Department of Energy
Washington, DC 20585

WM-00070

June 6, 2013

Ms. Madeline Roanhorse
Director Navajo AML Reclamation
Division of Natural Resources
The Navajo Nation
P.O. Box 1875
Window Rock, AZ 86515

Subject: Monitored Natural and Enhanced Attenuation of the Alluvial Aquifer and Subpile Soils at the Monument Valley, Arizona Site: Final Pilot Study Report

Dear Ms. Roanhorse:

Enclosed for your review is a copy of *Monitored Natural and Enhanced Attenuation of the Alluvial Aquifer and Subpile Soils at the Monument Valley, Arizona Site: Final Pilot Study Report, April 2013*. This report was prepared to provide DOE-LM with a technical basis for remedy options that could be applied in addressing groundwater contamination in the alluvial aquifer at the Monument Valley site.

The goal of the pilot studies was to gather landscape-scale information on the viability and practicality of natural and enhanced attenuation remedies for ammonium, nitrate, and sulfate in the source area (subpile) soils and alluvial aquifer at Monument Valley. It is anticipated that the pilot study findings presented in this report will support the process for developing compliance strategies for a Groundwater Compliance Action Plan for the Monument Valley site.

Please call me at (970) 248-6073 if you have any questions. Please address any correspondence to:

U.S. Department of Energy
Office of Legacy Management
2597 Legacy Way
Grand Junction, CO 81503

Sincerely,

Richard Bush
Site Manager

FSME 20

cc:
Document Control Desk, NRC
D. Orlando, NRC
L. Benally, Jr., NN UMTRA
S. Itsitty, NN EPA
E. Rich, NN EPA
D. Taylor, NN DOJ
G. Tom, NNFWS
D. Miller, Stoller (e)
File: MON 0410.02(A) (rc grand junction)

Sites\Monument Valley\6-5-13 Monument Valley Final Pilot Study Ltr (Roanhorse)

LMS/MON/S07670

Monitored Natural and Enhanced Attenuation of the Alluvial Aquifer and Subpile Soils at the Monument Valley, Arizona, Processing Site:

Final Pilot Study Report

April 2013

U.S. DEPARTMENT OF ENERGY | Legacy Management

This page intentionally left blank

LMS/MON/S07670

Monitored Natural and Enhanced Attenuation of the Alluvial Aquifer and Subpile Soils at the Monument Valley, Arizona, Processing Site:

Final Pilot Study Report

April 2013

This page intentionally left blank

Contents

Figure

Tables

Appendixes

Abbreviations*

ANOVA	analysis of variance
ATCA	*Atriplex canescens*
CFR	*Code of Federal Regulations*
cm	centimeters
DEA	Denitrification Enzyme Activity
DEI	Diné Environmental Institute
DOE	U.S. Department of Energy
EA	*Environmental Assessment of Groundwater Compliance at the Monument Valley Uranium Mill Tailings Site, Monument Valley, Arizona*
EC	electrical conductivity
EP	Evaporation Pond
EPA	U.S. Environmental Protection Agency
ESL	Environmental Sciences Laboratory
ET	evapotranspiration
ET_o	potential evapotranspiration
EVI	Enhanced Vegetation Index
EVS	Environmental Visualization System
f_c	fractional cover of vegetation
ft	feet
ft/day	feet per day
ft/yr	feet per year
g	grams
GCAP	Groundwater Compliance Action Plan
$g\ L^{-1}$	grams per liter
g/m^2	grams per square meter
ha	hectares
HCN	hydrocyanic acid
km	kilometers
L	liters
LAI	leaf area index
LM	Office of Legacy Management
m	meters
m^2	square meters

MAP	Management Action Process
MCL	maximum concentration limits
µg/g	micrograms per gram
mg	milligrams
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mm	millimeters
mm d^{-1}	millimeters per day
MNA	monitored natural attenuation
MODIS	Moderate Resolution Imaging Spectrometer
MPND	Most Probable Number of Denitrifiers
mrem	millirems
NDVI	Normalized Difference Vegetation Index
NEPA	National Environmental Policy Act
NIR	near infrared
NRC	U.S. Nuclear Regulatory Commission
pCi/g	picocuries per gram
PEIS	*Final Programmatic Environmental Impact Statement for the Uranium Mill Tailings Remedial Action Ground Water Project*
ppm	parts per million
r^2	coefficient of determination
SAVE	*Sarcobatus vermiculatus*
SD	standard deviation
SE	standard error
SOWP	*Final Site Observational Work Plan for the UMTRA Project Site at Monument Valley, Arizona*
t	metric ton or 1,000 kilograms
TOC	total organic carbon
UMTRA	Uranium Mill Tailings Remedial Action
UMTRCA	Uranium Mill Tailings Radiation Control Act
USGS	U.S. Geological Survey
VSP	Visual Sample Plan
WCR	Water Content Reflectometer
WFM	Water Flux Meters

*Contains abbreviations for the report and appendixes.

Executive Summary

The U.S. Department of Energy (DOE) Office of Legacy Management (LM) has completed a suite of pilot studies designed to evaluate, on a landscape scale, proposed passive and active remedies for ammonium, nitrate, and sulfate in an alluvial aquifer and in a source area at the Monument Valley, Arizona, Processing Site. Pilot studies are trial studies or experiments conducted to evaluate and demonstrate alternative remedies before a final remedial action is selected and implemented. The passive remedies, monitored natural and enhanced phytoremediation and denitrification, were evaluated as alternatives to active pumping and treatment technologies. Land-farm phytoremediation was evaluated as an alternative to conventional active remedies.

The pilot studies were carried out as directed in a DOE Work Plan (DOE 2004a) and a DOE Environmental Assessment (DOE 2005) to evaluate remedies for three components of the alluvial aquifer: subpile soils, shallow alluvial aquifer, and deep alluvial aquifer. Natural and enhanced phytoremediation using native desert plants and natural and enhanced microbial denitrification were evaluated as potential remedies for both the shallow portions of the alluvial aquifer and for a source of groundwater contamination, the soil remaining where a uranium mill tailings pile had been removed—subpile soils. As directed for deeper portions of the alluvial aquifer, land-farm phytoremediation was evaluated as a pump-and-treat option to supplement natural attenuation processes. As directed, the pilot studies also "demonstrated methods for monitoring performance of natural attenuation processes and enhancements" (DOE 2005).

A summary of pilot study methods and results follows for the subpile soils, shallow alluvial aquifer, and deep alluvial aquifer.

Subpile Soils

Enhanced phytoremediation and denitrification were evaluated as options for the subpile soils. The enhanced phytoremediation pilot study involved delineating, planting, and irrigating the entire denuded subpile soil area where ammonium and nitrate were shown to be elevated. Plantings of native fourwing saltbush shrubs matured within 5 years; native black greasewood transplants took longer to mature. Monitoring of soil water content and percolation flux and results of a soil salt balance study provided evidence that evapotranspiration from the mature plantings was preventing leaching of ammonium, nitrate, and sulfate into the alluvial aquifer—phytoremediation had cut off the subpile soil as a source of groundwater contamination. The plantings also extracted and metabolized nitrogen and sulfur from subpile soils, but not enough to account for a rapid drop in total soil nitrogen as monitored through soil sampling and analysis.

The enhanced denitrification pilot study involved deficit irrigation of the subpile planting—irrigating less than the amount of water removed by evapotranspiration—and supplying a carbon source in the irrigation stream. The pilot studies demonstrated, using a combination of direct assays of denitrification in source area soils and enrichment of N^{15} in soils undergoing nitrate loss, that irrigation-induced microbial denitrification was responsible for about a 50 percent drop in total subpile soil nitrogen. A hypothesis that supplying a carbon source through the irrigation stream would also enhance denitrification was supported by microcosm experiments but not supported by results of a field experiment.

If enhanced phytoremediation and denitrification were selected as remedies for the subpile soils, monitoring of plant health and soil water and maintenance of plantings and the irrigation system may be necessary at some level to assure continued isolation of the subpile soil as a source of groundwater contamination. Monitoring may also be necessary to determine whether deficit irrigation is continuing to enhance denitrification.

Shallow Alluvial Aquifer

The Environmental Assessment (DOE 2005) defined the shallow alluvial aquifer as alluvial groundwater "where the depth to the water table is less than 50 feet below the land surface." The pilot studies evaluated natural and enhanced phytoremediation, and natural and enhanced denitrification, as remedies for the shallow alluvial aquifer. The pilot studies also developed a protocol for landscape-scale monitoring of natural and enhanced phytoremediation for the alluvial aquifer, subpile soil, and land-farm.

Phytoremediation of the alluvial aquifer focused on hydraulic control and phytoextraction by populations of native phreatophytes that likely dominated the pre-milling ecology of the plume area. At the onset of the pilot studies, a large high-nitrate portion the plume had been denuded, and the remaining plume area had been heavily grazed by livestock. Although in poor health, these populations of black greasewood and fourwing saltbush were shown to be rooted in the plume, extracting small amounts of nitrogen and sulfur and transpiring aquifer water, potentially slowing dispersion—natural phytoremediation was ongoing, although at a reduced capacity. Enhanced phytoremediation entailed preventing grazing and revegetating denuded areas in large test plots, which increased transpiration rates up to six fold. During the course of the pilot studies, the general health of native phreatophyte populations improved in response to better grazing management in the region and, based on groundwater monitoring trends, apparently slowed or nearly stopped plume dispersion. Phytoextraction also increased. However, these healthier plants were still removing only a small percentage of plume nitrogen and sulfur.

The pilot studies also evaluated natural and enhanced denitrification in the shallow alluvial aquifer. First-order denitrification rate coefficients, which LM could use to project long-term nitrate attenuation in the alluvial aquifer, were comparable when calculated independently using laboratory microcosm experiments, field isotope fractionation analysis, and solute transport modeling. The composite natural attenuation rate coefficient was similar to the denitrification rate coefficients, indicating that microbially induced decay was primarily controlling nitrate attenuation. Ethanol increased denitrification rates by two orders of magnitude in microcosm experiments. Methanol also increased denitrification but at a slower rate. In field tests, ethanol injected into a high-nitrate portion of the aquifer dropped nitrate levels to below detection limits and increased nitrous oxide (a product of denitrification) in the injection wells and in downgradient observation wells. Denitrification rate coefficients were approximately 50 times larger than non-enhanced values. Ethanol injection also greatly increased rates of sulfate reduction. For the entire 20-month test, nitrate concentrations remained at levels three orders of magnitude below the initial values, indicating that the ethanol amendments may have a long-term impact on the local subsurface environment.

Deep Alluvial Aquifer

The Environmental Assessment (DOE 2005) defined the deep alluvial aquifer as alluvial groundwater "where the water table is generally more than 50 feet below the land surface." Although natural and enhanced phytoremediation are not options because roots do not extend to this depth, results of natural and enhanced denitrification as described above for the shallow alluvial aquifer are options for the deep alluvial aquifer. LM also evaluated land-farm phytoremediation "as an active remediation option if natural and enhanced attenuation processes are inadequate" (DOE 2005).

Land-farm phytoremediation, a type of pump-and-treat remedy, involves irrigating a crop of native shrubs with nitrate-contaminated groundwater pumped and piped from the alluvial aquifer. Results of a factorial field experiment demonstrated that a land farm with a crop of native fourwing saltbush shrubs may work well as an alternative remedy for the deep alluvial aquifer. Fourwing saltbush thrived when irrigated with plume water. Plant uptake and soil denitrification kept nitrate levels from building up in the land-farm soil; evapotranspiration limited recharge and leaching of nitrate and ammonia back into the aquifer; sulfate pumped from the plume was sequestered in the soil profile, most likely as gypsum; and the farm produced a native plant seed crop and forage that is safe for livestock. If land-farm phytoremediation is selected as a supplemental remedy for the deep alluvial aquifer, monitoring and maintenance of an operational land farm may include (1) monitoring of plant health, soil moisture profiles, and soil nitrogen and sulfate levels, (2) monitoring the effects of water extraction on well production and drawdown, (3) maintenance of the land-farm plantings, and (4) maintenance of the water extraction and irrigation system.

This page intentionally left blank

1.0 Introduction

The U.S. Department of Energy (DOE) Office of Legacy Management (LM) has completed a suite of pilot studies designed to evaluate remedies for groundwater contamination at the Monument Valley, Arizona, Processing Site. The Monument Valley Site is a former uranium mill located on Navajo land in northeastern Arizona (www.lm.doe.gov/MonValley/Sites.aspx). Pilot studies are trial studies or experiments conducted to evaluate and demonstrate alternative remedies before a final remedial action is selected and implemented. The pilot studies evaluated alternative remedies for contamination in an alluvial aquifer at the Monument Valley Site and in soils that are thought to be a source area for groundwater contamination. This final report reviews the pilot study directives and objectives; provides synopses of pilot study findings; and documents the rationale, designs, methods, and results for all activities. In other words, the report answers the questions—why did LM conduct the pilot studies, what was done, and what was found?

An *Environmental Assessment of Groundwater Compliance at the Monument Valley, Arizona, Uranium Mill Tailings Site* (EA) authorized the pilot studies. DOE prepared the EA to assess proposed actions for groundwater compliance and for the pilot studies (DOE 2005). Proposed pilot study actions were documented and authorized in *Monument Valley Groundwater Remediation Pilot Study Work Plan* (DOE 2004a). DOE carried out the actions proposed in the Work Plan to evaluate, on a landscape scale, passive remediation strategies and combinations and sequences of passive and active remediation strategies to comply with a U.S. Environmental Protection Agency (EPA) standard for groundwater nitrate and a Navajo Nation goal for remediation of groundwater sulfate (DOE 2005).

At the Monument Valley Site, levels of nitrogen and sulfur are elevated in the alluvial aquifer, and the contaminant plume is spreading away from the source area (subpile soils) where a uranium mill tailings pile once stood. The passive remediation strategies focused on monitored natural and enhanced attenuation. The suite of pilot studies evaluated natural and enhanced phytoremediation and bioremediation to remove nitrate, ammonium, and sulfate from the alluvial aquifer plume and subpile soils, and to hydraulically isolate the subpile source and slow plume dispersion. Land-farm phytoremediation, a type of active pump-and-treat strategy, was evaluated as an alternative to natural and enhanced attenuation. As directed (DOE 2004a, 2005), the pilot studies also demonstrated (1) methods for monitoring the performance of natural attenuation processes and enhancements and (2) land stewardship and reuse benefits of phytoremediation.

This final report is organized as follows. Section 2.0 provides a summary of regulatory requirements and DOE documents that were the basis for the pilot studies—why LM conducted the studies. Section 2.0 also reviews the objectives and scope of the studies as documented in the Work Plan (DOE 2004a), EA (2005), and subsequent status reports (DOE 2004b, 2006, 2007, 2008, and 2009)—what was done. Section 3.0 provides synopses of methods and results, addressing each of the Section 2.0 objectives—what was found. All sections direct the reader to applicable report appendixes that provide documentation of the studies including a list of scientific products: DOE reports, refereed journal publications, and proceedings papers. Most appendixes begin with abstracts. The key conclusions of the pilot studies, in Section 4.0, address the objectives as stated in the Work Plan and EA. A remote sensing method developed for monitoring phytoremediation, land stewardship benefits of the remedies, and educational outreach initiatives will be reported separately.

This page intentionally left blank

2.0 Background Information, Objectives, and Scope

This section reviews the regulatory and DOE background documents that directed and provided the rationale for the Monument Valley pilot studies. This section also reviews the objectives and scope of the pilot studies that were derived from the results of preliminary phytoremediation studies (DOE 2002), detailed Work Plan (DOE 2004a), and EA that assessed proposed pilot study actions (DOE 2005).

2.1 Background Documentation

The Monument Valley pilot studies were DOE actions carried out to protect human health and the environment as required by EPA groundwater standards defined in Title 40 Code of Federal Regulations (CFR) Part 192. Regulations in CFR Part 192 established procedures and numerical standards for remediation of residual radioactive materials in land, buildings, and groundwater as required under the 1978 Uranium Mill Tailings Radiation Control Act (UMTRCA). The regulations also require that DOE remedial actions be implemented with full participation of states, in consultation with affected tribes, and with the concurrence of the U.S. Nuclear Regulatory Commission (NRC). (Appendix A, Section A.2 provides a review of background information, regulatory requirements, and stakeholder interactions.)

The following sequence of DOE actions preceded, authorized, and documented the status of pilot studies at Monument Valley:

- Completion of an EA (DOE 1989) and the subsequent removal of tailings and other residual radioactive materials on or near the ground surface at Monument Valley.
- Completion of a Final Site Observational Work Plan (SOWP) for Monument Valley (DOE 1999) that was based on the framework established in a Programmatic Environmental Impact Statement (DOE 1996) to comply with the groundwater standards in 40 CFR 192.
- Completion of a work plan to assess the feasibility of phytoremediation, as recommended in the SOWP, for the subpile soils and for shallower portions of the alluvial aquifer (DOE 1998).
- Completion of *Draft Evaluation of Active Remediation Alternatives for the Monument Valley, Arizona, UMTRA Project Site* (DOE 2000), which evaluated active pumping strategies and treatment technologies for the alluvial aquifer.
- Completion of the preliminary phytoremediation feasibility studies at Monument Valley (DOE 2002) that were carried out to evaluate passive remediation compliance strategies presented in the SOWP as alternatives to active pumping and treatment strategies.
- Completion of a Work Plan (DOE 2004a) for the in-depth, landscape-scale phytoremediation and bioremediation pilot studies reported in this document.
- Completion of an EA (DOE 2005) that assessed actions proposed in the pilot study work plan and actions of proposed compliance strategies and provided authorization for the pilot studies to proceed.
- Completion of pilot study status reports that documented progress, preliminary results, and task improvements that were based on the knowledge gained (DOE 2004b, 2006, 2007, 2008, and 2009).

DOE entered into a cooperative agreement with the Navajo Nation as required by 40 CFR 192 and, following several departmental and public meetings, DOE and Navajo Nation agreed to proceed with the proposed pilot studies (Appendix A, Section A.3). However, Navajo Nation requested completion of the EA first to address the proposed pilot study actions and the proposed compliance strategies. DOE and Navajo Nation also agreed to postpone preparation of a Groundwater Compliance Action Plan (GCAP) for Monument Valley pending completion of the pilot studies.

2.2 Pilot Study Goals

The goal of the pilot studies, according to the EA, was "to gather additional information to support the compliance strategies proposed in this EA for the alluvial aquifer." The EA also stated that "the proposed compliance strategies for the alluvial aquifer in this EA are contingent upon the results of the proposed pilot studies."

The EA defined three distinct areas of concern for the alluvial aquifer: subpile soils, shallow alluvial aquifer, and deep alluvial aquifer. Table 1 is a summary of the compliance strategies for these three areas as proposed in the EA. Subpile soil is the soil remaining in the footprint of the New Tailings Pile after tailings were removed. The EA defined the shallow portions of the alluvial aquifer as "where the depth to the water table is less than 50 feet below the land surface," and the deep portions of the alluvial aquifer as "where the water table is generally more than 50 feet below the land surface." Phytoremediation would only apply to the subpile soils and shallow portions of the aquifer. Natural attenuation (referred to as natural flushing in the EA) would apply to the subpile soils and both the shallow and deeper portions of the alluvial aquifer. Although the EA proposed land-farm phytoremediation as an option for the deeper portions of the alluvial aquifer, it could also be applied to the shallow portions of the aquifer.

The compliance strategies were based, in part, on results of the initial phytoremediation feasibility studies (DOE 2002). The goal of the additional pilot studies was to evaluate the remedies proposed in the EA, in greater detail and at a landscape scale, for ammonium and nitrate in subpile soils and for nitrate and sulfate in both the shallow and deeper portions of the alluvial aquifer. The following general conclusions of the initial feasibility study supported the compliance strategies proposed in the EA (Section 3.1 in DOE 2005):

- Enhancement of phytoremediation, a passive remedy, can accelerate removal of ammonium and nitrate from the subpile soils. The enhancement is an irrigated planting of native fourwing saltbush in the subpile soils. Evapotranspiration in the planting apparently prevented leaching of nitrogen into the alluvial aquifer.
- Removal of nitrate from subpile soils was faster than anticipated if solely from uptake by the fourwing saltbush planting. Rapid removal of nitrate may be attributable to microbial processes.
- Two native phreatophytes, fourwing saltbush and black greasewood, where naturally rooted in the shallow aquifer, could remove nitrate at a faster rate if grazing is managed to enhance plant growth.
- Plantings of these phreatophytes in areas cleared of vegetation during the surface remediation could enhance natural phytoremediation if grazing of the plantings is restricted.

Table 1. Summary of DOE's Proposed Actions for Ammonium, Nitrate, and Sulfate in the Alluvial Aquifer at Monument Valley[a]

Aquifer	Area	Contaminants To Be Monitored	Compliance Strategy	Rationale
Alluvial	Subpile soils	Ammonium, nitrate	Passive remediation (natural flushing and phytoremediation)	Reduce concentrations of ammonium that could be a continuing source of nitrate contamination in the alluvial aquifer
	Shallow portions of aquifer	Nitrate, sulfate	Passive remediation (natural flushing and phytoremediation)	Reduce concentrations of nitrate and sulfate
	Deeper portions of aquifer	Nitrate, sulfate	Passive and/or active remediation (combination of natural flushing and land farming)	Reduce concentrations of nitrate and sulfate

[a] From Table 2 in *Environmental Assessment of Groundwater Compliance at the Monument Valley, Arizona Uranium Mill Tailings Site* (DOE 2005).

2.3 Objectives and Scope of Pilot Studies

This section reviews the overall objectives for the additional pilot studies, as proposed in the EA, and specific pilot study objectives and scope as approved in the Work Plan. The overall objectives support decision points in a DOE decision framework. The decision framework was created to illustrate how the results of the additional pilot studies would be used to sequentially evaluate natural attenuation, enhanced attenuation, and active land farming as potential remedies for the subpile soils and alluvial groundwater at Monument Valley (DOE 2004a, 2005):

1. Estimate the total capacity of natural attenuation processes that are reducing concentrations of groundwater contaminants and their source (subpile soils) at the site.
2. Investigate methods to enhance and sustain attenuation processes that could be implemented if the total capacity of natural processes is inadequate.
3. Demonstrate methods for characterizing attenuation rates, verifying short-term results, and monitoring performance of natural attenuation processes and enhancements.
4. Evaluate land farming as an active remedy option if natural and enhanced attenuation processes are both inadequate.

LM completed six pilot studies to acquire landscape-scale information, as proposed in the EA, and that support the decision framework. LM also evaluated potential risks to human health and the environment associated with pilot study activities and the remedies proposed in the EA. The pilot studies were implemented using large field plots, landscape-scale monitoring, and numerical modeling. Table 2 lists the titles, objectives, and scope (completed tasks) for the pilot studies as proposed in Work Plan, EA, and status reports. Table 2 also lists objectives of the risk evaluations. Section 3.0 provides synopses of the methods and results for each of the six pilot studies. Appendixes A through F provide documentation of the rationale, tasks, methods, and results of the pilot studies. Results of LM evaluations of potential risks to human health and the environment associated with the pilot studies and proposed remedies are reported in the pilot study synopses (Section 3.0) and Appendix G.

Table 2. Pilot Study Titles, Objectives, and Scope (Tasks Completed)

Title	Objective	Scope (Tasks Completed as Authorized in the EA, Work Plan, and Status Reports[a])
1. Control Subpile Soil Water Balance and Percolation	Enhance native vegetation establishment and evapotranspiration (ET) on source area soils to control the soil water balance, limit deep percolation, and prevent continued leaching of nitrate and ammonium into the alluvial aquifer.	1. Determined extent of subpile ammonium and nitrate. 2. Expanded subpile phytoremediation planting and irrigation system. 3. Investigated natural sources of vadose zone nitrate. 4. Monitored soil water content and percolation flux. 5. Monitored plant growth and related evapotranspiration. 6. Investigated causes and recourses for area of stunted plant growth.
2. Enhance Natural Attenuation in the Subpile Soils	Remove nitrate and ammonium from subpile soils by enhancing natural phytoremediation and bioremediation.	1. Monitored plant growth and related nitrogen uptake. 2. Sampled plant root abundance and distribution. 3. Sampled soil organic carbon. 4. Monitored changes in subpile soil ammonium and nitrate. 5. Evaluated natural and enhanced microbial denitrification. 6. Evaluated soil nitrification processes.
3. Evaluate Natural and Enhanced Phytoremediation of the Alluvial Aquifer	Evaluate and enhance natural phytoremediation by native phreatophytes rooted in the plume to remove plume nitrogen and, by increasing transpiration, to hydraulically limit the continued spread of the plume.	1. Evaluated historical modeling and monitoring of nitrate, ammonia, and sulfate in the alluvial aquifer. 2. Investigated rooting depths of native phreatophytes. 3. Evaluated phreatophyte transpiration and hydraulic control. 4. Evaluated effects of grazing management and revegetation on phytoremediation capacity for nitrogen uptake and transpiration. 5. Developed a remote sensing protocol to monitor natural and enhanced phytoremediation.
4. Evaluate Natural and Enhanced Denitrification in the Alluvial Aquifer	Characterize natural attenuation processes acting to reduce contaminant levels in the alluvial aquifer and investigate options for enhancing denitrification.	1. Investigated natural concentrations of alluvial nitrogen. 2. Modeled plume dynamics and natural attenuation processes. 3. Estimated natural denitrification in the alluvial aquifer based on nitrate concentrations and nitrogen isotope fractionation. 4. Evaluated carbon sources to enhance aquifer denitrification using laboratory microcosm assays. 5. Conducted field tests of the denitrification capacity and dispersion of ethanol injected into the alluvial aquifer.
5. Evaluate Land-Farm Phytoremediation	Evaluate land-farm phytoremediation, an active remedy alternative that involves pumping and irrigating a crop of native plants with nitrate-contaminated groundwater.	1. Conducted a feasibility study of land-farm phytoremediation. 2. Designed and constructed a land farm experiment to evaluate effects of different native shrub crops and irrigation nitrate levels on plant health, soil water, and soil nitrogen. 3. Characterized baseline physical and chemical properties of land-farm soils. 4. Monitored soil water content profiles using neutron hydroprobes. 5. Sampled for changes in soil nitrate and ammonium profiles. 6. Monitored crop health and growth using remote sensing.

Table 2 (continued). Pilot Study Titles, Objectives, and Scope (Tasks Completed)

Title	Objective	Scope (Tasks Completed as Authorized in the EA, Work Plan, and Status Reports[a])
6. Reduce Sulfate Levels as Possible	To the extent that is practical, reduce sulfate concentrations in the alluvial aquifer and sequester as soil sulfate in concert with remedies developed for groundwater nitrogen contamination.	1. Evaluated natural sources of sulfate in the alluvial aquifer. 2. Evaluated plant uptake of sulfate in subpile soils and alluvial aquifer. 3. Monitored changes in subpile soil sulfate profiles. 4. Monitored effects of ethanol injection into the alluvial aquifer on sulfate reduction. 5. Investigated gypsiferous soils as an analog of sulfate sequestration in a phytoremediation land farm. 6. Measured sequestration of sulfate in land farm soils.
Evaluate Potential Risks	Evaluate potential risks to human health and the environment related to the pilot studies and possible remedies.	1. Evaluated risks of plant uptake and livestock grazing for chemicals of potential concern in the subpile soil and groundwater. 2. Evaluated potential phytotoxicity of stained or colored subpile soils. 3. Investigated the potential health effects of manganese concretions in the subpile soils. 4. Conducted a radiological investigation of yellow crusts on the soil surface for the phytoremediation planting in the Evaporation Pond.

[a] DOE 2004a, 2005, 2006, 2007, 2008, 2009

This page intentionally left blank

3.0 Pilot Study Synopses

This section provides synopses of the passive and active remediation strategies LM evaluated through pilot studies at the Monument Valley, Arizona, Processing Site, as proposed in the Work Plan (DOE 2004a) and in support of compliance strategies proposed in the EA (DOE 2005). A goal of the pilot studies was to gather landscape-scale information on the viability and practicality of passive natural and enhanced phytoremediation and bioremediation as alternatives to conventional engineering remedies. Land-farm phytoremediation, an active pump-and-treat remedy, was also evaluated. Objectives, synopses of methods and results, and information concerning remedy monitoring and maintenance are presented for each of six pilot studies listed in Table 3. Monitoring and some level of maintenance may be necessary depending on the sequence or combination of passive and active remedies selected for the compliance strategy. The pilot study synopses also refer the reader to report appendixes that document scientific methods, data reduction, results, and pertinent literature, including pilot study publications.

Table 3. Pilot Study Field Plots and Methods

Title	Plot Labels in Figure 1	Field Methods
Control Subpile Soil Water Balance and Percolation	Subpile Soil Phytoremediation Planting and Irrigation	The 3.3 hectare subpile soil area with elevated ammonium and nitrate was planted primarily with fourwing saltbush to enhance transpiration and control percolation.
Enhance Natural Attenuation in the Subpile Soils	Subpile Soil Phytoremediation Planting and Irrigation	Portions of the subpile soil planting were deficit-irrigated with and without an ethanol amendment to test methods for enhancing denitrification.
Enhance Phytoremediation of the Alluvial Aquifer	Revegetation Test Plot East Revegetation Test Plot West Black Greasewood Grazing Exclosure Fourwing Saltbush Grazing Exclosure	Two methods were evaluated for enhancing phytoremediation of nitrate and transpiration (hydraulic control) of plume dispersion: - Control grazing of existing stands of native phreatophytes (black greasewood and fourwing saltbush) in 50 meter x 50 meter fenced plots overlying the nitrate plume. - Re-establish stands of native phreatophytes (fourwing saltbush) in two, 50 meter x 50 meter plots installed at different depths to groundwater.
Evaluate Natural and Enhanced Denitrification in the Alluvial Aquifer	Ethanol Injection Test Wells	Estimates of natural denitrification in the alluvial aquifer were based on nitrate distribution, nitrogen isotope fractionation, and modeling of plume dynamics and denitrification processes. Enhancement of denitrification in the alluvial aquifer with carbon sources was evaluated using microcosm assays and an array of ethanol injection and observation wells placed in a hot spot of the nitrate plume.
Evaluate Land-Farm Phytoremediation	Phytoremediation Land Farm	The land-farm phytoremediation option was evaluated within a 50 meter x 100 meter area. The field experiment was designed to compare effects of different native plant crops and nitrate concentrations in irrigation water on the fate of nitrogen, sulfate, and water in the soil profile.
Reduce Sulfate Levels as Possible	Subpile Soil Phytoremediation Planting and Irrigation Ethanol Injection Test Wells Phytoremediation Land Farm	Effects of the phytoremediation planting in the subpile soils, ethanol injection in the alluvial aquifer, and irrigation of the phytoremediation land farm, on sulfate sequestration and reduction, were evaluated in conjunction with test of remedies for ammonium and nitrate.

A fundamental feature of the pilot studies, and a basis given in the EA for conducting the studies, was the large scale of the field plots and tests. Evaluating the remedies proposed in the EA at an operative scale was an underlying goal. Figure 1 depicts field locations of the pilot studies at the Monument Valley Site on a 2010 satellite image. Table 3 matches pilot studies with their field plot locations and provides brief descriptions of the field methods.

3.1 Control Subpile Soil Water Balance and Percolation

3.1.1 Objective

Enhance native vegetation establishment and evapotranspiration (ET) on source area soils to control the soil water balance, limit deep percolation, and prevent continued leaching of nitrate and ammonium into the alluvial aquifer.

3.1.2 Synopsis

Two native shrubs, fourwing saltbush and black greasewood, dominated the pre-milling vegetation where the New Tailings Pile and Evaporation Pond once stood (Appendix A). Enhancing the reestablishment of the two shrub species in the subpile soils has cut off this source of contamination in the alluvial aquifer (Appendix B).

LM determined the extent of nitrate and ammonium contamination in the subpile soils, evaluated the capacity of natural phytoremediation, delineated an area that would benefit from enhanced phytoremediation, and then planted the entire subpile source area (see *Subpile Soil Phytoremediation Planting* in Figure 1) with fourwing saltbush and a few black greasewood seedlings (Appendix B, Sections B.1 and B.3). Seedling transplants were started in a greenhouse from native seed obtained in the region. Transplants were deficit-irrigated—given less water than they could potentially remove through transpiration—to supplement precipitation and hasten plant growth. By monitoring fractional canopy cover, leaf area index, foliage biomass, and root biomass with depth, LM documented rapid development of deep-rooted fourwing saltbush populations, originating both from transplants in the contamination zone and from plants surrounding the contamination zone that had "volunteered" from seeds produced by the transplants. Black greasewood transplants matured slowly compared to fourwing saltbush transplants. Periodic clipping of the stems of mature fourwing saltbush plants, effectively simulating moderate levels of grazing, stimulated annual regrowth and increased productivity and transpiration.

