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

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Abbreviations

(This list includes abbreviations for the report and the appendixes.)

ANOVA	analysis of variance
ATCA	*Atriplex canescens*
CFR	*Code of Federal Regulations*
cm	centimeters
cm^3 cm^{-3}	cubic centimeters per cubic centimeter
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
LAI	leaf area index
LM	Office of Legacy Management
m	meters
m^2	square meters

MCL	maximum concentration limit
µg/g	micrograms per gram
mg kg^{-1}	milligrams per kilogram
mg/L	milligrams per liter
mm	millimeters
mm day^{-1}	millimeters per day
MNA	monitored natural attenuation
MODIS	Moderate Resolution Imaging Spectrometer
MPND	Most Probable Number of Denitrifiers
mrem	millirem
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
SEM	standard error of the mean
SOWP	*Final Site Observational Work Plan for the UMTRA Project Site at Monument Valley, Arizona*
t	metric ton or 1000 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
‰	per mil (per thousand)

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 source area soils 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 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 nitrification and denitrification were evaluated as potential passive 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 an active pump-and-treat option to supplement natural and enhanced 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 bioremediation 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, landscape-scale estimates of evapotranspiration (ET), and a soil salt balance study provided evidence that ET from the mature plantings controlled leaching of ammonium, nitrate, and sulfate into the alluvial aquifer—phytoremediation 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 nitrification/denitrification pilot study involved deficit irrigation of the subpile planting—irrigating less than the amount of water removed by ET—supplying a carbon source in the irrigation stream, and then discontinuing irrigation. The pilot studies demonstrated, using a combination of direct assays of denitrification in source area soils and enrichment of ^{15}N in soils undergoing nitrate loss, that irrigation-induced microbial processes were responsible for a 50 percent drop in total subpile soil nitrogen between 2000 and 2007. Total N dropped another 30 percent between 2012 and 2014, after irrigation ceased. A hypothesis that supplying a carbon source (e.g., ethanol) through the irrigation stream would also enhance denitrification was supported by microcosm experiments but not supported by results of a field experiment.

Remediation of the subpile soils is nearly complete. Microbial processes have removed more than 80% of soil ammonium and nitrate, much of it after we discontinued irrigation, and ET by native shrub plantings has curtailed leaching of ammonium, nitrate, and sulfate into the alluvial aquifer. Microbial processes are expected to continue without irrigation. We recommend allowing natural succession to progress, maintaining fences to protect the plant community from livestock grazing, and periodic monitoring that includes (1) sampling of soil nitrate, ammonium, and sulfate, and (2) field inspections and remote sensing of vegetation health and ET.

Shallow Alluvial Aquifer

The Environmental Assessment (DOE 2005) defined the shallow alluvial aquifer as groundwater “where the depth to the water table is less than 50 feet (15 m) below the land surface.” The pilot studies evaluated natural and enhanced phytoremediation, and natural and enhanced bioremediation, as remedies for the shallow alluvial aquifer. The pilot studies also developed a remote sensing protocol for landscape-scale monitoring of natural and enhanced phytoremediation for the alluvial aquifer, subpile soil, and land farm.

Phytoremediation of the shallow alluvial aquifer focused on hydraulic control and phytoextraction by populations of native phreatophytes that likely dominated the pre-milling ecology of the contaminant plume area. At the onset of the pilot studies, the surface overlying a large, high-nitrate portion the plume was denuded, and vegetation in the remaining plume area was in poor condition due to overgrazing. 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 groundwater flow—natural phytoremediation was ongoing, although at a reduced capacity. Enhanced phytoremediation entailed preventing grazing and then revegetating the denuded area in large test plots, which increased transpiration rates up to 6-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, may have slowed plume dispersion.

We recommend using landscape-scale ET estimates to model effects of different land management scenarios (e.g., phreatophyte plantings and grazing protection) on groundwater flow and contaminant transport.

Although phytoextraction increased as grazing decreased, the healthier phreatophytes were still removing only a small percentage of plume nitrogen and sulfur. The pilot studies also evaluated natural and enhanced microbial processes in the shallow alluvial aquifer. First-order denitrification rate coefficients, which could be used 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. Also, results showing oxic redox conditions and correspondence of isotopic compositions of ammonium and nitrate were evidence of natural attenuation of ammonium via nitrification.

Ethanol increased denitrification rates by 2 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 3 orders of magnitude below the initial values, indicating that the ethanol amendments may have a long-term impact on the local subsurface environment.

We recommend a strategy that relies on natural nitrification and denitrification processes to remediate the shallow alluvial aquifer if modeling shows that ET can hydraulically slow groundwater flow and contaminant transport. More simply, if phytoremediation has cut off the source and could slow groundwater flow, then natural attenuation of the plume may be adequate. However, ethanol injection of hot spots should be considered if natural attenuation rates are determined to be inadequate after several additional years of groundwater monitoring.

Deep Alluvial Aquifer

The Environmental Assessment (DOE 2005) defined the deep alluvial aquifer as groundwater "where the water table is generally more than 50 feet (15 m) below the land surface." Although natural and enhanced phytoremediation are not options because roots do not extend this deep, natural and enhanced denitrification, as described above for the shallow alluvial aquifer, are also passive options for the deep alluvial aquifer. Land-farm phytoremediation was evaluated "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 how a land farm planted with native fourwing saltbush shrubs could be used 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 controlled 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. However, over the course of the study, extraction well yields dropped substantially, which could make large-scale pumping of the plume problematic.

We recommend using land-farm phytoremediation of the deep alluvial aquifer only if natural and enhanced attenuation remedies are determined to be inadequate. A land-farm design would need to address factors such as pumping rates, land-farm area, growing season, soil water balance, and extreme precipitation events. Monitoring and maintenance of an operational land farm would include (1) monitoring of plant health, soil moisture profiles, and soil nitrogen and sulfate profiles, (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.

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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) (DOE 2005) authorized the pilot studies. DOE prepared the EA to assess proposed actions for groundwater compliance and for the pilot studies. 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.

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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 40 CFR 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 the Monument Valley site:

- 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 the *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 for Monument Valley pending completion of the pilot studies.

2.2 Pilot Study Goals

The goal of the pilot studies, according to the 2005 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 (15 m) below the land surface," and the deep portions of the alluvial aquifer as "where the water table is generally more than 50 feet (15 m) 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 Section 3.1 of the EA (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 (DOE 2004a). 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 Attenuation 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 natural nitrification in the alluvial aquifer based on redox conditions and isotopic compositions of ammonium and nitrate. 5. Evaluated carbon sources to enhance aquifer denitrification using laboratory microcosm assays. 6. 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 former Evaporation Pond.

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

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3.0 Pilot Study Synopses

This section provides synopses of the passive and active remediation strategies LM evaluated by conducting 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 recommendations regarding remedy applications, 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 3.4-hectare (8.4-acre) subpile soil area with elevated ammonium and nitrate was planted primarily with fourwing saltbush to enhance transpiration and control percolation. Soil moisture profiles were monitored using neutron hydroprobes and water content reflexometers. Percolation was monitored using water fluxmeters. Evapotranspiration was estimated using a remote sensing algorithm.
Enhance Natural Attenuation in the Subpile Soils	Subpile Soil and Evaporation Pond 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. Irrigation was discontinued for the last 4 years of the study. Soil ammonium, nitrate, and sulfate were monitored by laboratory analysis of soil profile samples.(Phytoremediation of the Evaporation Pond was discontinued.)
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 × 50-meter fenced plots overlying the nitrate plume. • Re-establish stands of native phreatophytes (fourwing saltbush) in two, 50-meter × 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 evaluations of plume dynamics and nitrification 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.

Table 3 (continued). Pilot Study Field Plots and Methods

Title	Plot Labels in Figure 1	Field Methods
Evaluate Land-Farm Phytoremediation	Phytoremediation Land Farm	The land-farm phytoremediation option was evaluated within a 50-meter × 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 2015 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 this 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.

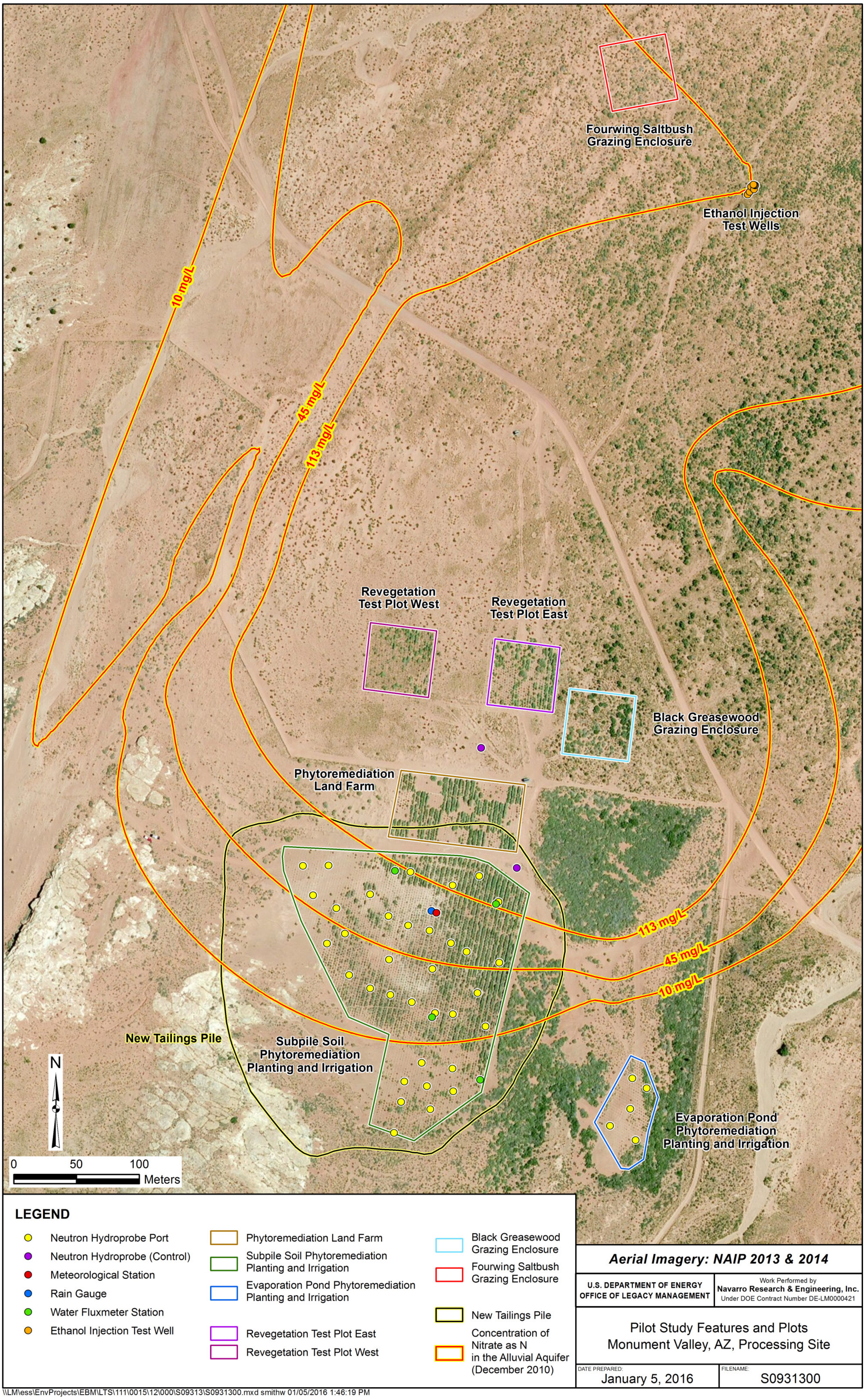

Figure 1. Locations of Pilot Study plots and Wells at the Monument Valley, Arizona, Processing Site

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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.

By monitoring soil moisture profiles and percolation flux rates, estimating ET using a remote sensing algorithm, and 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 meters [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, but measured zero percolation within the planting between 2000 and 2010. ET exceeded precipitation plus irrigation within the planting from 2000 to 2014 except in 2007, when irrigation was temporarily doubled to enhance denitrification. Electrical conductivity and ^{15}N enrichment data provided ancillary evidence that the planting controlled percolation. We did not observe a decrease in electrical conductivity over time which can indicate leaching of soluble ions. We did observe enrichment of ^{15}N which 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. Monitoring data can provide evidence as to whether subpile soils remain cut off as a source for nitrate and ammonium leaching into the alluvial aquifer.

- The health of subpile soil plantings and evapotranspiration were evaluated during onsite inspections and 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, leaf area index, and ET were evaluated using remote sensing methods (Appendixes B and E). These methods could be used to continue monitoring vegetation health and ET.
- Dead fourwing saltbush and black greasewood plants were replaced with 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 ET

requirements as determined from soil moisture data. Natural succession is expected to provide adequate ET in the future.

- Deficit irrigation, used to establish and maintain transplants in the first years of the pilot study, is no longer needed.
- 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. This existing instrumentation could be maintained to continue monitoring soil moisture and percolation until subpile soil remediation is complete.
- Soil moisture profiles were monitored at 40 locations using neutron hydroprobes. A 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. Neutron hydroprobe readings could be taken periodically to check trends and variability in soil moisture profiles until subpile soil remediation is complete.

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 aboveground 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 kilograms (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 2014, scientists measured an 82 percent drop in subpile soil nitrogen levels; total nitrogen levels dropped from 347 milligrams per kilogram (mg kg^{-1}) to 64 mg kg^{-1} (Appendix B, Section B.4.5).

Assays of denitrification and analyses of nitrogen isotopes in soil ammonium and nitrate support the hypothesis that microbial denitrification enhanced by irrigation caused the initial rapid removal of nitrate (reported as N), and that coupled microbial nitrification and denitrification processes were responsible for the drop in total N by 2014 (Appendix B, Section B.4.3). About 30 percent of the drop in total N occurred from 2011 to 2014, after irrigation ceased. In the laboratory, denitrification enzyme activity was 6 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 soil samples from irrigated soils than in samples from unirrigated soils. 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. Using ^{15}N enrichment values, scientists estimated that about 150 mg kg^{-1} of combined ammonium-N and nitrate-N was lost in the 32 years from 1968 to 2000, and another 282 mg kg^{-1} of total N was lost from 2000 to 2014. Hence, this process of natural attenuation of N was likely underway in the subpile soil before 2000, and was apparently enhanced by irrigating and protecting plantings of fourwing saltbush and black greasewood from grazing.

Scientists tested the hypothesis that supplying a carbon source through the irrigation system might enhance denitrification (Appendix B, Section B.4.4). 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 it 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 became a balancing act. If we increased irrigation rates to stimulate denitrification, soil moisture levels could exceed field capacity, and we would risk leaching more soil nitrogen into the alluvial aquifer (Section 3.1).

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 micrograms per gram (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. Nitrogen concentrations initially dropped rapidly—irrigation enhanced denitrification—and then leveled off. Nitrogen concentrations dropped again after irrigation ceased.

- Deficit irrigation is no longer needed to enhance denitrification.
- To determine if microbial processes are continuing to reduce soil nitrogen levels without irrigation, 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 should be used.

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

Scientists showed that black greasewood and fourwing saltbush, the native desert shrubs that curtailed leaching by controlling percolation and helped reduce nitrate and ammonium levels in the subpile soil (Sections 3.1 and 3.2), 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 naturally inhabit the area overlying the plume 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 the Monument Valley site 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 the ratio of heavier to lighter isotopes of oxygen and hydrogen in water, whereas the formation of raindrops tends to increase the ratio. These fractionation ratios provide a sort of fingerprint for water.

Water in the stems and leaves of plants will have isotope ratios similar to those in the source of water accessed by the plant roots, and these ratios can be used to determine where plants are receiving their water. At the Monument Valley site, water isotope ratios 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 2 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 5 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—that is, 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, and that ET in protected stands was 50–100 millimeters per year greater than precipitation. Landscape-scale ET estimates could be input to groundwater models to evaluate effects of different land management scenarios (e.g., phreatophyte plantings and grazing protection) on groundwater flow and contaminant transport.

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 sitewide 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. Phreatophytes protected from grazing may slow groundwater flow and contaminant transport. This pilot study also evaluated methods for monitoring phreatophyte health that could be used to manage grazing and continue to enhance plume phytoremediation.

- Scientists can use onsite inspections and, less frequently, remote sensing to visually evaluate the health of fourwing saltbush and black greasewood populations growing over the nitrate plume. 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). However, field observations in 2015 show that planted phreatophytes in the revegetation plots remained healthy during 4 years of drought after irrigation ceased in 2011, suggesting that plants are rooted in the alluvial aquifer. 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 a landscape scale, managing the seasonal 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 use groundwater modeling and monitoring to project and evaluate 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 Attenuation 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 of nitrate and ammonium are occurring in the alluvial aquifer (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 high 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 cleanup 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 2 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 concentration decreased by 3 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 day^{-1}. 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 rates of 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.

Finally, scientists evaluated the occurrence of natural attenuation of ammonium in groundwater. Results showing oxic redox conditions and correspondence of isotopic compositions of ammonium and nitrate confirmed natural nitrification. Ammonium concentration within the plume area was closely related to concentrations of uranium and a series of other trace elements. Evidence also suggested that the methods to enhance attenuation of ammonium and nitrate at the site may influence the transport and fate of the trace elements.

3.4.3 Remedy Monitoring and Maintenance

The results of the natural and enhanced attenuation pilot studies will be used to select and implement alternative remedies proposed in the EA for the alluvial aquifer. Natural nitrification and denitrification are occurring. The enhanced attenuation pilot study could be used to plan a larger-scale treatment system for hot spots in the shallow and deep 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 in the shallow aquifer, and multiple methods show that significant natural attenuation is occurring. However, groundwater monitoring data also show that plume nitrate concentrations have changed little in 15 years, possibly because of ongoing nitrification.

- The pilot studies indicate that natural attenuation of ammonium and nitrate is occurring. Groundwater modeling and monitoring could be used to determine if, over time, natural attenuation is adequate.
- If rates of natural attenuation are deemed to be inadequate, pilot study methods could be used to enhance denitrification by injecting ethanol. Nitrate concentrations in the injection and monitoring wells could be 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 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. However, over the course of the study, extraction well yields dropped substantially, which could make large-scale pumping of the plume problematic.

3.5.3 Remedy Monitoring and Maintenance

Land-farm phytoremediation of the deep aquifer would be considered only if natural and enhanced attenuation remedies were found to be inadequate. A land farm design would need to consider factors such as pumping rates, land farm area, growing season, soil water balance, and extreme precipitation events.

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. 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

EPA did not establish a groundwater standard for sulfate in 40 CFR 192, but the 2005 EA discusses the need to reduce sulfate concentrations in the shallower and deeper portions of the alluvial aquifer and in subpile soils. The intent was to achieve a remediation goal, as stated in the SOWP, of either 250 milligrams per liter (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 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 was 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 mg kg^{-1} occurred in almost all borings, with a maximum concentration of 2,975 mg kg^{-1}. 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 screen depths. Although natural sources of sulfate are present, scientists determined through stable isotope analyses that roughly three-fourths of the sulfates in the plume originated from sulfuric acid used in ore extraction, which oxidized to sulfate ions and leached from the source area to the plume, and that the sulfate plume will likely persist for many decades as it slowly migrates away from the source area.

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 sulfate and slow its spread 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 and enhanced 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 compliance strategies as proposed in the EA (DOE 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 Groundwater Compliance Action Plan to document the final selection of compliance strategies.

4.1 Subpile Soils

The pilot studies evaluated enhanced phytoremediation and enhanced microbial processes 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 ET from a planted field of native shrubs has cut off the subpile soils as a source for the groundwater plume and that soil microbial nitrification and denitrification cycles, initially enhanced by a limited amount of irrigation, have reduced total soil nitrogen by more than 80%.

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 initially 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 after 15 years, multiple lines of evidence confirmed that plant transpiration was controlling percolation and seepage of contaminants into the plume.

Transplanted 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 an initial rapid drop in soil nitrate, and that coupled microbial nitrification and denitrification processes were responsible for greater than 80% drop in total N after 15 years. 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.

Remediation of the subpile soils is nearly complete, and deficit irrigation is no longer needed. However, fences should be maintained to protect the plant community from livestock grazing, and periodic monitoring is recommended that includes sampling of soil nitrate, ammonium, and sulfate; field inspections; and remote sensing of vegetation health and ET.

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 soil 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 ensure continued isolation of the subpile soil as a source.
		Enhanced Attenuation	Microbial nitrification and denitrification processes removed more than 80% of total N after 15 years. 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 may have hydraulically slowed plume movement. 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, potentially 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. Landscape-scale ET estimates could be input to groundwater models to evaluate effects of different land management scenarios on groundwater flow and contaminant transport. Remote sensing was also used to monitor subpile soil and land-farm phytoremediation. (See pilot study results for subpile soils and the deep aquifer in this table.)
		Natural and Enhanced Denitrification	Nitrification and denitrification are naturally attenuating ammonium and nitrate in the shallow alluvial aquifer. First-order denitrification rate coefficients were comparable when calculated with laboratory microcosm experiments, field isotope fractionation analysis, and solute transport modeling. Oxic redox conditions and analyses of N isotope compositions of ammonium and nitrate were evidence of natural nitrification. Ethanol increased denitrification rates by 2 orders of magnitude in microcosm experiments. 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 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.

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 (15 m) 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, extract a small percentage of plume nitrogen and sulfate, and discharge shallow groundwater, potentially slowing contaminant transport. 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 6-fold. Over the course of the pilot studies, the health of native shrub populations outside the test plots also improved in response to better grazing management in the area. 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 attenuation of ammonium and nitrate in the alluvial aquifer were tested. Results showing oxic redox conditions and correspondence of isotopic compositions of ammonium and nitrate were evidence of natural nitrification. 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 denitrification. The occurrence and rate of denitrification were also 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 2 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 3 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 (15 m) 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 attenuation as described for the shallow alluvial aquifer (Section 4.2) 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). However, over the course of the study, extraction well yields dropped substantially, which could make large-scale pumping of the plume problematic. A land-farm design would need to consider factors such as pumping rates, land-farm area, growing season, soil water balance, and extreme precipitation events.

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.

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Angelita Denny, DOE Office of Legacy Management, manages operations at the Monument Valley, Arizona, Processing Site. Dr. Jody Waugh, Navarro Research and Engineering, Inc., directed the pilot studies for DOE with assistance from Navarro employees Linda Edwards, Jonathan Eng, David Foster, Susan Lyon, David Miller, Dr. David Peterson, Jeff Price, Linda Sheader, and Jeff Walters.

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Appendix A

Monument Valley, Arizona, Processing Site: Background Information

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Contents

Figures

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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 attenuation.

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) (15 miles) south of Mexican Hat, Utah, and about 21 km (13 miles) east of the scenic Monument Valley Tribal Park (Figure A-1). The nearest town is Dennehotso, about 8 km (5 miles) to the south. The site is on the west side of Cane Valley Wash at an elevation of approximately 1,460 meters (m) (4,790 feet) 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 (0.6 miles) 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

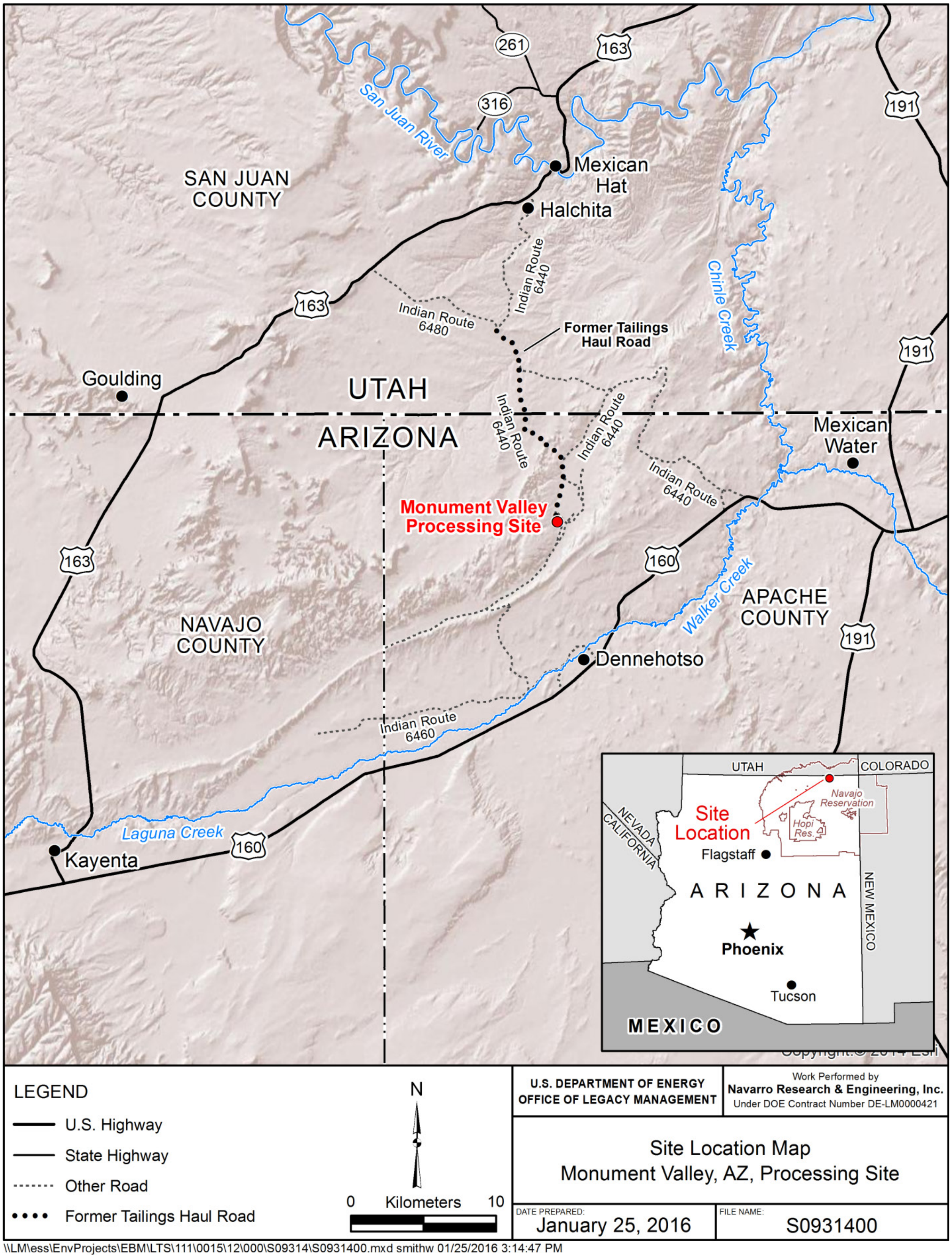

Figure A-1. Location map of the Monument Valley Processing Site.

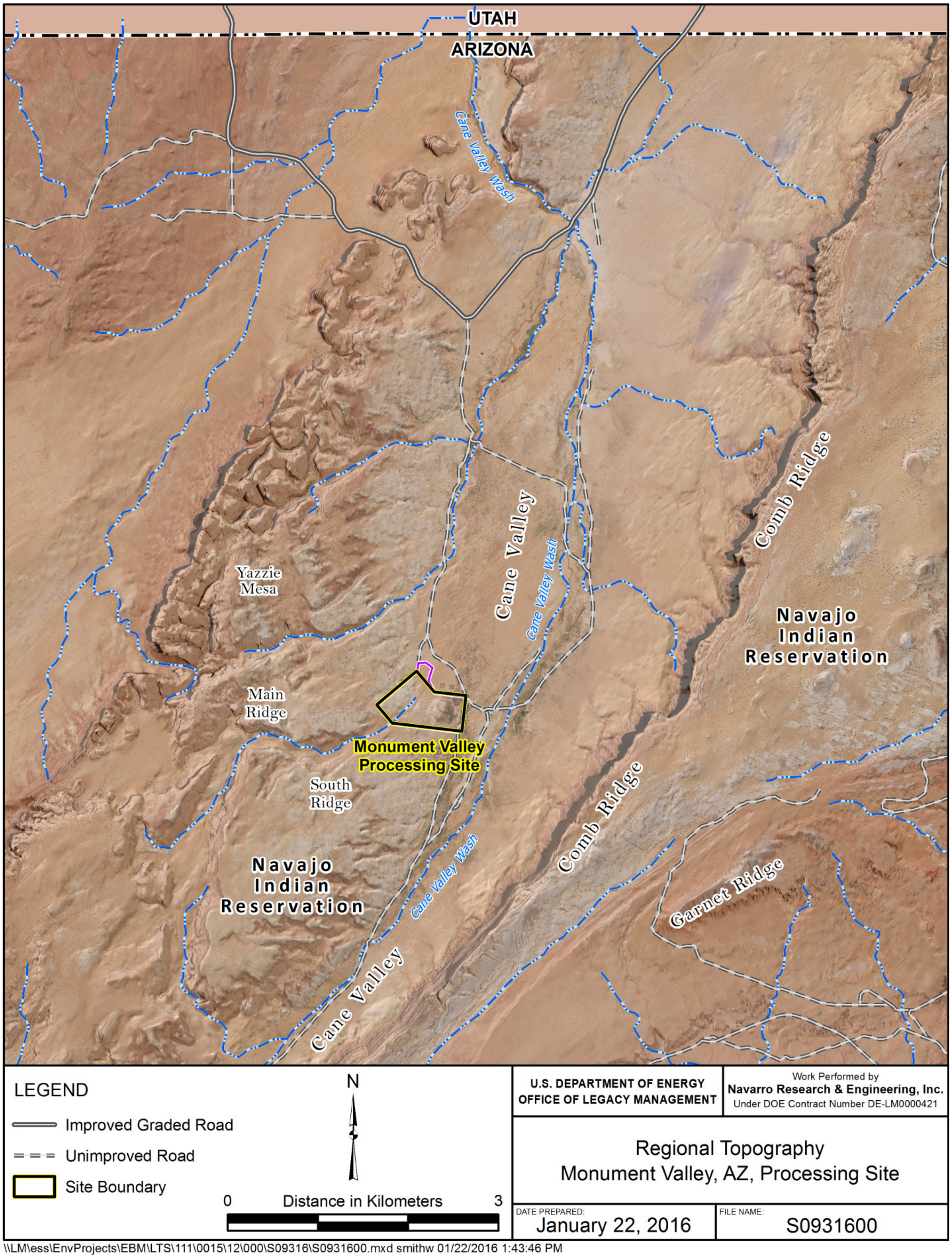

Figure A-2. Regional topography of the Monument Valley Processing Site.

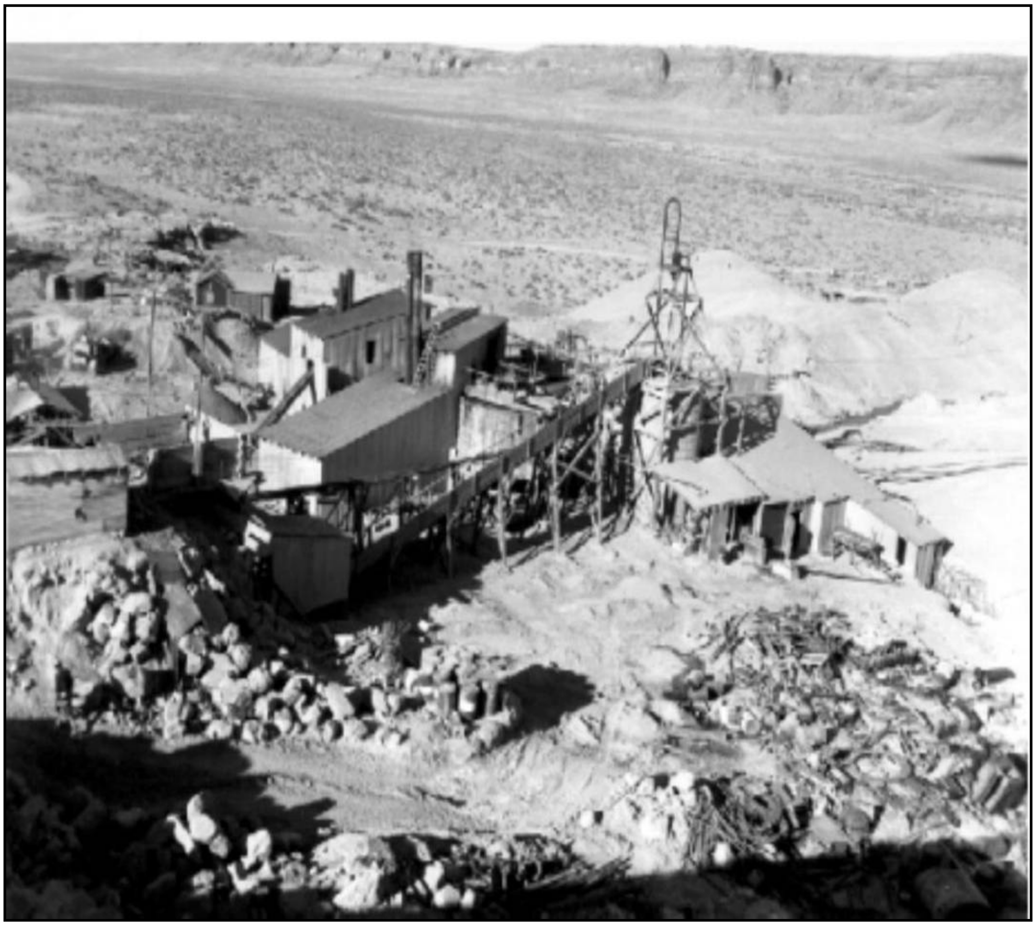

Figure A-3. Photograph of the Monument Valley mill in about 1960.

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 (17 miles) 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.

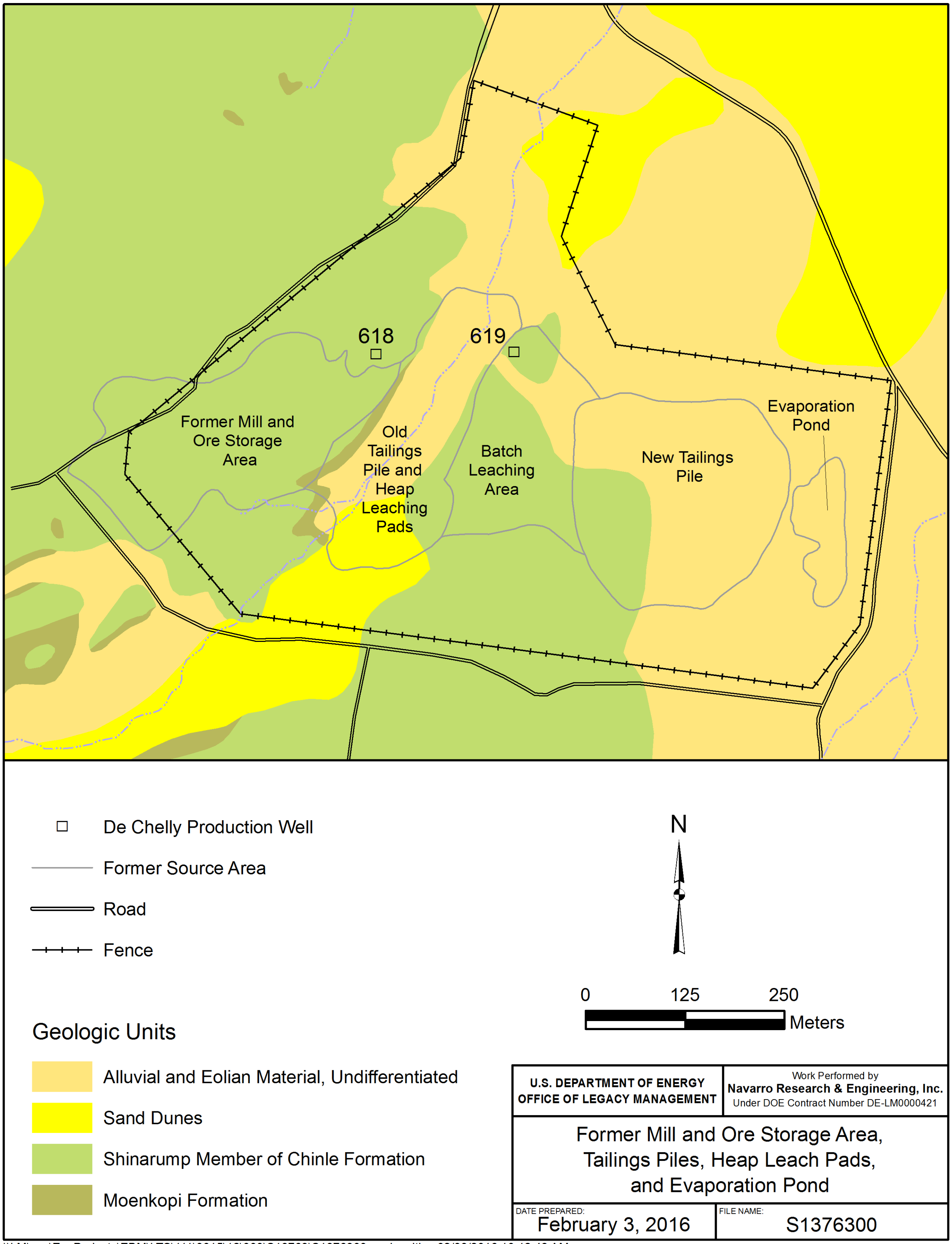

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Figure A-4. Locations of former Monument Valley mill and ore storage area, tailings piles, heap-leach pads, and evaporation pond (DOE 1999a).

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 Naagháí Bik'eh Hózhóón, which places human life in harmony with the natural world, DEI has helped guide researchers to look beyond traditional Western 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 of Arizona 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 Native 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 182 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 meters 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 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). Figure A-5 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 (26 feet) 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 (7 to 50 feet) below ground surface. The de Chelly aquifer consists of fine-grained sandstone that is approximately 150 meters (500 feet) 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 (160 feet).

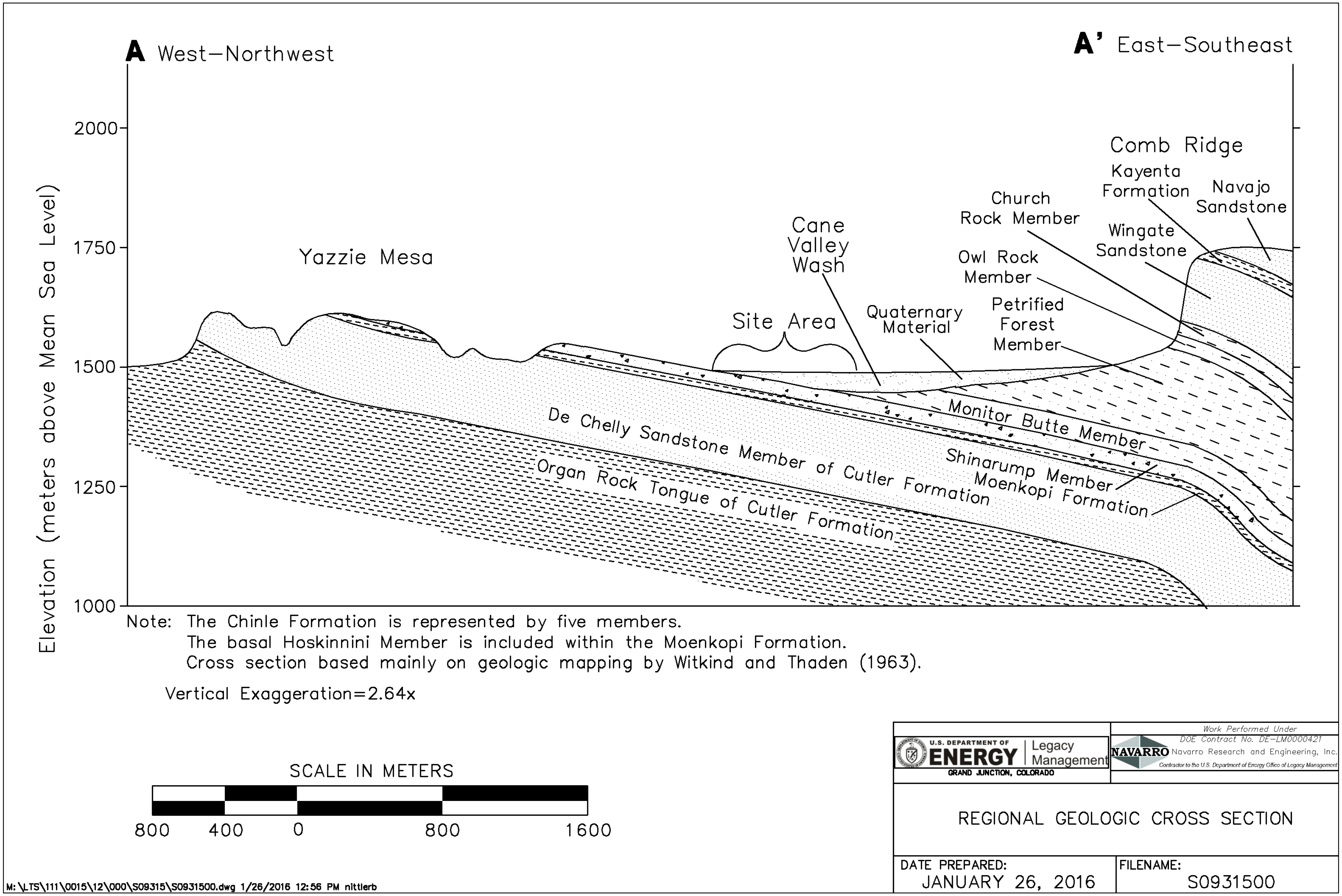

Figure A-5. Regional geologic cross section at the Monument Valley Processing Site (DOE 1999).

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 (30 to 40 feet). 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 vegetation 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).

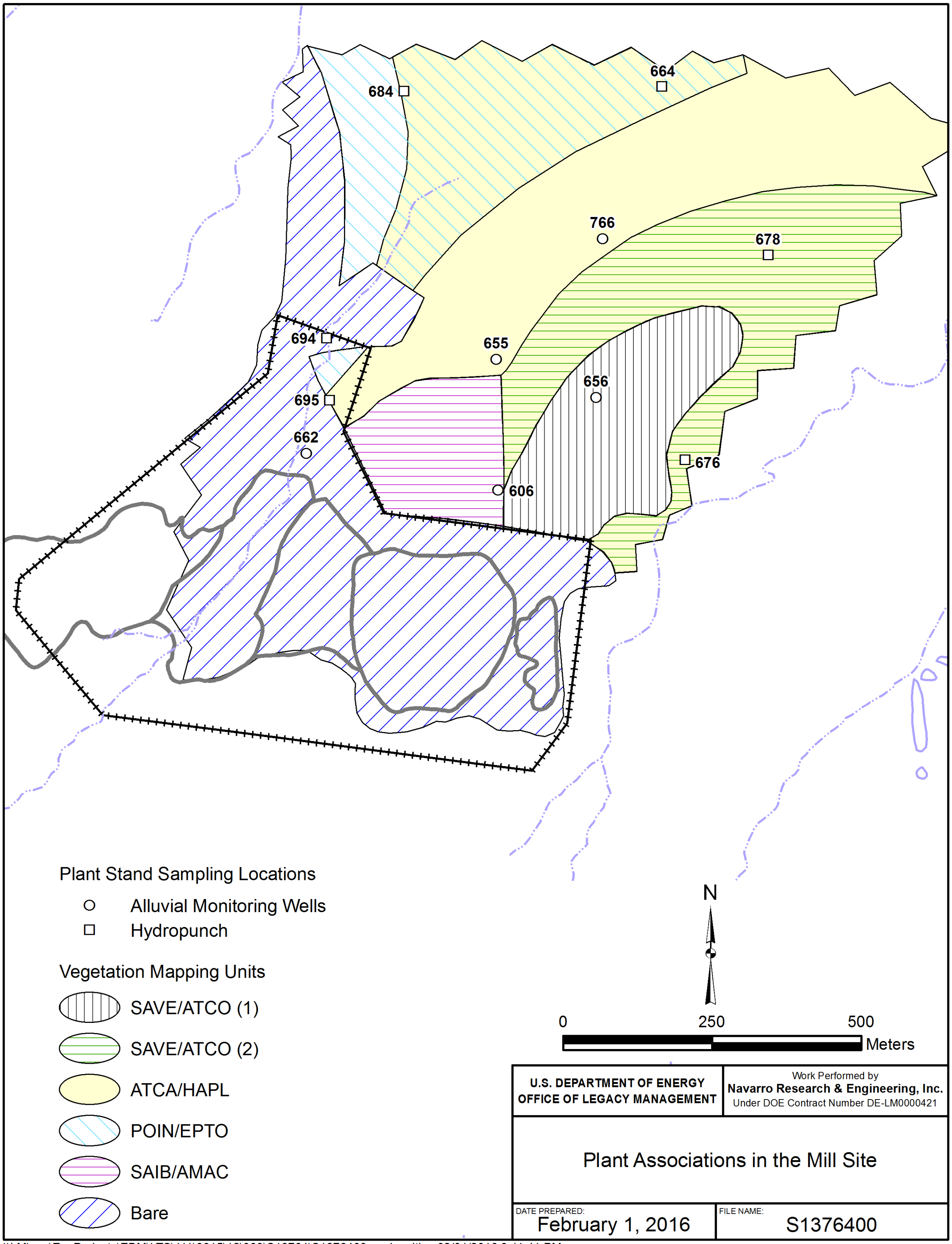

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Figure A-6. Plant associations at the Monument Valley site and extending north overlying the alluvial nitrate plume. Plant acronyms are formed by the first two letters of the genus followed by the first two letters of the species (see text).

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.

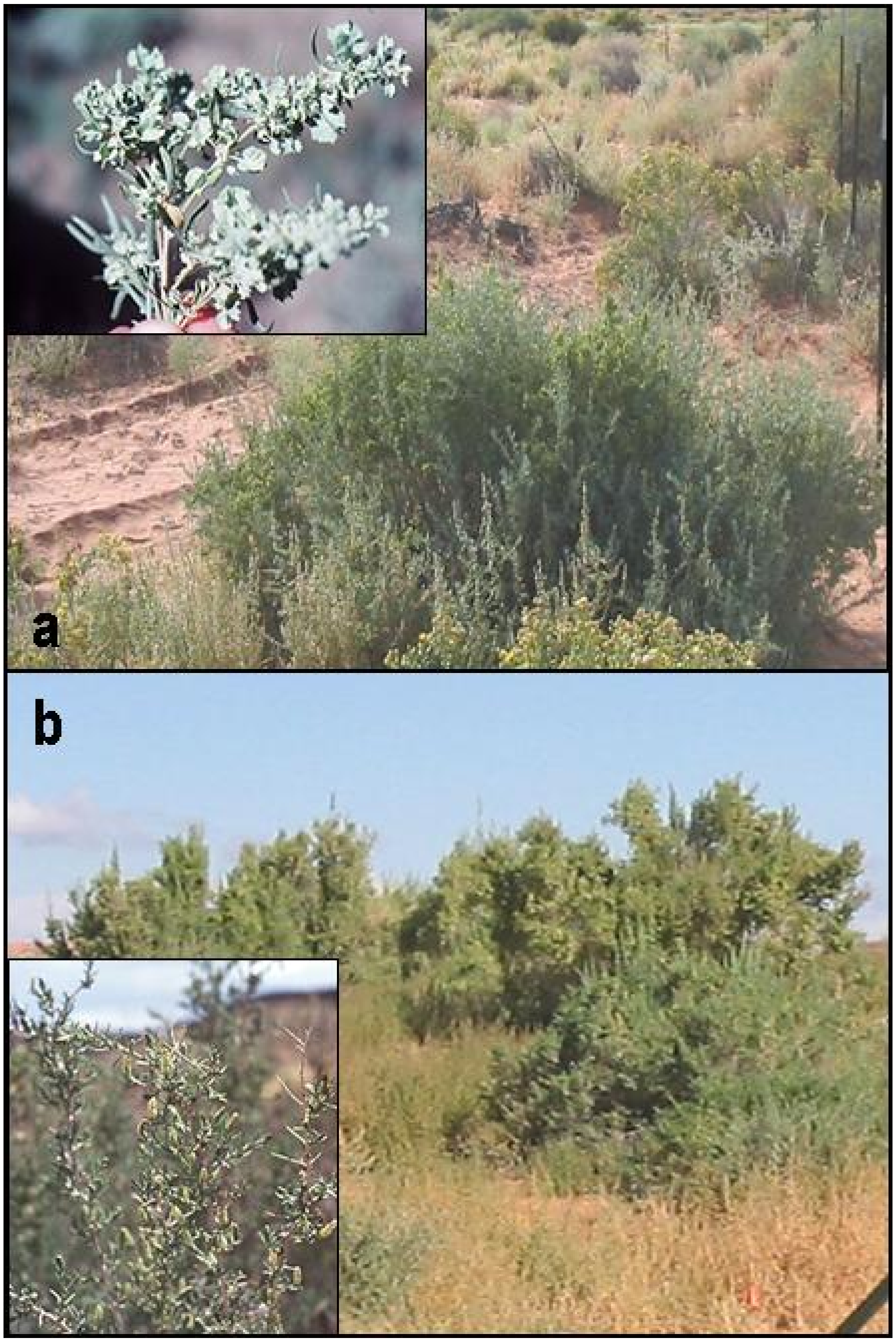

Figure A-7. Two native phreatophytes that grow over the Monument Valley nitrate plume: a) Atriplex canescens *(fourwing saltbush, or díwózhiishzhiin in Navajo), and b)* Sarcobatus vermiculatus *(black greasewood, or díwózhii_beii in Navajo).*

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

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The pilot studies show that a planting of native shrubs has cut off the source of the groundwater plume, and soil microbial nitrification and denitrification cycles, 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. Investigators first characterized the extent of soil nitrate and ammonium contamination, then planted a total of 3.4 ha. 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 support the premise that plant transpiration controlled 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. Over 15 years, total nitrogen levels dropped from 347 mg kg^{-1} to 64 mg kg^{-1}. Analysis of nitrogen isotopes support the hypothesis that coupled microbial nitrification and denitrification processes were responsible for the loss of N. LM scientists also tested the hypothesis that supplying a carbon source through the irrigation system might 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 milligrams per kilogram (mg kg^{-1}) dry weight of soil and ammonium (as NH_4) levels ranging from zero to 163 mg kg^{-1} dry weight of soil. Delineation of an initial 1.7-hectare (ha) phytoremediation field, planted in 1999 (Section B.3.1), was based on this second survey (Figures B-2 and B-3).

