DOE–LM/1254-2006

Soil and Ground Water Phytoremediation Pilot Studies at Monument Valley, Arizona

2005 Status Report

July 2006

U.S. Department of Energy

Office of Legacy Management

Work Performed Under DOE Contract No. DE–AC01–02GJ79491
for the U.S. Department of Energy Office of Legacy Management.

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Signature Page

Soil and Ground Water Phytoremediation Pilot Studies
at Monument Valley, Arizona, 2005 Status Report

Project Approval:

signature on original _____ _____

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Contents

Figures

Tables

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Executive Summary

The U.S. Department of Energy (DOE) Office of Legacy Management (LM), the Navajo Uranium Mill Tailings Remedial Action (Navajo UMTRA) program, and the University of Arizona (UA) are exploring natural remedies for ground water contamination at DOE's Legacy Management site near Monument Valley, Arizona. DOE removed radioactive tailings from Monument Valley, a former uranium millsite, in 1994. Nitrate and ammonium, used during the milling process, remain in a shallow ground water plume spreading from a millsite source. A conventional cleanup strategy might involve drilling wells and pumping ground water to a treatment facility on the surface. Pilot studies jointly funded by LM and UA are answering two questions: What is the capacity of natural processes to remove nitrate and slow plume dispersion, and if needed, can we efficiently enhance natural attenuation?

The pilot studies are focusing on plants and microorganisms to answer these questions. Where they have not been overgrazed by livestock or cleared during removal of radioactive tailings, deep-rooted plants are withdrawing nitrate water from both the millsite source and the plume, converting it into healthy plant tissue, a process called phytoremediation. Two native, desert phreatophytes—plants that send roots into ground water—are doing most of the work; fourwing saltbush and black greasewood. Also, by the time water approaches the far end of the plume, microorganisms have converted nearly half of the nitrate into harmless nitrogen gas, a process called microbial denitrification. Denitrification is also removing nitrate from the source area.

The studies show that significant rates of natural attenuation are reducing nitrate levels in both the source soil and ground water, and that some sustainable enhancements might be available to speed up the processes. Simply put, desert plants can control soil and ground water movement, cutting off the nitrate source and keeping the plume from spreading, while plants and primarily microorganisms remove nitrate from both.

Pilot Study Concepts and Goals

The goals of the pilot studies are (1) to understand, and (2) to evaluate enhancements of natural attenuation processes acting on the nitrate plume. Section 2.0 describes the concepts. "Enhanced Attenuation" (EA) is an expansion of the classical concept of "Monitored Natural Attenuation" (MNA) espoused by the Environmental Protection Agency (EPA). Two terms describe the differences: intervention and sustainability. An enhancement is an intervention implemented to increase the magnitude of attenuation by natural processes beyond what would occur without intervention. However, the enhancement must be sustainable—EA should not require continuous human intervention. The pilot studies are investigating sustainable enhancements that will achieve a favorable balance between processes that can slow the release of nitrate from the source area (defined as loading) and processes that can remove, degrade, or retard migration of nitrate in the alluvial plume. Section 2.0 includes a framework for applying results of the pilot studies at Monument Valley. The pragmatic goal is to provide the science necessary for LM and Navajo UMTRA to make informed decisions concerning a final remedy for the nitrate plume.

Pilot studies were originally proposed in 2004 (*Monument Valley Ground Water Remediation: Pilot Study Work Plan*. DOE-LM/GJ757-2004, Office of Legacy Management, U.S. Department of Energy), and then approved by LM and Navajo UMTRA in May 2005. Brief summaries of the purpose and 2005 status of tasks in the work plan follow. Report section numbers and page numbers are shown in parentheses.

Source Containment and Removal (Section 3.0)

Phytoremediation plantings, established in 2000 to slow loading of nitrate from the source area, were expanded in 2005. Tasks included characterizing the full extent of mill-related and natural sources of nitrate and sulfate, developing EA remedies that rely on plants and microbes to limit leaching and to remove the source, and demonstrating methods and instrumentation to monitor how well the EA remedies are working.

Delineate Extent of Mill-Related Contamination (p. 4)

Soils within source areas (footprints of the New Tailings Pile and the Evaporation Pond) were augered at designated grid points. Nitrate and ammonia were initially analyzed on site in a mobile laboratory. These results helped guide subsequent sampling. All samples were analyzed a second time in an analytical laboratory, and maps of soil nitrate and ammonia concentrations were produced for use in expanding the source area phytoremediation plantings (see below).

Investigate Natural Sources of Nitrate and Sulfate (p. 9)

Southwestern desert soils are known to naturally accumulate nitrate and sulfate. Both were sampled in the vadose zone overlying the plume and in the alluvial aquifer up gradient of the plume. In the vadose zone, nitrate levels were below detection limits in most samples, but sometimes exceeded 100 milligrams per kilogram (mg/kg) in the capillary fringe of the plume. Sulfate concentrations greater than 100 mg/kg occurred in almost all borings, hence the elevated concentrations likely represent naturally occurring zones or horizons of gypsum accumulation.

Wells were drilled into the alluvial aquifer using a geoprobe to characterize nitrate and sulfate up gradient of the plume. Nitrate levels were low, typical of desert ground water. These results and low levels in the vadose zone indicate that essentially all of the nitrate plume can be attributed to the mill site source. Up gradient sulfate levels were highly variable. This may be a response to localized recharge through sediments high in gypsum, or perhaps to upwelling and mixing of DeChelly ground water, that is low in sulfate, with localized recharge that is higher in sulfate.