Observations of transplants growing slowly in areas characterized by chemical soil staining raised concerns about the effectiveness of phytoremediation in those areas and about worker safety (Appendix B, Section B.3 and Appendix G, Section G.2). Results of soil sampling and greenhouse studies provided clues as to the causes of stunted growth, but an effective remedy was not found. The multicolored stains indicated that a heterogeneous mix of chemicals was present. Stained soils from poor-growth areas in the subpile soils were lower in copper and sulfate and higher in iron, magnesium, and calcium, which may have contributed to poor growth by interfering with plant uptake of nutritional ions. In the greenhouse, adding organic matter to stained soil enhanced fourwing saltbush growth, but micronutrient replacement experiments did not reveal any deficiencies. Manganese nodules were also observed, but manganese levels were within the range for natural soils and did not pose an exposure risk to workers at the site. A yellow precipitate observed in the area of the former evaporation ponds contained uranium and vanadium salts, but again levels were much lower than what would pose an exposure risk.

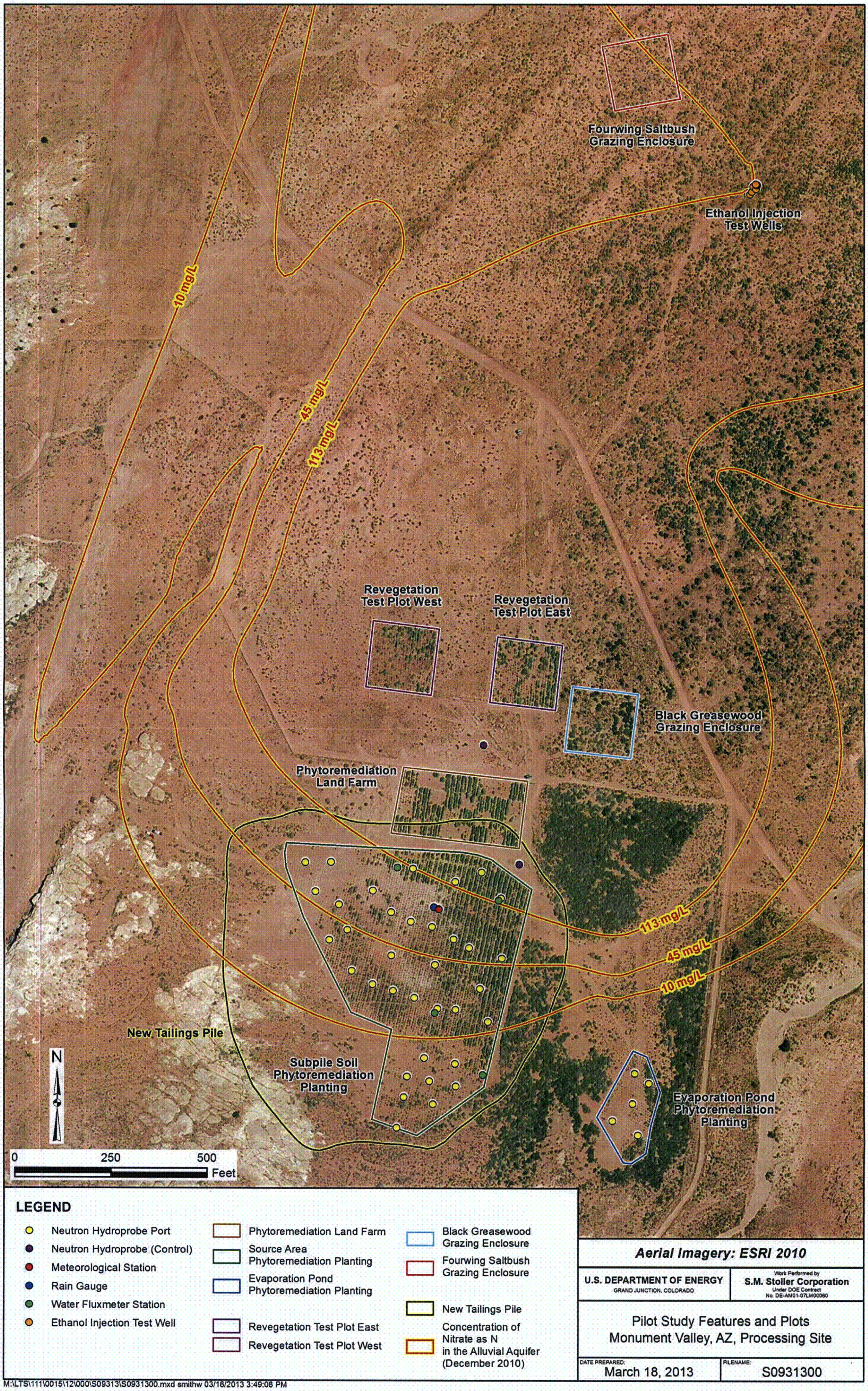


Figure 1. Locations of pilot study plots and wells at the Monument Valley, Arizona, Processing Site

This page intentionally left blank

By monitoring soil moisture profiles and percolation flux rates and by characterizing electrical conductivity and nitrogen isotopes in subpile soil profiles, scientists produced evidence supporting the hypothesis that mature fourwing saltbush and black greasewood plantings were controlling contaminant leaching (Appendix B, Section B.3). Soil moisture profiles, monitored monthly with a neutron thermalization hydroprobe in 40 ports (4.6-m deep) scattered throughout the subpile planting, remained below field capacity at all locations except on the east side where the ports reached groundwater. Results of real-time monitoring of moisture profiles and percolation flux at four locations (using water content reflectometers strung through the profile and water fluxmeters placed at the 3.7-m depth) corroborated the neutron hydroprobe data.

Scientists measured significant percolation flux in a denuded area outside the plantings, evidence of leaching without the plantings, but measured zero percolation within the planting. Electrical conductivity and ^{15}N enrichment data provided ancillary evidence. A decrease in electrical conductivity over time, which was not observed, can indicate leaching of soluble ions. Enrichment of ^{15}N, which was observed, can indicate that a loss of nitrate is due to microbial denitrification (Section 3.2) and not leaching.

3.1.3 Remedy Monitoring and Maintenance

This section describes the methods evaluated for monitoring and maintaining the health of fourwing saltbush and black greasewood plantings and monitoring soil moisture profiles, and that could be continued if phytoremediation is selected as a remedy for the subpile soils. Monitoring data can provide evidence as to whether subpile soils remain cut off and do not again become a source for nitrate and ammonium contamination leaching into the alluvial aquifer.

- The health of subpile soil plantings was evaluated during onsite inspections and/or using remote sensing. Observations of dieback, plant mortality, and changes in species composition were documented during the onsite inspections. Landscape-scale patterns and trends in canopy cover and leaf area index (an index of transpiration capacity) were evaluated using a remote sensing protocol (Appendix E).
- Dead fourwing saltbush and back greasewood plants were replaced with new transplants raised in the greenhouse from locally harvested seed. The ratio of saltbush to greasewood transplants was based on a comparison of observed growth rates, mortality rates, and transpiration requirements as determined from soil moisture data.
- Deficit irrigation of the subpile plantings could be maintained, decreased, or discontinued depending on the observed health of plantings and whether irrigation continues to enhance denitrification (Section 3.2).
- Clipping of fourwing saltbush stems every second or third year, simulating grazing, can stimulate plant growth and transpiration and delay plant mortality.
- Soil moisture profiles and percolation flux were monitored at four locations. This required periodic maintenance of a meteorological station, satellite monitoring stations equipped with water content reflectometers and water fluxmeters, and associated telemetry equipment.
- Soil moisture profiles were monitored at 40 locations using neutron hydroprobes. Historical hydroprobe and water content reflectometer data could be used to choose the appropriate monitoring frequency and seasonality. The neutron hydroprobe was calibrated using barrels filled with Monument Valley fine sand. The calibration accounted for the ranges of bulk density and volumetric moisture values that occur in the subpile soil planting.

- Field water storage capacity of subpile soils can be evaluated using existing water fluxmeters and statistical relationships of soil moisture measured with water content reflectometers and in adjacent neutron hydroprobe ports. Field water storage capacity test results, in combination with moisture profile monitoring, can be used as a basis for managing irrigation rates to ensure that soil water storage remains well below the field capacity.

3.2 Enhance Natural Attenuation in the Subpile Soils

3.2.1 Objective

Remove nitrate and ammonium from source area soils by enhancing natural phytoremediation and bioremediation.

3.2.2 Synopsis

A mixture of phytoremediation, but primarily microbial denitrification enhanced by irrigation, rapidly reduced nitrogen in the subpile soils (Appendix B, Section B.4; see *Subpile Soil Phytoremediation Planting* in Figure 1). Scientists estimated phytoremediation capacity by determining the productivity (annual above-ground biomass production) of fourwing saltbush and black greasewood and by annually sampling for nitrogen and sulfur content in new leaves and stems. Using this approach, scientists estimated that phytoremediation was annually removing about 350 kg of nitrogen and 55 kg of sulfur, a very small fraction of the estimated nitrogen and sulfur present in subpile soils.

Although native shrubs were slowly removing nitrate and ammonium—phytoremediation was indeed working—the phytoremediation capacity was too low to account for the relatively rapid drop in soil nitrogen levels that was measured. Between 2000 and 2010, scientists measured about a 50 percent drop in subpile soil nitrogen levels. Assays of denitrification and ^{15}N enrichment data support the hypothesis that microbial denitrification enhanced by irrigation caused the rapid removal of nitrogen. In the laboratory, Denitrification Enzyme Activity was six times higher and Most Probable Number of Denitrifiers was 20 times higher in irrigated compared to unirrigated subpile soil samples. Nitrous oxide production, the first product of denitrification, was about 30 times higher in irrigated versus unirrigated soil samples. Using assay chambers placed directly over the subpile soil in the field, scientists measured nitrous oxide production rates that were 10 to 20 times higher in irrigated compared to unirrigated soils. Scientists also measured significant enrichment of ^{15}N as soil nitrate levels dropped. Because bacteria preferentially use the more common ^{14}N isotope in their metabolism, including denitrification, residual nitrogen in the soil becomes progressively more enriched in ^{15}N as denitrification proceeds.

Scientists tested the hypothesis that supplying a carbon source through the irrigation system might enhance denitrification (Appendix B, Section B.4.3). Microbial denitrification requires a carbon source to support bacterial growth. The hypothesis was supported in laboratory studies, which indicated that ethanol stimulated more rapid rates of denitrification than other microbial carbon substrates, but was not supported by results of a subsequent field investigation. Ethanol distributed to fourwing saltbush and black greasewood transplants through the irrigation system caused an increase in nitrous oxide (indicating denitrification), but soil nitrate levels remained unchanged. Results indicated that denitrification rates were more influenced by soil moisture—

the wetter the soil the higher the rates—than by adding ethanol. Ethanol made a difference but only in wet soil. Hence, enhancing denitrification in subpile soils becomes a balancing act. Irrigation rates could be increased to stimulate denitrification, but if soil moisture levels exceed field capacity, we risk leaching soil nitrate into the alluvial aquifer (Section 3.1).

Although irrigation produced a significant reduction in soil nitrate and ammonium, such that about half of the total nitrogen was removed over 10 years, removal appeared to follow an exponential decay function (as might be expected for this enzyme-catalyzed process) with removal rates decreasing over time (Appendix B, Section B.4.4). Total nitrogen dropped from about 350 to 180 mg/kg N. Removal rates presumably slowed as soil nitrate and ammonium levels dropped, but also as transplants matured and evapotranspiration rates increased causing soil moisture levels to drop. During years when evapotranspiration dried soils causing nitrification, ammonium levels dropped and nitrate levels increased. Residual nitrate and ammonium are now highest at deeper soil depths. Deeper irrigation might enhance denitrification in these layers, but as indicated above, it might also cause leaching of nitrate into the plume.

Nitrate and sulfate occur naturally in desert soils. Atmospheric deposition, litter decay, and natural leaching in response to wet episodes cause accumulation of soil nitrate over long periods of time. Similarly, accumulation of calcium sulfate (gypsum) occurs when geologic parent materials are high in gypsum, as is the case at Monument Valley. Scientists measured natural levels of nitrate and sulfate in reference area soils for possible use in stipulating subpile soil cleanup levels (Appendix B, Section B.2). Scientists detected a zone of slight nitrate accumulation, no more than 120 µg/g NO_3-N, between about 7 and 9 m deep, and a zone of sulfate accumulation, up to 2,975 µg/g SO_4^{2-}, between about 1.5 and 6 m below the surface.

3.2.3 Remedy Monitoring and Maintenance

The pilot study evaluated options for monitoring nitrogen concentrations and moisture content in subpile soils. Irrigation might be continued if nitrogen concentrations continue to drop in response to a wetter soil. Conversely, irrigation rates might be discontinued when and if denitrification no longer responds to the added moisture.

- To determine if irrigation is continuing to enhance nitrogen loss, subpile soils could be sampled and analyzed for nitrate and ammonium (and sulfate) content and results compared to earlier values. For consistency, field and laboratory procedures developed for the pilot studies could be used.
- Deficit irrigation might be continued if total nitrogen concentrations continue to drop. Irrigation could be discontinued if the monitoring record suggests that nitrogen concentrations have leveled off asymptotically.
- The pilot study produced strong evidence that plant transpiration controlled percolation when the field was deficit-irrigated. Hence, irrigation should not be increased in an effort to enhance denitrification deeper in the soil profile, potentially risking a resumption of nitrogen leaching into the alluvial aquifer.

3.3 Evaluate Natural and Enhanced Phytoremediation of the Alluvial Aquifer

3.3.1 Objective

Evaluate and enhance natural phytoremediation by native phreatophytes rooted in the shallow plume to remove plume nitrogen and, by increasing transpiration, to limit the continued spread of the plume.

3.3.2 Synopsis

The native desert shrubs, black greasewood and fourwing saltbush, which curtailed leaching and helped reduce nitrate and ammonium levels in the subpile soil by controlling percolation (Sections 3.1 and 3.2) were shown by LM scientists to also extract and potentially slow the spread of nitrogen in the alluvial aquifer (Appendix C, Section C.1). Scientists explored the feasibility of plume phytoremediation, first by determining if the two plant species would naturally inhabit the area overlying and root into the plume, and second by estimating rates of plume nitrogen uptake and groundwater transpiration. Scientists then evaluated revegetation (see *Revegetation Test Plot East* and *Revegetation Test Plot West* in Figure 1) and grazing management (see *Black Greasewood Grazing Exclosure* and *Fourwing Saltbush Grazing Exclosure* in Figure 1) as options for enhancing plume phytoremediation.

Sustainable natural groundwater phytoremediation at Monument Valley would require well-adapted populations of native phreatophytes that can continue removing nitrogen and water without human intervention. By applying ecological tools called ordination and gradient analysis, in concert with maps of plume boundaries and depths to groundwater, scientists determined that the historical distributions of black greasewood and fourwing saltbush populations overlapped the plume footprint. This finding supported the premise that restoring these populations would enhance natural phytoremediation. Black greasewood populations dominated plume areas with a shallower depth to groundwater (about 5 to 10 m), and fourwing saltbush populations dominated the areas with a greater depth to groundwater (about 10 to 15 m).

Scientists analyzed stable isotopes of oxygen and hydrogen to test the hypothesis that black greasewood and fourwing saltbush populations were indeed rooted into and extracting water from the contaminated alluvial aquifer. Water molecules consist primarily of the ^{16}O and ^{1}H stable isotopes. Heavier stable isotopes of oxygen (^{18}O) and hydrogen (^{2}H, deuterium, or D) are also naturally present but as minor components of water. Natural hydrological cycling of water tends to alter ratios of the heavier isotopes to the lighter more common isotopes—a process called fractionation. For example, evaporation of water tends to decrease whereas the formation of raindrops tends to increase the ratio of heavier to lighter isotopes of oxygen and hydrogen in water. These fractionation ratios provide a sort of fingerprint for water.

Water in the stems and leaves of plants will have isotope ratios similar to the source of water accessed by the plant roots. For this reason, water "fingerprints" can be used to determine where plants are receiving their water. At the Monument Valley site, water isotope "fingerprints" suggested that wild fourwing saltbush and black greasewood populations were both obtaining most of their water from the top of the contaminated alluvial aquifer but also from the soil just above the aquifer. Black greasewood, an obligate phreatophyte, was more dependent than fourwing saltbush on aquifer water.

Scientists evaluated two options for enhancing plume phytoremediation: (1) revegetation of soils that had been scraped to remove surface contamination and (2) managing or restricting grazing. Excavation of soils contaminated with windblown tailings in the 1990s left a large denuded area overlying the proximal portion of the plume that has the highest nitrate levels. Closely browsed stands of fourwing saltbush and black greasewood overlying other portions of the plume were evidence of a history of heavy livestock use. Early small-plot studies provided evidence that, after about two years of irrigation, fourwing saltbush seedlings transplanted in denuded areas had rooted into the plume. Protecting these transplants from grazing (along with several wild fourwing saltbush and black greasewood plants that had rooted in the plume) greatly increased productivity, transpiration rates, and nitrogen uptake rates.

Given the encouraging results from these small-plot studies, scientists next installed 50 m × 50 m test plots to determine if comparable revegetation and grazing management results were possible on a landscape scale. Results were similar, although less striking. Irrigated transplants grew larger where the depth to the plume was relatively shallow, perhaps because these plants accessed plume nitrogen earlier. Protecting wild fourwing saltbush and black greasewood populations from grazing increased productivity, but not as much as in the small plots. During the course of the large-plot study, overall livestock grazing decreased throughout the area, so moderately grazed shrub populations outside the fenced plots were also healthier than before.

A goal of the plume phytoremediation enhancement pilot studies—revegetation and grazing management—was to increase phreatophyte uptake of plume contaminants. Scientists developed statistical relationships between small-scale sampling of vegetation on the ground and satellite imagery to develop landscape-scale estimates of nitrogen uptake and transpiration rates (Section 4.1). Annual nitrogen uptake rates were estimated from the dry weight of leaves (both species replace their leaves annually), nitrogen content of leaves, and fractional cover of both species as determined from Quickbird satellite images. Wild fourwing saltbush and black greasewood populations protected from grazing removed almost five times more nitrogen per acre than grazed plants. However, because overall uptake rates were relatively modest compared to the total mass of plume nitrogen, scientists turned to the enhancement of microbial denitrification as a second option for plume nitrate (Section 3.4).

Another goal of the plume phytoremediation enhancement studies was to increase phreatophyte transpiration rates—natural pumping of groundwater to the atmosphere—in an effort to slow the spread of the nitrate plume. Similar to the nitrogen uptake study, landscape-scale estimates of transpiration rates were based on statistical relationships between ground-level monitoring of plant transpiration and satellite imagery (Section 4.1). Scientists estimated transpiration rates for individual plants by monitoring stem flow of water using heat dissipation sensors. Landscape-scale transpiration rates were then extrapolated using the fractional cover and leaf area of those plants, and using similar vegetation abundance indices interpreted from satellite images. Past changes in transpiration rates were interpreted from archival satellite images. Results show that as livestock grazing pressure dropped between 2000 and 2010, phreatophyte health, abundance, and transpiration rates increased until annual transpiration exceeded annual precipitation—i.e., discharge from the plume was much greater than potential recharge. Results also show that by 2010, fourwing saltbush and black greasewood stands protected from grazing transpired twice as much water as grazed stands.

Results of groundwater monitoring between 1997 and 2010 (Appendix D) provide ancillary evidence that phytoremediation has the potential to favorably influence plume behavior. Although nitrate levels remained fairly constant, ammonia levels dropped significantly at the plume core in the vicinity of phytoremediation test plots. Nitrate levels dropped significantly along the eastern perimeter of the plume in an area where a mature, dense population of native back greasewood has become more productive in response to the site-wide reduction in livestock grazing. Finally, although the ammonia plume spread little if any over 14 years, the nitrate plume extended noticeably to the north, but only between 1997 and 2007. Between 2007 and 2010, when a drop in livestock grazing improved the health and transpiration rates for native phreatophytes rooted in the plume, the northern expansion of the nitrate plume appeared to have slowed or stopped.

3.3.3 Remedy Monitoring and Maintenance

Results of this pilot study indicate that reductions in plume nitrogen and a slowing of plume dispersion may have been a response to decreasing livestock grazing pressure that improved the productivity and transpiration of phreatophyte populations rooted in the aquifer. This pilot study also evaluated methods for monitoring phreatophyte health that could be used to manage grazing with the goal of continuing enhancing plume phytoremediation.

- The health of fourwing saltbush and black greasewood populations growing over the nitrate plume can be visually evaluated during onsite inspections and/or less frequently using remote sensing. Evidence of grazing pressure, shrub mortality, and changes in species composition can be documented during the onsite inspections. Landscape-scale patterns and trends in canopy cover and leaf area index can be tracked, and nitrogen uptake and transpiration rates calculated, both using the remote sensing protocol (Section 4.1).
- The pilot study ended before LM could test the hypothesis that transplants in the 50 × 50 m revegetation plots overlying the proximal portion of the plume are rooted into and extracting water from the plume (more time was needed for plants to mature). After at least one growing season without irrigation, oxygen and hydrogen isotope fractionation could be used to test this hypothesis.
- The pilot study demonstrated how grazing management can enhance plume phytoremediation in the area overlying the plume. On an landscape scale, managing the seasonality of grazing of fourwing saltbush and black greasewood would further enhance plant growth, transpiration, and nitrogen uptake. Moderate grazing of fourwing saltbush during the dormant season also increases biomass productivity.
- With an understanding of the influence of livestock grazing on phreatophyte health and abundance, LM could project effects of different grazing management scenarios on phreatophyte transpiration rates, plume water balance, plume migration, phreatophyte uptake of nitrogen, and plume nitrogen levels.

3.4 Evaluate Natural and Enhanced Denitrification in the Alluvial Aquifer

3.4.1 Objective

Characterize natural attenuation processes acting to reduce contaminant levels in the shallow and deeper portions of the alluvial aquifer and investigate options for enhancing denitrification.

3.4.2 Synopsis

A combination of solute-transport modeling, microcosm experiments, and nitrogen isotope fractionation analysis provided evidence that natural attenuation in the alluvial aquifer is controlled primarily by microbial denitrification (Appendix C, Section C.2.1). Scientists demonstrated the use of ethanol and methanol (see *Ethanol Injection Test Wells* in Figure 1), to significantly enhance denitrification in the alluvial aquifer and demonstrate the potential to rapidly attenuate nitrate where plume concentrations are highest (Appendix C, Section C.2.2). Modeling results also supported the feasibility of enhanced denitrification of "hot spots" given the relatively highly saturated hydraulic conductivity of the aquifer. Conversely, groundwater monitoring data (Appendix D) suggest that preferential flow may occur in at least parts of the aquifer, possibly complicating efforts to disperse ethanol within hot spots (Appendix E).

Scientists first characterized the capacity of naturally occurring processes acting to attenuate nitrate in the alluvial aquifer. Natural denitrification, if occurring rapidly enough, would provide a passive remedy for the nitrate plume to complement natural phytoremediation (Section 3.3). Natural denitrification gradually converts nitrate to innocuous nitrogen and nitrous oxide gases. Scientists evaluated the occurrence and rates of natural microbial denitrification through microcosm experiments, nitrogen isotopic fractionation analysis, and solute-transport modeling. The microcosm studies used water extracted from the plume to show, based on the fractionation of nitrogen isotopes, that natural microbial denitrification was indeed occurring. Denitrifying bacteria prefer the lighter ^{14}N isotope. The heavier ^{15}N isotope accumulated in residual nitrate as a microcosm experiment progressed, providing clear evidence that microbial denitrification was occurring.

With laboratory evidence in hand, scientists then estimated rates of denitrification in the plume by comparing nitrogen concentrations and fractionation in samples from several wells along the centerline of the plume. Enrichment of plume nitrate with the heavier ^{15}N isotope increased significantly with distance away from the plume source, showing that microbial denitrification is a major attenuation process. Geochemical data—changes in concentrations of ammonia, dissolved oxygen, and nitrate in wells along the plume centerline gradient—corroborated the isotope fractionation evidence. Scientists used the microcosm experiment results and well monitoring data to calibrate groundwater flow and solute-transport models. The numerical models were used to simulate rates of natural attenuation, including microbial denitrification, in the nitrate plume. LM could use denitrification rate coefficients derived from the pilot studies to project time periods for natural attenuation of nitrate in the alluvial aquifer.

Although the multiple lines of evidence indicate that natural attenuation is occurring and may eventually clean up the nitrate plume over time, groundwater monitoring data provide evidence of complexity in the groundwater system and, hence, uncertainty in projections of clean up times (Appendix D). While nitrate levels have dropped along the plume edge since 1997, nitrate concentrations along the plume axis have remained relatively constant or are increasing. Nitrification may well be the reason. Nitrification, the natural conversion of ammonia in the aquifer to nitrate, may be offsetting denitrification. Geochemical analyses in combination with monitoring data give evidence of simultaneous nitrification and denitrification. Dissolved oxygen content has decreased over time, primarily in the distal portions of the plume (nitrification requires oxygen). Whereas nitrate levels are increasing distally, ammonia levels are dropping in the plume core, and the nitrate plume extends farther from the source than the ammonia plume, all of which would be expected if nitrification is occurring. With evidence of offsetting nitrification and denitrification, scientists investigated options for enhancing and accelerating nitrate attenuation (Appendix C, Section C.2.2).

Groundwater flow and solute transport modeling supported the premise that enhancement efforts should focus on denitrification rather than other attenuation processes such as sorption, dispersion, or dilution. Results of a suite of laboratory experiments further supported the addition of a carbon substrate to enhance denitrification. Ethanol additions increased denitrification rates by two orders of magnitude in the laboratory. Methanol also increased denitrification, but at a slightly slower rate than ethanol.

Scientists next conducted two pilot-scale field tests to evaluate the efficacy of injecting ethanol directly into the alluvial aquifer to enhance denitrification. The first test was performed in 2010 using a push-pull injection method and the second, larger scale test was performed in 2011 using a single-well injection method with several downgradient monitoring wells. Both tests were conducted in an area of high nitrate concentration in the plume. For the push-pull test, a 5 percent solution of ethanol in plume water was injected in a well, additional plume water was added to *push* the ethanol solution into the aquifer immediately surrounding the well, and after a period of incubation, groundwater was *pulled* (or pumped) for analysis. The second, single-well injection test, conducted a year later, was designed to mimic the basic approach that would be used for a possible full-scale application. Ethanol was injected in an upgradient well, and then changes in nitrate and other constituents in the injection well and in six downgradient monitoring wells were used to estimate the effective reaction in front velocity and nitrate rebound.

For both tests, nitrate decreased by three orders of magnitude—to below the analytical detection limit—in the vicinity of the injection zones, and these low concentrations persisted for many months. The production of nitrous oxide, occurrence of nitrogen isotope fractionation, production of nitrogen gas bubbles, and observed changes in other redox-sensitive species are evidence that decreases in nitrate were caused by microbially mediated denitrification. For the single-well injection test, scientists estimated the advance of the reaction front, as detected in the downgradient monitoring wells, at roughly 0.1 to 0.17 m per day. Low nitrate concentrations persisted in injection and downgradient monitoring wells with little or no rebound—for more than 20 months in the push-pull injection well—despite the continued influx of high-nitrate groundwater that would eventually displace residual ethanol. Scientists hypothesized that this persistent denitrification may be attributable to die-off of bacterial populations as a carbon source.

Results of the ethanol injection tests are consistent with other project data. The estimated reaction front velocities are within ranges of pore water velocities expected based on the reported groundwater hydraulic conductivities and gradient. Rates of enhanced denitrification in the ethanol injection tests were similar to the earlier laboratory experiments using ethanol. Moreover, ethanol-induced denitrification rates were about 50 times greater than natural denitrification rates as determined using geochemical analysis, isotope fractionation, and numerical modeling.

3.4.3 Remedy Monitoring and Maintenance

The results of the natural and enhanced denitrification pilot studies will be used to select and implement alternative remedies proposed in the EA for the alluvial aquifer. Natural denitrificaiton is occurring. The enhanced denitrification pilot study could be used to plan a larger scale denitrification treatment system for nitrate hot spots in the alluvial aquifer. This option is based on the combined results of groundwater monitoring and the pilot studies discussed above. Groundwater monitoring records provide evidence that the improved health of phreatophyte populations has slowed the spread of the nitrate plume, and multiple methods show that significant natural denitrification is occurring. However, groundwater monitoring data also show that plume nitrate concentrations have changed little in 15 years, possibly because of ongoing nitrification. A larger scale enhanced denitrification could potentially increase groundwater nitrate reduction rates fifty-fold.

- The pilot studies indicate that natural denitrification is occurring. Groundwater could continue to be monitored using the existing wells to determine if, over time, natural denitrification is adequate.
- If rates of natural denitrification are not deemed to be adequate, pilot study results could be used to enhance denitrification by injecting either ethanol or methanol. Nitrate concentrations in the injection and monitoring wells used for the ethanol injection pilot study could be periodically resampled, as appropriate, to determine nitrate rebound rates, and the results could be used to design a larger scale enhanced denitrification treatment system.
- The ethanol injection pilot study results, groundwater nitrogen isotope fractionation results, groundwater flow and solute transport modeling, and the most current groundwater monitoring data could be used to design well locations, well spacing, ethanol or methanol concentrations, volume, injection procedures, and monitoring procedures for an enhanced denitrification system.
- Groundwater monitoring well selection and sampling frequencies could be optimized, and additional monitoring wells could be installed as needed to (1) improve groundwater monitoring efficiency, (2) improve LM's understanding of the effects of enhanced phytoremediation and microbial denitrification on plume dynamics, and (3) better project the groundwater cleanup time.

3.5 Evaluate Land-Farm Phytoremediation

3.5.1 Objective

Evaluate land-farm phytoremediation, an active remedy option that involves pumping and irrigating a crop of native plants with nitrate-contaminated groundwater.

3.5.2 Synopsis

The land-farm phytoremediation pilot study (see *Phytoremediation Land Farm* in Figure 1) was designed to evaluate an active remediation option (Appendix E). At the Monument Valley site, the land farming option, a type of pump-and-treat remedy, involved pumping and piping plume water from the alluvial aquifer and irrigating fields of native transplants with the nitrate-contaminated groundwater. Land-farm phytoremediation could be used as an option for both the shallower and deeper portions of the aquifer.

Scientists first evaluated the *feasibility* of irrigating a native shrub crop with nitrogen-contaminated groundwater (Appendix E, Section E.1). The feasibility study characterized rangeland conditions and trends, classified irrigable land, considered possible grazing management options, and used greenhouse studies to evaluate crop growth, nitrogen uptake, forage quality, phytotoxicity, and the potential for contaminating land-farm soils. Results of the feasibility study supported a plan to install the land-farm pilot study.

Scientists designed a factorial field experiment to evaluate native crops, irrigation methods, nitrogen application rates, and the fate of nitrogen and sulfate after irrigation (Appendix E, Section E.2). Overall, results of the experiment indicated that a land farm with a crop of native fourwing saltbush shrubs may work well as a backup remedy for the plume if other remedies prove to be insufficient. Fourwing saltbush thrived when irrigated with plume water. Plant uptake and soil denitrification kept nitrate levels from building up in the land-farm soil; plant transpiration limited recharge and leaching of nitrate and ammonia back into the aquifer; sulfate pumped from the plume was sequestered in the soil profile, most likely as gypsum (calcium sulfate); and the farm produced forage that is safe for livestock or as a native seed crop that could be used by the Navajo Nation for rangeland seeding or mine land reclamation.

3.5.3 Remedy Monitoring and Maintenance

This section highlights monitoring and maintenance activities that may be necessary, based on the results of the pilot study, if LM implements land-farm phytoremediation as a remedy for the deep alluvial aquifer at the Monument Valley Site.

- The feasibility of extracting plume water over an extended period of time, as would be needed for a land farm, could be evaluated by testing the production of wells and the behavior (e.g., drawdown) of groundwater in response to pumping.
- The size of the land farm was designed to be expanded or reduced as needed. Study plots originally planted with black greasewood, which grew poorly during the study, could be planted with fourwing saltbush, which grew vigorously. The irrigation system, designed to supply different concentrations of nitrate during the study, could be simplified to uniformly apply plume water over the farm.
- Operating a land farm would require routine maintenance of the extraction wells, irrigation system, and plantings. Maintaining the plantings could involve periodic clipping or livestock grazing of fourwing saltbush foliage to stimulate regrowth and replacement of dead or dying plants.
- The pilot studies developed several methods that could be used to monitor a phytoremediation land farm: (1) remote sensing of plant cover and leaf area (Section 4.1 and Appendix F), (2) monitoring soil moisture profiles relative to field capacity (to prevent leaching of nitrate back into the aquifer) using existing neutron hydroprobe ports (Section 3.1 and Appendix B), and (3) periodic sampling of nitrogen and sulfate levels in land-farm soil profiles (Section 3.1 and Appendix B).

3.6 Reduce Sulfate Levels as Possible

3.6.1 Objective

To the extent that is practical, reduce sulfate concentrations in the alluvial aquifer and sequester as soil sulfate in concert with remedies developed for groundwater nitrogen contamination.

