from this analysis, as are parameters on which there was relatively little data (e.g. groundwater chemistry data).

## B.2.1 General Information by COC Group

Table B-35: Site Type by COC Group

Site Type	Percent of Sites						
	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Federal</b>	32	33	36	8	16	7	10
<i>Air Force / ANG</i>	7	0	18	0	0	0	0
<i>Army</i>	1	0	0	0	0	0	0
<i>general DOD</i>	10	11	9	0	4	0	5
<i>DOE</i>	4	0	0	0	4	0	0
<i>miscellaneous</i>	1	6	0	0	0	0	0
<i>NASA</i>	3	6	0	3	0	7	0
<i>Navy</i>	7	11	9	5	8	0	5
<b>Manufacturing/ Industrial</b>	24	28	36	11	0	0	0
<b>Dry Cleaner</b>	30	0	0	0	4	0	0
<b>Service Station</b>	0	0	0	47	44	87	5
<b>Chemical Facility</b>	8	28	0	8	4	0	10
<b>Former MGP</b>	1	0	0	11	20	0	48
<b>Landfill / Lagoon / Waste Storage</b>	3	6	18	3	0	0	5
<b>Wood Treatment</b>	0	0	0	0	0	0	10
<b>Other</b>	5	11	27	16	12	7	19
<b><i>n</i></b>	<i>144</i>	<i>18</i>	<i>11</i>	<i>38</i>	<i>25</i>	<i>15</i>	<i>21</i>

Notes: Horizontal summation may yield greater than 100% because multiple contaminant groups were present at some sites. The category “general DOD” includes sites that were provided with the understanding that the site and its sector within the DOD complex would remain confidential and also project summaries that did not report the DOD sector in which the work was performed. “miscellaneous” is a federal facility that wanted its government sector to remain confidential.

Table B-36: DQC by COC Group

DQC	Number of Sites						
	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Class 1</b>	85	10	7	7	10	7	8
<b>Class 2</b>	78	6	2	2	9	6	11
<b>Class 3</b>	15	2	2	2	6	2	2
<b><i>mean</i></b>	<i>1.6</i>	<i>1.6</i>	<i>1.5</i>	<i>1.5</i>	<i>1.8</i>	<i>1.7</i>	<i>1.7</i>
<b><i>n</i></b>	<i>178</i>	<i>18</i>	<i>11</i>	<i>11</i>	<i>25</i>	<i>15</i>	<i>21</i>

Notes: Class 1 (most reliable) = project reports and journal articles, Class 2 = conference proceedings, online resources, Class 3 = vendor information

Table B-37: Presence of NAPL by COC Group

NAPL Indication	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Project Reports State that DNAPL is Present (%)</b>	51	53	67	11	18	0	42
<i>n</i>	111	15	9	18	11	8	12
<b>Project Reports State that LNAPL is Present (%)</b>	0	0	0	56	55	50	42
<i>n</i>	111	15	9	18	11	8	12
<b>Concentrations Reports above 1% of Solubility (%)</b>	49	23	50	na			
<i>n</i>	157	13	8				

Notes: na = not applicable. The three metrics are independent of each other. The third metric was only applied to chlorinated solvent sites.

Table B-38: Geology Group by COC Group

Geology Group	Percent of Sites						
	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Group A</b>	18	25	18	34	35	27	35
<b>Group B</b>	3	0	0	3	0	0	0
<b>Group C</b>	48	50	46	44	45	64	47
<b>Group D</b>	17	13	0	13	15	0	0
<b>Group E</b>	7	13	27	3	5	0	6
<b>Group F</b>	7	0	9	3	0	9	12
<i>n</i>	145	16	11	32	20	11	17

Notes: Horizontal summation may total more than 100% because multiple contaminant groups may have been present at a given site. Vertical summation may total more than 100% because of rounding of percentages.

Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )

Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )

Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)

Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

Table B-39: Goals of Remediation by COC Group

Goals of Remediation	Percent of Sites						
	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
Meet MCLs	28	17	50	48	67	75	36
Meet ACLs	28	17	10	19	13	8	0
Reduce Mass by a Given %	10	17	10	5	0	0	14
Reduce Mass and/or Time to Cleanup	34	58	50	33	20	17	36
Evaluate Effectiveness / Optimize	32	50	20	5	7	0	36
<i>n</i>	<i>110</i>	<i>12</i>	<i>10</i>	<i>21</i>	<i>15</i>	<i>12</i>	<i>14</i>

Notes: Horizontal summation may total more than 100% because multiple contaminant groups may have been present at a given site. Vertical summation may total more than 100% because some sites had more than one of the above goals.

### B.2.2 ISCO Design Parameters by COC Group

This section shows the various ISCO design parameters in ISCO-DB1 subdivided by COC group. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-40: Oxidant Used by COC Group

Oxidant Used	Percent of Sites						
	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
Permanganate	58	50	18	8	13	7	15
CHP	31	33	64	50	46	20	45
Persulfate	6	28	27	13	8	13	5
Ozone	8	6	9	21	25	53	40
Peroxone	1	6	0	3	4	13	5
Percarbonate	1	6	0	11	8	0	5
<i>n</i>	<i>154</i>	<i>18</i>	<i>11</i>	<i>38</i>	<i>24</i>	<i>15</i>	<i>20</i>

Notes: Horizontal may exceed 100% because multiple contaminant groups may have been present at a given site. Vertical summation may total more than 100% because of the six sites that used multiple oxidants.

Table B-41: TTZ by COC Group

TTZ	Percent of Sites						
	Chloroethenes	Chloroethanes	Chlorobenzenes	BTEX	TPH	MTBE	SVOCs
<b>Source</b>	55	53	20	54	47	42	44
<b>Source and Plume</b>	15	27	50	29	21	17	31
<b>Plume</b>	14	0	10	7	21	33	0
<b>Other (Pilot)</b>	16	20	20	11	11	8	25
<b><i>n</i></b>	<i>119</i>	<i>15</i>	<i>10</i>	<i>28</i>	<i>19</i>	<i>12</i>	<i>16</i>

Notes: Plume refers to aqueous phase concentrations of a COC higher than that COC's MCL. Source zone refers to areas with observed NAPL or aqueous phase concentrations greater than 1% of the solubility limit for that COC. Sites without NAPL or significant sorbed phase contamination were considered to have no saturated zone source (area and volume equal to 0).

Table B-42: Areal Extent of TTZ by COC Group

COC Group	Areal Extent (1000s sf)				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>Chloroethenes</b>	0.08	260	6	21	87
<b>Chloroethanes</b>	0.4	20	3.6	6	9
<b>Chlorobenzenes</b>	1.2	260	5.4	48	9
<b>BTEX</b>	0.4	32.6	9.6	11	19
<b>TPH</b>	0.6	48.6	19	18	11
<b>MTBE</b>	9.6	20	16	15	5
<b>SVOCs</b>	1	130	14	40	8

Table B-43: Volume of TTZ by COC Group

COC Group	Volume (1000s cf)				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>Chloroethenes</b>	0.2	9,100	130	469	78
<b>Chloroethanes</b>	15	540	126	184	6
<b>Chlorobenzenes</b>	20	9,100	72.3	1,280	9
<b>BTEX</b>	8	905	170	234	14
<b>TPH</b>	10	972	230	376	10
<b>MTBE</b>	190	905	240	385	5
<b>SVOCs</b>	8	9,100	216	1,270	10

Table B-44: Number of Pore Volumes of Oxidant Solution Delivered by COC Group

COC Group	Minimum	Maximum	Median	Mean	<i>n</i>
Chloroethenes	0.0040	56	0.10	1.4	58
Chloroethanes	0.0070	56	0.094	9.4	6
Chlorobenzenes	0.034	56	0.10	8.2	7
BTEX	0.086	0.32	0.18	0.19	4
TPH	0.017	0.65	0.18	0.31	5
MTBE	no data				
SVOCs	0.041	0.65	0.36	0.35	4

Table B-45: Number of Delivery Events by COC Group

COC Group	Minimum	Maximum	Median	Mean	<i>n</i>
Chloroethenes	1	9	2	2.3	110
Chloroethanes	1	5	1	1.7	16
Chlorobenzenes	1	10	2	3.4	9
BTEX	1	5	2	1.8	28
TPH	1	6	1	1.9	15
MTBE	1	3	1	1.4	10
SVOCs	1	6	1	2.0	14

Notes: Most MTBE sites were treated with ozone. While this oxidant is generally injected in a single delivery event, the duration of that delivery event ranges between months and years.

Table B-46: Use of Treatability Studies by COC Group - Full and Pilot Scale

	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
Percent Using Treatability Study	78	92	89	75	75	50	100
<i>n</i>	90	13	9	16	16	4	12

Notes: A lack of treatability testing was difficult to determine from project reports, and the field for these data were left blank if a treatability study was not mentioned unless it could be confirmed with project contacts that a treatability study was not performed.

Table B-47: Type of Treatability Study Performed - All Sites

Type of Study	Percent of Sites						
	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Demonstrate COC Degradation</b>	49	50	86	50	67	0	60
<b>Optimize Oxidant/Soil/Activator Ratios</b>	42	38	29	33	0	100	40
<b>Evaluate Secondary Groundwater Impacts</b>	10	0	14	0	33	0	10
<b>Evaluate Soils for Buffering or Activating Attributes</b>	7	0	0	0	0	0	10
<b>Measure NOD/SOD</b>	54	75	14	33	67	50	60
<b><i>n</i></b>	<i>59</i>	<i>8</i>	<i>7</i>	<i>6</i>	<i>3</i>	<i>2</i>	<i>10</i>

Notes: Vertical summation is greater than 100% because some treatability studies gathered multiple types of data from the above categories.