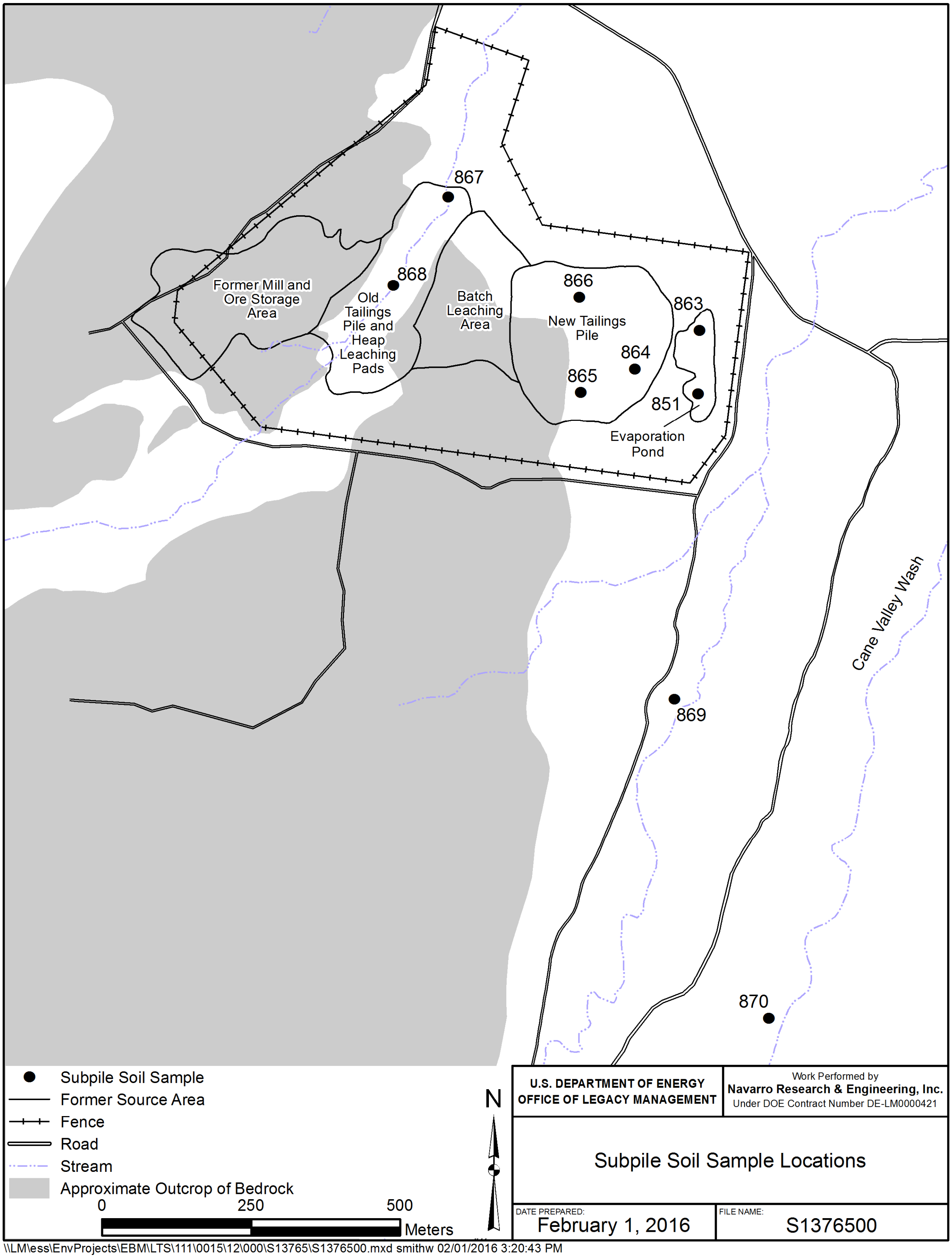

Figure B-1. Map of the Monument Valley site showing 1997 soil sampling locations and historical delineations of the mill and ore storage areas, Old Tailings Pile, New Tailings Pile, and Evaporation Pond. Elevated soil nitrate and ammonium were first detected at soil sample point 866.

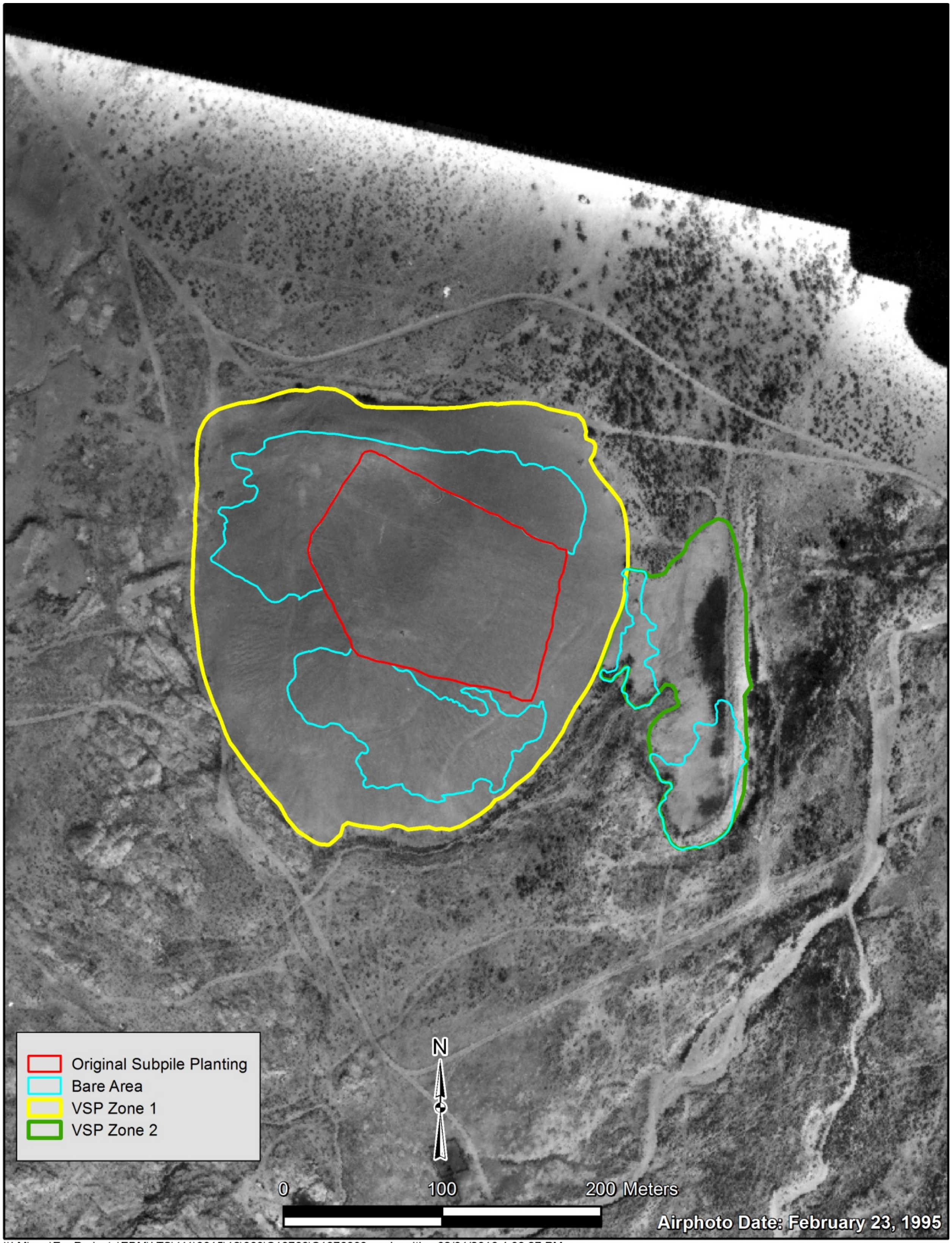

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Figure B-2. Pre-reclamation aerial photograph of source areas with New Tailings Pile (VSP Zone 1) and Evaporation Pond (VSP Zone 2) boundaries, and GPS-mapped demarcation of the 1999 subpile soil phytoremediation planting and adjacent bare soil areas.

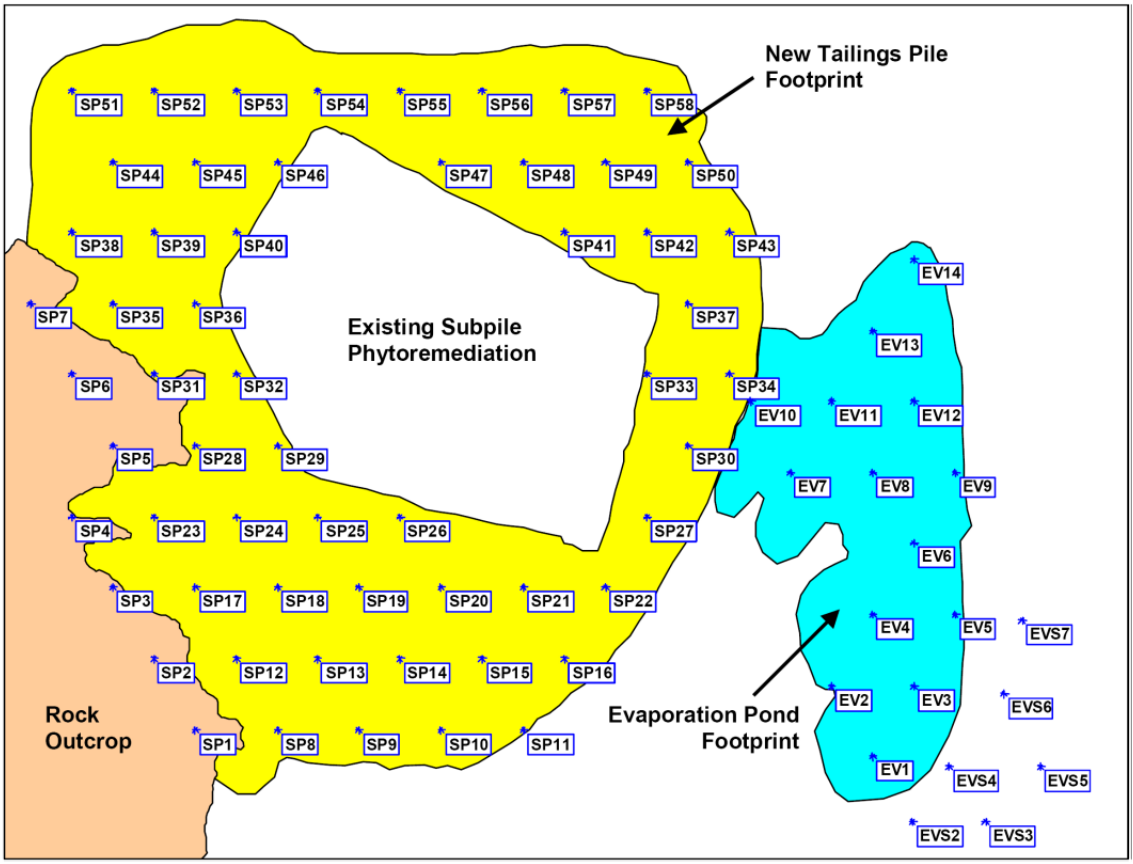

Figure B-3. Triangular grid sample points (about 30 m spacing) within the New Tailings Pile and Evaporation Pond footprints for the 2005 characterization. Points falling within the boundaries of the rock outcrop were omitted. The original 1999 phytoremediation field is also shown.

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).

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 meter (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 (PNNL 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 mg kg^{-1}, 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.

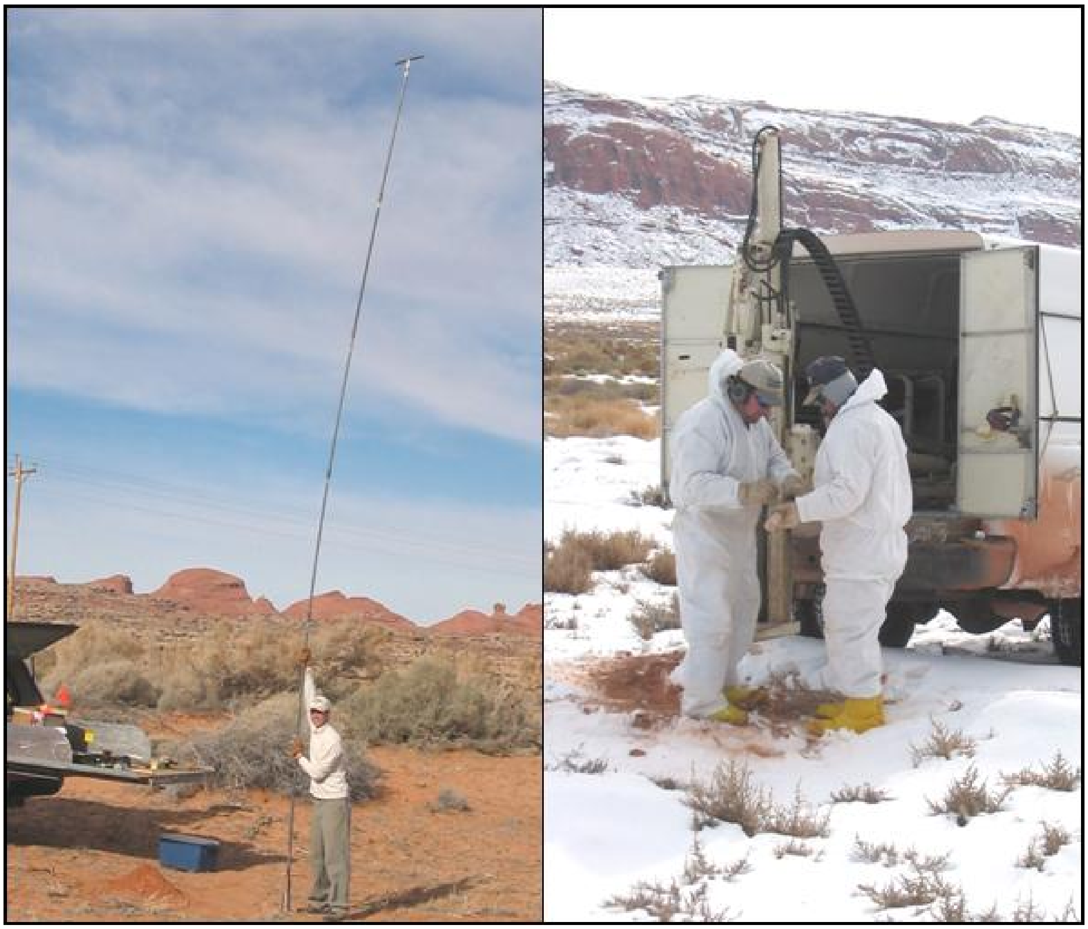

Figure B-4. Soil sampling with hand bucket augers (left) and a Geoprobe (right) to delineate hot spots and the extent of soil nitrate and ammonium within the footprints of the New Tailings Pile and Evaporation Pond.

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.

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.

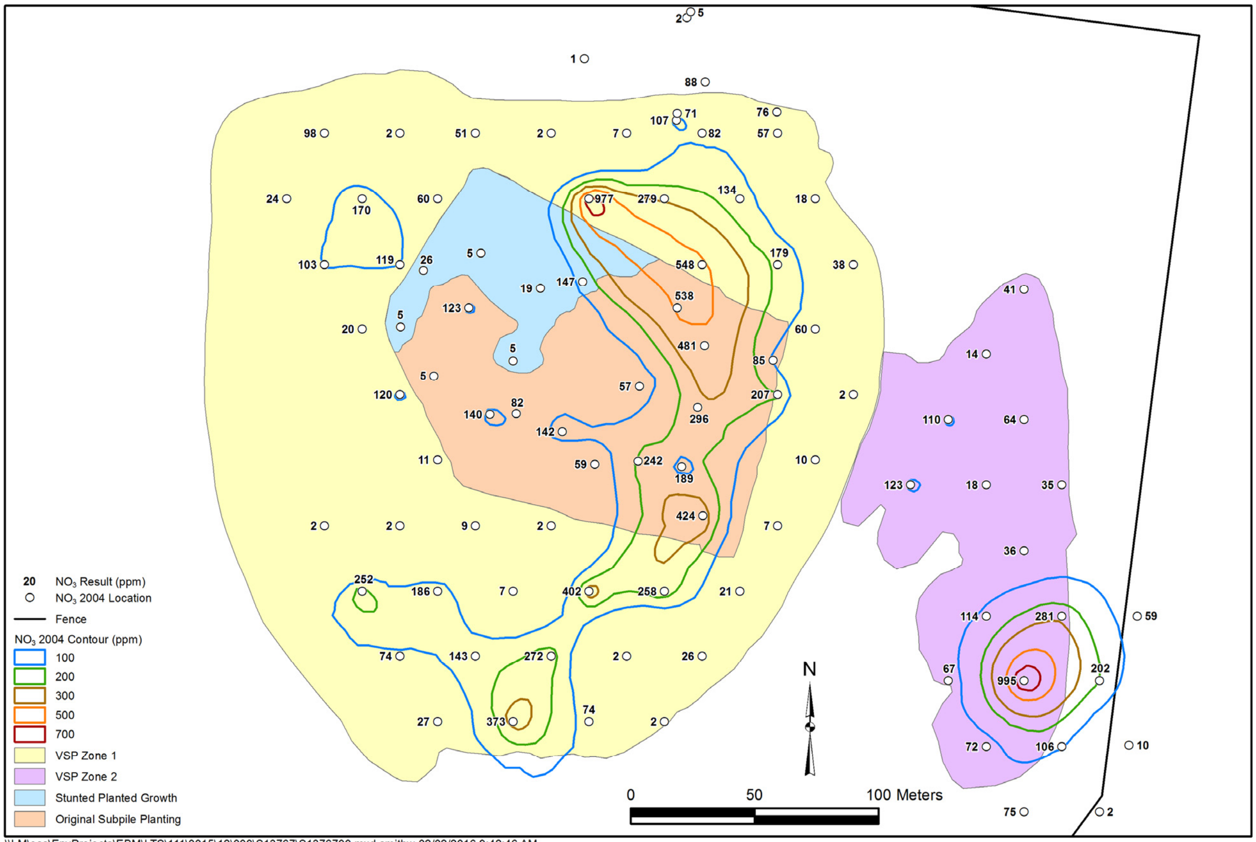

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Figure B-6. Map of nitrate (NO_3-N) concentrations in soil within the New Tailings Pile and Evaporation Pond source areas. Based on 2004–2005 sampling results.

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^{-1} to 977 mg kg^{-1} in the New Tailings Pile footprint. Areas with greater than 100 mg kg^{-1} NO_3-N extended both north and south of the 1999 planting. A hot spot with NO_3-N concentrations >100 mg kg^{-1} 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^{-1} to 650 mg kg^{-1} 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^{-1} at only one sampling location in the Evaporation Pond footprint.

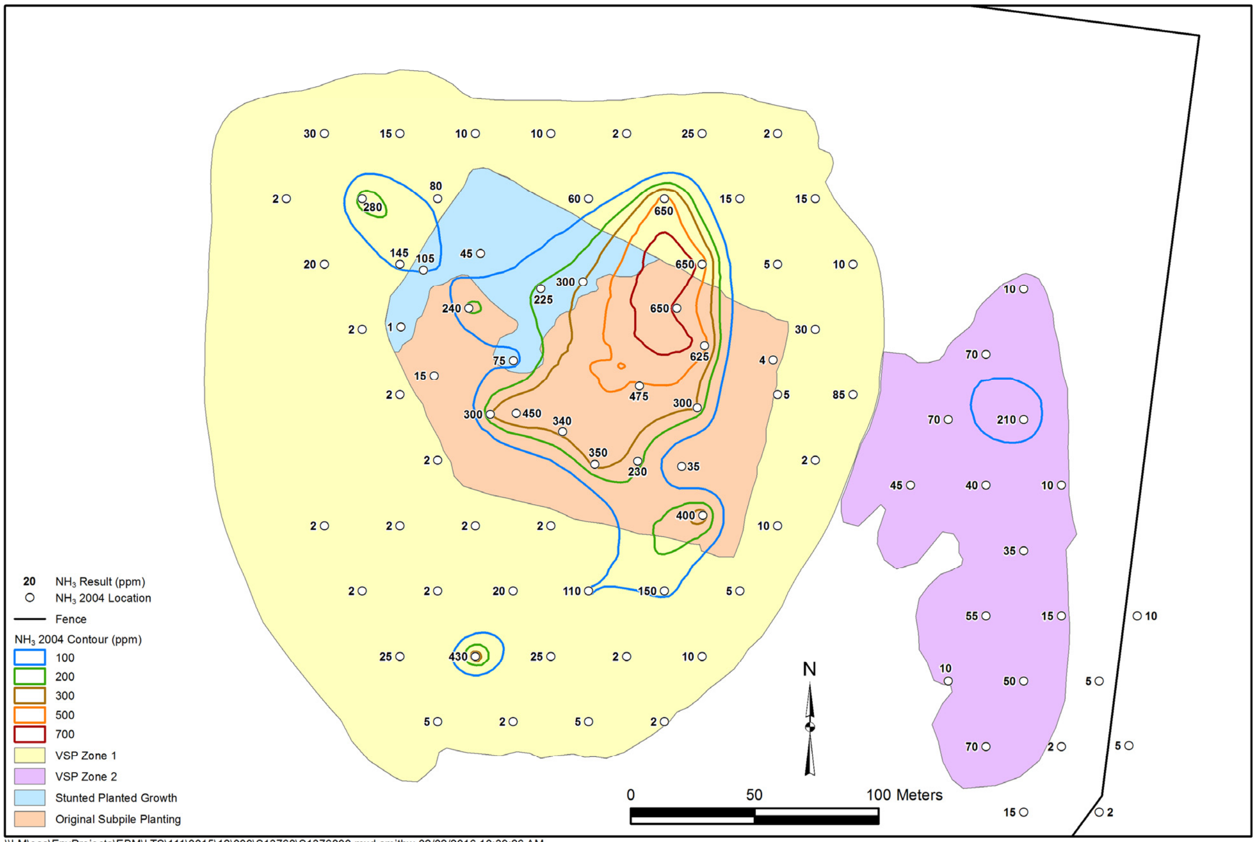

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Figure B-7. Map of ammonia (NO_3-N) concentrations in soil within the New Tailings Pile and Evaporation Pond source areas. Based on 2004–2005 sampling results.

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 fence line (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.

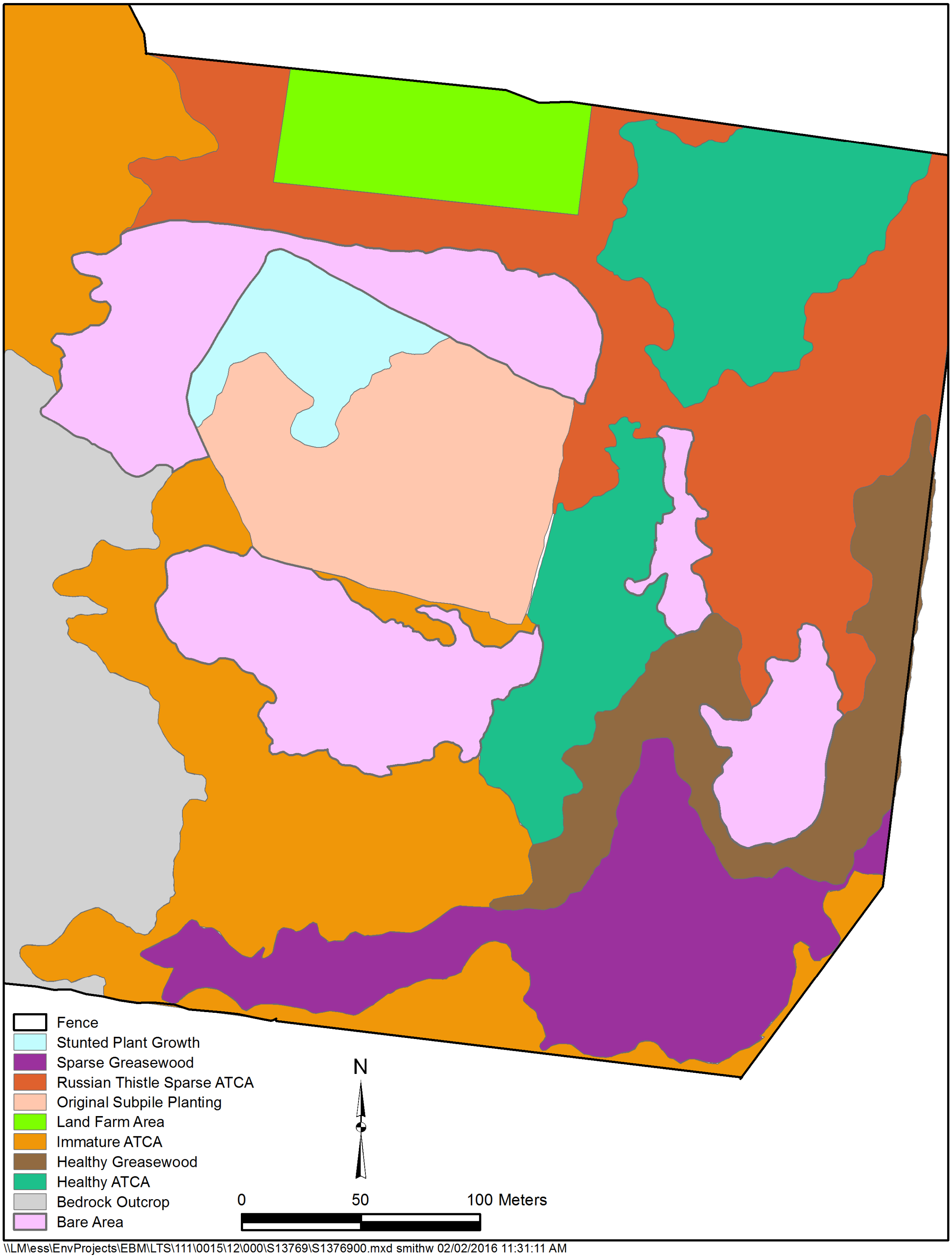

Figure B-8. Map of vegetation types, bare areas, rock outcrops, and the 1999 phytoremediation planting (including the stunted growth area). The map was created by subjectively delineating relevant mapping units using GPS.

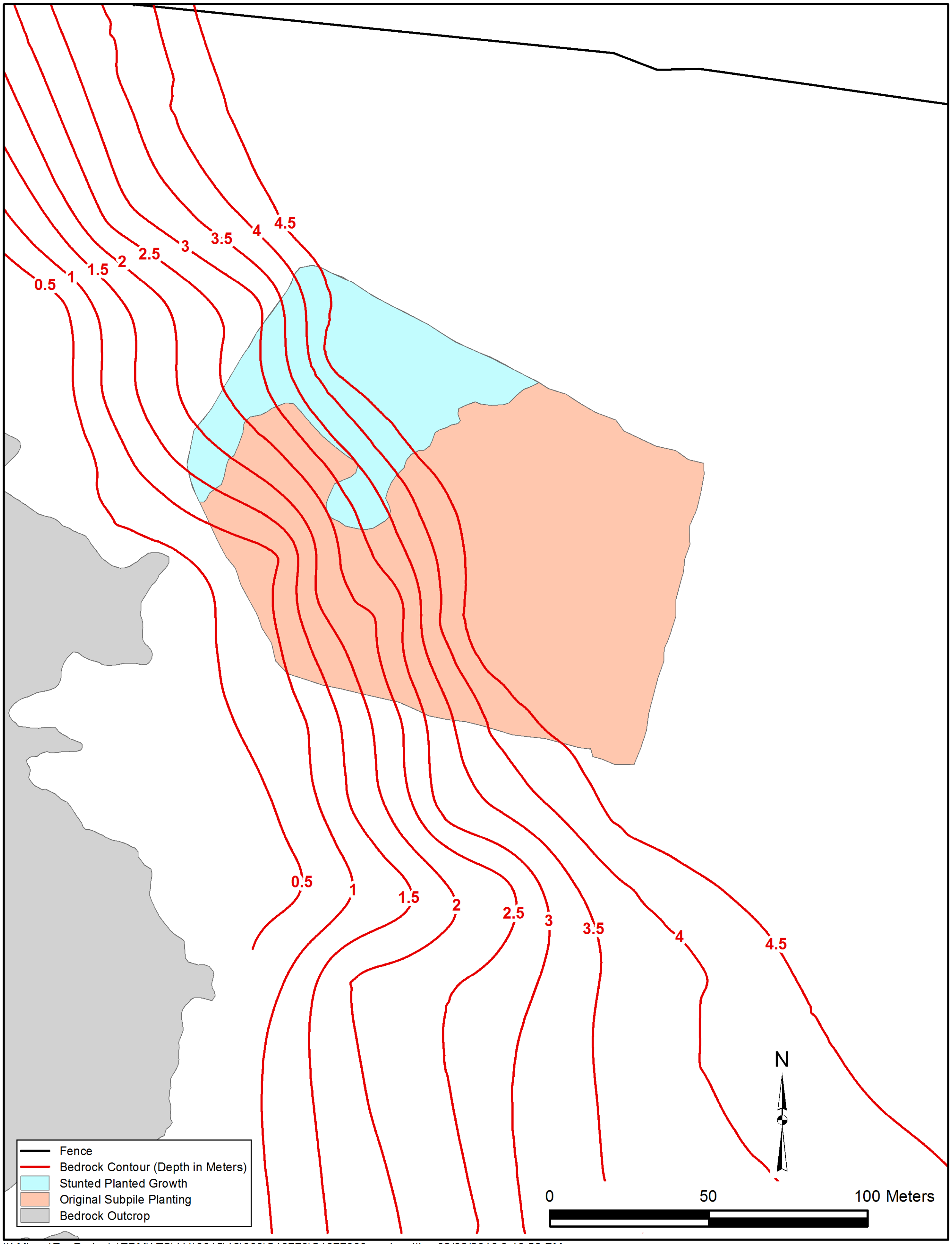

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Figure B-9. Rock outcrops and depth-to-bedrock contour map (depth in feet) in proximity of the original phytoremediation planting.

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.

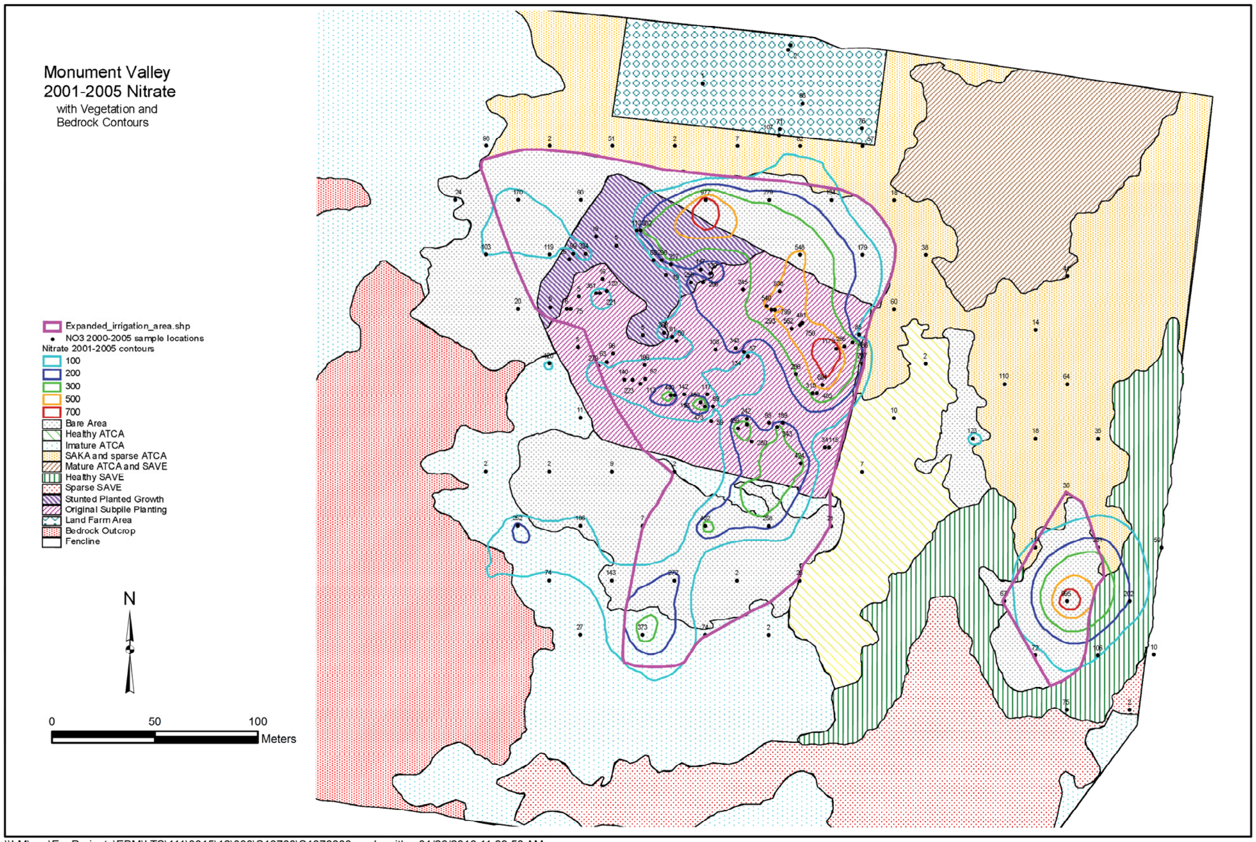

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Figure B-10. Outline of the 2006 source area phytoremediation planting or Extended Fields (the area within the magenta line boundary) superimposed on maps of existing vegetation, the 1999 phytoremediation planting, and soil nitrate distribution.

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).

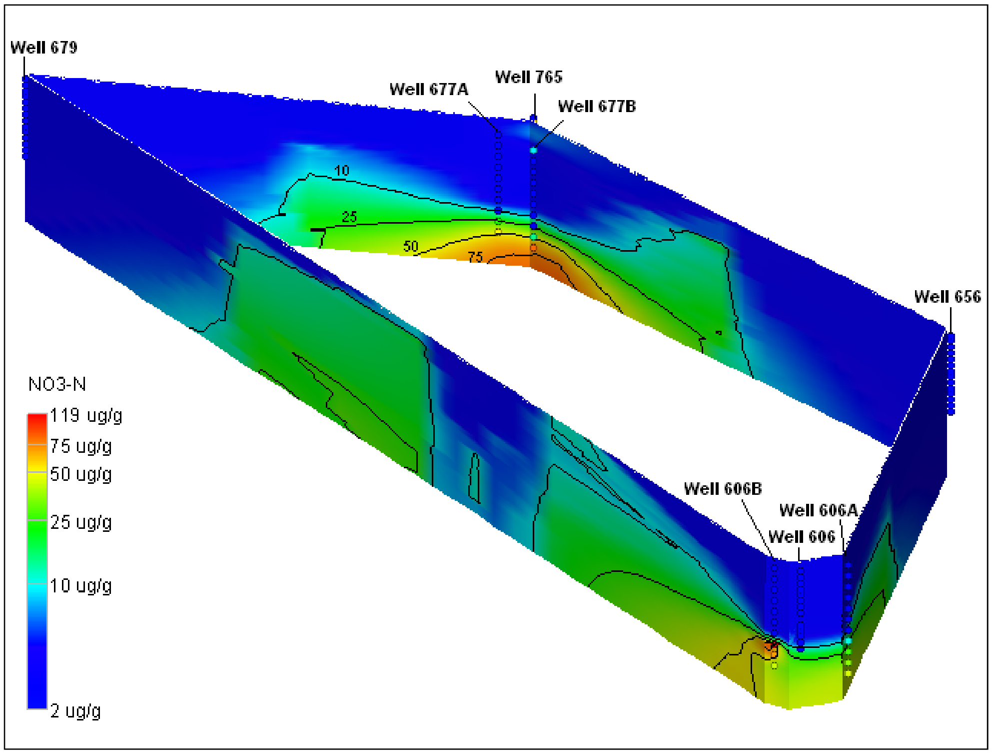

Figure B-11. EVS-generated solid-phase nitrate as N fence diagram for the vadose zone overlying the groundwater nitrate plume north of the Monument Valley site. View perspective is from the southwest looking to the northeast.

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.

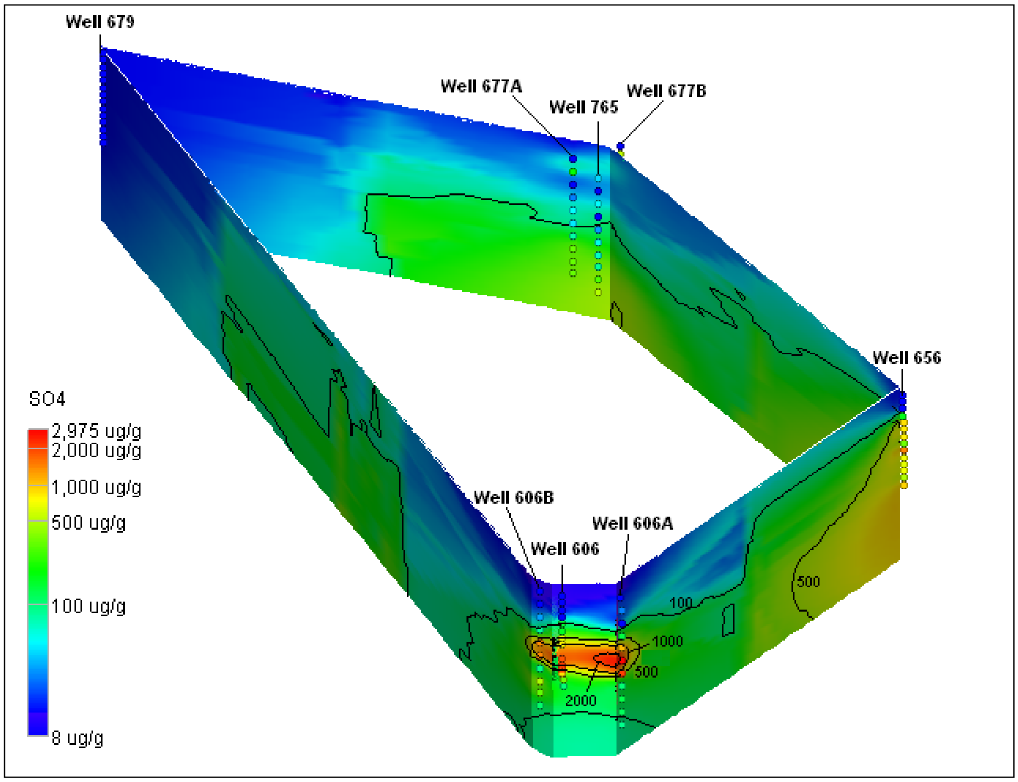

Figure B-12. EVS-generated solid-phase sulfate fence diagram for the vadose zone overlying the groundwater nitrate plume north of the Monument Valley site.
View perspective is from the southwest looking to the northeast.

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^{-1} (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 milligram per liter (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.

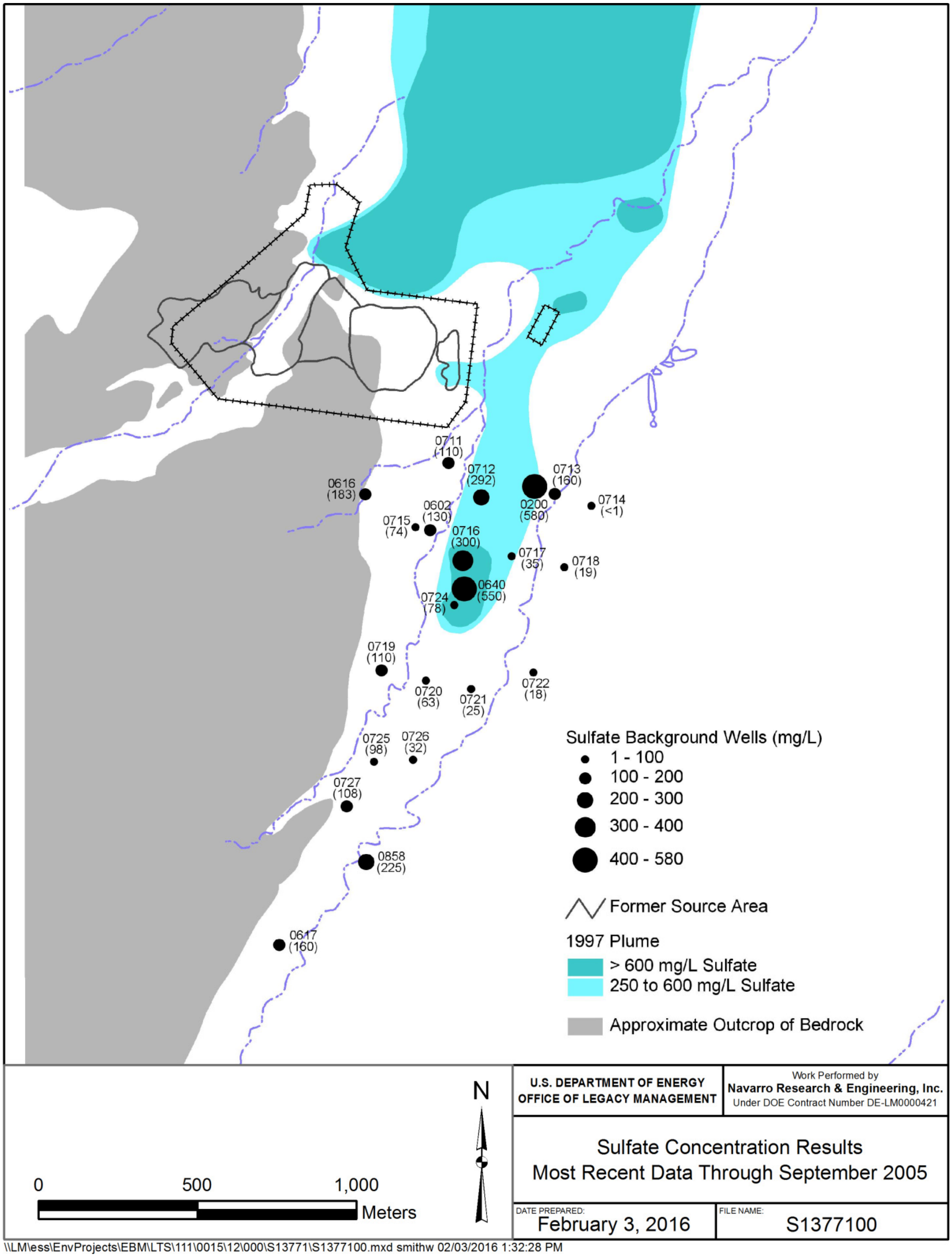

Figure B-13. Sulfate concentrations in upgradient alluvial wells.

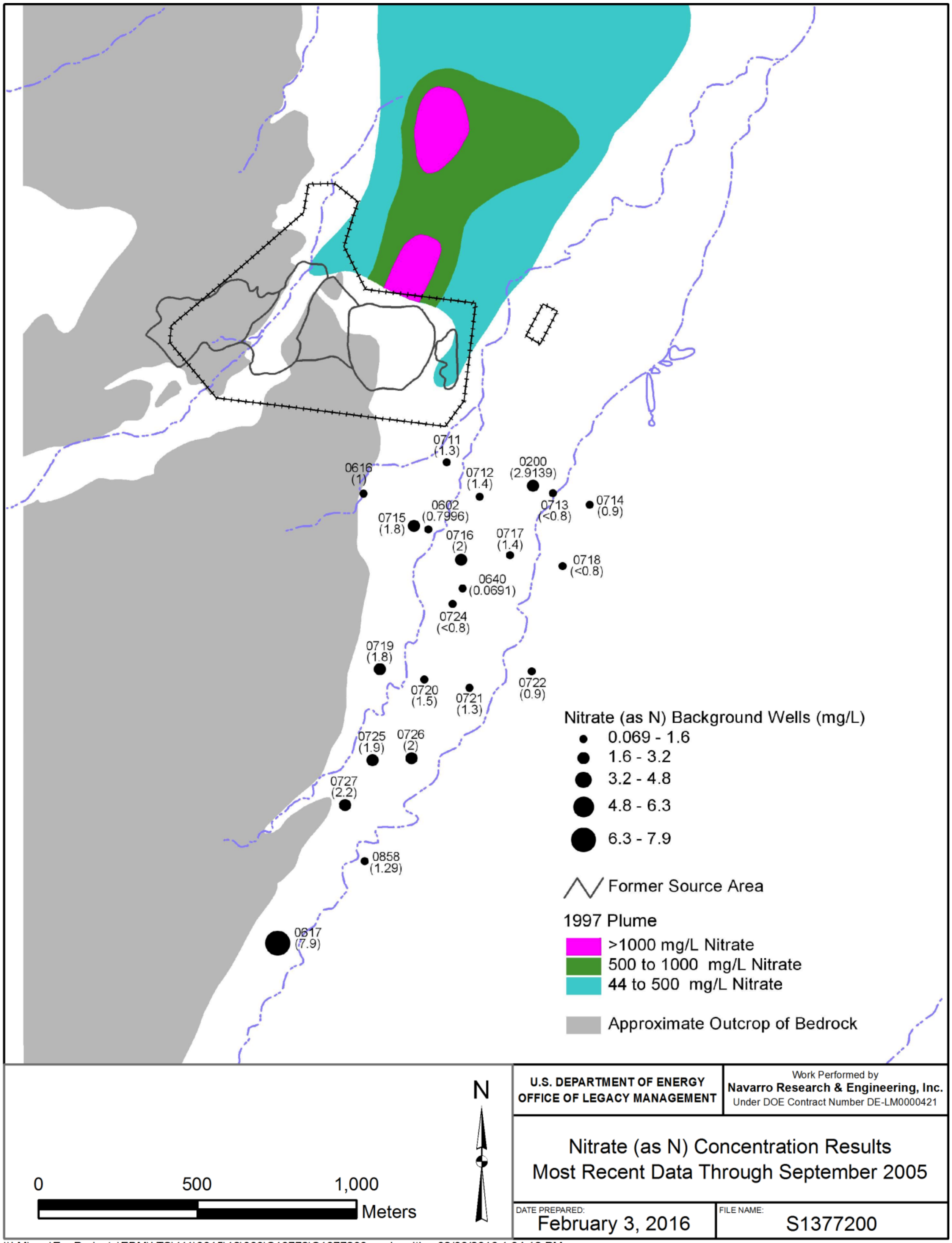

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Figure B-14. Nitrate (as N) concentrations in upgradient alluvial wells.

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^{-1} and ammonium concentrations averaged 34.2 mg kg^{-1}. 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 1.7 ha of land for a total of 3.4 ha of phytoremediation plots in the source area. Figure 1 in the main report shows the locations of the plantings within the footprint of the New Tailings Pile.

For most years we irrigated the plantings daily from March through October with approximately 3.8 L day^{-1} per plant for a total irrigation rate of 0.23 m yr^{-1} (range of 0.16−0.36 m yr^{-1}). In 2007, we doubled the irrigation rate to 0.46 m yr^{-1} to determine if additional water further enhanced denitrification. We reduced the irrigation rate back to 0.23 m yr^{-1} in 2008 because soil water content had increased at depth, and then discontinued irrigation in 2010. Irrigation rates were maintained lower than rates of potential evapotranspiration (ET_o) for mature saltbush plant canopies (typical rates are about 6 millimeters per day [mm day^{-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 the daily mean temperature, wind speed, relative humidity, and solar radiation.)

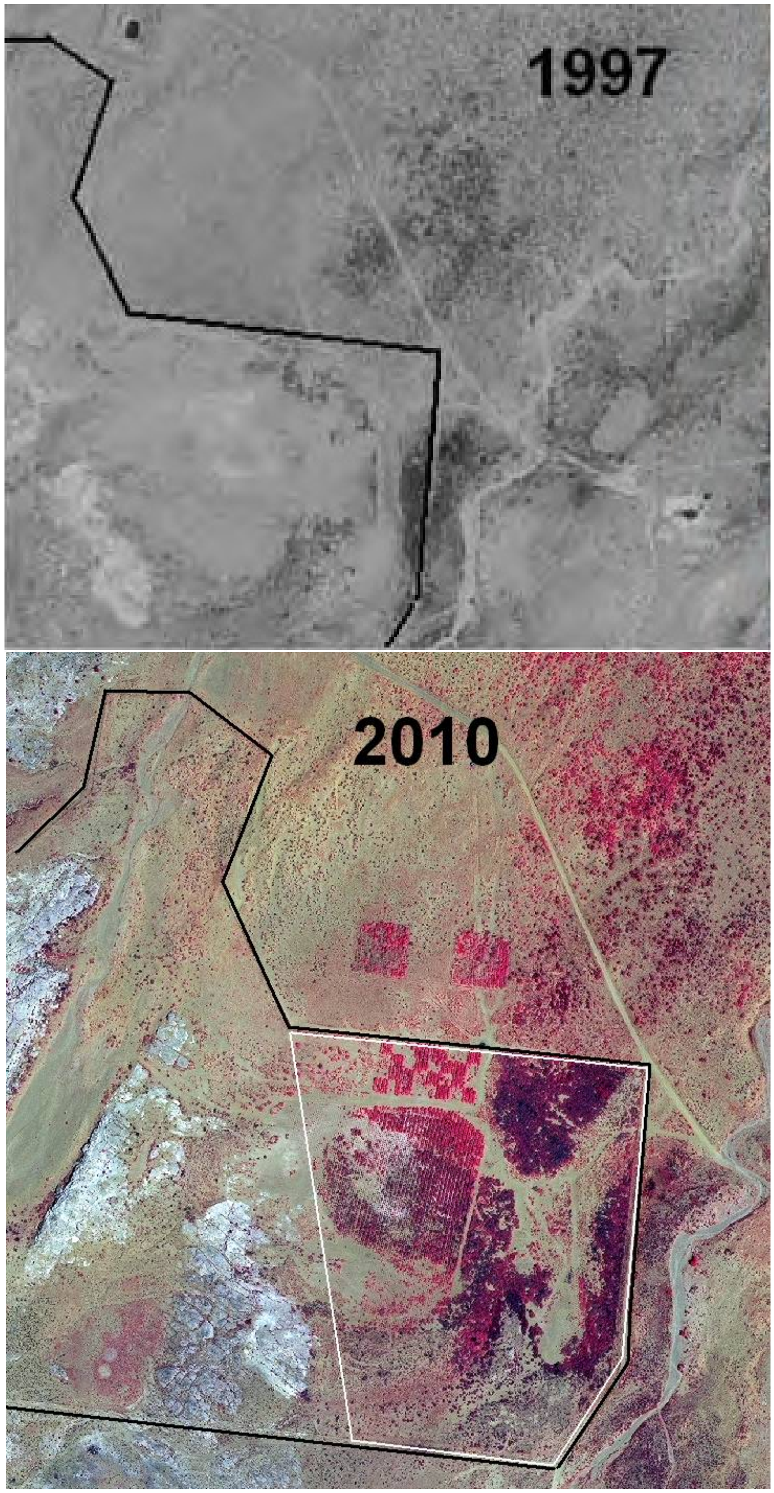


Figure B-15. Comparison of site vegetation on a black-and-white aerial photograph in 1997 (Top Panel) and on a Quickbird satellite image with vegetation shown in false-color red in 2010. The black line on both images denotes the fence line around the source area.

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.

B.3.2 Plant Canopy Growth and Development

Survival of plants in all phytoremediation plots in the source area was high until we discontinued irrigation in 2010. 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 area). Only the New Field North was free of stunted plants. Stunting appeared 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. By 2010, overall plant survival was >95%, and final plant cover in both plantings ranged from 40 to 70% (Breshlof et al. 2013). By 2014, a combination of no irrigation and drought had caused about 50% mortality of fourwing saltbush (*Atriplex canescens*, symbol ATCA), and grasses (mainly *Sporobolus* spp.) began replacing the shrubs. However, even though species composition changed, percent plant cover changed little after 2010 (Breshlof et al. 2013).

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-1 and 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 in 2010 for 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:

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

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 milligrams of dry roots per kilogram 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 mg dry weight, for a mean value of 0.128 mg per fragment (standard error [SE] = 0.075, n = 7). This assay procedure is only semiquantitative 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.