3.6.2 Synopsis

Although no EPA groundwater standards have been established under 40 CFR 192 for sulfate, the 2005 EA discusses the need to reduce sulfate concentrations in the shallower and deeper portions of the alluvial aquifer, and in the subpile soils, in an effort to achieve a remediation goal, as stated in the SOWP, as either 250 mg/L (the proposed Navajo Nation cleanup goal) or a sulfate-to-chloride ratio of 10.0 (DOE 1999). Groundwater monitoring over the past 15 years shows that groundwater sulfate concentrations are indeed dropping (Appendix D). Pilot study results provide evidence that options for enhancing natural phytoremediation and bioremediation of nitrate in the alluvial aquifer (Appendix C) and subpile soils (Appendix B) and active land-farm phytoremediation of nitrate (Appendix E), would also reduce sulfate levels.

Although sulfate is naturally present in soils and groundwater at the Monument Valley site (Appendix B, Section B.2), the former New Tailings Pile is thought to be the major source of sulfate downgradient in the alluvial aquifer (DOE 1999). Soluble gypsum (calcium sulfate) as sampled in the vadose zone above the sulfate plume likely accumulated over hundreds to thousands of years as rainwater leached naturally sulfate-rich eolian and fluvial sediments. Elevated sulfate levels found in the alluvial aquifer upgradient of the former New Tailings Pile may have originated in the Moenkopi Formation, a steeply dipping red sandstone high in gypsum. Concentrations greater than 100 μg/g occurred in almost all borings with a maximum concentration of 2,975 mg/kg. The highly variable upgradient sulfate levels can be attributed to many factors, including upwelling of artesian water from the DeChelley formation, variable surface water chemistries, and different well screening depths.

Enhanced phytoremediation pilot studies in the subpile soils (the former New Tailings Pile) have cut off the source of mill-related sulfate in the alluvial aquifer. As described in Section 3.1, by monitoring the soil water balance, scientists demonstrated how transpiration from mature plantings of native fourwing saltbush has controlled leaching of contaminants from source area soils. Groundwater monitoring data support this conclusion (Appendix D). Sulfate levels in monitoring wells just downgradient of the source area dropped by more than half between 1998 and 2011. Furthermore, scientists learned that as the fourwing saltbush plantings remove nitrogen from source area soils, they are also slowly depleting sulfate (Appendix B).

Pilot study results show that enhanced phytoremediation and bioremediation could remove and slow the spread of sulfate in the alluvial aquifer (Appendix C). Groundwater monitoring data suggest that sulfate hot spots have migrated downgradient over the past 15 years (Appendix D). As transpiration by native phreatophytes increased in response to better grazing management, the northern spread of the sulfate plume slowed. Slowing plume dispersion could increase the effectiveness of enhanced bioremediation of plume hot spots. The enhanced denitrification pilot study provided evidence that injection of ethanol in plume hot spots reduces both nitrate and sulfate concentrations. In both the push-pull and single well injection tests (Section 3.4), scientists measured significant drops in groundwater sulfate levels coincident with drops in nitrate, along with significant increases in hydrogen sulfide, suggesting that ethanol enhanced sulfate reduction as well as denitrification.

Finally, scientists designed the land-farm phytoremediation option to provide sustainable remediation of sulfate as well as nitrate (Section 3.5). Results of the land-farm pilot study produced evidence that sulfate in irrigation water pumped from the plume had accumulated in the soil profile, probably sequestered as gypsum. Sequestration of gypsum in land-farm soil is analogous to the natural formation of gypsiferous soils that occur in the area (Appendix B, Section B.2).

3.6.3 Remedy Monitoring and Maintenance

The pilot studies indicate that options evaluated for reducing nitrogen in the alluvial aquifer and source area at Monument Valley—natural attenuation, enhanced attenuation, and land farming—also reduce sulfate levels. The pilot studies produce the following information that could be used for monitoring and maintaining remedies that reduce sulfate:

- Upgradient sulfate concentrations in the alluvial aquifer could be used as a reasonable cleanup target for sulfate plume in the alluvial aquifer.
- Monitoring as described in Sections 3.1 and 3.2 and Appendixes B and C could be used to verify that subpile soil water content remains below the storage capacity and to determine if sulfate levels in subpile soils are changing.
- Natural attenuation of sulfate could be monitored using the existing well network (Appendixes C and D).
- Well selection and sampling frequencies for groundwater monitoring could be optimized to better track and project sulfate as well as nitrate plume dynamics.
- Levels of sulfate sequestered as gypsum in a land-farm soil profile could be monitored as described in Appendix E.

4.0 Conclusions

Results of the pilot studies at the Monument Valley, Arizona, Processing Site provide the information needed to select and implement the compliance strategies proposed in the EA (2005) for ammonium, nitrate, and sulfate in the alluvial aquifer. The EA proposed compliance strategies consisting of sequences or combinations of passive and active remediation for three components of the alluvial aquifer: subpile soils, shallow alluvial aquifer, and deep alluvial aquifer. Passive remedies included natural and enhanced phytoremediation and denitrification. The active remedy was land-farm phytoremediation. Table 4 provides summaries of pilot study results for each remedy evaluated. The EA also proposed a decision framework to use results of the pilot studies to guide the selection of remedies for each of the three components of the alluvial aquifer. LM will prepare a GCAP to document the final selection of compliance strategies.

4.1 Subpile Soils

The pilot studies evaluated enhanced phytoremediation and enhanced denitrification as remedies for the subpile soils. DOE considered the subpile soils, the soils remaining in the footprint of the New Tailings Pile after tailings were removed, to be a continuing source for contamination in the alluvial aquifer. The pilot study results show that an irrigated field of native shrubs has cut off the subpile soils as a source for the groundwater plume and that microbial denitrification, enhanced by irrigation, has rapidly reduced nitrogen levels in the soils.

The subpile soil area was planted with two native shrubs: fourwing saltbush and black greasewood. After the shrubs matured, plant transpiration removed precipitation stored in the soil and, in so doing, limited percolation, isolating the subpile source from the plume. Plants were deficit-irrigated—given less water than they could transpire under normal conditions. Five years after planting, a mature plant community consisting mostly of fourwing saltbush had established in the subpile soil, and multiple lines of evidence confirmed that plant transpiration was controlling percolation and seepage of contaminants into the plume.

Native shrubs are also slowly removing nitrate and ammonium from subpile soils but not fast enough to account for an initially rapid drop in soil nitrogen levels. The pilot studies confirmed that irrigation-enhanced microbial denitrification had caused the rapid drop in soil nitrogen. Scientists tested the hypothesis that supplying a carbon source through the irrigation system might also enhance denitrification in the subpile soils. This hypothesis was supported by a laboratory study but not supported by results of a subsequent field investigation.

Monitoring of plant health and soil water and maintenance of plantings and the irrigation system, at some level, may be necessary to assure continued isolation of the subpile source. Monitoring may also be necessary to determine whether deficit irrigation is continuing to enhance denitrification.

Table 4. Application of Pilot Study Results to Remedies Proposed in the EA (DOE 2005)

Area	Contaminants	Remedies Evaluated	Pilot Study Results
Subpile Soils	Ammonium, Nitrate	Enhanced Phytoremediation	A mature planting of native desert shrubs controlled the soil water balance, prevented percolation, and cut off the subpile as a source of contamination. Plants removed only small amounts of nitrogen and sulfate from the subpile soil. Monitoring and maintenance may be necessary to assure continued isolation of the subpile soil as a source.
		Enhanced Denitrification	Deficit irrigation (evapotranspiration > irrigation + precipitation) enhanced denitrification and removed half of total subpile soil nitrogen in five years. Future irrigation may or may not continue to enhance denitrification. Supplying carbon sources enhanced denitrification in lab tests but not in the field study.
Shallow Aquifer	Nitrate, Sulfate	Natural and Enhanced Phytoremediation	Native phreatophytes naturally transpired alluvial aquifer water and, evidently, hydraulically slowed plume dispersion. Native phreatophytes removed only small amounts of nitrogen and sulfate from the aquifer. Revegetation of denuded areas and management of grazing in other areas overlying the plume would greatly increase transpiration, enhancing hydraulic control. A remote sensing protocol was developed that can be used to monitor phreatophyte productivity, transpiration rates, and nitrogen and sulfate extraction rates. Remote sensing was also used to monitor subpile soil and land-farm phytoremediation. (see Pilot Study Results for Subpile Soils and the Deep Aquifer.)
		Natural and Enhanced Denitrification	First-order denitrification rate coefficients were comparable when calculated with laboratory microcosm experiments, field isotope fractionation analysis, and solute transport modeling. Microbial denitrification primarily controls nitrate attenuation in the alluvial aquifer. First-order denitrification rate coefficients could be used to project natural attenuation rates. Ethanol increased denitrification rates by 2 orders of magnitude in microcosm experiments. Methanol also increased denitrification but at a slightly slower rate. For field well tests of ethanol injection in a high-nitrate portion of the aquifer, nitrate levels dropped to below detection limits in both the injection wells and the downgradient observation wells with little or no rebound for at least 20 months. Ethanol injection also greatly increased rates of sulfate reduction.
Deep Aquifer	Nitrate, Sulfate	Natural Attenuation	First-order denitrification rate coefficients could be used to project natural attenuation rates in the deep aquifer as well as the shallow aquifer. Enhancement of denitrification by adding carbon substrates in injection wells may also apply to the deep aquifer (see above Pilot Study Results for Natural and Enhanced Denitrification of the Shallow Aquifer.)
		Land-Farm Phytoremediation	Land-farm phytoremediation is an active remedy. Native shrub crops were irrigated with high-nitrate water from the alluvial aquifer. Fourwing saltbush shrubs thrived on high-nitrate water; plant uptake and soil denitrification kept nitrate levels from building up in the land-farm soil; plant transpiration limited recharge and leaching of nitrate and ammonia back into the aquifer; sulfate pumped from the plume was sequestered in the soil profile, most likely as gypsum; and the farm produced a native plant seed crop and forage that is safe for livestock. Land-farm phytoremediation may also apply to the shallow aquifer.

4.2 Shallow Alluvial Aquifer

The EA (DOE 2005) defined the shallow alluvial aquifer as alluvial groundwater "where the depth to the water table is less than 50 feet below the land surface." The pilot studies evaluated natural and enhanced phytoremediation, and natural and enhanced denitrification, as remedies for the shallow alluvial aquifer. The pilot studies also developed a remote sensing protocol for monitoring phytoremediation of the alluvial aquifer. The protocol was also used to monitor subpile soil and land-farm phytoremediation (Sections 5.1 and 5.3).

Populations of the two native shrubs that dominated the pre-milling ecology of the site, fourwing saltbush and black greasewood, grow over large portions of the nitrate plume. These populations have been historically heavily grazed and were in poor health at the onset of the studies. Another large area overlying a high-nitrate portion of the plume was denuded during the surface remediation. The pilot studies demonstrated that these phreatophytic shrubs are naturally rooted in the plume, extracting a small percentage of plume nitrogen and sulfate, and transpiring enough plume water to hydraulically slow plume dispersion. Enhanced phytoremediation entailed preventing grazing of test-plot stands in poor health and revegetating test plots in the denuded area. In areas excluded from grazing, and potentially in revegetated plots, transpiration rates increased up to six fold. Over the course of the pilot studies, the health of native populations outside the test plots also improved in response to better grazing management in the area, evidently slowing or nearly stopping plume dispersion. Even though nitrogen and sulfur uptake rates also increased, plants removed only a small percentage of these plume contaminants.

Several methods for characterizing the occurrence and rate of natural nitrate attenuation in the alluvial aquifer were tested. Spatial and temporal nitrate concentration data collected from a transect of monitoring wells located along the plume centerline were analyzed to evaluate the overall rates of natural attenuation. The occurrence and rate of denitrification were evaluated through microcosm experiments, nitrogen isotopic fractionation analysis, and solute-transport modeling. First-order denitrification-rate coefficients calculated with each method were comparable. In addition, the composite natural attenuation rate coefficient was similar to the denitrification-rate coefficients, which suggests that microbially induced decay primarily controls nitrate attenuation in the aquifer.

In microcosm experiments, ethanol additions to alluvial aquifer water increased denitrification rates by two orders of magnitude. Methanol also increased denitrification but at a slightly slower rate. Injection of ethanol in a high-nitrate portion of the aquifer dropped nitrate levels to below detection limits in the injection wells and in downgradient observation wells. As the concentration of nitrate decreased, the concentration of nitrous oxide (a product of denitrification) increased. Results of compound-specific stable isotope analysis indicated that the nitrate concentration reductions were biologically mediated. In addition, changes in aqueous concentrations of sulfate, iron, and manganese indicated that the ethanol amendment caused a change in prevailing redox conditions; hence, sulfate concentrations also decreased. Denitrification rate coefficients estimated for the pilot tests were approximately 50 times larger than non-enhanced values. Nitrate concentrations in the injection zone remained at levels three orders of magnitude below the initial values for at least 20 months, indicating that the ethanol amendments had a long-term impact on the local subsurface environment.

4.3 Deep Alluvial Aquifer

The EA (DOE 2005) defined the deep alluvial aquifer as alluvial groundwater "where the water table is generally more than 50 feet below the land surface." Passive phytoremediation is not an option because the deep alluvial aquifer is below the rooting depth of native phreatophytes. Natural and enhanced denitrification, as described for the shallow alluvial aquifer (Section 5.2) are options. LM evaluated land-farm phytoremediation "as an active remediation option if natural and enhanced attenuation processes are inadequate" for the deeper alluvial aquifer, as directed in the EA (DOE 2005). Land-farm phytoremediation is also an option for the shallow alluvial aquifer.

Land-farm phytoremediation, a type of pump-and-treat remedy, involves irrigating plantings of native shrubs with nitrate-contaminated groundwater pumped from the alluvial aquifer. Results of a factorial field experiment demonstrated that a land farm with a crop of native fourwing saltbush shrubs may work well as a backup remedy for the plume if other remedies prove to be insufficient. Fourwing saltbush thrived when irrigated with plume water. Plant uptake and soil denitrification kept nitrate levels from building up in the land-farm soil; plant transpiration limited recharge and leaching of nitrate and ammonia back into the aquifer; sulfate pumped from the plume was sequestered in the soil profile, most likely as gypsum (calcium sulfate); and the farm produced a native plant seed crop and forage that is safe for livestock. Monitoring and maintenance of an operational land farm could include (1) the effects of extracting plume water over an extended period of time on extraction well production and drawdown, (2) maintenance of the extraction and irrigation system, (3) maintenance of the plantings, and (4) monitoring of plant health, soil moisture profiles, and soil nitrogen and sulfate levels.

5.0 References

DOE (U.S. Department of Energy), 1989. *Environmental Assessment of Remedial Action at the Monument Valley Uranium Mill Tailings Site, Monument Valley, Arizona*, Final, UMTRADOE/AL-0368, prepared by U.S. Department of Energy, UMTRA Project Office, Albuquerque, New Mexico.

DOE (U.S. Department of Energy), 1996. *Final Programmatic Environmental Impact Statement for the Uranium Mill Tailings Remedial Action Ground Water Project*, DOE/EIS-0198, Grand Junction Projects Office, Grand Junction, Colorado.

DOE (U.S. Department of Energy), 1998. *Monument Valley Ground Water Remediation Work Plan: Native Plant Farming and Phytoremediation Pilot Study,* U.S. Department of Energy Grand Junction Office, Grand Junction, Colorado, August.

DOE (U.S. Department of Energy), 1999. *Final Site Observational Work Plan for the UMTRA Project Site at Monument Valley, Arizona*, MAC-GWMON 1.1, U.S. Department of Energy Grand Junction Office, Grand Junction, Colorado, April.

DOE (U.S. Department of Energy), 2000. *Draft Evaluation of the Active Remediation Alternatives for the Monument Valley, Arizona, UMTRA Project Site*, GWMON 10.6, U.S. Department of Energy Grand Junction Office, Grand Junction, Colorado, June.

DOE (U.S. Department of Energy), 2002. *Phytoremediation of Nitrogen Contamination in Subpile Soils and in the Alluvial Aquifer at the Monument Valley, Arizona, Uranium Mill Tailings Site*, GJO-2002-312-TAR, UMTRA Ground Water Research Project, U.S. Department of Energy Grand Junction Office, Grand Junction, Colorado.

DOE (U.S. Department of Energy), 2004a. *Monument Valley Ground Water Remediation Pilot Study Work Plan: Monitored Natural Attenuation, Enhanced Attenuation, and Land Farming Pilot Studies*, DOE-LM/GJ757-2004, Office of Legacy Management, U.S. Department of Energy, Grand Junction, Colorado.

DOE (U.S. Department of Energy), 2004b. *Phytoremediation of the Nitrogen-Contaminated Subpile Soil at the Former Uranium Mill Tailings Site in Monument Valley, Arizona: 2004 Status Report*, DOE-LM/GJ768-2004 (ESL-RPT-2004-07), Environmental Sciences Laboratory, U.S. Department of Energy, Grand Junction, Colorado.

DOE (U.S. Department of Energy), 2005. *Environmental Assessment of Ground Water Compliance at the Monument Valley, Arizona, Uranium Mill Tailings Site, Final*, DOE/EA 1313, U.S. Department of Energy, Office of Legacy Management, Grand Junction, Colorado.

DOE (U.S. Department of Energy), 2006. *Soil and Ground Water Phytoremediation Pilot Studies at Monument Valley, Arizona: 2005 Status Report*, DOE-LM/1254-2006, U.S. Department of Energy Office of Legacy Management, Grand Junction, Colorado.

DOE (U.S. Department of Energy), 2007. *Natural and Enhanced Attenuation of Soil and Ground Water at Monument Valley, Arizona, and Shiprock, New Mexico: 2006 Status Report*, DOE-LM/1428, U.S. Department of Energy Office of Legacy Management, Grand Junction, Colorado.

DOE (U.S. Department of Energy), 2008. *Natural and Enhanced Attenuation of Soil and Groundwater at Monument Valley, Arizona, and Shiprock, New Mexico, DOE Legacy Waste Sites: 2007 Pilot Study Status Report*, LMS/MON/S04243, U.S. Department of Energy Office of Legacy Management, Grand Junction, Colorado.

DOE (U.S. Department of Energy), 2009. *Natural and Enhanced Attenuation of Soil and Ground Water at Monument Valley, Arizona, and Shiprock, New Mexico: 2008 Status Report*, LMS/MON/S04243, U.S. Department of Energy Office of Legacy Management, Grand Junction, Colorado.

Glenn, E.P., W.J. Waugh, J. D. Moore, C. McKeon, and S. Nelson, 2001. Evaluation of revegetation methods at an abandoned uranium mill site on the Colorado Plateau, Arizona. *Journal of Environmental Quality* 30:1154-1162.

Waugh, W.J., E.P. Glenn, P.H. Charley, B. Maxwell, and M.K. O'Neill. 2011. *Helping Mother Earth Heal: Dine' College and Enhanced Natural Attenuation Research at U.S. Department of Energy Uranium Processing Sites on Navajo Land.* In: Burger, J. (ed.) Stakeholders and Scientists: Achieving Implementable Solutions to Energy and Environmental Issues. Springer, New York.

Appendix A

Monument Valley, Arizona, Processing Site: Background Information

This page intentionally left blank

Contents

Figures

This page intentionally left blank

This Appendix provides a summary of background information for the Monument Valley processing site compiled from DOE reports and other literature. The information was necessary to formulate pilot study objectives, develop experimental designs and methods, and interpret results. Included are (1) the history of milling and remediation at the Site, (2) regulatory requirements and guidance, (3) stakeholder participation, and (4) descriptions of the environmental setting with pertinent information on soils, hydrogeology, and plant ecology.

This Appendix also provides a brief description of monitored natural and enhanced attenuation (MNEA) concepts. Natural attenuation research gained momentum in the 1990s as an alternative to conventional engineering approaches for soil and groundwater remediation. Enhanced attenuation research followed in the 2000s. The concepts involve (1) efforts to characterize and gain an understanding of naturally occurring processes that act to transform, sequester, and slow migration of contaminants in soil and groundwater, (2) evaluations of ways to enhance or accelerate those processes, and (3) tools for monitoring natural attention.

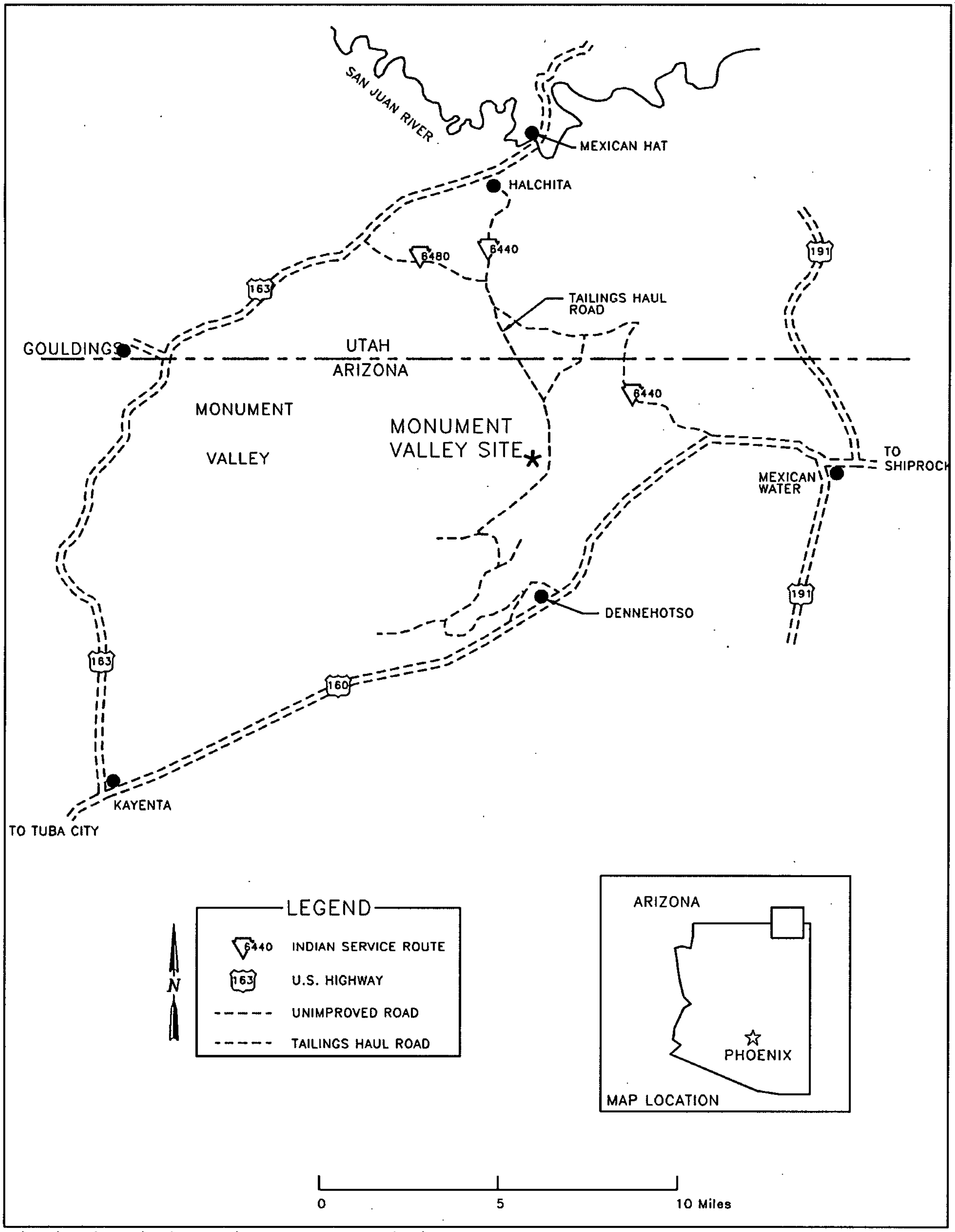
LM investigated two natural attenuation processes at Monument Valley: phytoremediation and microbial denitrification. Phytoremediation relies on plants to extract, transform, and contain contaminants. Unlike typical applications in more mesic environments that use introduced trees such as hybrid poplars, the Monument Valley pilot studies focused on the role of native desert shrubs rather than introducing non-native plants. Similarly, microbial denitrification studies at Monument Valley involved indigenous microorganisms to transform nitrate in both soil and groundwater.

The Monument Valley, Arizona, Processing Site is located on the Navajo Nation in northeastern Arizona, 24 kilometers (km) south of Mexican Hat, Utah, and about 21 km east of the scenic Monument Valley Tribal Park (Figure A–1). The nearest town is Dennehotso, about 8 km to the south. The site is on the west side of Cane Valley Wash at an elevation of approximately 1,460 meters (m) above sea level, and is bordered on the west by Yazzie Mesa and on the east by Comb Ridge, the most prominent topographic feature in the area (Figure A–2).

A.1 History

Uranium was first discovered in 1942 approximately 1 km west of the site. An estimated 696,000 metric tons of uranium and vanadium ore were mined from the deposit between 1943 and 1968 when the mill closed and the lease with the Navajo Nation expired. From 1955 until 1964, ore was processed by mechanical milling, using an upgrader to crush the ore and separate it by grain size, followed by chemical flocculation. The finer-grained material, higher in uranium content, was shipped to other mills such as the one at Shiprock, New Mexico, for chemical processing. Coarser-grained materials were stored onsite in the Old Tailings Pile. Figure A–3 is an early photograph of the mill site.

From 1964 until 1968 an estimated 998,000 metric tons of tailings and low-grade ore were processed using batch and heap leaching. Uranium and vanadium were batch-leached by flowing sulfuric acid solution through sandy tailings placed in lined steel tanks. Heap leaching consisted of percolating a sulfuric acid solution through crushed, low-grade ore spread on polyethylene sheeting. Both operations used ammonia, ammonium nitrate, and quicklime (calcium oxide) to produce a bulk precipitate of concentrated uranium and vanadium. The tailings and processing solutions were discharged to the New Tailings Pile and the Evaporation Pond downslope from



M:\LTS\111\0015\02\S01318\U0131800.DWG 07/30/04 10:40am J50191

Figure A–1. Location map of the Monument Valley Processing Site.

Modified from the USGS 15' Dennehotso, Arizona, topographic map, 1952 ed.

0 1 2 miles

Explanation	
═══	Improved Graded Road
········	Unimproved Road
—×—×—	Fenced Site Boundary

m:\lts\111\0015\02\s01319\s0131900.cdr

Figure A–2. Regional topography of the Monument Valley Processing Site.

Figure A–3. Photograph of the Monument Valley mill in about 1960.

the processing area. The mill closed in 1968, and most of the mill buildings were removed shortly thereafter. The footprints of the New Tailings Pile (the primary source area for alluvial aquifer contamination) and associated processing facilities are illustrated in (Figure A–4).

The total volume of contaminated material at the site was 720,000 cubic meters on 34 hectares (ha). All of the source materials and other site-related contamination were hauled to the Mexican Hat, Utah, disposal cell 27 km to the north. The surface remedial action began in 1992 and was completed in May 1994. Contaminated materials, defined as tailings and soils with radium-226 concentrations exceeding 15 picocuries per gram (pCi/g), were removed. However, analysis of soil within the footprint of the tailings piles after tailings were removed indicated that residual ammonium and nitrate may be contributing to nitrogen contamination in a shallow, alluvial aquifer. Nitrate is the constituent of greatest concern in alluvial groundwater because concentrations exceed the EPA groundwater standard (discussed below) of 44 milligrams per liter (mg/L) for nitrate, or 10 mg/L nitrate as N.

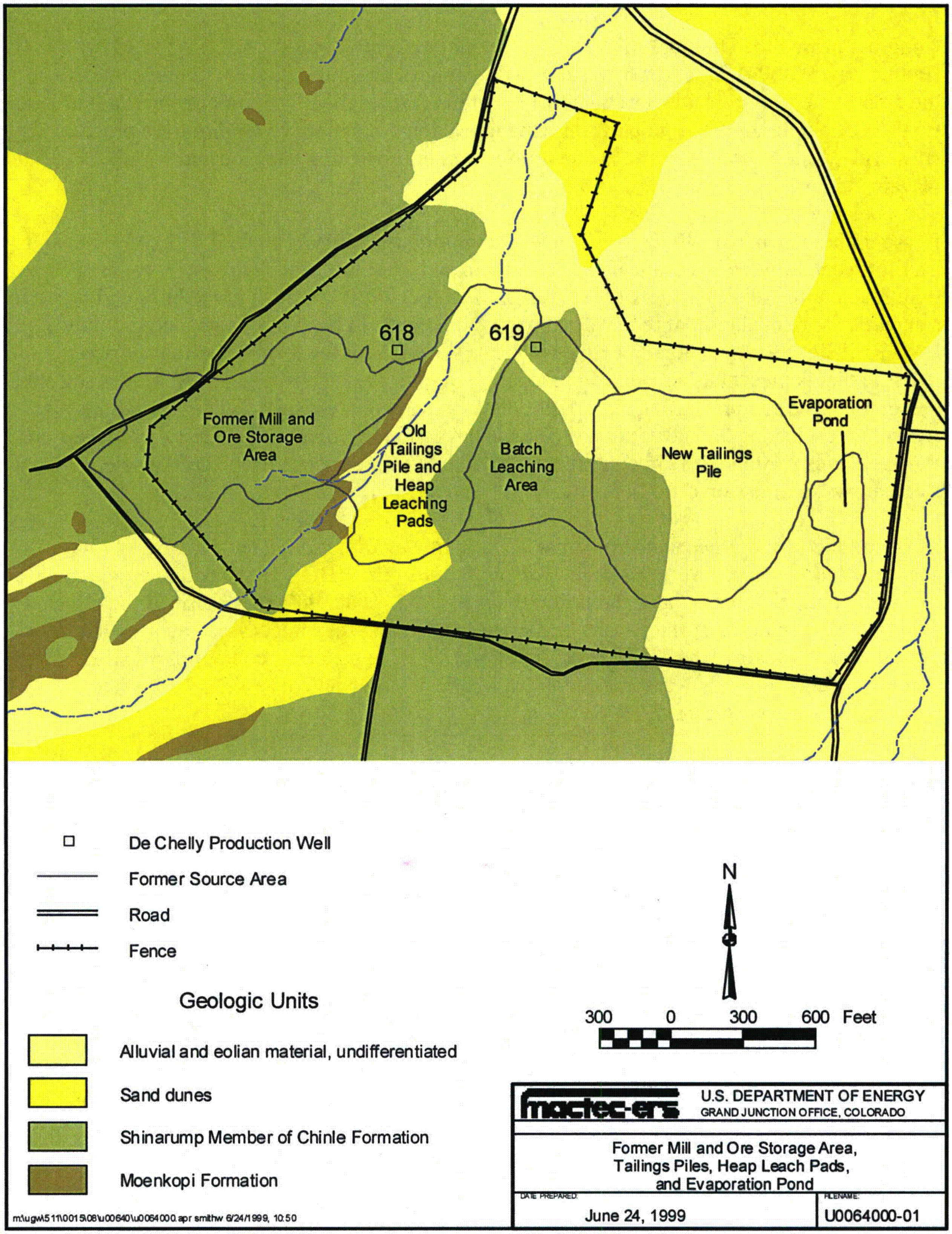


Figure A–4. Locations of former Monument Valley mill and ore storage area, tailings piles, heap-leach pads, and evaporation pond (DOE 1999a).

A.2 Regulatory Framework

Congress passed the Uranium Mill Tailings Radiation Control Act (UMTRCA) in 1978 (Public Law 95-604). UMTRCA was enacted to control and mitigate risks to human health and the environment from residual radioactive materials that resulted from processing uranium ore. UMTRCA authorized DOE to perform remedial action at 24 inactive uranium-ore processing sites. The Monument Valley site is one of four former processing sites located within the Navajo Nation.

EPA regulations in Title 40 *Code of Federal Regulations* Part 192 (40 CFR 192), "Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings," were established to implement the requirements of UMTRCA. The regulations establish procedures and numerical standards for remediation of residual radioactive materials in land, buildings, and groundwater. UMTRCA defines residual radioactive materials as "waste in the form of tailings or other material that is present as a result of processing uranium ores at any designated processing site, and other waste at a processing site which relates to such processing…." The regulations also require that selection and performance of remedial action be completed with full participation of states, in consultation with affected tribes, and with the concurrence of the U.S. Nuclear Regulatory Commission (NRC).

DOE completed the *Environmental Assessment of Remedial Action at the Monument Valley Uranium Mill Tailings Site, Monument Valley, Arizona* (EA) (DOE 1989) before conducting surface remediation of the land and mill tailings in 1992. That 1989 EA described the affected environment, including surface water and groundwater, and the effects associated with removal of tailings and debris at the Monument Valley site. Surface materials contaminated with residual radioactive contaminants were interred at the Mexican Hat, Utah, disposal cell. Surface remediation was completed in 1994.

After the source of groundwater contamination is removed, EPA regulations require that the site be evaluated to determine if contaminant concentrations in groundwater comply with EPA standards in 40 CFR 192. The *Final Programmatic Environmental Impact Statement for the Uranium Mill Tailings Remedial Action Ground Water Project* (PEIS) (DOE 1996b) provides a general discussion of groundwater contamination at the 24 former processing sites. The PEIS also provides a framework for selecting site-specific groundwater compliance strategies that comply with EPA regulations.