Table B-48: Use of Treatability Studies by COC Group - Full Scale Only

	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Percent Using Treatability Study</b>	67	80	83	70	56	33	100
<b><i>n</i></b>	<i>51</i>	<i>5</i>	<i>6</i>	<i>10</i>	<i>9</i>	<i>3</i>	<i>7</i>

Notes: A lack of treatability testing was difficult to determine from project reports, and the field for these data were left blank if a treatability study was not mentioned unless it could be confirmed with project contacts that a treatability study was not performed.

Table B-49: Use of Pilot Studies by COC Group - Full Scale Only

	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Percent Performing Pilot Study</b>	58	75	67	67	55	83	57
<b><i>n</i></b>	<i>60</i>	<i>8</i>	<i>6</i>	<i>12</i>	<i>11</i>	<i>6</i>	<i>7</i>

Notes: Only full scale applications are included in this analysis because pilot testing is only a relevant pre-design test relative to full scale applications.

Table B-50: Use of Coupling by COC Group – Full and Pilot Scale Only

	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Percent of Sites Using Coupling</b>	71	77	100	94	93	92	69
<b>Percent Coupled Before ISCO</b>	53	54	75	83	64	83	54
<b>Percent Coupled During ISCO</b>	19	8	13	33	21	33	31
<b>Percent Coupled After ISCO</b>	33	23	38	17	43	8	31
<i>n</i>	95	13	8	18	14	12	13



Table B-51: Coupling Techniques by COC Group

	Percent of Sites						
	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b><i>Technology Implemented Before ISCO</i></b>							
<b>Excavation</b>	41	33	75	71	54	64	56
<b>Air Sparging</b>	5	0	0	6	15	27	11
<b>SVE</b>	20	11	0	6	23	46	11
<b>Bioventing</b>	0	0	0	0	0	9	0
<b>P&amp;T</b>	27	56	25	18	0	9	22
<b>EFR</b>	3	0	0	0	0	0	0
<b>DPE</b>	2	0	0	0	0	0	0
<b>EISB</b>	5	11	0	0	0	0	11
<b><i>Technology Implemented Concurrently with ISCO</i></b>							
<b>Excavation</b>	6	0	0	0	0	0	0
<b>Air Sparging</b>	2	0	0	6	8	9	11
<b>SVE</b>	6	0	0	12	8	18	33
<b>P&amp;T</b>	11	11	13	12	8	9	22
<b>DPE</b>	3	0	0	0	0	0	0
<b>Surfactant/ Cosolvent</b>	5	0	0	0	0	0	0
<b>EISB</b>	0	0	0	12	0	9	0
<b><i>Technology Implemented After ISCO</i></b>							
<b>Excavation</b>	11	0	0	0	8	0	11
<b>P&amp;T</b>	9	11	13	12	15	0	22
<b>Air Sparging</b>	0	0	0	0	8	9	0
<b>Biosparging</b>	0	0	13	0	0	0	0
<b>SVE</b>	3	0	13	0	8	9	0
<b>DPE</b>	3	0	0	0	0	0	0
<b>EISB</b>	21	22	13	0	15	0	11
<b>MNA</b>	26	11	13	6	15	0	0
<b><i>n</i></b>	<b><i>66</i></b>	<b><i>9</i></b>	<b><i>8</i></b>	<b><i>17</i></b>	<b><i>13</i></b>	<b><i>11</i></b>	<b><i>9</i></b>

Notes: MNA was only entered as a coupling technique when project reports specifically called out that it was to be used after ISCO. Due to this fact, it is likely that the use of MNA following ISCO is underestimated.

### B.2.3 ISCO Results by COC Group

This section shows results achieved by ISCO treatment projects in ISCO-DB1 subdivided by COC group. The definition of each of these metrics is as described in Section 3.3.3 of the body of the text. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-52: Percentage of Sites Attaining Closure by COC Group – Full Scale Only

	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Percent Attaining Closure</b>	20	17	0	43	38	63	22
<i>mean DQC</i>	1.4	1.6	1.2	2.0	1.4	1.5	1.5
<i>n</i>	50	6	5	7	8	8	9

Notes: Site closure is defined as the completion of active remediation and monitoring, and includes the attainment of MCLs, ACLs, or other standards, and may include requirements of institutional and engineering controls. This metric was only applied to full scale sites because pilot tests are generally not expected to lead to site closure.

Table B-53: Percentage of Sites Meeting Goals by COC Group

	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Percent Meeting MCLs</b>	13	0	0	0	43	60	0
<i>mean DQC</i>	1.3	1.0	1.3	1.3	1.4	1.2	1.0
<i>n</i>	24	1	3	3	7	5	2
<b>Percent Meeting ACLs</b>	39	0	no data	33	0	no data	no data
<i>mean DQC</i>	1.3	1.0		2.0	1.0		
<i>n</i>	23	1		3	2		
<b>Percent Reduced Mass by a Given %</b>	50	100	0	0	no data	no data	100
<i>mean DQC</i>	1.2	1.0	1.0	1.0			1.0
<i>n</i>	10	2	1	1			1
<b>Percent Reduced Mass and/or Time to Cleanup</b>	74	67	75	100	100	100	80
<i>mean DQC</i>	1.4	1.2	1.0	2.0	2.3	2.0	1.6
<i>n</i>	31	6	4	6	3	2	5
<b>Percent Evaluated Effectiveness / Optimized</b>	94	100	100	100	100	no data	100
<i>mean DQC</i>	1.4	1.2	2.5	3.0	1.0		1.5
<i>n</i>	31	6	2	1	1		4

Notes: The above table includes all five types of remediation goals included in ISCO-DB1, ranging from attaining MCLs (most stringent) to evaluating ISCO at the field-scale (least stringent). The percentages refer the frequency with which projects attempted and met these particular goals.

Table B-54: Percentage of Sites Attaining MCLs by COC Group

	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Percent Attaining MCLs</b>	3	0	0	0	25	60	0
<i>mean DQC</i>	1.4	1.6	1.4	2.1	1.6	1.2	1.4
<i>n</i>	105	14	7	12	12	5	8

Notes: This table includes all sites in each COC group irrespective of their goals. The values are lower than the previous table, which included only sites that intended to reach MCLs.

Table B-55: Percent Reduction in Maximum Groundwater VOC Concentrations by COC Group

COC Group	Percentage Reduction				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>Chloroethenes</b>	-146	99.7	54	47	56
<b>Chloroethanes</b>	-146	99.7	54	47	6
<b>Chlorobenzenes</b>	-15	97	24	38	7
<b>BTEX</b>	49	99.99	94	84	7
<b>TPH</b>	99	99.99	99.9	99.9	2
<b>MTBE</b>	83	99.99	99	96	4
<b>SVOCs</b>	21	99	60	60	2

Notes: The mean DQCs are 1.2, 1.3, 1.3, 2.3, 1.5, 1.0, and 2.0, respectively. Note that the results shown in this table are technically for co-contaminants for TPH or SVOC sites because the primary contaminants in these groups are not VOCs

Table B-56: Percentage of Sites with Rebound by COC Group

	Chloro-ethenes	Chloro-ethanes	Chloro-benzenes	BTEX	TPH	MTBE	SVOCs
<b>Percent of Sites with Rebound</b>	72	67	100	38	43	29	25
<b><i>n</i></b>	54	9	2	8	7	7	4
<b>For Rebound Sites, Percentage of MWs w/ Rebound</b>	50	25	55	29	25	29	50
<b><i>n</i></b>	22	1	2	2	1	2	1

Notes: The second metric is applied only to sites that experienced rebound. It is calculated as the mean value of the percentage of well locations that experienced rebound each of the sites where rebound occurred. Using BTEX as an example, among the sites reviewed, 38% experienced rebound at one or more locations in the treatment zone after ISCO. When rebound did occur, it occurred at 29% of well locations on average.

Table B-57: Total Project Cost by COC Group

COC Group	Total Project Cost (1000s U.S. \$)				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>Chloroethenes</b>	28.4	1,670	270	430	40
<b>Chloroethanes</b>	15	360	170	160	8
<b>Chlorobenzenes</b>	1,670	1,670	1,670	1,670	1
<b>BTEX</b>	15	360	170	160	8
<b>TPH</b>	15	263	200	170	4
<b>MTBE</b>	15	263	200	170	4
<b>SVOCs</b>	151	1,670	220	520	5

Table B-58: Unit Cost by COC Group

COC Group	Total Unit Cost (U.S. \$ / cubic yard treated)				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>Chloroethenes</b>	2	4,720	120	430	28
<b>Chloroethanes</b>	36	190	110	110	2
<b>Chlorobenzenes</b>	5	5	5	5	1
<b>BTEX</b>	28	90	36	50	3
<b>TPH</b>	36	510	271	270	2
<b>MTBE</b>	no data				
<b>SVOCs</b>	5	510	30	140	4

Notes: Total unit cost is defined as the total cost divided by the volume of the TTZ.

### B.3 Summary Statistics by Oxidant Type

This section presents summary statistics on the case studies subdivided by the oxidant used. As with the previous subsections, this list of tables includes all DQC groups and both full and pilot scale applications except when otherwise noted. This section follows a similar format to the previous subsections, covering general information, COC and geological information, ISCO design data, and results in that order. The formula  $MnO_4$  refers to both potassium and sodium permanganate,  $S_2O_8$  refers to sodium persulfate, and peroxone is ozone catalyzed with hydrogen peroxide. These abbreviations are used in some tables for the sake of keeping the labels compact.