Determine Causes and Recourses for Stunted Plant Growth (p. 19)

An area of poor plant growth occurs in the western third of the original source area planting. Plant growth, plant nutrient status, soil chemistry, and soil compaction in the poor-growth area and elsewhere in the planting were compared. The results indicate that stunted growth is likely due to an excess of calcium that may be inhibiting plant uptake of micronutrients including iron and copper. Bulk density measurements show that soils were significantly less compacted inside than outside the poor-growth area. A greenhouse experiment was set up in collaboration with faculty and students at the Tsalie campus of Dine College to test the hypothesis that high soil calcium levels are interfering with the ability of plants to absorb Cu and Fe and growth inhibition can be reversed by adding Cu and Fe to the soil.

Expand Source Area Planting and Irrigation System (p. 26)

Past evaluations have shown that the original source area planting was exceptionally effective in limiting deep percolation and leaching of nitrate and in removing nitrate from the soil,

principally through microbial denitrification. Criteria for expanding the source area planting were developed based on the (1) extent of elevated nitrate and ammonia in the tailings pile and evaporation pond footprint, (2) extent of bare areas, (3) plant community characteristics including maturity of volunteer saltbush and greasewood, and (4) depth to bedrock. The expansion totaled approximately four additional acres, doubling the size of the source area phytoremediation. The infrastructure for the expanded irrigation system was installed including replacement of the original system that had outlived its design life.

Monitor Soil Water and Recharge (p 32)

The original planting has been irrigated yearly since 2000, with the exception of 2003. An objective was to irrigate less than plants can use (defined as deficit irrigation) to preclude leaching of nitrate. Soil moisture has been measured monthly since 2000 in 20 neutron hydroprobe ports arrayed systematically within the planting, and in ports installed off the field in non-irrigated soil. Results suggest that moisture levels in the irrigated planting are below field capacity except at lower depths where probe ports extend into the aquifer. An additional 20 neutron hydroprobe ports were installed in the expanded source area planting. Wicking lysimeters will be installed in 2006 to measure percolation flux directly.

Monitor Canopy Growth and Total Nitrogen (p. 33)

Growth and N-uptake by native desert shrubs, mainly fourwing saltbush planted in the source area, have been monitored since 2000. Plant growth has increased by tenfold since 2000 and by about 8 percent since 2004. The cumulative N-uptake, estimated by multiplying plant-N content by plant productivity (biomass gain per year), is approximately 206 killograms (kg).

Evaluate Denitrification and Nitrification in the Subpile Soil (p. 35)

Yearly soil sampling since 2000 indicates that nearly half of the source area nitrate has been removed, much more than can be attributed to plant uptake alone. A salt-balance evaluation and a study of ^{15}N enrichment in the residual nitrate show that the nitrate loss can be attributed to microbiological processes and not leaching. A soil microcosm study indicated that nitrification occurs when source area soils are drier, and denitrification occurs at higher moisture contents. The microcosm denitrification results were similar to values observed in the field plot during times when soils were wet. This study supports the hypothesis that increasing irrigation rates will increase denitrification. Because plants rapidly extract water in the summer, the best strategy might be to irrigate throughout the year, allowing water to accumulate in the profile during winter when plants are inactive, thereby enhancing microbial denitrficiation. Plants would then remove this water during the summer growing season.

Measure Root Distribution and Abundance (p. 40)

Measurements of root distribution and abundance are needed to evaluate the subsurface component of phytoremediation and fine-tune the irrigation system. Roots will be viewed with a small camera in transparent tubes to determine the (1) depths at which shrubs are extracting water, (2) relative amounts of annual root growth and productivity, and (3) spatial variability in root growth compared with above-ground characteristics of the planting. This activity will begin in 2006.

Measure Soil Organic Carbon (p. 40)

Total organic carbon (TOC) in a soil is indicative of the potential for dentrification activity. TOC content in the source area planting was found to be low, hence denitrification activity is likely carbon-limited. TOC was highest in the upper soil profile and likely attributable to decaying plant roots and leaf litter. Batch studies of denitrification from plume samples show that ethanol greatly stimulates denitrification. Addition of ethanol to soil microcosms in the laboratory stimulated denitrification ten fold, suggesting that enhancement of denitrification can be achieved by supply additional water and a carbon source to the subpile soil. An ethanol injection study designed to stimulate denitrification in the source area is planned for 2006.

Natural Attenuation of Ground Water (Section 4.0)

The studies in this section identified and evaluated the capacity of natural attenuation processes acting on the nitrate plume. As with the source area studies, phytoremediation and microbial dentirification were the key processes evaluated. The goal is to determine if the total capacity of natural processes will achieve remediation requirements in a timely manner, assuming that source loading can be curtailed as indicated above.

Determine Depth to Ground Water within Phreatophyte Populations (p. 41)

Phreatophytes are a class of plants that send their roots down to ground water. This task produced a simple map of depths to ground water where existing native phreatophyte populations occur overlying the nitrate plume. Monitor well data were used to produce the map. Depths to ground water range from 30 feet (ft) to 40 ft where fourwing saltbush grow, and 20 ft to 30 ft where the vegetation is dominated by black greasewood.

Partition Plant Water and Nitrate Sources Using Stable Isotopes (p. 41)

Fourwing saltbush and black greasewood, if rooted into the nitrate plume, may be contributing to natural attenuation in two ways: transpiration of water from the plume, slowing its dispersion from the site, and uptake of nitrate from the plume. Stable isotope methods were used to evaluate plant extraction of water and nitrate. Water contains a small proportion of the heavy isotopes; ^{18}O and D (Deuterium), in addition to the more common ^{16}O and H. Natural nitrogen sources also contain a small proportion of ^{15}N in addition to ^{14}N. Stem water samples from plants growing over the plume should have the same isotope composition as the source of water accessed by their roots. Similarly, the nitrogen isotope composition of plant tissues can indicate if plants are extracting nitrate from the plume. Similarly, the nitrogen isotope composition of plant tissues can indicate if plants are extracting nitrate from the plume.