EPA regulations outline several criteria for determining compliance with groundwater standards:

- A characterization/monitoring program to determine background groundwater quality.
- Identification of residual radioactive materials present and whether concentrations of these constituents exceed background or maximum concentration limits (MCLs) established in 40 CFR 192 (Table 1 to Subpart A).
- The extent of contamination as a result of residual radioactive materials.
- Potential risks to human health and the environment.

To comply with these criteria, DOE completed the *Final Site Observational Work Plan for the UMTRA Project Site at Monument Valley, Arizona* (SOWP) (DOE 1999a), a site evaluation and findings, and an update of the original Baseline Risk Assessment (DOE 1996a). The Baseline Risk Assessment evaluated potential human health and ecological risks that could result from exposure to residual radioactive materials. Fieldwork was completed in 1997 and 1998, and the recommended compliance strategies, which are the basis for the proposed action in the EA (DOE 2005), are documented in the final SOWP. Project documents that provided guidance for the SOWP include the *UMTRA Ground Water Management Action Process (MAP) Document* (DOE 1999b) and the *Technical Approach to Groundwater Restoration* (DOE 1993). The proposed pilot study objectives and actions were authorized in *Monument Valley Ground Water Remediation: Pilot Study Work Plan* (DOE 2004).

The 2005 EA focused on compliance strategies for the alluvial (uppermost) aquifer at Monument Valley. Nitrate is the primary contaminant of concern in the alluvial aquifer. Three components of the alluvial aquifer were differentiated: subpile soils (source area), shallow alluvial aquifer, and deeper alluvial aquifer. The 2005 EA proposed, as compliance strategies, passive remediation for the subpile soils and shallow alluvial aquifer, and passive or active phytoremediation for the deeper alluvial aquifer.

According to the 2005 EA, the goal of the pilot studies was "to gather additional information to support the compliance strategies proposed in this EA for the alluvial aquifer" and that "the proposed compliance strategies for the alluvial aquifer in this EA are contingent upon the results of the proposed pilot studies." The conclusions and recommendations of these pilot studies interpret "passive" remediation to include both natural and enhanced attenuation as defined by DOE (SRNL 2006): "Any type of human intervention that might be implemented in a source-plume system that increases the magnitude of or accelerates attenuation by natural processes beyond what occurs without intervention." Therefore, as presented herein, passive remediation includes planting native shrubs overlying the alluvial aquifer and in the source area to enhance phytoremediation, and injection of ethanol in the alluvial aquifer to enhance microbial denitrification. "Active" remediation, as proposed in the 2005 EA and as investigated by these pilot studies, refers to land-farm phytoremediation, the irrigation of a farm of native shrubs using alluvial groundwater pumped from the nitrate plume.

A.3 Stakeholder Interactions

DOE has interacted with and received concurrence from Navajo Nation officials during the planning and implementation of enhanced attenuation pilot studies for contaminated soils and groundwater at Monument Valley. DOE also consulted with Diné College faculty on cultural aspects of enhanced attenuation, and funded internships for students in the College's DEI.

A.3.1 Navajo Nation

To comply with EPA regulatory requirements concerning consultation with tribes, DOE entered into a cooperative agreement with the Navajo Nation and held numerous meetings over several years with representatives of the Navajo Nation, including representatives of the Navajo Uranium Mill Tailings Remedial Action (UMTRA) Project, the Navajo EPA, the Navajo Water Code Administration, and the Navajo Department of Justice, to address concerns at the Monument Valley site. In addition, work plans, status reports, technical publications, and other documents were provided to the Navajo Nation for their review and comment.

The alluvial aquifer at Monument Valley is used to water livestock and could potentially be used as a source of domestic water. To minimize risks to potential water users in the short term, DOE met with Navajo Nation representatives on September 21, 1999, and agreed to install a water supply system to serve the Monument Valley area. The Navajo Tribal Utility Authority, in cooperation with the Bureau of Indian Affairs, prepared the appropriate National Environmental Policy Act (NEPA) documentation for the alternate water supply. A well was installed upgradient in the de Chelly aquifer and a water line and infrastructure were completed in September 2003.

On October 7, 1999, comments were received from the Navajo Nation on the draft Ground Water Compliance Action Plan, which would implement the proposed action, phytoremediation plus active pump and treat, that had been identified in the draft version of this EA. On October 25, 1999, DOE announced the availability of the draft EA. Comments were received from the Navajo Nation on December 8, 1999. By letter dated December 20, 1999, from DOE to the Navajo Nation, DOE suspended completion of the EA pending resolution of comments. On February 24, 2000, DOE met with representatives of the Navajo Nation at Mexican Hat, Utah, to discuss the feasibility of implementing phytoremediation and land farming remedies for groundwater contamination. In addition, DOE conducted an alternatives evaluation (DOE 2000a) to ensure that all feasible alternatives to remediate groundwater had been considered.

In June 2000, DOE and the Navajo Nation agreed to conduct additional pilot studies for the alluvial aquifer prior to completing the EA. DOE and Navajo UMTRA representatives held field meetings on September 17, 2000, and May 8, 2003, at Monument Valley with local residents, stakeholders, Navajo Nation agency officials, and Indian Health Services representatives to discuss the pilot study and potential related actions. These actions could include a grazing management plan, rights-of-way, land withdrawal, and institutional controls. At a meeting between DOE and the Navajo Nation on November 12, 2003, in Durango, Colorado, the Navajo Nation agreed to move forward with the pilot studies. Results of the proposed pilot studies would be the basis for remediation of the alluvial aquifer and subpile soils.

In accordance with DOE's NEPA policy and regulations, pilot studies would normally be completed before an EA is begun. However, the Navajo Nation had requested that the EA be completed to address the entire scope of DOE's proposal, including the pilot studies and proposed compliance strategies. This would allow the Navajo Nation to consider rights-of-way, land withdrawal, institutional controls, and other actions comprehensively and simultaneously. Preparation of a final EA and a GCAP (Groundwater Compliance Action Plan) were postponed pending completion of the pilot studies. The Navajo Nation agreed that if the pilot studies indicate that the proposed remedies for the alluvial aquifer would not comply with EPA standards and remediation goals, additional NEPA assessment and documentation may be necessary.

The final remedial action at the Monument Valley site will be selected and performed in compliance with EPA regulations, Navajo Nation regulations, and the cooperative agreement, and with the concurrence of NRC.

A.3.2 Diné College

DEI has become a strategic partner with DOE and Navajo Nation in efforts to develop and implement sustainable and culturally acceptable remedies for soil and groundwater contamination at uranium mill tailings processing and disposal sites on Navajo Nation land. DEI is a center for environmental education, research, and community outreach located on the Shiprock, New Mexico, campus of Diné College, the Navajo Nation institution of higher education. As a stakeholder, DEI has played a key role in shaping the philosophy of remedial actions, advancing the science of sustainable remedies, bridging communication and interaction among other stakeholders, listening to and responding to the concerns of the Navajo people, and training a new generation of scientists to address the uranium mining legacy and other environmental and energy issues on the Navajo homeland.

Through an educational philosophy grounded in the Navajo traditional living system called Sá'ah Naaghái Bik'eh Hózhóón, which places human life in harmony with the natural world, DEI has helped guide researchers to look beyond traditional engineering approaches and seek more sustainable remedies for contaminated soil and groundwater at the former uranium mill site near Monument Valley, Arizona. Following this philosophy, researchers are asking first, what is Mother Earth already doing to heal a land injured by uranium mill tailings, and second, what can we do to help her? This led researchers to investigate applications involving natural and enhanced attenuation remedies.

DEI faculty and students worked side by side with university and LM scientists on the enhanced attenuation pilot studies aimed at developing sustainable remedies for contaminated soil and groundwater at Monument Valley (Waugh et al. 2011). Diné College faculty, student interns, and local residents have contributed to several aspects of the pilot studies including site characterization, sampling designs, installation and maintenance of plantings and irrigation systems, monitoring, and data interpretation.

DEI's insight and experience implementing an educational policy that fosters diversity of thought, the joining of tradition and science, and the importance of community, has been instrumental in building stakeholder relations. With firsthand knowledge of human health and environmental issues associated with the Navajo uranium legacy, lifelong practice of Navajo Way of Life, and experience directing community outreach programs, DEI faculty have been influential in helping mediate communication and interaction among stakeholders including federal regulators and administrators, scientists, Navajo Nation agencies, and the Navajo people.

A.4 Environmental Setting

Evaluations of natural and enhanced attenuation require a thorough understanding of the environmental setting. This section is a brief summary of the climate, soils, hydrogeology, and plant ecology at the Monument Valley site. More detailed descriptions of the environmental setting, baseline conditions, and a site conceptual model can be found in DOE's Final SOWP for Monument Valley (DOE 1999a). The site conceptual model consisted of an interpretation of site characterization data collected before 1998, and an understanding at that time of the extent and magnitude of contamination, exposure pathways, and risk to public health and the environment. The site conceptual model was the basis for the groundwater compliance strategy and remediation objectives as proposed at that time. A revised site conceptual model incorporating new information produced by these pilot studies will be included in the GCAP.

A.4.1 Climate

The Monument Valley site is semiarid with 163 millimeters (mm) average annual precipitation. Wetter months are July through August and December through February. May and June are generally drier. Summer precipitation typically occurs as high-intensity, short-duration storms, and winter precipitation occurs as low-intensity, longer-duration storms. Average daily low temperatures are below freezing from November through March. Summers are warm with daily high temperatures of 32 to over 37 °C. The annual pan evaporation averages 2,141 mm. Average pan evaporation rates exceed precipitation every month except January. The highest pan evaporation rates, greater than 250 mm per month, occur from May through August.

A.4.2 Soils

Thick Quaternary alluvial, eolian, and some lacustrine deposits underlie the site. The more common and widespread eolian deposits are well-sorted, fine-grained to very fine grained quartz sand. Less common fluvial materials, deposited in minor stream channels and in alluvial fans, consist of coarser sands and pebbles as large as 20 mm. Coarse deposits up to several feet thick occur at the base of the Quaternary deposits. Elsewhere, coarse layers are thin, sporadic, and discontinuous. Layers consisting of silt and clay fractions, also thin and sporadic, were deposited in a shallow lakes or stream channels.

The surface soil is reddish-yellow sand (mesic, arid, typic torripsamment) with about 15 percent silt and clay overlying limestone bedrock. Soils have a relatively high electrical conductivity (EC) value in surface samples, with calcium (Ca) as the principal cation. Organic matter content is only 0.6 percent, and pH is neutral to slightly alkaline. Gypsiferous and calcareous layers have formed in these desert soils. Large areas along the valley floor covered with thin white crust of gypsum and gypsite are evidence of natural gypsiferous soils. Calcareous horizons occur as white layers within a meter of the soil surface. In some exposed stream cuts, the calcareous layer occurs as an indurated calcic horizon about 1 m thick.

A.4.3 Hydrogeology

The hydrogeology of the site and the nature and extent of contamination are discussed in detail in the Final SOWP (DOE 1999a). is a regional geologic cross section showing the relative location of the former processing site. The three main aquifers at the site are, from the ground surface down, the alluvial in Quaternary sediments, Shinarump, and de Chelly aquifers. Depth to groundwater in the alluvial aquifer ranges from less than a meter in Cane Valley Wash to slightly more than 18 m downgradient from the site. The footprint of the New Tailings Pile (see Figure A–5) is in an isolated recharge area that converges with the Cane Wash alluvial aquifer just east of the footprint. This alluvial aquifer is recharged by occasional infiltration from precipitation and upward leakage from the semiconfined Shinarump. Depth to groundwater in the Shinarump ranges from 2 to 15 m below ground surface. The de Chelly aquifer consists of fine-grained sandstone that is approximately 150 meters thick in the site area. Groundwater in the de Chelly is present under artesian conditions in three wells south and east of the site and may be unconfined in areas west of the site, where the maximum measured depth to groundwater is about 50 m.

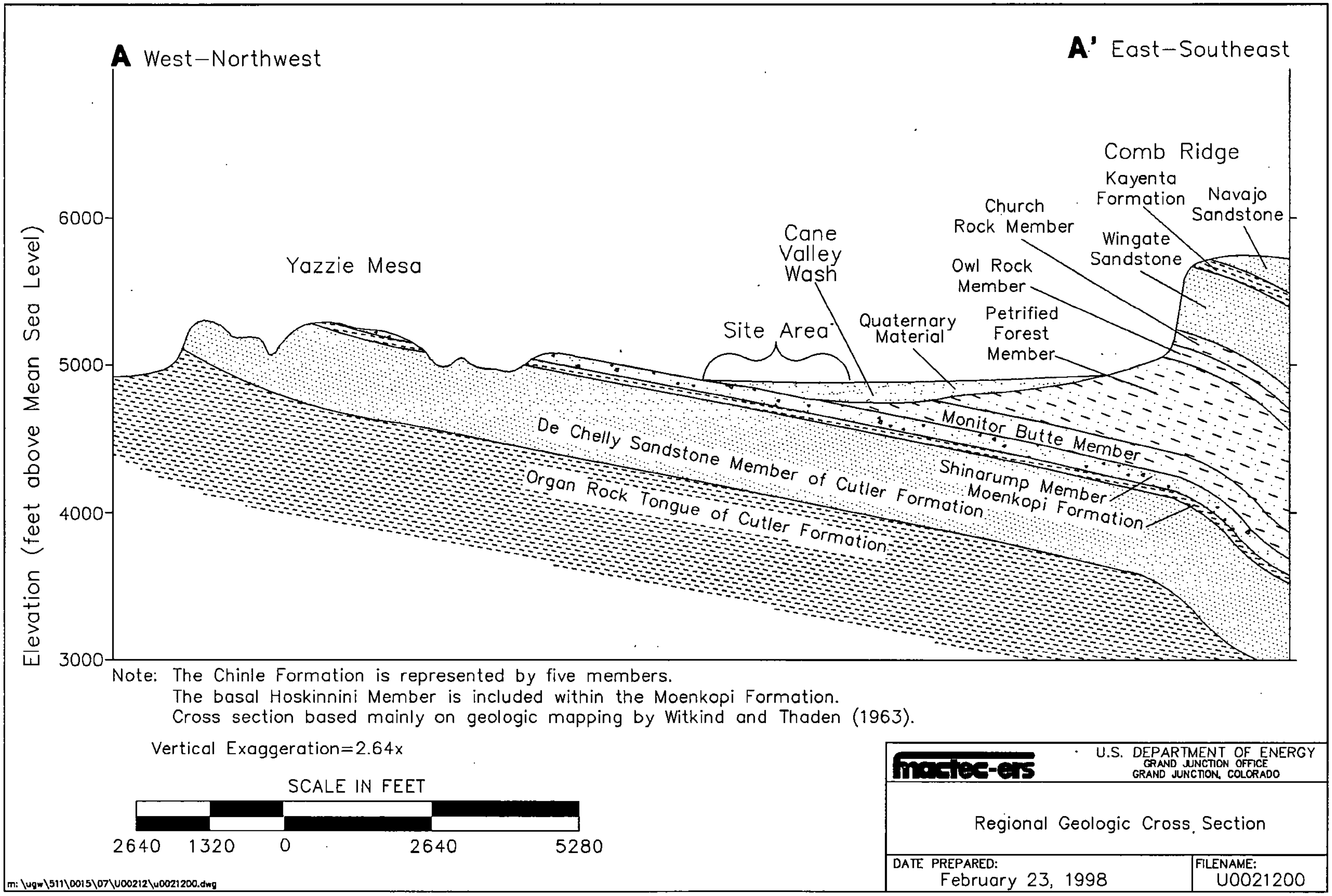


Figure A–5. Regional geologic cross section at the Monument Valley Processing Site (DOE 1999).

The alluvial aquifer underlying the site consists mainly of windblown and some water-deposited, fine- to medium-grained sands. In the area of the alluvial nitrate plume, the depth to groundwater is between 9 and 12 m. The average hydraulic conductivity of the portion of the alluvial aquifer containing the nitrate plume was estimated to be 6.5 m/day. Flow is to the north-northeast.

Assuming an effective porosity of 0.25 and a hydraulic gradient of 0.007 to 0.012, the groundwater velocity ranged from 0.2 to 0.3 m/day. At these velocities, the nitrate plume would have taken 15 to 25 years to reach its farthest extent in 1997 (about 1,700 m downgradient). In the centroid of the plume, the average hydraulic gradient was estimated at 0.0095 with a groundwater velocity of 0.25 m/day. These values indicate it would have taken approximately 22 years for the portion of the nitrate plume that is above background to reach its 1997 extent.

A.4.4 Plant Ecology

The occurrence and relative abundance of plant species, coupled with knowledge of their physiological and ecological tolerances, provided measures of the health of the ecosystem and evidence of environmental conditions that are of importance for phytoremediation planning. The DOE SOWP (DOE 1999a) provides detailed results of a 1997 characterization of local plant ecology. A summary follows.

Plant cover in stands near monitoring wells was characterized, and stands were then grouped into associations using simple ordination and gradient analysis techniques (Barbour et al. 1999). Because species composition and cover vary across the site as a continuum rather than as discrete units, a simple gradient analysis of dominant species was used to group stands. Results of the gradient analysis suggested that some dominant species are associated and that associations overlap—a given stand may occur in more than one association. Four associations were delineated, named for their two most abundant shrubs. Plant acronyms, in capital letters, are formed by the first two letters of the genus followed by the first two letters of the species. For example, the acronym for *Atriplex canescens* is ATCA.

- *Sarcobatus vermiculatus* (black greasewood) and *Atriplex confertifolia* (shadscale), or SAVE/ATCO.
- *Atriplex canescens* (fourwing saltbush) and *Haplopappus pluriflorus* (jimmyweed), or ATCA/HAPL.
- *Poliomintha incana* (bush mint) and *Ephedra torreyana* (joint fir), or POIN/EPTO.
- *Salsola iberica* (Russian thistle) and *Ambrosia acanthicarpa* (bur ragweed) or SAIB/AMAC.

Production of a vegetation map (Figure A–6) involved (1) mapping stand locations on the 1995 aerial photograph; (2) identifying vegetation patterns in the photograph, under magnification, that were consistent with the plant associations; (3) outlining mapping unit boundaries using a combination of stand locations and vegetation patterns; and (4) returning to the field to check the reliability of the photograph interpretation. Acronyms of dominant plants in associations are used for mapping unit titles in (Figure A–6).

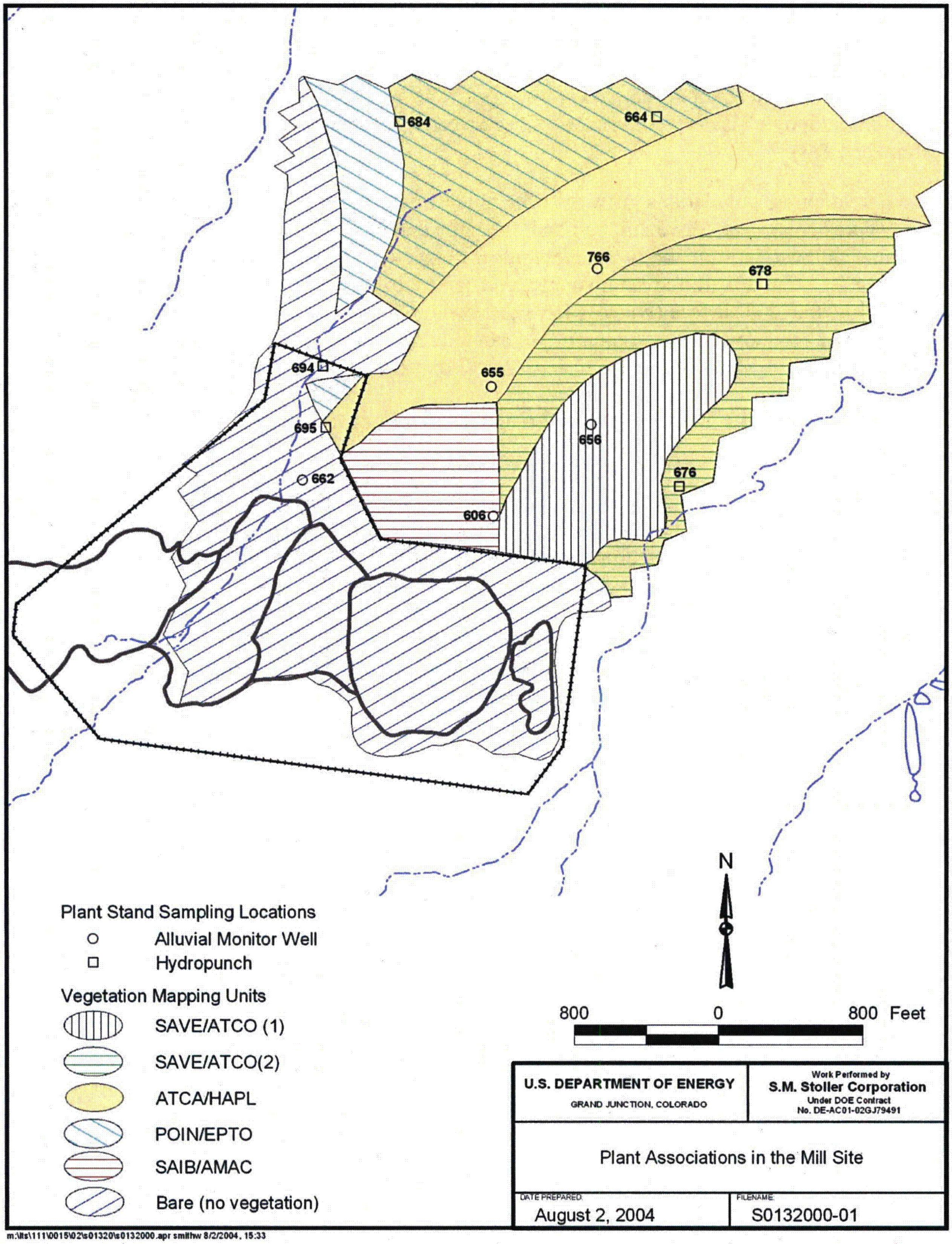


Figure A–6. Plant associations at the Monument Valley site and extending north overlying the alluvial nitrate plume. Plant acronyms are formed by the first two letters of the genus followed by the first two letters of the species (see text).

Phreatophytes at the Monument Valley site may act, in essence, as passive, solar-powered, pump-and-treat systems for nitrate and ammonia in the alluvial aquifer. Phreatophytes are capable of sending their roots into the water table, or into the capillary fringe overlying the water table. Thus they are able to produce vigorous growth even during periods of severe drought. The term "phreatophyte" is derived from two Greek words that literally mean "well plant" (Meinzer 1923).

Two phreatophyte populations grow over the plume area (Figure A–7): *Sarcobatus vermiculatus* and *Atriplex canescens* (díwózhii_beii and díwózhiishzhiin in Navajo, and black greasewood and fourwing saltbush in English). *S. vermiculatus* is considered to be an obligate phreatophyte requiring a permanent groundwater supply, and can transpire water from aquifers as deep as 18 m below the land surface (Nichols 1993). *A. canescens* is a facultative phreatophyte; it takes advantage of groundwater when present but can tolerate periods of low water availability. The rooting depth of *A. canescens* may exceed 12 m (Foxx et al. 1984).

A.5 Natural and Enhanced Attenuation Concepts

Before and into the early 1990s, most large-scale attempts to clean up contaminated soil and groundwater focused on engineering strategies. Engineering approaches included excavating and hauling large volumes of soil to landfills, and drilling wells and pumping large volumes of water to the surface for treatment (National Research Council 2000). By the mid-1990s, research and experience had revealed several shortcomings. Excavating and hauling contaminated soil can damage natural ecosystems and potentially expose workers or nearby residents. Also, many conventional pump-and-treat remedies for groundwater contamination had not achieved cleanup goals (National Research Council 2000). Overall, engineered remedies have not always been successful in restoring contaminated soil and groundwater.

As awareness of the limitations of engineering approaches grew, research began revealing more fully how naturally occurring processes in soils and groundwater can transform or prevent the migration of contaminants (National Research Council 2000). Reliance on natural attenuation has increased as a consequence. Natural attenuation is now considered a tool for supplementing or even replacing engineered treatment systems. In some cases, including sites with uranium mill tailings contamination, natural attenuation can be used to manage groundwater contamination that remains after engineering approaches have removed or isolated the source of contamination (DOE 1996b). The term *monitored natural attenuation* (MNA), as an alternative to active engineering approaches, "…refers to the reliance on natural attenuation processes to achieve site-specific remedial objectives within a time frame that is reasonable compared to that offered by other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater." (EPA 1999)

The natural physical, chemical, or biological processes most often referenced that can degrade or dissipate contaminants in soil and groundwater include aerobic and anaerobic biodegradation, dispersion, volatilization, and sorption (for example, see Ford et al. 2008). Phytoremediation is another attenuation process that is often categorized separate from microbiological, physical, and chemical processes. Phytoremediation and microbial denitrification are the natural attenuation processes LM and collaborators have investigated as an alternative to engineered approaches for nitrate and ammonia in soil and groundwater at the Monument Valley site.

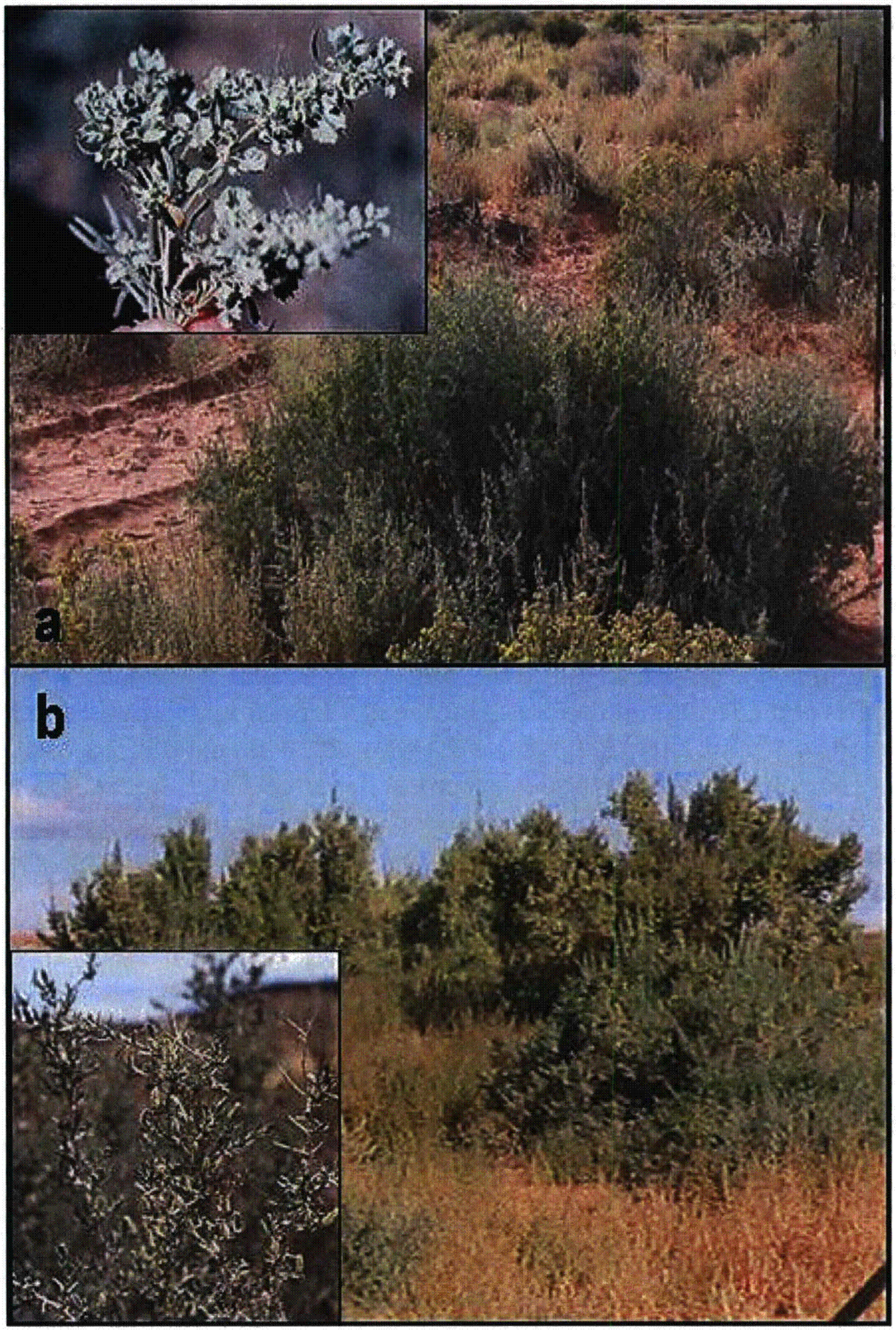


Figure A–7. Two native phreatophytes that grow over the Monument Valley nitrate plume: a) Atriplex canescens *(fourwing saltbush, or díwózhiishzhiin in Navajo), and b)* Sarcobatus vermiculatus *(black greasewood, or díwózhii_beii in Navajo).*

Although the basic idea is quite old, the concept of using plants for natural attenuation didn't take root until the 1970s, and since then it has been studied and applied primarily in wetland and humid upland settings. The U.S. Environmental Protection Agency (EPA) defines phytoremediation as a set of technologies that use different types of plants for containment, destruction, or extraction of contaminants (EPA 2000). Some general categories of phytoremediation include degradation, the breakdown of contaminants in the root zone or through plant metabolism; extraction, the accumulation of contaminants in shoots and leaves and subsequent harvesting of the crop to remove the contaminant from the site; immobilization, sequestration of contaminants in soil; and hydraulic control, enhancing ET to slow the spread groundwater plumes. A review of literature suggests that research using native desert phreatophytic shrubs for phytoremediation in the arid environment of the Monument Valley site is new and innovative. (Note that for the purposes of this document, evapotranspiration or ET refers to water removed from the soil or groundwater by plant transpiration.)

Microbial denitrification, as discussed here, is a technology that encourages growth and reproduction of indigenous microorganisms to enhance denitrification in both soil and the saturated zone. Denitrification ultimately produces molecular nitrogen (N_2) through a multistep process that results first in the intermediate gaseous nitric oxide (NO), then nitrous oxide (N_2O) (Tiedje 1994). Denitrification completes the cycle by returning molecular N_2 to the atmosphere. The process is performed primarily by heterotrophic bacteria and several species of bacteria that may be involved in the complete reduction of nitrate to nitrogen gas. Denitrification requires electron donors such as organic matter or another carbon source to reduce oxidized forms of nitrogen.

Although natural attenuation has been accepted elsewhere by regulatory agencies for many years, *enhanced* attenuation has only recently been forwarded by the scientific community as a distinct strategy. In 2003, DOE introduced the concept of enhanced attenuation and developed the technical basis and documentation to use enhanced attenuation as a transition between active, engineered remedies and sustainable remedies that rely solely on natural processes (SRNL 2006). The enhanced attenuation concept is a departure from the classical definition of MNA (EPA 1999). An *enhancement* is any type of human intervention that might be implemented in a source-plume system that increases the magnitude of or accelerates attenuation by natural processes beyond what occurs without intervention.

Enhanced attenuation is a strategy that bridges the gap between active, engineered solutions, and passive MNA. A successful enhancement is also a sustainable manipulation—it does not require continuous, long-term intervention. Hence, enhanced attenuation requires a short-term, sustainable manipulation of a natural attenuation process leading to a reduction in mass flux of contaminants. In many cases, sustainable enhancements of natural processes are needed to achieve a favorable balance between the release of contaminants from a source (source loading) and attenuation processes that degrade or retard migration of contaminants in resultant plumes. With regard to pilot studies at the Monument Valley site, enhanced attenuation refers to sustainable interventions that enhance phytoremediation of nitrate and ammonia, ET for hydraulic control, and microbial denitrification.

Appendix B

Source Containment and Removal

This page intentionally left blank

Contents

Figures

Tables

This page intentionally left blank

The pilot studies show that an irrigated field of native shrubs has cut off the source of the groundwater plume, and microbial dentrification, enhanced by irrigation, has rapidly reduced nitrogen levels in the source area soils.