### B.3.1 General Information by Oxidant Type

This section shows results of the general information and site conditions in ISCO-DB1 subdivided by the oxidant used in remediation. Unless otherwise noted, all scales of implementation are included.

Table B-59: Site Type by Oxidant

Site Type	Percent of Sites					
	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Federal</b>	27	32	8	18	0	14
<i>Air Force / ANG</i>	10	3	4	0	0	0
<i>Army</i>	1	0	0	0	0	0
<i>general DOD</i>	5	13	4	9	0	14
<i>DOE</i>	6	3	0	0	0	0
<i>miscellaneous</i>	1	0	0	0	0	0
<i>NASA</i>	2	1	0	0	0	0
<i>Navy</i>	1	12	0	9	0	0
<b>Manufacturing/ Industrial</b>	28	20	4	46	0	14
<b>Dry Cleaner</b>	31	16	19	0	0	0
<b>Service Station</b>	1	11	35	9	60	29
<b>Chemical Facility</b>	5	3	0	9	20	29
<b>Former MGP</b>	0	9	12	0	0	0
<b>Landfill / Waste Storage</b>	2	0	8	0	0	0
<b>Wood Treatment</b>	1	0	8	0	20	0
<b>Other</b>	7	11	15	18	0	14
<b><i>n</i></b>	83	76	26	11	5	7

Notes: Horizontal summation may yield greater than 100% because multiple contaminant groups were present at some sites. The category “general DOD” includes sites that were provided with the understanding that the site and its sector within the DOD complex would remain confidential and also project summaries that did not report the DOD sector in which the work was performed. “miscellaneous” is a federal facility that wanted its government sector to remain confidential.

Table B-60: DQC by Oxidant

DQC	DQC (# of sites)					
	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Class 1</b>	47	31	11	6	3	1
<b>Class 2</b>	42	28	15	3	2	1
<b>Class 3</b>	4	20	1	3	0	5
<i>mean</i>	<i>1.5</i>	<i>1.9</i>	<i>1.6</i>	<i>1.8</i>	<i>1.4</i>	<i>2.6</i>
<i>n</i>	<i>93</i>	<i>79</i>	<i>27</i>	<i>12</i>	<i>5</i>	<i>7</i>

Notes: Class 1 (most reliable) = project reports and journal articles, Class 2 = conference proceedings, online resources, Class 3 = vendor information

Table B-61: Presence of NAPL by Oxidant - Full and Pilot Scale Applications

	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Percent of Project Reports Stating that DNAPL Was Present</b>	48	49	22	50	0	33
<i>n</i>	<i>63</i>	<i>47</i>	<i>18</i>	<i>8</i>	<i>4</i>	<i>3</i>
<b>Percent of Project Reports Stating that LNAPL Was Present</b>	2	15	28	0	25	67
<i>n</i>	<i>63</i>	<i>47</i>	<i>18</i>	<i>8</i>	<i>4</i>	<i>3</i>
<b>Percent of Projects Reporting Concentrations above 1% Solubility</b>	67	70	42	85	0	100
<i>n</i>	<i>67</i>	<i>44</i>	<i>12</i>	<i>7</i>	<i>3</i>	<i>1</i>

Notes: The first two metrics are based on statements made in project documents reviewed. The third metric is independent of the others, and is applied only to chlorinated solvent sites.

Table B-62: COC Groups Present by Oxidant

COC Group	Percent of Sites					
	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Chloroethenes</b>	95	61	44	50	25	29
<b>Chloroethanes</b>	7	7	0	25	25	14
<b>Chlorobenzenes</b>	2	7	4	25	0	0
<b>BTEX</b>	1	26	30	25	25	57
<b>TPH</b>	2	15	22	8	25	29
<b>MTBE</b>	0	4	30	8	50	0
<b>SVOCs</b>	2	11	26	0	25	14
<b><i>n</i></b>	<i>87</i>	<i>72</i>	<i>27</i>	<i>12</i>	<i>4</i>	<i>7</i>

Notes: Vertical summation may exceed 100% because multiple contaminants were present at some sites.

Table B-63: Geology Group by Oxidant

Geology Group	Percent of Sites					
	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Group A</b>	15	25	21	10	60	29
<b>Group B</b>	4	0	0	10	0	14
<b>Group C</b>	40	51	67	60	40	43
<b>Group D</b>	23	13	4	0	0	0
<b>Group E</b>	11	6	0	10	0	14
<b>Group F</b>	8	6	8	10	0	0
<b><i>n</i></b>	<i>86</i>	<i>69</i>	<i>24</i>	<i>10</i>	<i>5</i>	<i>7</i>

Table B-64: Goals of Remediation by Oxidant

Goals of Remediation	Percent of Sites					
	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Meet MCLs</b>	32	30	71	33	50	20
<b>Meet ACLs</b>	26	37	5	0	25	20
<b>Reduce Mass by X%</b>	7	13	0	11	25	0
<b>Reduce Mass and/or Time to Cleanup</b>	37	22	10	56	25	60
<b>Evaluate Effectiveness / Optimize</b>	31	20	24	56	25	20
<b><i>n</i></b>	<i>62</i>	<i>46</i>	<i>21</i>	<i>9</i>	<i>4</i>	<i>5</i>



### B.3.2 ISCO Design by Oxidant

This section shows results of ISCO design parameters in ISCO-DB1 subdivided by the oxidant used in remediation. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-65: Delivery Method by Oxidant

Delivery Method	Percent of Sites					
	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
Well Injection	37	58	0	50	0	0
Direct Push	28	25	0	10	0	100
Sparge Points	0	0	96	0	100	0
Infiltration	19	4	0	10	0	0
Injectors	0	23	0	0	0	0
Recirculation	13	0	0	30	0	0
Fracturing	9	4	0	0	0	0
Mixing	4	0	0	0	0	0
Horizontal Well Injection	0	0	9	0	0	0
<i>n</i>	78	57	22	10	5	4

Notes: Vertical summation may exceed 100% because multiple delivery techniques were used at some sites.

Table B-66: TTZ by Oxidant

TTZ	Percent of Sites					
	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
Source	61	55	40	18	0	50
Source and Plume	12	23	20	46	25	17
Plume	10	13	35	9	50	0
Other	17	9	5	27	25	33
<i>n</i>	69	56	20	11	4	6

Table B-67: Areal Extent of TTZ by Oxidant

Oxidant	Areal Extent (1000s sf)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	0.08	220	6.4	19	43
CHP	0.18	260	9.3	22	50
Ozone	2.1	43	13	15	8
Persulfate	0.6	5.4	2.7	3	6
Peroxone	6	19	13	13	3
Percarbonate	0.4	2.5	1.2	1	6

Table B-68: Volume of TTZ by Oxidant

Oxidant	Volume (1000s cf)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	0.2	3,600	110	290	40
CHP	0.71	9,100	130	530	45
Ozone	38	1,000	320	440	10
Persulfate	15	54	19	26	6
Peroxone	190	270	260	240	3
Percarbonate	10	23	17	17	2

Table B-69: Injected Oxidant Concentration by Oxidant

Oxidant	Concentration (g/L)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	0.21	1,340	24	71	59
CHP	10	600	190	300	37
Ozone	no data				
Persulfate	40	270	160	150	8
Peroxone	no data				
Percarbonate	80	80	80	80	1

Notes: Oxidant concentration in this table is the concentration of the oxidant solution as it was injected into the subsurface, and does not account for dilution with activators or injected water conducted in situ. Concentrations of ozone and peroxone could not be calculated because of a lack of data. The maximum concentration of permanganate is that which was injected as a slurry during fracturing.

Table B-70: Oxidant Concentration after Mixing with Activator by Oxidant

Oxidant	Concentration (g/L)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	0.21	993	23	69	40
CHP	10	395	91	136	23
Ozone	no data				
Persulfate	45	135	100	99	5
Peroxone	no data				
Percarbonate	no data				

Notes: This table adjusts the oxidant concentration to account for the injected activator and/or water, assuming complete in situ mixing of the oxidant and other injected fluids.

Table B-71: Design Radius of Influence by Oxidant

Oxidant	Radius of Influence (ft)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	2	50	14	19	29
CHP	3	55	15	16	30
Ozone	15	50	25	28	5
Persulfate	10	15	13	13	6
Peroxone	10	25	21	19	4
Percarbonate	4	6	6	5	6

Notes: The data on which this table is based were entered based upon statements in the project documents about the planned ROI or measured from to-scale plans showing the injection grid. When measuring from plans, it was assumed that the system was designed to distribute oxidant radially from the injection points and provide complete coverage of the TTZ unless otherwise stated.

Table B-72: Observed Radius of Influence by Oxidant

Oxidant	Radius of Influence (ft)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	5	50	25	26	11
CHP	8	25	15	16	6
Ozone	35	40	38	38	2
Persulfate	12	23	20	18	3
Peroxone	22	40	31	31	2
Percarbonate	4	4	4	4	1

Notes: The data on which this table is based are from statements in project reports regarding oxidant distribution observed during field-scale application. When a range of observed influences was given, the observed radius was assumed to be the mean of those two numbers unless the project documents stated otherwise. The permanganate applications include fracturing delivery methods.