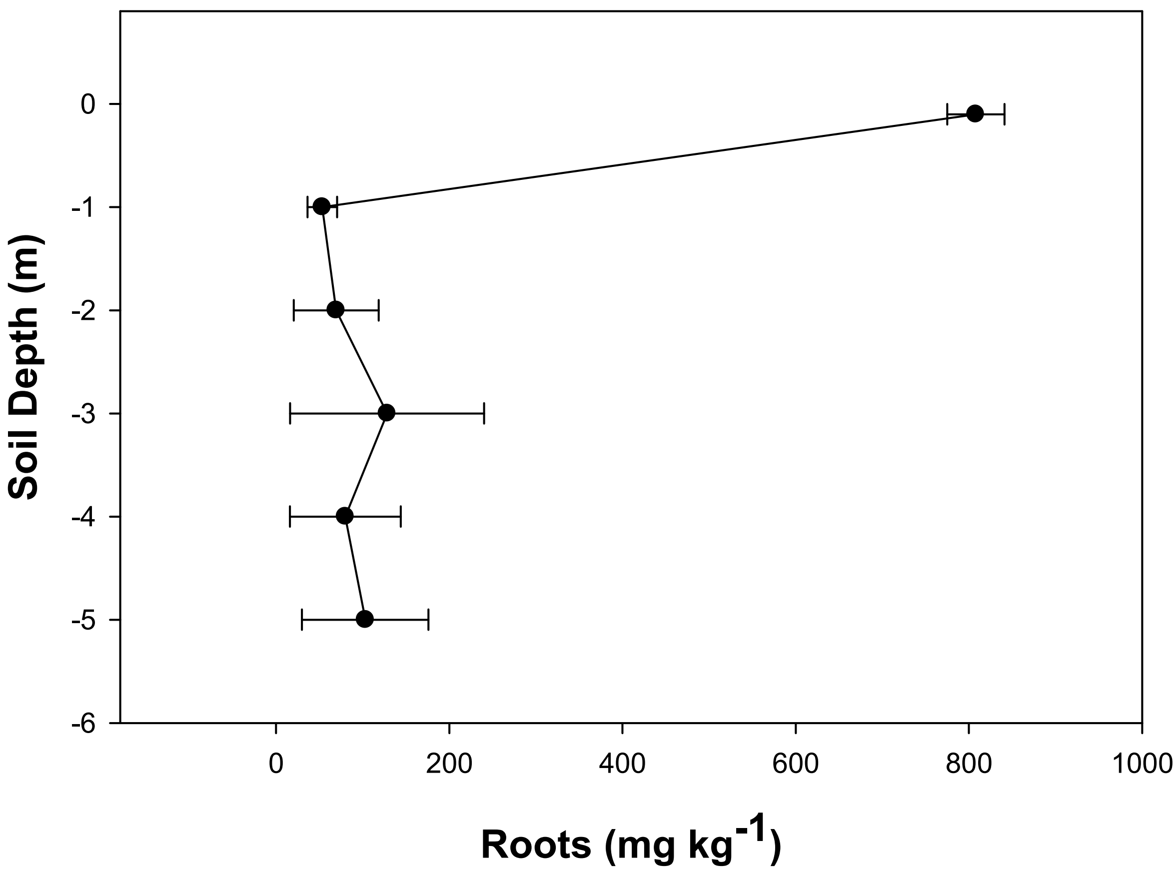


Figure B-17. Root content of soils in phytoremediation plots as a function of soil depth. Bars are standard errors of means.

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 Tsaile, 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 (standard deviation [SD] = 0.34) and sulfur averaged 0.284 percent (SD = 0.127). 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 Content and Percolation Monitoring

Monitoring Methods

Scientists began monitoring soil moisture profiles in 1999 using a fast neutron thermalization (neutron hydroprobe) method (Ward and Whitman 2009) and added monitoring with water content reflectometers (WCRs) (Kim and Benson 2002) and water flux meters (WFMs) (Gee et al. 2002, 2009) in 2006. Thin-walled PVC tubes served as neutron hydroprobe ports. We installed 20 ports in the Old Field in 1999 and 20 more in the Extended Field in 2006, all evenly distributed over the fields (McKeon et al. 2005; Jordan et al. 2008). We recorded neutron counts with a Campbell Pacific Nuclear Model DR 503 hydroprobe in each port at 0.3 m intervals to a maximum soil depth of 5 m except where bedrock occurred at shallower depths. We divided field counts by shielded counts (count ratios) and applied a calibration based on soil bulk density and count ratios obtained for dry and saturated site soils (Jordan et al. 2008). We measured neutron counts monthly in all ports, March through October from 2000 to 2010 and again in July 2015, to determine how lack of irrigation affected soil moisture.

In 2006, scientists installed WCRs and WFMs at four locations within the plantings (one in the Old Field and three in the Extended Field) for real-time monitoring of soil moisture profiles and percolation flux. Each instrument cluster consisted of one WFM placed at a depth of 3.7 m and four WCRs placed above the WFM at 0.3–0.6 m, 0.9–1.2 m, 1.8–2.1 m, and 2.7–3.0 m depths. WCRs were calibrated in the laboratory following the methods of Kim and Benson (2002). WFMs consist of a funnel to direct water from the soil into a passive wick to control soil moisture tension, emptying into a miniature tipping-bucket water gage (similar to a rain gage), and a pipe or chimney extending above the funnel to minimize divergent flow (Gee et al. 2002, 2009). We calibrated WFMs annually by injecting 100 mL of water through tubes that extended to the surface. Data from WCRs and WFMs were downloaded regularly using a telemetry system (Bush et al. 2010).

Monitoring Results

Monthly mean soil water content in the irrigated subpile soil plantings, determined by neutron hydroprobe, was relatively constant at 0.11–0.12 $cm^3\ cm^{-3}$ from 2006 through 2010 (Figure B-20A), and below the soil water content at field capacity, about 0.15 $cm^3\ cm^{-3}$. Water content increased slightly in 2007, the year we increased irrigation volume, and then decreased in 2008 when we adjusted irrigation back to 0.23 m yr^{-1}. Mean soil water content in July 2015, 5 years after irrigation ceased, was still 0.110 $cm^3\ cm^{-3}$ (standard error of the mean [SEM] = 0.003), not significantly different than during years with irrigation ($P = 0.63$). Soil water content increased with depth, but for most ports, it remained at or below field capacity even at the 5 m depth (Figure B-20B). However, for 2 of the 40 ports, soil water content remained consistently at saturation (0.24 $cm^3\ cm^{-3}$) at the 5 m depth, even in 2015, 5 years after irrigation ceased; the two ports occur in an area where the water table is shallower than 5 m. Soil moisture levels tended to be lowest from May to September during the growing season (Figure B-20C).

WCR readings also indicated that soil water content was below field capacity in the top 1.2 m (Figure B-21). Readings at Stations 3 and 4 were consistently below field capacity at all soil depths from 2006 to 2015. At Station 1, soil water content at the 3 m depth rose above field capacity in 2010 (Figure B-21), but then the profile dried markedly after we discontinued irrigation. By contrast, at Station 2, soil water content at 3 m increased markedly after irrigation ceased in 2010, possibly because of the high plant mortality in the immediate area. WFMs recorded no net recharge at stations in the Old and Extended Fields from 2006 through 2010. One of the four WFMs recorded a percolation flux rate of 9.7 millimeters per year (mm yr^{-1}) from 2010 through 2014, after irrigation ceased. This WFM is in area where, after 2011, erosion caused runoff water to channel and pond after storm events, and groundwater elevation seasonally increased as determined by soil sampling (B.4.1) and WCR measurements.

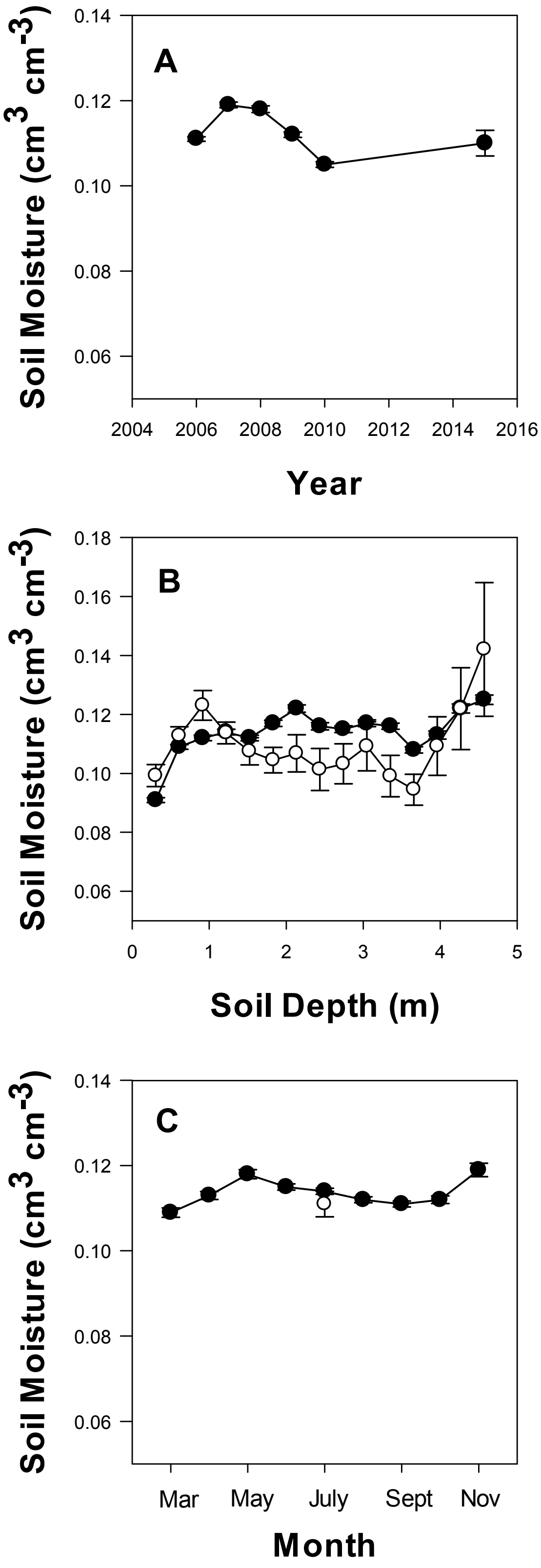


Figure B-20. Soil moisture contents measured by neutron hydroprobe in the subpile soil at the Monument Valley UMTRCA site showing means per year.(A), means by soil depth (B), and means per month during the growing season (C). Open symbols in B and C show results for July, 2015, 5 years after irrigation was discontinued. Errors bars are standard errors of means.

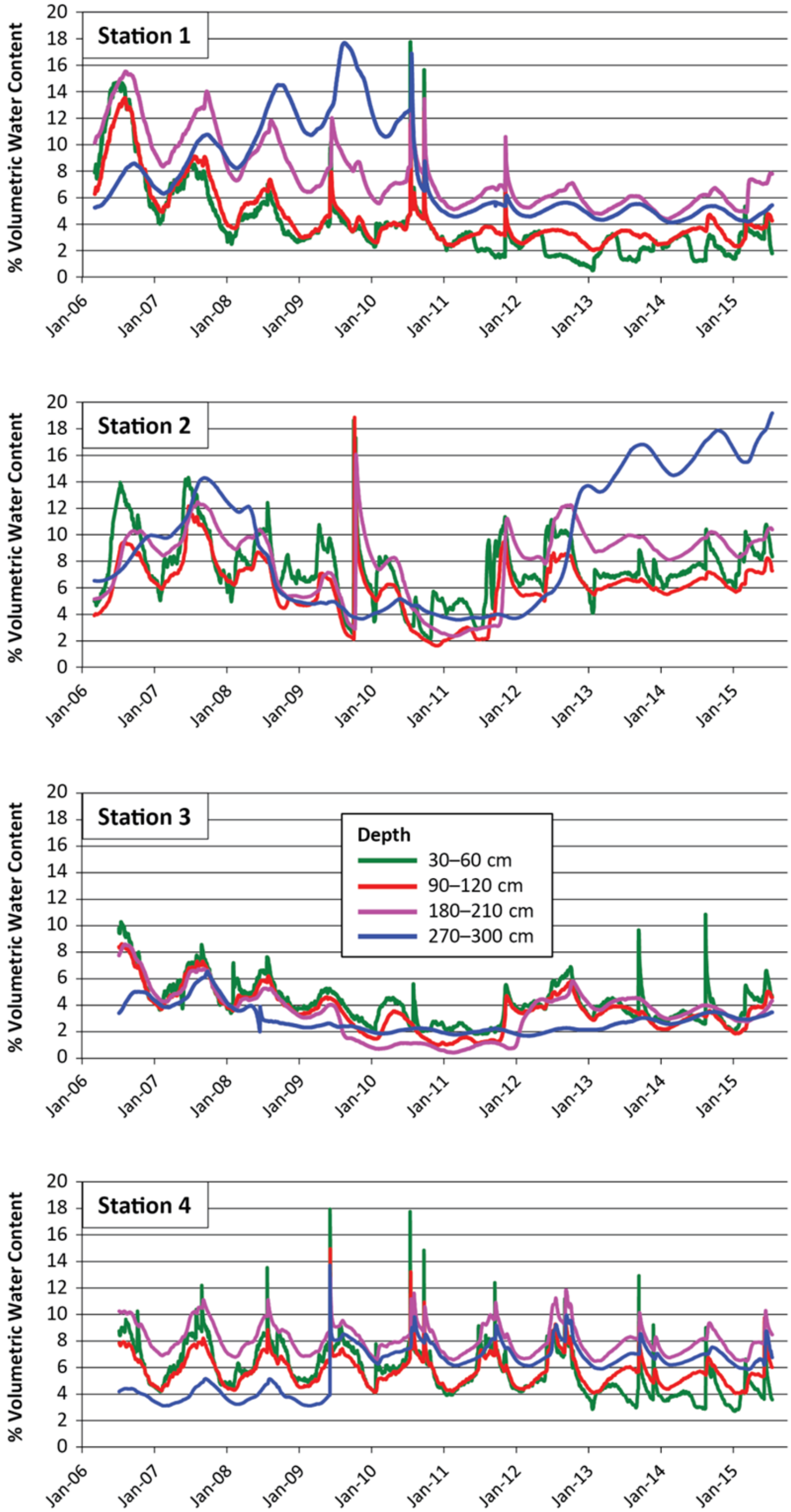


Figure B-21. Soil moisture contents measured by water content reflectometers in the Old Field (Stations 1 and 2) and the Extended Field (Station 3 and 4) at different depths in the subpile soil profile at the Monument Valley UMTRCA site.

B.3.7 Estimation of Evapotranspiration

We calculated an approximate annual water balance for the subpile soil area by subtracting ET from precipitation (PPT) plus irrigation. We estimated monthly ET using a remote sensing algorithm. The algorithm empirically relates Enhanced Vegetation Index (EVI) data from the Moderate Resolution Imaging Spectrometer (MODIS) sensors on the Terra satellite with maximum daily air temperatures (T_{max}) and with ET measured at eddy covariance and Bowen ratio moisture flux towers at 13 riparian phreatophyte sites in in Arizona and New Mexico (Nagler 2005a,b). We modified the algorithm for ATCA and black greasewood (*Sarcobatus vermiculatus*, symbol SAVE) using 2 years of sap flux measurements at the Monument Valley site (Glenn et al. 2008) as follows:

$$ET = 11.5 * (1 - e^{-1.63*EVIsc})*0.883/[1+e^{-(T_{max} - 27.9)/2.57}] \quad (1)$$

EVI_{sc} is MODIS EVI stretched between a maximum value, representing full plant cover, and a minimum value, representing bare soil:

$$EVI_{sc} = 1 - (EVI_{max} - EVI)/(EVI_{max} - EVI_{min}) \quad (2)$$

We set EVI_{max} at 0.542 and EVI_{min} at 0.091, based on values from the 13 flux tower sites, resulting in an EVI_{sc} of 0.0 for bare soil and an EVI_{sc} of 1.0 for full vegetation. EVI_{sc} values can exceed 1.0, for example, for alfalfa fields. Negative EVI values can also occur for surface water and are excluded from analyses.

T_{max} is the mean daily maximum temperature (°C) for each 16-day period of MODIS data collection. T_{max} was better correlated with ET at the tower sites than any other meteorological variable or combination of variables, including potential ET (ET_o). The first term in Equation (1), $(1 - e^{-1.63*EVIsc})$, is based on the equation for the absorption of light by a canopy, with EVI_{sc} replacing leaf area index in the formula. The second term, $0.883/[1 + e^{-(T_{max} - 27.9)/2.57}]$, assumes a sigmoidal response of ET to T_{max}, with a center point at 27.9 °C. These equations were based on the observed response of phreatophyte ET to EVI and T_{max} at the tower sites. Numerical coefficients in Equation (1) were derived using best-fit regression analysis. The original equation developed for riparian phreatophytes (Nagler et al. 2005b) included an additional constant, 1.03 mm day^{-1}, to account for the fact that tower ET did not go to zero even when plants were dormant. This term was dropped for the Monument Valley analysis because, given the sparse vegetation, ET frequently does go to zero. Equation (1) adequately reproduced sap flux data for ATCA and SAVE in the source area and matched annual PPT values for the entire UMTRCA site (subpile soil and plume areas) within 6% for the years 2000–2007 (Glenn et al. 2008).

Figure B-22 shows results of a partial water balance for the subpile soil plantings. ET exceeded PPT plus irrigation in all years except 2007, when we temporarily doubled irrigation. Averaged over all years, ET exceeded PPT plus irrigation by 27% ($P < 0.001$ by *t* test). After we discontinued irrigation in 2010, ET was more than double PPT (259 mm yr^{-1} versus 115 mm yr^{-1}, $P < 0.001$). The high ET might be attributable to the desert phreatophytes, ATCA and SAVE, tapping groundwater (Breshlof et al. 2013), or an unmeasured amount of runoff that the subpile soil area received from surrounding sandstone uplands (DOE 1999, 2005). By contrast to ET in the subpile soil area, estimates of ET over the plume were correlated with annual PPT ($r = 0.75$, $P = 0.002$), with mean values of 145 mm yr^{-1} (SE = 11.0) for ET and 161 mm yr^{-1} (SE = 11.4) for PPT (not significantly different, $P = 0.11$).

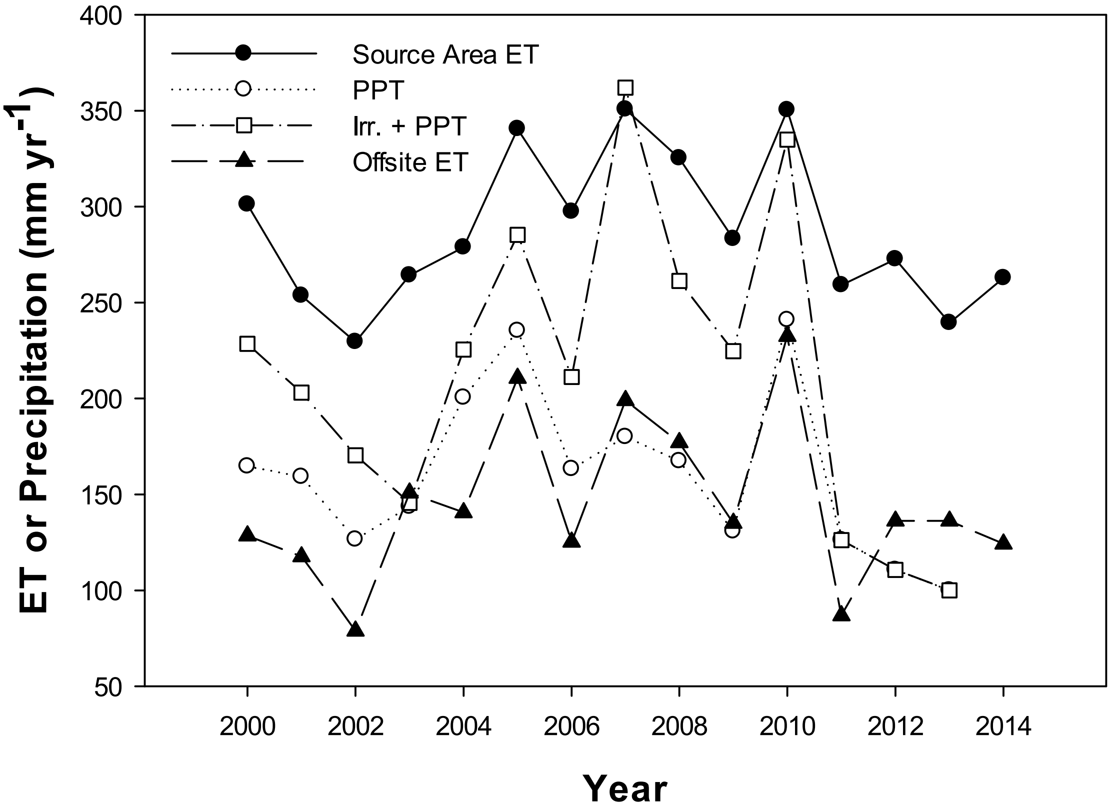


Figure B-22. Annual water balance components for the subpile soil area at the Monument Valley UMTRCA site, 2000–2014, showing ET, precipitation (PPT), and irrigation plus PPT. ET over the plume (offsite ET) is also shown.

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 the 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 Soil Sampling and Analysis Methods

We sampled subpile soil annually using hand augers in the vicinity of each hydroprobe port and analyzed the samples for nitrate as N, ammonium as N, and sulfate as SO_4^{2-}. Samples were taken at 0.3 m intervals to a maximum depth of 5 m (Figure B-23). All samples were analyzed in the DOE's Environmental Sciences Laboratory. Samples were air-dried and sieved, then 20 g samples were mixed with 50 mL of 1 M potassium chloride, stirred for 2 hours, and centrifuged to remove particulates. This procedure was repeated once, and the combined supernatants were filtered and analyzed by ion chromatography for nitrate and by Hach spectrophotometry for ammonium and sulfate.

Figure B-23. 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.

We collected soil samples for ^{15}N analysis at 1 m and 4 m depths, at eight locations within the Old Field in 2004 and at eight locations within the Extended Field in 2007. Samples were analyzed for nitrate, ammonium, and ^{15}N isotopes of each compound at the SIRFER Laboratory at the University of Utah, Salt Lake City, UT. We reported ^{15}N enrichment as $\delta^{15}N$ relative to an atmospheric standard in ‰ (Kendall and Aravena 2000). We calculated values forε using a simplified form of the Rayleigh Equation:

$$\varepsilon = (\delta^{15}\mathrm{N}S_t - \delta^{15}\mathrm{N}S_0)/\ln f \qquad (3)$$

where S_t and S_0 are enrichment values of samples at time t and time zero, respectively, ln is the natural logarithm, and f is the fraction of unreacted product at time t (Mariotti et al. 1981). For our samples, we plotted $\delta^{15}N$ values of nitrate and ammonium versus the natural logarithm of concentrations of each, and we assumed that the slope of the line was equal to ε (Kendall and Aravena 2000). The major assumptions in this analysis are that starting concentrations were uniform in the soil profile and that different concentrations measured in the samples represent different decay rates over time rather than different starting concentrations (Kendall and Aravena 2000).

We analyzed time courses of nitrate, ammonium, and sulfate concentrations by one-way analysis of variance (ANOVA) with year of sample as the categorical variable, and by linear regression analyses to determine decay rates. ANOVA, linear regression analyses, and other tests were performed with SigmaPlot software (Systat Software, Inc., San Jose, CA). Variances around means are reported as standard errors of means (SEM).

B.4.2 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 ton 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).

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, 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).

B.4.3 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-24). The value of $\delta^{15}N$ decreased linearly with the natural logarithm of the concentrations for both nitrate and ammonium (Figure B-25). Enrichment factors for $\delta^{15}N$ were similar for nitrate ($\varepsilon = -4.76‰$) and ammonium ($\varepsilon = -5.22‰$) (not significantly different at $P < 0.05$). However, the $\delta^{15}N$ line plot for nitrate was about −16‰ lower than the line plot for ammonium (Figure B-25).

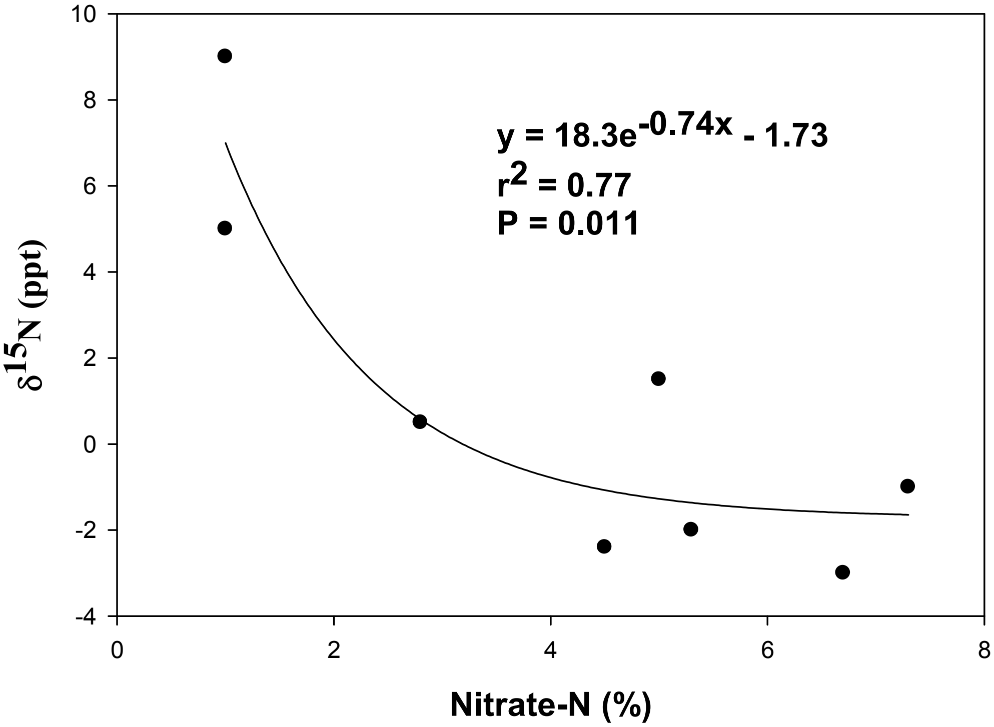


Figure B-24. ^{15}N enrichment versus nitrate concentration in pooled samples from source area soils, 2000–2002. ^{15}N enrichment is expressed as $\delta^{15}N$ in units of parts per thousand relative to ^{15}N content in atmospheric samples of nitrogen gas. The relationship followed an exponential decay function as expected for ^{15}N enrichment due to microbial denitrification. See Appendix A for more information on ^{15}N enrichment methods and interpretation.

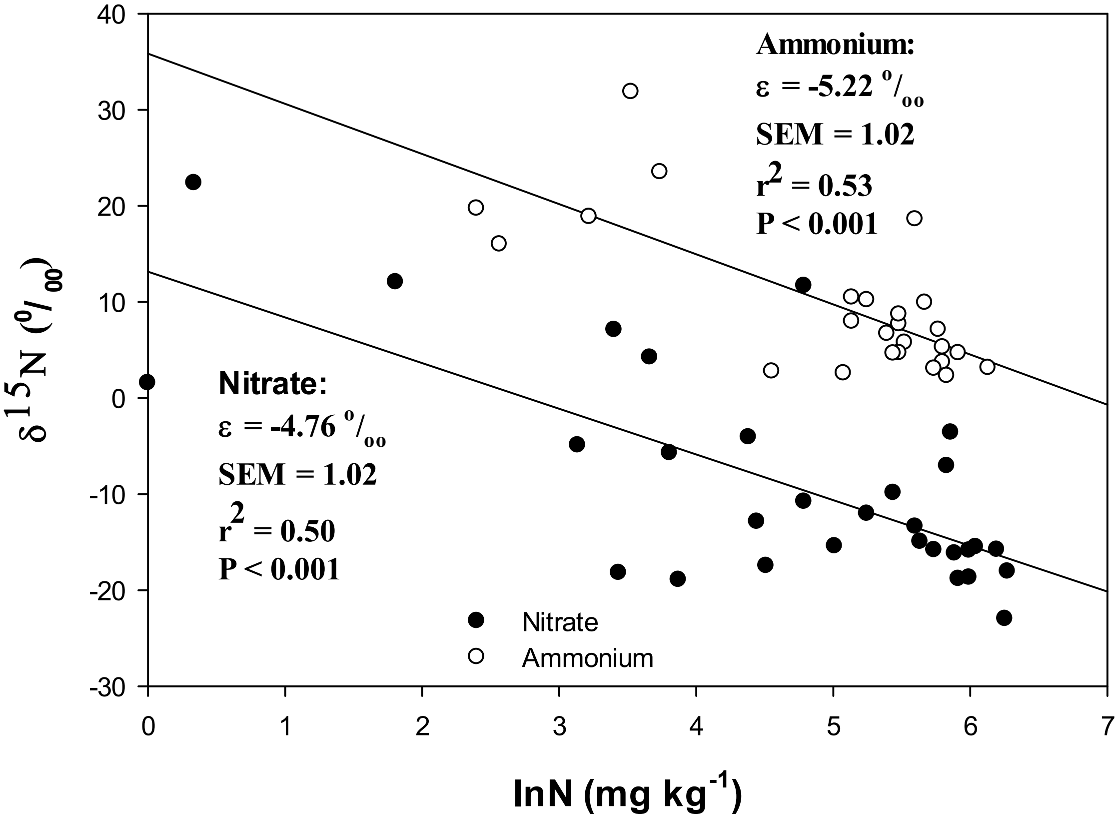


Figure B-25. Regression of ^{15}N enrichment values ($\delta^{15}N$) for nitrate and ammonium as a function of ln(concentration) in samples from the subpile soil at the Monument Valley UMTRCA site.

B.4.4 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.4.5 Changes in Nitrate, Ammonium, and Sulfate, 2000–2014

Concentrations of nitrate-N and ammonium-N in the Old Field in 2000 were 163 mg kg^{-1} (SEM = 14.7) and 184 mg kg^{-1} (SEM = 20.0), respectively. Mean nitrate-N and ammonium-N levels in the Old Field decreased by 78% and 86%, respectively, from 2000 to 2014 (Figure B-26). Mean annual reduction rates, based on linear regression, were 5.5 mg kg^{-1} yr^{-1} for nitrate-N, 9.55 mg kg^{-1} yr^{-1} for ammonium-N, and 15.1 mg kg^{-1} yr^{-1} for total N (Figure B-26). Final levels of nitrate-N and ammonium-N in 2014 were 23.5 mg kg^{-1} (SEM = 8.9) and 40.4 mg kg^{-1} (SEM = 18.5), respectively. In contrast, sulfate levels appeared to rise from 2007 to 2009, then decreased to 2007 levels by 2014 (Figure B-26); however, an ANOVA indicated no significant differences in sulfate levels among years ($F = 1.38$, $P = 0.23$). The mean sulfate concentration for all years was 2007 mg kg^{-1} (SEM = 152).

Soil nitrate profiles in the Old Field were initially greater at depth, and reductions in soil nitrate over time occurred at all depths (Figure B-27A). Soil ammonium profiles were similar (Figure B-27B), except that levels were lower than nitrate at shallower depths and higher at greater depths. Soil sulfate profiles were different; levels were highest near the surface and decreased with depth, and with no apparent loss of sulfate from the profile over time (Figure B-27C).

Nitrate and ammonium also decreased with time in the Extended Fields planted in 2006 (Figure B-28). Nitrate decreased after an initial lag period, whereas ammonium decreased steadily over all years. An ANOVA, with year as the categorical variable, indicated that decreases were significant for both nitrate ($F = 4.83$, $P < 0.001$) and ammonium ($F = 2.61$, $P = 0.035$) and, similar to observations in the Old Field, initial levels were 79–83% lower by 2014. An ANOVA also indicated that sulfate levels did not differ by year ($F = 2.06$, $P = 0.086$) (Figure B-26). By 2014, the remaining ammonium and nitrate occurred only in a few hot spots in subpile soil profiles (Figure B-29).

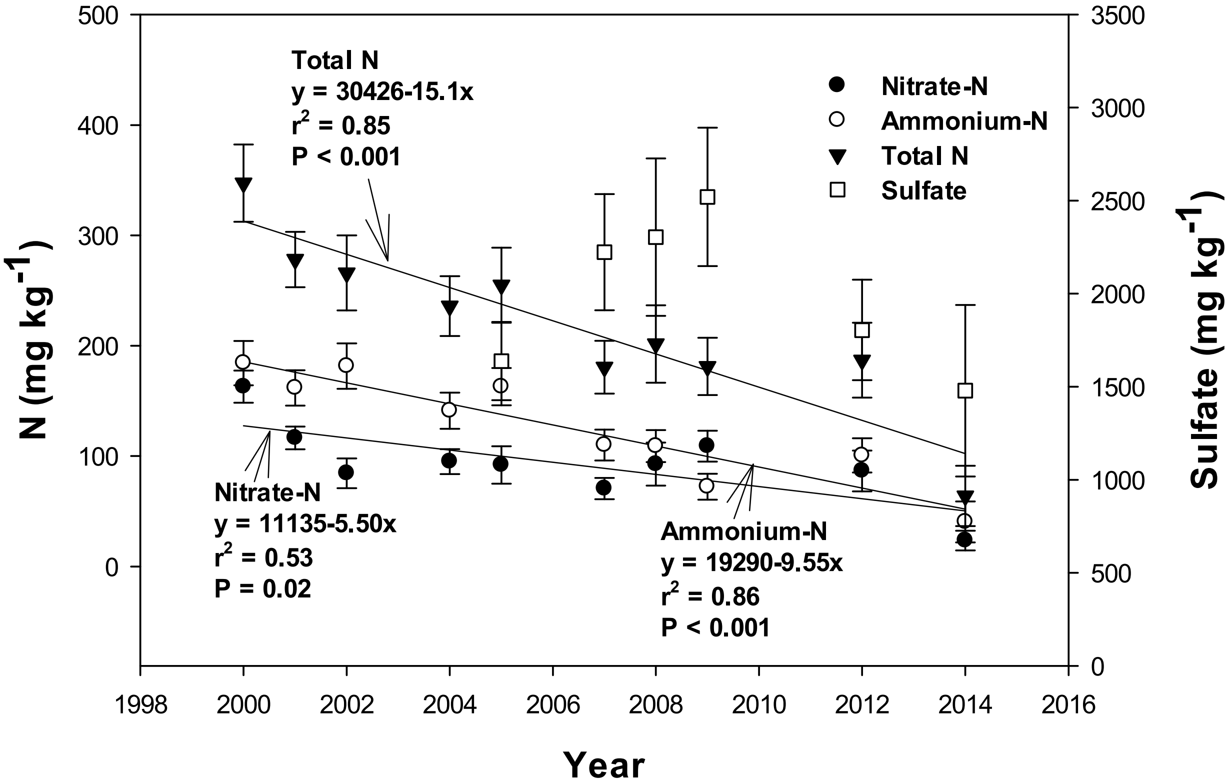
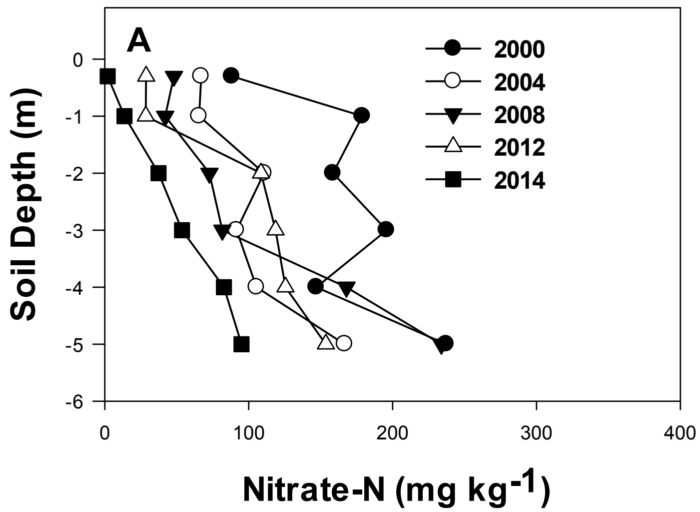
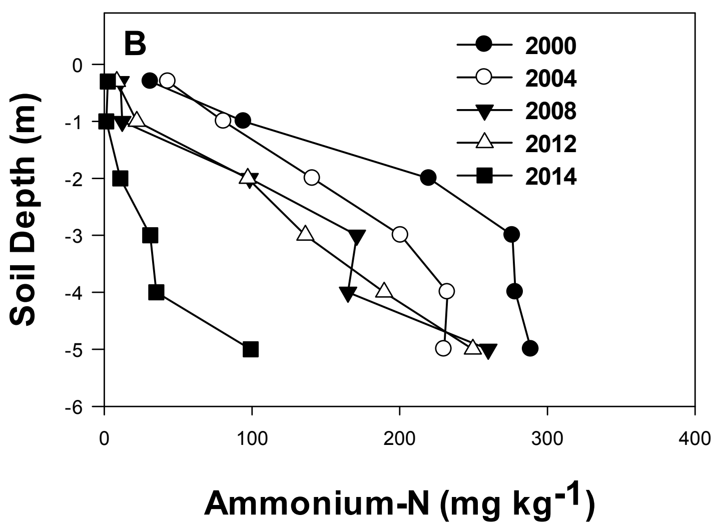


Figure B-26. Means and standard errors for concentrations of nitrate-N, ammonium-N, and sulfate in the subpile soil of the Old Field at the Monument Valley UMTRCA site, 2000–2014. Error bars are standard errors of means. Sulfate was first measured in 2005.





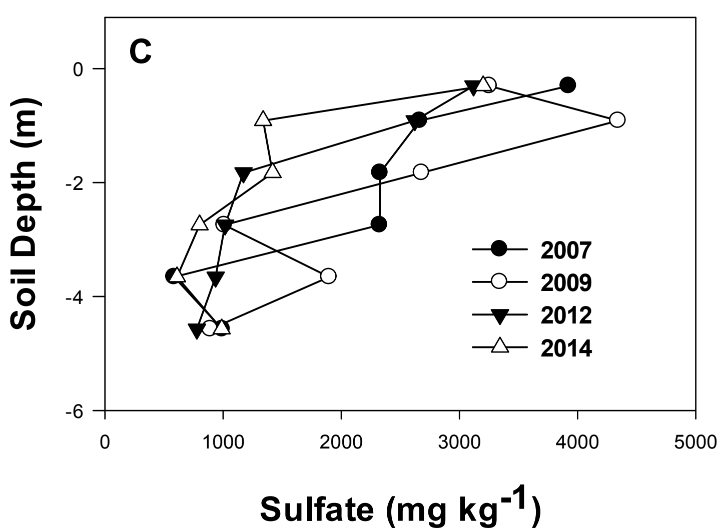


Figure B-27. Distribution of nitrate (A), ammonium (B), and sulfate (C) by soil depth over time in the Monument Valley UMTRCA site subpile soil.

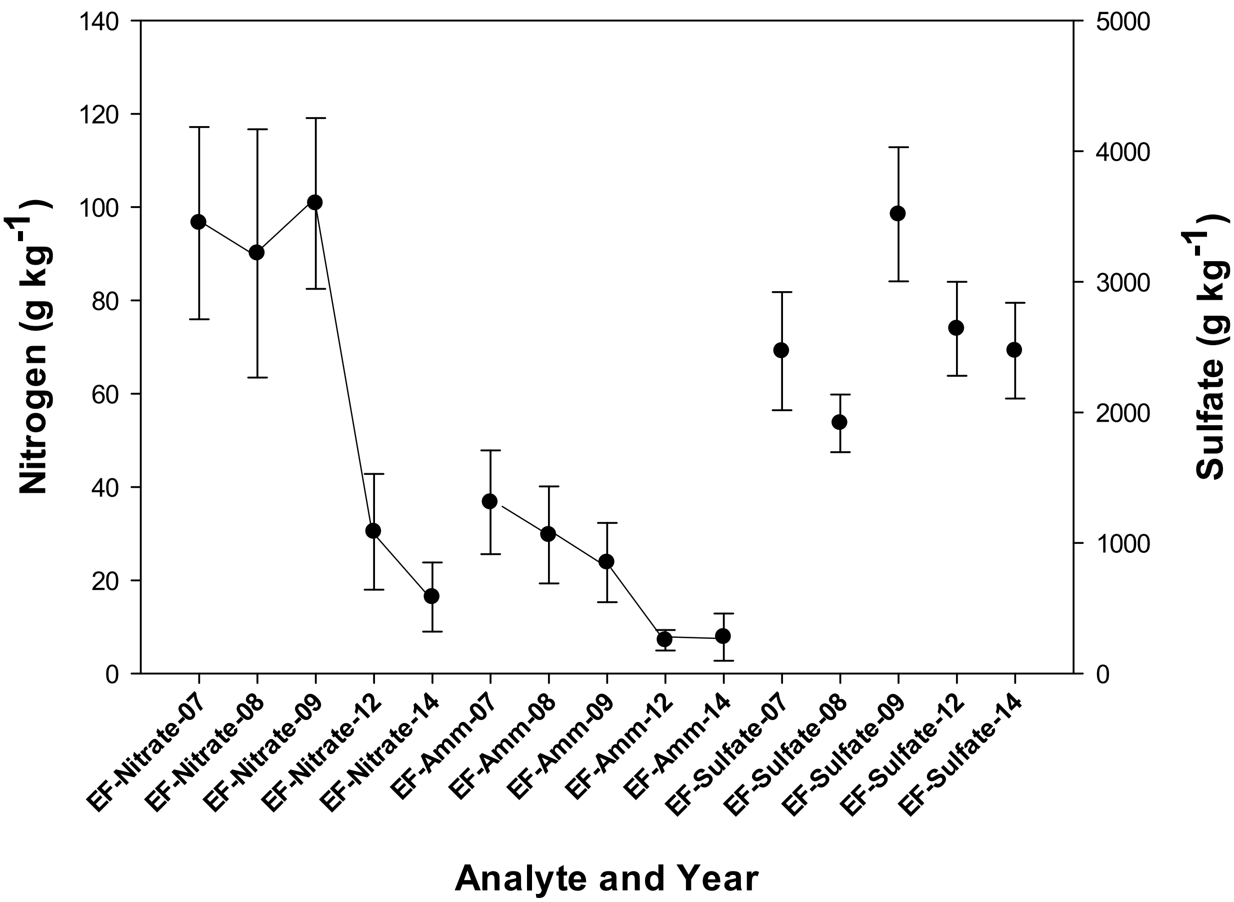


Figure B-28. Mean and standard errors of subpile soil nitrate-N, ammonium-N, and sulfate in the Extended Field at the Monument Valley UMTRCA site.

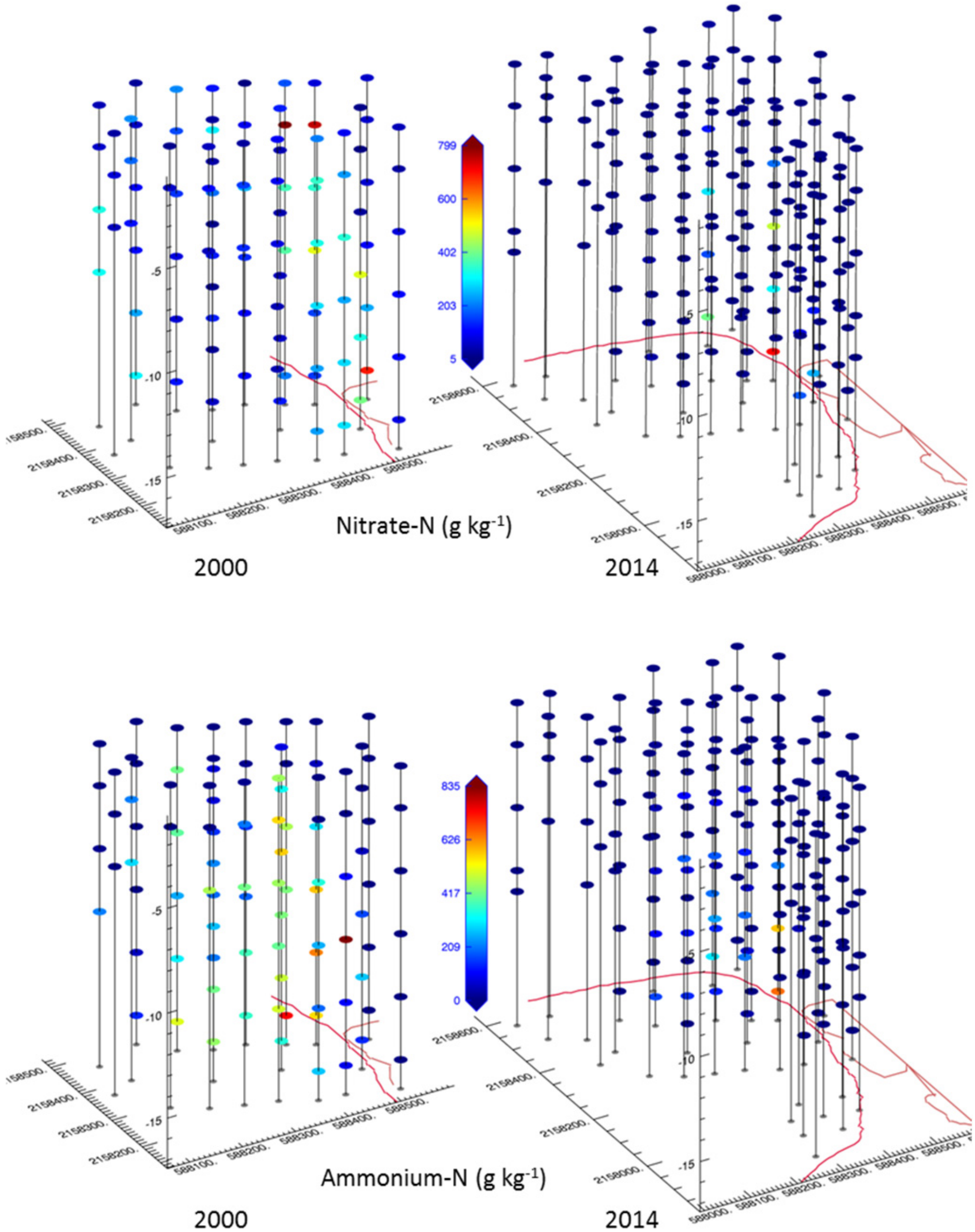


Figure B-29. Spatial distributions of nitrate-N and ammonium-N in subpile soil profiles for the Old Field in 2000 and for the Old Field and Extended Field in 2014 at the Monument Valley UMTRCA site *(x and y axes are State Plane in US feet, and the z axis is soil depth in negative feet).*

B.5 Source Containment and Removal Discussion

Ammonia was the main nitrogen source used in ore processing at the site, although some ammonium nitrate was also used (DOE 2005). This commercial ammonia would likely have had $\delta^{15}N$ close to 0.0‰ (Freyer and Aly 1974). We measured values of 2 to 3‰ in subpile soil samples with the highest ammonium concentrations (about 500 mg kg^{-1} as N in Figure B-25), a level that might have been close to N levels in the subpile soil when the mill was decommissioned. Using this assumption, we estimated that about 150 mg kg^{-1} of N was lost in the 32 years from 1968 to 2000, compared to 282 mg kg^{-1} lost from 2000 to 2014. Hence, a process of natural attenuation of N was likely underway in the subpile soil before 2000 and was apparently enhanced by irrigated plantings of ATCA and SAVE, and fencing the site to prevent grazing.

Nitrate-N from ammonium nitrate used for ore processing would likely have had $\delta^{15}N$ values of 2–3‰ depending on the manufacturer (Freyer and Aly 1974), whereas we measured $\delta^{15}N$ values of about −16‰ in subsoil samples with the highest nitrate concentrations (also about 500 mg kg^{-1} as N). We concur with Miao et al. (2013a) that the depletion of ^{15}N observed in soil ammonium samples relative to nitrate was due to microbial conversion of ammonium to nitrate in the tailings pile and soil. The parallel $\delta^{15}N$ enrichment lines in Figure B-25 also indicate loss of N through coupled nitrification and denitrification (Kendall and Aravena 2000). A similar coupled process occurs in the alluvial aquifer plume but at a slower rate (Jordan et al. 2008; Carroll et al. 2009; Borden et al. 2012; Miao et al. 2013a).

Coupled nitrification and denitrification systems are found in soils and sediments with adjacent anoxic and oxic microsites, because nitrification is carried out by facultative aerobes, while denitrification requires anaerobic conditions (Kendall and Aravena 2000; Kremen et al. 2005). It appears that nitrification and denitrification occurred most rapidly in the upper soil layers of the subpile soil where oxygen would be more abundant, while deeper soil layers initially retained large amounts of unreacted ammonium. However, by 2014 even deep layers of soil showed a marked reduction in both nitrate and ammonium.

Our values of ε for $\delta^{15}N$ enrichment were similar to values found for denitrification in soil and groundwater systems undergoing rapid denitrification due to the presence of large amounts of nitrate (−5‰ to −8‰), whereas slower rates lead to greater fractionation and, therefore, larger (more negative) values of ε (Mariotti et al. 1988). The ε value for the plume during ethanol-stimulated nitrification and denitrification was −8‰ (Miao et al. 2013a), similar to our results for the subpile soil.

Leaching occurred during and after milling operations (DOE 1999, 2005) and was evaluated as a possible reason for the decrease in subpile soil nitrogen levels between 2000 and 2014. The subpile soil receives an unknown amount of runoff from the surrounding uplands. Storm runoff across this area created a few small channels and may have contributed to localized recharge as measured in one WFM. However, four lines of evidence suggest that leaching was not a broadly important factor once the fenced plantings became established. First, sulfate levels were highest at the soil surface and did not decrease significantly over the study period, opposite of patterns observed for nitrate and ammonium. Leaching would have resulted in movement of sulfate from the surface to deeper in the profile and an overall reduction in concentration similar to that observed for nitrate and ammonium. Second, soil water content was at or below field capacity for almost all soil profiles sampled over the 14-year course of the study, and we detected no net percolation flux with the four WFMs during the 10-year irrigation period. Third, groundwater nitrate-N and ammonium-N levels immediately downgradient of the subpile soils dropped to <5 mg L^{-1} (although levels have increased farther downgradient), indicating a recent lack of nitrogen movement from the subpile soils into the alluvial aquifer (Miao et al. 2013a). Finally, the partial water balance analysis suggests that ET for our ATCA and SAVE plantings now removes twice the amount of water that the subpile soil receives as PPT.

Our irrigated plantings did not remove sulfate in the subpile soil, probably because redox conditions in the vadose zone did not favor sulfate reduction (Miao et al. 2013b). However, the plantings did *isolate* sulfate in the subpile soil. ET from ATCA and SAVE plantings appeared to curtail sulfate leaching. Groundwater monitoring results for 2009 and 2010 included sulfate levels of 39–330 mg kg^{-1}in wells immediately downgradient of the subpile soils, compared to levels of 17–130 mg kg^{-1} for upstream control wells, and 370–1500 mg kg^{-1} for wells in the plume (Miao et al. 2013b). Stable isotope analyses indicated that the subpile soil area was the source of high levels of sulfate in the alluvial aquifer for approximately 40 years (Miao et al. 2013b), but enhancing or accelerating reestablishment of the desert phreatophyte community has now cut off that source.

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Appendix C

Natural and Enhanced Attenuation of Groundwater

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The roles of desert shrubs (phytoremediation) and microbial processes (nitrification and denitrification), which were shown to help contain and remove contamination from the source area (Appendix B), were also investigated as possible remedies for contaminated groundwater. As with the source area (subpile soils), LM scientists first characterized natural phytoremediation and microbial denitrification in the alluvial aquifer, and then evaluated ways to enhance these natural processes.

Fourwing saltbush and black greasewood plants naturally pump water from the top of the alluvial aquifer and from deep soil layers above the aquifer, thereby potentially limiting plume dispersion. These plants also extract small amounts of nitrogen and sulfur from the aquifer. Field plot studies found that revegetation of denuded areas and grazing management in other areas overlying the plume can greatly enhance water extraction by these native phreatophytic plants.

Modeling and isotope studies provided evidence that nitrate in the alluvial aquifer is naturally undergoing microbial denitrification, albeit at a slow rate, with an estimate that between 40 percent to 60 percent of the original nitrate in the plume has been converted to innocuous nitrogen gas over the past 40 years. Injection of ethanol into selected wells markedly increased rates of denitrification and also stimulated conversion of sulfate to hydrogen sulfide. Modeling results show that enhanced plume denitrification may be technically feasible given the high hydraulic conductivity of the alluvial aquifer sands.

Enhanced attenuation can be defined as initiating and/or augmenting natural and sustainable attenuation processes. The goal is to increase the magnitude of natural processes beyond that which occurs without intervention. Enhanced attenuation approaches may be implemented if it cannot be shown with a high level of certainty that the total capacity of *natural* attenuation processes are capable of attaining groundwater remediation objectives. The pilot studies are focusing on enhancements that are sustainable—that do not require long-term, continuous intervention. The goals for enhanced attenuation of groundwater at Monument Valley are to slow plume movement, extract nitrate and sulfate, and increase microbial denitrification.