The ^{18}O and D results support the hypothesis that black greasewood is an obligate phreatophyte rooted into the plume, whereas fourwing saltbush is a facultative phreatophyte that uses both plume water and vadose zone water. The ^{15}N results support the hypothesis that both plant species extract nitrate from the plume.

Estimate Sulfate Uptake Rates in Phreatophytes (p. 46)

Although sulfate is not addressed in EPA ground water standards (40 CFR 192), the former mill is a source for elevated sulfate in alluvial ground water; therefore, sulfate will be addressed in the final remedy. These pilot studies are improving our understanding of attenuation processes for

sulfate, and helping to establish reasonable treatment goals. Background concentrations, natural plume sources, and uptake of sulfur by plants are all issues addressed by these studies. This task, scheduled to begin in 2006, will estimate sulfate uptake rates by phreatophytes currently rooted in the alluvial aquifer.

Evaluate Denitrification in the Plume Using Stable Isotopes (p. 47)

Nitrate levels in the alluvial aquifer decrease downgradient from the source area and have also decreased over time. Part of the decrease is likely due to dilution, but part of the nitrate may have been lost to microbial denitrification. A natural process called "^{15}N enrichment" in the plume provided a preliminary estimate of denitrification. The "^{15}N enrichment" study evaluated the ratio of the natural isotopes of nitrogen (^{15}N and ^{14}N) in the plume. Biological denitrification favors ^{14}N over ^{15}N; therefore, as denitrification proceeds, the residual nitrate remaining in the plume becomes enriched in ^{15}N. Preliminary results suggest that up to a 60 percent drop in nitrate from the source out to the leading edge of the plume can be attributed to denitrification.

Monitor and Model Plume Dynamics (p. 48)

This task, scheduled to begin in 2006, will update well monitoring data, document recent changes in nitrate and sulfate plumes, construct relatively simple models of the capacity of natural attenuation processes, and model responses of plumes to attenuation enhancements.

Enhanced Attenuation (Section 5.0)

Enhanced attenuation (EA) remedies should increase the magnitude of attenuation by natural processes beyond that which occurs without intervention. EA approaches will be considered if natural attenuation alone is shown to be incapable of attaining ground water remediation objectives. These studies are focusing on measures to enhance growth of native phreatophytes overlying the plume and of denitrifiers within the plume. The goals are to slow plume movement and remove nitrate and sulfate.

Install Landscape-Scale Grazing Protection and Revegetation Plots (p. 51)

Preliminary DOE studies found that phreatophyte transplants could be established in small exclosure plots, and with managed irrigation, send roots 30 ft or more into the nitrate plume. Protecting wild phreatophytes from grazing doubled the biomass productivity, transpiration rate, and N-uptake rate. This task installed large grazing protection (exclosure) plots and irrigated plantings (revegetation plots established in bare areas) overlying the plume to determine if similar results could be attained on a landscape scale. The irrigation system was designed to deliver water to transplants for 2 years or until plant roots contact ground water.

Monitor Plant Growth and Nitrate and Sulfate Uptake Rates (p. 52)

This task, scheduled to begin in 2006, will monitor plant survival, plant abundance (canopy cover, canopy volume, leaf area index, and annual biomass), and nitrate and sulfate in plant tissues in both the revegetation and exclosure plots. Monitoring will be conducted annually at the end of the growing season. The results will be used to estimate increases in water, nitrate, and sulfate uptake rates.

Estimate Phreatophyte Evapotranspiration (ET) Under Current and Possible Future Land Use Scenarios (p. 54)

Stable isotope data for water and nitrate in the plume ecosystem show that the plant community is helping to control the spread of the plume, through evapotranspiration (ET), and that denitrification is removing nitrate from the plume. Beginning in 2006, ET will be evaluated in the grazing exclosure plots and revegetation plots overlying the plume to test the feasibility of enhancing plant growth and ET. This task will test methods to scale up from stem and plant ET measurements to landscape measurements using satellite remote sensing.

Conduct Soil Column Study of Carbon Sources (p. 54)

Given the success of efforts to enhance denitrification in the source area, this task was developed to evaluate similar methods for enhancing denitrification in the plume. Enhanced bioremediation generally involves addition of nutrients to stimulate microbial populations. Batch studies, followed by column studies, found that ethanol stimulated denitrification, whereas acetate, glucose, and formate were not as effective. The column studies were inconclusive with regard to the actual rates of denitrification that could be achieved.

Active Ground Water Remediation: Land Farming (Section 6.0)

If pilot studies show that natural and enhanced attenuation processes are inadequate or unsustainable, then active remedies will be considered. The pilot studies are evaluating land farming as a form of active phytoremediation. The shallow nitrate plume would be pumped and used to fertilize crops such as native plants to produce seed for mine land reclamation. The Land Farm pilot study is addressing several issues, including land suitability for irrigation, cropping system selection, nitrate uptake and toxicity, fate and toxicity of sulfate, irrigation management, farm operation requirements, and long-term land use.

Develop Experimental Design (p. 59)

An experiment was designed to answer specific questions, with confidence, about crop types, nitrate concentrations, irrigation rates, residual soil nitrate and sulfate accumulation, crop productivity, and crop safety (toxicity). The design, called a randomized split plot, consists of four nitrate levels and two crops replicated and arranged in 32 equal-size plots.