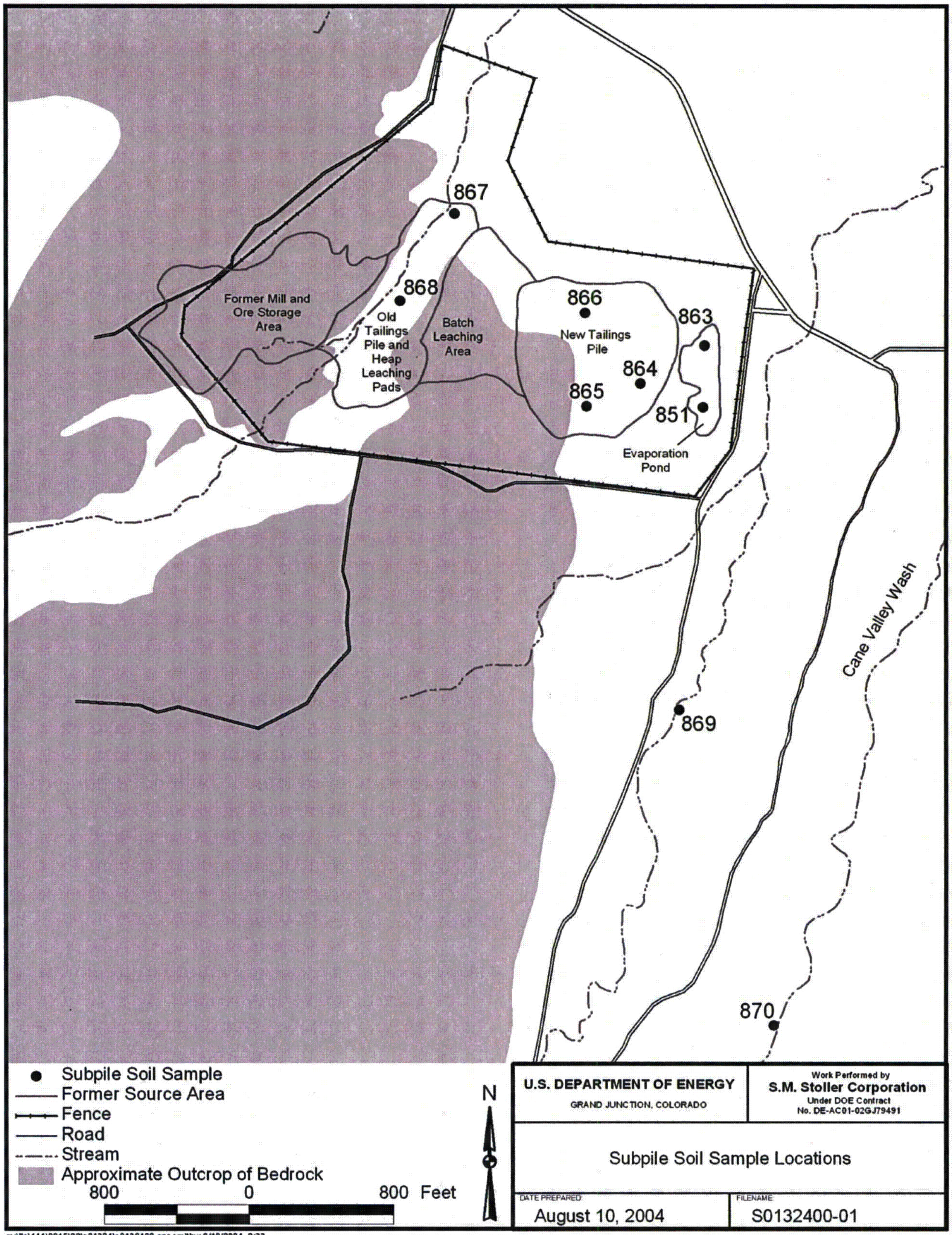
The residual source area (subpile soils) for the plume—the nitrate- and ammonium-contaminated soils remaining after tailings were removed—was planted with two native shrubs, fourwing saltbush and black greasewood. The purposes of the plantings were to (1) transpire precipitation stored in the soil and, in so doing, limit percolation, cutting off the source from the plume, and (2) extract nitrate and ammonium. After characterizing the extent of soil nitrate and ammonium contamination, a 3.3 ha area was planted. Plants were deficit irrigated—given less water than they could transpire under normal conditions. Soil moisture measurements provided evidence that little if any water escaped below the root zone. A few years after planting, a mature plant community consisting mostly of fourwing saltbush had established in the subpile soil, and multiple lines of evidence confirmed that plant transpiration was controlling seepage of contaminants into the plume.

Native shrubs were also slowly removing nitrate and ammonium from subpile soils, but not fast enough to account for an initially rapid drop in soil nitrogen levels. Ensuing work confirmed that irrigation-enhanced microbial denitrification had caused the rapid drop in soil nitrogen. LM scientists tested the hypothesis that supplying a carbon source through the irrigation system might also enhance denitrification. This hypothesis was supported by a laboratory study, but not supported by results of a subsequent field investigation.

B.1 Subpile Soil Characterization

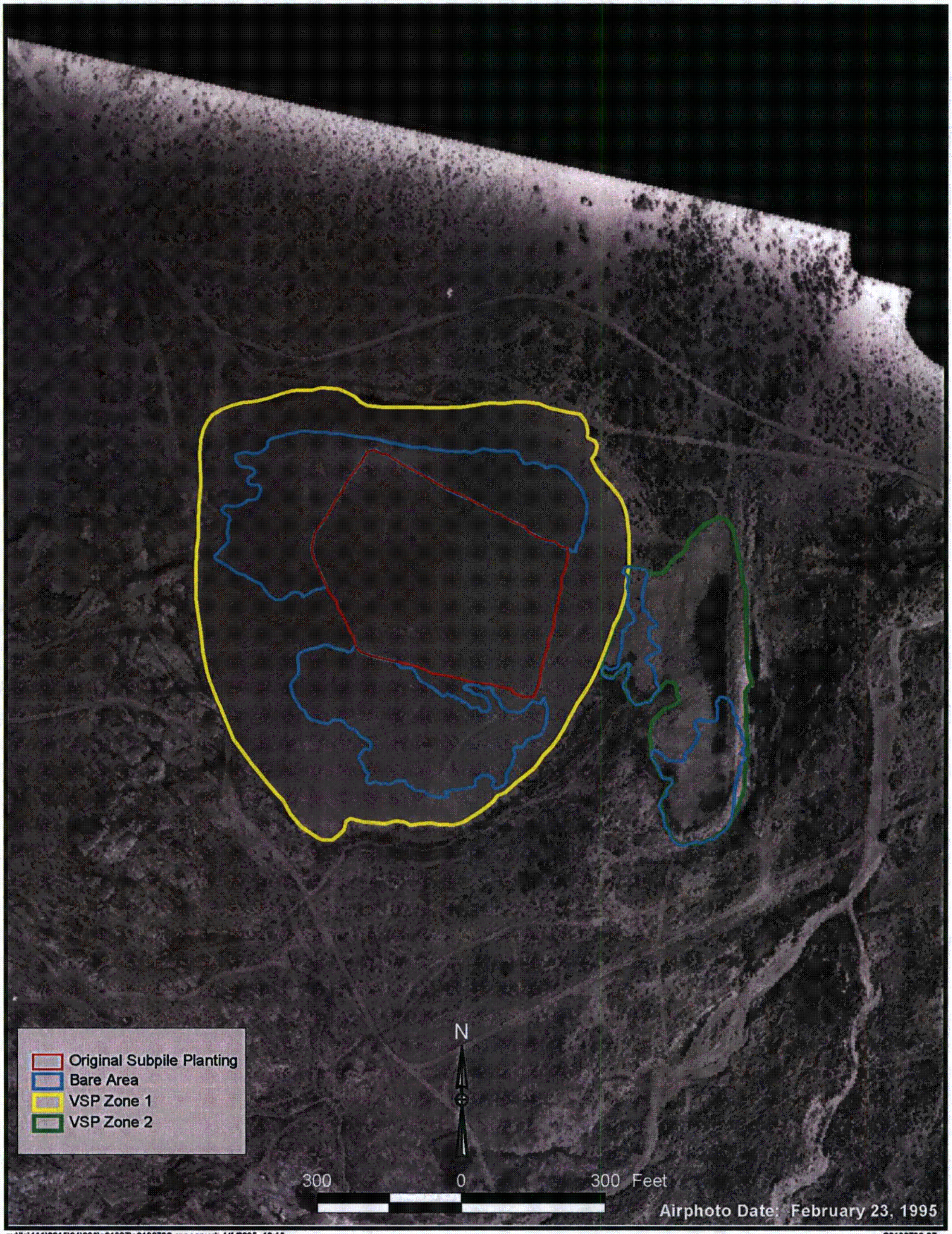
Characterization of the subpile soil, the former location of the New Tailings Pile, progressed through three stages. The initial discovery of an ammonium hot spot in 1997 was based on a single sample location, point 866 (Figure B–1, DOE 1999a). A second survey, conducted in June 1997, included analysis of both nitrate and ammonium levels from subpile soils sampled along radial transects away from location 866 (DOE 2002). Results of this second sampling event indicated that subpile soils contained elevated levels of nitrate (as NO_3) ranging from 45 to 1,060 mg/kg dry-weight of soil and ammonium (as NH_4) levels ranging from zero to 163 mg/kg dry-weight of soil. Delineation of an initial 1.7 ha phytoremediation field, planted in 1999 (Section B.3.1), was based on this second survey (Figures B–2 and B–3).

After the 1999 planting proved to be exceptionally effective in removing nitrate from the subpile soil, in part through plant uptake but principally through microbial denitrification (Section B.4.1), in 2005 scientists conducted a third, more comprehensive characterization that led to an expansion of the irrigated planting. This final effort focused on the former location of the New Tailings Pile (Figure B–1). The Old Tailings Pile (Figure B–1), a waste product of mechanical crushing and separating operations beginning in 1955, was not considered to be a source of nitrate or ammonium. Other than flocculants, no chemicals were used in the milling process that produced the Old Tailings Pile. Starting in 1964, batch and heap leaching of ore used sulfuric acid, ammonia, and ammonium nitrate. The leaching waste was discharged to the New Tailings Pile. The Evaporation Pond to the east (Figure B–1) was probably used to retain seepage from the New Tailings Pile. The final subpile soil characterization was constrained within the historical boundaries of the New Tailings Pile and the Evaporation Pond. Historical footprints of these source areas were delineated using aerial photographs taken in 1995 before tailings were removed (Figure B–2).



m:\lts\111\0015\02\s01324\s0132400.apr smithw 8/10/2004, 8:33

Figure B–1. Map of the Monument Valley site showing 1997 soil sampling locations and historical delineations of the mill and ore storage areas, Old Tailings Pile, New Tailings Pile, and Evaporation Pond. Elevated soil nitrate and ammonium were first detected at soil sample point 866.



m:\lts\111\0015\04\003\s01697\s0169700.apr carverh 4/1/2005, 10:43 S0169700-07

Figure B–2. Pre-reclamation aerial photograph of source areas with New Tailings Pile (VSP Zone 1) and Evaporation Pond (VSP Zone 2) boundaries, and GPS-mapped demarcation of the 1999 subpile soil phytoremediation planting and adjacent bare soil areas.

B.1.1 Sampling Methods

Soils within the footprint of the New Tailings Pile and the Evaporation Pond were sampled incrementally to a depth of 4.5 m and analyzed for ammonium and nitrate content. The objectives of the sampling design were to detect the presence of locally elevated concentrations—hot spots—and to delineate the greatest extent of the source area as a basis for expanding the phytoremediation planting. The sampling design consisted of a triangular grid pattern with random starting points (Gilbert 1987) and 30 m spacing. Visual Sample Plan (VSP) software (Battelle 2005) was used to calculate a grid spacing considered to be adequate to detect hot spots. VSP uses an algorithm to produce a sample location map (Figure B–3) with x:y coordinates designed to detect an elliptical hot spot area of approximately 214 square meters (m^2) with a 95 percent probability of detection (Singer 1975). A hot spot was defined as an area with soil nitrate as N concentrations of >100 milligrams per kilogram (mg/kg), and the reference hot spot shape and size were based on 1997 sampling results (DOE 2002). Sample points, located using GPS, were flagged and 100–300 gram (g) samples were taken at depths of 0.3, 0.9, 1.8, 2.7, 3.7, and 4.6 m (or to bedrock or the water table) using hand augers and a Geoprobe (Figure B–4). Sampling began December 6–10, 2004, and was completed January 17–18, 2005.

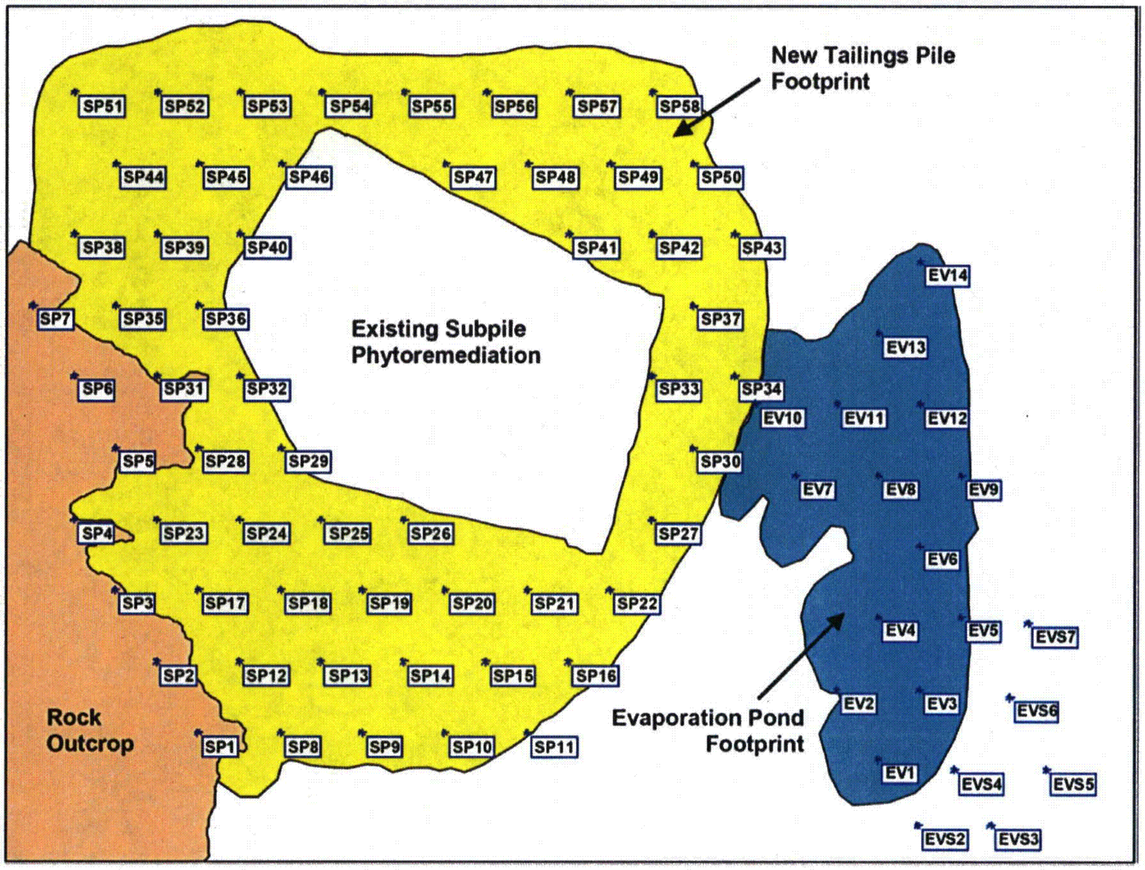


Figure B–3. Triangular grid sample points (about 30 m spacing) within the New Tailings Pile and Evaporation Pond footprints for the 2005 characterization. Points falling within the boundaries of the rock outcrop were omitted. The original 1999 phytoremediation field is also shown.

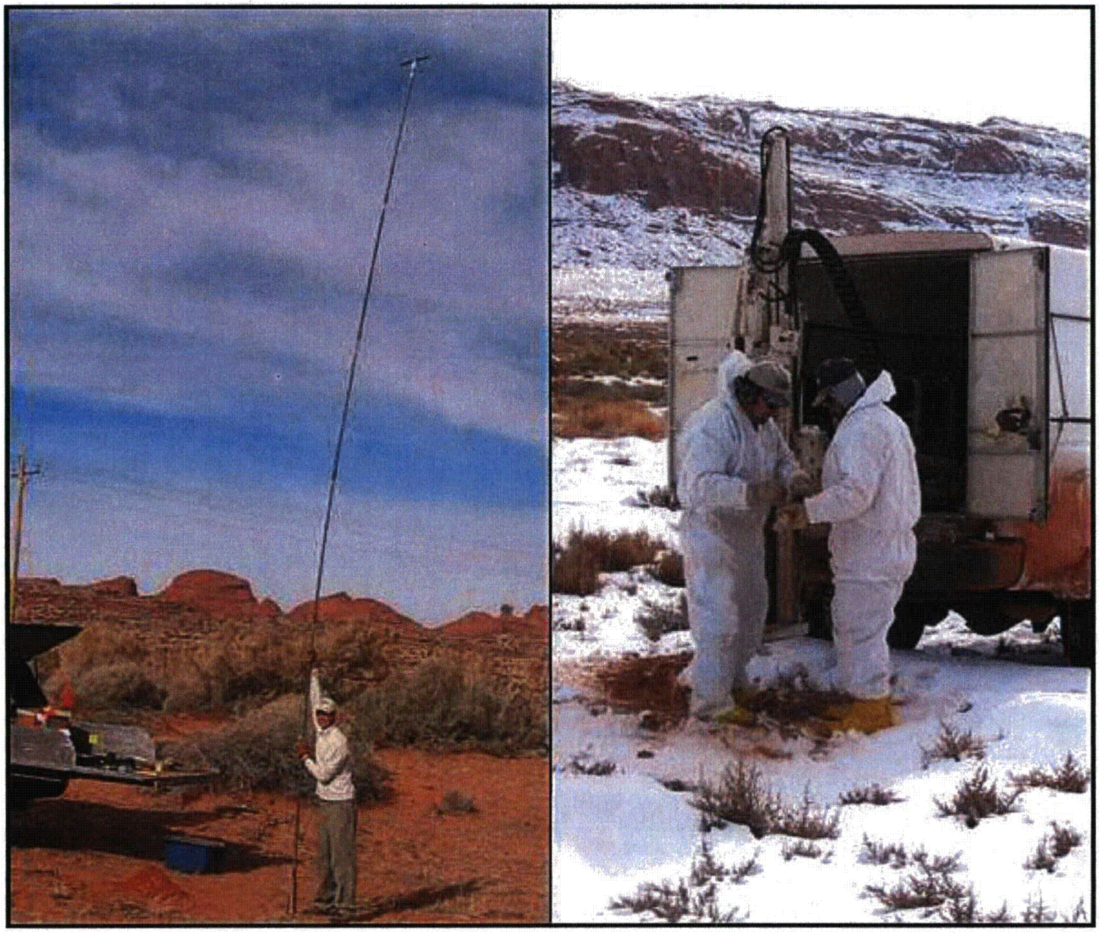


Figure B–4. Soil sampling with hand bucket augers (left) and a Geoprobe (right) to delineate hot spots and the extent of soil nitrate and ammonium within the footprints of the New Tailings Pile and Evaporation Pond.

The New Tailings Pile footprint was sampled starting close to the boundary of the 1999 planting and continuing outward toward the footprint boundary. Samples were analyzed initially in the Environmental Sciences Laboratory (ESL) Mobile Laboratory for ammonium and nitrate content as they were collected (Figure B–5). Where concentrations were elevated, sampling continued outward to the next closest grid point. All grid locations within the Evaporation Pond were sampled. Six additional points (EVS2 through EVS7) were sampled outside the Evaporation Pond footprint after field analyses revealed high nitrate concentrations near the eastern edge (Figure B–6). All samples were analyzed a second time at the DOE ESL in Grand Junction using a procedure for extraction of ammonia and nitrate using potassium chloride (DOE 2011).

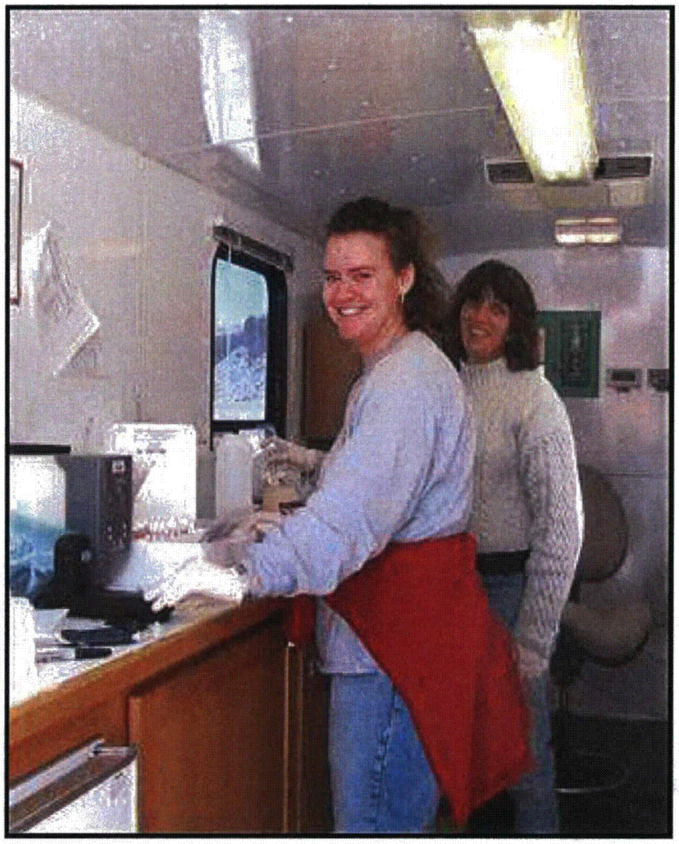


Figure B–5. University of Arizona graduate students Casey McKeon and Fiona Jordan conducting nitrate analyses in the ESL Mobile Laboratory during characterization of hot spots and the full extent of source area soil contamination.

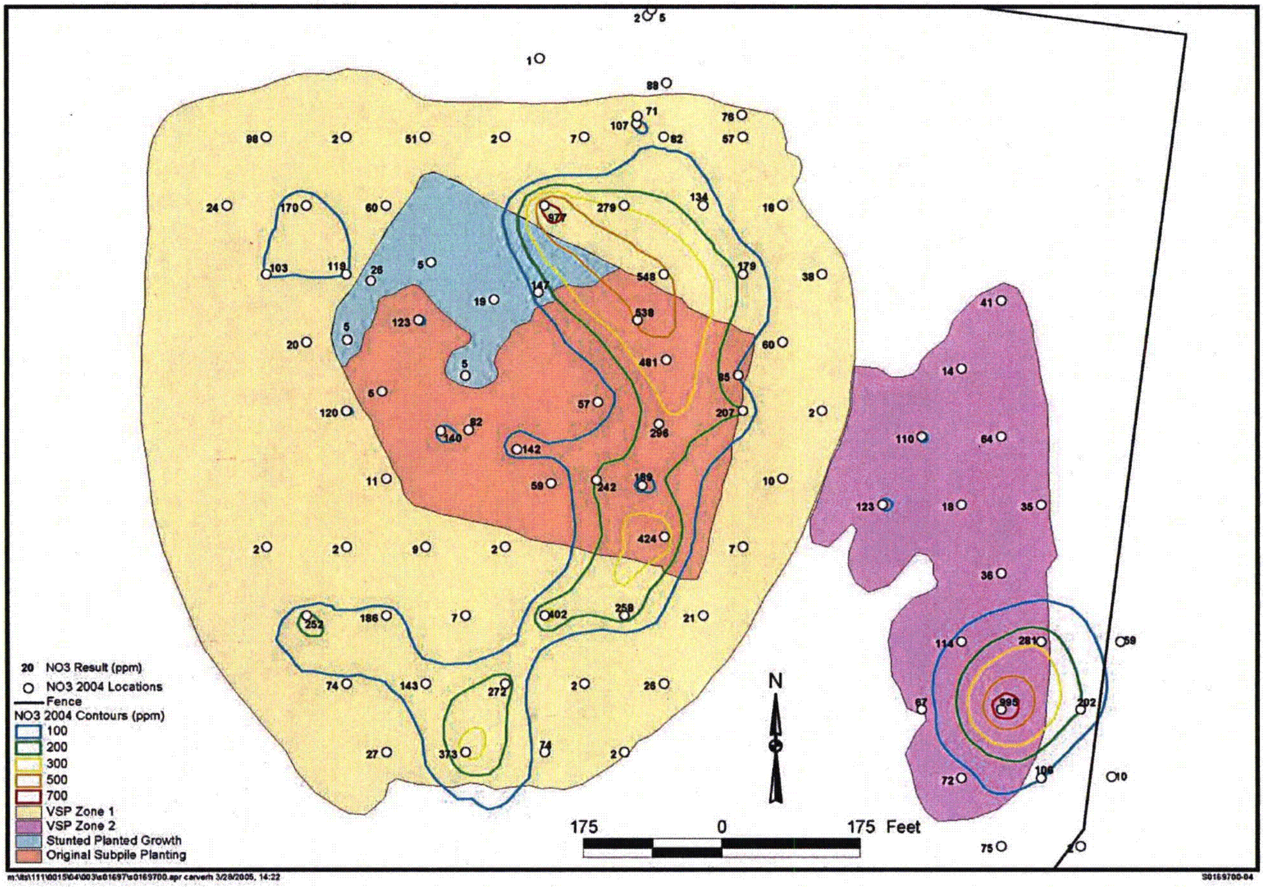


Figure B–6. Map of nitrate (NO_3-N) concentrations in soil within the New Tailings Pile and Evaporation Pond source areas. Based on 2004–2005 sampling results.

B.1.2 Results

Soil concentrations of nitrate as N (NO_3-N) and ammonia as N (NH_3-N) in the source areas are shown in Figure B–6 and Figure B–7, respectively. Data points within the 1999 source area planting were from routine annual monitoring (DOE 2004b). These figures were created by importing data and shape files to Environmental Visualization System (EVS) software and running a kriging routine to interpolate and extrapolate concentration maps from the data.

Both NO_3-N and NH_3-N were highly variable laterally and vertically within the source areas. The figures show the highest values within the vertical profile at each sampling location. Concentrations of NO_3-N ranged from less than 5 mg/kg to 977 mg/kg in the New Tailings Pile footprint. Areas with greater than 100 mg/kg NO_3-N extended both north and south of the 1999 planting. A hot spot with NO_3-N concentrations >100 mg/kg and approximately 200 ft wide was detected at the southern end of the Evaporation Pond footprint and extending east of the footprint. Concentrations of NH_3-N ranged from less than 5 mg/kg to 650 mg/kg in the New Tailings Pile footprint; the highest levels were within the boundaries of the 1999 planting. NH_3-N concentrations exceeded 100 mg/kg at only one sampling location in the Evaporation Pond footprint.

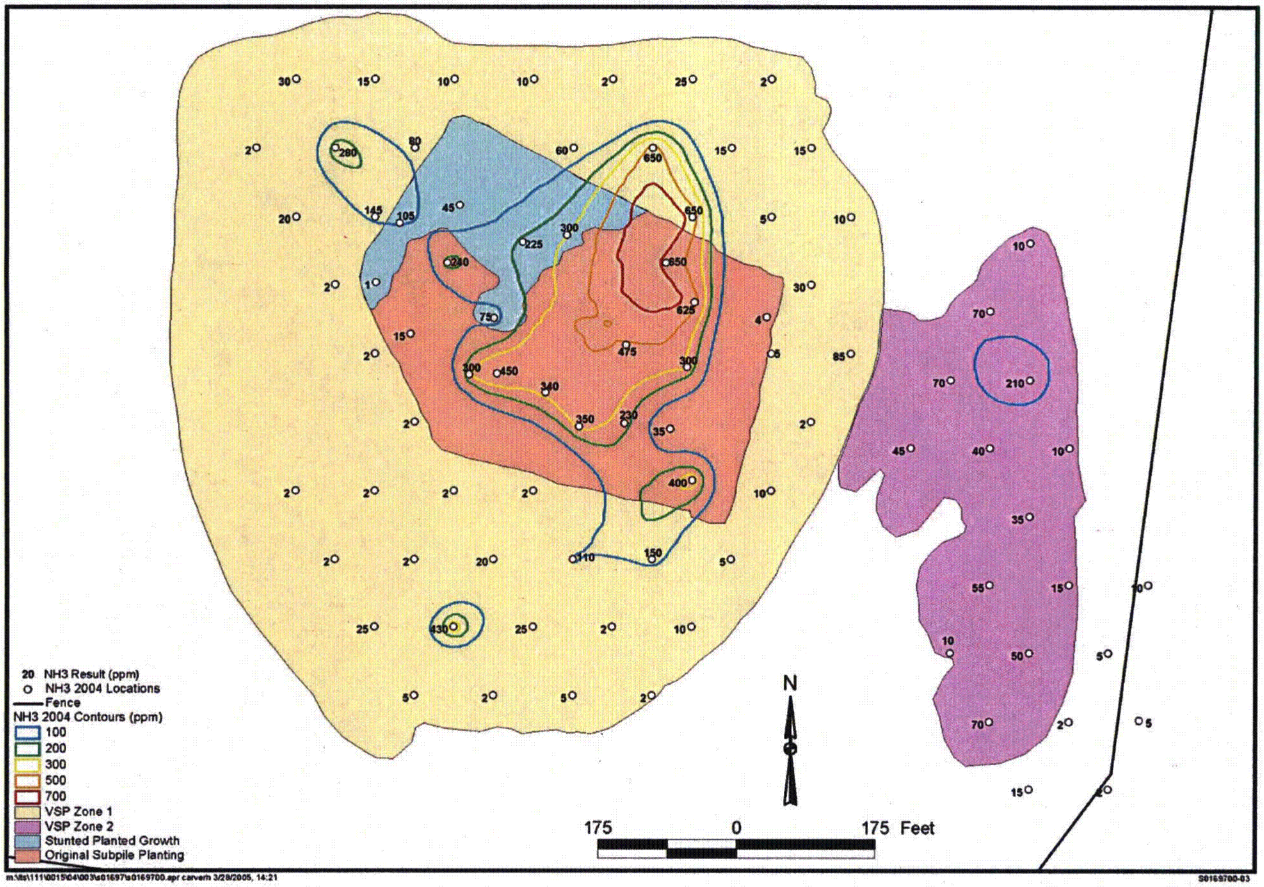


Figure B–7. Map of ammonia (NO_3-N) concentrations in soil within the New Tailings Pile and Evaporation Pond source areas. Based on 2004–2005 sampling results.

B.1.3 Delineation of 2006 Phytoremediation Field

Several factors were considered in the development of a map for the expanded source area planting, including the following: (1) extent of elevated soil nitrate and ammonia concentrations in the source areas, (2) extent of denuded areas, (3) vegetation including the distribution and maturity of volunteer fourwing saltbush, and (4) depth to bedrock.

Site characterization results (Section B.1.2) provided a map of the extent of soil nitrate and ammonium in footprints of the New Tailings Pile and Evaporation Pond. These data were also used as a baseline for comparison with subsequent annual sampling results used to monitor the response of soil nitrate and ammonium to actions taken to enhance phytoremediation and denitrification in the source area (Section B.4.4).

ET by recent volunteer saltbush and greasewood within the fenceline (Figure B–8) is likely controlling the soil water balance and preventing percolation and leaching of contaminants within these stands, and these native plants are also removing nitrate. Therefore, rather than disturb these native plant populations, natural phytoremediation was allowed to progress without intervention. A contour map showing depth to bedrock (Figure B–9) was created using sample points where bedrock was encountered during the systematic grid sampling.