The role of native shrubs in controlling the source area water balance through transpiration (Appendix B, Section B.3), which prevents deep percolation and leaching of contaminants, led to the hypothesis that these same shrubs, functioning as phreatophytes (plants that root into and extract groundwater) could transpire groundwater and slow the spread of the contaminant plumes. Similarly, the rapid loss of nitrate and ammonium from the source area due to microbial processes (McKeon et al. 2005; Jordan et al. 2008) led to the hypothesis that similar microbial processes might be operating in the plume and could be enhanced by supplying carbon substrates. These topics were addressed through pilot studies and modeling. The major findings are presented in the following sections. As in previous sections of this report, more detailed discussions can be found in the technical products—reports and publications—cited herein.

C.1 Groundwater Phytoremediation

The potential natural vegetation overlying the plume is dominated by two phreatophytic shrubs, fourwing saltbush and black greasewood. Phreatophytes are deeply rooted plants that extract water from shallow aquifers. Black greasewood (*Sarcobatus vermiculatus*) is an obligate phreatophyte—it must extract groundwater to survive—while fourwing saltbush (*Atriplex* *canescens*), and some other *Atriplex* species, are facultative phreatophytes capable of extracting water from both the aquifer and the vadose zone above the aquifer.

Plant communities dominated by these two species occur over many millions of hectares of intermountain basins in the western U.S. where, as is the case at the Monument Valley site, recharge creates shallow aquifers under valley floors (Nichols 1994; Steinwand et al. 2001; Lin et al. 1996). These communities are capable of controlling the basin water balance through their use of groundwater for transpiration. However, where the phreatophyte have been overgrazed, as occurs at the Monument Valley site, the local water balance can switch from net discharge to net recharge due to a reduction in phreatophyte transpiration.

Where rooted into the alluvial aquifer plume at Monument Valley, these phreatophytic shrub species could be contributing to natural attenuation in two ways. First, they could be extracting water from the plume, slowing its movement away from the site. Second, they could be extracting nitrate and sulfate from the plume to support plant growth. If the shrub populations are indeed extracting water, nitrogen, and sulfur from the plume, their contribution to remediation could potentially be enhanced through grazing management and revegetation in areas overlying the plume.

The pilot studies of natural and enhanced phytoremediation of groundwater at Monument Valley addressed the following topics:

- The relationship between the natural distribution of phreatophytes and the depth to groundwater
- Evidence of phreatophyte rooting depths and zones of water extraction
- The feasibility of enhancing natural phytoremediation through revegetation and grazing management
- Rates of nitrogen and sulfur uptake by plants rooted in the alluvial aquifer
- Rates of water extraction—transpiration—by phreatophytes rooted in the alluvial aquifer and potential slowing of plume dispersion

C.1.1 Plant Communities and Depth to Groundwater

A simple contour map of depths to groundwater superimposed over a distribution map of native phreatophyte populations and associated plant communities (Figure C-1), coupled with isotope data showing where plants are extracting water and nitrogen from the plume (Section C.1.2), was used to select areas for evaluating the feasibility of methods to enhance plume phytoremediation (Section C.1.3). The contours of depth to groundwater were derived from well completion data (DOE 1999a) and vadose zone sampling.

The vegetation distribution map was created using a modified relevé method to characterize plant cover in stands near monitoring wells, and then stands were grouped into associations using simple ordination and gradient analysis techniques (e.g., Barbour et al. 1999). Associations were identified by first grouping stands with similar species composition and cover. Because species composition and cover vary across the site as a continuum rather than as discrete units, no clear breaks between groups of stands were apparent. Therefore, a simple gradient analysis of dominant species was used to group stands.

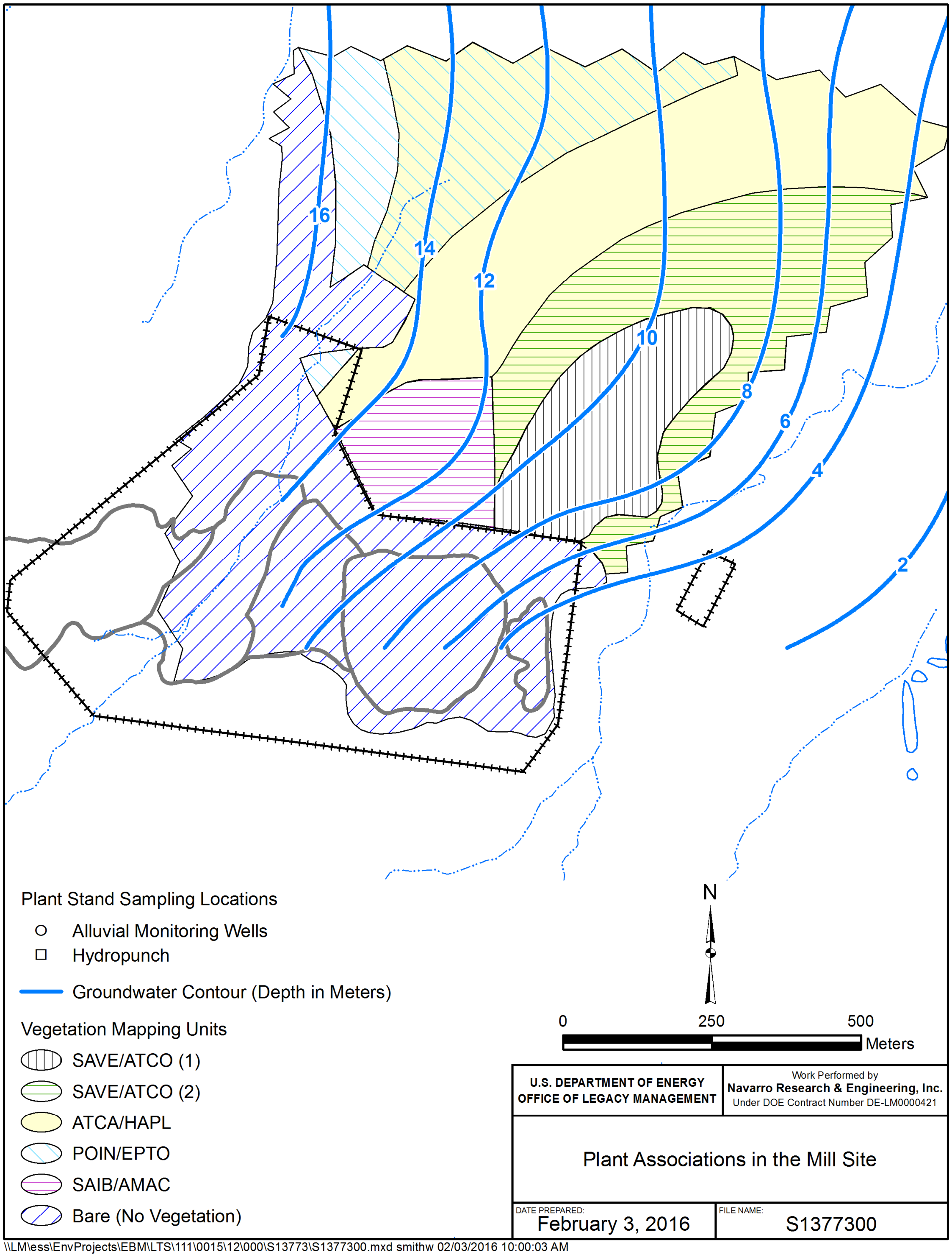

Figure C-1. Contour map of depths to groundwater superimposed on a map of plant associations. Plant acronyms are as follows: SAVE = Sarcobatus vermiculatus *(black greasewood), ATCO* = Atriplex confertifolia *(shadscale), ATCA* = Atriplex canescens *(fourwing saltbush), HAPL* = Haplopappus pluriflorus *(jimmyweed), POIN* = Poliomintha inicana *(bush mint), EPTO* = Ephedra torreyana *(joint fir), SAIB* = Salsola iberica *(Russian thistle), and AMAC* = Ambrosia acanthacarpa *(bur ragweed).*

Production of a vegetation map 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 (DOE 2004b).

Depths to groundwater range from 9 to 12 m (30 to 40 ft) within the fourwing saltbush association (*Atriplex canescens,* or ATCA) association and from 6 to 9 m (20 to 30 ft) within the black greasewood association (*Sarcobatus vermiculatus,* or SAVE). Revegetation plots were installed within the denuded area along a depth gradient from east to west and overlying nitrate "hot spots" so as to span ranges of depth to groundwater (Section C.1.3)

C.1.2 Phreatophyte Rooting Depth

Before initiating large-scale studies of groundwater phytoremediation, LM scientists first needed strong evidence that native phreatophytes were rooted in the alluvial aquifer at Monument Valley. According to the literature, black greasewood roots can penetrate 10-20 m or deeper to access groundwater (Nichols 1993, 1994). Given the apparent influence of the depth to groundwater on the distributions of black greasewood and fourwing saltbush overlying the alluvial aquifer (Section C.1.1), scientists tested the hypothesis that these native shrubs were indeed rooted into the contamination plume and were extracting water, nitrogen, and sulfur from the plume, contributing to natural attenuation of contaminants. If this hypothesis was true, then the extraction rates might be increased by enhancing the health and growth rates of these plant populations.

For phytoremediation studies in the source area (Appendix B, Section B.3.3), stable isotope data for source area soils provided direct evidence that roots penetrated to at least 5 m. Similarly, LM scientists used stable isotopes of oxygen (^{18}O) and hydrogen (^{2}H, also known as deuterium [D]) to test the hypothesis that black greasewood and fourwing saltbush overlying the alluvial aquifer are rooted even deeper, accessing groundwater.

^{18}O and D are naturally present as minor constituents of water, along with the more common ^{16}O and ^{1}H isotopes. These isotopes fractionate within the hydrological cycle (Clark and Fritz 1997; Cook and Herczeg 2000; Kendall and McDonnell 1998). Seawater normally contains the highest concentration of the heavy isotopes and is used as a standard to calculate the degree of heavy isotope enrichment in other water samples. Enrichment is expressed as δ^{18}O or δD, in units of per thousand (‰), similar to the use of atmospheric nitrogen as a standard for ^{15}N enrichment as discussed earlier (Appendix B, Section B.3.3). When seawater evaporates to form clouds, the isotopes fractionate due to gravity; the atmospheric water molecules have lower concentrations of the heavy isotopes (negative δ values) than the source seawater. The opposite occurs when rainwater forms; gravitational fractionation produces rain that is more enriched in heavy isotopes (less negative δ values) than the source water in the clouds. Furthermore, the residual moisture in clouds becomes ever more depleted in heavy isotopes (more negative δ values) following sequential rainfall events. As a result, each rainfall event has a characteristic "signature" of heavy isotopes.

In the southwestern U.S., summer rains tend to have less negative δ values than winter rains, because summer rains originate from the nearby Gulf of Mexico and Gulf of California, whereas winter rains originate in the northern Pacific Ocean and have been depleted of much of their heavy isotopes through rainfall events as they pass over the continent on their way to the southwestern deserts. Plots of δD versus $\delta^{18}O$ fall along a meteoric water line characteristic of water samples originating from rainfall events (Lin et al. 1996). On the other hand, terrestrial water samples that have undergone evaporation form an "evaporative series," plotting along a line having shallower slope than the meteoric water line. The point at which the evaporative series intersects the meteoric water line indicates the isotope enrichment values of the original rainfall event giving rise to the evaporative series. Finally, water taken up by plants has the same isotope signature as the source water accessed by the roots; hence, water extracted from stem samples can be matched to environmental water samples to determine where the plant got its water.

These relationships, as illustrated for Monument Valley in Figure C-2, are based on summer rain, aquifer, and soil and plant stem moisture samples taken in 2000-2003 (McKeon et al. 2005). Summer rain at Monument Valley fell along the meteoric water line determined by a more extensive sample set from at nearby Page, Arizona (Lin et al. 1996). Well samples also fell along the meteoric water line, closer to the winter rains than summer rains. Well samples clustered close together, indicating that water in the aquifer at the depth of the wells was mixed and probably recharged by rapidly infiltrating winter rain events from the surrounding uplands. On the other hand, plant stem water fell along an evaporative series apparently originating from winter rains falling directly over the plume area. This was assumed to be deep soil moisture as it did not match isotope signatures of summer rain water or soil water down to 5 m soil depth.

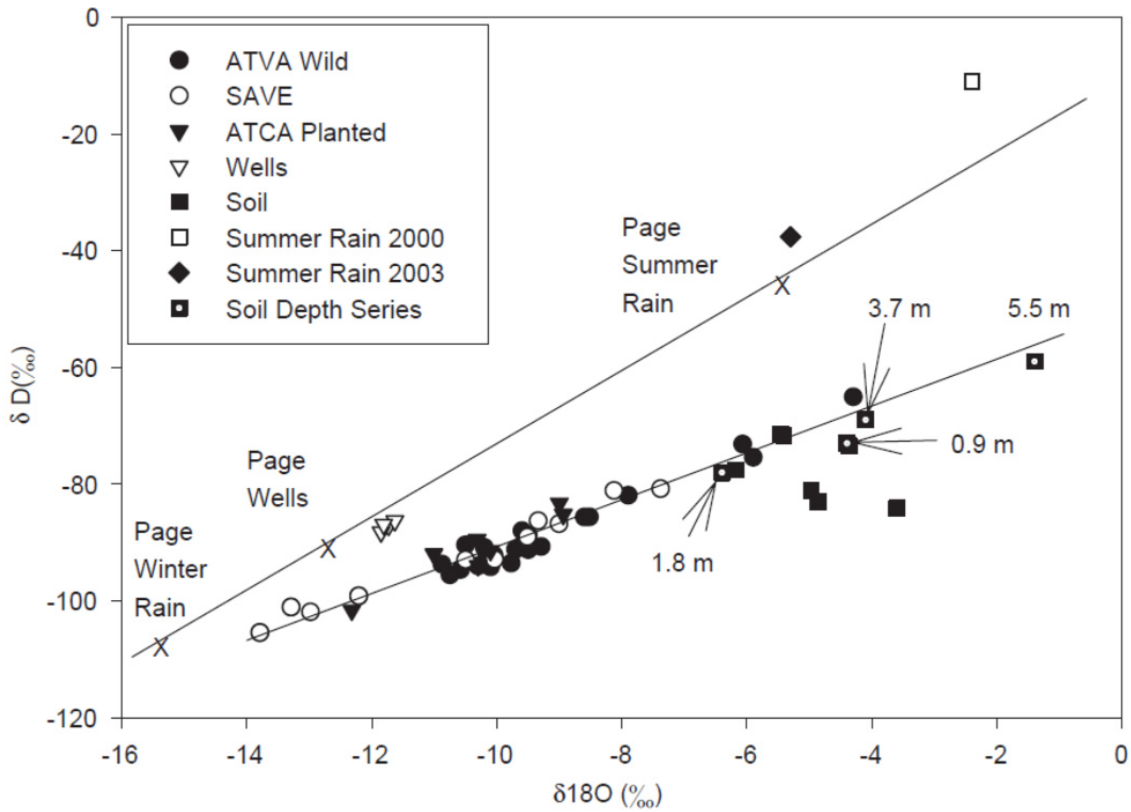

Figure C-2. $\delta^{18}O$ and δD values for soil, water, and plant tissues collected in 2000 and 2003 at the Monument Valley UMTRA site. Reference data for wells and rainwater for Page, Arizona (Lin et al. 1996), are shown plotted along the Page local meteoric water line. Plant stem water and soil pore water are shown plotted along an apparent local evaporation line.

In 2005, scientists augered two deeper holes down to the top of the water table near wells 606 and 677 (Jordan et al. 2008). These holes were located in mixed stands of black greasewood and fourwing saltbush plants overlying the plume. Soil water, groundwater, and plant water samples were analyzed for isotopes. Black greasewood and fourwing saltbush plants growing near the auger hole were sampled, including plants that had been transplanted and protected from livestock in fenced exclosures (Section C.1.3) as well as wild black greasewood and fourwing saltbush plants.

At well 606, which is closer to the source area, the water table was 9 m deep. At this depth soil nitrate levels varied from near background levels at the surface to >100 ppm at the water table. Soil moisture levels were low in the vadose zone down to the 5 m depth, then increased with depth to about 10 percent gravimetric moisture content until the top of the aquifer was encountered. The water above the alluvial aquifer was very low in nitrate, and so it was assumed to be rainwater stored in the vadose zone above the capillary fringe of the aquifer, which would have been high in nitrate. The auger hole near well 677, further downgradient from the source area, was relatively dry down to the top of the aquifer at 10 m. Nitrate levels increased abruptly from near-background to >100 ppm at the top of the aquifer (Figure C-3).

Water isotope values for these samples are shown in Figure C-4. Soil moisture samples from the surface to the 3 m soil depth had higher (less negative) values for oxygen and hydrogen isotopes, compared to values from 4 m down to the top of the aquifer. Plants in and out of exclosures near the wells had enrichment values within the range measured at the top of the aquifer at well 677 and in the aquifer and in moist soil above the aquifer at well 606.

The combination of soil moisture profiles, nitrate profiles, and water isotope results suggest that wild fourwing saltbush and black greasewood had rooted down to and were intercepting water both from soil water in the vadose zone just above the capillary fringe of the aquifer and from the top of the plume, with black greasewood being more dependent on aquifer water than fourwing saltbush.

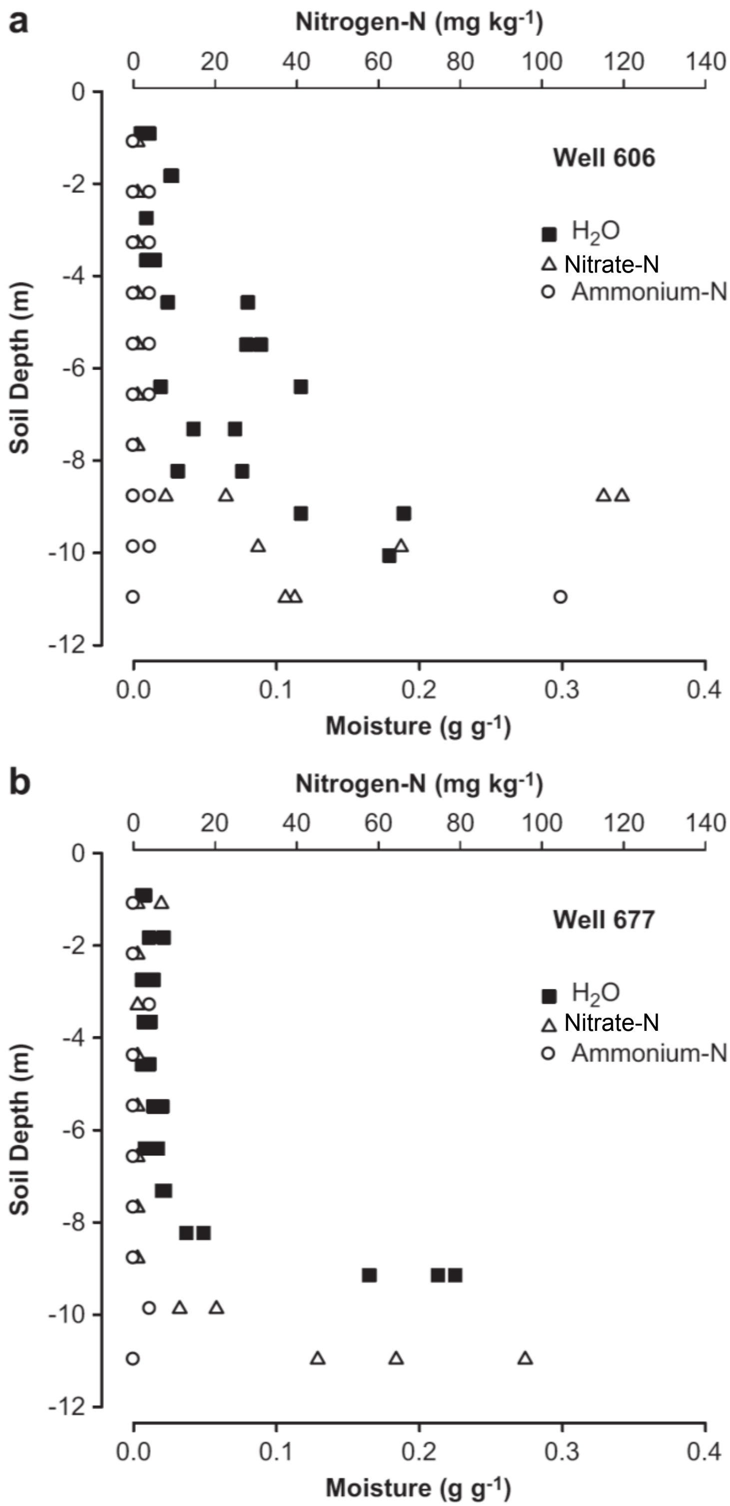

Figure C-3. Relationship between moisture content, nitrate concentrations, and ammonium concentrations as a function of soil depth at sites near well 606 (a) and well 677 (b) over the Monument Valley contamination plume (see Jordan et al. 2008).

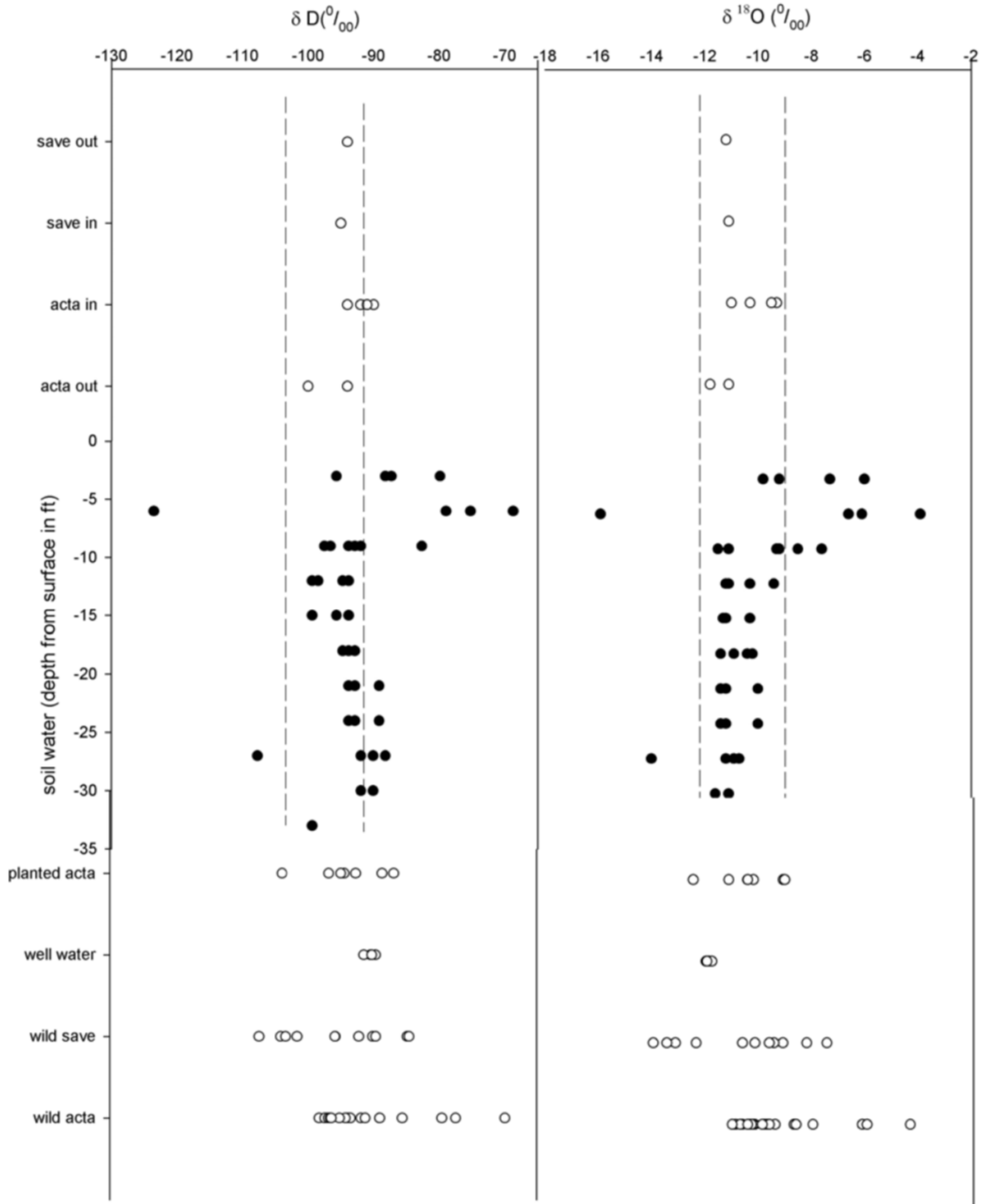

Figure C-4. $\delta^{18}O$ and δD isotope enrichment values in water extracted from soil samples collected at different depths over the alluvial plume near well 606 and well 677. The graph also shows the isotope values in water extracted from stem sample of black greasewood (SAVE) and fourwing saltbush (ATCA) plants growing over the plume near the wells (top of graph), of saltbush plants that were grown from seedling in exclosures, and of wild plants growing at different locations over the plume (bottom of graph).

C.1.3 Enhanced Plume Phytoremediation: Grazing Management and Revegetation

Grazing management and revegetation were evaluated as methods for enhancing phreatophyte growth and phytoremediation. Early grazing management studies at the Monument Valley site indicated that grazing protection may have positive effects on biomass productivity, ground cover, and rates of phreatophyte transpiration and nitrogen uptake (McKeon et al. 2006; Glenn et al. 2008). Similarly, early revegetation studies indicated that native phreatophytes could be planted and, with irrigation, become rooted in the alluvial aquifer within three years. Given these early positive results, LM scientists designed follow-up pilot studies to evaluate grazing management and revegetation as means for enhancing plume phytoremediation on a landscape scale.

Populations of native phreatophytes (black greasewood and fourwing saltbush) growing over the plume have historically been degraded by heavy grazing. In addition, populations of these shrubs growing north of the former New Tailings Pile were deliberately cleared during the initial tailings remediation work, prior to the excavation of soils contaminated by windblown tailings, leaving a large denuded area overlying proximal portions of the plume and with the highest nitrate levels.

C.1.3.1 Early Studies

The early phytoremediation enhancement studies found that protecting native black greasewood and fourwing saltbush plants from grazing could double biomass productivity, transpiration rates (rates of water extraction from the aquifer), and nitrogen-uptake rates (DOE 2004b, McKeon et al. 2006). The early phytoremediation studies also found that greenhouse-grown transplants could be successfully established and grow vigorously for several years in small fenced plots and, with managed irrigation, send roots down 30 feet into the nitrate and sulfate plume.

The early studies were conducted using grazing exclosures constructed around 24 plant pairs (12 fourwing saltbush and 12 black greasewood) of similar initial size (1−3 m^3 canopy volume per plant). One plant of each pair was enclosed within a 2 by 2 by 1.5 m chainlink fence for protection from grazing while the other plant was left unprotected. Canopy volume, ground cover area, biomass, and density were measured for each shrub when exclosures were constructed in June 1998, and then annually in September or October for 3 consecutive years.

Plants were subsampled for tissue analysis. Tissue samples were collected of all new, annual growth of leaves, small stems, and often seeds. The dry weights of the samples were measured, and representative portions of the samples were analyzed for total nitrogen content using the Kjeldahl method (Tabatai 1996). An ammonia ion selective electrode was used to determine ammonia nitrogen values, and a nitrate ion electrode was used to determine nitrate nitrogen values (American Public Health Association 1998).

Initially the canopy volumes of shrubs inside and outside grazing exclosures were similar. During the three growing seasons, canopy volumes of shrubs inside exclosures increased by 2−4 times the starting values, whereas the size of grazed plants outside the exclosures remained unchanged (Figure C-5). Differences in biomass per m^2 of canopy cover were not significant between grazed and ungrazed plants of either species; however, the net annual productivity of ungrazed plants was approximately 1.5 times that of the grazed plants. Grazed plants had significantly ($P < 0.05$) lower total N content than ungrazed plants, and black greasewood plants had higher total N content than fourwing saltbush (Table C-1). Ungrazed plants had higher levels of nitrate-N than grazed plants ($P < 0.05$). Plants that were excluded from grazing also contained significantly higher ($P < 0.05$) concentrations of total sulfur than grazed plants (Table C-2).

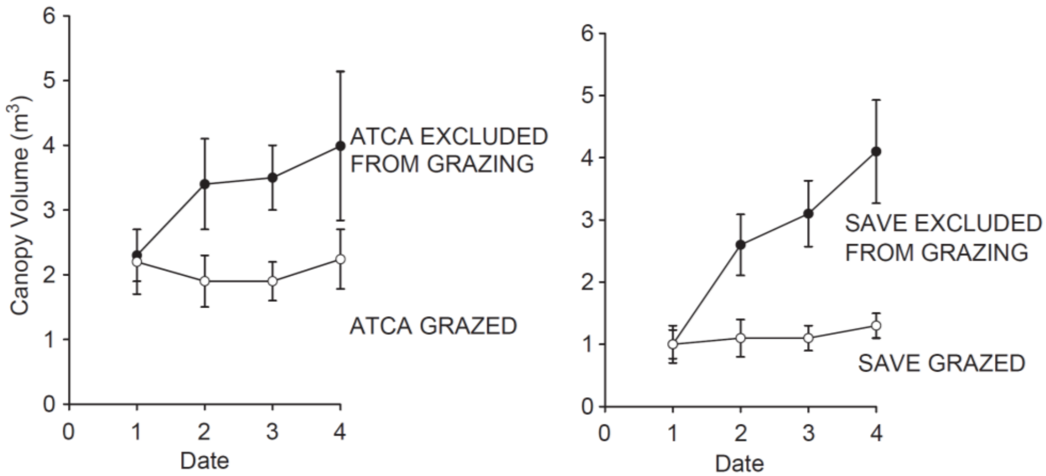

Figure C-5. Canopy volumes for fourwing saltbush (ATCA) and black greasewood (SAVE) plants either grazed or protected from grazing during 3 growing seasons at the Monument Valley site. Each data point is the mean of 12 plants; error bars show standard errors of the mean. Date 1 is June 1998, Date 2 is October 1998, Date 3 is March 1999, and Date 4 is September 2000.

Table C-1. Total nitrogen and nitrate on a dry-weight basis of A. canescens *and* S. vermiculatus *leaves under ungrazed and grazed conditions for plants harvested in 2000. Two-way analysis of variance (ANOVA) with plant type and grazing condition as a dependent variable showed that black greasewood had significantly (P < 0.05) higher nitrogen content than fourwing saltbush; Black greasewood plants under ungrazed conditions had significantly higher nitrogen than under grazed conditions. Nitrate results were not different by plant type (P > 0.05) but ungrazed plants had significantly greater nitrate-N than grazed plants. Table shows means and (standard errors).*

	A. canescens		***S. vermiculatus***	
	Ungrazed	**Grazed**	**Ungrazed**	**Grazed**
Nitrogen (%)	2.14 (0.12)	2.05 (0.15)	2.76 (0.17)	2.26 (0.08)
Nitrate (mg N kg $^{-1}$)	727 (95)	590 (69)	951 (139)	558 (60)

Table C-2. Sulfate-S and Total Sulfur (dry-weight basis) of A. canescens *and* S. vermiculatus *leaves for plants under ungrazed and grazed conditions in 2000. Table shows means and (standard deviations).*

Plant	**Sulfate-S Ungrazed (ppm)**	**Sulfate-S Grazed (ppm)**	**Total S Ungrazed (%)**	**Total S Grazed (%)**
A. canescens	513 (323)	374(257)	0.461 (0.244)	0.271 (0.156)
S. vermiculatus	430 (308)	375 (353)	0.332 (0.09)	0.253 (0.052)

The results show that productivity and canopy volume of both shrub species increased markedly when grazing was eliminated. This rapid growth in response to protection from grazing is further evidence that the plants are rooted into the alluvial aquifer (Section C.1.2), as a rapid growth response would not be expected if plants were rooted into the predominantly dry soil over the plume. Nitrogen content of the plant tissues also increased slightly and nitrate-N increased markedly in response to grazing protection. These results corroborate other studies of grazing effects in the Navajo Nation (Brotherson et al. 1983, Lash et al. 1999).

Small livestock exclosures were also used to determine if black greasewood and fourwing saltbush seedlings would establish and survive if transplanted in denuded areas over the plume. Seeds of both species, collected near Tuba City, Arizona, were germinated in a greenhouse. The subspecies of fourwing saltbush, (*Atriplex canescens* ssp. *angustifolia*) exhibits better survival and growth when used in revegetation projects (Glenn et al. 2001). In June 1998, ten plants of each species were transplanted into six exclosures located over the plume near well 606 (three exclosures) and well 765 (3 exclosures). Plants were irrigated once each week with 8 liters of clean groundwater from June to October 1998.

By May 1999 fourwing saltbush transplants had a 90 percent survival rate and reached an average height of over 0.5 m, whereas black greasewood had only a 45 percent survival rate and reached a mean height of only about 0.15 m. By October 2001, fourwing saltbush dominated and completely filled each exclosure plot, reaching heights exceeding 2 m (Figure C-6). By contrast, black greasewood transplants remained small and most did not survive to the third growing season. On the basis of the results of this early study, fourwing saltbush *(A. canescens* ssp. *Angustifolia)* appeared to be a good candidate for revegetation of denuded areas and enhancing phytoremediation of the plume.

Figure C-6. Exclosure plots near well 606 planted with fourwing saltbush and black greasewood in June 1998 and irrigated from June to October 1998. This photo was taken in July 2002 during an extended drought, providing anecdotal evidence that transplants had rooted in groundwater.

C.1.3.2 Landscape-Scale Studies

Based on these positive results of the early studies, indicating that phytoremediation can be enhanced by controlling grazing, LM scientists installed large plots protected from grazing to determine if similar results were possible on a landscape scale.

Two 50 m by 50 m plots within existing populations of fourwing saltbush and black greasewood overlying the plume were fenced to protect populations from grazing. Plots were established in locations where the potential benefits of grazing protection were greatest: (1) areas with relatively mature stands of these shrubs, (2) areas where roots were known to be tapping the aquifer, and (3) areas where nitrate concentrations in the alluvial aquifer are relatively high. One fourwing saltbush exclosure was established north of the source area where the populations had been severely overgrazed. A black greasewood exclosure was established in a relatively dense population stand nearer the source area (Figure C-7).

Two other exclosures (East and West Revegetation Exclosures) were established in an area that had been cleared of vegetation in the past (Figure C-7) and, when exclosures were constructed in 2005, only annual weeds grew there. As with the early studies, fourwing saltbush and black greasewood seedlings grown in the greenhouse were planted. Seedlings were transplanted on 2 m × 2 m spacing and then irrigated using a drip system at a rate of approximately 50 cm/year. These plots have been surveyed for plant growth by ground transects and remote sensing methods (Appendix F) through 2010. Figure 1 in the report shows the locations of the 50 m by 50 m grazing exclosure plots and revegetation plots as they appeared in 2010.

The large exclosures have been effective in enhancing phreatophyte growth over the plume, although not as dramatically as in the small exclosures in the earlier study. The difference can be attributed to reduced grazing pressure over the entire area. Whereas in the early study, major differences in plant growth inside versus outside could be attributed to heavy grazing, differences were less significant because of relatively moderate grazing during the more recent study; populations outside the enclosures also grew healthier.

Based on 2010 remote sensing results (Appendix F), the fourwing saltbush grazing exclosure plot had 35.3 percent canopy cover compared to a cover of 29 percent in unprotected fourwing saltbush stands. Percent canopy cover in the black greasewood exclosure was 66.9 percent, compared to 40.9 percent outside the exclosure. The East and West Revegetation Exclosure plots had 76.3 percent and 48.0 percent canopy cover by 2010, respectively, based on remote sensing data, compared to near-zero shrub growth before seedlings were transplanted. The differences between these plots may be attributable, at least in part, to depth to groundwater, which was approximately 30 ft at the East Plot and 40 ft at the West Plot.

About half the canopy cover in these protected plant communities consisted of phreatophytes while the other half consisted of non-phreatophytic shrubs, forbs, and grasses (Table C-3).

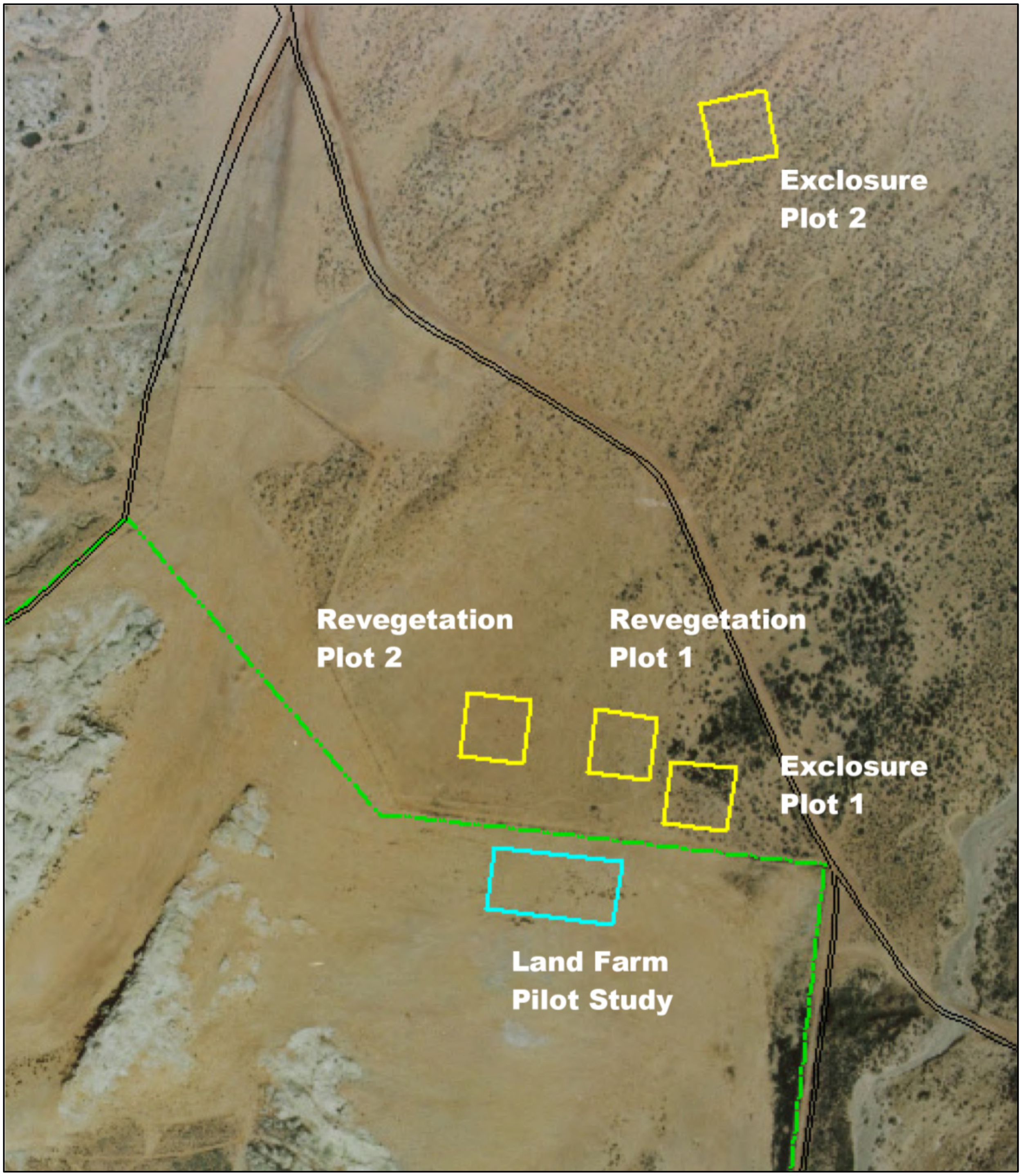

Figure C-7. Aerial photograph of plume area taken prior to installation of the pilot studies showing GPS boundaries of grazing Exclosure Plot 1 (black greasewood) and Exclosure Plot 2 (fourwing saltbush), Revegetation Plots 1 (East) and 2 (West) (all in yellow), the land-farm pilot study plot (blue; Appendix E), and the mill site remediation fence line (green).

Table C-3. Percent plant canopy cover inside and outside grazing exclosure plots.

Cover Type	Black Greasewood Inside	Black Greasewood Outside	Fourwing Saltbush Inside	Fourwing Saltbush Outside
Atriplex canescens	15.8	6.5	15.7	15.1
Sarcobatus vermiculatus	16.0	5.4	-	-
Atriplex confertifolia	0.2	0.4	-	-
Total phreatophyte shrubs	*32.0*	*12.3*	*15.7*	*15.1*
Gutierrezia sarothrae	-	0.2	-	-
Poliomintha incana	-	-	0.5	0.9
Vanclevea stylosa	-	-	2.2	1.7
Total non-phreatophyte shrubs	*0.0*	*0.2*	*2.7*	*2.6*
Ambrosia acanthicarpa	-	1.4	1.8	2.6
Bassia scoparia	-	0.2	-	-
Chamaesyce revoluta	-	-	1.5	0.3
Chenopodium sp.	-	-	1.8	0.5
Descurainia sophia	-	-	0.7	0.1
Grindelia squarrosa	-	-	0.6	-
Mentzelia multiflora	-	0.1	0.2	0.1
Salsola tragus	32.3	24.5	17.4	22.8
Sphaeralcea coccinea	-	-	0.2	-
Suaeda moquinii	1.4	1.0	-	-
Total forbs	*33.7*	*26.2*	*24.2*	*26.4*
Sporobolus contractus	-	-	0.1	-
Sporobolus cryptandrus	-	-	1.3	0.2
Achnatherum hymenoides	-	-	0.5	-
Total grasses	*0.0*	*0.0*	*1.9*	*0.2*
Plant litter	5.4	4.7	8.2	5.4
Bare ground	28.8	55.8	48.1	50.3
Total vegetative cover	*65.7*	*38.7*	*42.6*	*44.1*

C.1.4 Plant Uptake of Nitrogen and Sulfur

LM scientists analyzed nitrogen and sulfur contents of leaf tissue samples of fourwing saltbush and black greasewood rooted in the plume to estimate annual uptake rates (DOE 2007), and then extrapolated the results over large areas of the plume using remote sensing and estimates of fractional cover of these two phreatophytic shrubs (Appendix F).

Leaf material was harvested from 0.25 m^2 quadrats on eight randomly selected saltbush and greasewood plants growing over the plume. Dry weight of leaves plus seeds was multiplied by nitrogen content (3.14%, S.E. = 0.2) or sulfur content (0.66%, S.E. = 0.04), and then by fractional vegetation cover for areas of the plume, to calculate annual nitrogen and sulfur uptake rates for the plume. Both species replace their leaves annually, and so the tissue concentrations based on leaf weights were interpreted as a minimum measure of annual elemental uptake rates—the values exclude branch and root growth (S.E. is standard error of the mean). Dry weight of saltbush leaves was 508 grams per square meter (g/m^2) (S.E. = 55) while greasewood was 276 g/m^2 (S.E. = 32). The mean value of 392 g/m^2 was used, thus assuming an equal proportion of plants over the plume.

The area over the plume was divided into three distinct vegetation zones (Table C-4): a densely populated, 4.9 ha stand of volunteer fourwing saltbush just east of the source area and within the fence (protected from grazing); a 20.6 ha stand of less densely populated black greasewood just north of the source area; and a 162 ha area of relatively sparse fourwing saltbush covering most of the rest of the plume. The evaluation was based on nitrogen and sulfur content of leaf samples. Again, both plant species replace their leaves annually, so the results represent annual uptake rates.

Table C-4. Area, plant cover, and uptake of sulfur and nitrogen based on leaf dry weight for three areas over the Monument Valley contamination plume. ATCA = Atriplex canescens *(fourwing saltbush) and SAVE =* Sarcobatus vermiculatus *(black greasewood).*

Area Description	Area (ha)	Plant Cover (%)	Sulfur Uptake (kg/yr)	Sulfur Uptake (kg/yr/ha)	Nitrogen Uptake (kg/yr)	Nitrogen Uptake (kg/yr/ha)
Volunteer ATCA Inside Fence	4.9	24.1	30.7	6.3	146	29.8
Dense SAVE Outside Fence	20.6	9.75	52.1	2.5	248	12.0
Sparse ATCA Outside Fence	162	5.24	220	1.4	1,045	6.5

Nitrogen uptake for the entire area overlying the plume was 1,439 kg/yr and sulfur uptake was 296 kg/yr. Although substantial, these estimates of uptake rates are relatively modest compared to the total amount of contamination in the plume, roughly 9.6×10^7 kg nitrogen and 2.7×10^{10} kg sulfur, based on data from the SOWP (DOE 1999).

C.1.5 Groundwater Extraction: Phreatophyte Transpiration

An objective of the plume pilot studies was to evaluate methods for limiting the continued spread of the alluvial aquifer plume by enhancing plant transpiration (natural pumping of water back to the atmosphere). The study employed a combination of transpiration measurements on individual plants and remote sensing methods to monitor the effects of grazing on LAI, fractional cover (f_c), and ET. Journal publications of this research are appended.

Two native phreatophytic shrubs are rooted in the alluvial aquifer (Section C.1.2): fourwing saltbush (*Atriplex canescens,* or ATCA) and black greasewood (*Sarcobatus vermiculatus,* or SAVE). Given the literature on the ecohydrology of these two phreatophytes, LM scientists evaluated the concept that ET of groundwater by these two plant species could potentially slow the movement of the contaminant plume, as a type of groundwater hydraulic control (EPA 2000).

Because the site has historically been heavily grazed by livestock, the study focused on a comparison of transpiration rates for (1) areas overlying the plume that are grazed and (2) areas protected from grazing. Results of an evaluation of grazing management and revegetation, considered to be the most practical methods for enhancing plume phytoremediation, are presented in Section C.1.3. Appendix F describes the research that led to the development of remote sensing monitoring protocols that were used for this study. A journal publication (Bresloff et al. 2013) provides thorough documentation of the remote sensing research (see Appendix J).

Transpiration rates of fourwing saltbush and black greasewood rooted in the plume were measured in 2006 and 2007 using sap flow sensors attached to branches on individual plants inside and outside livestock exclosures (Glenn et al. 2009). Sap flow sensors (Figure C-8) introduce a precise amount of heat into the plant through a wire wrapped around the stem. Temperatures are measured by thermocouples placed in the stem upstream and downstream of the heating wire, and outside the insulating layer around the stem section. Temperature differences between the stem temperature at the heating wire and at the three points away from the heating wire are used to solve an energy balance equation to determine diffusive and convective heat losses. Convective heat loss is due to heat carried away from the stem section by water moving in the transpiration stream, thus providing a measure of water flow though the plant.

Estimates of landscape-scale transpiration rates were derived from the stem sap flow measurements using the LAI and f_c values of those plants (Figure C-9), and then extrapolated over larger areas of the plume using satellite remote sensing methods (Appendix F). High-resolution Quickbird images, on which individual shrubs are discernible, were used to develop relationships between ground measurements of LAI and $f_{c,}$ and values of the NDVI on images. These results were then scaled to longer time frames using archival Landsat imagery for which NDVI values were inter-calibrated with Quickbird images.

This approach for estimating ET on a landscape scale indicates that fourwing saltbush and black greasewood shrubs had relatively high LAI and canopy level transpiration rates (Table C-5), and that the f_c of plants was the controlling factor for their water consumption over different areas of the plume. Table C-6 shows that over the whole site, annual precipitation exceeded ET from 2000 to 2004, but was slightly lower than ET from 2005 to 2010 due to revegetation of the source area and reduced grazing over the plume. Table C-6 also shows that the more dense stands of ATCA and SAVE, protected from grazing, used up to twice the annual precipitation, demonstrating the potential of the shrub community to control the site water balance, and provide groundwater hydraulic control under favorable conditions.

The results also show that ET is approximately equal to annual precipitation over the entire site. However, in exclosure plots where fourwing saltbush and black greasewood were protected from grazing, plants developed higher f_c and LAI values, and ET exceeded annual precipitation, with the excess assumed to come from groundwater discharge. Therefore, grazing management could be an effective method to slow migration of the contaminant plume in the shallow alluvial aquifer at this and similar sites in the western U.S.

*Figure C-8. Wiring for a heat-dissipation stem flow sensor on a black greasewood (*Sarcobatus vermiculatus*) plant rooted in the alluvial aquifer at the Monument Valley site (top photo), and photovoltaic panel, batteries, and datalogger to power and record data from the stem flow sensor (bottom photo).*

*Figure C-9. Local residents Ben and Mary Stanley sampling foliage to estimate LAI and fractional cover of a black greasewood (*Sarcobatus vermiculatus*) plant as part of the phreatophyte transpiration study at the Monument Valley site.*

*Table C-5. Summary of LAI and sap flow data for ATCA (*Atriplex canescens*, fourwing saltbush) and SAVE (*Sarcobatus vermiculatus*, black greasewood) plants growing over the Monument Valley contamination plume. Mean values were pooled across species and grazing treatments but separated by year based on analysis of variance (ANOVA) results. 2006 values were significantly lower than 2007 values for each variable (P < 0.05).*

	LAI 2006	**LAI 2007**	**2006 ET Leaf $(mm/m^2)/d$**	**2007 ET Leaf $(mm/m^2)/d$**	**2006 ET Canopy $(mm/m^2)/d$**	**2007 ET Canopy $(mm/m^2)/d$**
ATCA In	2.96	3.78	1.66	2.95	4.91	11.15
ATCA Out	3.19	4.47	2.81	4.38	8.96	19.58
SAVE In	3.71	3.98	3.06	6.72	11.35	26.75
SAVE Out	2.05	4.45	3.07	4.42	6.29	19.67
Mean	2.96	3.85	2.66	4.74	7.97	16.79
SE	0.22	0.27	0.27	0.69	1.16	2.59
N	31	32	13	17	13	17

Notes:
In = inside livestock exclosures
Out = outside livestock exclosures
SE = standard error of the mean
N = sample size
$(mm/m^2)/d$ = millimeters per square meter per day

Table C-6. Potential evapotranspiration (ET_o), precipitation, and ET estimated by Moderate Resolution Imaging Spectrometer (MODIS) satellite imagery for areas at the Monument Valley site. Means and standard errors (SE) are shown for 2000-2004 and 2005-2010. All values are mm yr^{-1}.

Year	ET_o	Precipitation	Inside Fence	Outside SAVE	Outside ATCA	Whole Site
2000	1573	168	189	146	123	144
2001	1499	214	145	149	122	136
2002	1482	143	103	99	99	90
2003	1508	146	183	191	147	169
2004	1461	212	185	159	129	146
Mean (SE)	1504 (19)	176 (17)	161 (17)	148 (15)	124 (8)	137 (13)
2005	1463	267	282	220	196	195
2006	1452	155	206	157	110	143
2007	1465	167	306	235	199	200
2008	1421	193	259	248	160	162
2009	1432	107	193	184	114	150
2010	1419	234	310	356	242	268
Mean (SE)	1442 (8)	187 (26)	259 (20)	233 (28)	170 (21)	186 (19)

C.2 Natural and Enhanced Plume Denitrification

The Monument Valley pilot studies evaluated the feasibility of relying on natural attenuation processes to remediate contamination in soil beneath the former New Tailings Pile (referred to as the source area) and an alluvial aquifer (referred to as the plume) spreading away from the source area. The evaluation focused on the roles of native desert plants (phytoremediation) and microorganisms (bioremediation). Source area phytoremediation and bioremediation were addressed in Appendix B and plume phytoremediation was addressed in Section C.1. This section first reviews modeling and monitoring methods used to evaluate ongoing natural microbial denitrification in the plume (C.2.1), and then reviews the results of a field study designed to enhance natural denitrification. Journal publications of this research are in Appendixes I and J.

C.2.1 Natural Plume Denitrification

Natural attenuation of nitrate is the combined effect of several naturally occurring processes, such as biodegradation, sorption, and dispersion, that decrease the concentrations of chemicals in the aquifer over time (Rivett et al. 2008; Smith et al. 2006; Tartakovsky et al. 2002). Sorption was determined for nitrate in column studies (Jordan et al. 2008), and for nitrate in the plume by mobility relative to chloride (Carroll et al. 2009). Spatial and temporal nitrate concentration data was collected from a transect of monitoring wells located along the plume centerline and was used to model dispersion and sorption processes (Carroll et al. 2009).