Design Irrigation System (p. 60)

An irrigation system, designed to supply correct mixtures of nitrate plume and clean water to the land farm study plots, was installed in 2005.

Characterize and Monitor Soil Chemical Properties (p. 62)

Baseline soil chemical properties were characterized in the Land Farm. The baseline data were necessary for later evaluation of plant uptake rates, denitrification rates, and soil accumulation of nitrate and sulfate. Results show that soil nitrate and sulfate levels vary greatly laterally and vertically within the Land Farm. Ammonia levels were below detection limits.

Characterize Soil Physical Properties (p. 67)

This task, scheduled to begin in 2006, will determine baseline physical and hydraulic properties of the Land Farm soils.

Monitor Soil Water (p. 67)

The purpose of this task is to monitor soil moisture profiles in the Land Farm to detect seasonal wetting fronts and to monitor and adjust irrigation rates. Neutron hydroprobe ports installed previously will be used to measure soil moisture in the Land Farm beginning in Spring 2006.

Monitor Crop Growth and Productivity (p. 67)

This task, scheduled to begin in Fall 2006, will seasonally monitor the survival, growth, biomass production, and seed production for the different crops and nitrate irrigation levels in the Land Farm.

Evaluate Nitrification and Denitrification Processes (p. 68)

This task will monitor nitrification and denitrification in Land Farm soils. Results will be used to help establish optimal nitrate irrigation rates for plant growth (phytoremediation) and denitrification/nitrification. This task will begin in Fall 2006.

Investigate Gypsiferous Soil Analogs (p. 68)

Some plume sulfate will accumulate in Land Farm soils. Earlier calculations suggested that most of the sulfate would precipitate in the soil as gypsum, a common salt in desert soils high in sulfur and calcium. This task, scheduled to begin in 2007, will investigate the occurrence, genesis, and morphology of gypsiferous soils in the vicinity of the Monument Valley site. These analogs will be used to evaluate the feasibility of creating gypsiferous horizons in the Land Farm soil as a remedy for sulfate.

Manage and Market Seed Crop (p. 68)

A preliminary investigation found that a fourwing saltbush seed crop grown at the Monument Valley site may be worth up to $10,000 per acre. This task, scheduled to begin in 2007, will contact coalmines and other potential users of native plant seed on the Navajo Nation, to determine if a market exists and if establishing a local enterprise is feasible.

Test Plant Toxicity and Simulate Grazing (p.69)

Pumping and irrigating plume water on the Land Farm must not increase risk. This task, scheduled to begin in Fall 2006, will monitor the safety of plants and soil for both livestock and wildlife, and, if feasible, evaluate grazing as an alternative use of Land Farm crops. To achieve these objectives, tissues of fourwing saltbush, black greasewood, and any other crops, will be analyzed for toxic levels of nitrate, hydrocyanic acid, sulfate, total sulfur, and metals of concern. Plant tissues will also be analyzed for nutritional content including crude protein, ash, fiber, fat, lignin, and energy content.

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1.0 Introduction

The U.S. Department of Energy (DOE) is conducting pilot studies of remedies for a contaminated alluvial aquifer at the former uranium mill tailings site in Monument Valley, Arizona. Nitrate, ammonium, and sulfate levels are elevated in the aquifer. A DOE environmental assessment (EA) mandated the pilot studies to evaluate and demonstrate alternative remedies before a final strategy is selected (DOE 2004a). Preliminary studies suggested that natural and enhanced phytoremediation may be viable options for reducing nitrate and sulfate levels in the alluvial aquifer and at the plume source, and are consistent with revegetation and land management goals for the site (DOE 2002, 2004b). Phytoremediation relies on the roots of plants to remove, degrade, and slow migration of contaminants. In May 2005, DOE and the Navajo Nation jointly approved a second and final phase of pilot studies as proposed in a work plan published by DOE in 2004 (DOE 2004c). The purpose of this final phase is to evaluate the capacity of natural and sustainable processes, and methods to enhance natural processes that degrade and slow migration of contaminants both in the alluvial aquifer and at its source. Phytoremediation is but one of the natural and sustainable processes that may be contributing to the degradation and isolation of contaminants.

This report is a summary of work conducted on the Monument Valley pilot studies in 2005. Section 2.0 presents a strategy for using pilot study results to select a final remedy that focuses on natural and enhanced attenuation processes. The balance of the report provides summaries of the purpose, results thus far, and a path forward for each task in the pilot study work plan. Section 3.0 addresses source containment and removal tasks; Section 4.0, natural attenuation of ground water; Section 5.0, enhanced attenuation; and Section 6.0, land farming, a type of active ground water phytoremediation.

2.0 Natural and Enhanced Attenuation Strategy

Before and into the early 1990s, most large-scale attempts to clean up contaminated soil and ground water 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 (NRC 2000). By the mid 1990s, studies and experience had revealed several shortcomings (NRC 1994). Excavations can damage natural ecosystems and potentially expose workers or nearby residents. Many conventional pump-and-treat remedies for ground water contamination have not achieved cleanup goals (NRC 2000). Overall, engineered remedies have not always been successful in restoring contaminated soil and ground water.