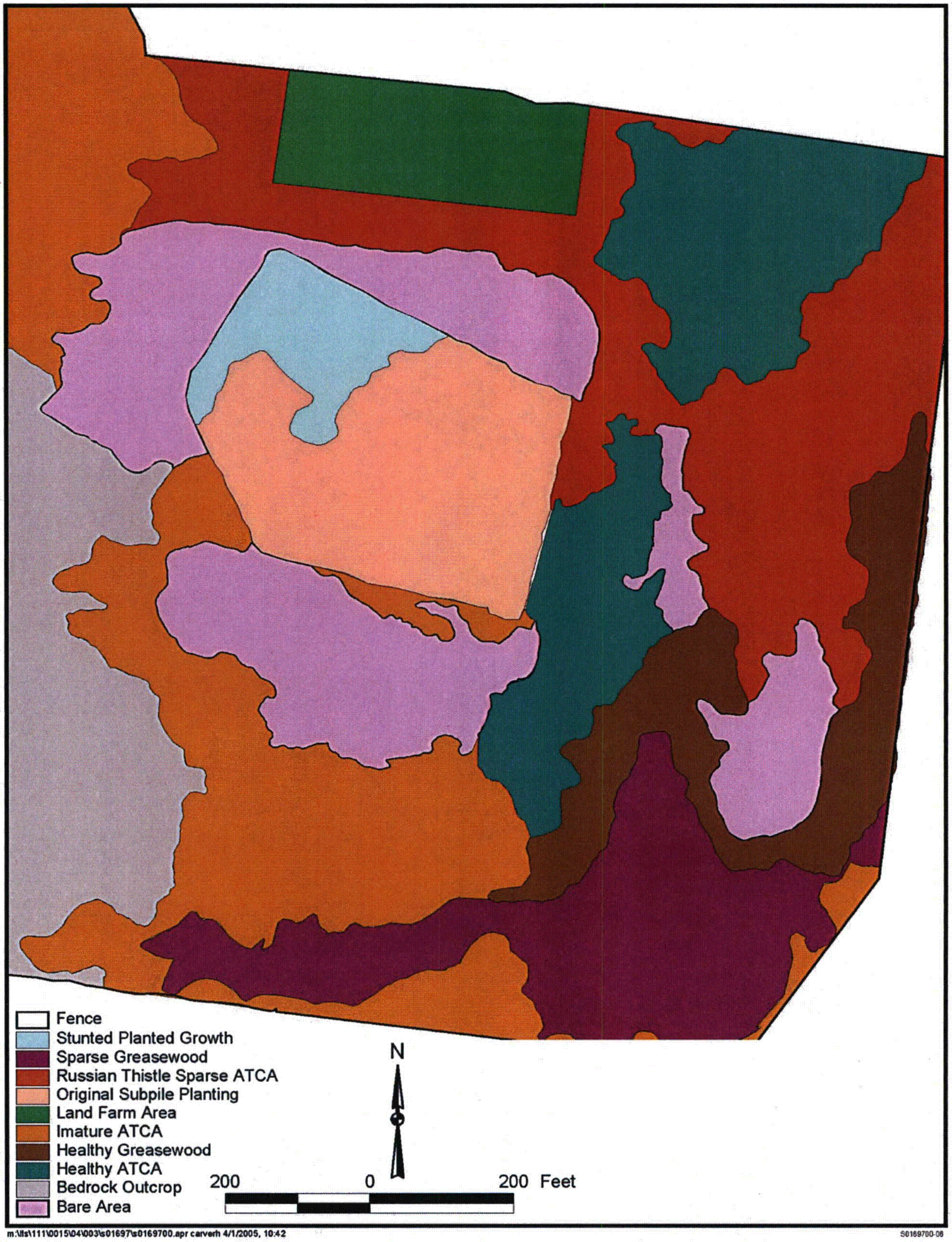


Figure B–8. Map of vegetation types, bare areas, rock outcrops, and the 1999 phytoremediation planting (including the stunted growth area).
The map was created by subjectively delineating relevant mapping units using GPS.

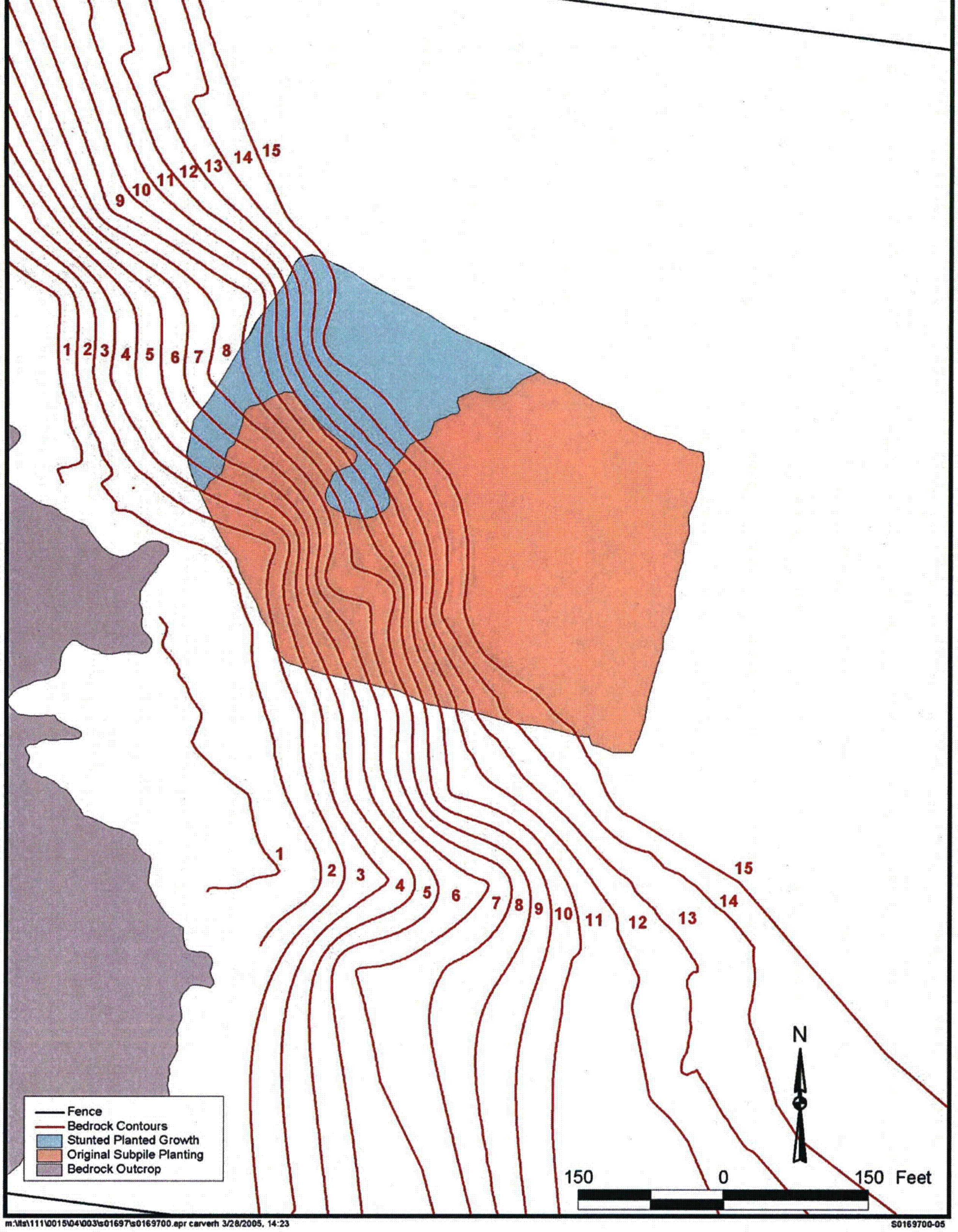


Figure B–9. Rock outcrops and depth-to-bedrock contour map in proximity of the original phytoremediation planting.

The area chosen for the 2006 phytoremediation planting is shown in Figure B–10 (the area within the magenta line boundary). The planting encompassed the majority of the 1999 planting, areas within the New Tailings Pile footprint both north and south of the 1999 planting, and an area within the Evaporation Pond footprint. Delineation of the expanded planting relied on the maps of nitrate and ammonia distribution (Figures B–6 and B–7), vegetation (Figure B–8), and depth to bedrock (Figure B–9). The selected planting area satisfied the following criteria: (1) nitrate (NO_3-N) and/or ammonia (NH_3-N) levels near or greater than 100 parts per million (ppm), (2) bare or sparsely vegetated soils, and (3) depth to bedrock exceeding 5 ft.

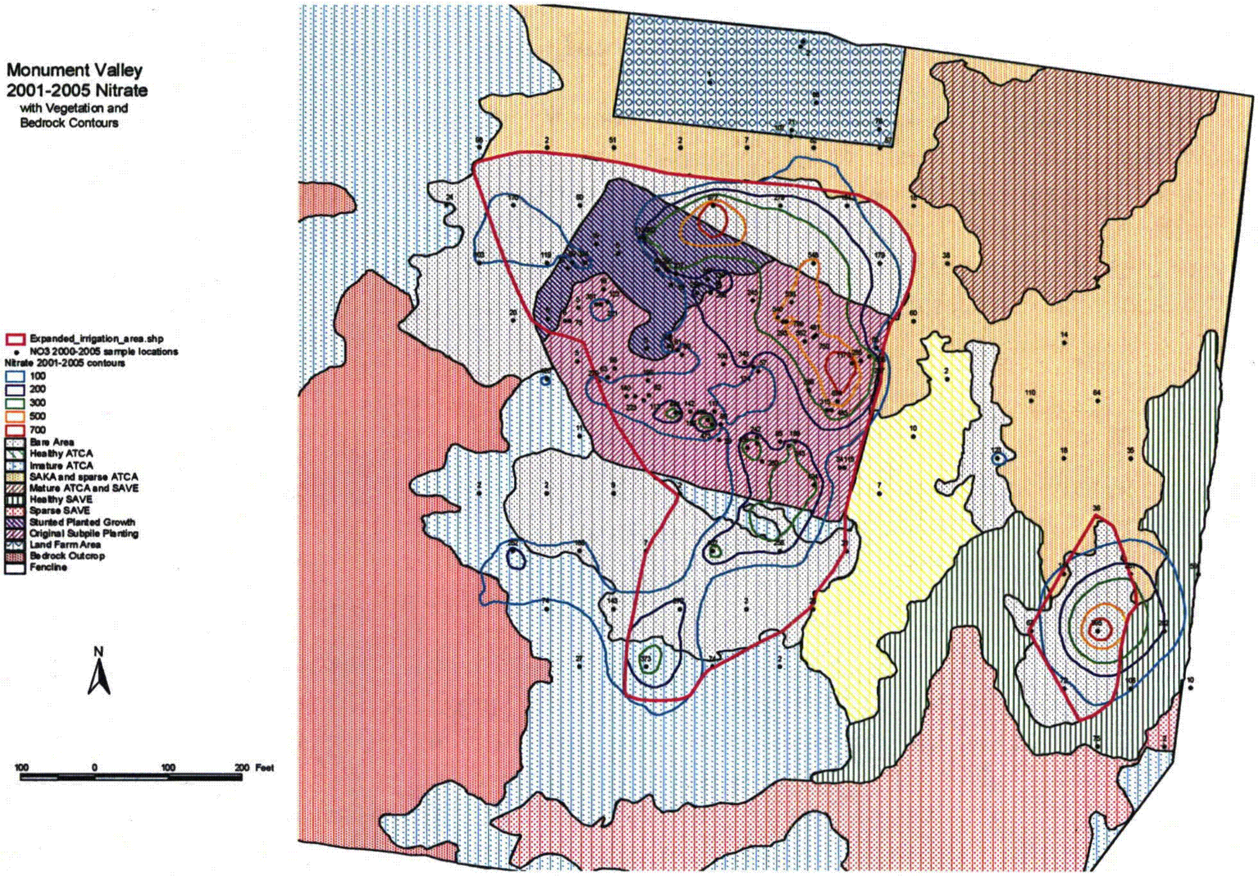


Figure B–10. Outline of the 2006 source area phytoremediation planting or Extended Fields (the area within the magenta line boundary) superimposed on maps of existing vegetation, the 1999 phytoremediation planting, and soil nitrate distribution.

Most but not all bare areas with elevated NO_3-N or NH_3-N were included in the 2006 planting. Some areas already supported mature or establishing greasewood and saltbush stands; natural phytoremediation is ongoing in these areas and enhancement efforts (e.g., soil preparation and planting) would set back the favorable ecological succession. The southern tip of the new planting was an exception. The nitrate hot spot was in a sparse, immature stand of saltbush. This area was irrigated to accelerate plant growth, stimulate denitrification, and increase ET. A small area in the southwest corner of the New Tailings Pile footprint has elevated NO_3-N or NH_3-N, but depth to bedrock was shallow. Because of relatively low contaminant mass and the likelihood that irrigation would cause leaching rather than prevent it, this area was also omitted from the 2006 planting. Some of the bare areas to the north and south, with low NO_3-N or

NH_3-N concentrations, were included in the planting to reduce deep percolation and help control contaminant movement into the alluvial plume.

In spring 2006, compacted portions of the new planting areas were ripped, the original irrigation system was replaced and extended to water the 2006 field expansion, and seedlings started in a University of Arizona greenhouse from local seed sources were transplanted on 2 m spacing (DOE 2006). The locations of the original 1999 phytoremediation planting and the 2006 expansion of the planting (Extended Fields) are shown in Figure B–10.

B.2 Natural Sources of Nitrate, Ammonia, and Sulfate

Southwestern deserts are known to naturally accumulate nitrate and sulfate in soil horizons, in the vadose zone, and in groundwater. Natural sources may be contributing to nitrate and sulfate in the alluvial aquifer at Monument Valley. The purpose of a 2005 task was to investigate the occurrence and mobility of natural sources of nitrate and sulfate, both in the vadose zone overlying the plume and in the alluvial aquifer upgradient of the plume. This information could be used to establish reasonable cleanup goals for the alluvial plume. This study took place in 2005 (DOE 2006).

B.2.1 Vadose Zone

Atmospheric deposition and litter decay during the Holocene are the presumed source of vadose zone nitrate (Walvoord et al. 2003). Accumulation occurs over long periods of time as nitrate in soil is leached in response to episodic wetting events. Similarly, accumulation of calcium sulfate (gypsum) in desert soils can occur especially where geologic parent materials are high in gypsum, as is the case at Monument Valley.

Soils and vadose-zone sediments, sampled in 2006 from varying depths at locations overlying the alluvial nitrate and sulfate plumes, were analyzed at the ESL in Grand Junction. Samples were collected (1) using a hand auger near wells 606, 656, 679, and 765, every half-meter from the surface down to a depth of 7 meters, and (2) using a Geoprobe at two locations each near wells 606 and 677, about every meter from the surface down to at least 9 m (Figure B–11).

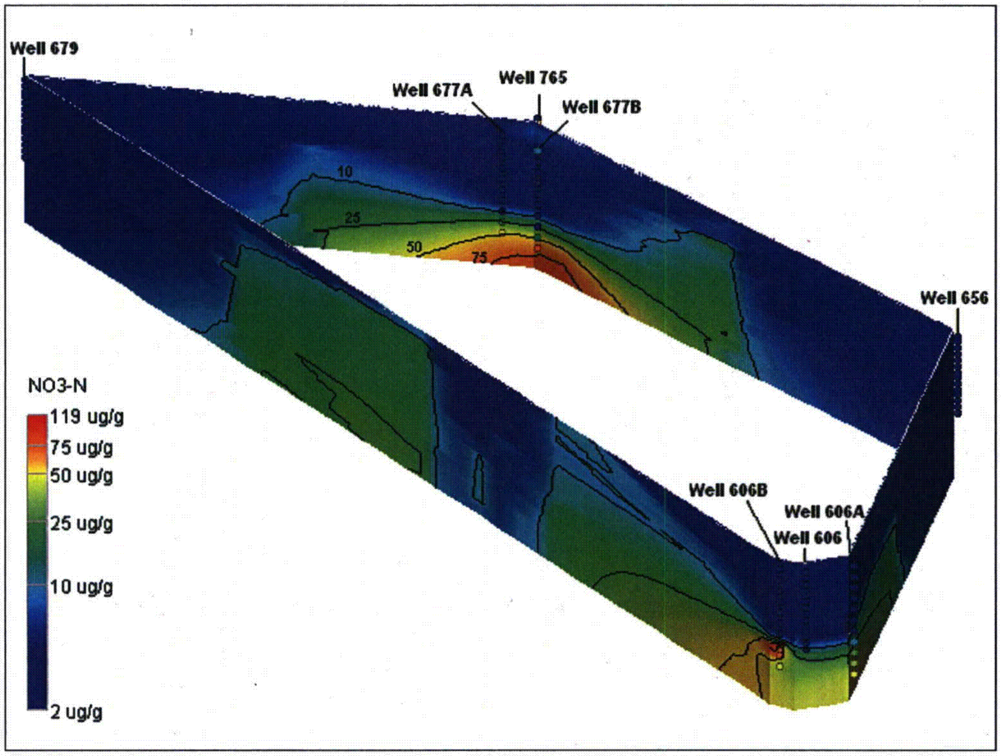


Figure B–11. EVS-generated solid-phase nitrate as N fence diagram for the vadose zone overlying the groundwater nitrate plume north of the Monument Valley site. View perspective is from the southwest looking to the northeast.

Results shown in Figure B–11 and Figure B–12 are "fence diagrams" created from the combined data sets using a modeling software program called EVS. An EVS kriging of the data provided interpolation between wells (confidence is greater for interpolated information between closely spaced wells than between wells spaced farther apart). Nitrate (NO_3-N) values in the vadose zone ranged from < 5.6 (detection limit of the analytical procedure) to 119.6 micrograms per gram (µg/g). Detectable nitrate concentrations occurred primarily in the vadose zone between the surface and 7 m below the surface, and in groundwater between 9 and 11 m below the surface.

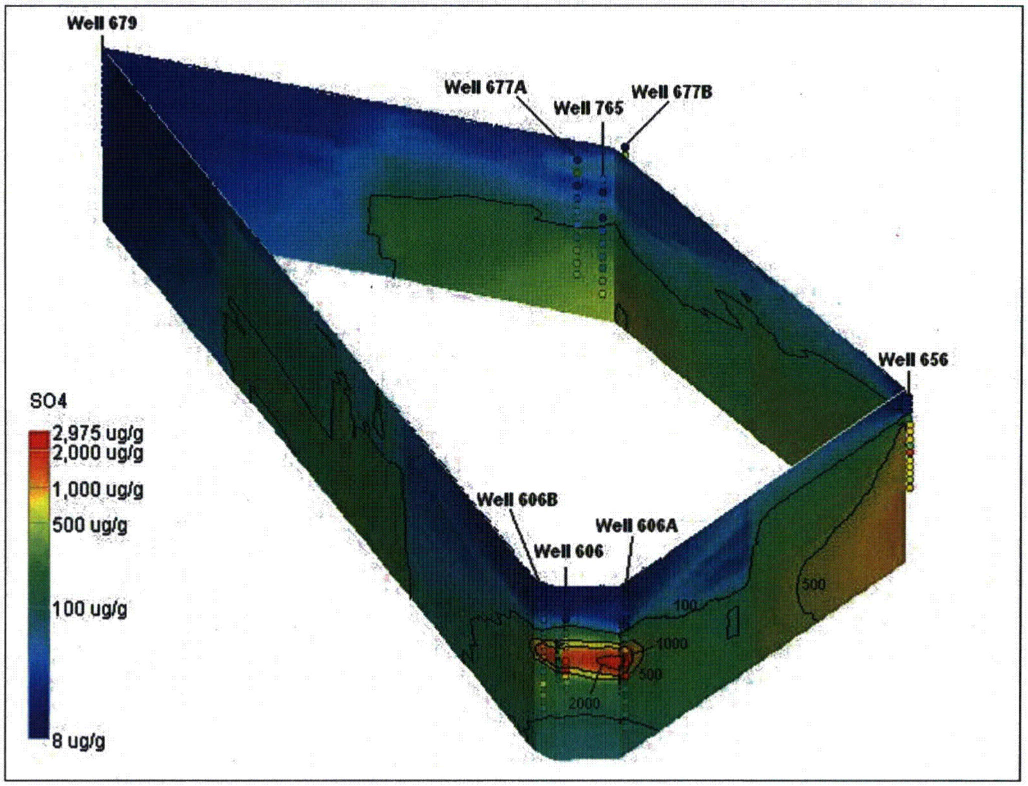


Figure B–12. EVS-generated solid-phase sulfate fence diagram for the vadose zone overlying the groundwater nitrate plume north of the Monument Valley site. View perspective is from the southwest looking to the northeast.

Walvoord et al. (2003) found natural reservoirs of nitrate at depths ranging from approximately 1 to 5 m in areas with healthy native vegetation, and from 9 to 11 m below the surface, as we found at Monument Valley, where deserts had been irrigated or where ET rates were low. However, at Monument Valley, natural nitrate accumulation and plume nitrate may be indistinguishable. The high nitrate layer was just above and continuous with the alluvial plume; therefore, vadose zone nitrate at Monument Valley may be attributable to the capillary fringe of the plume. However, even if the vadose zone nitrate layer is naturally occurring, concentrations are relatively low, so LM considers the mill site to be the major nitrate source for the alluvial nitrate plume.

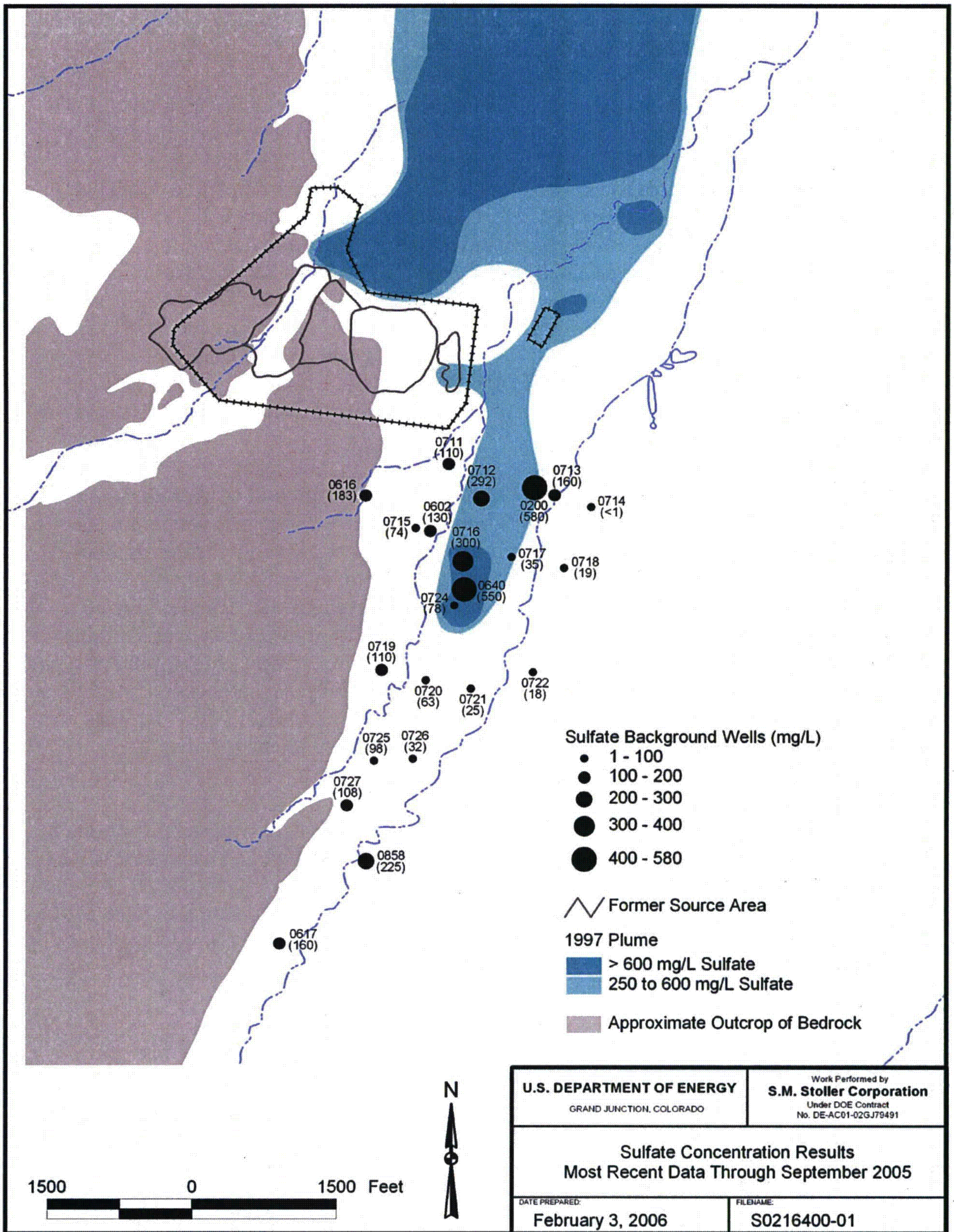
Sulfate (SO_4^{2-}) concentrations in the vadose zone above the plume ranged from < 25.0 (below the detection limit of the analytical procedure) to 2,975 mg/kg (reported as µg/g). Concentrations greater than 100 µg/g occurred in all borings except near well 679. The elevated concentrations likely represent naturally occurring zones of gypsum ($CaSO_4^{2-}$) accumulation. The highest SO_4^{2-} levels were found in a distinct layer in borings near well 606 between about 1.5 and 6 m below the surface. More diffuse zones of SO_4^{2-} accumulation occurred throughout the vadose zone profile near wells 656, 677, and 765. Soluble gypsum salts derived from sulfate-rich eolian and fluvial sediment often accumulate where rainwater moves the salts down in the vertical profile. The depths of accumulation can vary in response to surface ecology and disturbances—the greater the disturbance, the lower the ET, resulting in greater infiltration and leaching of gypsum salts. However, as with nitrate, given the relatively low values, the mill site is considered to be the major source of alluvial water sulfate.

B.2.2 Upgradient Alluvial Groundwater

An initial characterization of background concentrations of sulfate and nitrate in the alluvial aquifer upgradient of the plume at the Monument Valley site (DOE 1998) indicated highly variable concentrations of these dissolved ions, particularly sulfate. The high degree of variability could be attributable to many factors including unknown completion depths of existing wells, unknown production rates, effects of the occurrence and quality of surface water, perched groundwater that may not be representative of the deeper alluvial aquifer, and influences of artesian groundwater from the de Chelly Sandstone (DOE 1998). Another factor influencing groundwater composition is the variability in geologic strata it contacts. For example, the Moenkopi Formation contains gypsum that would contribute sulfate to groundwater (Appendix A, Figure A–5). The geologic beds are steeply dipping in the Cane Creek area; thus, the alluvial groundwater makes contact with a variety of strata within and upgradient of the project site (DOE 1998). For these reasons, 19 new borings were drilled in 2005; 16 were made into monitoring wells (DOE 2006).

Groundwater concentrations of sulfate and nitrate (as N) in background or upgradient alluvial wells are shown in Figure B–13 and Figure B–14, respectively. The highly variable concentrations of SO_4^{2-} are suggestive of a groundwater system containing water from local recharge. Surface water in the intermittent streams is likely to have highly variable concentrations due to variable degrees of evaporation. The groundwater samples may be reflecting this variation. Another explanation for the variability is the presence of a mixing zone where upwelling groundwater from the de Chelly Sandstone mixes with groundwater originating from local recharge. de Chelly groundwater is low in SO_4^{2-} whereas local recharge is likely a source of higher concentrations resulting from concentrations observed in the Frog Pond area located along Cane Wash, about 1,000 ft downstream of the upgradient sampling area (DOE 1998).

Nitrate concentrations are relatively low throughout the upgradient alluvial sampling area. Nitrate (as N) concentrations range from less than 0.8 mg/L to 7.9 mg/L. The highest value was observed in a sample of groundwater collected from the most southern well (0617). These low concentrations are typical of many groundwaters and could result from natural or anthropogenic sources. The low NO_3^- concentrations upgradient, coupled with relatively low nitrate levels in the vadose zone overlying the plume (Section B.2.1), indicate that essentially all of the NO_3^- in the plume is due to contamination from the mill site.



m:\lts\111\0015\04\001\s02164\s0216400.apr smithw 2/3/2006, 12:54

Figure B–13. Sulfate concentrations in upgradient alluvial wells.

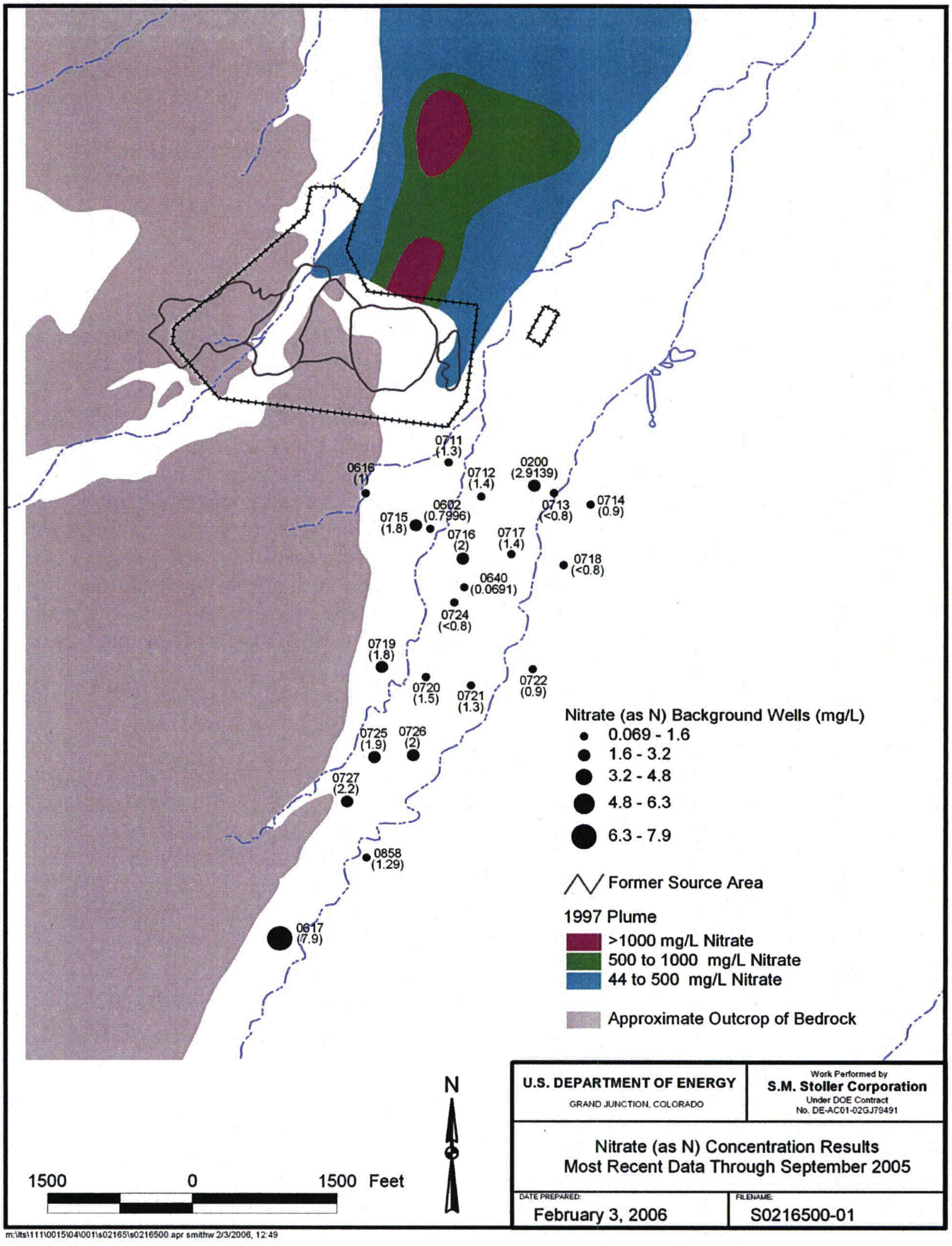


Figure B–14. Nitrate (as N) concentrations in upgradient alluvial wells.

B.3 Phytoremediation with Native Shrubs

The objectives for phytoremediation in the source area were (1) control migration of contaminants from the source area into the alluvial aquifer by increasing ET and (2) promote uptake of nitrate, ammonium, and sulfate contamination in plant tissues. Much of the source area was devoid of plant cover in 1997 when phytoremediation was initiated (Figure B–15, Top Panel), but the site now supports a high density of planted and volunteer shrubs (mainly fourwing saltbush) inside the fence and surrounding the source area (Figure B–15, Bottom Panel).

B.3.1 Planting and Irrigation

The first phytoremediation field in the source area (designated the Old Field) was delineated based on a field survey of ammonium and nitrate concentrations in a radial pattern centered around a single hot spot of ammonium contamination found in the initial site survey (Section B.1). In 1997 nitrate and ammonium were measured in soil cores at 0–3 m soil depths along radial survey lines extending 100–150 m from the initial hot spot. Nitrate concentrations averaged 378 mg/kg and ammonium concentrations averaged 34.2 mg/kg. A 1.7 ha drip irrigated field that encompassed the contaminated area around the hot spot was constructed and planted in 1999 (DOE 2002). Plants were spaced 2 m apart within and between rows. There were a total of about 4,000 plants, 99 percent of which were fourwing saltbush transplants and 1 percent black greasewood. In 2005, further surveys were conducted in the source area to see if additional pockets of contamination were present (Section B.1). As a result, the planting was expanded in 2006 creating four new plots or fields (Figure B–16). These were designated New Fields North, West, and South, and Evaporation Pond. The new fields added 1.6 ha of land for a total of 3.3 ha of phytoremediation plots in the source area. Figure 1 shows the locations of the 1999 planting (Old Field) and 2006 plantings (New Fields) within the footprint of the New Tailings Pile.

Each plant is individually irrigated, typically for 2–3 hours per day at a rate of 2 liters (L) per hour, for a total application of 1.0–1.5 mm/d on an aerial basis over the fields. However, exact irrigation volumes have varied depending on the performance of the drip irrigation system. Furthermore, temporary increases in irrigation volume were tested in 2007 (DOE 2008). Irrigation rates have been maintained lower than rates of potential evapotranspiration (ET_0) for mature saltbush plant canopies (typical rates are about 6 mm d^{-1} in summer at this location). Hence, the plants are deficit irrigated; they are provided with enough supplemental water to stimulate growth but not enough to produce drainage below the root zone. (Note, potential ET is a mathematical calculation of ET requiring as input: daily mean temperature, wind speed, relative humidity, and solar radiation.)