Table B-73: Oxidant Loading Rate by Oxidant

Oxidant	Oxidant Loading Rate (g oxidant / kg media)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	0.021	60	0.4	6.4	36
CHP	0.052	24	1.2	3.1	19
Ozone	0.0040	1.9	0.1	0.5	4
Persulfate	0.3	34	5.1	8.7	6
Peroxone	0.011	0.011	0.011	0.011	1
Percarbonate	8.8	8.8	8.8	8.8	1

Table B-74: Number of Pore Volumes Delivered by Oxidant

Oxidant	Number of Pore Volumes (-)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	0.004	56	0.155	2.3	32
CHP	0.0055	0.66	0.073	0.1	26
Ozone	no data				
Persulfate	0.007	1.7	0.57	0.7	6
Peroxone	no data				
Percarbonate	0.65	0.65	0.65	0.7	1

Notes: The 56 pore volume application was a fractured rock site at which permanganate was delivered via an infiltration gallery.

Table B-75: Number of Delivery Events by Oxidant

Oxidant	Number of Delivery Events				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	1	10	2	2.3	65
CHP	1	6	2	2.5	57
Ozone	1	1	1	1.0	15
Persulfate	1	2	1	1.4	10
Peroxone	1	1	1	1.0	5
Percarbonate	1	2	2	1.8	6

Notes: Ozone and peroxone are delivered in a single event over a long duration of time as shown in the following table.

Table B-76: Duration of Delivery Events by Oxidant

Oxidant	Duration of Delivery Events (days)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	1	135	4	13	45
CHP	1	245	6	18	42
Ozone	10	820	210	333	15
Persulfate	2	20	4	7	7
Peroxone	210	365	288	288	3
Percarbonate	4	4	4	4	1

Table B-77: Use of Treatability Studies by Oxidant – Full and Pilot Scale Applications

	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
Percent Using Treatability Study	78	78	43	100	33	100
<i>n</i>	50	45	7	8	3	2

Notes: A lack of treatability testing was difficult to determine from project reports, and the field for these data were left blank if a treatability study was not mentioned unless it could be confirmed with project contacts that a treatability study was not performed.

Table B-78: Use of Treatability Studies by Oxidant - Full Scale Applications Only

	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
Percent Using Treatability Study	68	68	43	100	0	no data
<i>n</i>	31	28	7	4	2	

Notes: A lack of treatability testing was difficult to determine from project reports, and the field for these data were left blank if a treatability study was not mentioned unless it could be confirmed with project contacts that a treatability study was not performed.

Table B-79: Use of Pilot Studies by Oxidant - Full Scale Applications Only

	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
Percent Performing Pilot Study	65	53	50	100	50	0
<i>n</i>	37	32	8	4	2	1

Notes: Only full scale applications are included in this analysis because pilot testing is only a relevant pre-design test relative to full scale applications.

Table B-80: Use of Coupling by Oxidant

	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Percent of Sites Using Coupling</b>	68	88	84	67	100	50
<b>Percent Coupling Before ISCO</b>	56	63	63	67	100	0
<b>Percent Coupling During ISCO</b>	19	20	42	11	0	50
<b>Percent Coupling After ISCO</b>	30	50	11	0	0	0.0
<b><i>n</i></b>	<i>57</i>	<i>40</i>	<i>19</i>	<i>9</i>	<i>4</i>	<i>2</i>

Table B-81: Coupling Techniques by Oxidant

Coupling Technique	Use of Coupling (Percent of Sites)					
	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b><i>Technology Implemented Before ISCO</i></b>						
<b>Excavation</b>	44	49	63	67	50	0
<b>Air Sparging</b>	3	0	31	17	25	0
<b>SVE</b>	21	14	25	0	50	0
<b>Bioventing</b>	0	0	6	0	0	0
<b>P&amp;T</b>	31	17	19	33	0	0
<b>EFR</b>	0	6	0	0	0	0
<b>DPE</b>	3	0	0	0	0	0
<b>EISB</b>	5	0	0	0	25	0
<b><i>Technology Implemented Concurrently with ISCO</i></b>						
<b>Excavation</b>	8	3	0	0	0	0
<b>Air Sparging</b>	0	0	19	0	0	0
<b>SVE</b>	0	6	44	0	0	0
<b>P&amp;T</b>	18	6	6	17	0	0
<b>DPE</b>	3	3	0	0	0	0
<b>Surfactant/Cosolvent</b>	3	6	0	0	0	0
<b>EISB</b>	0	3	0	0	0	100
<b><i>Technology Implemented After ISCO</i></b>						
<b>Excavation</b>	10	9	6	0	0	0
<b>P&amp;T</b>	15	6	0	0	0	0
<b>Air Sparging</b>	0	0	6	0	0	0
<b>Biosparging</b>	0	3	0	0	0	0
<b>SVE</b>	3	6	6	0	0	0
<b>DPE</b>	3	3	0	0	0	0
<b>EISB</b>	13	34	0	0	0	0
<b>MNA</b>	26	26	0	0	0	0
<b><i>n</i></b>	<b><i>39</i></b>	<b><i>35</i></b>	<b><i>16</i></b>	<b><i>6</i></b>	<b><i>4</i></b>	<b><i>1</i></b>

Notes: MNA was only entered as a coupling technique when project reports specifically called out that it was to be used after ISCO. Due to this fact, it is likely that the use of MNA following ISCO is underestimated. Persulfate, peroxone, and percarbonate are the more recently developed of the oxidants. Because post-ISCO coupling technologies are often implemented years after ISCO, it is likely coupling had not yet occurred at these sites as opposed to these oxidants inherently not using post-ISCO couples.

### B.3.3 ISCO Results by Oxidant

This section shows the results achieved by ISCO subdivided by the oxidant used in remediation. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-82: Percentage of Sites Attaining Closure by Oxidant – Full Scale Only

	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Percent Attaining Closure</b>	16	27	50	0	50	no data
<i>mean DQC</i>	<i>1.4</i>	<i>1.5</i>	<i>1.6</i>	<i>1.3</i>	<i>1.3</i>	
<i>n</i>	<i>32</i>	<i>22</i>	<i>12</i>	<i>4</i>	<i>2</i>	

Notes: Site closure is defined as the completion of active remediation and monitoring, and includes the attainment of MCLs, risk-based standards, and may include requirements of institutional and engineering controls. This metric was only applied to full scale sites because pilot tests are generally not expected to lead to site closure.

Table B-83: Percentage of Sites Meeting Goals by Oxidant

	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Percent Meeting MCLs</b>	0	10	50	0	100	0
<i>mean DQC</i>	<i>1.1</i>	<i>1.5</i>	<i>1.3</i>	<i>1.0</i>	<i>1.0</i>	<i>1.0</i>
<i>n</i>	<i>15</i>	<i>10</i>	<i>8</i>	<i>3</i>	<i>1</i>	<i>1</i>
<b>Percent Meeting ACLs</b>	39	39	0	no data	no data	100
<i>mean DQC</i>	<i>1.5</i>	<i>1.2</i>	<i>1.0</i>			3.0
<i>n</i>	<i>13</i>	<i>13</i>	<i>1</i>			<i>1</i>
<b>Percent Reduced Mass by a Given %</b>	33	40	no data	100	100	no data
<i>mean DQC</i>	<i>1.3</i>	<i>1.2</i>		1.0	1.0	
<i>n</i>	<i>3</i>	<i>5</i>		<i>1</i>	<i>1</i>	
<b>Percent Reduced Mass and/or Time to Cleanup</b>	76	88	100	80	100	100
<i>mean DQC</i>	<i>1.3</i>	<i>1.6</i>	<i>2.0</i>	<i>1.2</i>	<i>1.0</i>	<i>3.0</i>
<i>n</i>	<i>21</i>	<i>8</i>	<i>1</i>	<i>5</i>	<i>1</i>	<i>2</i>
<b>Percent Evaluated Effectiveness / Optimized</b>	94	88	100	100	100	100
<i>mean DQC</i>	<i>1.5</i>	<i>1.5</i>	<i>2.0</i>	<i>1.4</i>	<i>1.0</i>	<i>1.0</i>
<i>n</i>	<i>18</i>	<i>8</i>	<i>3</i>	<i>5</i>	<i>1</i>	<i>1</i>

Notes: The above table includes all five types of remediation goals included in ISCO-DBI, ranging from attaining MCLs (most stringent) to evaluating ISCO at the field-scale (least stringent). The percentages are the percent of sites that attempted and met each particular goal.



Table B-84: Percentage of Sites Attaining MCLs by Oxidant

	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Percent Attaining MCLs</b>	0	2	31	0	50	0
<i>mean DQC</i>	1.4	1.5	1.5	1.3	1.0	2.6
<i>n</i>	55	45	13	8	2	5

Notes: This table includes all sites in each COC group irrespective of their goals. The percentage values are lower than the previous table, which included only sites that intended to reach MCLs.

Table B-85: Percent Reduction in Maximum Groundwater VOC Concentrations by Oxidant

COC Group	Percentage Reduction				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>Permanganate</b>	-27	99.7	51	51	27
<b>CHP</b>	-146	99	56	49	26
<b>Ozone</b>	54	99.99	96	82	5
<b>Persulfate</b>	-6.1	80	24	38	5
<b>Peroxone</b>	no data				
<b>Percarbonate</b>	49	70	60	60	2

Notes: The mean DQCs are 1.1, 1.4, 1.2, 1.0, and 3.0, respectively. This table includes all COCs as well as sites with and without DNAPL and LNAPL.