Based on the finding that microbial denitrification was taking place in the source area (McKeon et al. 2005), LM scientists conducted laboratory and field assays to see if denitrification occurred in the plume as well. If present, natural denitrification could represent a passive form of site remediation, with nitrate gradually converted to nitrogen and nitrous oxide gasses over time. Furthermore, ammonium and sulfate in the plume could also undergo microbial transformations that could reduce their levels in the aquifer through coupled nitrification-denitrification and formation of hydrogen sulfide gas, respectively.

^{15}N and denitrification assays, as part of laboratory microcosm studies, were used to evaluate the conversion of nitrate to nitrogen and nitrous oxide gasses (Jordan et al. 2008). From these data, LM scientists developed a model (the MT3DMS Model) of first-order rate coefficients for natural attenuation and denitrification. The model was then compared to measurements of nitrate, ammonium, and oxygen in observation wells from 1985 to 2007, producing calibrated estimates of rates of natural attenuation and of enhanced attenuation (Carroll et al. 2009).

Laboratory assays showed that denitrification occurred in samples collected from the plume, with a projected half-life of nitrate of 1-4 years under laboratory conditions (Table C-7). Furthermore, adding a carbon substrate (ethanol or methanol) increased the rate of denitrification by two orders of magnitude (Figure C-10). These results were checked by determining the ^{15}N enrichment factor in the residual nitrate in the reaction vessels. As expected, ^{15}N accumulated in the residual nitrogen fraction, because ^{14}N is the preferred form of nitrogen for microbial denitrification.

Table C-7. Natural, ethanol-, and methanol-enhanced denitrification first-order rate coefficients obtained from laboratory microcosm concentration data.

First-order Rate Description	k (hr^{-1})	k (yr^{-1})	Half-life (yr)
2006-natural	2.00×10^{-5}	0.2	3.96
2007-natural	8.33×10^{-5}	0.7	0.95
2006-with ethanol	3.30×10^{-3}	28.9	0.02
2007-with ethanol	2.00×10^{-3}	17.5	0.04
2007-with methanol	1.95×10^{-3}	17.1	0.04

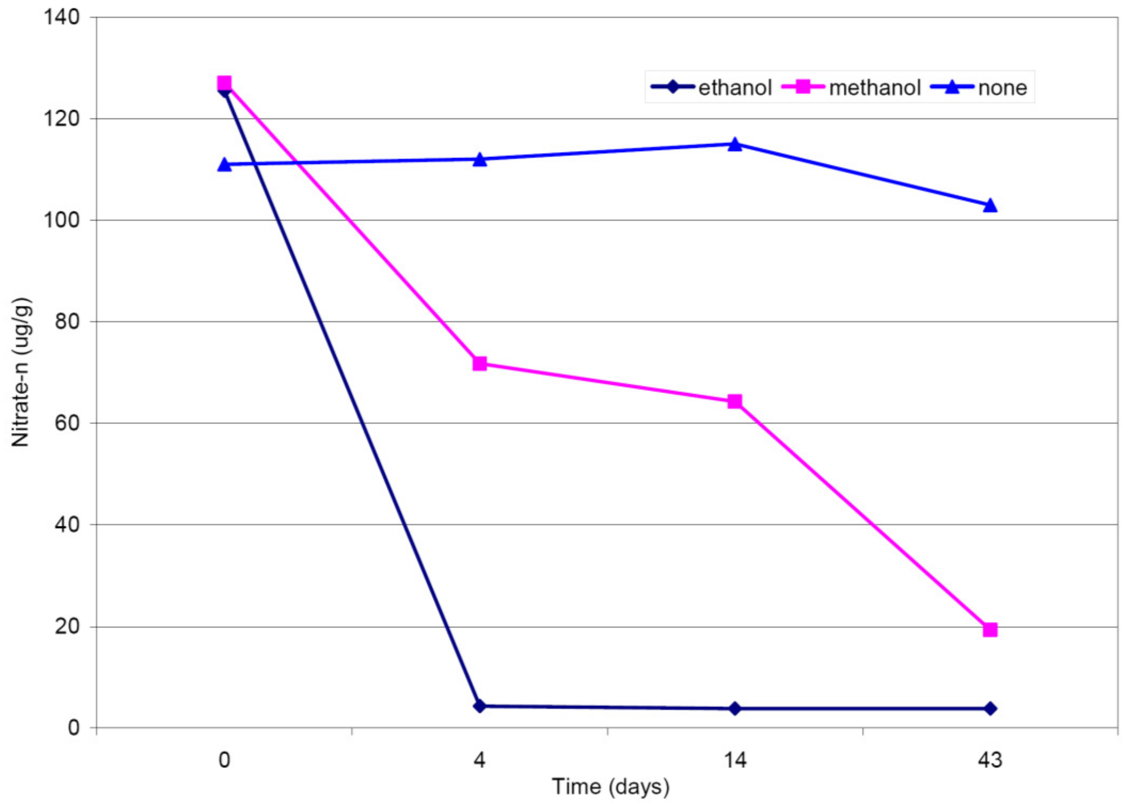

Figure C-10. Microcosm nitrate depletion in soil slurries with or without methanol or ethanol amendment (DOE 2008, Jordan et al. 2008).

These laboratory rates cannot be extrapolated directly to field conditions. Therefore, scientists estimated field rates by measuring nitrate concentrations and ^{15}N enrichment values in samples taken from plume wells at increasing distances from the source area, up to 2,000 m away at the leading edge of the plume (Figure C-11). Nitrate decreased in concentration with increasing distances from the source (Figure C-11a), presumably due to dilution of the original nitrate due to recharge of the plume as well as by denitrification. ^{15}N enrichment also increased with distance (Figure C-11b), and a plot of ^{15}N enrichment versus nitrate concentration showed an inverse relationship between ^{15}N enrichment and nitrate loss (Figure C-11c), as expected for microbial denitrification.

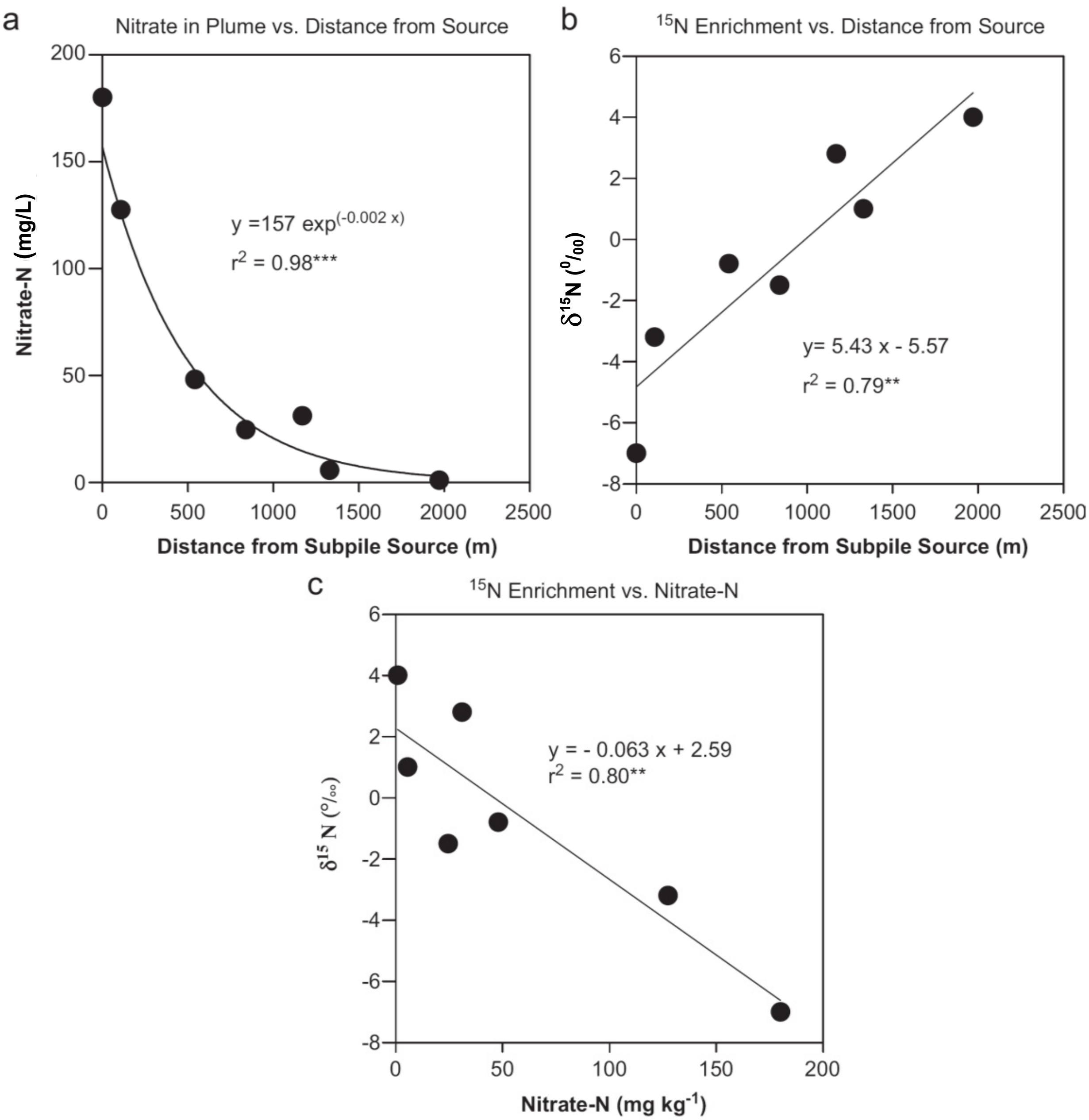

*Figure C-11. Nitrate (a) and ^{15}N isotope enrichment (b) in the Monument Valley contamination plume as a function of distance from the source area, and ^{15}N-nitrate enrichment as a function of nitrate concentration in the same samples (c). Significance levels are denoted as ** (P < 0.01) and *** (P < 0.001).*

The discrimination of ^{14}N over ^{15}N is calculated as an enrichment factor (ε) as:

$$\varepsilon = (\delta_s(t) - \delta_{s0})/\ln C_t/C_0$$

where:
$\delta_s(t)$ is the enrichment value of the sample at time (t)
δ_{s0} is the enrichment factor of the original source of nitrate
C_t and C_0 are the final and starting concentrations of nitrate, respectively

Values of ε are usually negative, with more negative numbers indicating greater discrimination of ^{14}N over ^{15}N. For this analysis, we assumed that samples taken just outside the source area represented $\delta_s(t)$ and C_0, while samples at the leading edge of the plume represented δ_{s0} and C_t. Our calculated value of ε was −1.7, typical of mixed systems where nitrate is attenuated by physical processes such as dispersion and sorption as well as by microbial nitrification. On the other hand, pure denitrification determined in laboratory assays produces values of ε ranging from -10 to -23 (Blackmer and Bremner 1977) (our laboratory value was -9.63). If we apply the range of values for pure denitrification to our mixed system, we can estimate that from 1968 when the mill closed to 2008, approximately 40-60 percent of the original nitrate in the plume was lost to denitrification, for a half-life of approximately 40 years.

Miao et al. (2013) evaluated the natural attenuation of ammonium in groundwater. They collected samples from 14 wells in the plume and analyzed major cations and anions, trace elements, and isotopic composition of ammonium and nitrate. Their results showing oxic redox conditions and correspondence of isotopic compositions of ammonium and nitrate confirmed the natural attenuation of ammonium via nitrification. Moreover, they observed that ammonium concentration within the plume area was closely related to concentrations of uranium and a series of other trace elements, including chromium, selenium, vanadium, iron, and manganese. They hypothesized that ammonium-nitrate transformation processes influence the disposition of the trace elements through mediation of redox potential, pH, and possibly aqueous complexation and solid-phase sorption. Despite the generally relatively low concentrations of trace elements present in groundwater, their transport and fate may be influenced by remediation of ammonium or nitrate at the site.

C.2.2 Enhanced Plume Denitrification and Sulfate Reduction

At the rate now occurring in the aquifer, many decades may be required for nitrate levels to decay to compliance levels by natural denitrification alone. On the other hand, the laboratory assays suggested that denitrification could be greatly enhanced by injecting a carbon substrate into the plume. This appeared to be feasible due to the limited volume of the aquifer with high concentrations of nitrate, and the high hydraulic conductivity of the aquifer sediments. Two field trials were conducted to test this option, a push-pull experiment and a natural gradient experiment. The experiments were initiated in 2009 and monitored through 2011 (Borden et al. 2011).

The push-pull experiment injected 5 percent ethanol dissolved in plume water into well 765 (Figure C-12) screened at 17-27 m soil depth, located in an area of high nitrate concentration in the plume. Additional groundwater was then added to push the ethanol solution into the aquifer surrounding the well casing. Water was then pumped from the well casing to retrieve the injection solution, and it was tested for nitrate, ethanol, and nitrous oxide to determine the rate of denitrification. Over 48 hours, nitrate levels decreased to background levels (Figure C-13) and nitrous oxide levels increased (Figure C-14), indicating that denitrification occurred. In addition, changes in aqueous concentrations of sulfate, iron, and manganese indicated that the ethanol amendment caused a change in prevailing redox conditions. The results of compound-specific stable isotope analysis for nitrate-nitrogen indicated that the nitrate concentration reductions were biologically mediated. Denitrification rate coefficients estimated for the pilot tests were approximately 50 times larger than resident-condition (non-enhanced) values obtained from prior characterization studies conducted at the site (Carroll et al. 2009). The nitrate concentrations in the injection zone have remained at levels three orders of magnitude below the initial values for many months (Figure C-13), indicating that the ethanol amendments had a long-term impact on the local subsurface environment.

The single-well natural gradient experiment injected ethanol in one well, and detected its rate of movement and effect on nitrate levels in a series of downgradient observation wells. The purpose was to see if the rate of movement of ethanol in the aquifer was sufficient to make enhanced denitrification practical at this site. As in the first experiment, denitrification was rapid at the injection site, well 729 (Figure C-13). The redox potential in the soil changed, and it was confirmed that sulfate was converted to hydrogen sulfide. Sulfate concentrations began to decrease a few weeks after the injection, coincident with the depletion of nitrate, and by month 9, were below 10 mg/L. After a time lag, denitrification was detected at the downgradient observation wells, with the direction of movement determined to be northwesterly and the rate of movement calculated as 0.1 m day^{-1}. As in the first experiment, once nitrate levels decreased, they did not rebound over the measurement period of several months. This indicates that residual denitrification activity after ethanol injection can keep pace with nitrate renewal rates. This could occur if microbial biomass developed from the injection of ethanol was recycled as a substrate for later generations of denitrifying bacteria. The results are positive in showing that ethanol injection has a long-lasting effect on aquifer nitrate levels.

These results support the premise that it would be feasible to enhance denitrification by injecting ethanol into hot-spot areas of the plume. The plume currently has two hot spots of high-nitrate concentrations, each apparently with a footprint area of about 2 ha (Appendix D, Section D.2). Using the rate of movement of 0.1 m day^{-1}, a single injection well could treat an area of roughly 0.4 ha yr^{-1}. Therefore, it may be possible to treat the hot-spot areas with five injection wells each.

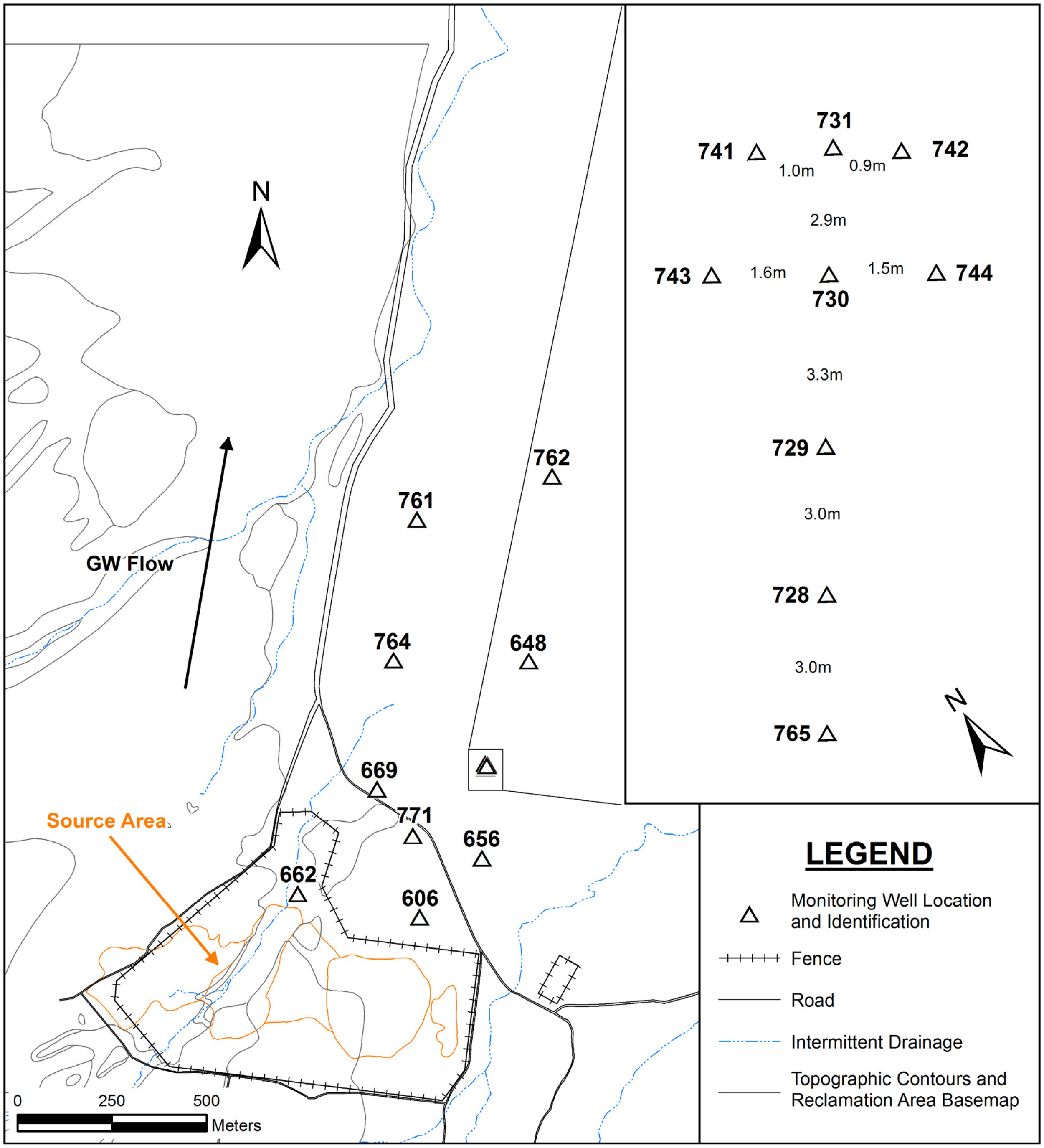

Figure C-12. Illustration of the Monument Valley site showing the source area and selected monitoring wells. The inset shows the arrangement of injection and monitoring wells used for the push-pull and single well gradient test. Ethanol was first injected into well 765 in the push-pull experiment. Ethanol was then injected into well 729 and monitored in the downgradient wells in the natural gradient experiment.

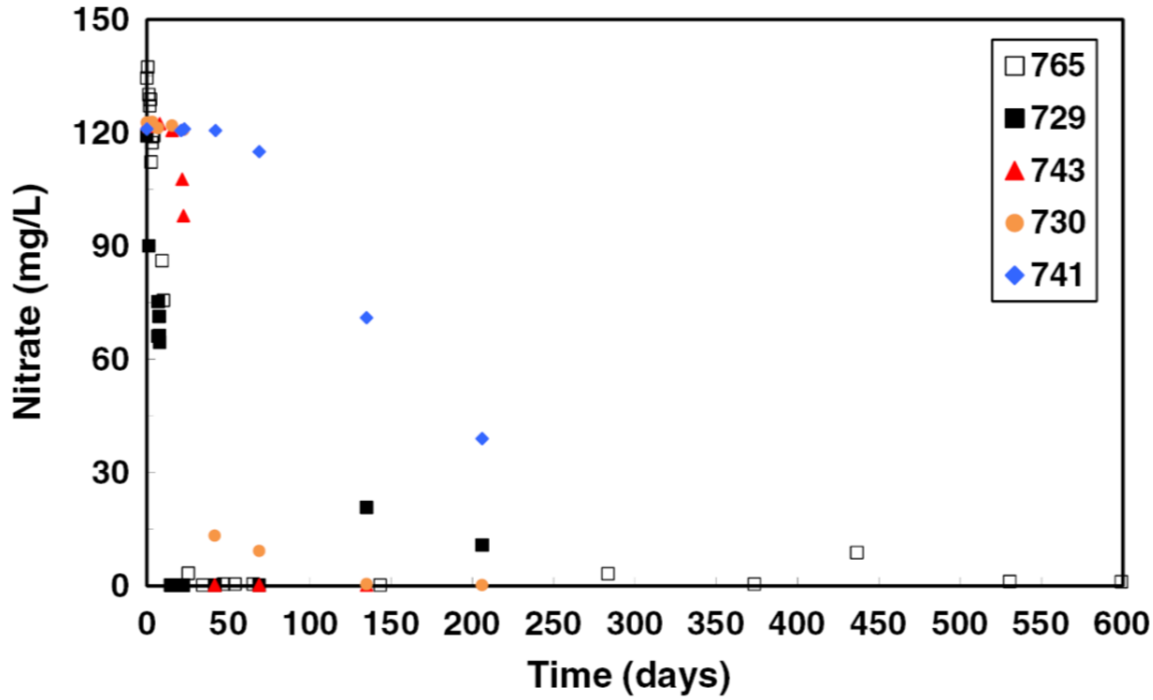

Figure C-13. Long-term nitrate concentrations measured for the push-pull test (injection well 765) and for the single-well injection test (injection well 729 and monitoring wells 743, 730, and 741). Time 0 corresponds to the start of ethanol injection.

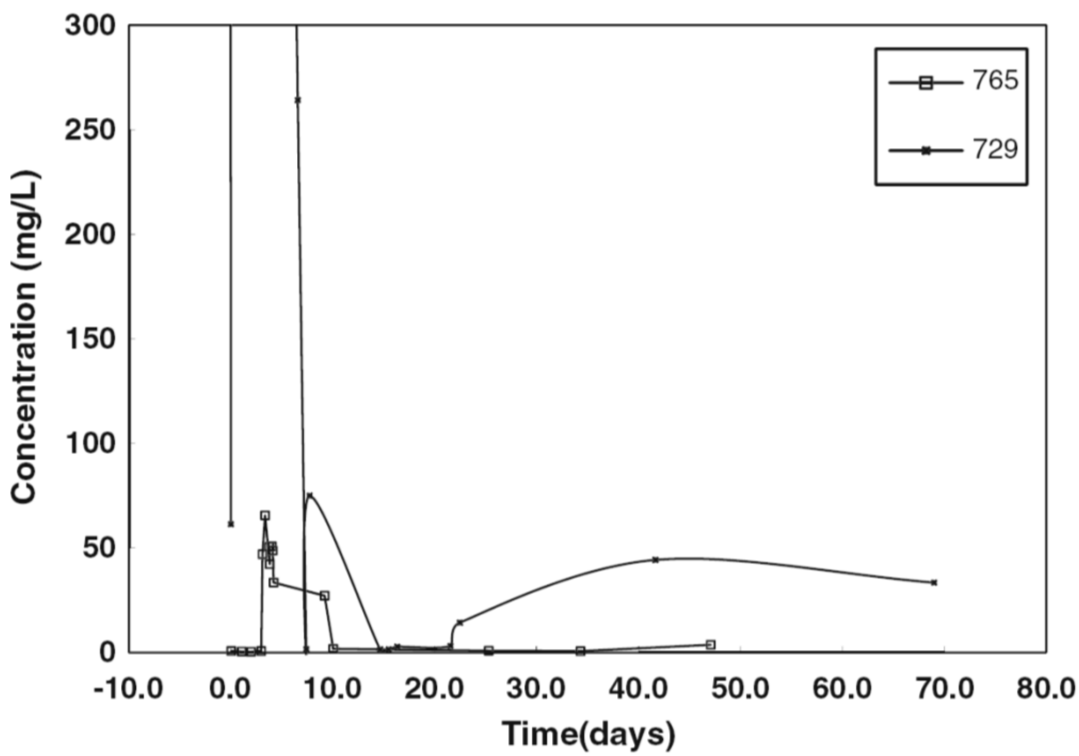

Figure C-14. Nitrous oxide concentrations measured for the push-pull test (injection well 765) and for the single-well injection test (injection well 729). Time 0 corresponds to the start of ethanol injection.

Appendix D

Review of Groundwater Modeling and Monitoring

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Contents

Figures

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This Appendix reviews mathematical modeling performed historically for the Monument Valley site and routine groundwater monitoring data for the alluvial aquifer. The modeling (1) produced quantitative estimates of alluvial aquifer properties and (2) evaluated several groundwater remedies that rely on aquifer pumping. Water chemistry data collected as part of routine monitoring are displayed in the form of contour maps of nitrate, ammonia, and sulfate concentrations. These maps, and graphs of contaminant concentrations at selected wells, are used to illustrate how the nitrate, ammonia, and sulfate plumes have changed during a 14-year period between the late 1990s and 2010. Possible causes of observed plume changes are also discussed. LM and Navajo Nation could use the historical groundwater monitoring data as a baseline for evaluating how well enhanced attenuation remedies, as reported herein, are working if implemented.

Historical computer modeling of groundwater flow at the Monument Valley site was performed to identify natural flow directions in the alluvial aquifer and to estimate the speed with which nitrate, ammonia and sulfate migrated from contaminant source areas in past years. Once flow directions and groundwater speeds were identified, additional computer modeling was conducted to simulate groundwater pumping remedies that might be implemented to clean up contaminants remaining in the aquifer. DOE had proposed pump-and-treat remedies before investigating enhanced natural attenuation remedies as alternatives (DOE 2000a).

Characterization of the site's hydrogeology and contamination in the alluvial aquifer was completed in 1997. Monitoring of groundwater levels and contaminant concentrations began shortly thereafter. The results of multiple years of groundwater sampling illustrate how ammonia, nitrate, and sulfate plumes have evolved in the alluvial aquifer since the late 1990s. Contour maps representative of contaminant plumes at different times over a 14-year period, and temporal plots of contaminant concentrations at several wells downgradient of the New Tailings Pile footprint, are used to demonstrate how source-area remediation and various phytoremediation tests have impacted contamination in the aquifer.

D.1 Modeling

Mathematical modeling of groundwater flow at contaminated sites is often performed for the purpose of better understanding how historical groundwater movement contributed to existing contaminant plumes. The modeling is very useful for estimating the values of aquifer properties that control the speed of migrating groundwater and for developing ways to clean up groundwater contamination. Once a reliable flow model has been developed, it is common for groundwater scientists to run the model many times in the interest of evaluating various groundwater remediation methods, such as groundwater pumping at specific wells. The model run of each groundwater remedy is an approximate prediction of how the contamination will be gradually removed from water in the subsurface.

Groundwater modeling at Monument Valley focused on the simulation of steady-state flow in the alluvial aquifer in areas located downgradient of former ore processing operations at the site. Several different conceptualizations of the groundwater system were tested with automated model calibration software before identifying a model that performed best in matching measured groundwater levels in the study area. The selected steady-state model was subsequently used in conjunction with computer-based optimization algorithms designed to identify efficient methods for cleaning up the alluvial aquifer. Application of these techniques to a variety of proposed groundwater remedies based on pump-and-treat technology resulted in the identification of an optimal remediation strategy.

D.1.1 Steady-State Flow

A steady-state flow model was developed for the alluvial aquifer at Monument Valley (DOE 2000b) using software developed and maintained by the U.S. Geological Survey (USGS). Sixteen different conceptual models were considered in the process of developing the steady-state flow model. Each conceptual model was calibrated using the USGS code MODFLOW (McDonald and Harbaugh 1988), a finite-difference simulator that can account for three-dimensional groundwater flow in heterogeneous domains, and using the automated parameter estimation techniques within the UCODE software (Poeter and Hill 1998). The steady-state flow model ultimately selected to represent groundwater flow in the alluvial aquifer at the site produced a reasonable match to observed groundwater levels at numerous wells monitored in the area north of the New Tailings Pile footprint.

All models considered in the UCODE analyses were two-dimensional with a single model layer of spatially variable thickness representing the alluvial aquifer. A spatially varied field of elevations representing the base of the alluvial aquifer (i.e., top of bedrock) was developed from available well construction information and adopted in the flow simulations. The model runs were conducted using version 3.50 of the graphical user interface called Groundwater Vistas (Environmental Simulations Inc. 1997), a Windows-driven package that contains graphical pre- and post-processors for MODFLOW models and facilitates easy data entry, data-file modification, program execution, and analysis of modeling results.

The final steady-state model assumed that hydraulic conductivity was spatially uniform (1.66 meters per day [m/day] or 5.44 feet per day [ft/day]) throughout the aquifer and that all parts of the aquifer receives recharge at a constant rate of 0.025 m (3 inches) per year. Five different ET zones, each with a distinct ET loss rate that depended largely on observed depth to groundwater, were employed in the model.

The selected model produced a steady-state flow field with an average horizontal, north-northeast gradient of about 0.0085 (dimensionless) and average linear velocities that generally averaged between 18 to 21 meters per day (60 and 70 feet per year [ft/yr]). Though the model performed well (DOE 2000b) in matching observed groundwater levels at numerous monitoring wells, observed lengths of the nitrate and sulfate plumes (approximately 1370 m or 4,500 ft) at the site in 1997 and 1998 indicated that the model-generated velocities were not large enough to have produced the plumes apparently caused by discharged process chemicals at the former mill site in the mid-1960s. A subsequent modeling effort conducted by Carroll and others (2009) that attempted to match observed nitrate concentrations in the alluvium at several different times between 1993 and 2007 showed results that inferred groundwater velocities on the order of 75 to 85 m/yr (250 to 280 ft/yr) occur in the aquifer. This in turn suggested that the hydraulic conductivity of 1.66 m/day used throughout the DOE flow model was probably too low. The Carroll model (Carroll et al. 2009), which was based on aquifer testing results summarized in the SOWP, used a hydraulic conductivity of about 5 m/day (16 ft/day) in the initial 600 m (2,000 ft) of aquifer located downgradient of assumed nitrate sources in the vicinity of the New Tailings Pile, and a conductivity of about 7.6 m/day (25 ft/day) beyond the 600-m distance.

D.1.2 Early Groundwater Remedy Simulations

The SOWP (DOE 1999a) recommended that phytoremediation techniques, in conjunction with groundwater extraction and treatment, be used to remediate nitrogen-containing contaminants at the Monument Valley site. In the interest of designing an effective and efficient groundwater extraction system, the model ultimately selected to represent steady-state flow in the alluvial aquifer (DOE 2000b) was used to evaluate the relative merits of a variety of well-field configurations and pumping plans. This was accomplished with an optimization algorithm called the Brute Force method, as incorporated in the Groundwater Vistas (Environmental Simulations Inc. 1997) software package. The Brute Force technique combined groundwater flow simulations of a proposed pumping strategy with particle tracking to identify the flow paths and groundwater travel times that resulted from that strategy. The flow modeling was performed using MODFLOW and the particle tracking was conducted with the USGS package MODPATH (Pollock 1994). Optimization focused on maximizing the amount of contaminant mass removed while minimizing the number of wells needed to extract the mass, thereby minimizing overall groundwater remediation costs (DOE 2000c).

Two fundamentally different groundwater extraction strategies were considered in the optimization modeling runs: one that returns treated water to the aquifer (non-consumptive use) and one that does not (consumptive use). In addition to a single well field designed for pumping at a constant total rate for the duration of the cleanup action involved with each strategy, phased approaches were also evaluated with the strategies. The phased approach assumed that pumping would be concentrated in select locales during the first several years of remediation (Phase 1) for the purpose of removing contaminant hot spots, which was then followed with plume-wide groundwater extraction (Phase 2) to meet aquifer restoration goals within a specified time frame.

Three different well-field design alternatives were simulated under the non-consumptive use strategy. Each of these assumed that the groundwater would be pumped from vertical wells in the nitrate plume and that extracted groundwater would be returned to the alluvial aquifer at three upgradient locations, each representing a 76-m (250-ft) long infiltration trench. Multiple model simulations, differing with respect to the duration of hot-spot removal and total remediation time, were conducted under the three alternatives. Subsequent analysis of the optimization modeling for the non-consumptive use strategy indicated that optimal aquifer remediation would be achieved through Phase 1 pumping for 5 years to remove hot spots followed by an additional 15 years of Phase 2 pumping from the nitrate plume as a whole.

Assessment of the consumptive use strategy also examined three different alternatives that varied according to duration of hot-spot removal and total remediation time (DOE 2000c). Though the exact processes leading to consumption of the pumped groundwater were not specified, use of the water to supply a spray evaporation system or support a land-farm phytoremediation operation were mentioned as possible candidates. Ultimately, an optimal remedy was identified that called for 5 years of hot-spot removal followed by 20 years of plume-wide groundwater extraction, a solution that was similar to the recommended alternative under the non-consumptive use strategy.

Though the various active remediation designs considered in the modeling (DOE 2000c) helped to identify optimal pumping alternatives, no attempt has since been made to pursue pump-and-treat methods for aquifer cleanup. Alternatively, the purpose of this report is to recommend a groundwater remediation approach that utilizes either natural or enhanced attenuation processes, or some combination thereof.

D.2 Monitoring

Before and after the mathematical modeling, groundwater elevations and the concentrations of contaminants in the groundwater were measured. The collection of water-level and concentration data at regular time intervals during the months and years after model predictions have been made is called groundwater monitoring, and the data collected during each monitoring event provides a snapshot of how aquifer cleanup is progressing. By comparing individual snapshots with model predictions of aquifer remediation, groundwater scientists can determine whether the remedy is working as expected. If the aquifer is not cleaning up as fast as predicted, scientists may decide to modify the groundwater remedy or select a new one.

Extensive site characterization work was conducted in 1997 to develop a comprehensive understanding of groundwater flow and transport processes at the site. This work involved geophysical surveys, the drilling and logging of multiple wells, water-level measurements, and groundwater sampling and analysis. Prior to finalization of the SOWP (DOE 1999a), additional groundwater chemistry data were collected as a result of two sampling events in 1998. The 1998 data collection effort served not only to further describe natural groundwater chemistry in the vicinity of the site but also to confirm the lengths of the ammonia, nitrate, and sulfate plumes in the alluvial aquifer and the concentrations of these constituents in their respective plumes, particularly along each plume's longitudinal axis. The axes of the plumes appeared to be collinear, indicating that all three plumes originated in the vicinity of the New Tailings Pile footprint.

Groundwater monitoring has been conducted routinely at the Monument Valley site since 1997, with sampling occurring once a year in some years and twice during others. The results of sampling in 1997 and 1998 can be used to describe starting configurations for contaminant plumes that have evolved in the alluvial aquifer through 2010. The following report sections discuss the degree to which the plumes of ammonia, nitrate, and sulfate have changed, if at all, during that time period. Possible reasons for the observed changes are given in the interest of developing a more thorough understanding of contaminant fate at the site.

D.2.1 Ammonia

The disposition of the ammonia plume can be approximately discerned by examining contour maps of ammonia as nitrogen (NH_3[N]) concentration in 1997 and 1998 (Figure D-1), June 2007 (Figure D-2) and December 2010 (Figure D-3). These three figures imply that the northern extent of the ammonia plume over a period of 14 years has remained about 900 m (3,000 ft) north of the New Tailings Pile footprint, far short of 1350 m (4,500 ft) plume lengths that have been ascribed to nitrate and sulfate plumes north of the New Tailings Pile footprint. Comparison of the 1997-1998 and 2010 plume maps suggests that ammonia concentrations at five wells in and near the plume core (606, 655, 656, 770, 771) decreased steadily by as much 10 to 50 percent between these two times. Whereas this is basically true for wells 606, 656, and 770, a temporal plot of ammonia concentrations at several site wells between 1997 and 2010 (Figure D-4) shows that consistently decreasing concentrations were not observed at wells 655 and 771. Though NH_3-N levels at these two co-located wells fluctuated greatly from 1997 through 2010, no discernible, steadily decreasing trends in concentration were observed in the water samples collected from them.

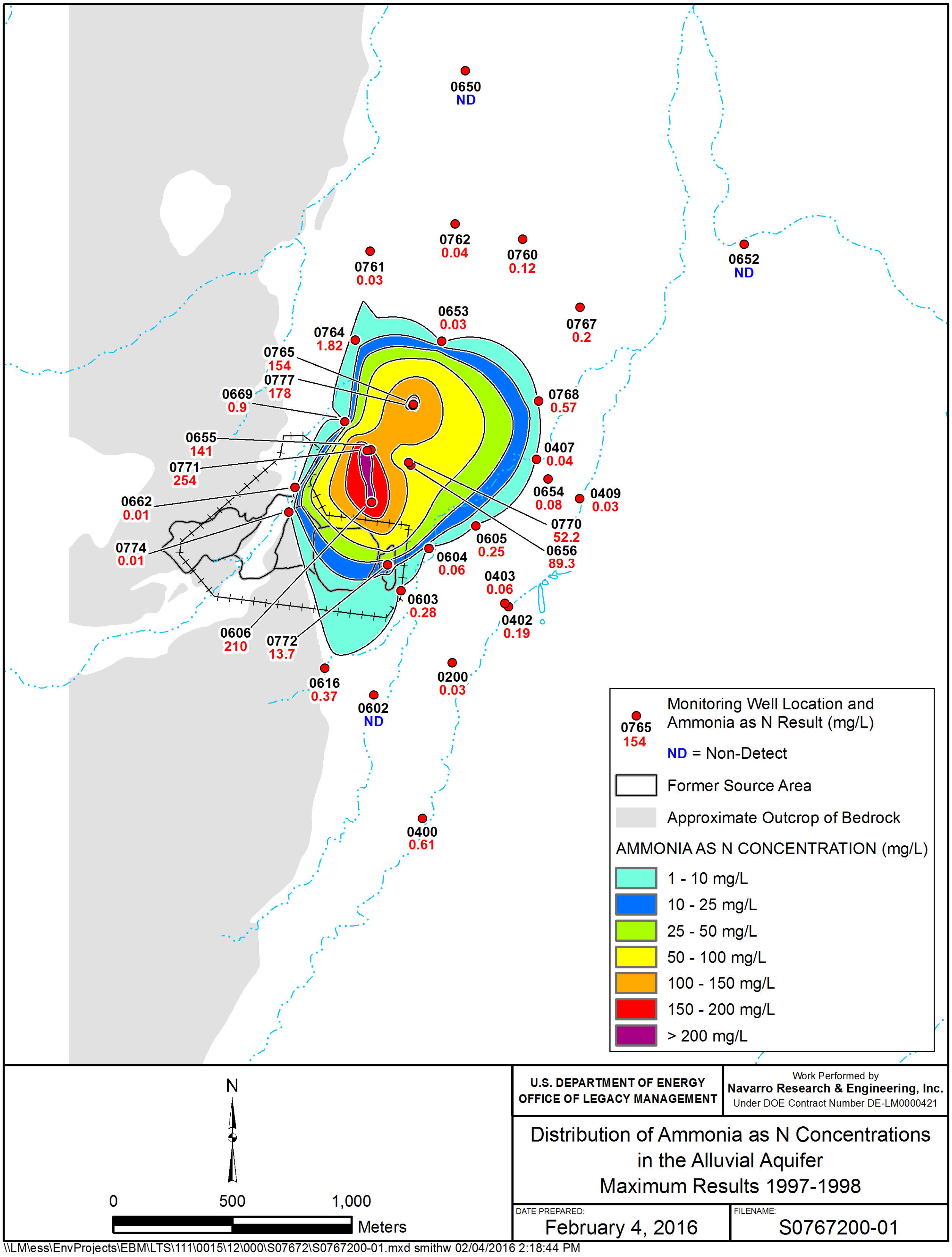

Figure D-1. Distribution of maximum ammonia (as N) concentrations during 1997 and 1998.

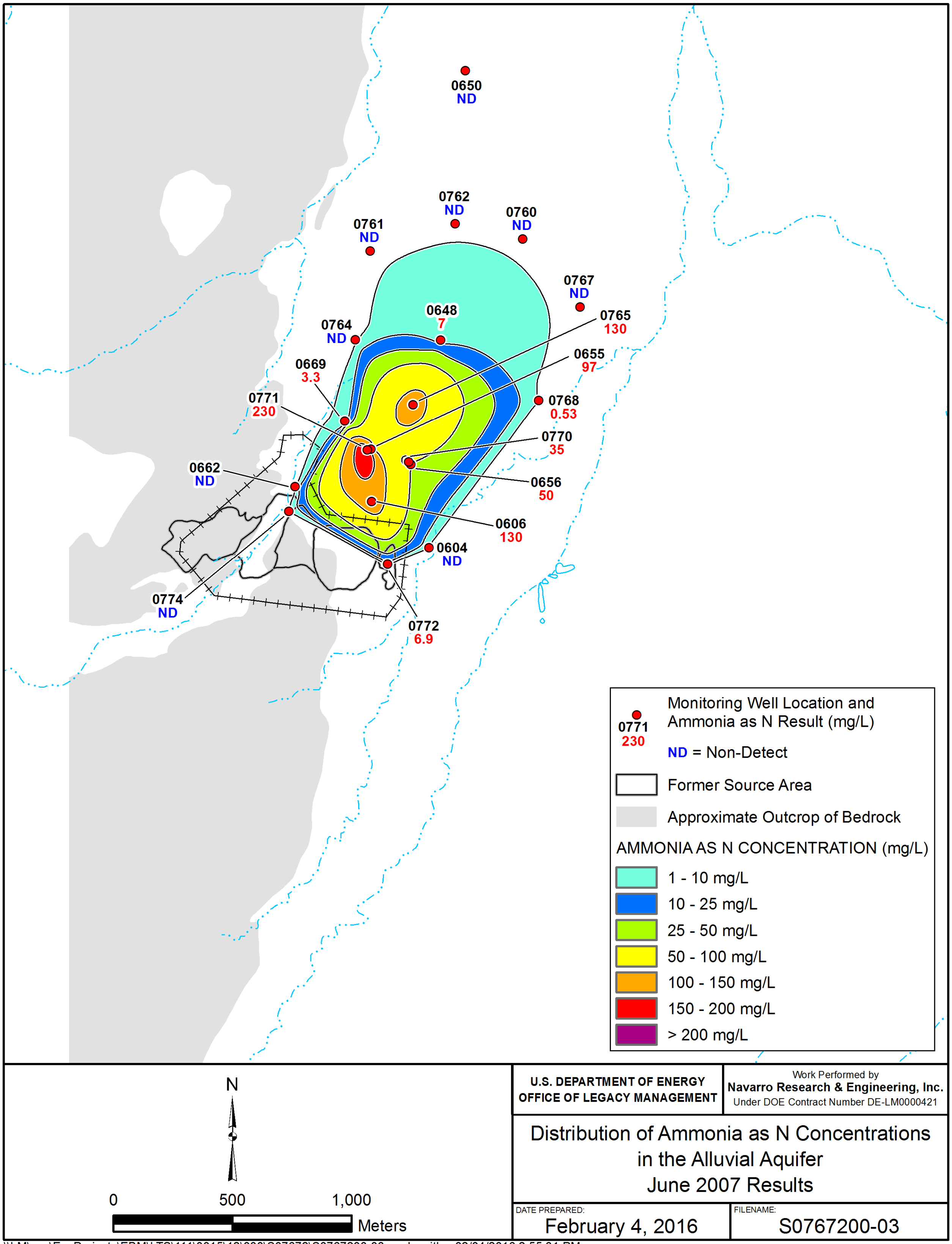

Figure D-2. Distribution of ammonia (as N) concentrations in June 2007.

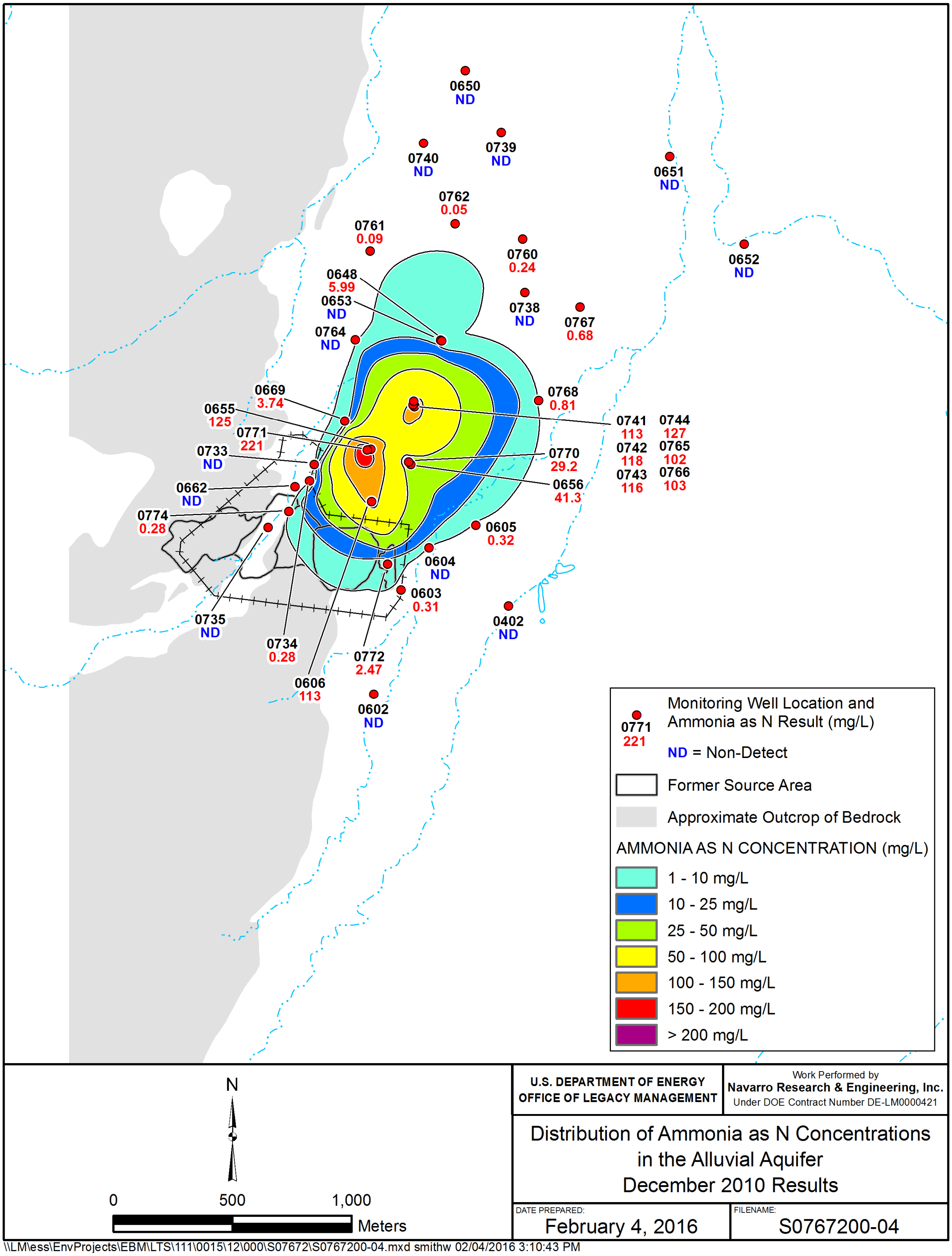

Figure D-3. Distribution of ammonia (as N) concentrations in December 2010.

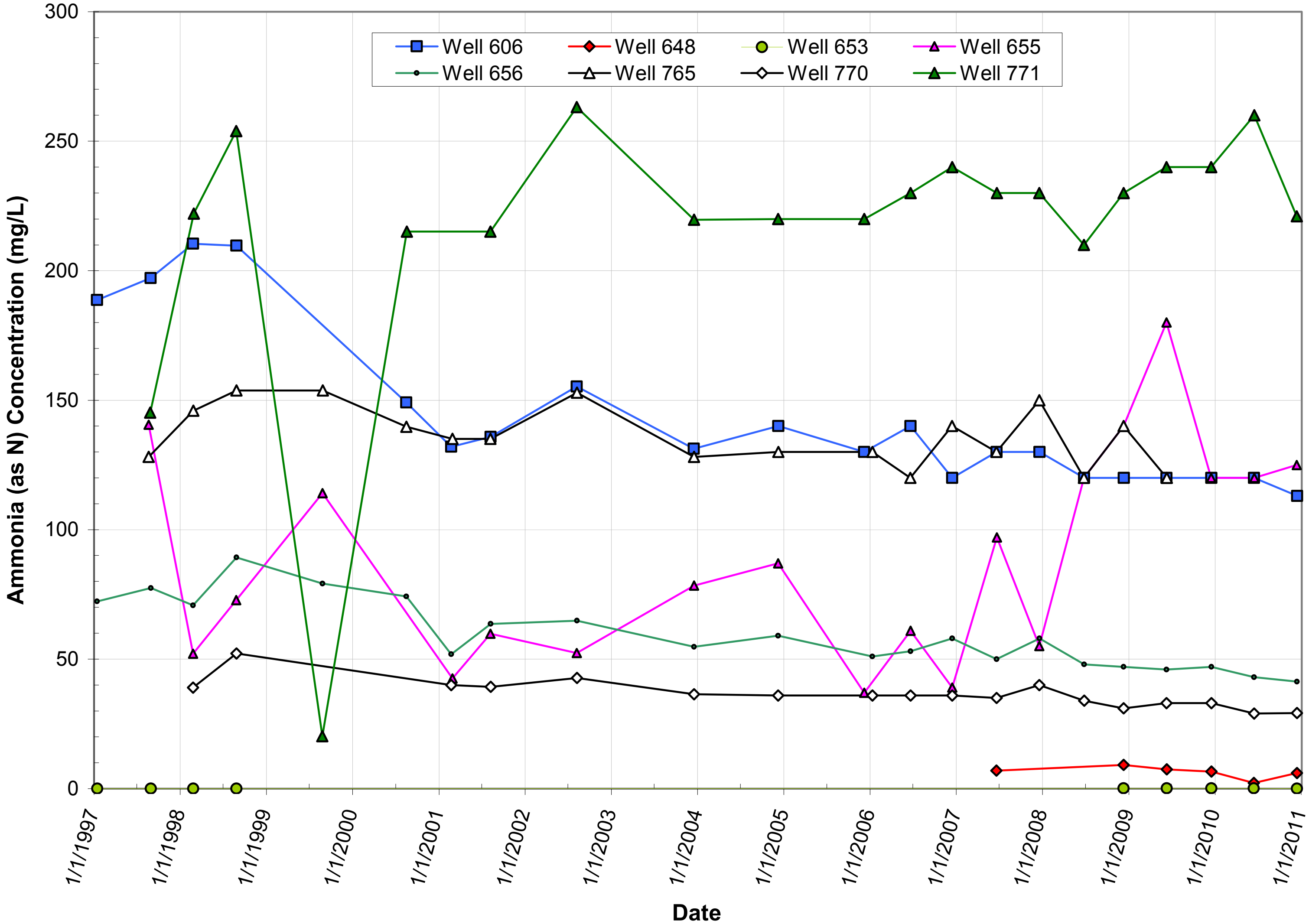

Figure D-4. Ammonia (as N) concentrations along and near the plume axis from 1997 to 2010.

Well 606 lies in the center of a 50 m by 50 m square plot that was used for phytoremediation testing. Fourwing saltbush were planted in the test plot in 2005, and the plants gradually reached a healthy, mature state. Hence, the decrease in ammonia concentration by about half at this location between 1997-1998 and 2010 (210 to 113 mg/L NH_3[N]) is probably attributable to ammonia uptake by the roots of this phreatophyte planting. Though it is also possible that the recharge irrigation water applied to the test plot during the first few years of the phytoremediation testing helped to dilute underlying groundwater, subsurface monitoring in the test plot indicated that deep migration of the applied water during and shortly after the irrigation period was limited. Consequently, dilution was unlikely to have impacted ammonia levels in well 606 to the degree shown in Figure D-4.