B.3.2 Plant Canopy Growth and Development

Survival of plants in all phytoremediation plots in the source area was high. Survival of plants in the Old Field was 80 percent during the first season, with some plants lost due to malfunction of the irrigation system. Dead plants were replaced and the irrigation system repaired, and survival from 2000 to 2001 was 97 percent. Survival of transplants in the new fields was also high, ranging from 96 to 98 percent over the first two growing seasons. Despite high survival rates, many plants in both planting years exhibited stunting over the first season, and these plants grew slowly over subsequent years. Stunting affected about 30 percent of plants in the Old Field, and the majority of plants in the New Field West, the New Field South, and the Evaporation Pond

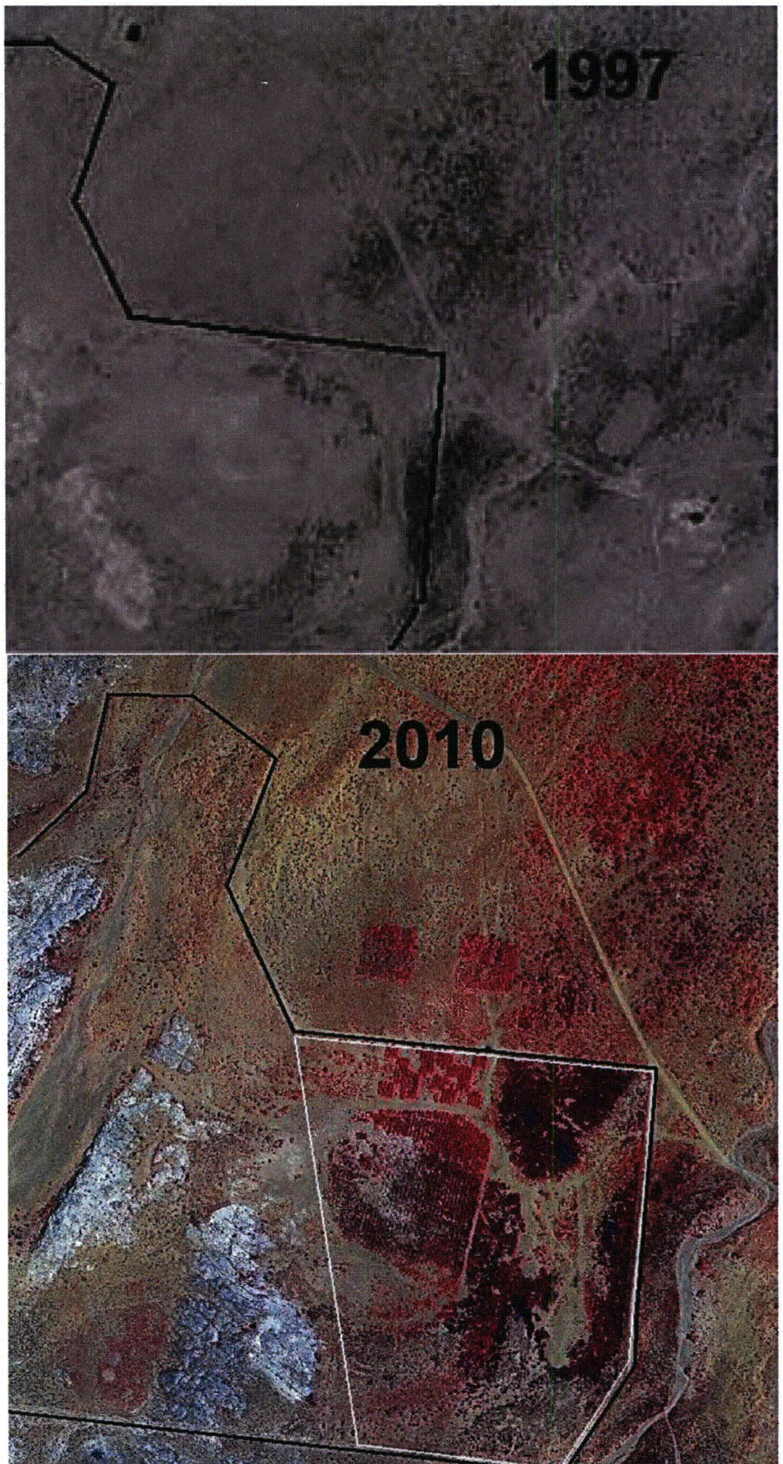


Figure B–15. Comparison of site vegetation on a black-and-white aerial photograph in 1997 (Top Panel) and on a Quickbird satellite image with vegetation shown in false-color red in 2010. The black line on both images denotes the fence line around the source area.

Figure B–16. Cane Wash, Arizona, residents Ben and Mary Stanley transplanting fourwing saltbush seedlings in the 2006 phytoremediation pilot study at the New Fields at the Monument Valley site.

area). Only the New Field North is apparently free of stunted plants. Stunting appears to be associated with the chemistry of the surface soil layer in some parts of the source area and is discussed in Section B.3.4.

Percent plant cover, leaf area index (LAI), and Normalized Difference Vegetation Index (NDVI), estimated in 2010 by ground and satellite imagery, are in Table B–1and locations are in Figure F–1, Appendix F, "Remote Sensing Monitoring of Phytoremediation". Plant growth (mainly fourwing saltbush) has occurred not only in the phytoremediation plots but also as volunteer plants throughout the fenced area encompassing the source area. Plants in the Old Field and in the densely vegetated volunteer ATCA area inside the fence have developed high plant cover (50–70 percent), but plant vigor has decreased judging by LAI and NDVI measurements. These stands are undoubtedly water-limited and may have become partly senescent.

Table B–1. Percent cover, LAI, and NDVI of the source area (subpile soils) phytoremediation plantings in the Old Field (1999 planting), New Fields (2006 plantings), and in a volunteer stand of Atripelx canescens (ATCA or fourwing saltbush).

Area	Cover (%)	LAI	NDVI
Old Field	51.4	0.69	0.143
New Field North	60.1	1.65	0.230
New Field South	31.1	0.58	0.167
New Field West	4.1	0.16	0.120
New Field EP	27.8	0.18	0.141
Volunteer ATCA	70.8	-	0.147

Detailed plant surveys were conducted during 2002–2009 and results are documented in Monument Valley Pilot Studies Status Reports (Section 6.0). By 2010, a mature plant community had developed over an area of approximately 11 ha in the source area, consisting of planted and volunteer plants (white polygon in Figure B–15, Bottom Panel). Final plant cover in this area was 47 percent based on remote sensing results (Appendix F). Biomass harvesting was conducted in 2006 and 2007 and correlated with canopy cover. A linear relationship was found:

$$\text{Biomass (kg m}^{-2}) = 1.39 \times f_c$$

where f_c is fractional cover, $r^2 = 0.95$ (r^2 is the coefficient of determination). Based on this equation and areas of the plots, the standing crop of biomass in the phytoremediation plots is 6.9 t (metric ton) in the New Fields and 12.1 t in the Old Field, and 71.2 t over the 11 ha area delineated in Figure B–15, Bottom Panel.

B.3.3 Root Penetration

A key concern was whether plants would develop deep root systems capable of intercepting soil moisture and contaminants throughout the soil profile, which is 2–5 m deep overlying limestone bedrock in the source area. Rooting depth was measured by taking 250 g soil samples from auger samples collected from 0.1 m to 5 m soil depths in April 2009. Samples were collected from the Old Field and from New Fields North, South, and West. Roots were present in samples as root fragments of varying length. Root fragments were extracted by suspending soil samples in 1 L of brine solution (400 g/L NaCl), which floated root fragments to the surface. Foam was settled by spraying the surface with a small amount of ethanol, and then root fragments were recovered by carefully decanting the surface layer containing roots into a funnel with filter paper. Root fragments on the filter paper were then counted under a 10× binocular microscope.

Results were expressed as mg of dry roots per kg of soil by recovering, air-drying, and weighing a subsample of root fragments from seven of the soil samples. These were near-surface samples with high root content, so root fragments could be easily separated from other material on the filter papers and quantified. A total of 496 root fragments weighed 63.4 milligrams (mg) dry weight, for a mean value of 0.128 mg per fragment (Std Error = 0.075, n = 7). This assay procedure is only semi-quantitative due to the high variance in weights per root fragment. Fragments were not weighed directly in all samples because the filter papers contained soil particles and other material that would overestimate the weight of roots in samples with sparse root content.

Root content was highest at the soil surface, as expected because this zone is the first to receive irrigation water. However, root content was relatively constant at about 80 mg kg^{-1} from 1 to 5 m soil depth (Figure B–17). Results were similar in the New Fields and the Old Field, showing that roots quickly penetrated to the bottom of the profile. Hence, plant roots accessed the entire soil profile in the phytoremediation plots, but they were most concentrated in the top 10 centimeters (cm) of the soil profile.

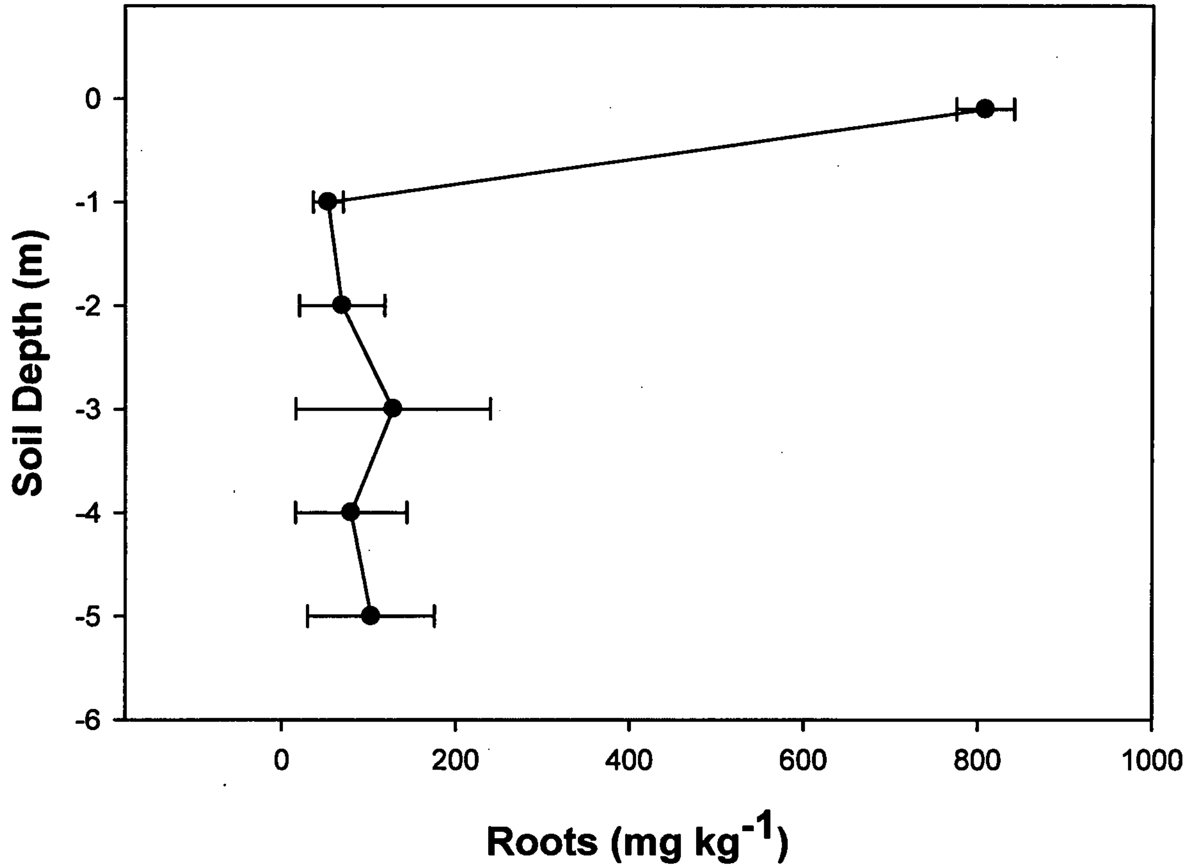


Figure B–17. Root content of soils in phytoremediation plots as a function of soil depth. Bars are standard errors of means.

B.3.4 Stunted Plant Growth: Causes and Recourses

Considerable effort was spent trying to understand the causes for stunted growth in some parts of the source area planting. Some of these areas coincided with areas of apparent chemical staining of the surface soil, visible on aerial photographs and Quickbird images in the Old Field (Figure B–18). One objective was to see if the soil could be amended to restore plant growth; a second objective was to determine if there were human health risks associated with chemical residues on the soil.

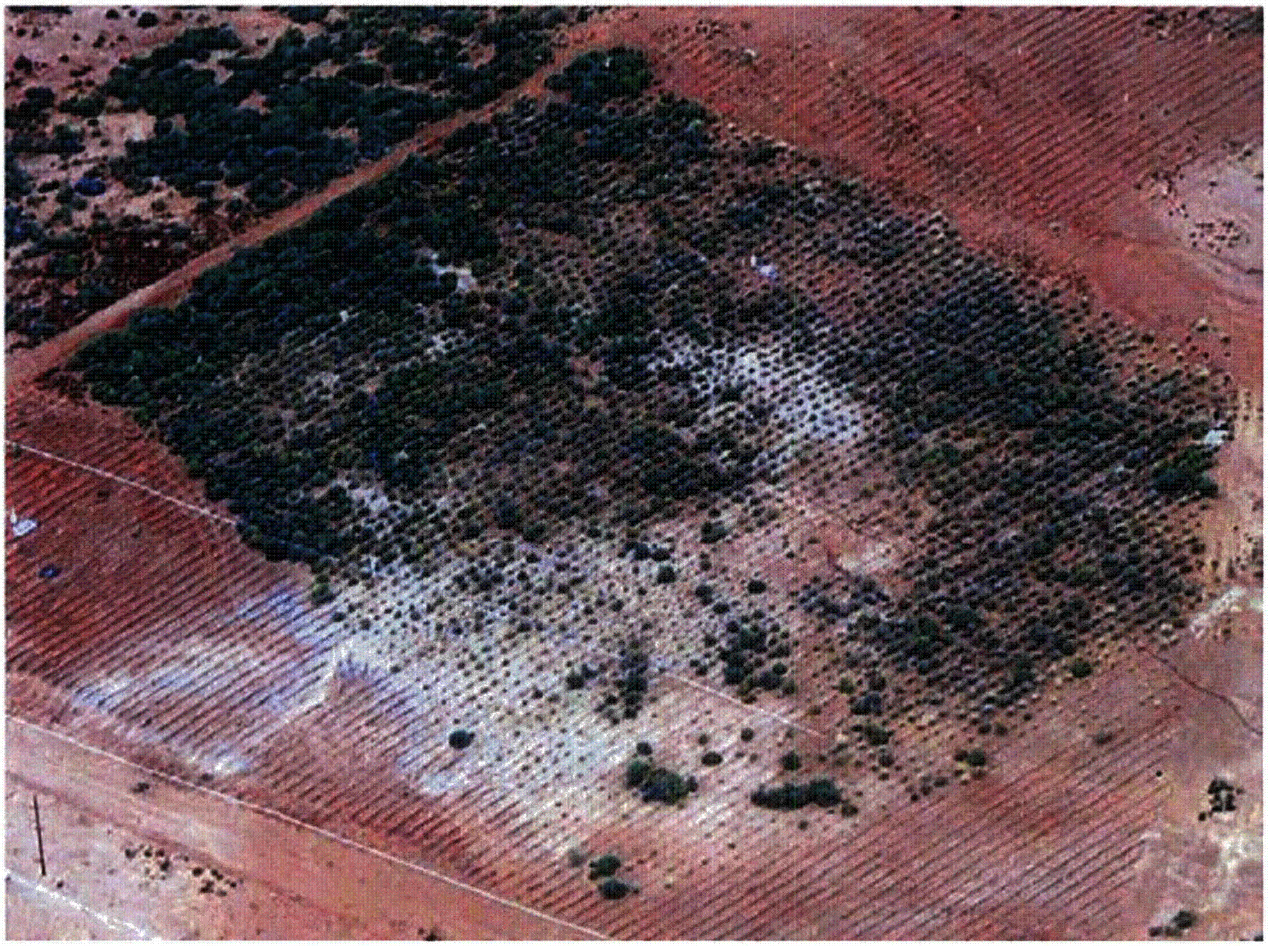


Figure B–18. Aerial view of the source area phytoremediation plantings in 2006, showing areas of chemical staining in white.

In 2005, greenhouse experiments were conducted with sudan grass grown in soil collected from stunted-growth and good-growth area of the Old Field (DOE 2006). Sudan grass grew poorly in soil from the stunted-growth areas. Further greenhouse trials were conducted in 2006 by students at Diné College in Tsalie, Arizona (Figure B–19) growing fourwing saltbush in stained soil (DOE 2008). Adding organic potting mix to the stained soil enhanced the growth of fourwing saltbush, but a series of replacement experiments with micronutrients did not reveal any micronutrient deficiencies.

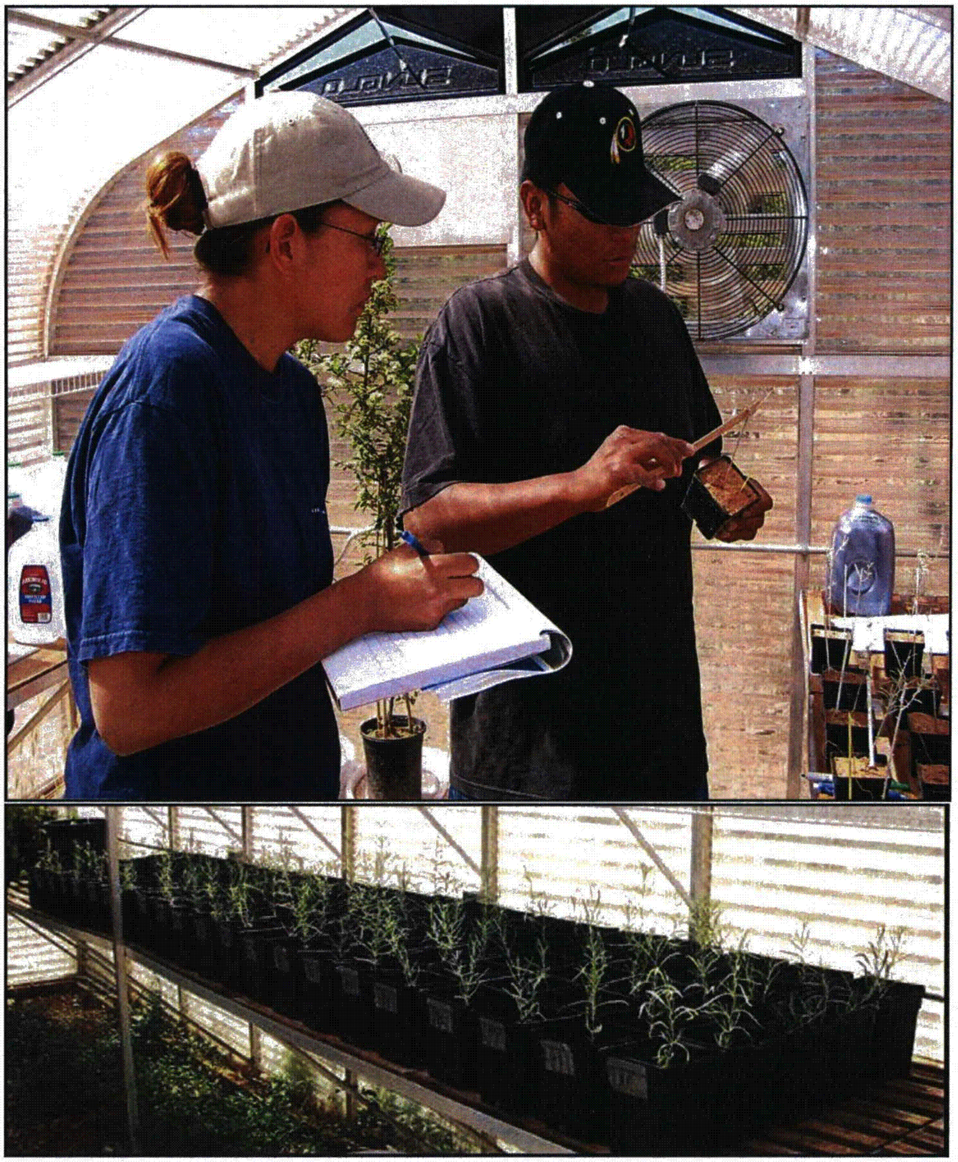


Figure B–19. Top Panel: Diné College students Alverae Laughter and Westin Lee measuring fourwing saltbush plants as part of a greenhouse study of stunted growth and micronutrient supplements at the Tsaile, Arizona campus. Bottom Panel: Atriplex plants 4 weeks after the start of the greenhouse experiment. Plants were sown in the stained soil both with and without potting mix and both with and without micronutrient amendments.

The stains observed at the site consisted of different colored materials (red, gray, yellow, and black) suggesting a heterogeneous mix of chemicals were present. Soil samples from the poor-growth areas were lower in copper and sulfate and higher in calcium, iron, and magnesium than soils from good-growth areas. Calcium was present in very high amounts in the stained areas of the Old Field and might have contributed to stunting by interfering with plant uptake of nutritional ions. Plant tissues did not accumulate uranium or other heavy metals to levels of concern for grazing animals. Manganese nodules, which are precipitates of manganese and iron, were also observed in the stained areas. However, analyses of manganese levels in stained soil samples showed that concentrations were within the range of natural soils and did not pose an exposure risk to workers onsite (DOE 2009). A yellow precipitate was noted in areas of the former Evaporation Pond, and these were tested for radioactivity and chemical composition. Uranium and vanadium salts were found in the precipitates, but at levels that were two orders of magnitude lower than would pose an exposure risk to workers onsite (DOE 2010).

An effective remedy for stunted plant growth was not found. Application of organic mulch to the plants in their early stage of growth appeared promising. Scientists thought that after plants reached a critical size, they might extend their roots through the stained layers and into uncontaminated soil, and continue to grow. This occurred with several individual plants However, areas of the Old Field planted in 1999 still have low plant cover and stunted plants, so surface treatments alone are not sufficient to promote good plant growth in these areas.

B.3.5 Plant Uptake of Nitrogen and Sulfur

Nitrogen concentrations were measured annually in plant tissues (leaf and stem samples) from 2001 to 2008, and sulfur was measured in 2007 and 2008 (see the Status Reports in Appendix I). Plant nitrogen content averaged 1.82 percent (SD = 0.34) and sulfur averaged 0.284 percent (SD = 0.127) (SD is the standard deviation). On the basis of biomass estimates (Section B.3.2), plants in source area phytoremediation plots removed 346 kg of nitrogen and 54 kg of sulfur from the soil. These are relatively small amounts compared to the amount of nitrogen and sulfur contaminants initially present in the source area soils (DOE 2002, 2007). However, much larger amounts of nitrate and ammonium have been removed from the source area by microbiological processes stimulated by irrigation of the phytoremediation plots (Section B.4).

B.3.6 Soil Water Balance and Recharge

Soil moisture content was monitored monthly during each irrigation season, 2000 to 2010, with a neutron thermalization hydroprobe. Twenty hydroprobe ports were distributed over the Old Field and an additional 40 were installed in New Fields in 2006. Also in 2006, 16 Water Content Reflectometers (WCRs) and four Water Flux Meters (WFMs) were installed in the phytoremediation plots. One WFM was installed in the Old Field and the other three were in the northeast, northwest and southeast areas of the 2006 New Fields (DOE 2007). WFMs were installed at 370 cm soil depth, and four WCRs were installed above the WFM at each station at 30–60, 90–120, 180–210 and 270–300 cm soil depths. WCRs measure soil water content by electrical conductivity and data are reported on a daily basis. WFMs directly measure the actual downward flux of water through the soil by collecting mobile water via a funnel and wick then quantifying water flux with a tipping bucket collection and weighing device.

Up to 2006, soil moisture levels tended to be stable and below field capacity (about 15 $cm^3\ cm^{-3}$) throughout the Old Field. In 2006, irrigation rates were increased to stimulate additional plant growth, especially in the newly planted areas. Irrigation rates were increased from 165 mm/yr in 2006 to 496 mm yr^{-1} in 2007. This extra water led to an accumulation of moisture in the root zone of some of the plots, and in 2008 irrigation was reduced to 285 mm/yr, which has been maintained through 2010.

Figure B–20 shows soil moisture readings from WCRs averaged over all irrigation zones. A clear seasonal trend in soil moisture is apparent at the 30–60 cm, 90–120 cm, and 180–210 cm soil depths. Water content is highest in summer (July) and lowest in winter (February); this trend is expected because irrigation water is applied April through September or October. Moisture content decreased with soil depth, and also by year for the first three soil depths. Spikes of high soil moisture are evident in the 30–60 cm depth, presumably due to summer monsoon rains. These spikes are dampened at greater depths. Soil moisture in the top part of the profile was highest in 2006, because the New Fields were being irrigated but had not yet developed a plant cover, and moisture accumulated in the soil profile. Soil moisture was significantly higher in the New Fields compared to the Old Field in that year (Figure B–21). Soil moisture also was high in 2007 due to the more aggressive irrigation schedule, but decreased to low levels by 2010 as the new plants developed and irrigation volume was reduced. The soil moisture content at 270–300 cm depth was relatively low, but tended to increase in fall and winter, perhaps due to the infiltration of rainfall and excess irrigation water to that soil depth. However, WFMs have shown no net flux of water at the 370 cm depth since they were installed.

In 2010, soil moisture levels remained below field capacity throughout the profile and were not increasing with depth as might be expected if moisture was percolating past the root zone. The strategy for revegetation of the site and deficit irrigation the plantings appears to have been successful in controlling the site water balance and limiting recharge over the source area. The source area likely supports as much vegetation as is possible at current rates of precipitation and irrigation.

B.4 Soil Nitrification and Denitrification

When the phytoremediation study commenced in 1999, scientists assumed that inorganic nitrogen would slowly convert to organic forms through uptake by transplanted native shrubs, fourwing saltbush and black greasewood, resulting in a slow reduction of inorganic nitrogen in the source area soils. As the study progressed it became apparent that microbial processes were causing soil nitrogen levels to drop at a much faster rate than expected. With this knowledge, research efforts shifted to evaluations of ways to enhance microbial processes.

B.4.1 Rapid Nitrate Loss from the Source Area Soil

The soil in the Old Field initially contained an estimated 36 metric tons of inorganic nitrogen in the form of nitrate and ammonium ions. Plants had converted just 0.35 metric tons of this inorganic nitrogen into organic nitrogen over 10 years (about 1 percent removed per year) (Section B.3). However, the initial loss of nitrogen from the source area soil profile was unexpectedly rapid, with nitrate-N dropping from 164 mg kg^{-1} to 82 mg kg^{-1} between 2000 and 2002 (Table B–2). The decrease occurred throughout the field and was statistically significant ($P < 0.001$). Ammonium levels decreased by less than 10 percent over the same period ($P > 0.05$) (Table B–3). Neutron hydroprobe readings showed that the soil profile was not at field capacity and water fluxmeter monitoring detected no deep percolation (Section B.3.6) so that leaching from the profile by irrigation was not a likely explanation for the loss of nitrate. This was confirmed by a salt balance study, which showed that loss of nitrate could explain the small drop in EC noted in soil samples from 2000 to 2002 (McKeon et al. 2005). If leaching had removed the nitrate, the EC should have decreased more substantially due to loss of other soluble ions in the soil profile.

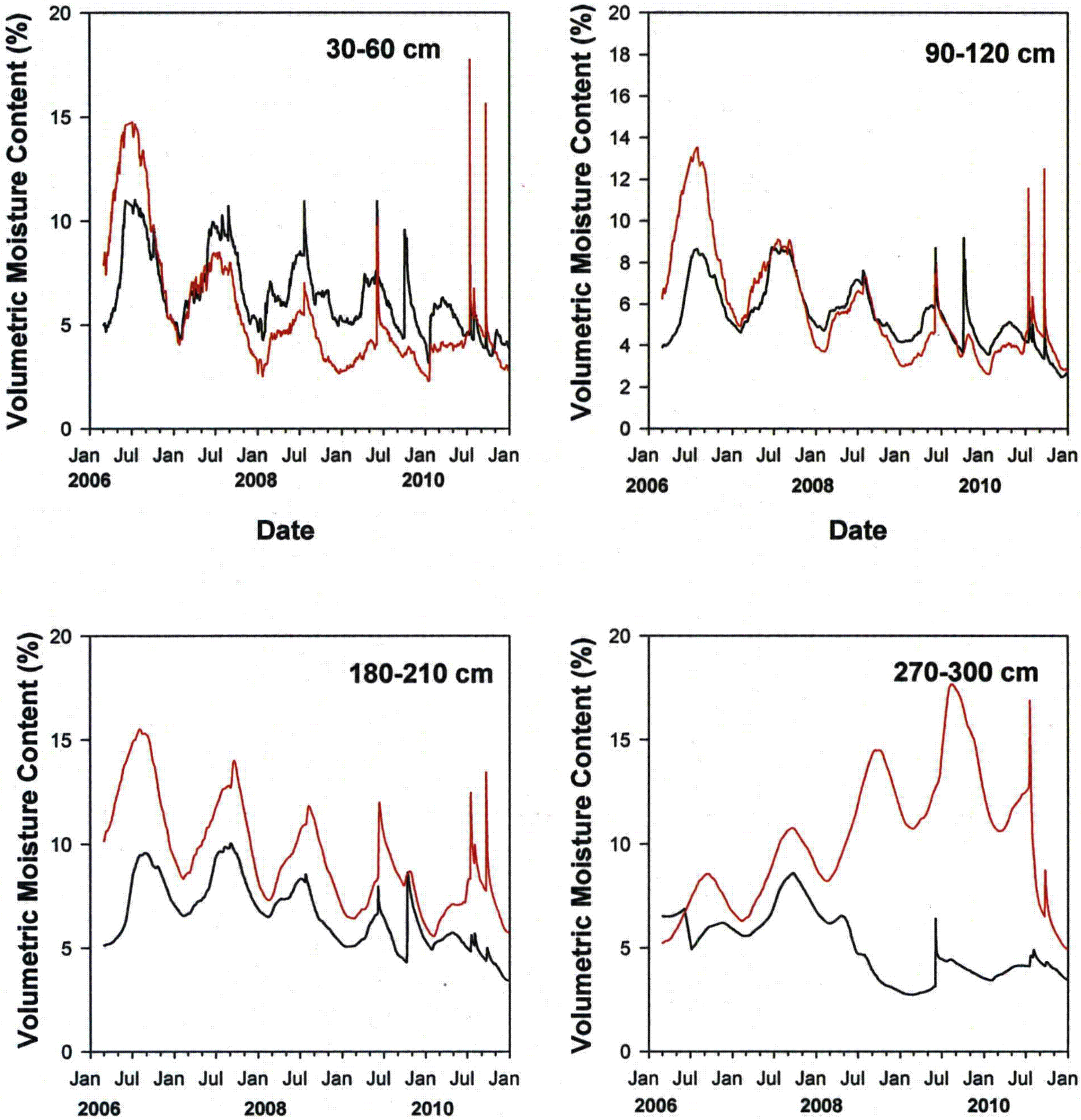


Figure B–20. Soil moisture content at four soil depths in phytoremediation plots, measured by Water Content Reflectometers. Results are daily means of water content for three monitoring stations in New Fields (black line) and one in the Old Field (red line).