Table B-86: Percentage of Sites with Rebound by Oxidant

	MnO <sub>4</sub>	CHP	Ozone	S <sub>2</sub> O <sub>8</sub>	Peroxone	Percarbonate
<b>Percent of Sites with Rebound</b>	78	57	27	50	0	no data
<i>n</i>	32	21	11	2	1	
<b>For Rebound Sites, Percentage of MWs w/ Rebound</b>	48	53	28	no data	na	no data
<i>n</i>	11	10	3			

Notes: na = not applicable. MWs = monitoring wells. The second metric is applied only to sites that experienced rebound. It is calculated as the mean value of the percentage of well locations that experienced rebound each of the sites where rebound occurred. Using MnO<sub>4</sub> as an example, among the sites reviewed, 78% experienced rebound at one or more locations in the treatment zone after ISCO. When rebound did occur, it occurred at 48% of well locations on average.

Table B-87: Total Project Cost by Oxidant

Oxidant	Total Project Cost (1000s U.S. \$)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	32	1,410	240	350	25
CHP	28.4	1,670	270	420	14
Ozone	35	1,240	160	280	10
Persulfate	15	15	15	15	1
Peroxone	185	357.5	270	270	3
Percarbonate	no data				

Table B-88: Unit Costs by Oxidant

Oxidant	Unit Total Project Cost (U.S. \$ / cubic yard treated)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Permanganate	2	4,720	130	250	17
CHP	5	1,080	130	210	10
Ozone	25	60	44	44	2
Persulfate	no data				
Peroxone	28	40	32	32	2
Percarbonate	no data				

#### B.4 Summary Statistics by Geologic Media

This section presents summary statistics based on the six Geology Groups into which the sites were placed. The classification system used to group the sites based on geologic media is repeated below and described thoroughly in Section 3.3.1 above, and these groups are mutually exclusive.

- Group A - Permeable ( $K > 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )
- Group B - Impermeable ( $K < 10^{-5}$  cm/s) and homogeneous ( $K_{\max}/K_{\min} < 1000$ )
- Group C - Permeable ( $K > 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )
- Group D - Impermeable ( $K < 10^{-5}$  cm/s) and heterogeneous ( $K_{\max}/K_{\min} > 1000$ )
- Group E - Consolidated material with low matrix porosity (generally igneous and metamorphic rocks)
- Group F - Consolidated material with high matrix porosity (generally sedimentary rocks)

### B.4.1 General Information by Geology Group

This section shows results of the general information and site conditions in ISCO-DB1 subdivided by the Geology Group. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-89: Site Type by Geology Group

Site Type	Percent of Sites						
	Group A	Group B	Group C	Group D	Group E	Group F	Group BEF
<b>Federal</b>	18	0	28	28	20	29	21
<i>Air Force / ANG</i>	3	0	8	4	0	7	3
<i>Army</i>	0	0	0	0	0	0	0
<i>general DOD</i>	0	0	8	16	13	7	9
<i>DOE</i>	0	0	4	8	0	7	3
<i>miscellaneous</i>	0	0	1	0	0	0	0
<i>NASA</i>	0	0	3	0	0	0	0
<i>Navy</i>	15	0	3	0	7	7	6
<b>Manufacturing/ Industrial</b>	8	25	20	36	47	29	36
<b>Dry Cleaner</b>	18	25	28	16	0	29	15
<b>Service Station</b>	18	0	10	8	0	7	3
<b>Chemical Facility</b>	5	25	4	4	13	0	9
<b>Former MGP</b>	3	0	6	0	7	0	3
<b>Landfill / Waste Storage</b>	5	25	0	0	7	0	6
<b>Wood Treatment</b>	5	0	2	0	0	0	0
<b>Other</b>	26	25	1	8	13	7	12
<b><i>n</i></b>	<b>39</b>	<b>4</b>	<b>96</b>	<b>25</b>	<b>15</b>	<b>14</b>	<b>33</b>

Notes: The category “general DOD” includes sites that were provided with the understanding that the site and its sector within the DOD complex would remain confidential and also project summaries that did not report the DOD sector in which the work was performed. “miscellaneous” is a federal facility that wanted its government sector to remain confidential.

Table B-90: Data Quality Classification Values by Geology Group

DQC	DQC (# of sites)						
	Group A	Group B	Group C	Group D	Group E	Group F	Group BEF
<b>Class 1</b>	18	2	53	12	4	7	13
<b>Class 2</b>	18	1	37	14	9	7	17
<b>Class 3</b>	8	2	10	5	2	0	4
<i>mean</i>	<i>1.8</i>	<i>2.0</i>	<i>1.6</i>	<i>1.8</i>	<i>1.9</i>	<i>1.5</i>	<i>1.7</i>
<i>n</i>	<i>44</i>	<i>5</i>	<i>100</i>	<i>31</i>	<i>15</i>	<i>14</i>	<i>34</i>

Notes: Class 1 (most reliable) = project reports and journal articles, Class 2 = conference proceedings, online resources, Class 3 = vendor information

Table B-91: COCs Present by Geology Group

COCs Present	Percent of Sites						
	Group A	Group B	Group C	Group D	Group E	Group F	Group BEF
<b>Chloroethenes</b>	61	100	71	86	71	83	83
<b>Chloroethanes</b>	9	0	8	7	14	0	7
<b>Chlorobenzenes</b>	5	0	5	0	21	8	13
<b>BTEX</b>	26	20	14	14	7	8	10
<b>TPH</b>	16	0	9	10	7	0	3
<b>MTBE</b>	7	0	7	0	0	8	3
<b>SVOCs</b>	14	0	8	0	7	17	10
<i>n</i>	<i>43</i>	<i>5</i>	<i>97</i>	<i>29</i>	<i>14</i>	<i>12</i>	<i>30</i>

Notes: The sum of the percent values in each column may be greater than 100% because some sites had multiple COCs present.

Table B-92: Presence of NAPL by Geology Group - Full and Pilot Scale Applications

	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Percent of Project Reports Stated that DNAPL Was Present</b>	44	50	46	29	89	40	62
<i>n</i>	32	2	72	17	9	10	21
<b>Percent of Project Reports Stated that LNAPL Was Present</b>	22	0	8	6	0	10	5
<i>n</i>	32	2	72	17	9	10	21
<b>Percent of Project Documents Reporting Concentrations above 1% Solubility</b>	72	50	65	63	88	77	79
<i>n</i>	22	2	63	16	8	9	19

Notes: The last of the three metrics was only applied to chlorinated solvent sites.

Table B-93: Goals of Remediation by Geology Group

<b>Goal of Remediation</b>	<b>Percent of Sites</b>						
	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Meet MCLs</b>	43	0	35	31	27	38	29
<b>Meet ACLs</b>	27	50	22	56	9	0	10
<b>Reduce Mass by X%</b>	3	0	12	6	18	0	10
<b>Reduce Mass and/or Time to Cleanup</b>	20	50	37	13	46	38	43
<b>Evaluate Effectiveness / Optimize</b>	20	0	31	13	46	38	38
<i>n</i>	30	2	78	16	11	8	21

Notes: The sum of the percent values in each column may be greater than 100 because some sites had multiple goals for their remediation.

#### B.4.2 ISCO Design by Geology Group

This section shows a summary of ISCO design parameters subdivided by the Geology Group. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-94: Oxidant Selected by Geology Group

Oxidant	Percent of Sites						
	Group A	Group B	Group C	Group D	Group E	Group F	Group BEF
Permanganate	33	60	38	68	60	50	50
CHP	41	0	40	32	33	29	29
Persulfate	5	20	6	0	7	7	7
Ozone	12	0	17	3	0	14	14
Peroxone	7	0	2	0	0	0	0
Percarbonate	5	20	3	0	7	0	0
<i>n</i>	42	5	98	31	15	14	14

Table B-95: Delivery Method by Geology Group

Delivery Method	Percent of Sites						
	Group A	Group B	Group C	Group D	Group E	Group F	Group BEF
Well Injection	47	0	33	37	69	30	44
Direct Push	24	100	24	37	8	10	22
Sparge Points	21	0	16	5	0	10	4
Infiltration	3	0	9	5	15	40	22
Injectors	5	0	9	5	8	10	7
Recirculation	5	0	9	0	15	10	11
Fracturing	0	25	9	5	8	0	7
Mixing	0	0	0	16	0	0	0
Horizontal Well Injection	0	0	1	0	0	0	0
<i>n</i>	38	4	80	19	13	10	44

Notes: The sum of percentages in columns may total greater than 100% because multiple delivery techniques were used at some sites.

Table B-96: TTZ by Geology Group

TTZ	Percent of Sites						
	Group A	Group B	Group C	Group D	Group E	Group F	Group BEF
Source	48	75	53	65	64	33	56
Source and Plume	30	0	19	10	14	33	19
Plume	9	0	16	15	7	11	7
Other (Pilot)	12	25	12	10	14	22	19
<i>n</i>	33	4	81	20	14	9	27

Table B-97: Areal Extent of TTZ by Geology Group

Geology Group	Areal Extent (1000s sf)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Group A	0.18	110	9.0	14	25
Group B	2.5	10	3.5	5	3
Group C	0.20	260	7.0	20	64
Group D	0.23	120	8.2	20	17
Group E	1.2	49	5.4	14	5
Group F	0.08	130	37.0	51	4
Group BEF	0.08	130	7.7	24	12

Table B-98: Volume of TTZ by Geology Group

Geology Group	Volume (1000s cf)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Group A	0.71	1,700	130	250	25
Group B	1.7	160	81	81	2
Group C	1.2	2,200	120	260	58
Group D	1.2	3,600	150	440	15
Group E	54	970	72	390	5
Group F	0.2	9,100	2,500	3,500	4
Group BEF	0.2	9,100	160	1480	11

Table B-99: Use of Treatability Studies by Geology Group - Full and Pilot Scale Applications

	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Percent Using Treatability Study</b>	55	100	83	80	80	60	75
<b><i>n</i></b>	20	1	64	15	10	5	16

Notes: A lack of treatability testing was difficult to determine from project reports, and the field for these data were left blank if a treatability study was not mentioned unless it could be confirmed with project contacts that a treatability study was not performed.