Similar decreases in ammonia concentration by about half at wells 656 and 770 between 1997-1998 and 2010 were also probably the result of a phytoremediation pilot study. These two wells are in the center of a mature stand of black greasewood that was historically overgrazed. Since about 2000, the stand has recovered as the grazing pressure declined to become a healthy population that has the capacity to remove ammonia via root uptake.

The low NH_3-N concentrations seen consistently at co-located wells 648 and 653 (Figure D-4), which are at the leading edge of the ammonia plume, indicate the plume is not progressing farther to the north. Historical ammonia concentrations at well 765, located approximately 275 m (900 ft) south of wells 648 and 653, provide further evidence that the plume is not migrating northward. Despite the fact that NH_3-N levels at this well were consistently high (>100 mg/L) between 1997-1998 and 2010, the concentrations remained relatively constant and showed no signs that they were steadily increasing. Note that concentration data for well 765 beyond early 2009 are omitted from Figure D-4 because a push-pull test of enhanced attenuation conducted in the well in the second half of 2009 impacted local contaminant concentrations.

Ammonia concentrations in groundwater samples from co-located wells 655 and 771 from 1997-1998 through 2010 (Figure D-4) are of particular interest because of the sizable differences in concentration typically observed between them. Though the wells were installed about 15 m (50 ft) from each other, NH_3-N levels at well 771 have commonly been 2 to 3 times the comparable concentrations observed at well 655. Possible reasons for the disparity in ammonia concentration can be surmised by examining the well logs for the respective wells. These indicate that each well is screened over a 6 m (20 ft) vertical interval, the midpoint elevation of the screen in well 771 is 8.4 m (27.5 ft) lower than the midpoint elevation of the well 665 screen, and overlap of the two screened intervals is limited to 0.76 m (2.5 ft). In addition, the geologic log for the deeper well (771) indicates the possible presence of fine-grained materials, particularly clay, in the bottom 3 m (10 ft) of the well borehole, whereas no such fine-grained sediment is observed in the shallower well. These observations suggest that ammonia concentrations have the potential to vary noticeably with depth in the aquifer, with concentrations in this part of the plume increasing with depth. However, it also possible that aquifer heterogeneity is primarily responsible for the disparate concentrations, such that the clay apparently present in a deeper horizons at well 771 is somehow related to higher ammonia levels.

The potential for contaminant concentrations to vary noticeably over short distances in the aquifer can be further analyzed by examining NH_3-N levels in co-located wells 656 and 770 between 1997-1998 and 2010 (Figure D-4). These two latter wells are also located about 15 m (50 ft) from each other and the screened interval in well 770 is deeper than that in well 656.

Vertical separation between the screened intervals for the wells is less dramatic than at the well 655/771 pair, as the midpoint elevations for the respective screens differ by 3.4 m (11 ft) and screen overlap is 1.2 m (4 ft). In addition, neither of the geologic logs for the two locations indicates the presence of clayey material. The ammonia concentrations in the two wells tend to be close in magnitude, with the shallower well (656) during recent years consistently exhibiting NH_3-N concentrations that are about 30 percent larger than equivalent concentrations in the deeper well (770). Obviously, the larger concentrations observed in the shallower well contradicts the notion that concentrations tend to increase with depth. As previously discussed, wells 656 and 770 are located in a phytoremediation test plot, but it is unclear whether apparent root uptake of ammonia associated with the testing played a role in creating larger NH_3-N levels at the shallower vertical interval in the aquifer.

Though it is clear that dissolved ammonia concentrations can vary significantly over relatively short distances, the limited data presented above for the two sets of co-located wells (wells 655 and 771, wells 656 and 770) are inadequate for deciphering all factors influencing ammonia levels in a local area. Nevertheless, the fact that NH_3-N concentrations at one well location can be as much as 2 to 3 times the value of comparable concentrations in a well as little as 15 m (50 ft) away implies that aquifer heterogeneity has the potential to strongly influence spatial distributions of contaminants in site groundwater. Accordingly, the possibility that local contaminant migration mostly occurs within preferential flow paths (i.e., zones of higher hydraulic conductivity; Zheng and Gorelick 2003) cannot be discounted.

D.2.2 Nitrate

Plume maps displaying nitrate as nitrogen (NO_3[N]) concentrations at the site in 1997-1998, 2000, 2007, and 2010 are presented in Figures D-5, D-6, D-7, and D-8, respectively. An obvious progression observed in nitrate distribution over this time period is an extension of the plume to the north, manifested by a gradual increase in concentration at well 762, located near the plume's leading edge, about 1350 m (4,500 ft) north of the New Tailings Pile footprint. As shown in the plume maps, NO_3-N concentrations at this location appeared to increase steadily from about 17 mg/L in 1997-1998 to greater than 95 mg/L in December 2010. A temporal plot of nitrate levels at wells along and near the plume axis (Figure D-9) reveals that nitrate increased in concentration at well 762 between 1997 and late 2008 (~130 mg/L), and subsequently decreased to a constant concentration of about 100 mg/L thereafter. A slight but steady increase in NO_3-N concentration at well 650 from less than 0.3 mg/L in 1997 to greater than 2 mg/L in 2010 also suggests that the leading edge of the nitrate plume migrated farther north during the 14-year monitoring period.

Co-located wells 655 and 771 also experienced discernible upward trends in nitrate concentration from the late 1990s through 2010 (Figures D-5 through D-8), with both wells exhibiting increases in NO_3-N level on the order of 40 to 50 mg/L since 1998 (Figure D-9). The reason for the gradual rise in concentration in the vicinity of these wells is unknown. Note that the disparity in NO_3-N concentration at wells 655 and 771 during the monitoring period was far less than comparable differences observed for ammonia (Figure D-4). Nonetheless, as in the case of ammonia, the larger nitrate concentrations were typically observed in well 771 (Figure D-9), which is screened at a greater depth than well 655.

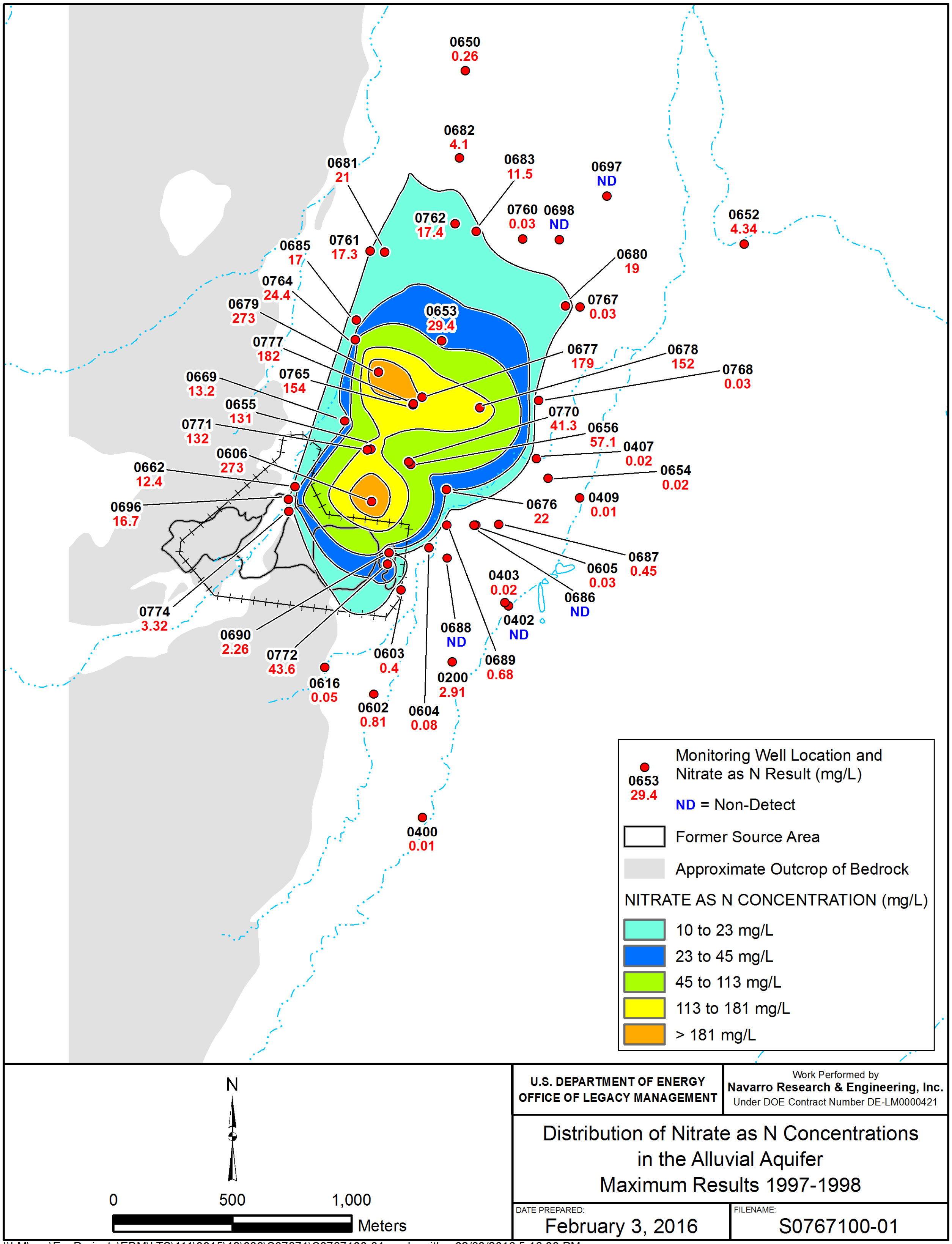

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Figure D-5. Distribution of maximum nitrate (as N) concentrations in the alluvial aquifer during 1997 and 1998.

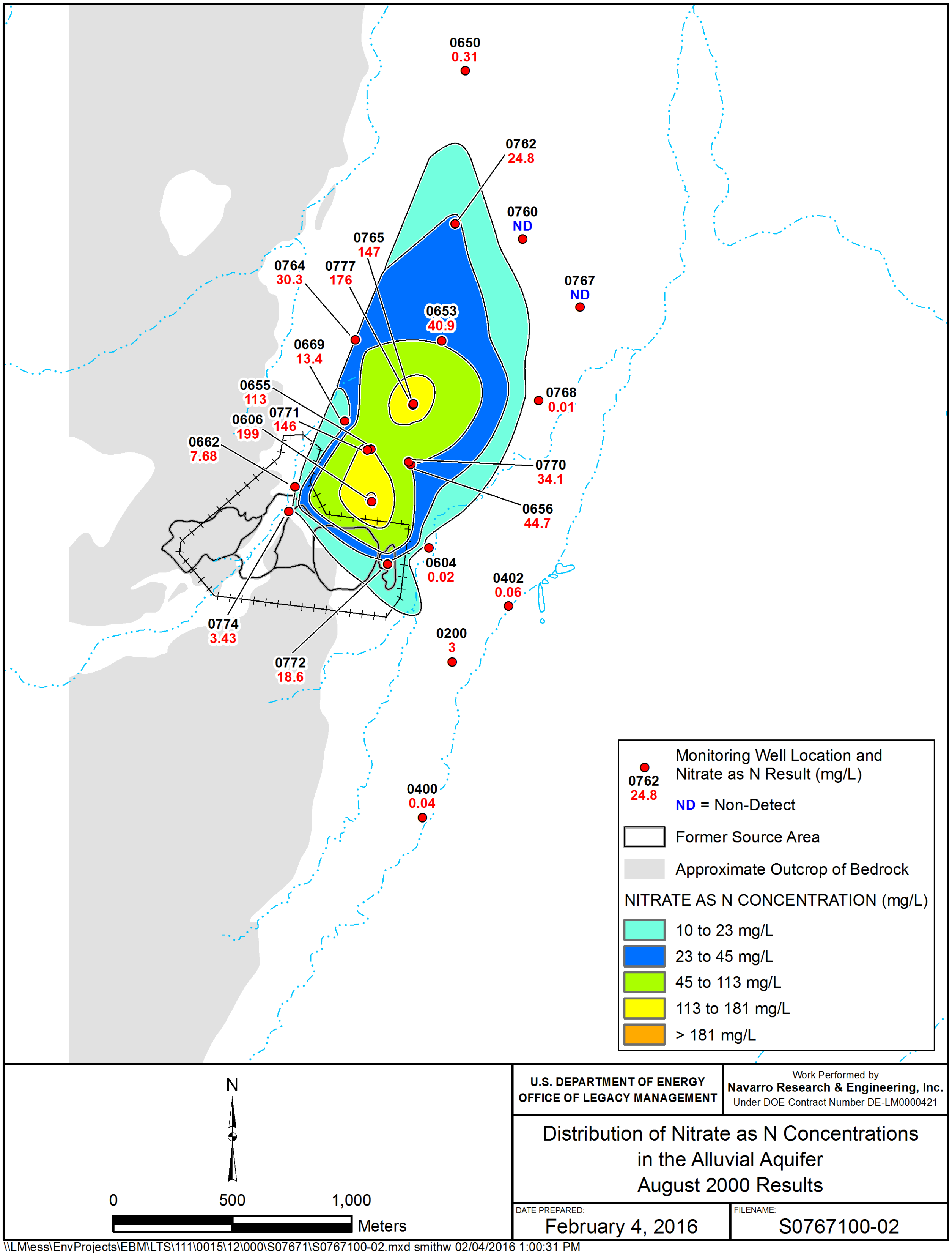

Figure D-6. Distribution of nitrate (as N) concentrations in the alluvial aquifer in August 2000.

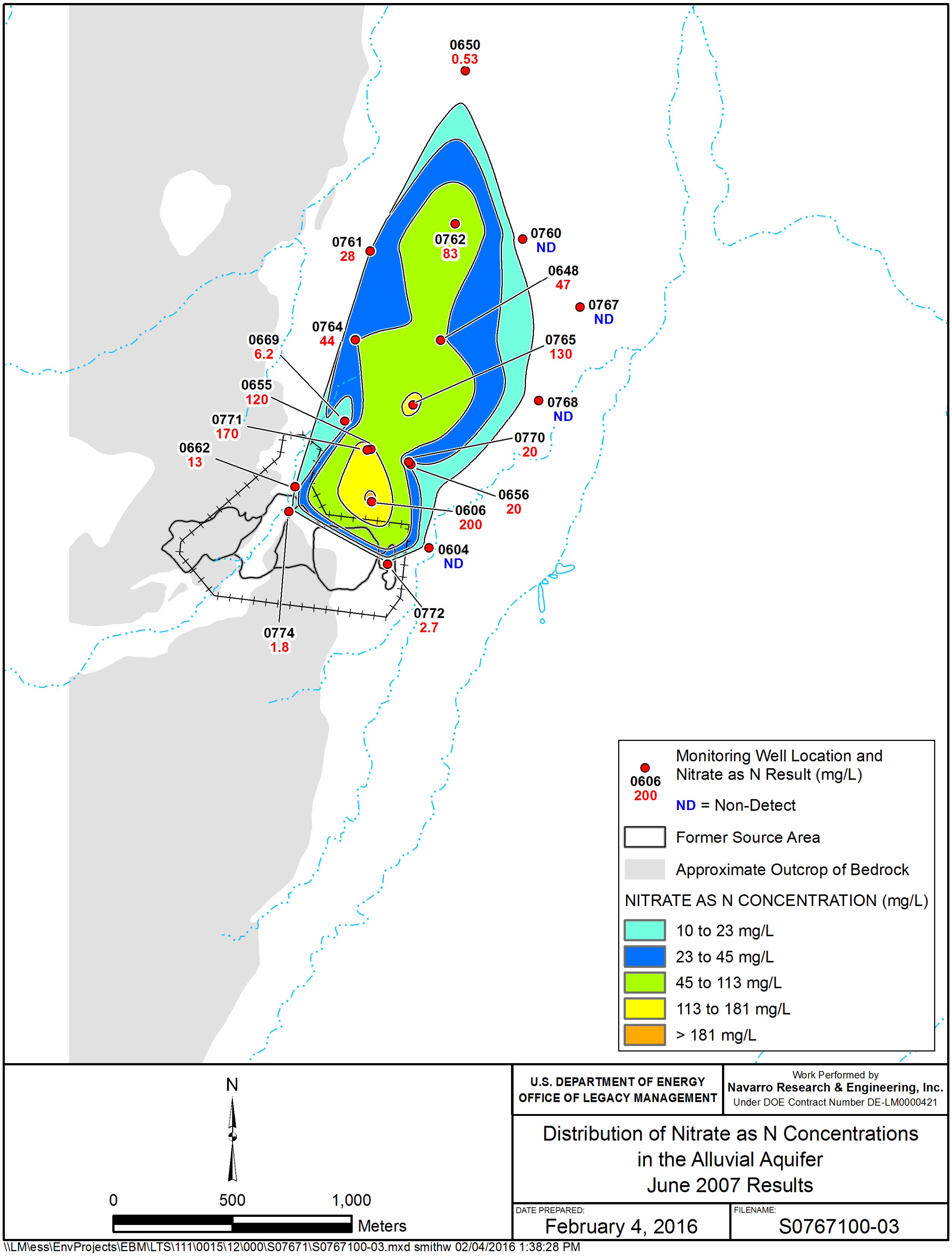

Figure D-7. Distribution of nitrate (as N) concentrations in June 2007.

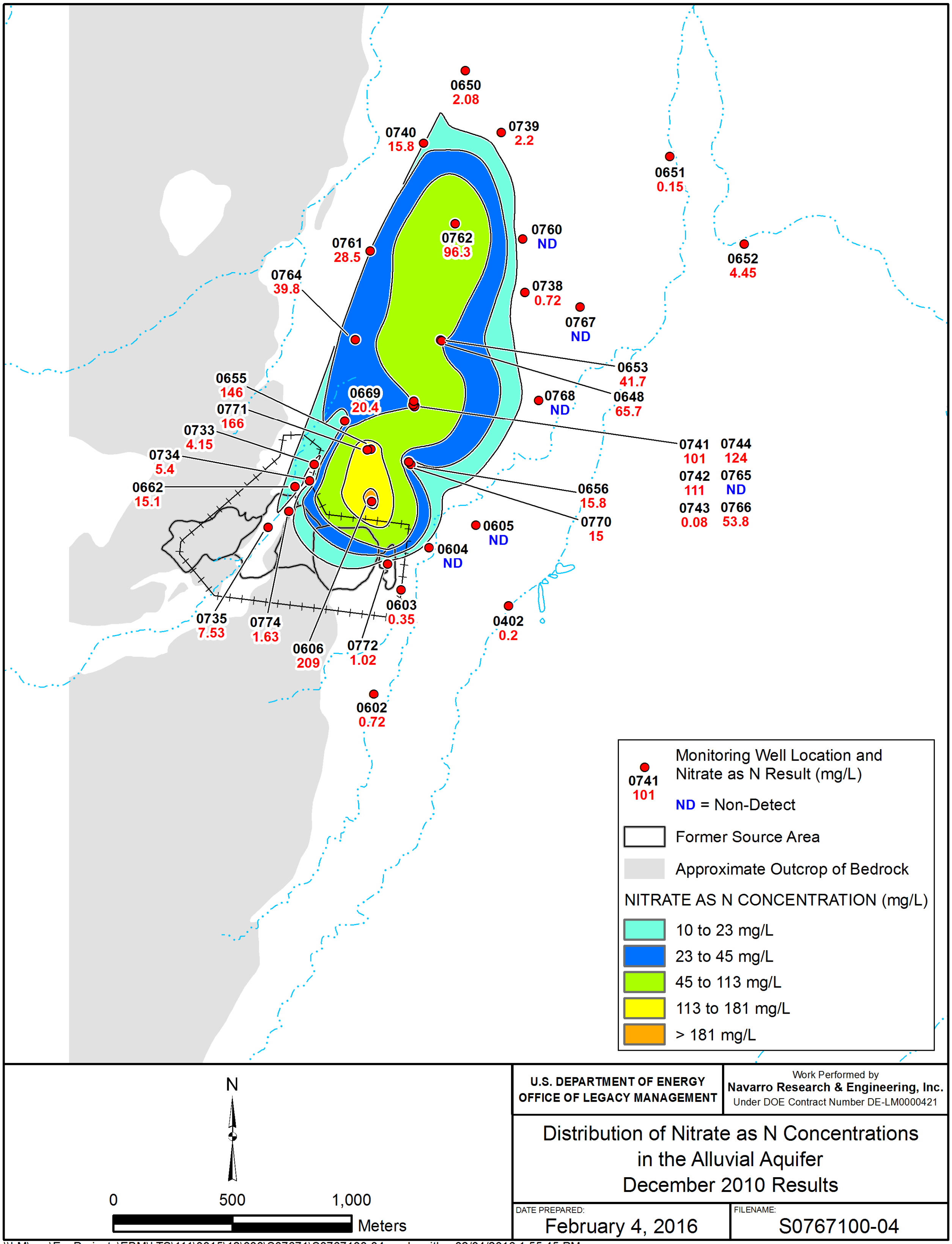

Figure D-8. Distribution of nitrate (as N) concentrations in December 2010.

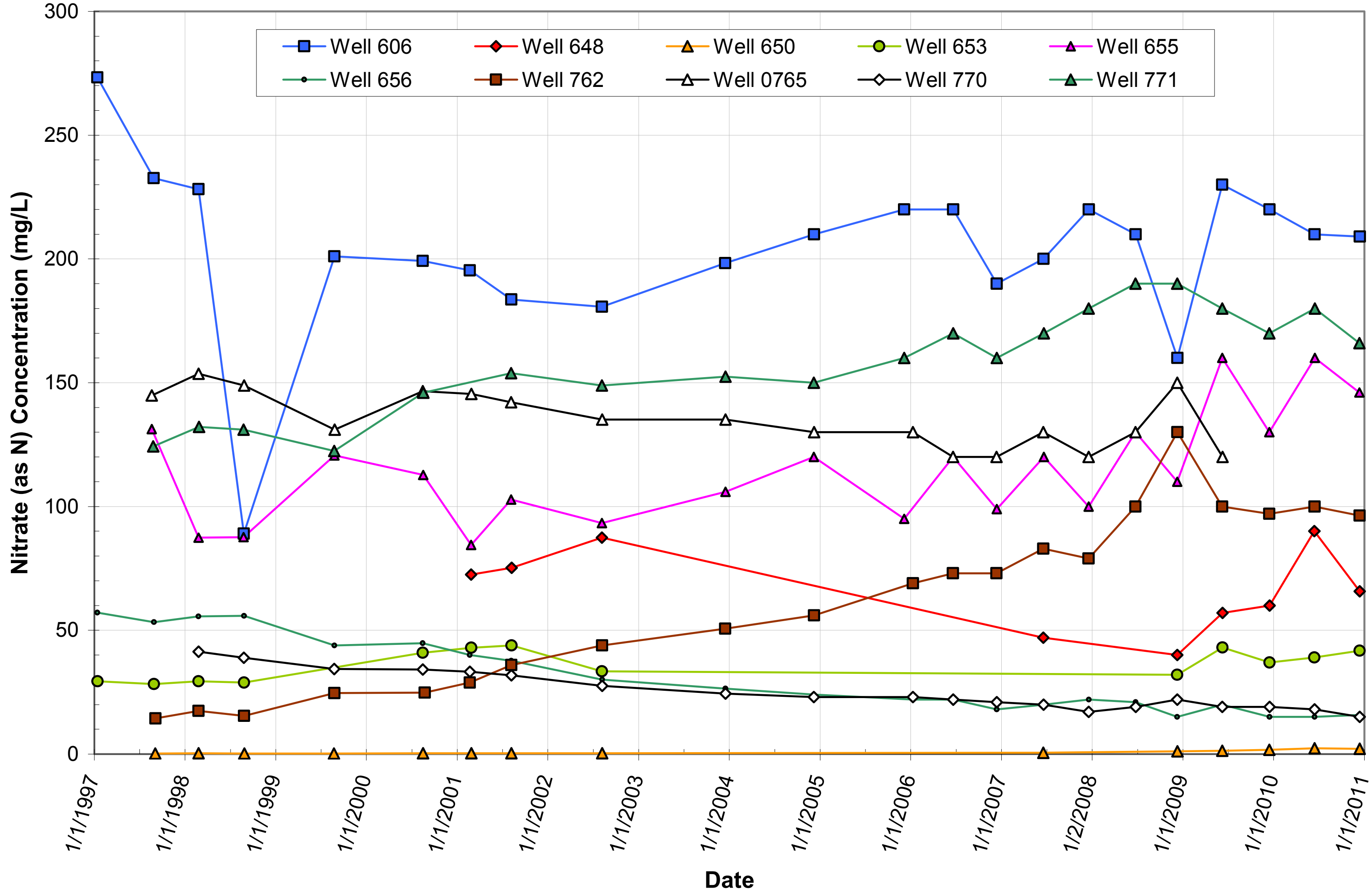

Figure D-9. Nitrate (as N) concentrations along and near the plume axis from 1997 to 2010.

In contrast to ammonia behavior, nitrate levels during 14 years of monitoring at well 606 did not show a clear decreasing trend. Rather, NO_3-N concentrations at this well mostly remained above 200 mg/L since 1997 (Figure D-9), despite fluctuating significantly. This observation indicates that attempts at phytoremediation in the test plot surrounding well 606 had no discernible impact on local nitrate contamination.

As indicated by the temporal plot of NO_3-N concentrations (Figure D-9), co-located wells 648 and 653 tended to exhibit relatively constant nitrate levels during the years that they were monitored. Because these wells lie about 240 m (800 ft) hydraulically upgradient of well 762, which is representative of the nitrate plume's leading edge, the relatively stable concentrations in each suggest that, during the 14 years of monitoring, nitrate was feeding into the local portion of the plume at the same rate that it was migrating farther to the north. Nitrate in wells 648 and 653 was also of interest because the wells are only 4.9 m (16 ft) apart and the midpoint elevations of their screened intervals are within 1.5 m (5 ft) of each other, yet nitrate levels in the former were consistently 10 to 50 mg/L larger than comparable concentrations in the latter. This observation supported a previous observation that contaminant concentrations have the potential to vary significantly over short distances in the alluvial aquifer. Again, the data provide evidence for the presence of preferential flow paths.

Similar to observed nitrate in wells 648 and 653, NO_3-N concentrations in well 765 remained relatively constant between 1997-1998 and 2010 (see Figures D-5 through D-9), providing evidence of a balance between nitrate influx and efflux in the portion of the plume sampled by this well. As in the case of ammonia, NO_3-N concentration data collected at well 765 after the first half of 2009 were omitted from Figure D-9 because a push-pull test of enhanced attenuation conducted at this location in the second half of 2009 impacted local contaminant concentrations. The plume map in Figure D-8 shows that the enhanced attenuation testing had reduced nitrate to non-detect levels at well 765 as of 2010.

In contrast to the consistently different ammonia concentrations measured at co-located wells 656 and 770 (Figure D-4), NO_3-N levels in these two wells remained very close in magnitude during the 13 years between 1998 and 2010 (Figure D-9). The difference in ammonia concentration between the two locations averaged about 10 mg/L from early 1998 through early 2001, but differences in subsequent years tended to remain within about 3 mg/L. Though it is difficult to find a reason for differing ammonia concentrations between the neighboring wells when comparable nitrate levels were very similar, it is possible that variable impacts of phytoremediation testing in the vicinity of the wells contributed to this apparent paradox. Regardless of the cause of the contradictory observations regarding ammonia and nitrate, gradually decreasing NO_3-N concentrations at both wells 656 and 770 between 1997-1998 and 2010 (Figures D-5 through D-9) suggests that the phytoremediation testing was helping to attenuate local nitrate levels.

Comparison of the NO_3-N plume contours for 1997-1998 conditions (Figure D-5) with subsequent plume maps in 2000, 2007, and 2010 (Figures D-6 through D-8) suggests that the nitrate plume was wider during the start of the 14-year monitoring period than it was in later years. This observation stems from the fact that the isopleths plotted in the 1997-1998 map made use of nitrate concentrations measured in June 1997 at well 678, a hydro-punch well that was abandoned shortly after it was first drilled. Thus, without the benefit of subsequently measured concentrations at this location, the plume contours representing conditions in 2000, 2007, and 2010 implied a narrower plume. Additional nitrate concentrations from sampling locations east of well 678 (wells 768 and 767) have never yielded data that are indicative of a plume that expands farther to the east than shown in Figures D-6 through D-8.

The observed tendency of concentrations at wells along and near the nitrate-plume axis (606, 655, 771, 765, 648, 653) to either remain relatively constant or increase over the 14-year monitoring period suggests that biologically mediated denitrification in the alluvial aquifer, if it is occurring, is mildly impacting the plume core. It is possible, however, that denitrification may take place along the east and west edges of the nitrate plume, where mixing of dissolved organic carbon in the aquifer with electron acceptors is potentially enhanced.

D.2.3 Sulfate

Of the three contaminants that impact the alluvial aquifer, sulfate showed the greatest tendency to attenuate in groundwater during the 14-year monitoring period. This tendency was seen primarily in wells located in the southern half of the sulfate plume, as shown in the succession of plume maps for 1997-1998 (Figure D-10), 2000 (Figure D-11), 2007 (Figure D-12) and 2010 (Figure D-13). As illustrated in a temporal plot of sulfate concentrations (Figure D-14), five of the monitoring wells in the southern half of the plume (606, 653, 656, 770, 765) experienced gradual, and mostly steady, decreases in sulfate concentration. Using the starting and ending concentrations presented in Figure D-14, the calculated drop in concentration at these wells fell in the range of 40 to 55 percent. These findings strongly suggest that the source of the sulfate was greatly reduced, if not terminated, at some time in the early 2000s. Phytoremediation in the source area has greatly limited percolation and may have curtailed deep percolation of sulfate once the plants matured (Appendix B, Section B.3). Therefore, it is logical to assume that source area remediation is responsible for much, if not all, of the sulfate attenuation in the southern half of the plume.

The greatest decrease in sulfate mass was observed at well 771, where sulfate levels were higher than 3,500 mg/L in 1997 and 1998, but had been reduced to less than 1,500 mg/L in December 2010 (Figure D-14). This large decline in concentration contrasts with the behavior of sulfate in co-located well 655, which generally maintained sulfate levels that fluctuated between 1,500 and 2,000 mg/L from 1997 to late 2007, and subsequently decreased to about 1,000 mg/L in late 2010. As a result of this behavior, sulfate concentrations in wells 656 and 771 tended to remain close in magnitude between 2005 and 2010. Though it is difficult to pinpoint why sulfate levels differed greatly between the two wells at the start of the 14-year monitoring period yet approximated each other at a later time, it is likely that the previously discussed vertical offset of screened intervals in the respective wells (Section B.2.1) and the apparent presence of clay near the bottom of the deeper well (771) helped play a role.

Well 648, co-located with well 653, showed a clear decrease in sulfate concentration from about 1,700 mg/L in 2001 to about 900 mg/L in 2007, and remained slightly below 1,000 mg/L through 2010. During sampling events when both of the co-located wells were sampled, their sulfate concentrations tended to stay close in value, generally differing by no more than 200 mg/L. Nevertheless, the frequent difference in observed concentration between two locations separated by 4.9 m (16 ft) confirmed the potential for contaminant levels to vary significantly over very small distances.

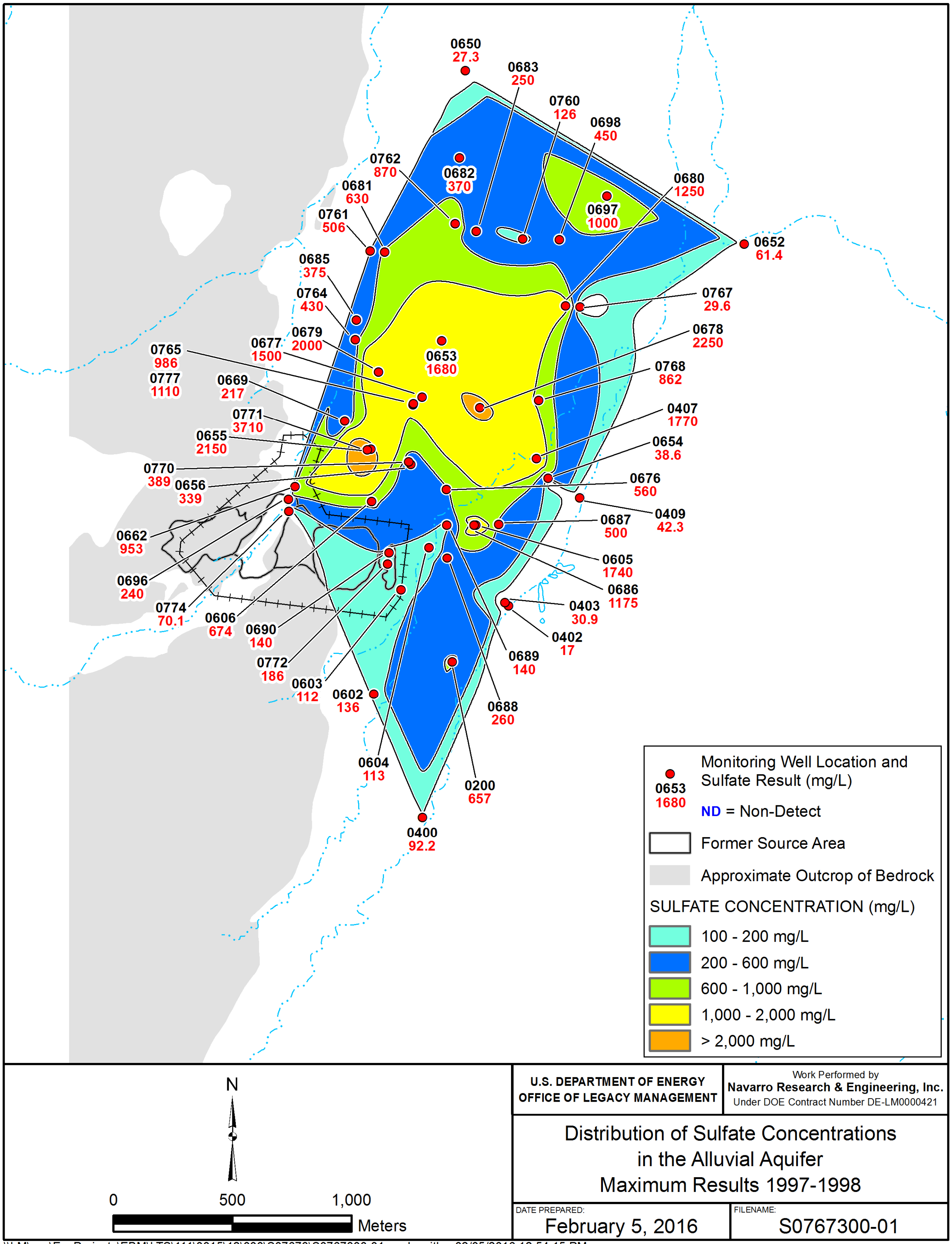

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Figure D-10. Distribution of maximum sulfate concentrations during 1997 and 1998.

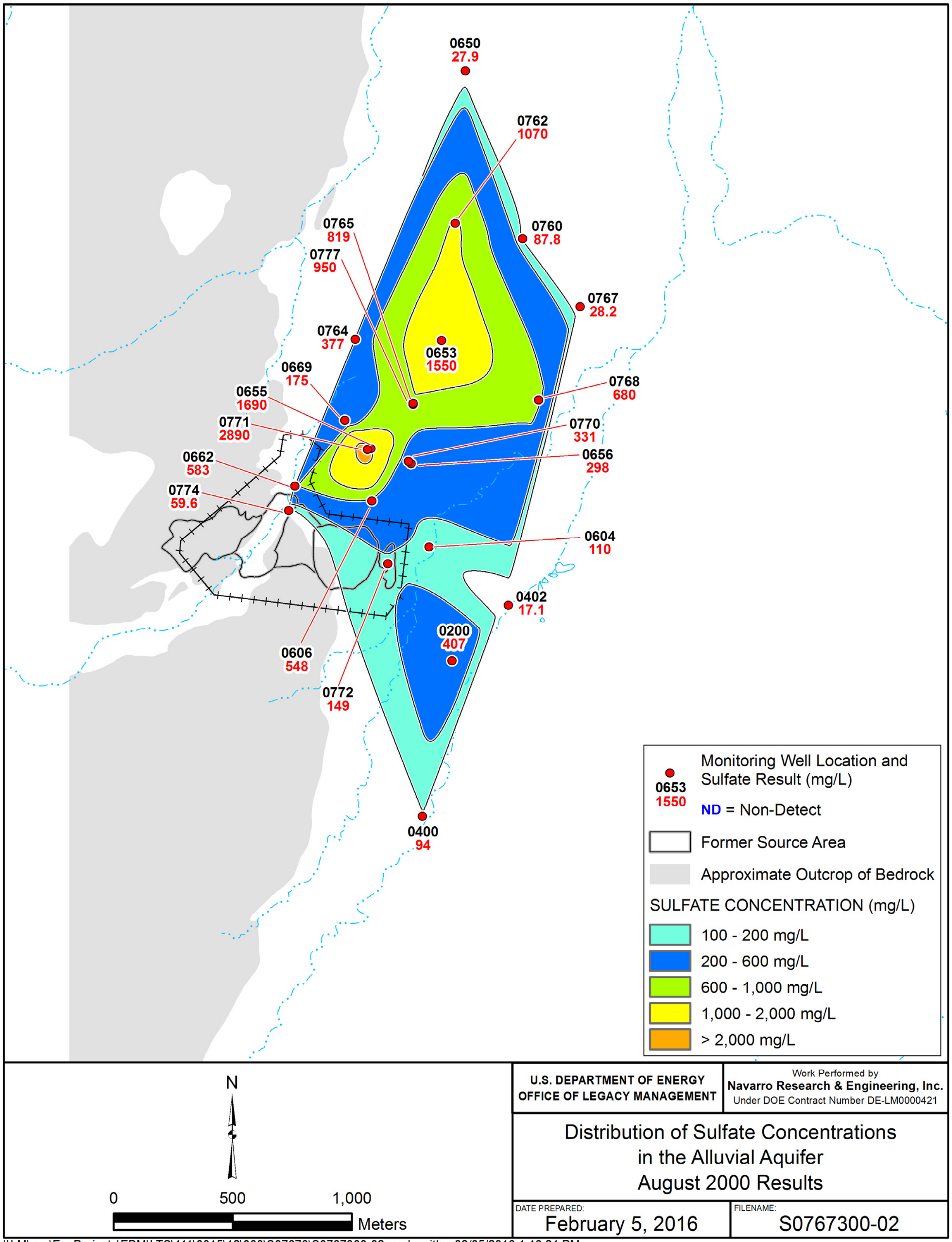

Figure D-11. Distribution of sulfate concentrations in August 2000.

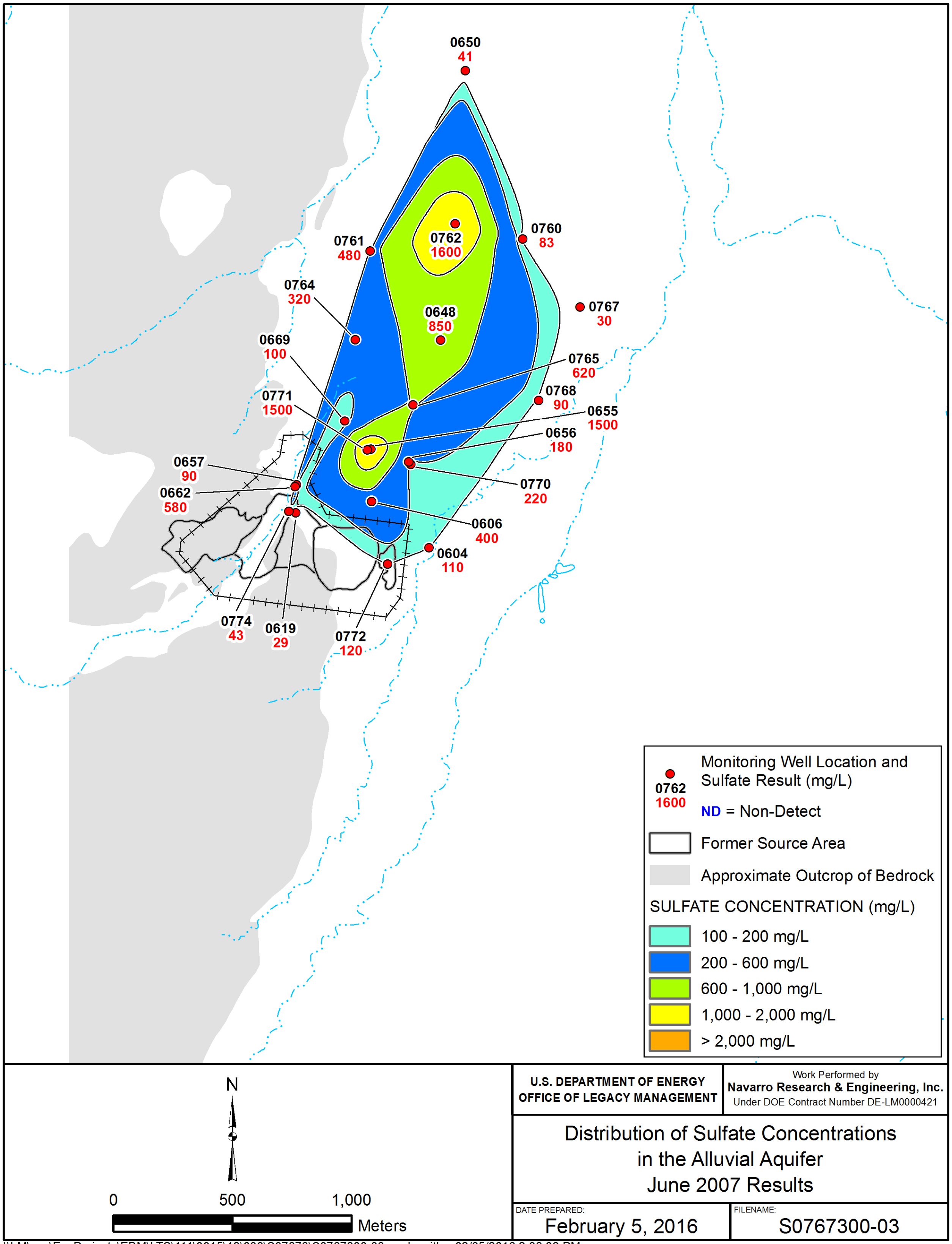

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Figure D-12. Distribution of sulfate concentrations in June 2007.

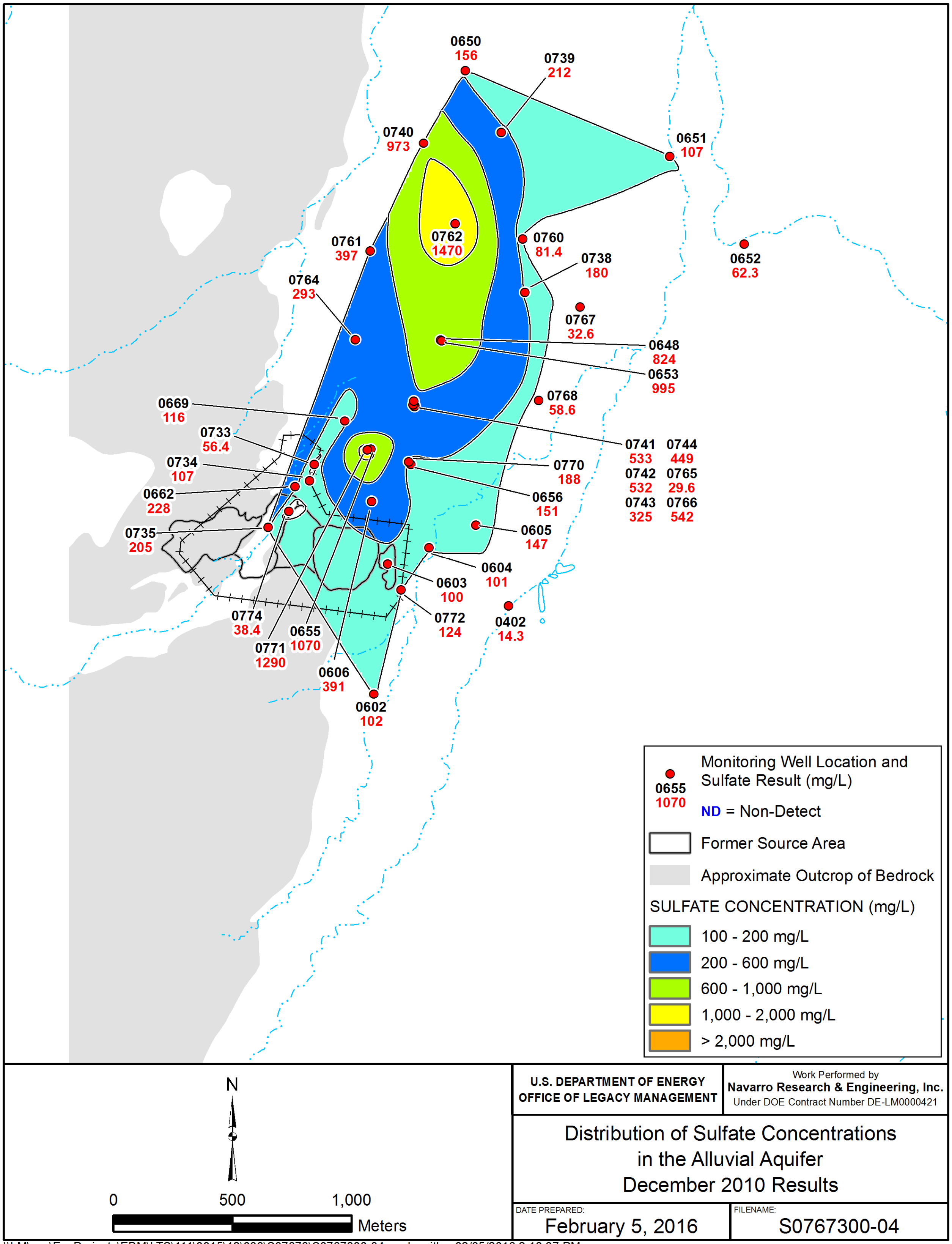

Figure D-13. Distribution of sulfate concentrations in December 2010.

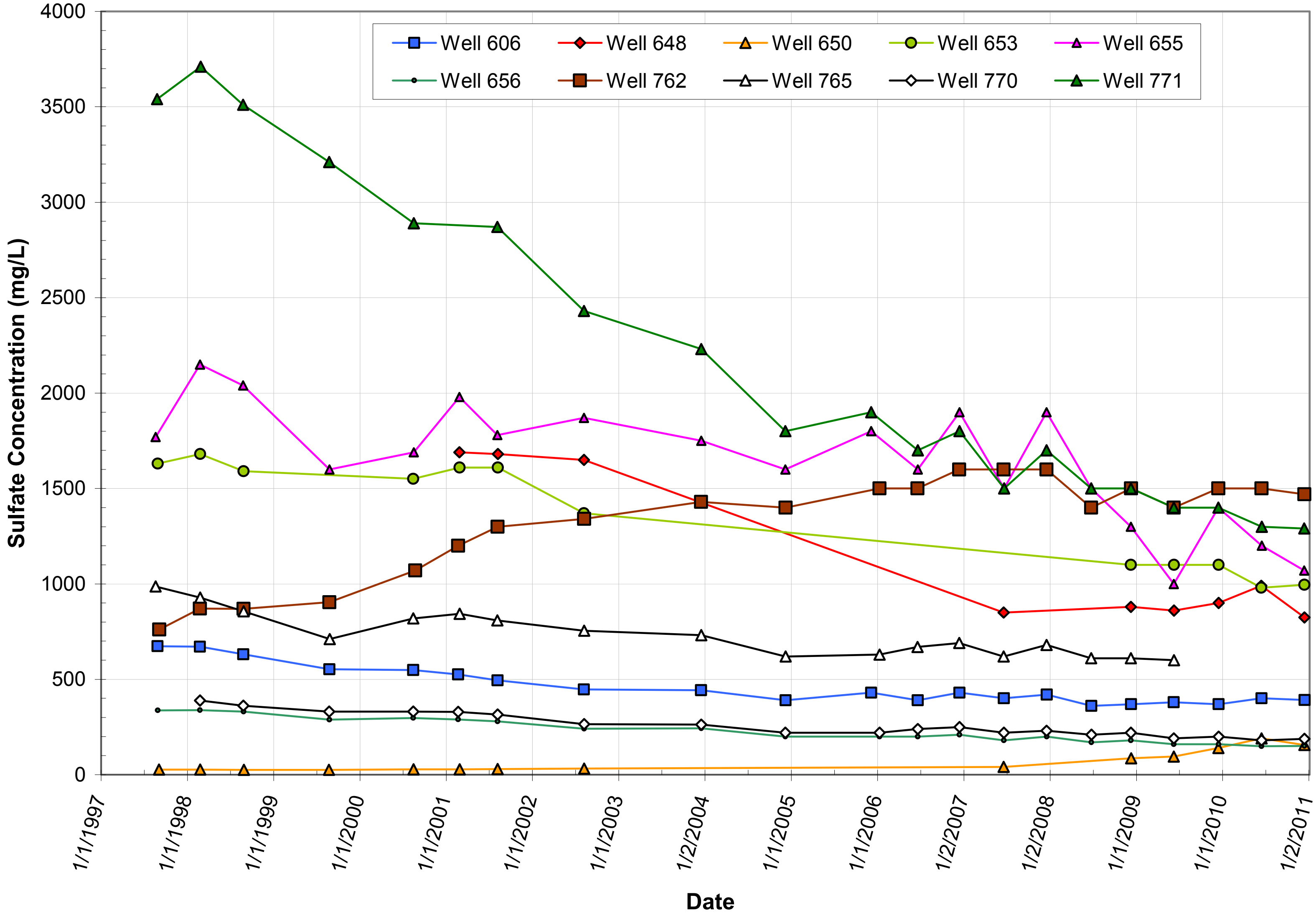

Figure D-14. Sulfate concentrations along and near the plume axis from 1997 to 2010.

In contrast to the mostly declining sulfate levels at the above-mentioned wells, wells 762 and 650 in the northern half of the plume showed clear increases in concentration from 1997 through 2010 (Figures D-10 through D-14). The combination of this latter observation and obviously decreasing concentrations in wells to the south suggests that the center of mass of the sulfate plume had been migrating northward during the 14 years of monitoring. Such an effect comports with the hypothesis that source area phytoremediation has largely, if not completely, cut off site-related influxes of sulfate on the south end of the plume. Alternatively, biologically mediated sulfate reduction is unlikely to have been the cause of such a decrease given that the alluvial aquifer environment is considered to be chemically oxidizing. Regardless of the cause of declining sulfate levels in the southern half of the plume and increasing concentrations in the northern half, the recent occurrence of elevated concentrations at well 650 (156 mg/L in December 2010), some 1980 m (6,500 ft) north of the source area, indicates that sulfate has the potential to migrate farther in the alluvial aquifer than ammonia and nitrate.

The sulfate plumes illustrated in Figures D-10 through D-13 indicate that sulfate contamination at relatively high levels has been observed to the south and southeast of the New Tailings Pile area in addition to the north. Rather than originating as contamination associated with former operations at the Monument Valley site, these latter occurrences of sulfate in groundwater appear to derive naturally from the leaching of gypsum in Moenkopi Formation sandstone and associated gypsiferous soils south and southeast of former tailings areas.

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Appendix E

Active Groundwater Phytoremediation: Native Plant Land Farming

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Contents

Figures

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The Monument Valley pilot studies were designed to provide DOE and Navajo Nation policymakers with an alternative or backup remedy for the alluvial aquifer plume if, over time, natural and enhanced attenuation remedies are found to be inadequate. Native plant land farming is the alternative. At the Monument Valley site, land farming, a type of pump-and-treat remedy, involves irrigating fields of native transplants with nitrate-contaminated groundwater pumped from the alluvial aquifer.