As awareness of the limitations of engineering approaches grew, research began revealing more fully how naturally occurring processes (natural attenuation) in soils and ground water can transform or prevent the migration of contaminants (NRC 2000). Reliance on natural attenuation has increased as a consequence. Natural attenuation is now often 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 ground water contamination remaining after engineering approaches have removed or isolated the source of contamination (DOE 1996). 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 ground water." (EPA, 1999)

In 2003, DOE introduced the concept of enhanced attenuation (EA) and is now developing the technical basis and documentation to use EA as a transition between active engineered remedies and sustainable remedies that rely solely on natural processes (Early et al., 2006). The EA concept is a departure from classical EPA (1999) definition of MNA. An *enhancement* is any type of intervention that might be implemented in a source-plume system that increases the magnitude of attenuation by natural processes beyond what occurs without intervention. *Enhanced attenuation* is the result of applying an enhancement that *sustainably* manipulates a natural attenuation process leading to an increased reduction in mass flux of contaminants (Early et al., 2006). 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 processes that degrade or retard migration of contaminants in resultant plumes.

These pilot studies are designed to evaluate MNA and EA as the primary components of a final remedy for the alluvial aquifer at the Monument Valley site (DOE 2004b). Figure 1 illustrates a decision framework for using pilot study results to choose a final strategy. The framework is based on the assumption that natural and sustainable processes existing at the site have the capacity, either with or without enhancements, to remediate source area soils and the alluvial aquifer in an acceptable time frame. An overview of the steps of the decision process follows (see DOE 2004c, Section 4.0).

2.1 Evaluate Natural Attenuation Processes

The first step is to identify and estimate the contribution of natural processes acting to degrade and disperse nitrate and sulfate in the shallow plume and at its source. DOE has already shown that phytoremediation is a significant process. The attenuation capacity is the sum of all natural processes that act to lower contaminant mass as the shallow ground water moves away from the source. Monitoring well data provide an indirect indication of the total attenuation capacity. Characterization data will give estimates of the contributions of all key processes. The adequacy of MNA is measured as the mass balance of contaminants entering the shallow aquifer, from the both mill site and natural sources, and the capacity or sum of natural attenuation processes acting to lower contaminants levels in the aquifer. If the evaluation projects high confidence that contaminant loading is less than the sum of removal/dispersal processes, such that remediation objectives for the aquifer can be achieved in a reasonable time frame, then MNA will be selected as the final remedy.

2.2 Evaluate Natural Attenuation Enhancements

If the natural attenuation capacity is not sufficient to reduce nitrate and sulfate concentrations in shallow ground water to acceptable levels, then the next step is to determine whether *enhancements* can raise the attenuation capacity beyond what is occurring naturally. The pilot studies are designed to answer the following questions: (1) Is the incremental increase in attenuation capacity provided by enhancements enough? (2) Are enhancements sustainable

without costly and prolonged intervention? If the answers to these questions are a confident *yes*, then a combination of MNA and EA will be recommended as the final remedy.

2.3 Evaluate Active Phytoremediation

Land farming is a form of active phytoremediation. Shallow contaminated ground water is pumped and used to fertilize crops such as native plants for seed that could be marketed for mine land reclamation. The land farm pilot study is addressing several issues: land suitability for irrigation, cropping system selection, nitrate uptake and toxicity, fate and toxicity of sulfate, irrigation management, farm operation requirements, and land management. If pilot study results show that combinations of MNA, EA, and/or land farming are inadequate to achieve remediation objectives for Monument Valley, then other remedies will be considered.