Table B-100: Use of Treatability Studies by Geology Group - Full Scale Applications Only

	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Percent Using Treatability Study</b>	25	100	75	70	100	33	75
<b><i>n</i></b>	12	1	40	10	4	3	8

Notes: A lack of treatability testing was difficult to determine from project reports, and the field for these data were left blank if a treatability study was not mentioned unless it could be confirmed with project contacts that a treatability study was not performed.

Table B-101: Use of Pilot Studies by Geology Group - Full Scale Applications Only

	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Percent Performing Pilot Study</b>	29	100	59	85	100	33	78
<b><i>n</i></b>	17	1	44	13	5	3	9

Notes: Only full scale applications are included in this analysis because pilot testing is only a relevant pre-design test relative to full scale applications.



Table B-102: Use of Coupling by Geology Group

	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Percent of Sites Using Coupling</b>	77	no data	77	57	100	89	94
<b>Percent Coupling Before ISCO</b>	57		55	57	86	78	81
<b>Percent Coupling During ISCO</b>	23		24	14	29	11	19
<b>Percent Coupling After ISCO</b>	30		38	14	43	11	25
<b><i>n</i></b>	<i>30</i>		<i>66</i>	<i>14</i>	<i>7</i>	<i>9</i>	<i>16</i>

Table B-103: Coupling Techniques by Geology Group

Coupling Technique	Percent of Sites						
	Group A	Group B	Group C	Group D	Group E	Group F	Group BEF
<b><i>Technology Implemented Before ISCO</i></b>							
<b>Excavation</b>	48	no data	38	78	71	75	73
<b>Air Sparging</b>	4		10	0	0	0	0
<b>SVE</b>	17		26	11	0	0	0
<b>Bioventing</b>	0		2	0	0	0	0
<b>P&amp;T</b>	26		22	22	29	13	20
<b>EFR</b>	4		2	0	0	0	0
<b>DPE</b>	0		0	0	0	13	7
<b>EISB</b>	0		2	11	0	0	0
<b><i>Technology Implemented Concurrently with ISCO</i></b>							
<b>Excavation</b>	0	no data	8	0	0	0	0
<b>Air Sparging</b>	9		2	0	0	0	0
<b>SVE</b>	17		6	11	0	13	7
<b>P&amp;T</b>	0		12	11	29	13	20
<b>DPE</b>	4		2	0	0	0	0
<b>Surfactant/ Cosolvent</b>	0		6	0	0	0	0
<b>EISB</b>	4		2	0	0	0	0
<b><i>Technology Implemented After ISCO</i></b>							
<b>Excavation</b>	9	no data	12	0	0	0	0
<b>P&amp;T</b>	4		10	0	29	0	13
<b>Air Sparging</b>	0		2	0	0	0	0
<b>Biosparging</b>	0		2	0	0	0	0
<b>SVE</b>	9		4	0	0	0	0
<b>DPE</b>	4		2	0	0	0	0
<b>EISB</b>	17		22	11	14	0	7
<b>MNA</b>	26		20	22	14	13	13
<b><i>n</i></b>	23		50	9	7	8	15

Notes: MNA was only entered as a coupling technique when project reports specifically called out that it was to be used after ISCO. Due to this fact, it is likely that the use of MNA following ISCO is underestimated.

#### B.4.3 ISCO Results by Geology Group

This section shows the results achieved by ISCO subdivided by the Geology Group. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-104: Percentage of Sites Attaining Closure by Geology Group – Full Scale Only

	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Percent Attaining Closure</b>	47	50	13	29	0	25	20
<i>mean DQC</i>	1.4	1.5	1.5	1.3	1.6	1.2	1.4
<i>n</i>	15	2	38	7	4	4	10

Notes: Site closure is defined as the completion of active remediation and monitoring, and includes the attainment of MCLs, risk-based standards, and may include requirements of institutional and engineering controls. This metric was only applied to full scale sites because pilot tests are generally not expected to achieve site closure.

Table B-105: Percentage of Sites Meeting Goals by Geology Group

	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Percent Meeting MCLs</b>	33	no data	11	0	0	0	0
<i>mean DQC</i>	1.4		1.2	1.0	1.5	1.5	1.3
<i>n</i>	9		19	3	2	2	4
<b>Percent Meeting ACLs</b>	29	100	50	33	0	no data	50
<i>mean DQC</i>	1.4	2.0	1.3	1.3	2.0		2.0
<i>n</i>	7	1	12	6	1		2
<b>Percent Reduced Mass by a Given %</b>	100	no data	43	100	0	no data	0
<i>mean DQC</i>	1.0		1.1	1.0	1.5		1.5
<i>n</i>	1		7	1	2		2
<b>Percent Reduced Mass and/or Time to Cleanup</b>	100	100	78	100	80	80	67
<i>mean DQC</i>	2.0	2.0	1.4	1.0	1.4	1.4	1.3
<i>n</i>	6	1	23	2	5	5	9
<b>Percent Evaluated Effectiveness / Optimized</b>	100	no data	95	100	100	100	88
<i>mean DQC</i>	2.0		1.4	1.0	1.6	1.6	1.5
<i>n</i>	6		21	2	5	5	8

Notes: The above table includes all five types of remediation goals included in ISCO-DB1, ranging from attaining MCLs (most stringent) to evaluating ISCO at the field-scale (least stringent).

Table B-106: Percentage of Sites Attaining MCLs by Geology Group

	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Percent Attaining MCLs</b>	13	0	3	0	0	0	0
<i>mean DQC</i>	1.6	1.5	1.5	1.3	1.6	1.6	1.4
<i>n</i>	24	2	71	15	10	10	17

Notes: This table includes all sites in each Geology Group irrespective of their goals. The values are lower than the previous table, which included only sites that attempted to reach MCLs.

Table B-107: Percent Reduction in Maximum Groundwater VOC Concentrations by Geology Group

<b>Geology Group</b>	<b>Percentage Reduction</b>				
	<b>Minimum</b>	<b>Maximum</b>	<b>Median</b>	<b>Mean</b>	<b><i>n</i></b>
<b>Group A</b>	-6.1	99	77	67	11
<b>Group B</b>	70	70	70	70	1
<b>Group C</b>	-146	99.7	58	47	39
<b>Group D</b>	-5.5	99.99	43	47	9
<b>Group E</b>	24	97	61	61	4
<b>Group F</b>	3	40	21	21	3
<b>Group BEF</b>	3	97	43	47	8

Notes: The mean DQCs are 1.3, 3.0, 1.3, 1.1, 1.8, 1.0 and 1.6 for Geology Groups A through BEF, respectively.

Table B-108: Percentage of Sites with Rebound by Geology Group

	<b>Group A</b>	<b>Group B</b>	<b>Group C</b>	<b>Group D</b>	<b>Group E</b>	<b>Group F</b>	<b>Group BEF</b>
<b>Percent of Sites with Rebound</b>	35	100	65	75	100	100	89
<i>n</i>	17	1	34	8	4	4	9
<b>For Rebound Sites, Percentage of MWs w/ Rebound</b>	56	no data	49	52	29	29	36
<i>n</i>	3		15	4	2	2	3

Notes: The second metric is applied only to sites that experienced rebound. It is calculated as the mean value of the percentage of well locations that experienced rebound each of the sites where rebound occurred. Using Group A as an example, among the sites reviewed, 35% experienced rebound in one or more well locations in the treatment zone after ISCO. When rebound did occur, it occurred at 56% of well locations on average.

Table B-109: Total Project Cost by Geology Group

Geology Group	Total Project Cost (1000s U.S. \$)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Group A	28.4	1,240	160	240	13
Group B	109	109	109	109	1
Group C	32.2	1,410	270	410	32
Group D	35	590	190	230	6
Group E	no data				
Group F	222	1,670	950	950	2
Group BEF	109	1,670	220	670	3

Table B-110: Unit Cost by Geology Group

Geology Group	Unit Total Project Cost (U.S. \$ / cubic yard treated)				
	Minimum	Maximum	Median	Mean	<i>n</i>
Group A	25	1,080	110	220	8
Group B	no data				
Group C	2	1,570	105	280	22
Group D	53	4,720	2,390	2,390	2
Group E	no data				
Group F	5	5	5	5	1
Group BEF	5	5	5	5	1

## B.5 Summary Statistics by Presence of NAPL

This section presents summary statistics from the ISCO-DB1 subdivided by the presence of NAPL in the treated area. There were three metrics used to assess the presence of NAPL. The first two are whether or not the project documents stated that DNAPL or LNAPL were present, and are termed LNAPL Reported and DNAPL Reported in the tables that follow. The third metric is whether or not groundwater concentrations were measured above 1% of that compound's solubility limit, labeled >1% of Solubility. This metric is based off of EPA's guidance, and was applied only to chlorinated compounds (EPA 1992, EPA 1993). None of these three metrics are mutually exclusive. Both LNAPL and DNAPL were observed at a few sites. And the DNAPL Reported and >1% of Solubility metrics have considerable overlap as would be expected.