Results show that a land farm with a crop of native fourwing saltbush shrubs should work well as a backup remedy for the plume if other remedies are found 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 remained in the soil profile, perhaps sequestered as gypsum (calcium sulfate); and the land farm produced both forage that is safe for livestock and a native seed crop that could be used by the Navajo Nation for rangeland or mine land reclamation.

LM evaluated land farming as a pump-and-treat option for the Monument Valley nitrate plume. LM considered land farming to be the most feasible active (as opposed to passive) remedy for both nitrate and sulfate in the alluvial aquifer and authorized a pilot study in 2004 (DOE 2004c). If successful as a pilot study, LM may implement land farming if, over time, monitoring shows that natural or enhanced attenuation remedies prove to be inadequate. LM considers land farming to be a form of active phytoremediation.

The land-farm pilot study at Monument Valley involved pumping plume water and irrigating a crop of native shrubs planted on land disturbed during remediation of tailings. With the land-farm option, pumping would continue until nitrate concentrations in the alluvial aquifer drop below the 44 mg/L (or 10 mg/L nitrate as N) MCL.

The land-farm pilot study was designed to serve several functions:

1. Reduce nitrate and ammonia levels in the alluvial aquifer by pumping and irrigating a native shrub crop, converting nitrate and ammonia into useful plant biomass.
2. Reduce sulfate levels in the alluvial aquifer by pumping plume water, irrigating the land farm, and sequestering groundwater sulfate as calcium sulfate in the soil profile, analogous to natural gypsiferous soils in the area.
3. Improve rangeland conditions and produce a cash crop such as native plant seed for use in rangeland revegetation or mine land reclamation.

This section is a summary of (1) a land-farm feasibility study, (2) the pilot study experimental design, (3) results of plant growth, nitrogen uptake, and water management, and (4) results of soil nitrogen and sulfur sampling after 4 years of irrigation with plume water. Appendix H addresses rangeland improvements and other beneficial uses.

E.1 Land Farming Feasibility

The feasibility of irrigating a native shrub crop to recover nitrogen and sulfur from the alluvial groundwater plume rested on several factors:

1. Existing rangeland ecology,
2. Land suitability for irrigation,
3. Adaptability of native plants for cropping,
4. Attainable nitrate levels based on irrigation and pumping rates,
5. Nitrogen uptake rates toxicity to plants,
6. Fate and potential toxicity of soil sulfate, and
7. Crop water requirements and deficit irrigation rates.

These issues were addressed through a series of investigations that included characterization of rangeland conditions and trends, irrigable land classification, discussions of grazing management options with the Navajo Nation, greenhouse studies of crop growth and nitrogen uptake, and an evaluation of potential forage quality, phytotoxicity, and farm soil contamination. Results of these investigations, documented by DOE (DOE 2004b, pp. 8-1 to 8-6), supported a plan to install a field study, in 2005, to evaluate the response of two native shrub crops to different nitrate concentrations in irrigation water.

E.2 Methods

E.2.1 Experimental Design

A factorial field experiment was designed to address several issues that DOE and Navajo Nation would need to resolve before proceeding with a large-scale native plant land farm:

- Which native crop is most efficient in using nitrate?
- What is an optimum irrigation rate to remove as much nitrogen and sulfur as possible while limiting deep percolation and leaching of contaminants back into the aquifer?
- What is the optimum nitrate concentration in irrigation water?
- Will sulfate and nitrate accumulate in the soil and in what forms?
- How productive are the crops?
- Are crops irrigated with plume water safe for livestock? (This issue is addressed in Appendix G.)

A factorial experimental design consists of a treatment structure and a design structure. The treatment structure of an experiment refers to the factors that will be compared and controlled, and design structure refers to how field plots will be arranged and how treatments are assigned to the plots (Milliken and Johnson 1992).

The treatment structure for the land farm pilot study consisted of two main factors: (1) nitrate concentration in irrigation water and (2) crops in the cropping system. Four nitrate treatment levels (as nitrate) were derived from the results of greenhouse studies (DOE 2004b; pp. 8-7 to 8-9): 250 mg/L, a level not likely toxic to crop plants or to livestock feeding on the crop; 500 mg/L, a level not likely toxic to crops but possibly toxic to livestock; 750 mg/L, a level possibly toxic to crops; and a clean water control. Two native shrubs, fourwing saltbush (*Atriplex canescens,* or ATCA) and black greasewood (*Sarcobatus, vermiculatus* or SAVE) were selected as crop plants. Seedlings grown from locally collected seed in a greenhouse were transplanted on a 2 m grid spacing.

A randomized split-block design structure developed for the study (Figure E-1) consisted of a 50 × 100 m area divided into four blocks. Four plots in each block received the four different nitrate levels. Each plot was split at random and planted, half with fourwing saltbush and the other half with black greasewood, for a total of 32 equal-size split-plots receiving four replications of 8 different treatment combinations (nitrate level × crop). Figure 1 in the report shows the location of the land farm pilot study as it appeared in 2010.

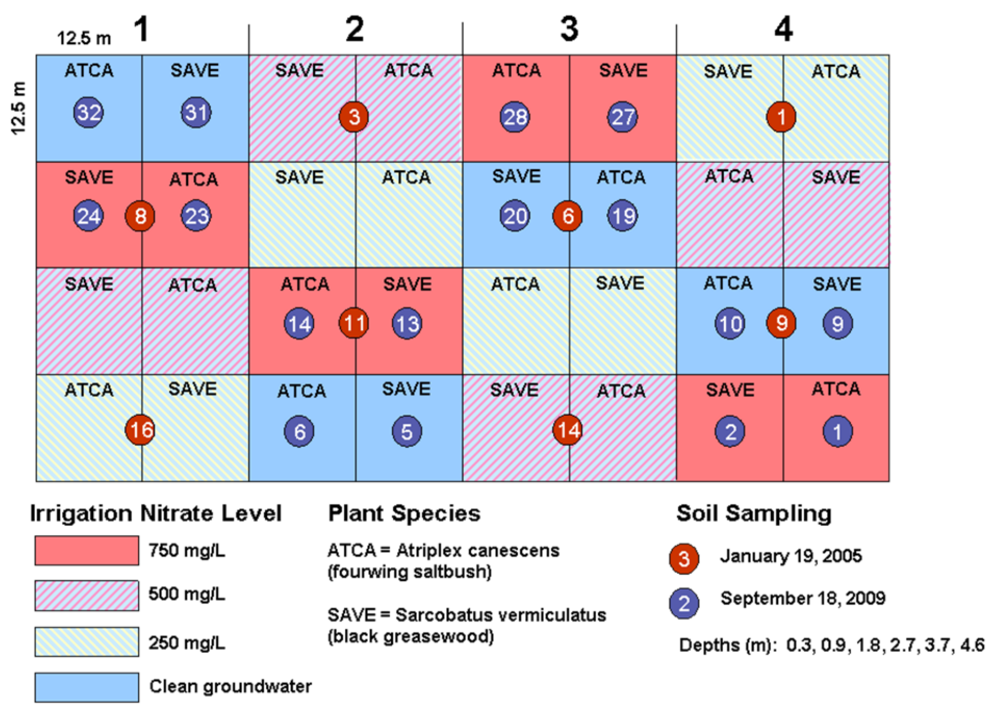


Figure E-1. Illustration of randomized split-block experimental design showing plots for nitrate treatment levels and shrubs species, and soil sampling locations and times.

E.2.2 Irrigation System

Water was delivered to the land farm from two wells: clean water pumped from well 618, a DeChelley aquifer well, and nitrate-contaminated water pumped from well 649, a well completed in 2000 in relatively high-nitrate alluvial groundwater about 283 meters directly north of the land farm. The four nitrate levels were achieved using a drip irrigation system with solenoid valves that alternated between well 618 and well 649. Plants in the control or no nitrate plots received 1 gallon of "clean" water per day from well 618. Plants in the 250 mg/L nitrate plots were irrigated for 30 minutes with water from well 649 and 90 minutes with water from well 618 for a total of 1 gallon per day. Plants in the 500 mg/L nitrate plots were irrigated for 90 minutes with well 649 water and 30 minutes with well 618 water. Plants in the 750 mg/L plots received 1 gallon of contaminated water per day from well 649. Irrigation of the land-farm plots began in fall of 2005.

In May 2006, pumping from well 649 was drawing down the groundwater elevation causing the pump to suck air before completing its 2-hour pumping cycle. Hence, the plots assigned the higher nitrate concentrations were receiving less irrigation water than the others. Lowering the pump in the well did not alleviate the problem, nor did splitting the irrigation cycle. As a result, the treatment structure and irrigation schedule were modified to regain consistency in irrigation volumes across all plots. Beginning in May 2007, only plots assigned the 750 ppm nitrate level received plume water from well 649, while all other plots received clean water from well 618.

E.3 Results

E.3.1 Crop Growth, Transpiration, and Nitrogen Uptake

The pilot study results show that during a 4-year monitoring period, fourwing saltbush was superior to black greasewood as a phytoremediation crop. For all treatment combinations, fourwing saltbush had lower mortality rates, grew larger, had greater leaf area and transpiration rates, and took up more nitrogen than black greasewood. Comparisons were made in 2006 and again in 2010 using different methods.

E.3.1.1 2006 Results

In October 2006, survival, growth, and productivity for the different combinations of crops and nitrate irrigation levels were compared. A total of 60 randomly distributed plants (3−5 plants per plot) were measured. Shrub canopy area was estimated from cross-sectional diameters using the formula for an ellipsoid. Plant volume was estimated using the formula for a hemispheroid. Above-ground biomass and total N were estimated based on a canopy volume-weight relationship established previously. Total N was determined by combustion using a CNS-2000 analyzer for 16 individual plants harvested per plot. Plant survival was estimated by census.

In June 2006 we noted that many of the plants had been eaten down by rabbits. Efforts to replace them with new seedlings failed. Black greasewood suffered more from herbivory than fourwing saltbush. Protecting plants in biodegradable mesh cages, in fall 2006, was successful.

Nitrogen uptake was significantly ($P < 0.05$) greater for fourwing saltbush plants harvested from the 750 mg/L nitrate plots compared to plants receiving clean water (DOE 2007; p 3-27). However, estimates of total biomass were not significantly different among treatments, most likely due to variation in irrigation amount and not a response to nitrate toxicity. Plants receiving 750 mg/L nitrate took up no more N than plants receiving 250 mg/L nitrate, reflecting differences in plant growth responses to irrigation.

E.3.1.2 2010 Results

Plant cover and leaf area in the land-farm plots were evaluated in 2010 using a Quickbird satellite image (Figure E-2). The sharp contrast between the bright false-color red fourwing saltbush plots and the adjacent mostly bare black greasewood plots, visible as a checkerboard pattern in Figure E-2, clearly illustrates the greater abundance of fourwing saltbush.

Figure E-2. July 10, 2010, Quickbird image composed of pan-sharpened black-and-white and red-blue-green bands plus the near infrared (NIR) shown in false-color red to highlight plants. Block numbers and plot boundaries, corresponding to Figure E-1, are highlighted in white.

LAI and plant canopy cover were estimated using Quickbird data that was calibrated and validated against ground monitoring data. LAI, defined as green leaf area per unit ground area, is often used to estimate transpiration rate. By 2010, the LAI of fourwing saltbush (LAI ≈ 5.0) plots was significantly greater ($P < 0.001$) than the black greasewood LAI (LAI ≈ 2.0 - 3.0) for all nitrate treatments (Figure E-3A). Percent cover, defined as the percentage of ground surface area beneath or "covered" by plant canopy, was more variable but also significantly greater ($P < 0.001$) in fourwing saltbush plots (Figure E-3B).

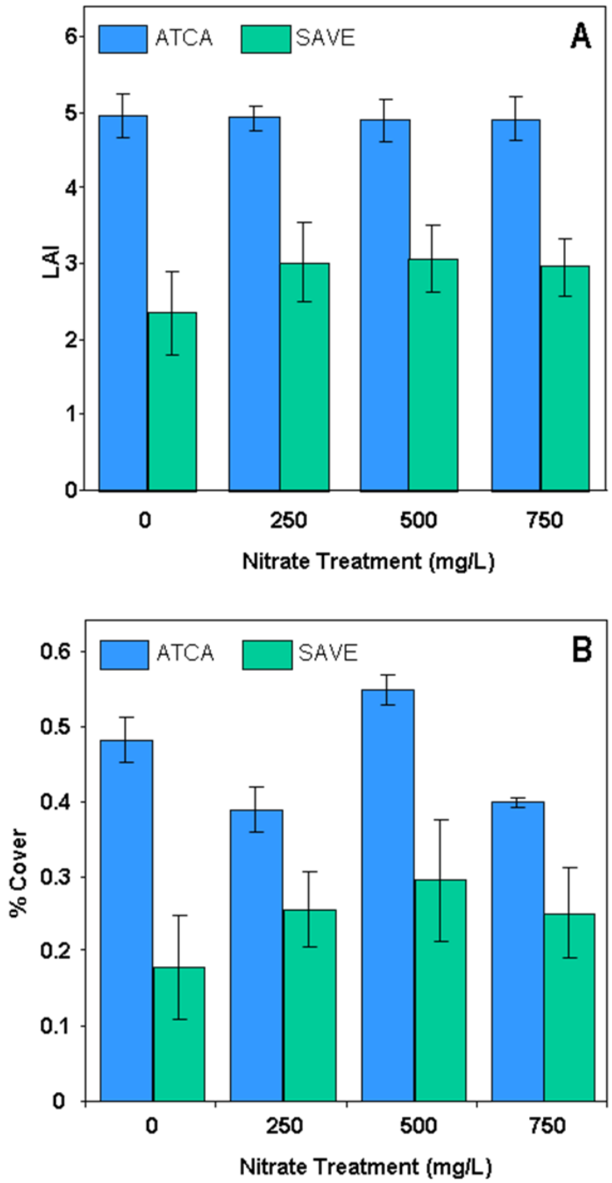
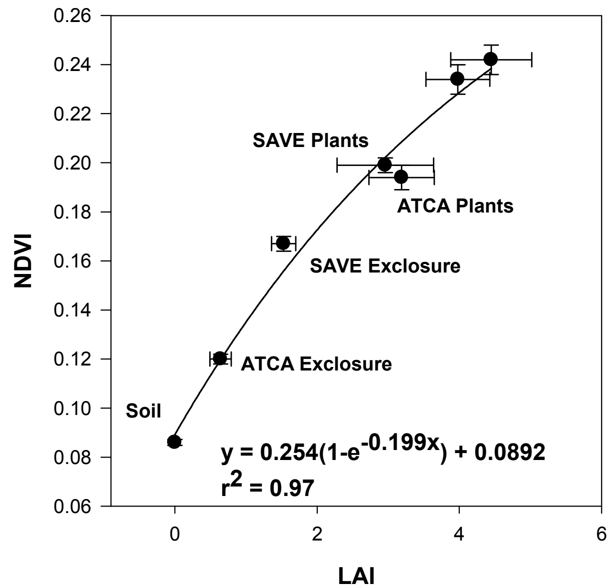


*Figure E-3. (A) Leaf area index (LAI) and (B) percent cover of fourwing saltbush (*Atriplex canescens*, or ATCA) and black greasewood (*Sarcobatus vermiculatus*, or SAVE) for irrigation water nitrate treatments. Bars are one standard error of the mean. Analysis of variance (ANOVA) results show that species differences are significant at P < 0.001.*

Field observations revealed that much of the LAI and percent cover in the black greasewood plots, estimated using Quickbird, is attributable to volunteer fourwing saltbush plants. The Quickbird analysis did not differentiate the two species. Therefore, differences in the LAI and percent cover of the two species were likely greater than the Quickbird interpretation indicates.

Estimates of LAI and percent plant cover were derived from a July 2010 Quickbird satellite image with 0.5 m resolution in the visible spectrum and 2 m resolution for the NDVI. NDVI is calculated from red and NIR bands. Percent cover was estimated by classifying pixels as either bare soil or vegetation using a program in ERDAS software (www.erdas.com). Estimates using this approach were compared to cover estimated from a visual inspection of images using a point intercept method (Figure E-4).



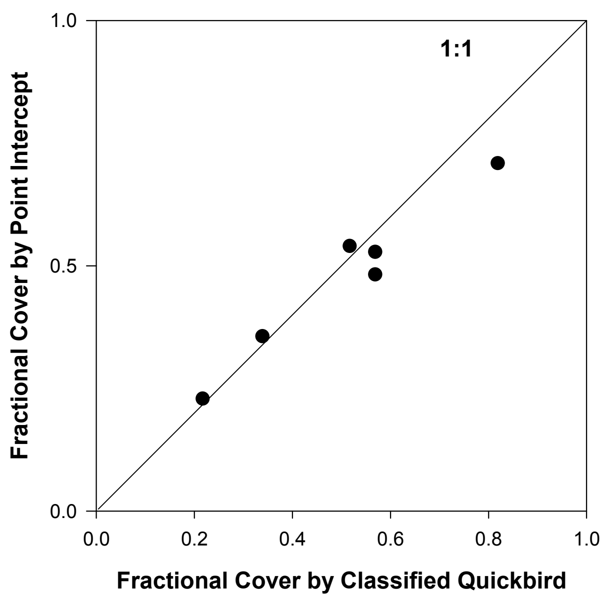


Figure E-4. Top: LAI measured on the ground by leaf harvesting versus NDVI using Quickbird. Bottom: Fractional cover estimated visually on Quickbird using a point intercept method versus an automated method using a pixel classification program in ERDAS.

LAI was calculated from NDVI in areas of interest using a regression of LAI values measured in 2007 with a Licor 2000 LAI Meter against leaf harvesting data. LAI was measured on individual plants and extended to stands of plants by multiplying LAI by fractional cover determined on the July 2010 Quickbird image (Figure E-4).

Although survival and growth of fourwing saltbush far exceeded black greasewood during the 5-year study, greasewood may take longer to establish and so, over a longer period of time, may close the gap with fourwing saltbush. By 2010, the few 11-year old greasewood seedlings planted in 1999 in the source area (Appendix B) were about the same size as their fourwing saltbush neighbors.

E.3.2 Soil Water Monitoring

Volumetric soil water content (θ) was monitored monthly during the growing season from March 2006 through October 2010 using a neutron hydroprobe (Gardner 1986). Thin-walled polyvinyl chloride access tubes, 457 cm deep by 5.7 cm i.d., were installed in 16 locations in 2002 during construction of an earlier land-farm study (DOE 2002). DOE terminated the earlier study before the installation was complete. In the current experimental design, eight access tubes occur within ATCA plots and the other eight within SAVE plots. Neutron counts were recorded at depths of 30, 61, 91, 122, 152, 183, 213, 244, 274, 305, 335, 366, 396, 427, and 457 cm.

The neutron hydroprobe was calibrated in barrels using soils from Monument Valley, compacted to achieve the bulk density of the land-farm soil, and wetted incrementally to prescribed gravimetric water contents. The calibration produced the following linear relationship:

$$\theta = 1.93 \times 10^{-5} * (\text{neutron count} - 1.81 \times 10^{-2})$$

Soil water storage (S) was calculated from neutron hydroprobe measurements of θ using a trapezoidal approximation by Green et al. (1986) as follows:

$$S = \theta_1 Z_1 + \sum_{i=2}^{n} [(\frac{\theta_{i-1} + \theta_i}{2})(Z_i - Z_{i-1})]$$

where:
θ_1 and Z_1 are the water content and depth for the uppermost measurement
θ_i is the volumetric water content measured at the *i*th point in the profile
Z_i is the depth of the *i*th point in the profile
n is the total number of points.

Soil profiles were significantly drier in ATCA plots than in SAVE plots, reflecting the higher survival, productivity, and transpiration of ATCA as a land-farm crop. Mean values of θ for ATCA (0.11) and SAVE (0.14), averaged over all plots, depths, and months, were significantly different at $P < 0.001$. Mean values of S for ATCA (691 mm) and SAVE (929 mm) were also significantly different at $P < 0.001$.

Time series of soil water storage (S) over the 4-year monitoring period reflect contrasts in the growth and development of ATCA and SAVE crops (Figure E-5). The SAVE plots started out slightly wetter than ATCA plots. However, after irrigation commenced, S values increased steadily over the first two years for both species. But in 2008, the third growing season, the ATCA plots began to dry while the SAVE plots continued to get wetter. This is likely attributable to an increase in leaf area and transpiration by ATCA as illustrated in Figure E-2.

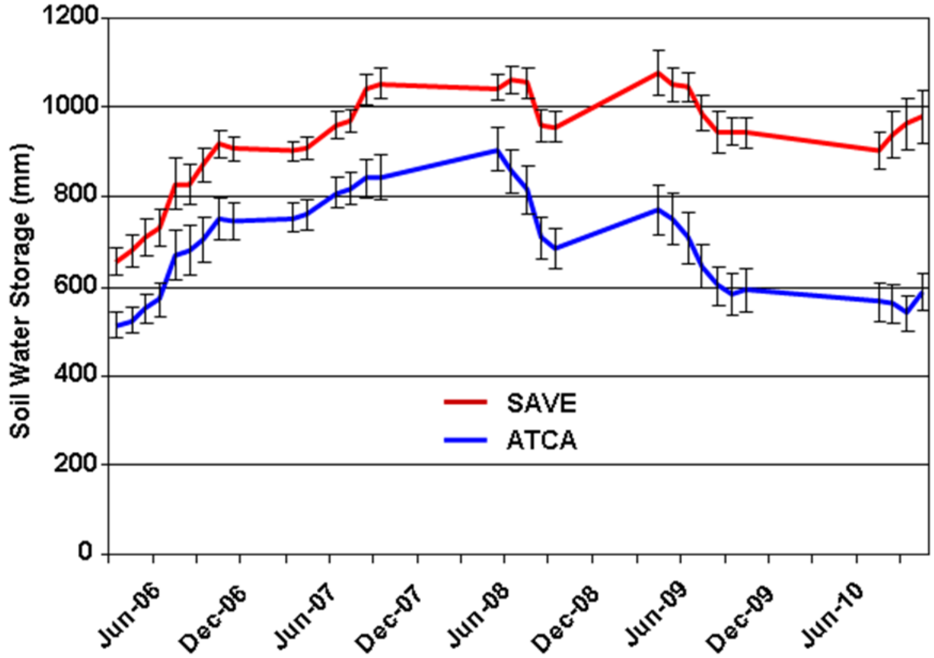


Figure E-5. Changes in soil water storage in Sarcobatus vermiculatus *(SAVE) and* Atriplex canescens *(ATCA) land-farm plots monitored monthly during the growing season using a neutron hydroprobe. Error bars = standard error of the mean.*

By 2010, ATCA that had volunteered in the SAVE plots were maturing and leaf area (Figure E-3) and transpiration rates were likely high enough to cause the slight drop in water storage (Figure E-5).

E.3.3 Soil Nitrogen and Sulfur

Land-farm soil sampling data show that irrigation with plume water resulted in little if any accumulation of soil nitrate, probably due in part to plant uptake and denitrification in the fourwing saltbush plots, and in part to leaching in plots where transpiration was inadequate. However, irrigation with plume water did result in an accumulation of sulfate in the soil profile, and perhaps sequestration as calcium sulfate (gypsum).

Soil profiles in the land farm were sampled in 2005, at the beginning of the study, and again in 2009 (Figure E-1). The objective of the 2005 sampling, which occurred before the design layout was finalized, was to develop mean baseline levels of nitrate, ammonia, and sulfate and to map spatial distributions in the land farm. Soil profiles were sampled at eight locations. The objectives in 2009 were (1) to determine changes in mean soil levels of nitrate, ammonia, and sulfate over time and (2) to test for treatment effects. In 2009, soil profiles were sampled in the center of all plots receiving clean water and 750 mg/L nitrate water. During both sampling events and at all sampling locations, samples (approximately 500 g each) were removed from the soil profile at depths of 0.3, 0.9, 1.8, 2.7, 3.7, and 4.6 m (1, 3, 6, 9, 12, and 15 ft) using a 50-millimeter (2-inch) diameter hand auger.

Figure E-6 and Figure E-7 map soil nitrate and sulfate distribution in the land farm in 2005. The maps, created using EVS software, are mean concentrations of nitrate and sulfate for all depths at each sampling location. Results show that baseline concentrations of both nitrate and sulfate varied considerably across the site, ranging from < 5.6 µg/g (detection limit) to 778 µg/g for nitrate as nitrogen, and from < 25 µg/g (detection limit) to 4,185 µg/g for sulfate. The high spatial variability in soil nitrate and sulfate in 2005 may have masked detection of some treatment effects when soil profiles were sampled again in 2009.

Figure E-8 compares 2005 with 2009 mean values of soil nitrate, ammonia, and sulfate for all treatments combined. Values are means for all depths and locations. Analysis of variance (ANOVA) results show that mean ammonia-N and nitrate-N values changed little over four years of irrigation, but sulfate levels were significantly less by 2009 ($P < 0.001$), possibly due to leaching in the black greasewood plots. An ANOVA evaluation of treatment effects in 2009 indicated that soil sulfate levels were significantly greater ($P < 0.001$) in plume water plots than in clean water plots, suggesting an accumulation of sulfate from irrigation with plume water. Results also show that mean nitrate-N levels are significantly different for water and plant treatments at $P < 0.1$. Figure E-9 values are means of all depths for each treatment.

The source of treatment effects on soil nitrate-N depicted in Figure E-9 was clarified by comparing profiles of nitrate concentrations with depth (Figure E-10). ANOVA results show that nitrate-N levels in the lower soil profile of the ATCA (fourwing saltbush) plots were significantly greater than all other upper or lower profiles ($P < 0.001$). One interpretation of the nitrate profiles, and the overall loss of sulfate between 2005 and 2009, is that the poor growth and low transpiration in SAVE (black greasewood) plots allowed leaching of nitrate and sulfate whereas high productivity and transpiration in ATCA (fourwing saltbush) plots limited leaching and caused nitrate accumulation in the lower profile.

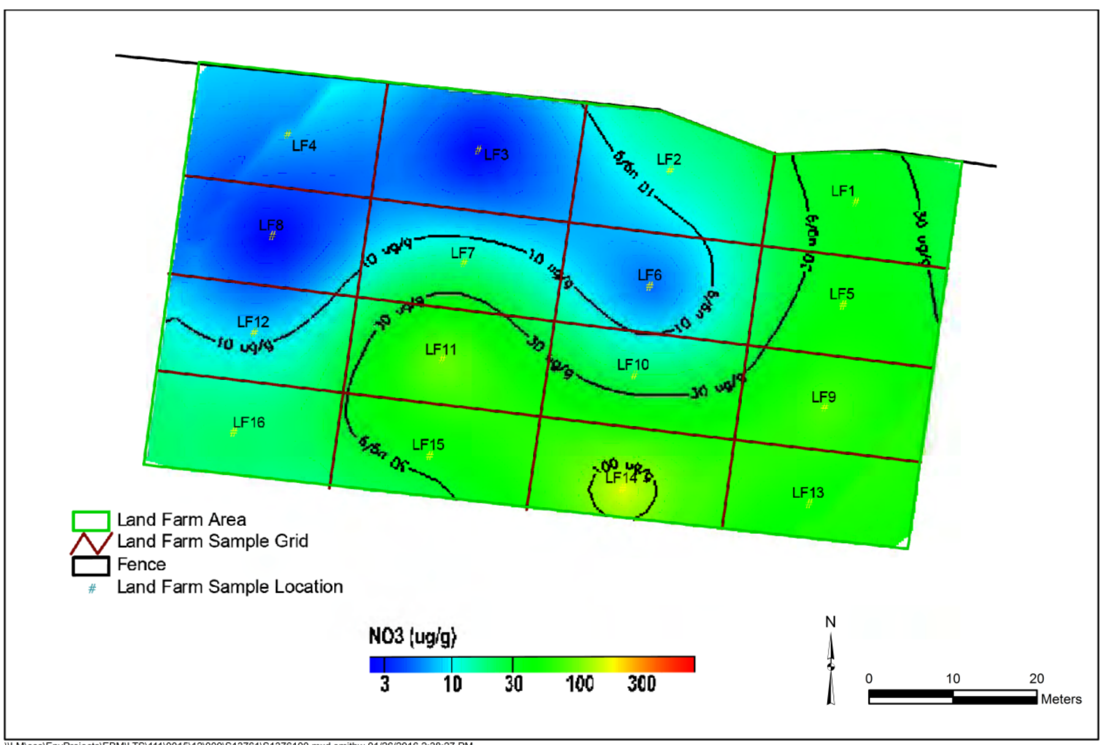


Figure E-6. Map of baseline soil nitrate distribution in the land farm created using mean concentrations at each sampling location.

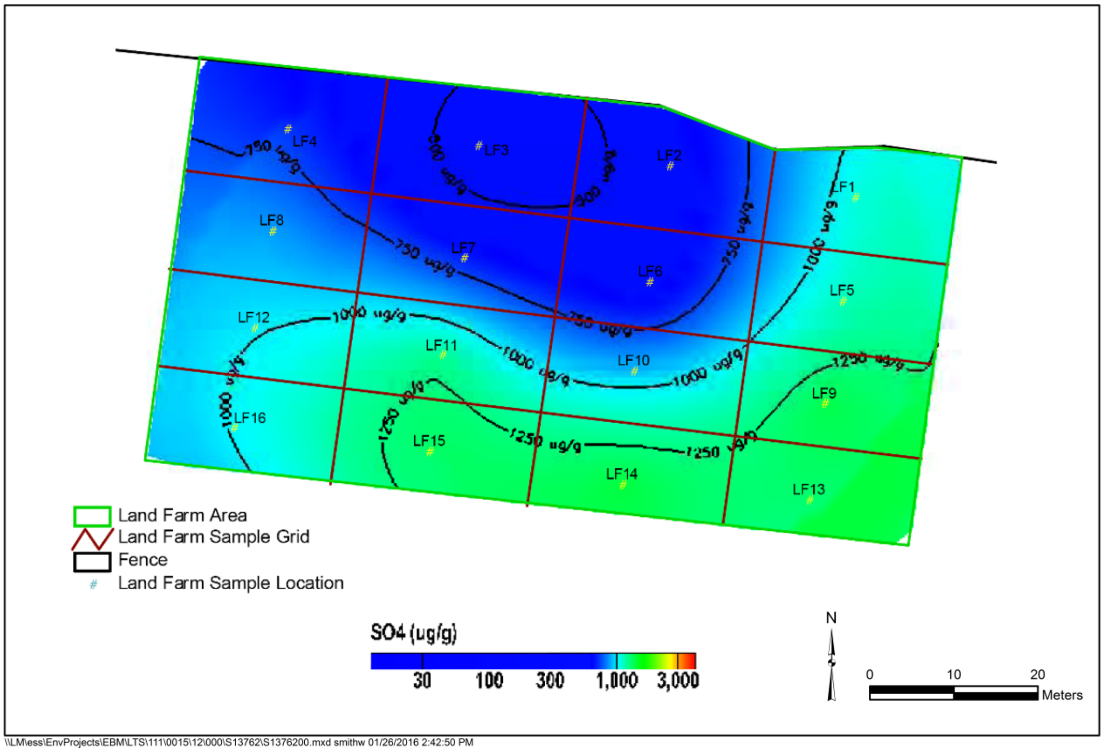


Figure E-7. Map of baseline soil sulfate distribution in the land farm created using mean concentrations at each sampling location.

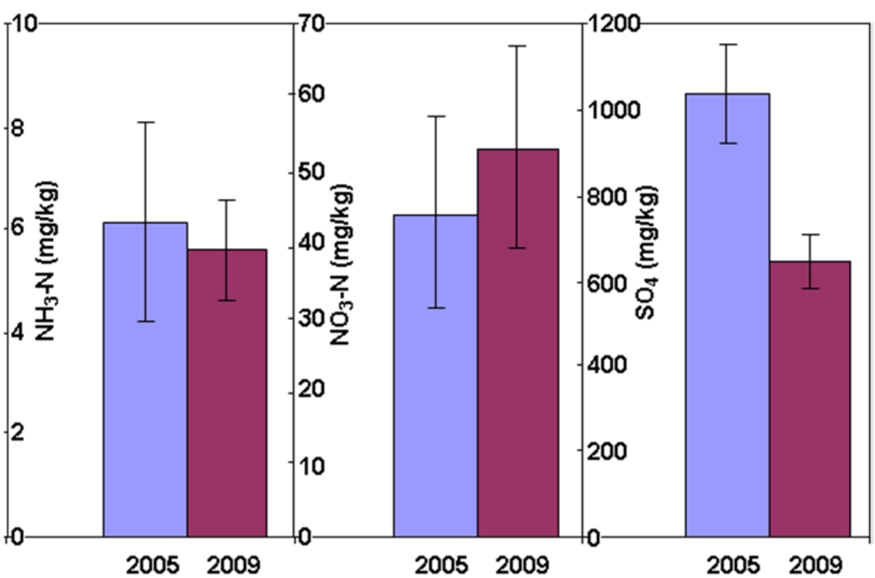


Figure E-8. Comparison of mean soil ammonia-N, nitrate-N, and sulfate concentrations for combined treatments in the land farm study in 2005 and 2009.

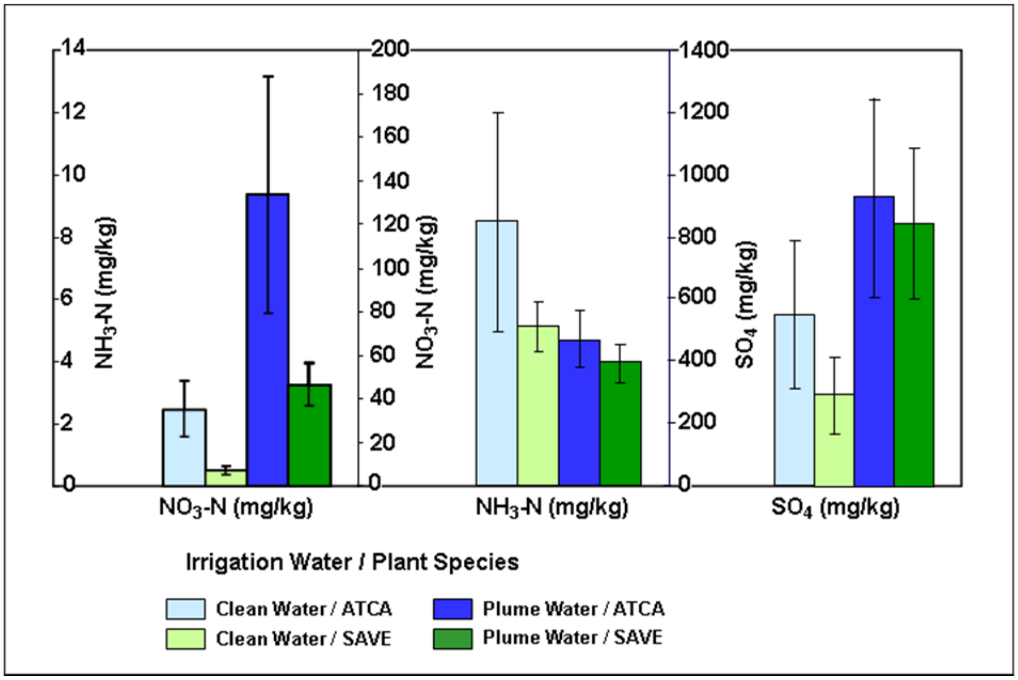


Figure E-9. Comparisons of soil ammonia-N, nitrate-N and sulfate levels in 2009 for the different irrigation water and plant treatments in the land farm study.

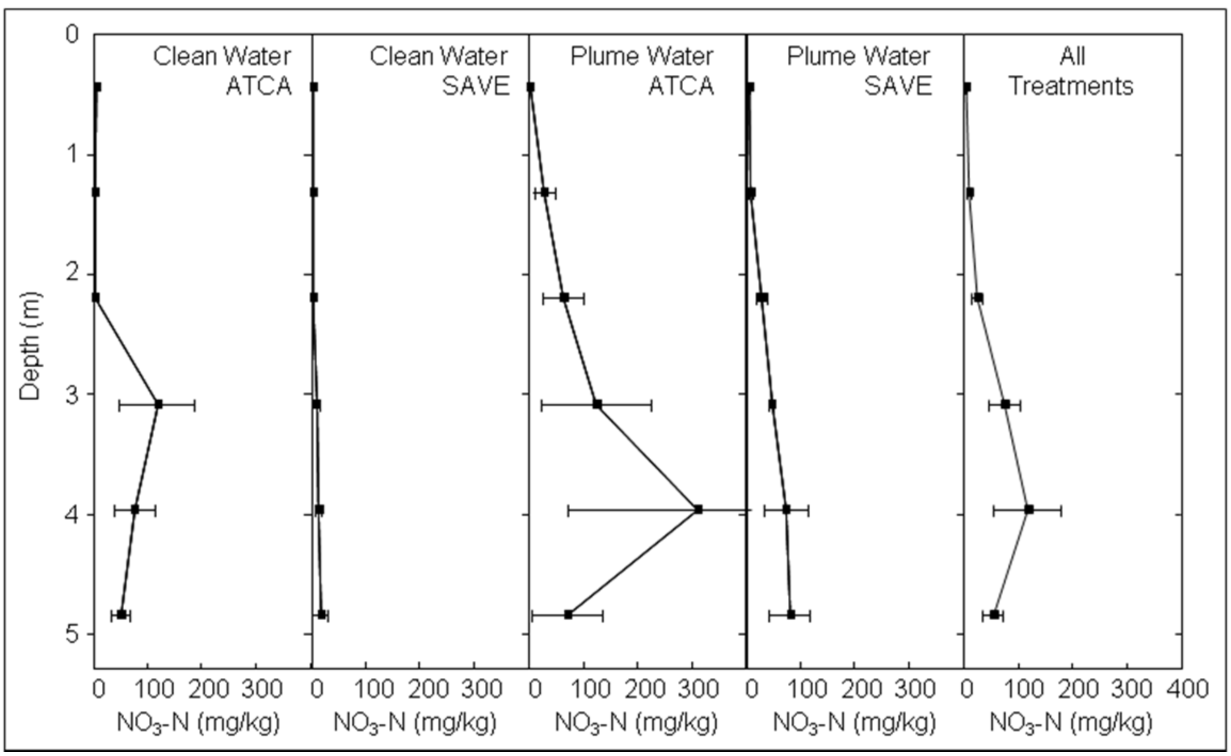


Figure E-10. Mean soil nitrate-N with depth for irrigation water and plant treatments in the Monument Valley land farm study.

Appendix F

Remote Sensing Monitoring of Phytoremediation

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A remote sensing protocol was developed as an efficient means for long-term monitoring of vegetation and ET. If phytoremediation becomes part of the final remedy for the source area or the plume, phreatophyte health and transpiration would be key long-term indicators of remedy performance. Development of the remote sensing protocol involved calibration of satellite images with important characteristics of vegetation as measured on the ground. Satellite images included annual Quickbird and Landsat images, and 16-day images from the Moderate Resolution Imaging Spectrometer (MODIS) sensors on the Terra satellite. The key vegetation performance indicators are leaf area index, fractional vegetation cover, and plant water use (ET).

The successful calibration allowed project scientists to quantify and compare—on a landscape scale—effects of grazing and revegetation practices on phreatophyte health and phytoremediation performance. Prior to the pilot studies, much of the Monument Valley site landscape had been heavily grazed, leaving populations of native phreatophytes (fourwing saltbush and black greasewood) in poor ecological condition. Over the past 10 years, however, livestock numbers and grazing pressure has been reduced over the site, and, using the remote sensing protocol, project scientists have quantified improvements in the health, fractional cover, and ET of phreatophyte populations. Results show that, as a consequence of improved grazing practices, the plume area appears to have converted from an area of recharge (less water used by plants than arrives as precipitation) to one of discharge (plant water use exceeds precipitation), indicating that water from the plume is being removed. This is good news with respect to phytoremediation. A healthy plant community may be capable of slowing or stopping the further migration of the contaminant plume.

The Monument Valley site covers about 230 ha, including the source area and the surface footprint over the contamination plume in the alluvial aquifer. Vegetation can play a key role in controlling the water balance of a desert site such as Monument Valley (Naumber et al. 2005; Nichols 1993, 1994, 2000). The two dominant shrubs at the site are *Sarcobatus vermiculatus* (SAVE) and *Atriplex canescens* (ATCA), both of which are phreatophytes that extract water from the vadose zone as well as the alluvial aquifer (Jordan et al. 2008). When these shrubs are protected from grazing they can develop abundant plant cover (McKeon et al. 2006) with high transpiration rates (Glenn et al. 2009). As phreatophytes, populations of these species, when healthy, can transpire more water than arrives as precipitation, with the difference extracted from groundwater. Theoretically, this groundwater discharge will slow or reverse the spread of groundwater contamination away from the source area. Then again, this site has a history of heavy grazing by livestock, which can greatly reduce plant health and transpiration rates, potentially accelerating the spread of contaminants away from the source area due to recharge of the aquifer from percolation of precipitation over the site and runoff from adjacent uplands.

Contaminants in the source area soils and in the alluvial aquifer include nitrate, ammonium, and sulfate. Concentrations of all three appear to be gradually decreasing due to natural attenuation processes as characterized by monitoring and modeling (Appendix D). However, natural or even enhanced attenuation of the source area and plume will likely take several decades (Appendix C). A healthy plant community may reduce the risk that contaminants will migrate further away from the site during this time. Therefore, monitoring the progress of natural and enhanced attenuation should include tracking the health or condition of phreatophyte populations in response to changing land management practices.

Remote sensing can provide economical, long-term, non-intrusive monitoring of phreatophyte health and water use. This section is an overview of the methods project scientists used to develop a monitoring protocol. The methods essentially are a calibration of fractional vegetative cover, LAI, and ET as measured extensively on the ground at the site from 1999 to 2010, and as measured by satellite imagery. More complete documentation of the methods development is appended as a technical journal manuscript. In addition to describing methods development, this section also gives an overview of the application of the protocol to document changes from 2000 to 2010 in phreatophyte cover, ET, and the site water balance in response to changing grazing management practices and the maturation of phytoremediation plantings.

F.1 Land Areas Monitored

Pilot remediation studies at the site are documented in DOE Status Reports (Appendix I). Figure F-1 and Figure F-2 show different natural and planted vegetation units that were of importance for the pilot studies. In 1999, a 1.7 ha plot, designated the Old Field, was established in the fenced source area that included the former New Tailings Pile and evaporation ponds. This area was planted primarily with fourwing saltbush shrubs with about 1 percent black greasewood shrubs, on a 2 m × 2 m spacing. These plantings have been drip-irrigated each growing season since 1999, from April to October, with between 0.16 to 0.36 m yr^{-1} of non-contaminated water. This Old Field was established over hot spots of soil nitrate and ammonium contamination. Additional areas to the north, south, and west of the plot, and over the former evaporation ponds, were planted in 2006 based on additional contaminant surveys (Appendix B). In Figure F-2 these areas are designated New Fields North, West, South and Evaporation Pond (EP), respectively, for a total area of 1.6 ha. These plantings have been drip-irrigated since 2006 similar to the Old Field.

Four small grazing exclosure plots (50 m × 50 m fenced areas) were also established to determine vegetation response to grazing exclusion (Appendix C, Section C.1.3). Two of these, designated ATCA Exclosure and SAVE Exclosure, were established in 2005 around existing plant communities overlying the alluvial aquifer plume. Two more plots, designated East Exclosure and West Exclosure, were established in 2006 in an area that had been denuded. These plots were also planted primarily with fourwing saltbush shrubs on a 2 m × 2 m spacing and drip irrigated similar to the other plantings. In addition, an irrigated area designated Pilot Farm (50 m × 100 m) containing small plots of fourwing saltbush and black greasewood was established to evaluate whether irrigating fields of native transplants with nitrate-contaminated water pumped from the alluvial aquifer could be used as an alternative groundwater remedy.

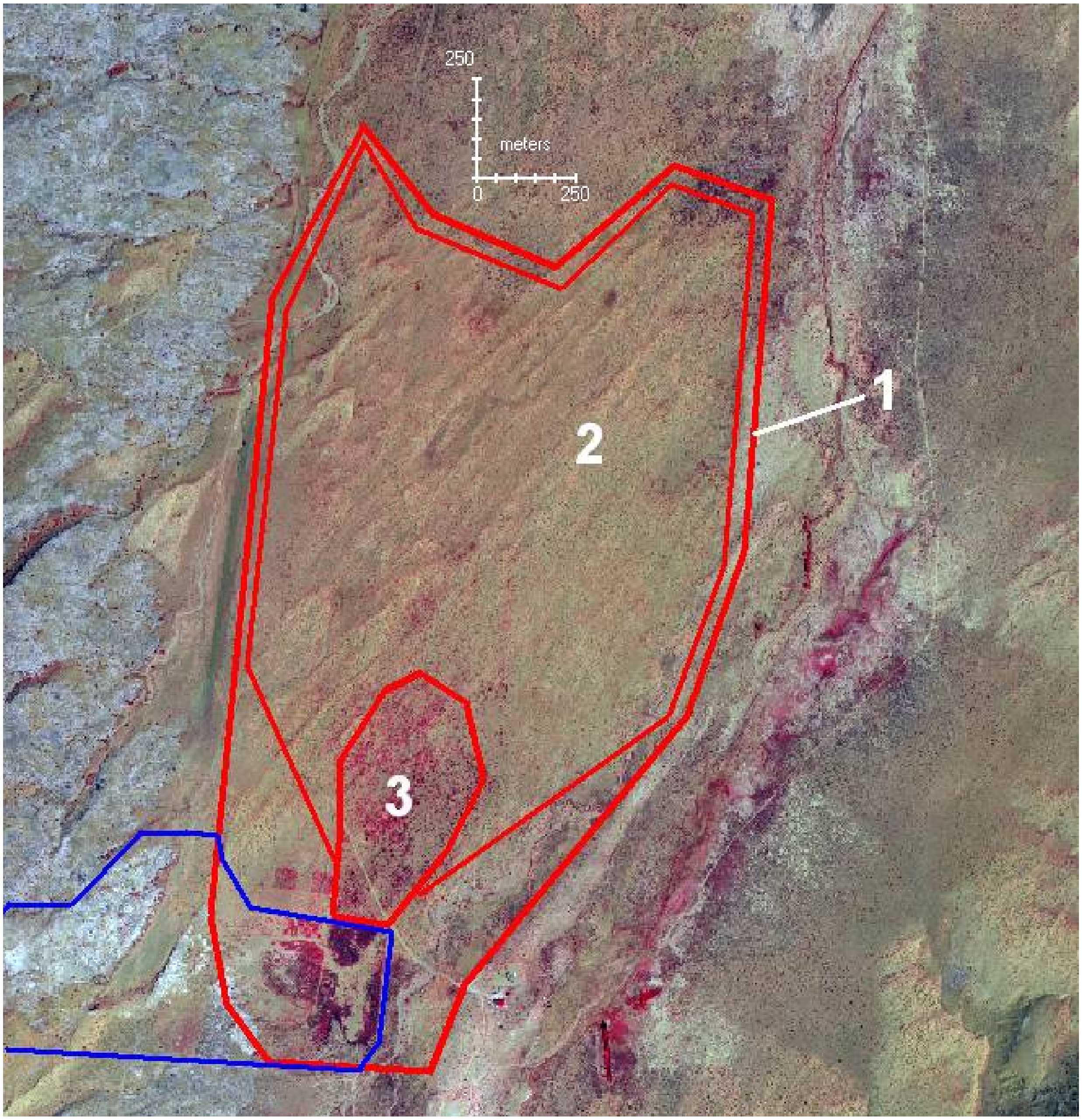


Figure F-1. Areas of interest at the Monument Valley site: (1) the whole site; (2) the Outside ATCA zone; and (3) the Outside SAVE zone. The blue line shows the fence line around the source area.

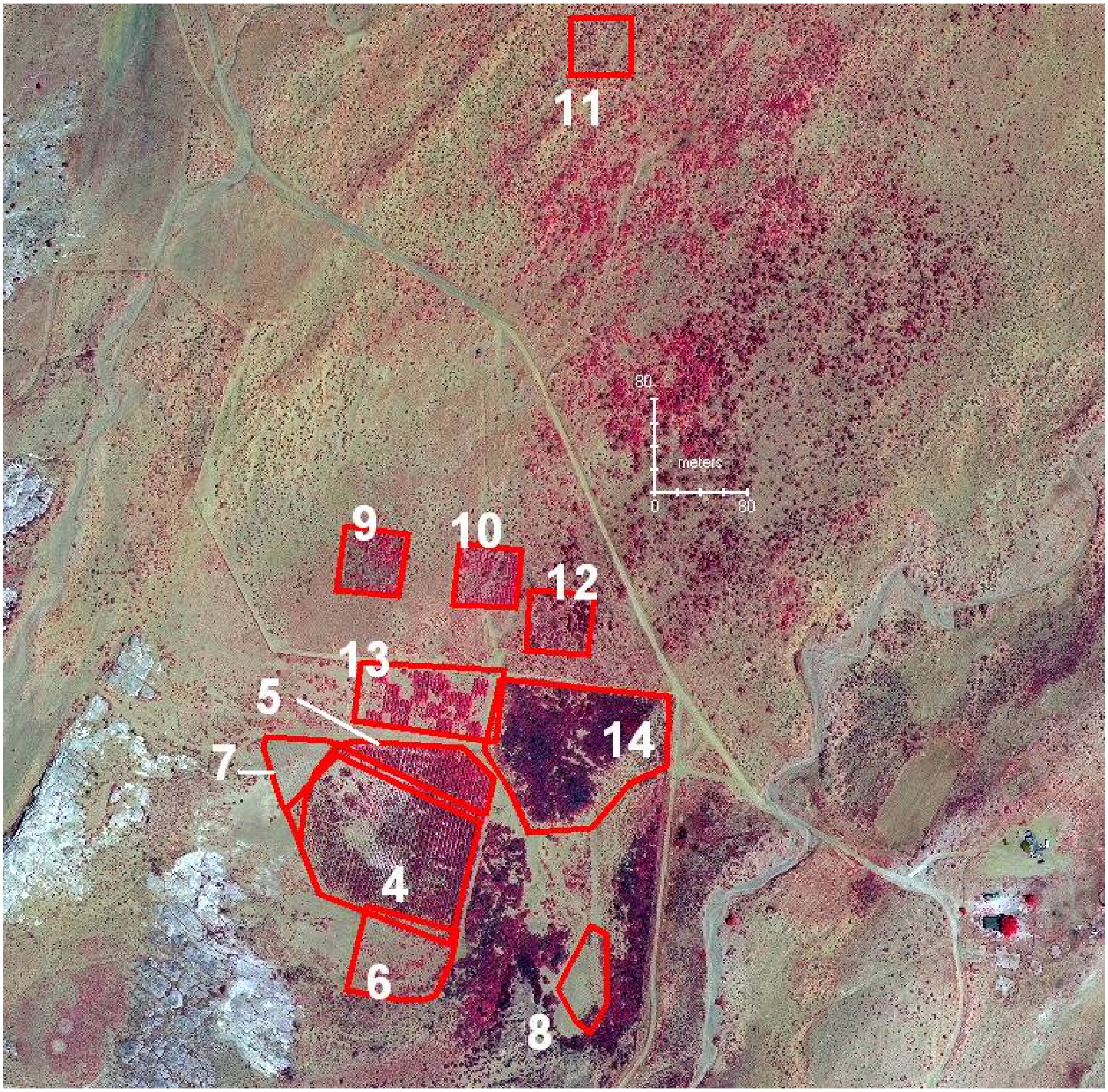


Figure F-2. Areas of interest at the Monument Valley UMTRA site: (4) the Old Field; the New North (5), New South (6), New West (7), and Evaporation Pond Fields (8); irrigated and planted West (9) and East (10) livestock exclosures; unirrigated exclosures in natural stands of ATCA (11) and SAVE (12); the pilot land farm (13); and a volunteer stand of ATCA (14) inside the source area fence.