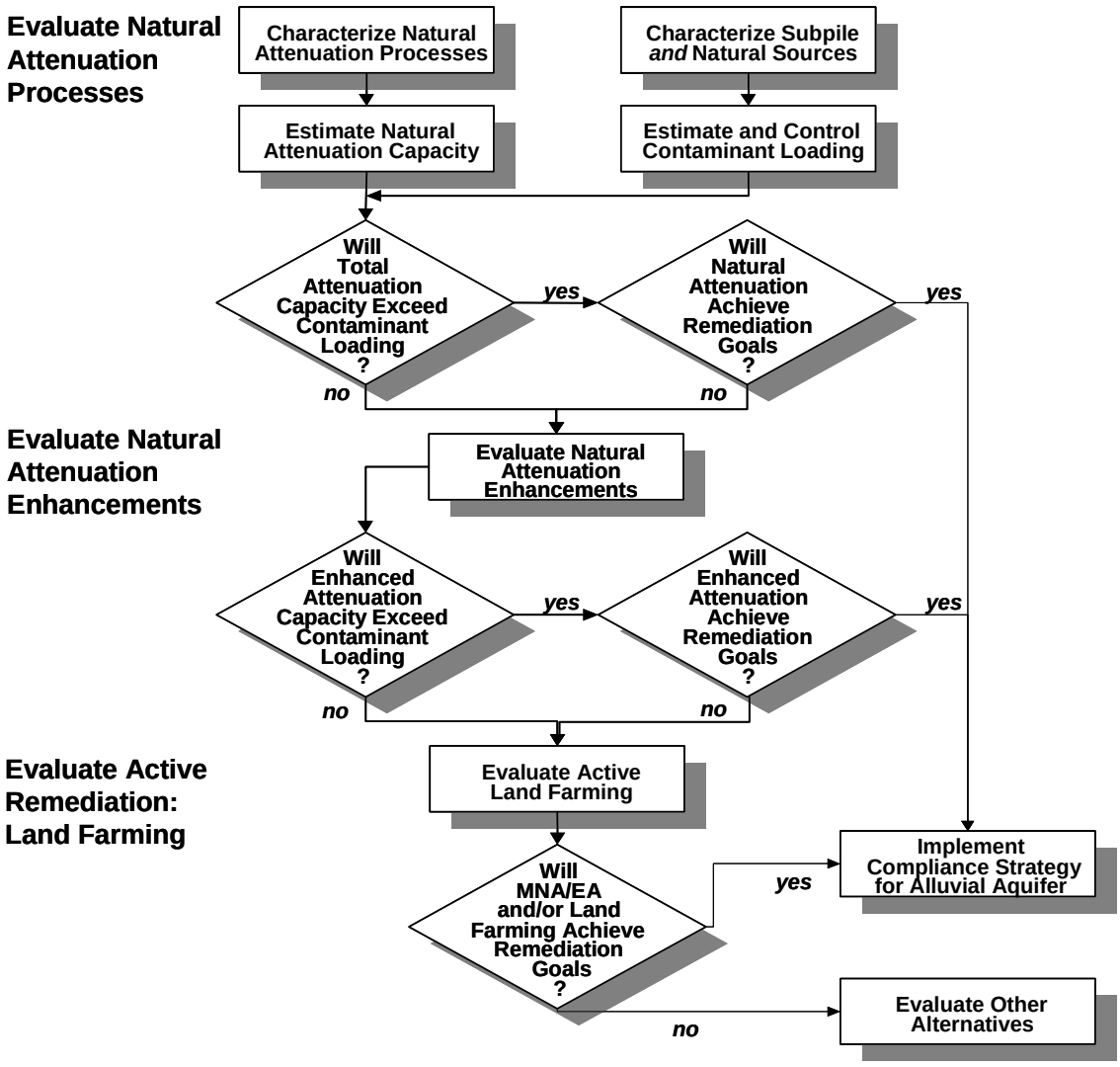

Figure 1. Framework for applying pilot study results to choose a final remedy for the alluvial aquifer at Monument Valley.

3.0 Source Containment and Removal

The final remedy for the alluvial aquifer will include measures to contain and remove mill-related sources of contamination. Efforts to clean the ground water may be unsuccessful if source loading is not curtailed. In 1994, DOE completed a mandated remediation of *radioactive* constituents of tailings and soils at the site. Materials with radium-226 concentrations exceeding 15 picocuries per gram were removed and hauled to a disposal cell near Mexican Hat, Utah. However, in 1997, soil sampling within the footprint of a former tailings pile (subpile soil) discovered elevated levels of ammonium and nitrate, ranging from 45−1,060 mg kg^{-1} and 0−273 mg kg^{-1}, respectively. The subpile soil is assumed to be a continuing source of contamination for the alluvial aquifer extending to the north.

This section addresses the isolation and removal of mill-related sources of nitrogen assumed to be entering the alluvial aquifer. Tasks include characterizing the extent of mill-related and natural sources of nitrate and sulfate, developing EA remedies that rely on plants and microbes to limit leaching and remove the source, and testing of monitoring methods and instrumentation to determine if the EA remedies are working.

3.1 Delineate Extent of Mill-Related Contamination

The purpose of this task was to determine the full extent and concentrations of ammonium and nitrate in mill-related source areas. Mechanical crushing and separating operations beginning in 1955 produced a coarse-grained tailings pile, the Old Tailings Pile (Figure 2). Other than flocculants, no chemicals were used; hence the Old Tailings Pile is not considered to be a source. Starting in 1964, batch and heap leaching of ore used sulfuric acid, ammonia, and ammonium nitrate. These chemical solutions were discharged to the New Tailings Pile (Figure 2). An evaporation pond to the east was probably used to retain seepage from the New Tailings Pile. Source area sampling during 2005 was constrained within the historical boundaries of the New Tailings Pile and the evaporation pond.

3.1.1 Methods

Soils within the footprint of the New Tailings Pile and the Evaporation Pond were sampled to a depth of 15 feet (ft) and analyzed for ammonium and nitrate content. The objective of the sampling design was to detect the presence of local areas of elevated concentrations—hot spots—as a basis for expanding the source area phytoremediation. The sampling design consisted of a systematic grid with random starting points (Gilbert 1987, pp. 119-131). Sample locations were spaced 100 ft apart in a triangular grid pattern.

Sampling was generally confined within the boundaries of the New Tailings Pile and Evaporation Pond. Historical footprints of these source areas were delineated from aerial photographs taken before tailings were removed (Figure 3). Visual Sample Plan (VSP) software (Battelle 2005) calculated grid spacing using an algorithm developed by Singer (1975), and produced a sample location map (Figure 4) with x:y coordinates. The calculation used an elliptical hot spot area approximately 2300 ft^2 (the reference hot spot shape and size were based on 1997 sampling results; DOE 2002), and a 95 percent probability of detection. A hot spot was defined as an area with soil nitrate (NO_3^--N) concentrations of ≥100 mg/kg. Sample points, located using GPS, were flagged and 100-300 g samples were taken at depths of 1, 3, 6, 9, 12

and 15 ft (or to bedrock or the water table) using hand augers and a Geoprobe. Sampling began December 6-10, 2004, and was completed January 17-18, 2005.