The groups based on these three NAPL metrics are presented along with sites at which NAPL was not present. This fourth group is all sites that do not fall into any of the three categories above. In the case of chlorinated solvents, projects that reported concentrations exceeding the 1% of solubility criterion were not included in the No NAPL category even if project documents made no mention of the possibility of DNAPL.

As with the previous sections, several tables showing summary statistics of NAPL and non-NAPL sites follow. These include general site information, contaminant and subsurface characteristics, ISCO design, and results, in that order.

#### *B.5.1 General Information by NAPL Presence*

This section shows results of the general information and site conditions in ISCO-DB1 subdivided by the presence of NAPL. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-111: Site Type by NAPL Presence

Site Type	Percent of Sites			
	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
<b>Federal</b>	6	31	27	28
<i>Air Force / ANG</i>	0	2	1	11
<i>Army</i>	0	0	0	1
<i>general DOD</i>	6	9	8	7
<i>DOE</i>	0	6	5	2
<i>miscellaneous</i>	0	2	1	0
<i>NASA</i>	0	3	2	2
<i>Navy</i>	0	9	10	5
<b>Manufacturing/Industrial</b>	6	23	27	19
<b>Dry Cleaner</b>	0	28	33	16
<b>Service Station</b>	53	0	1	13
<b>Chemical Facility</b>	0	6	6	6
<b>Former MGP</b>	12	3	0	4
<b>Landfill / Waste Storage</b>	0	3	2	2
<b>Wood Treatment</b>	12	2	1	1
<b>Other</b>	12	6	4	13
<i>n</i>	17	64	84	124

Notes: Horizontal summation may yield greater than 100% because multiple types and indicators of NAPL may have been present at a given site. The category “general DOD” includes sites that were provided with the understanding that the site and its sector within the DOD complex would remain confidential and also project summaries that did not report the DOD sector in which the

work was performed. “miscellaneous” is a federal facility that wanted its government sector to remain confidential.

Table B-112: DQC by NAPL Presence

	DQC (# of sites)			
	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
<b>Class 1</b>	4	42	55	56
<b>Class 2</b>	10	21	24	59
<b>Class 3</b>	3	2	5	25
<i>mean</i>	<i>1.9</i>	<i>1.4</i>	<i>1.4</i>	<i>1.8</i>
<i>n</i>	<i>17</i>	<i>65</i>	<i>84</i>	<i>140</i>

Notes: Class 1 (most reliable) = project reports and journal articles, Class 2 = conference proceedings, online resources, Class 3 = vendor information

Table B-113: Geology Type by NAPL Presence

Geology Group	Percent of Sites			
	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
<b>Group A</b>	47	22	20	19
<b>Group B</b>	0	2	1	4
<b>Group C</b>	40	51	50	47
<b>Group D</b>	7	8	12	20
<b>Group E</b>	0	12	9	5
<b>Group F</b>	7	6	9	5
<i>n</i>	<i>15</i>	<i>65</i>	<i>82</i>	<i>112</i>

Notes: Horizontal summation of the percent values in each column may be greater than 100% because sites may contain more than one type of NAPL and because the two DNAPL metrics are not exclusive.

Table B-114: Goals of Remediation by NAPL Presence

Goal of Remediation	Percent of Sites			
	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
Meet MCLs	40	19	21	51
Meet ACLs	40	33	31	15
Reduce Mass by X%	0	14	12	7
Reduce Mass and/or Time to Cleanup	20	35	38	26
Evaluate Effectiveness / Optimize	10	28	28	29
<i>n</i>	10	57	68	73

Notes: Percentages in each column may sum to more than 100% because some sites reported multiple goals.

### B.5.2 ISCO Design by NAPL Presence

This section shows ISCO design parameters subdivided by the presence of NAPL. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-115: Oxidant by NAPL Presence

Oxidant	Percent of Sites			
	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
Permanganate	6	52	54	42
CHP	44	41	37	34
Persulfate	0	8	7	8
Ozone	31	6	6	14
Peroxone	6	0	0	3
Percarbonate	13	2	1	3
<i>n</i>	16	64	83	130



Table B-116: Oxidant Delivery Method by NAPL Presence

Delivery Method	Percent of Sites			
	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
Well Injection	8	43	45	36
Direct Push	33	22	25	20
Sparge Points	42	2	3	19
Infiltration Trench/Gallery	8	5	11	10
Injectors	8	13	8	4
Recirculation	0	15	13	4
Fracturing	0	10	8	4
Mixing	0	2	3	2
Horizontal Well Injection	8	0	0	1
<i>n</i>	<i>12</i>	<i>60</i>	<i>76</i>	<i>94</i>

Table B-117: TTZ by NAPL Presence

TTZ	Percent of Sites			
	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
Source	54	70	64	37
Source and Plume	23	17	20	20
Plume	8	0	1	27
Other (Pilot)	15	14	15	17
<i>n</i>	<i>13</i>	<i>59</i>	<i>75</i>	<i>82</i>

Table B-118: Areal Extent of TTZ by NAPL Presence

NAPL Group	Areal Extent (1000s sf)				
	Minimum	Maximum	Median	Mean	<i>n</i>
LNAPL Reported	1.8	25	6.3	11	6
DNAPL Reported	0.2	130	4.8	13	44
>1% of Solubility	0.1	130	4.7	13	56
No NAPL	0.2	260	10	24	60

Table B-119: Volume of TTZ by NAPL Presence

NAPL Group	Volume (1000s cf)				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>LNAPL Reported</b>	10	150	38	53	6
<b>DNAPL Reported</b>	1.2	9,100	82	470	40
<b>&gt;1% of Solubility</b>	0.2	9,100	71	390	52
<b>No NAPL</b>	0.71	3,600	190	410	55

Table B-120: Number of Pore Volumes Delivered by NAPL Presence

NAPL Group	Number of Pore Volumes (-)				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>LNAPL Reported</b>	0.09	0.7	0.37	0.37	2
<b>DNAPL Reported</b>	0.006	56	0.13	2.2	32
<b>&gt;1% of Solubility</b>	0.005	56	0.12	1.8	39
<b>No NAPL</b>	0.004	2.9	0.11	0.34	28

Table B-121: Number of Delivery Events by NAPL Presence

NAPL Group	Number of Delivery Events				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>LNAPL Reported</b>	1	6	1	1.9	13
<b>DNAPL Reported</b>	1	10	2	2.9	50
<b>&gt;1% of Solubility</b>	1	10	2	2.6	68
<b>No NAPL</b>	1	6	1	1.8	83

Table B-122: Use of Treatability Studies by NAPL Presence - Full and Pilot Scale Applications

	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
<b>Percent Using Treatability Study</b>	67	77	76	79
<b><i>n</i></b>	6	47	53	58

Table B-123: Use of Treatability Studies by NAPL Presence - Full Scale Applications Only

	<b>LNAPL Reported</b>	<b>DNAPL Reported</b>	<b>&gt;1% of Solubility</b>	<b>No NAPL</b>
<b>Percent Using Treatability Study</b>	50	66	63	68
<b><i>n</i></b>	4	32	35	28

Table B-124: Use of Pilot Studies by NAPL Presence - Full Scale Applications Only

	<b>LNAPL Reported</b>	<b>DNAPL Reported</b>	<b>&gt;1% of Solubility</b>	<b>No NAPL</b>
<b>Percent Using Pilot Study</b>	67	59	54	63
<b><i>n</i></b>	6	34	41	38

Table B-125: Incidence of Program Modification by NAPL Presence

	<b>LNAPL Reported</b>	<b>DNAPL Reported</b>	<b>&gt;1% of Solubility</b>	<b>No NAPL</b>
<b>Percent Modified During Implementation</b>	60	66	58	56
<b><i>n</i></b>	5	29	38	36

Table B-126: Use of Coupling by NAPL Presence

	<b>LNAPL Reported</b>	<b>DNAPL Reported</b>	<b>&gt;1% of Solubility</b>	<b>No NAPL</b>
<b>Percent of Sites Using Coupling</b>	90	80	76	73
<b>Percent Coupling Before ISCO</b>	70	57	58	61
<b>Percent Coupling During ISCO</b>	20	25	22	22
<b>Percent Coupling After ISCO</b>	10	45	41	22
<b><i>n</i></b>	10	49	59	64

Table B-127: Coupling Technology by NAPL Presence

Coupling Technique	Percent of Sites			
	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
<b><i>Technology Implemented Before ISCO</i></b>				
<b>Excavation</b>	67	39	42	54
<b>Air Sparging</b>	11	0	2	13
<b>SVE</b>	11	21	20	19
<b>Bioventing</b>	0	0	0	2
<b>P&amp;T</b>	11	28	31	19
<b>EFR</b>	0	3	4	2
<b>DPE</b>	0	0	0	2
<b>EISB</b>	0	3	2	4
<b><i>Technology Implemented Concurrently with ISCO</i></b>				
<b>Excavation</b>	0	8	7	2
<b>Air Sparging</b>	0	0	0	6
<b>SVE</b>	11	8	7	10
<b>P&amp;T</b>	11	13	11	8
<b>DPE</b>	0	3	4	2
<b>Surfactant/Cosolvent</b>	0	5	4	2
<b>EISB</b>	11	0	0	2
<b><i>Technology Implemented After ISCO</i></b>				
<b>Excavation</b>	0	8	9	8
<b>P&amp;T</b>	11	15	11	2
<b>Air Sparging</b>	0	0	0	2
<b>Biosparging</b>	0	3	2	0
<b>SVE</b>	0	5	7	2
<b>DPE</b>	0	3	4	2
<b>EISB</b>	0	21	20	17
<b>MNA</b>	0	31	31	10
<b><i>n</i></b>	<b>9</b>	<b>39</b>	<b>45</b>	<b>48</b>

Notes: MNA was only entered as a coupling technique when project reports specifically called out that it was to be used after ISCO. Due to this fact, it is likely that the use of MNA following ISCO is underestimated.