Additional areas of interest in Figure F-1 and Figure F-2 are a stand of volunteer fourwing saltbush plants that established inside the site fence and immediately adjacent, a natural stand of dense, mainly black greasewood plants north of the fence, designated Outside SAVE. Sparse stands of mainly fourwing saltbush plants, designated Outside ATCA, dominated the area overlying the plume to the north.

F.2 Ground Vegetation Surveys

Annual surveys of plant cover, LAI, and standing biomass were conducted from 2000 to 2010 within the areas shown in Figure F-1 and Figure F-2. In 2006 and 2007, transpiration of individual fourwing saltbush and black greasewood plants were measured, using sap flux sensors, in the ATCA and SAVE Exclosure plots and on adjacent grazed plants (Glenn et al. 2009). Although sap flux sensors measure just the transpiration component of ET, the site soil is normally dry and direct evaporation from the soil is assumed to be fairly low, so, by convention, the term ET is used in this report for water loss through the plants. Livestock stocking rates were not directly monitored during this period, but from 2000 to about 2004, grazing pressure was significant, as indicated by poor plant health. After the green-up of shrubs in May and June each year, sheep, cattle, and horses grazed the new growth of both species, removing most of the new leaves and even pruning back new and old shoots. Starting in 2005, grazing pressure appeared much lower. In addition, the source area has been fenced since 1999, excluding grazing except occasionally when fences are down and animals enter.

F.3 Remote Sensing Methods

Time-series imagery from 2000 to 2010 was obtained from the MODIS sensors on the Terra satellite (250 m resolution). This satellite has nearly daily coverage of the globe and data are supplied as preprocessed vegetation indices or other products in 16-day composite increments. Project scientists used the MOD13Q1 Enhanced Vegetation Index (EVI) product for analyses of ET. EVI data were combined with maximum daily temperature data (obtained from the PRISM website) to calculate ET using an algorithm calibrated with sap flux data collected onsite (Glenn et al. 2009). Visual changes in site vegetation were also analyzed using Landsat TM-5 images obtained in the summers of 2000, 2005, 2007, and 2009.

Fine-level estimates of percent cover and LAI were made on Quickbird satellite images obtained for the summers of 2006, 2007, 2009, and 2010, with 0.5 m resolution in visible and 2 m resolution for the NDVI, calculated from red and NIR bands. Percent cover was estimated by converting pixels into two classes, representing bare soil or vegetation, using an unsupervised classification program in ERDAS software. The accuracy of the classification system was tested by comparing these estimates of groundcover with estimates determined by visual inspection of images using a point intercept method. This was accomplished for areas representing a wide range of cover conditions by placing a grid over the area of interest on the Quickbird image and scoring each grid intersection as either vegetated or bare soil in Adobe Photoshop. The same areas were then classified in ERDAS to determine percent cover by the automated method.

LAI was calculated from NDVI in areas of interest using a regression of measured LAI values from a Licor 2000 LAI Meter in 2010 and leaf harvesting methods in 2007. LAI was measured on individual plants and was extended to stands of plants by multiplying LAI by fractional cover determined on a Quickbird image acquired on July 10, 2010.

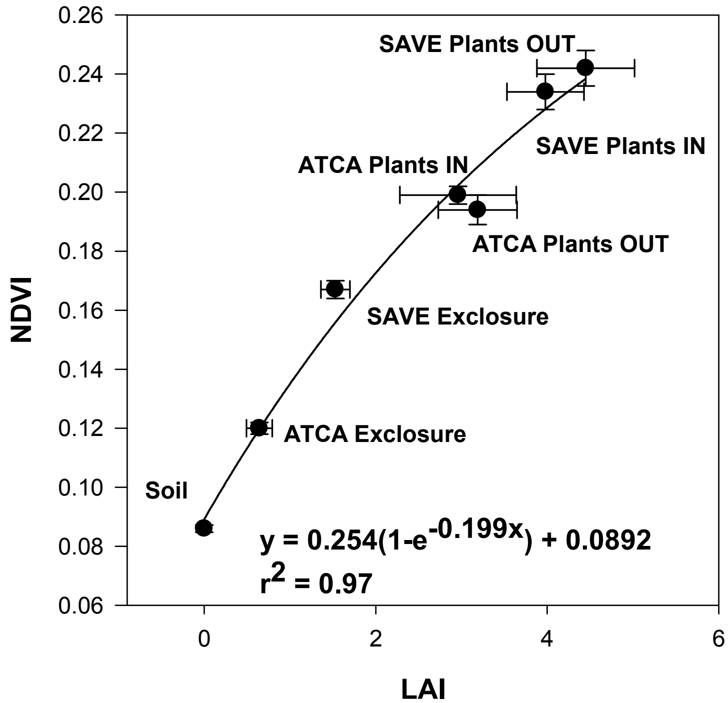
F.4 Vegetation Monitoring Results

F.4.1 Site Conditions in 2010 by Quickbird

Ground measurements of LAI determined by leaf-harvesting methods were accurately predicted by NDVI values (Figure F-3A). Fractional cover determined on a two-class Quickbird image had a near 1:1 correspondence with percent cover determined by ground transect methods (Figure F-3B). Table F- 1 gives NDVI, percent cover, and LAI values for areas of interest in Figure F-1 and Figure F-2. The Old Field and Inside ATCA areas had high cover but low LAI. Both of these stands had grown to exceed their water supply and were undoubtedly water stressed. They were also composed of older plants that had accumulated a great deal of thatch and woody stem material within the stands. The most vigorous planted area was the New Field North, with 60.1 percent cover and an LAI of 1.65. The other New Field areas had lower cover and LAI, especially the New Field West, perhaps due to chemical contaminants in the soil that also affected portions of the Old Field. The irrigated plants in the East and West Exclosures and the Pilot Farm also had high cover and LAI. The unirrigated ATCA and SAVE Exclosures each had higher cover and LAI than unprotected plants in Outside SAVE and Outside ATCA zones, showing that protection from grazing enhances plant growth. Over the whole site, plant cover averaged 31.2 percent and LAI was 0.65. Fourwing saltbush and black greasewood accounted for about half of the total vegetation cover as determined by ground transect methods.

Table F- 1. NDVI, percent vegetation cover, and leaf area index for areas of interest at the Monument Valley site based on analysis of a July 10, 2010, Quickbird satellite image.

Site No.	Description	NDVI	Cover (%)	LAI
1	Whole Site	0.172	31.2	0.65
2	Outside ATCA	0.175	29.0	0.70
3	Outside SAVE	0.193	40.9	0.97
4	Old Field	0.143	51.4	0.69
5	New Field North	0.230	60.1	1.65
6	New Field South	0.167	31.1	0.58
7	New Field West	0.120	4.1	0.16
8	New Field EP	0.141	27.8	0.18
9	Exclosure West	0.200	76.3	1.08
10	Exclosure East	0.223	48.0	1.44
11	ATCA Exclosure	0.195	35.3	1.01
12	SAVE Exclosure	0.203	66.9	1.13
13	Pilot Farm	0.208	31.4	1.20
14	Inside ATCA	0.147	70.8	-



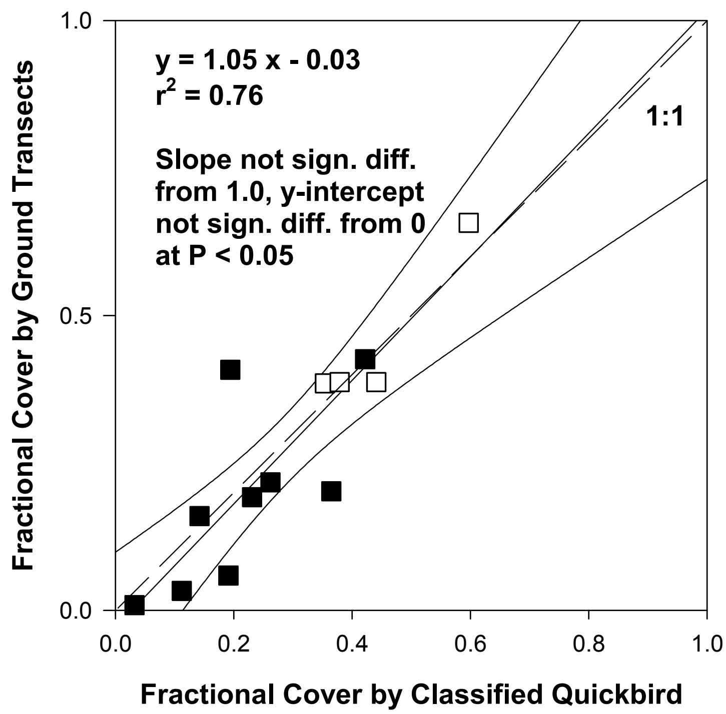


Figure F-3. (Above) Relationship between leaf area index (LAI) measured by leaf-harvesting and fractional ground cover measurements inside and outside exclosure plots and NDVI values on 2007 and 2010 Quickbird images. (Below) Relationship between fractional cover measured inside and outside exclosure plots by line transects and fractional cover estimated on classified Quickbird images. Closed squares are from 2007 measurements and open squares are from 2010.

F.4.2 ET and Vegetation Changes, 2000-2010 by MODIS and Landsat

Landsat images show a clear increase in vegetation intensity over the site from 2000 to 2009 (Figure F-4). Estimated ET rates by MODIS imagery of the site over four years are in Figure F-4. The area inside the fence showed a marked increase in ET after 2005 due to the growth of the irrigated and volunteer plants. However, the Outside ATCA and Outside SAVE areas also showed an increase in ET after 2005. This was attributed to reduced grazing compared to earlier years. ET measured by sap flow sensors in 2006 and 2007 matched the rates predicted from MODIS EVI and the maximum daily temperature. Figure F-5 shows no clear relationship between ET and precipitation on a monthly basis over the study period. This was also evident from a plot of mean monthly values of ET and precipitation averaged over multiple areas and years (Figure F-6). ET followed a regular seasonal pattern, low in winter and high in summer, whereas precipitation was highest in late summer and winter, and was lowest in early and mid-summer when ET was highest. This is a typical pattern for desert phreatophytes in the western U.S. (Lin et al. 1996).

Annual totals of potential ET (ET_o), estimated ET for areas of interest at the site, and precipitation are in Table F-2. ET for Inside, Outside SAVE, and the Whole Site areas were significantly ($P < 0.05$) correlated with the year; the correlation for the Outside ATCA area was marginally significant ($P = 0.078$). The correlations with the year were due to the increase in ET across the site after 2004 (see Table F-2). This increase was due presumably to reduced grazing, since neither ET_o or precipitation increased over that time period. ET was not significantly correlated with precipitation. However, onsite measurements of precipitation were only available from 2007 to 2010; data for previous years were interpolated from widely spaced reporting stations by the PRISM Climate Group (University of Oregon) and they did not match well with the onsite data for the years of overlap. For the 4 years for which onsite precipitation data were available, both precipitation and ET were lowest in 2009 and highest in 2010, suggesting that precipitation is one of the factors controlling annual ET.

Figure F-5 and Table F-2 show that fourwing saltbush and black greasewood plants are able to utilize a large portion of the annual precipitation even when it arrives at a time when plants are not active; presumably winter rains percolate into deep soil layers and are used to support plant ET in summer (Lin et al. 1996). High rainfall use efficiency is evident by comparing annual precipitation with annual ET. Over the whole site, ET was equal to 99 percent of precipitation from 2005 to 2010, compared to only 78 percent from 2000 to 2004.

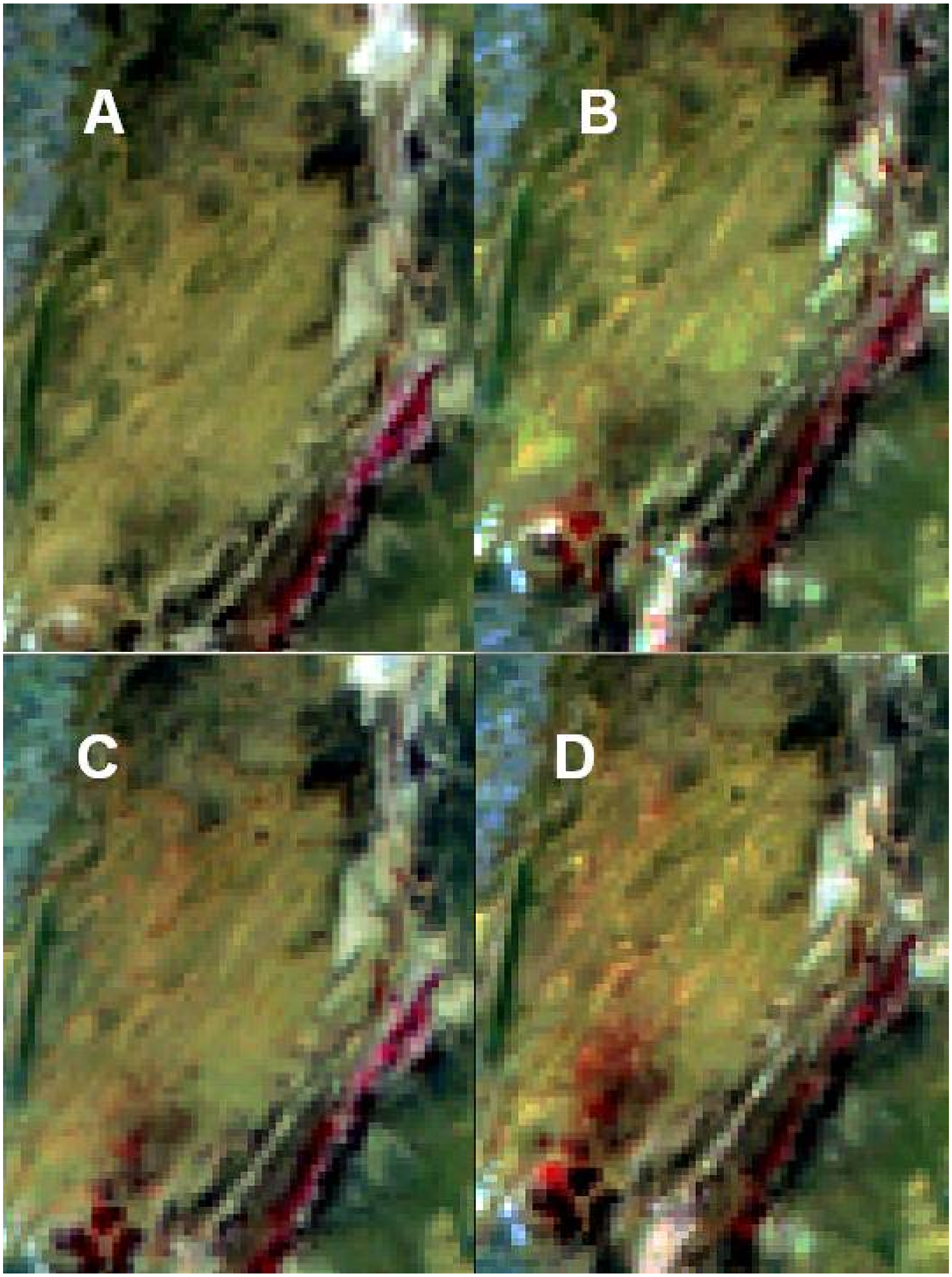


Figure F-4. False-color Landsat Thematic Mapper 5 images of the Monument Valley site with the near infrared band denoting vegetation shown in red. Images are summer scenes for 2000 (A), 2005 (B), 2007 (C), and 2009 (D).

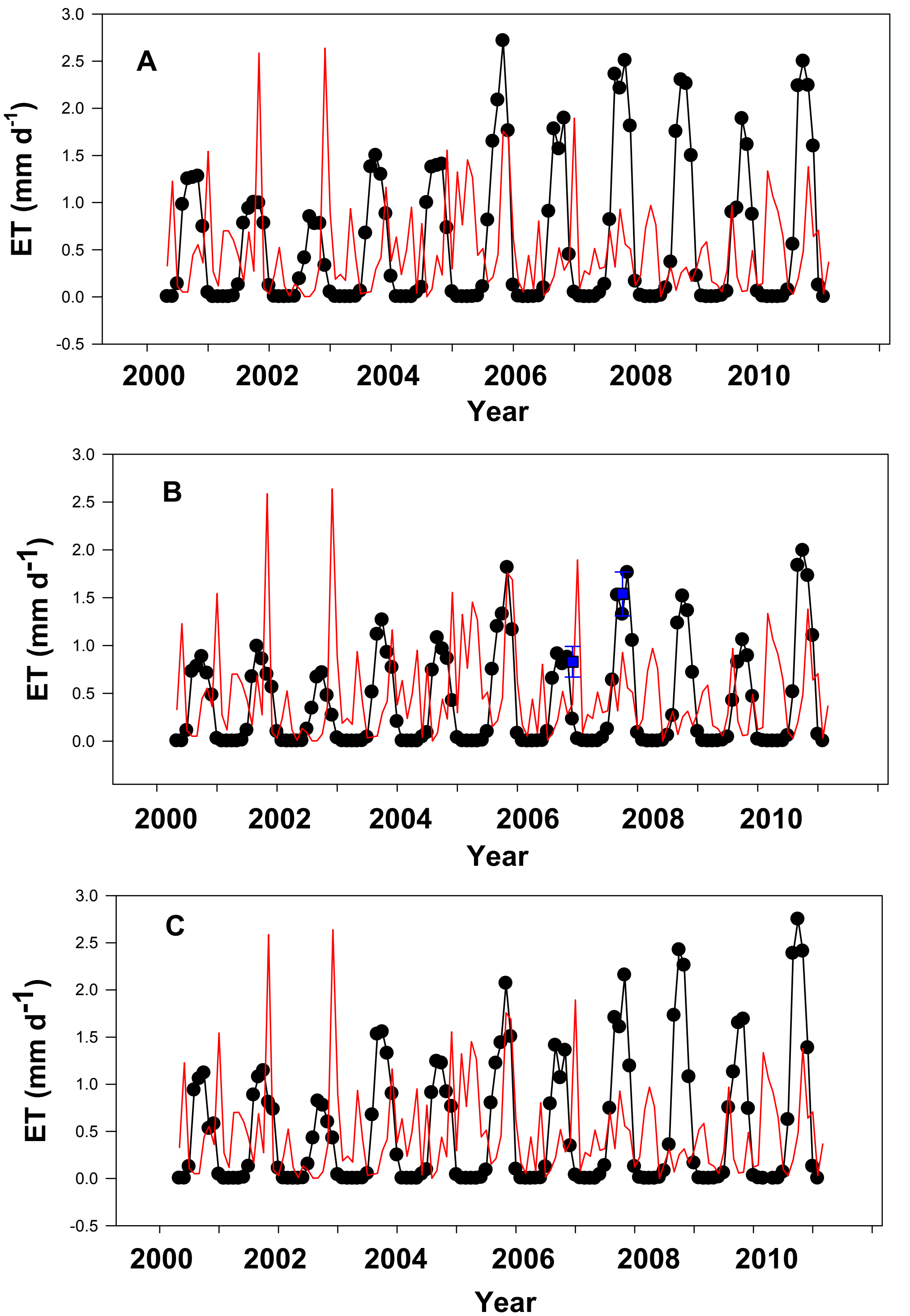


Figure F-5. ET in mm d^{-1} (black dots) estimated from MODIS Enhanced Vegetation Index and air temperature for the plants inside the source area fence (A); in the Outside ATCA zone (B); and in the Outside SAVE zone (C). The red lines are precipitation in mm d^{-1}. The inside-fence area was represented by four MODIS pixels encompassing 24 ha; the Outside SAVE area was represented by two MODIS pixels contained wholly within the area of interest; and the Outside ATCA area was represented by a rectangle of 4 × 5 pixels within the area of interest. Blue squares in (B) show ET measured by sap flow sensors in 2006 and 2007 and projected over the ATCA zone based on LAI and fractional cover.

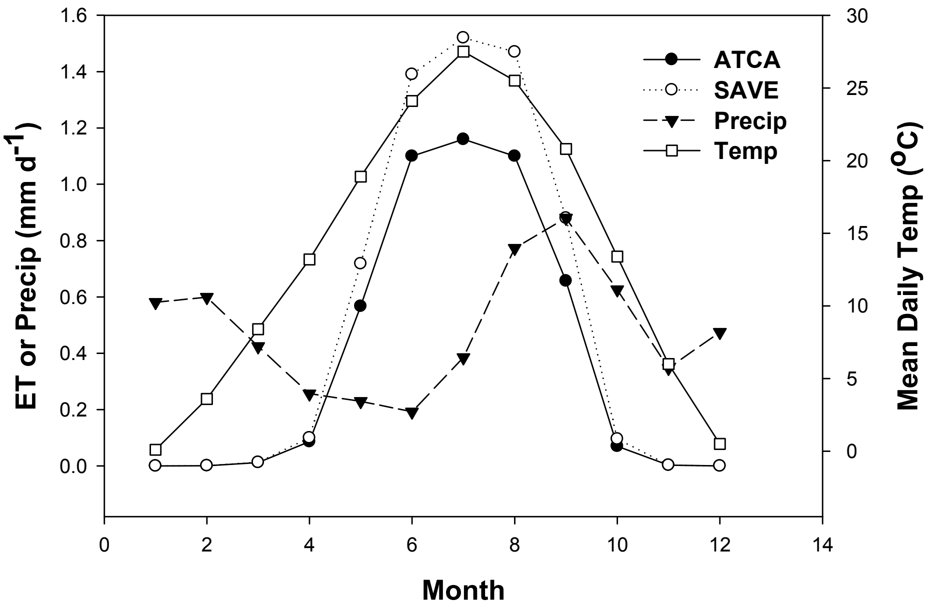


Figure F-6. Annual cycles of ET, precipitation, and air temperature in the Outside ATCA and Outside SAVE areas, averaged over years for 2000-2010.

Table F-2. Potential evapotranspiration (ET_o) and, precipitation, and ET estimated by MODIS satellite imagery for areas at the Monument Valley UMTRA site. Means and standard errors (SE) are shown for 2000-2004 and 2005-2010.

Year	ET_o	Precipitation	Estimated ET			
			Inside Fence	Outside SAVE	Outside ATCA	Whole Site
	mm year^{-1}					
2000	1573	168	189	146	123	144
2001	1499	214	145	149	122	136
2002	1482	143	103	99	99	90
2003	1508	146	183	191	147	169
2004	1461	212	185	159	129	146
Mean (SE)	1504 (19)	176 (17)	161 (17)	148 (15)	124 (8)	137 (13)
2005	1463	267	282	220	196	195
2006	1452	155	206	157	110	143
2007	1465	167	306	235	199	200
2008	1421	193	259	248	160	162
2009	1432	107	193	184	114	150
2010	1419	234	310	356	242	268
Mean (SE)	1442 (8)	187 (26)	259 (20)	233 (28)	170 (21)	186 (19)

Precipitation exceeded ET over all areas of the site from 2000 to 2004, suggesting that the site water balance favored recharge, which may be a factor in the expanding of the contamination plume. On the other hand, ET exceeded precipitation in the source area and in the SAVE stand outside the fence from 2005 to 2010. Irrigation water applied to 4 ha in the source area contributed an additional 60 mm yr^{-1} of water to the area represented by the 4 MODIS pixels

(24 ha) selected to represent the Inside Fence area; hence precipitation plus irrigation (247 mm yr^{-1}) approximately equaled ET (259 mm yr^{-1}) for this part of the site. This is expected, as there is no aquifer under most of the source area and the plants were dependent on precipitation and irrigation. On the other hand, black greasewood outside the fence could have been using groundwater as well as precipitation, because ET exceeded precipitation, and, in previous studies (McKeon et al. 2006; Jordon et al. 2008), plants over this part of the plume were shown to be extracting water from the alluvial aquifer based on stable isotope values.

F.5 Conclusion and Recommendations

The remote sensing method developed here for monitoring vegetation dynamics and ET at Monument Valley, using a combination of annual Quickbird images and 16-day MODIS images, should be accessible into the foreseeable future. Quickbird images are commercial products supplied by Digital Globe, Inc., which recently added another satellite, WorldView 2, to its fleet. Replacement satellites are also planned for NASA's Terra satellite, which acquires MODIS images.

The results suggest that from 2000 to 2010, the area over the plume appears to have switched from recharge to discharge of the aquifer. This could have important implications for the migration of contaminants away from the site. Increased vegetation cover and ET was due partly to revegetation projects conducted over the source area, and partly due to an observed decrease in grazing over the plume. Since vegetation dynamics and grazing pressure will continue to vary in the future, continued monitoring of the site by remote sensing is recommended.

Appendix G

Risk Evaluations

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Contents

Figures

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The overall goal of Monument Valley pilot studies is to generate the science needed for sustainable protection of human health and the environment. The pilot studies focused on the contaminants of concern in the alluvial aquifer, nitrate, ammonium, and sulfate. The pilot studies revealed several natural processes that are acting to contain and remove these constituents from soil and groundwater, and the studies produced strong landscape-scale evidence that these processes can be enhanced and accelerated. As the pilot studies progressed, project scientists also considered whether enhancements might actually create risk to human health and the environment.

This section is a summary of evaluations of potential risks associated with plant uptake of contaminants, grazing of phytoremediation plantings by livestock, and constituents that may have caused soils to become stained over the course of the pilot studies, possibly as a result of soil ripping and irrigation.

G.1 Plant Uptake and Grazing

Project scientists conducted greenhouse, modeling, and field studies to evaluate uptake of soil and groundwater constituents and potential toxic effects for phytoremediation plants and for animals that might consume those plants. The toxicity studies focused on uranium, nitrogen, and sulfur, but also addressed other chemicals of concern.

G.1.1 Chemicals of Potential Concern

With respect to risks associated with plant uptake, project scientists were concerned primarily with accumulation of NO_3, SO_4, hydrocyanic acid, strontium, vanadium, uranium, and manganese within the plants, and how accumulation of these constituents could affect the quality of forage for livestock. A thorough discussion of potential toxic effects of these constituents is presented in an earlier phytoremediation report (DOE 2002). A summary follows.

Some plants accumulate hydrocyanic acid (HCN), commonly called prussic acid and a derivative of NO_3. HCN is usually not present in plants, but some plants can accumulate cyanogenetic glycoside. Plants that contain the glycoside have the potential to cause HCN toxicity when consumed by ruminants such as cattle and sheep. HCN interferes with the ability of oxygen to enter body cells thus causing suffocation at the cellular level (Strickland et al. 1995). In the Southwest, the plants most likely to cause HCN poisoning are sorghums. The potential is greatest for Johnson grass and the least for true sudan grasses. At Monument Valley, therefore, HCN poisoning of livestock would be of greatest concern if plume water were used to irrigate sorghums. The accumulation of nitrate is also of concern when feeding livestock. High nitrate accumulation in plant tissues also results in oxygen deprivation. But again, this would be of greatest concern only if plume water were used to irrigate sorghums.

Sulfur (S) toxicity could theoretically occur in livestock if levels are high enough for microflora to convert S to hydrogen sulfide in the gastrointestinal tract. However, it takes large amounts of S to start producing hydrogen sulfide. There are no established limits on S/SO_4 for cattle and sheep diets. An apparent maximum tolerable level for sheep is 0.4 percent dietary S as sodium sulfate (Subcommittee on Mineral Toxicity in Animals 1980).

Strontium (Sr) is an alkaline earth metal closely related to calcium (Ca). Strontium is processed in plants and animals similarly to Ca but the processing is less efficient. The effects of Sr on livestock are more pronounced when there are small concentrations of Ca present. Young animals fed small Ca and large Sr concentrations develop “strontium rickets,” which affects bone growth (Colvin and Creger 1967). Assuming that animals have adequate Ca in their diet, plants containing up to 2,000 µg Sr g^{-1} can be tolerated (Subcommittee on Mineral Toxicity in Animals 1980).

Manganese (Mn) is an essential element for both plant and animal growth. However, Mn toxicity can result as an interference with iron causing a decreased production of hemoglobin. Sheep and cattle should not be fed diets containing more than 1,000 µg Mn g^{-1} (Subcommittee on Mineral Toxicity in Animals 1980).

Vanadium (V) has also been shown to be an essential element in animal diets, but can also be toxic by inhibiting enzymes and causing the lysis of cells. However, there is no established maximum tolerable limit for V (Subcommittee on Mineral Toxicity in Animals 1980).

Uranium (U) has been shown to be essential in small amounts for plant growth but not essential for animal growth. Toxicity to animals by U occurs in the kidney due to cell damage. Most animals do not absorb large amounts of U through digestion and there is little data on feeding U to farm animals. A safe concentration of dietary U for rats appears to be 400 mg U kg^{-1} (Subcommittee on Mineral Toxicity in Animals 1980).

G.1.2 Greenhouse Studies

Greenhouse studies were conducted at the University of Arizona primarily to evaluate varieties of sudan grass for hay production. Scientists evaluated varieties of sudan grass as an early candidate for the phytoremediation land farm (Appendix E). The studies used soil and water from the site to assess the feasibility of growing crop plants of forage quality (DOE 2002). A previous greenhouse study conducted with soil and water from a different uranium mill tailings site found this to be a feasible approach (Baumgartner et al. 2000a, 2000b).

Five types of crop plants were evaluated in the greenhouse: alfalfa, sudan grass, Sweet sudan grass, Sorghum-sudan grass, and the fourwing saltbush. The selection of crops was based on a literature search on the effects of high-nitrate irrigation water, on guidance from the DOE client, and on the suitability of land at Monument Valley for growing irrigated crops. The study used soils from the source area and from north of the source area, the proposed location for the land-farm study (Appendix E). Irrigation water treatments included 1,000, 500, and 83 mg/L NO_3 from wells 648, 777, and 778, respectively.

The best plant growth occurred on soil from north of the source area where the land-farm study was eventually conducted. Plant growth was inhibited in soils from the tailings pile footprint. Growth on all three soils improved with the addition of organic matter.

One thousand mg/L nitrate (measured as NO_3) in water was lethal to most plants. This toxicity was alleviated by the addition of organic matter to the soil. One thousand and 500 mg/L NO_3 in water resulted in plant tissue concentrations of NO_3 above recommended feeding values for cattle. At 83 mg/L NO_3 in the water, alfalfa did not accumulate NO_3 to excessive levels. All other plant types accumulated nitrate close to or above 5,000 mg/kg NO_3, the highest amount of nitrate considered safe for feeding ruminants. Plants grown with organic matter and watered with 1,000 mg/L NO_3 accumulated NO_3 up to 20 times the safe feeding level. HCN accumulation was lowest in Piper sudan grass with a mean below the lower toxic limit. Both Sweet sudan grass and Sorghum-sudan grass accumulated HCN above toxic levels. Sulfur as sulfate (SO_4) in dried plant tissues accumulated to harmful concentrations in alfalfa grown with water containing 83 mg/L NO_3 and 620 mg/L SO_4. Plants did not accumulate Sr, Mn, V, or U to harmful levels.

The main conclusion of the study was that alfalfa would be a better choice for hay production because sudan grass is more likely to accumulate toxic amounts of HCN and NO_3. Fourwing saltbush could also be grown as a hay crop or for grazing. However, because fourwing saltbush can accumulate nitrate, at least on the basis of this greenhouse study, a seed crop may be a more acceptable alternative because it would help alleviate toxicity concerns. Fourwing saltbush would be safe for short duration grazing if irrigated with plume water.

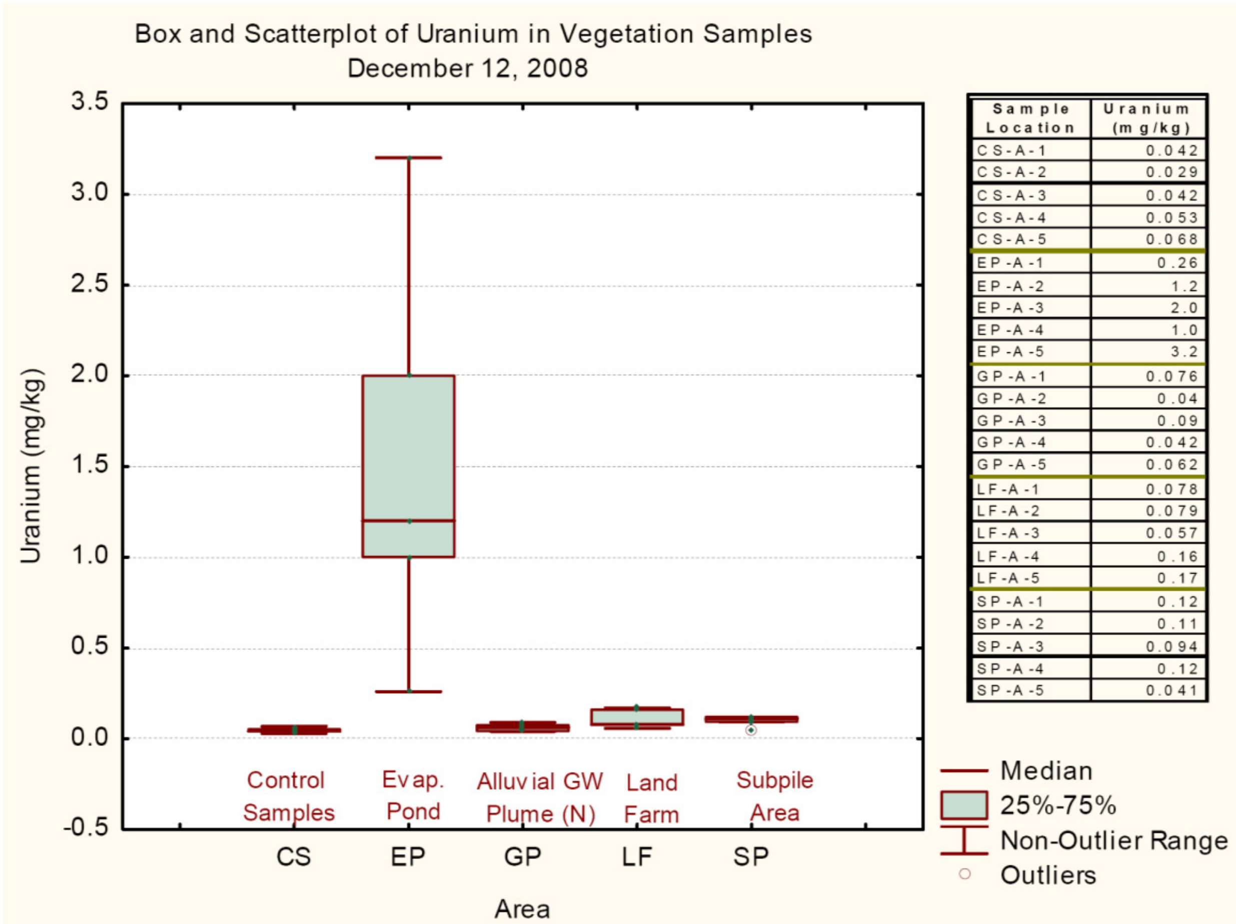
G.1.3 Field Studies of Plant Uptake

Field studies of plant tissue accumulation of nitrogen and uranium provide some information on possible toxicity if phytoremediation plantings were to be grazed continuously by livestock. This section is a summary of the field studies.

Nitrate toxicity is sometimes a problem for livestock (Sections G.1.1 and G.1.2). However, nitrate is the primary form of nitrogen, a plant nutrient, and is a normal constituent of plants. Whether nitrate accumulates in plants to toxic levels depends on the rate of uptake from the soil and the rate that plants convert it to nitrite, ammonia, and amino acids. As a rule, forage containing less than 5,000 ppm (0.5 percent) nitrate on a dry matter basis is safe. Project scientists determined total nitrogen content of plant tissues as part of the phytoremediation field study, but did not evaluate nitrate content. In the source area phytoremediation plantings, total nitrogen content of leaf and stem tissue ranged from 1.24 percent to 2.17 percent over 5 years, 2000-2005 (DOE 2006). If future land management were to include grazing, nitrate content of plant tissues would need to be determined.

Although most animals do not absorb large amounts of U through digestion and there is little data on U toxicity to farm animals, 400 mg kg^{-1} has been used as a safe dietary threshold (Section G.1.1). In 2008, project scientists sampled stem and leaf tissue for fourwing saltbush plants growing in different locations at Monument Valley. Five plants each were sampled in the source (subpile) planting, in the land-farm planting, in the Evaporation Pond planting, overlying the alluvial nitrate plume, and at a control site (an area south of the mill site that had not been disturbed by milling or remediation activities).

Results in Figure G-1 show that the highest concentrations of uranium were found in the former Evaporation Pond. The concentrations in vegetation samples from the former Evaporation Pond were similar to, and in some cases higher than, those found in evaporation pond soils. Concentrations of uranium in fourwing saltbush from all other areas were significantly lower and similar to the control samples. All uranium concentrations were over two orders of magnitude less than the stated dietary threshold.



Sample Location	Uranium (mg/kg)
CS-A-1	0.042
CS-A-2	0.029
CS-A-3	0.042
CS-A-4	0.053
CS-A-5	0.068
EP-A-1	0.26
EP-A-2	1.2
EP-A-3	2.0
EP-A-4	1.0
EP-A-5	3.2
GP-A-1	0.076
GP-A-2	0.04
GP-A-3	0.09
GP-A-4	0.042
GP-A-5	0.062
LF-A-1	0.078
LF-A-2	0.079
LF-A-3	0.057
LF-A-4	0.16
LF-A-5	0.17
SP-A-1	0.12
SP-A-2	0.11
SP-A-3	0.094
SP-A-4	0.12
SP-A-5	0.041

Figure G-1. Box and scatter plot of uranium (mg kg^{-1} dry weight) in tissue samples of fourwing saltbush growing in different locations at Monument Valley (DOE 2010).

G.2 Evaluation of Stained Soils

At different times during the course of the pilot studies, project scientists observed colored or "stained" soils in the source area plantings. This section is a summary of investigations concerning the potential toxicity of stained soils to plants and to humans.

G.2.1 Stained Subpile Soils

Project scientists have observed poor plant growth in the western part of the subpile planting since 1999. Satellite images show this area of poor growth as a whitish stain (Figure G-2). Previous analyses of soil samples from areas with both poor and good growth suggested that nitrate, sulfate, calcium, magnesium, strontium, and vanadium were higher in the poor-growth areas. Concentrations of iron, manganese, phosphate, potassium, sodium, and uranium were significantly lower in the poor-growth areas. Therefore, stunted growth of fourwing saltbush shrubs may be due to the combined effects of both an excess and a deficiency of several ions. In a previous greenhouse study, growth of sudan grass in soil obtained from a poor-growth area was significantly less than growth in a soil sample taken from a good-growth area. Chemical analysis of sudan grass tissue samples was inconclusive as to the causative agents of poor growth. Tests also found that soil bulk densities, another suspected cause of poor plant growth, were not significantly different in poor-growth and good-growth areas. A follow-up greenhouse study determined that moderate additions of iron and copper fertilizer improved plant survival but not growth.

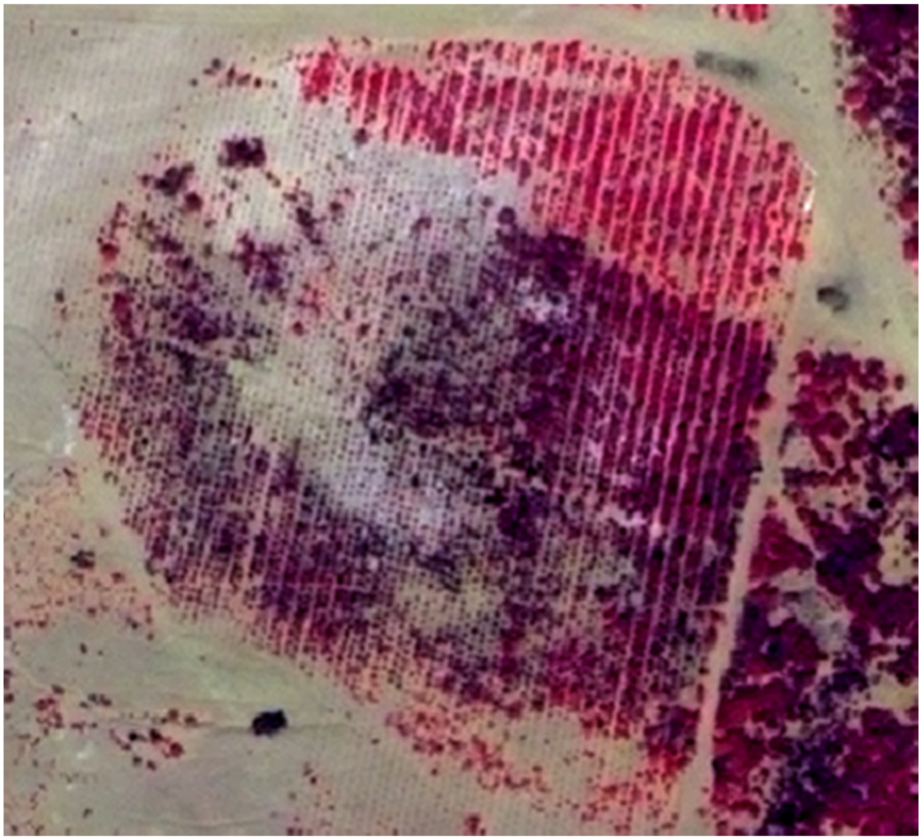


Figure G-2. False-color 2009 Quickbird images showing whitish colored soil and areas of poor plant growth in the western portion of the subpile phytoremediation planting.

G.2.2 Manganese Toxicity Investigation

Parts of the subpile planting also have a shallow layer of black mottled material below the whitish soil surface in areas of stunted plant growth. Project scientists identified Mn and iron (Fe) concretions in samples from the mottled soil areas. They hypothesized that oxides of Mn at different oxidation states may have been deposited in the soil as a consequence of milling, and that these different oxidation states could be responsible for the "rainbow" appearance of colors around drip emitters in the stained areas. This section is a summary of a follow-up effort to determine the source of Mn concretions and to evaluate the potential health risks of Mn dust at the site (DOE 2009). The major findings follow:

- Chemical analyses of the concretions show that they are indeed aggregates enriched in Mn and Fe.
- Although the onset of irrigation may have mobilized Mn, and the Mn oxides may be precipitating, most of the mobilization of Mn at this site likely occurred during the leaching of uranium-rich minerals with acid.

- The levels of Mn are within values for normal soils, and they are well below any levels of concern for human health risks.

G.2.3 Evaporation Pond Crusts

In 2009, yellow- and green-colored deposits or soil crusts were noticed on the surface of the phytoremediation plantings in the Evaporation Pond. Sample analyses determined that the deposits were high in vanadium and uranium. In 2010, DOE conducted a radiological investigation, independent of the pilot studies, to evaluate the potential dose to workers resulting from exposure to radiological constituents in Evaporation Pond soils (DOE 2010). Highlights of the investigation follow:

- When the site was remediated between 1992 to 1994, all areas of the site, including the former Evaporation Pond, were verified clean under the UMTRCA surface soil cleanup standard of 5 pCi/g radium-226 (Ra-226) and the subsurface standard of 15 pCi/g. NRC approved the Monument Valley cleanup on April 5, 2001.
- Although the Evaporation Pond probably represents worst-case conditions in terms of contamination, post-cleanup verification studies, as corroborated by NRC, indicate that cleanup commitments were fulfilled.
- Because fourwing saltbush in the former Evaporation Pond had poor growth rates compared to other plantings, project scientists sampled yellow and green stains as a possible source of poor growth and determined that the stains had elevated levels of uranium and vanadium.
- As a best management practice, DOE conducted a radiological screening because of the higher-than-expected uranium results. Results indicated higher-than-anticipated gamma levels in the area.
- A follow-up soil sampling from the former Evaporation Pond found uranium-234 plus uranium-238 levels from 31 to 985 pCi/g. The ratio between uranium-234 and uranium-238 was consistently close to 1. The concentrations of thorium and radium were much lower than those of uranium, and the highest measured value for radium was less than 2 pCi/g.
- To ensure that workers have not been exposed to excessive dose levels from isotopic uranium in surface soils, risk calculations were performed. Risks were estimated using an allowable exposure rate of 25 millirems (mrem) per year, the highest measured results for the isotopes of uranium, and very conservative exposure assumptions. The results indicate that risks are well below the allowable exposure rate of 25 mrem per year.

Appendix H

Beneficial Land Use

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Contents

Figures

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The Monument Valley pilot studies investigated potential beneficial land uses as part of an overall remedy. The contaminants of concern, nitrate and ammonium, are also the dominant sources of nitrogen in desert soil, an essential element for plant growth. Therefore, although seemingly a contradiction, nitrate and ammonium should be viewed both as contamination with respect to groundwater quality, but also as a resource with respect to plant nutrition and growth.

The levels of nitrogen in soil and groundwater at Monument Valley produce abundant foliage and seed growth. The phytoremediation plantings produce seed crops that the Navajo Nation could harvest for mine-land reclamation and rangeland restoration. Harvested seed may be worth $10,000 per acre. Fourwing saltbush is highly palatable to livestock and wildlife. Livestock grazing or harvesting saltbush foliage for hay, if managed correctly, could actually stimulate plant growth and enhance phytoremediation. Fourwing saltbush also has traditional, medicinal value to Native Americans.

An objective of the Monument Valley pilot studies is to evaluate options for exploiting nitrogen contamination to fertilize native plants for possible beneficial land reuse as seed and forage crops. This is possible because the primary contaminants of concern in the alluvial aquifer and in the plume source area soils are nitrate and ammonium. This section reviews the role nitrogen plays in rangeland ecosystems, and how nitrogen contamination at Monument Valley could be utilized to increase native plant forage and seed production.

H.1 Ecological Importance of Nitrate and Ammonium

An understanding of potential beneficial uses of nitrogen contamination must start with a review of the ecological role of nitrogen. Nitrogen is an essential element for plants—without it, there would be no life as we know it. Nitrogen is required for many important structural, genetic, and metabolic compounds in plant cells. Nitrogen is a major component of chlorophyll, the compound by which plants use sunlight energy to produce sugars from water and carbon dioxide—photosynthesis. It is also a major component of amino acids, the building blocks of proteins. Some proteins act as structural units in plant cells while others act as enzymes, making possible many of the biochemical reactions on which life is based. Nitrogen is a component of energy-transfer compounds, such as ATP (adenosine triphosphate), which allow cells to conserve and use the energy released in metabolism. Finally, nitrogen is a significant component of nucleic acids such as DNA, the genetic material that allows cells and whole plants to grow and reproduce.

Although nitrogen is one of the most abundant elements on earth, plant productivity in desert ecosystems is commonly limited by insufficient soil nitrogen (Whitford 2002). The most abundant form of nitrogen, gaseous nitrogen (N_2) molecules in the atmosphere, is not directly available to most plants that need it. Plant-available nitrogen exists primarily in soils as organic nitrogen compounds, ammonium ions (NH_4^+), and nitrate ions (NO_3^-). In desert ecosystems, the plant-available forms of nitrogen are inorganic ammonium and nitrate.

Typically, nitrogen reserves become depleted or altered in disturbed landscapes, such as at the Monument Valley site, because the healthy cycling of nitrogen through the ecosystem is inhibited or prevented. Restoration ecologists often apply nitrogen fertilizer under these conditions, in the form of ammonium or nitrate, to help jumpstart nitrogen cycling and enhance revegetation. Monument Valley is unique. At Monument Valley, elevated levels of ammonium and nitrate in soil and shallow groundwater can be viewed both as contamination with respect to groundwater quality, but also as a resource to be utilized with respect to plant nutrition and growth.

H.2 Land Reuse: Seed and Forage Crops

Atriplex canescens (fourwing saltbush) is one of the most widely distributed and important native shrubs on rangelands in the western United States including the Intermountain, Great Basin, and Great Plains regions. It is an important forage plant in western deserts of the United States and is widely used for reclamation of drastically disturbed lands and for rangeland restoration. Historically, fourwing saltbush has probably been the most seeded of all Western shrubs (Aldon 1972, Booth 1985). As a pioneer shrub it has proven useful for accelerating and directing plant succession on mined lands and degraded rangelands, especially when transplants are used (Glenn et al. 2001, Watson et al. 1995). The species comprises at least six distinct varieties that appear to be adapted to local soil and climate regimes (Glenn et al. 1996; Glenn and Brown 1997). For revegetation on Navajo mine lands, the diploid variety *angustifolia* was found to be better adapted for rapid establishment on disturbed sandy soils than the slower-growing variety *occidentalis*.

Phytoremediation plantings at Monument Valley produce fourwing saltbush seed crops annually that the Navajo Nation could harvest for mine-land reclamation and rangeland restoration (Waugh et al. 2010). As fertilizer, the nitrogen contamination has resulted in luxuriant growth of fourwing saltbush and abundant seed in the pilot study plantings (Figure H-1). In fall 2001, project scientists harvested about 50 kg of fourwing saltbush seed; about 2 kg or more of seed from each of several mature plants. There were about 4,000 plants in the subpile phytoremediation planting, half of which are female (fourwing saltbush are dioecious; separate male and female plants), so 2,000 plants × 2 kg gives a potential yield of 4,000 kg of seed. The field is 1.6 ha, so the potential yield is 2,500 kg/ha. Seed companies charge up to $66/kg ($30/lb) for seed with the wings milled off. If the seed companies pay as little as $10/kg ($4.50/lb) for bulk seed, this would be a return of $25,000/ha (about $10,000/acre). Saltbush seeds are harvested by stripping or beating the ripe fruits into shoulder hoppers, boxes, or bags, or onto tarps spread under the bushes. Vacuum or reel type harvesters may also be used (McArthur et al. 2004).

Fourwing saltbush is also highly palatable browse for most livestock and big game and could be managed for grazing or harvesting. It is palatable to cattle, sheep, and deer throughout the growing season, and provides nutritious winter browse on many areas as a fall and winter browse plant for bighorn sheep, antelope, and elk. With minimal toxicity risks (Appendix G), Monument Valley fourwing saltbush plantings could be made available for livestock belonging to local residents. The plantings would need to be closely managed for short duration grazing in the winter to maintain plant health. Plants continuously browsed by cattle usually develop a hedged form and produce relatively little growth. Managed grazing may actually improve phytoremediation capacity. Moderate browsing by livestock for short durations can significantly stimulate fourwing saltbush growth, whereas plants protected from browsing for a year or more respond with progressively less leader production as length of protection time increases (Price et al. 1989). Fourwing saltbush can also be cut and windrowed with a hay-swather and then combine-harvested for seed or fodder (Carlson et al. 1984).

Figure H-1. Seed production (light green) of fourwing saltbush transplants in the source area phytoremediation planting at Monument Valley, September 22, 2010.

H.3 Ethnobotany

Fourwing saltbush also has traditional, medicinal value for Native Americans (Moerman 2009). Among other traditional uses, Native Americans boil fresh fourwing saltbush roots with a little salt and drink half-cupful doses for stomach pain and as a laxative. Roots are ground and applied as a toothache remedy. Leaf or root tea is taken as an emetic for stomach pain and bad coughs. Soapy lather from leaves is used for itching and rashes from chickenpox or measles. Fresh leaf or a poultice of fresh or dried flowers is applied to ant bites. Leaves are used as a snuff for nasal problems. Smoke from burning leaves is used to revive someone who is injured, weak, or feeling faint.

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Appendix I

List of Publications, Reports, and Presentations

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LM funded the pilot studies at the Monument Valley site to gain the knowledge (science) and tools (technology) as a basis for informed, efficient, and cost-effective remediation strategies for the alluvial aquifer and subpile soils. By publishing, LM subjected the pilot studies to scholarly scrutiny by independent communities of experts in these fields of research; this process is known as refereeing. Publishing provides a measure of credibility and enables others to utilize these contributions to the science and technology of enhanced natural attenuation. Listed below are a book chapter and peer-reviewed pilot study publications in scientific journals and symposia proceedings followed by lists of DOE reports and technical presentations. The full-text journal articles are available on request.

Book Chapter

Waugh, W.J., E.P. Glenn, P.H. Charley, B. Maxwell, and M.K. O'Neill, 2011. *Helping Mother Earth Heal: Diné 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, New York.

Journal and Proceedings Publications

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Appendix J

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