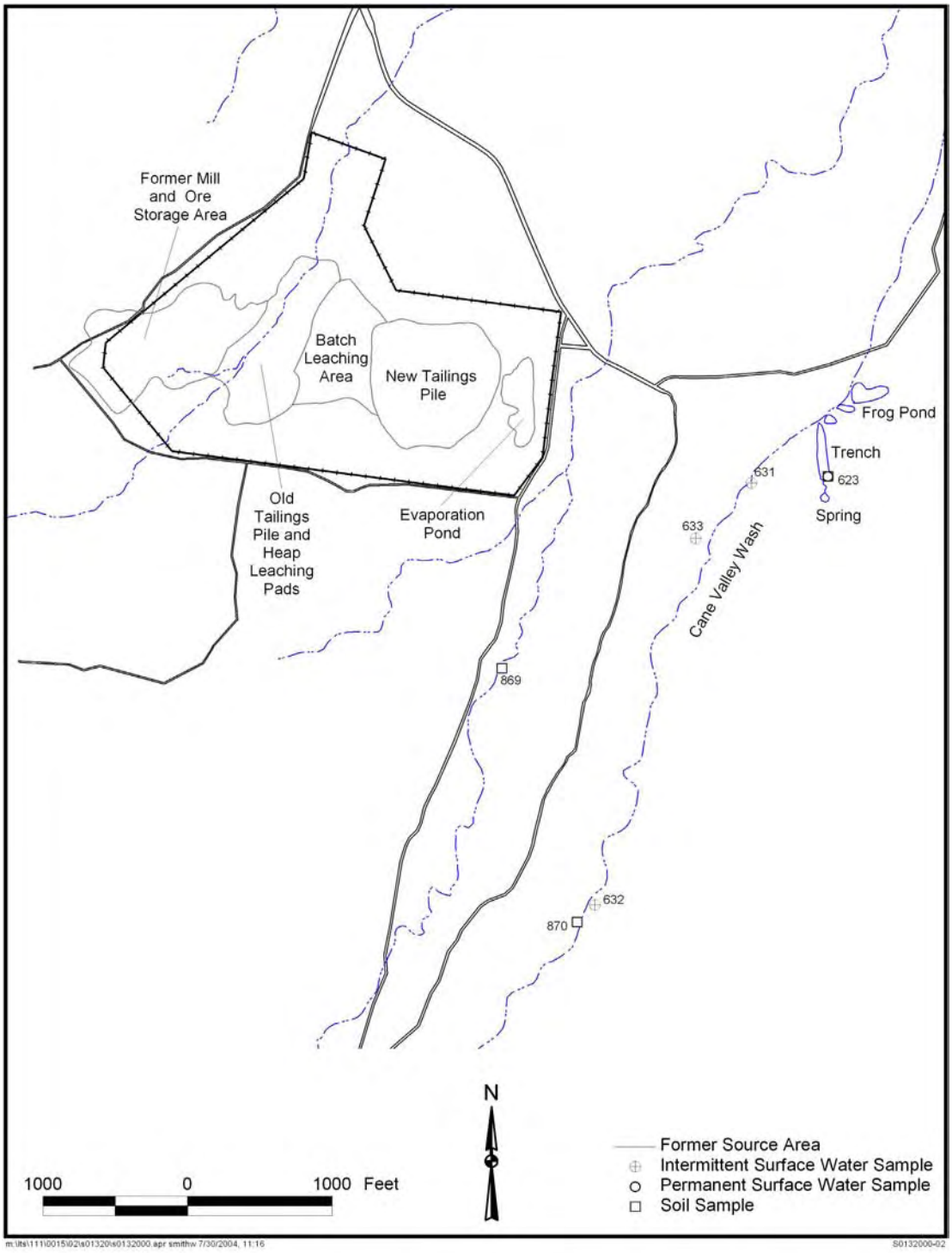

Figure 2. Map of potential source areas for the alluvial plume.