### B.5.3 ISCO Results by NAPL Presence

This section shows results achieved by ISCO subdivided by the presence of NAPL. Unless otherwise noted, all scales of implementation and all DQC values are included.

Table B-128: Attainment of Site Closure by NAPL Presence – Full Scale Applications Only

	<b>LNAPL Reported</b>	<b>DNAPL Reported</b>	<b>&gt;1% of Solubility</b>	<b>No NAPL</b>
<b>Percent Attaining Closure</b>	60	9	13	37
<i>mean DQC</i>	1.7	1.3	1.3	1.6
<i>n</i>	5	32	40	30

Table B-129: Percentage of Sites Meeting Goals by NAPL Presence

	<b>LNAPL Reported</b>	<b>DNAPL Reported</b>	<b>&gt;1% of Solubility</b>	<b>No NAPL</b>
<b>Percent Meeting MCLs</b>	0	0	0	25
<i>mean DQC</i>	1.7	1.1	1.2	1.2
<i>n</i>	3	8	12	24
<b>Percent Meeting ACLs</b>	33	35	39	57
<i>mean DQC</i>	2.0	1.2	1.1	1.6
<i>n</i>	3	17	18	7
<b>Percent Reduced Mass by a Given %</b>	no data	38	44	67
<i>mean DQC</i>		1.3	1.2	1.0
<i>n</i>		8	9	3
<b>Percent Reduced Mass and/or Time to Cleanup</b>	100	63	68	100
<i>mean DQC</i>	2.0	1.2	1.2	1.9
<i>n</i>	2	19	25	14
<b>Percent Evaluated Effectiveness / Optimized</b>	100	94	95	94
<i>mean DQC</i>	1.0	1.4	1.3	1.8
<i>n</i>	1	16	19	17

Notes: The above table includes all five types of remediation goals included in ISCO-DB1, ranging from attaining MCLs (most stringent) to evaluating ISCO at the field-scale (least stringent).

Table B-130: Percentage of Sites Attaining MCLs by NAPL Presence

	<b>LNAPL Reported</b>	<b>DNAPL Reported</b>	<b>&gt;1% of Solubility</b>	<b>No NAPL</b>
<b>Percent of All Sites Attaining MCLs</b>	0	0	0	10
<i>mean DQC</i>	1.7	1.3	1.3	1.6
<i>n</i>	7	55	69	59

Notes: This table includes all sites in each of the three groups indicating NAPL presence, whereas the previous table calculated the percentage of sites meeting MCLs among only those projects that stated that MCLs were one of the goals of their ISCO remediation.

Table B-131: Percent Reduction in Maximum Groundwater VOC Concentrations by NAPL Presence

COC Group	Percentage Reduction				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>LNAPL Reported</b>	no data				
<b>DNAPL Reported</b>	-146	99.7	48	42	33
<b>&gt;1% of Solubility</b>	-146	99.7	50	44	44
<b>No NAPL</b>	-6.1	99.99	68	63	28

Notes: The mean DQCs for the three metrics with data are 1.1, 1.1, and 1.6, from top to bottom.

Table B-132: Percentage of Sites with Rebound by NAPL Presence

	LNAPL Reported	DNAPL Reported	>1% of Solubility	No NAPL
<b>Percent of Sites with Rebound</b>	0	71	78	56
<b><i>n</i></b>	5	28	36	34
<b>For Rebound Sites, Percentage of MWs w/ Rebound</b>	na	43	54	44
<b><i>n</i></b>		13	18	10

Notes: na = not applicable. The second metric is applied only to sites that experienced rebound. It is calculated as the mean value of the percentage of well locations that experienced rebound each of the sites where rebound occurred. Using >1% Solubility as an example, among the sites reviewed, 78% experienced rebound at one or more locations in the treatment zone after ISCO. When rebound did occur, it occurred at 54% of well locations on average.

Table B-133: Total Project Cost by NAPL Presence

NAPL Group	Total Project Cost (1000s U.S. \$)				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>LNAPL Reported</b>	55	222	190	160	6
<b>DNAPL Reported</b>	106	1,670	400	630	18
<b>&gt;1% of Solubility</b>	73	1,670	380	580	20
<b>No NAPL</b>	15	1,240	180	250	29

Table B-134: Unit Project Cost by NAPL Presence

NAPL Group	Unit Total Project Cost (U.S. \$ / cubic yard treated)				
	Minimum	Maximum	Median	Mean	<i>n</i>
<b>LNAPL Reported</b>	94	510	300	300	2
<b>DNAPL Reported</b>	5	4,720	170	570	14
<b>&gt;1% of Solubility</b>	5	4,720	160	530	15
<b>No NAPL</b>	2	1,570	42	260	16





## APPENDIX C: DETAILS OF RANDOMIZATION TEST

This appendix discusses the theory and implementation of the randomization test used to perform the statistical analyses in the body of the text. The randomization test is a non-parametric test that uses repeated random sampling to evaluate the likelihood that an observed difference between two groups with respect to a particular parameter arose by chance. The null hypothesis is that the mean (or another statistic) of the two groups are the same. The alternative hypothesis is the larger of the two is in fact significantly greater based on a one directional significance test. It is similar to a Student's t test but does not require that the data be normally distributed (Navidi 2006). It also does not require assumptions regarding the similarity of probability distributions between the two samples, nor does it require that the data being analyzed be a continuous variable (Lunneborg 2000). The test is performed by calculating the difference in mean (or another statistic such as the trimmed mean or median) between the two groups, which are not required to have the same sample size. The data are then aggregated, and a two new samples of the same size as the reported samples are randomly selected. The means of these new random samples and the difference between them are recorded. This process is repeated 1,000 times or more. The p-value of the test is calculated by dividing the number of randomly generated samples whose result was higher than the observed result by the total number of randomly generated samples.

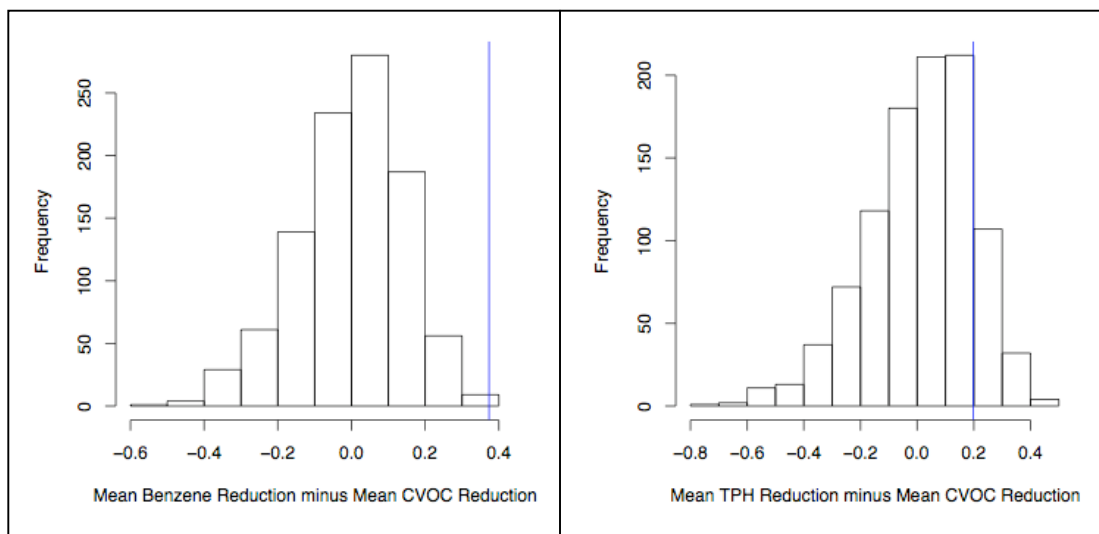
As applied to the data in ISCO-DB1, the randomization test was implemented using the software package R (v. 2.6.1) previously described in the geospatial analysis section. To keep the computer runtimes at a manageable level, the data were randomly sampled 1,000 times. In situations in which the p-value was close to that which would make the result either significant or insignificant at the 95% confidence level, the test was repeated to confirm the result. R scripts can be acquired by contacting the author at [fkrembs@hotmail.com](mailto:fkrembs@hotmail.com).

The randomization test was performed using either the arithmetic mean, a trimmed arithmetic mean that removed the top and bottom 10% of the sample, or the median. The untrimmed mean was used for binary variables, which were used to track whether or not a particular event occurred, such as meeting MCLs. The trimmed mean

was used for continuous data as a more robust statistic than the mean, but one that would include more values in the analysis than the median.

Some results of output of several randomization tests are shown in Figure C-1. These are presented here to illustrate in graphical terms what the randomization test does. Such graphs were not created for each analysis. This figure shows the probability distribution generated for the randomization tests comparing percent reductions in Benzene versus total CVOCs and TPH versus total CVOCs. Both panels in Figure C-1 are based on the mean values. The blue line represents the actual difference in the statistic (mean or median) between the two groups. The p-value calculated is the same as the area to the right of the blue line.

Figure C-1: Randomization Test Histograms



The p-value of the test shown in the left hand panel is 0.001, indicating that the result is significant at the 95% confidence level. The p-value of the test shown in the right hand panel is 0.134, indicating that the result is not significant at the 95% confidence level.