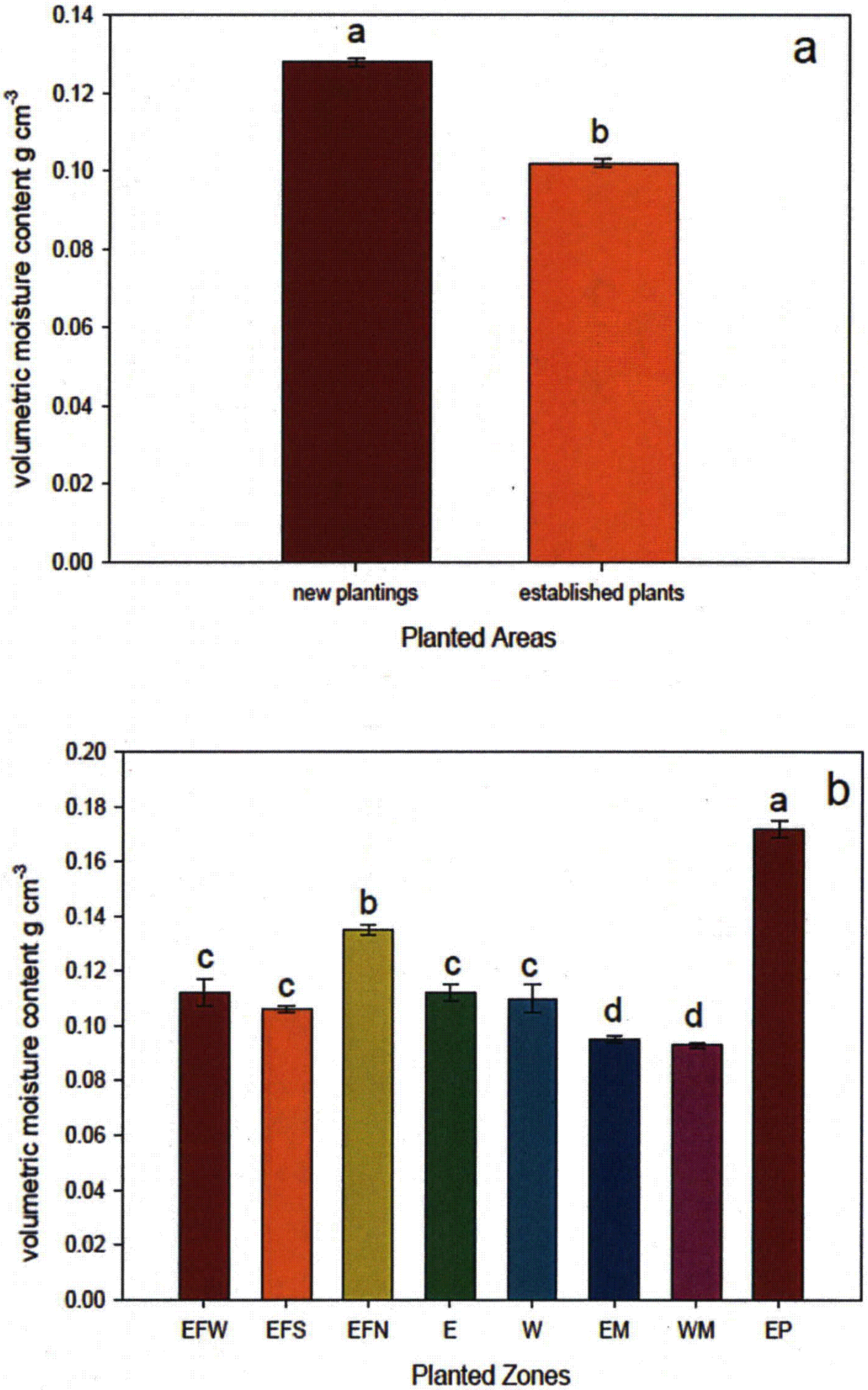


Figure B–21. Mean soil moisture contents in New and Old Field phytoremediation plots in 2006. Means across zones are shown in (a) and means of individual zones are in (b). EFW – extended field west; EFS – extended field south; EFN – extended field north; E, W, EM and WM – east, west, east middle and west middle zones of the Old Field; EP – Evaporation Pond field. Error bars are standard errors and bars with different letters are significantly different at $P < 0.05$.

Table B–2. Nitrate-N concentrations (mg kg^{-1}) in soil samples from the Old Field, 2000 to 2004. The field is divided into four irrigation zones that were each sampled at 2–5 locations near neutron hydroprobe ports. Values are means with standard errors of means in parentheses.

Zone/Depth (m)	2000	2001	2002	2004	Number of Samples
Zone 1					
0.3	71.8 (37.6)	100.8 (41.1)	22.6 (37.1)	25.9 (23.1)	5
0.9	90.6 (25.2)	31.2 (10.5)	7.0 (5.3)	42.9 (34.7)	5, 5, 5, 4
1.8	186.7 (73.9)	52.0 (21.1)	9.3 (6.1)	36.1 (28.8)	3, 3, 4, 4
2.7	218.0 (103.0)	77.5 (60.5)	10.9 (16.3)	27.8 (25.0)	2, 2, 2, 3
3.6	235.0	23.0	48.1		1
4.5	302.0	46.0	57.3		1
Zone 2					
0.3	92.6 (35.5)	112.6 (58.2)	44.1 (47.3)	61.6 (26.5)	5
0.9	154.4 (42.0)	44.0 (13.2)	51.1 (73.5)	39.7 (20.2)	5
1.8	111.2 (33.4)	69.8(34.3)	35.1 (24.1)	43.1 (36.4)	5
2.7	67.8 (24.6)	113.3 (35.8)	34.7 (22.1)	38.4 (29.7)	4, 4, 5, 4
3.6	77.0 (31.9)	90.7 (73.3)	49.5 (39.8)	61.5 (52.5)	3, 3, 3, 2
4.5	113.0 (12.0)	133.5 (35.5)	74.8 (10.8)	59.1 (17.3)	2, 2, 2, 4
Zone 3					
0.3	126.0 (34.3)	95.0(30.1)	73.4 (53.4)	92.9 (36.9)	5
0.9	276.5 (141.1)	116.0 (52.2)	82.6 (54.4)	60.9 (26.9)	5
1.8	213.2 (64.4)	146.2(58.2)	106.0 (41.2)	137.7 (72.3)	5
2.7	180.4 (65.3)	119.0 (53.6)	84.7 (62.1)	147.9 (75.5)	5
3.6	123.6 (35.7)	95.7 (27.9)	58.6 (48.7)	104.1 (39.6)	5, 4, 4, 5
4.5	170.3 (28.8)	164.7(108.8)	107.0 (76.3)	229.1 (111)	4, 3, 5, 4
Zone 4					
0.3	62.0 (13.8)	131.8 (40.9)	145.4 (104.5)	81.5 (55.3)	5
0.9	217.8 (138.4)	181.8(81.6)	74.9 (75.9)	122.6 (73.1)	5
1.8	173.4 (70.9)	170.8 (43.8)	88.2 (87.2)	134.5 (47.4)	5
2.7	286.6 (85.4)	185.6(55.6)	87.3 (97.1)	128.9 (39.9)	5
3.6	227.0 (118.8)	166.8(27.5)	312.7 (432.2)	156.7 (37.4)	5
4.5	322.6 (106.1)	240.8 (20.3)	283.8 (229.8)	181.6 (71.0)	5, 4, 5, 5
Average	**164**	**116**	**82**	**91**	

Table B–3. Ammonium-N concentrations (mg kg^{-1}) in soil samples from the Old Field, 2000 to 2004. The field is divided into four irrigation zones which were each sampled at 2–5 locations near neutron hydroprobe ports. Values are means with standard errors of means in parentheses.

Zone/Depth (m)	2000	2001	2002	2004	Number of Samples
Zone 1					
0.3	2.5 (1.2)	66.8 (53.5)	1.9 (0.83)	1.52 (0.51)	5
0.9	44.9 (45.5)	121.9 (62.1)	10.3 (11.1)	5.82 (3.98)	5, 5, 5, 4
1.8	102.7 (93.2)	146.7 (109.1)	57.8 (77.8)	85.3 (65.0)	3, 3, 4, 4
3.6	56.0	43.0	7.5		1
4.5	140.0	113.0	77.5		1
Zone 2					
0.3	8.2 (2.0)	55.3 (42.9)	12.3 (18.9)	1.37 (0.51)	5
0.9	155.2 (73.3)	110.8 (53.2)	93.3 (76.0)	74.6 (57.6)	5
1.8	329.6 (60.9)	200.2 (50.2)	196.1 (152.0)	191.5 (80.9)	5
2.7	287.0 (60.4)	226.1 (50.2)	257.0 (144.2)	230 (89)	4, 4, 5, 4
3.6	310.0 (60.4)	244.3 (22.6)	220.8 (141.2)	227.5 (62.5)	3, 3, 3, 2
4.5	360.0 (145.0)	349.5 (90.5)	290.0 (420.0)	251.7 (11.81)	2, 2, 2, 4
Zone 3					
0.3	109.6 (87.0)	116.1 (91.6)	131.4 (158.9)	95.8 (60.4)	5
0.9	183.2 (113.6)	257.7 (87.5)	270.8 (219.5)	186.0 (81.8)	5
1.8	397.6 (70.1)	258.9 (72.9)	332.0 (136.1)	205.1 (84.8)	5
2.7	340.4 (49.2)	360.3 (48.9)	400.0 (31.62)	286 (58.0)	5
3.6	432.1 (69.2)	380.3 (45.2)	410.0 (389.1)	307 (40.9)	5, 4, 4, 5
4.5	432.0 (105.0)	206.8 (84.2)	460.0 (159.4)	320 (113)	4, 3, 5, 4
Zone 4					
0.3	4.8 (1.2)	19.2 (5.0)	2.4 (1.8)	81.9 (79.5)	5
0.9	11.4 (9.6)	19.9 (10.1)	92.5 (178.8)	35.2 (19.7)	5
1.8	90.5 (54.3)	94.1 (70.0)	101.8 (199.1)	77.9 (74.3)	5
2.7	316.8 (167.0)	114.4 (100.8)	181.3 (221.6)	168.6 (108)	5
3.6	203.0 (118.8)	206.1 (103.6)	234.7 (278.4)	175.1 (103)	5
4.5	159.4 (103.7)	230.0 (90.4)	290.1 (278.5)	143.3 (120)	5, 4, 5, 5
Average	**191**	**168**	**173**	**148**	

The most likely remaining explanation for the rapid loss of nitrate was microbial denitrification stimulated by application of irrigation water to the soil. Denitrification produces nitrous oxide and diatomic nitrogen gasses, which vent from the soil into the atmosphere. Scientists recognized this as a potentially significant finding because microbial processes could dramatically speed up the remediation of inorganic nitrogen compounds in the source area and perhaps also in the aquifer. Therefore, considerable effort was expended in testing the denitrification hypothesis, quantifying loss of nitrate and ammonium over time with intensive annual soil sampling (Figure B–22), and seeing if the process could be enhanced by supplying a carbon substrate through the irrigation system. The soil denitrification and nitrification research at Monument Valley, summarized below, is well documented (McKeon et al. 2005; Jordan et al. 2008; and the Status Reports in Appendix I).

Figure B–22. Diné College students Garry Jay and Rita White sampling source area soils with a bucket auger. Annually from 2000 to 2009, samples were extracted to a depth of 5 meters at 40 random points within the irrigated plantings.

B.4.2 Evidence for Denitrification in the Source Area

Two lines of evidence supported the hypothesis that microbial denitrification was responsible for the rapid loss of nitrate: direct assays of denitrification in source area soils and enrichment of ^{15}N in soils undergoing nitrate loss. Denitrification activity was measured both in the laboratory in soils collected from the site, and in the field using assay chambers placed over the soil.

In the laboratory, soil samples from irrigated and unirrigated areas in the source area were assayed for Denitrification Enzyme Activity (DEA) and Most Probable Number of Denitrifiers (MPND). DEA and MPND were positive in both irrigated and unirrigated soil samples, but DEA was 6 times higher in irrigated compared to unirrigated samples ($P < 0.05$), and MPND counts were 20 times higher ($P < 0.05$). Nitrous oxide is the first product of denitrification, and soils collected from the irrigated area had about 30 times the rate of nitrous oxide production as unirrigated soils when placed in reaction chambers in the laboratory. Unsupplemented soils (no water or substrate added) had rates of nitrous oxide production consistent with observed rates of nitrate loss from the field. Assay chambers were also placed directly over the soil onsite, and rates of nitrous oxide production were 10–20 times higher ($P < 0.05$) in irrigated compared to unirrigated sites in the source area.

^{15}N enrichment is another signal of microbial denitrification. Bacteria preferentially use the more common ^{14}N isotope in their metabolism, including denitrification. Therefore, residual nitrogen in the soil becomes progressively more enriched in ^{15}N as denitrification proceeds. On the other hand, if nitrate is lost due to physical processes such as leaching, no ^{15}N enrichment is expected in the residual nitrate pool. Scientists extracted residual nitrate from source area irrigated soil samples collected from 2000 to 2004 and assayed them for total nitrate, ^{14}N-nitrate, and ^{15}N-nitrate. The samples showed significant enrichment in ^{15}N as nitrate levels decreased over time (Figure B–23).

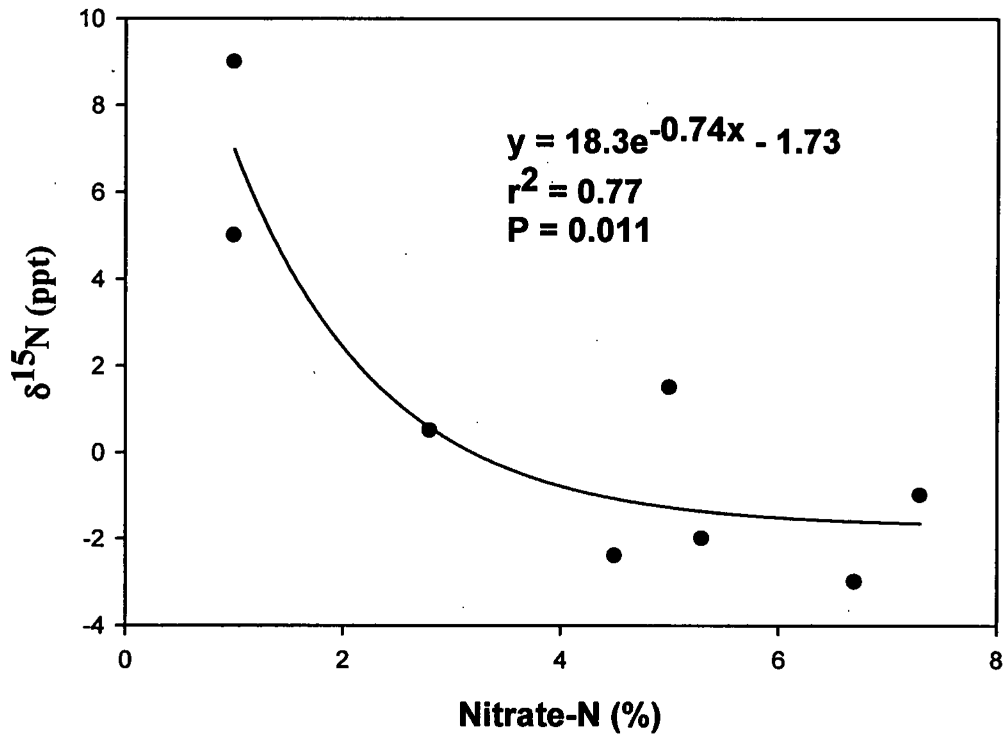


Figure B–23. ^{15}N enrichment versus nitrate concentration in pooled samples from source area soils, 2000–2002. ^{15}N enrichment is expressed as $\delta^{15}N$ in units of parts per thousand relative to ^{15}N content in atmospheric samples of nitrogen gas. The relationship followed an exponential decay function as expected for ^{15}N enrichment due to microbial denitrification. See Jordon et al. (2008) in Appendix A for more information on ^{15}N enrichment methods and interpretation.

B.4.3 Effect of Ethanol on Denitrification in the Source Area

After initially high rates of nitrate loss slowed, and nitrate levels actually increased slightly from 2002 to 2004, scientists began considering methods to stimulate denitrification in the soil. Microbial denitrification requires a carbon source to support bacterial growth as well as nitrate, which serves as an energy source. Soil assays in 2005 showed that total organic carbon (TOC) levels were very low (0.02–0.07 percent) and appeared to be negatively correlated with nitrate content (higher nitrate levels were associated with lower TOC levels). Therefore, the thinking was that denitrification might be carbon-limited in the source area. Laboratory assays showed that addition of ethanol, a microbial carbon substrate, greatly stimulated denitrification in soil samples from the source area.

In 2006 scientists tested the ability of ethanol injected into the irrigation system to enhance denitrification. Ethanol was distributed into selected irrigation lines at a concentration of 0.15 percent in the irrigation stream. Soil samples were collected monthly, May to September, and assayed for moisture content, nitrate, ammonium, and nitrous oxide production at 0.3 m, 1.3 m, and 2.7 m soil depths. Addition of ethanol significantly ($P < 0.5$) increased nitrous oxide production (indicating denitrification) in soil samples, but the effect was rather small, and no net decrease in soil nitrate was measured in the soil samples over the summer. Despite irrigation, soil moisture levels were low (4–8 percent on a gravimetric basis) in all treatments, and a multivariate analysis showed that soil moisture rather than presence of ethanol was the most important factor influencing nitrous oxide production in the soil. The growth of plants in the phytoremediation plots led to rapid removal of irrigation water as plant transpiration, producing lowered levels of soil moisture after 2002. Denitrification and microbial growth require high soil moisture levels, leading to the conclusion that ethanol alone could not enhance denitrification in this water-limited system.

B.4.4 Changes in Nitrate, Ammonium, and Sulfate, 2000–2010

Nitrate, ammonium and sulfate concentrations in the Old Field from 2000 to 2010 are shown in Figure B–24. Nitrate levels fell sharply from 2000 to 2002 then increased slightly through 2010. Ammonium concentrations decreased after 2002, falling from 191 mg kg^{-1} in 2000 to 72 mg kg^{-1} in 2010. Nitrate plus ammonium levels decreased from 355 mg kg^{-1} in 2000 to 181 mg kg^{-1} in 2010, a 49 percent reduction. Loss of ammonium was attributed to microbial nitrification of ammonium under aerobic conditions, followed by denitrification by denitrifying bacteria. This hypothesis was supported by analyses of ^{15}N enrichment in source area soils (Figure B–25). Soil samples taken throughout the source area showed a negative regression of ^{15}N enrichment on both nitrate and ammonium concentrations, and the slopes of nitrate and ammonium enrichment were similar. Bacteria-mediated conversion of ammonium to nitrate favors ^{14}N over ^{15}N, so residual ammonium in the soil became enriched in ^{15}N, and then denitrification of nitrate converts nitrate to nitrous oxide and diatomic nitrogen gasses, resulting in a net loss of inorganic nitrogen from the soil. Soil pools of both ammonium and nitrate become enriched in ^{15}N as coupled nitrification and denitrification proceeds.

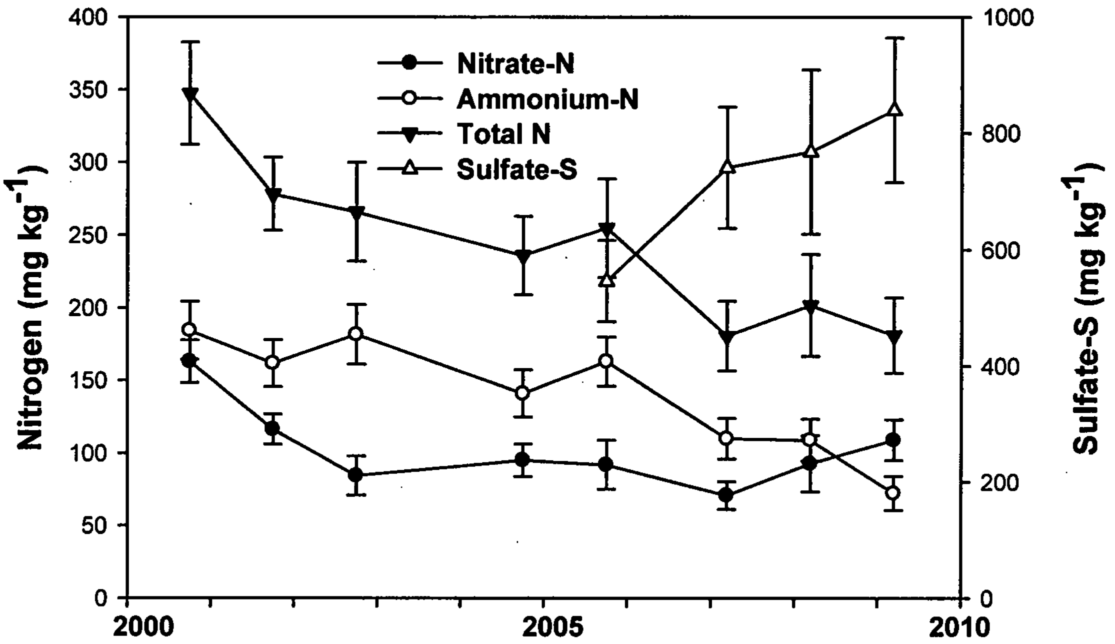


Figure B–24. Concentrations of nitrate, ammonium, nitrate + ammonium (Total N), and sulfate in soil samples from the Old Field, 2000 to 2010. Error bars are standard errors of means. Sulfate was first measured in 2005.

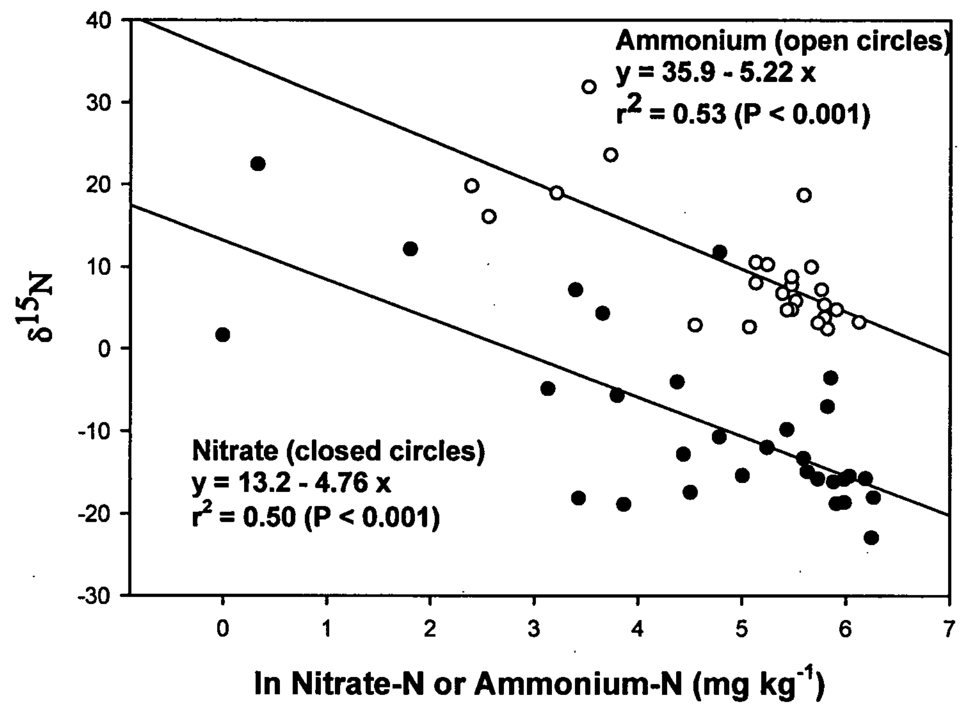


Figure B–25. ^{15}N enrichment in parts per thousand in nitrate and ammonium extracted from source area soils as a function of the natural logarithm of their concentrations in the soil. Slopes of linear regression lines were not significantly different. Scatter in the data are due to the presumed heterogeneous distribution of initial concentrations of nitrate and ammonium in the soil profile.

Figure B–24 shows that the rate of nitrogen loss has decreased over time. This is expected, because as the substrates for nitrification and denitrification decrease, rates of these processes decrease as well. On the other hand, sulfate (measured from 2005 onward) showed an increase in the soil profile over time (Figure B–24). The irrigation water contains about 250 mg L^{-1} sulfate, and a gradual increase in sulfate is expected in the absence of leaching. Figure B–26shows the distribution of nitrate, ammonium, and sulfate by soil depth in 2010. Nitrate and ammonium increased with soil depth. This partially reflects their initial distribution in 2000 (Tables B–2 and B–3), and partially the depths at which nitrogen loss was greatest between 2000 and 2010. Loss of nitrogen was highest in the middle soil depths (1–3 m for nitrate and 2–3 m for ammonium) (Figure B–27). Sulfate followed a different pattern. It was highest at the soil surface and decreased with soil depth (Figure B–26). This distribution suggests that sulfate accumulated in the surface layers due to deposition of sulfate from the irrigation supply, supporting the conclusion from soil moisture monitoring that the soil profile remained unleached through the study period.

Figure B–28 shows mean values of nitrate, ammonium and sulfate for the Old Field and New Fields in 2010. Nitrate, ammonium, and sulfate were very low in the East and West Exclosure Plots, which are located in uncontaminated soil outside the source area fence. Nitrate and ammonium levels are reduced compared to initial 2007 values in all the plots, but nitrate in the New Field North was still very high (193 mg kg^{-1}) in 2010, reduced from 265 mg kg^{-1} in 2007.

B.4.5 Conclusions

Microbial processes produced a significant reduction in soil nitrate and ammonium, such that about half of the total nitrogen was removed over 10 years. However, removal appeared to follow an exponential decay function, as expected for enzyme-catalyzed processes, with removal rates decreasing with time. Removal rates presumably slowed due to reduction in levels of the substrates nitrate, and ammonium. However, other processes may have also slowed removal rates. Soil moisture became limiting as the plants grew and absorbed more of the irrigation water. Furthermore, soil moisture levels were low (Section B.3.6) and residual nitrate and ammonium were highest at deeper soil depths over much of the planting. Deeper irrigation could enhance nitrate and ammonium levels in the deeper soil layers, but this could also result in leaching of nitrates from the source area into the plume. Sulfate levels increased most likely due to deposition of sulfate from irrigation water.

Phytoremediation combined with microbial process were successful in controlling the source area water balance and in reducing nitrogen contaminants. However, complete remediation of the source area may take many years due to the very high initial levels of contaminants and the apparent diminishing effectiveness of microbial processes over time.

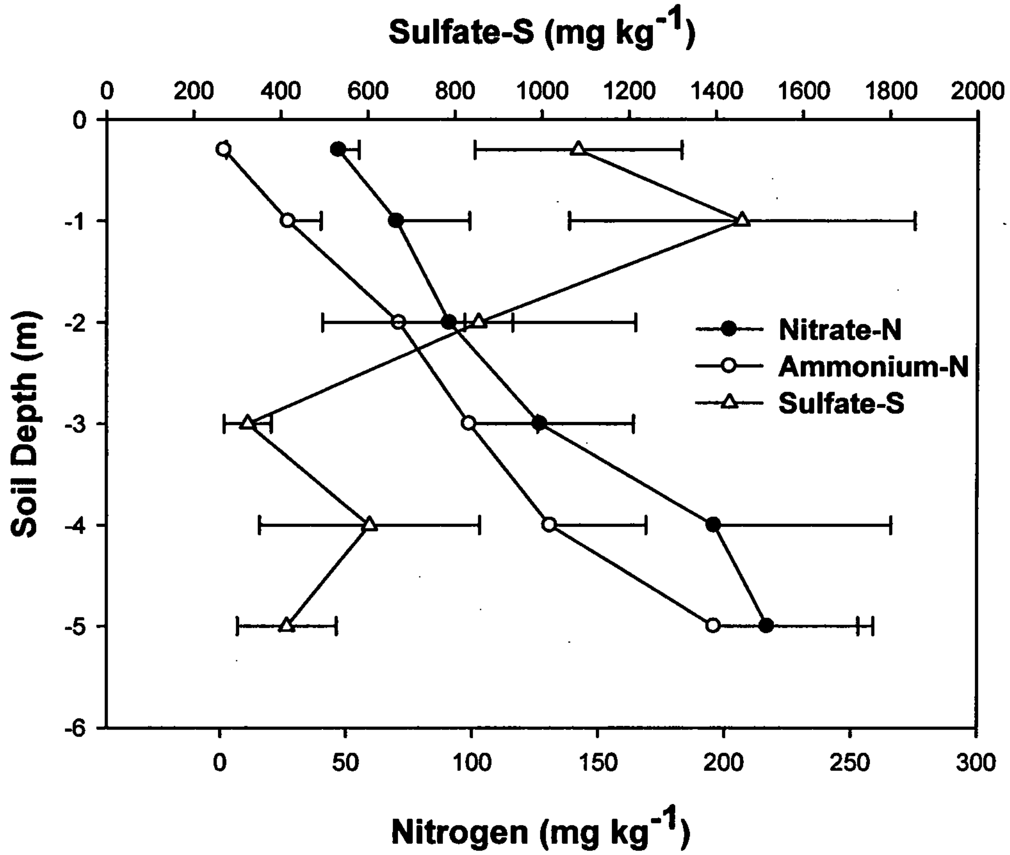


Figure B–26. Distribution of nitrate, ammonium, and sulfate as a function of soil depth in source area soil samples from the Old Field in 2010.
Error bars are standard errors of means.

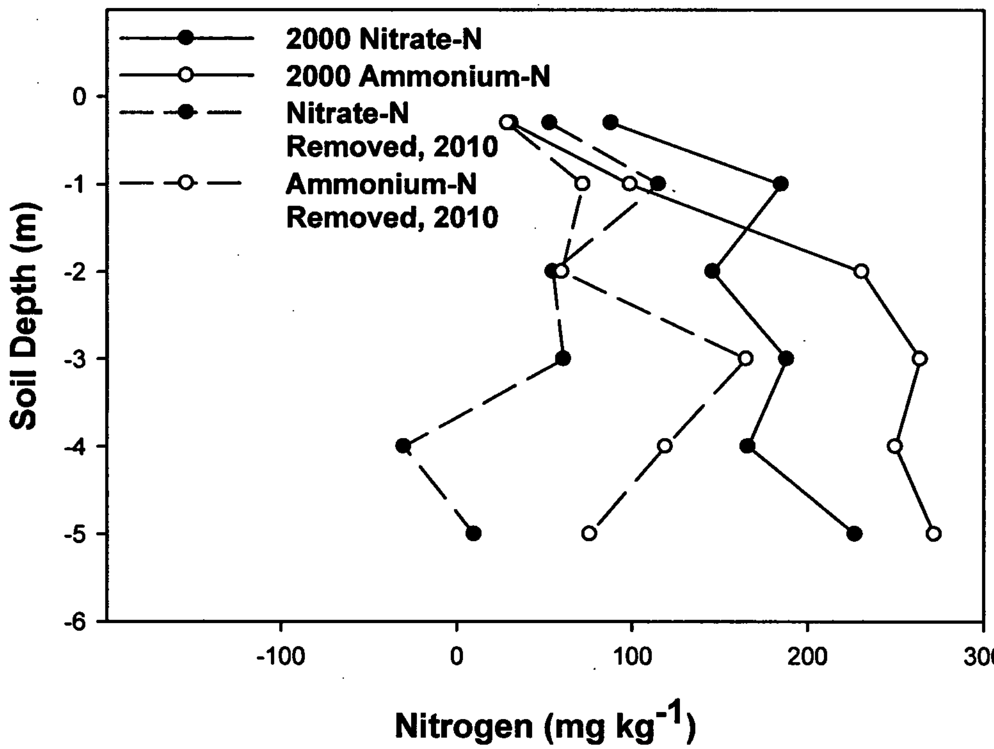


Figure B–27. Initial concentrations of nitrate and ammonium in the Old Field, 2000, and the amount of nitrate and ammonium removed by 2010, as a function of soil depth.

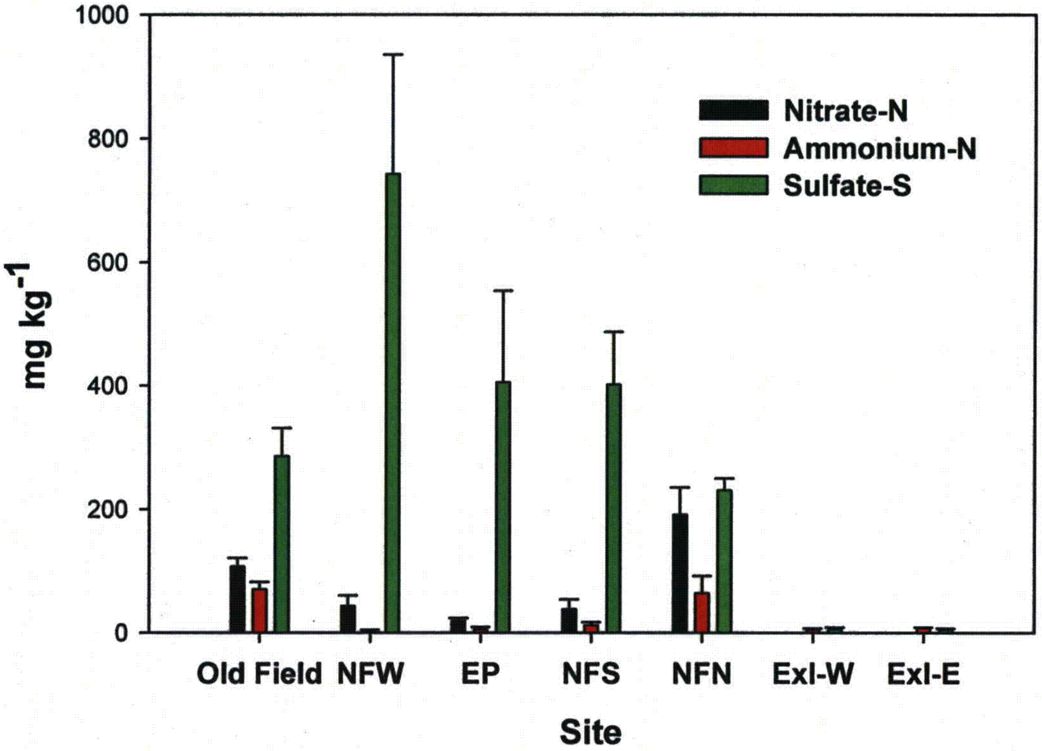


Figure B–28. Nitrate, ammonium, and sulfate concentrations in the Old Field and New Fields in 2010. NFW = New Field West; EP = Evaporation Pond; NFS = New Field South; NFN = New Field North; ExI-W and ExI-E = East and West Exclosure Plots. The Old Field was planted in 1999 and the New Fields were planted in 2006.