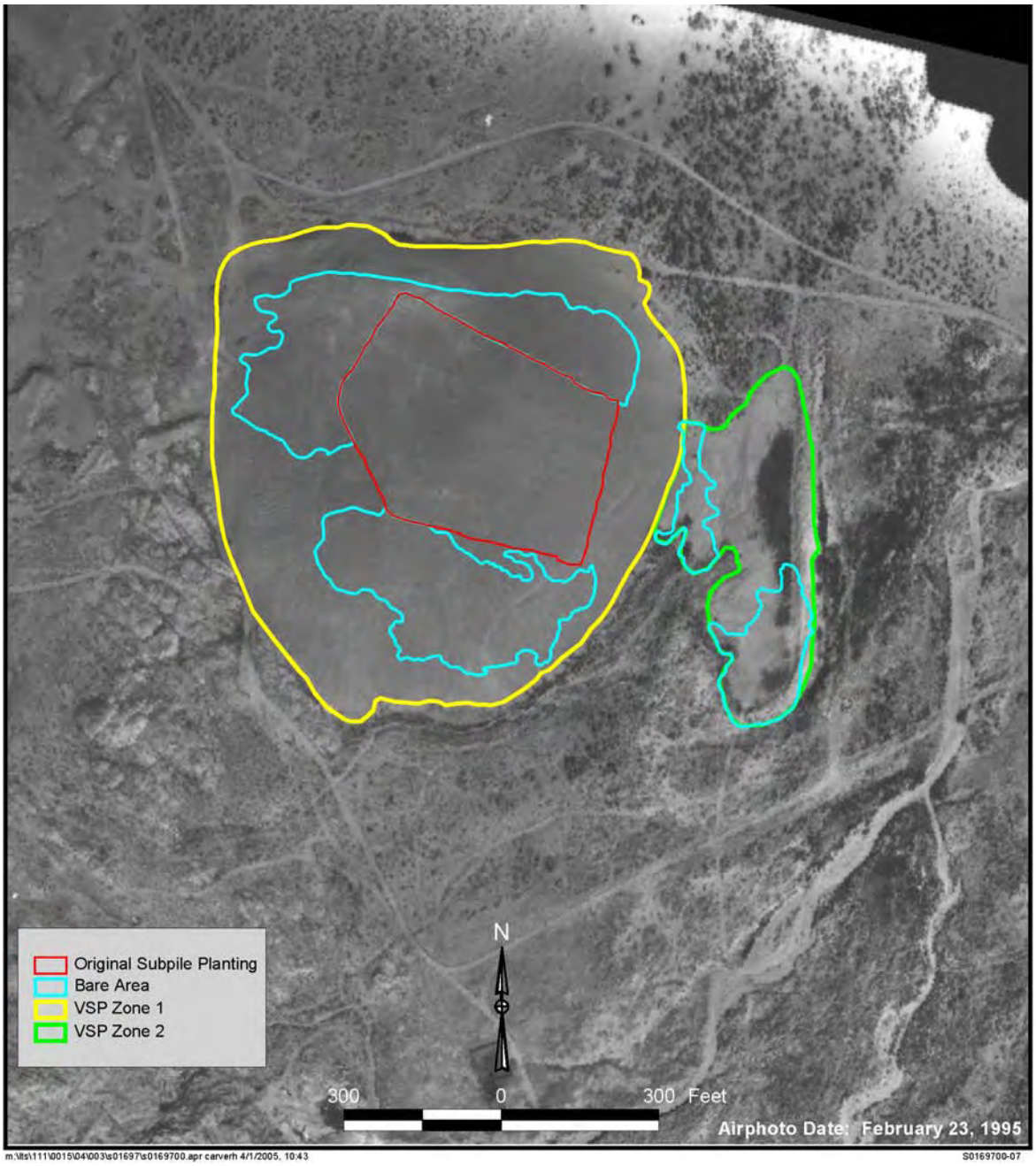

Figure 3. Pre-reclamation aerial photograph of source areas with New Tailings Pile (VSP Zone 1) and Evaporation Pond (VSP Zone 2) boundaries, and GPS-mapped demarcation of the original subpile phytoremediation planting and adjacent bare areas.

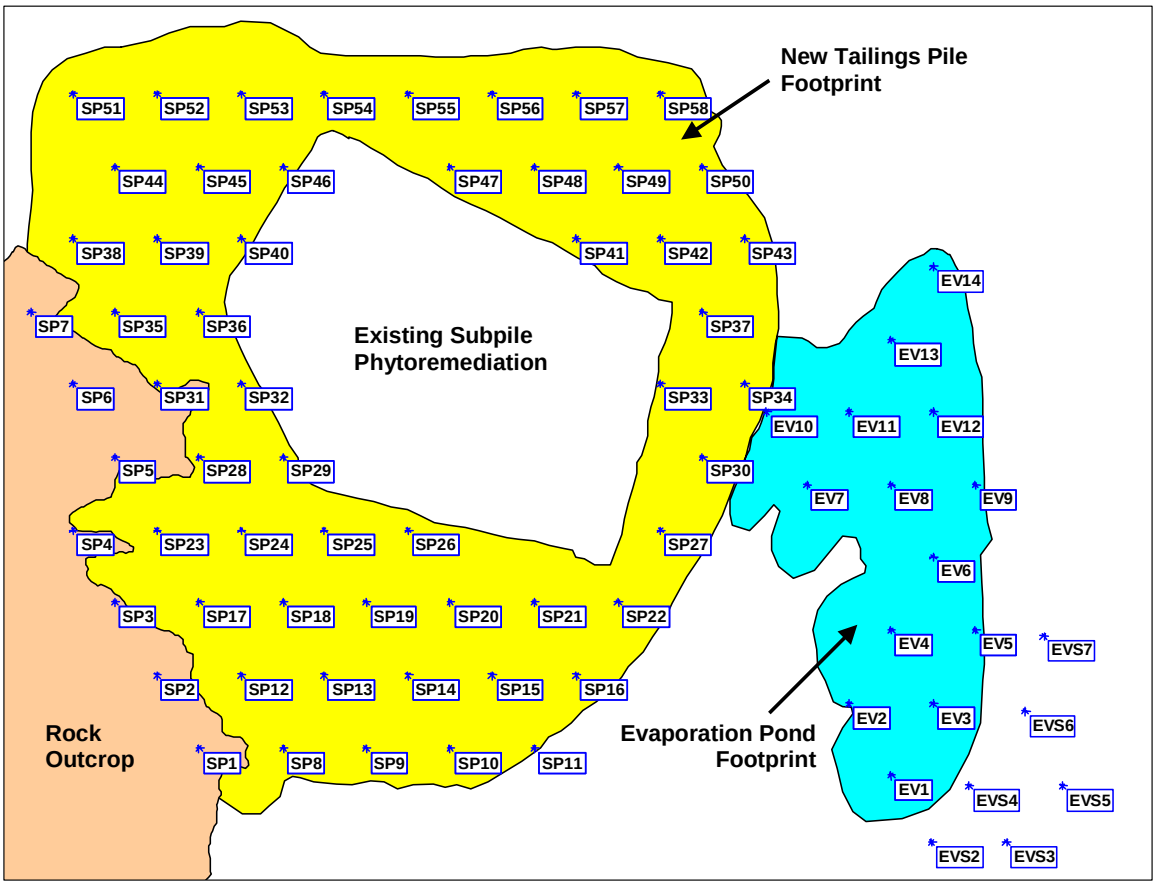

Figure 4. Triangular grid sample points (100 ft spacing) within the New Tailings Pile and Evaporation Pond footprints. Points falling within the boundaries of the rock outcrop were omitted.

Sampling in the New Tailings Pile footprint began at locations closest to the existing phytoremediation planting and then continued outward toward the historical boundary. Samples were analyzed in the ESL Mobile Laboratory for ammonium and nitrate content as they were collected in the field. Selection of subsequent sampling locations relied on these preliminary results; where concentrations were elevated, sampling continued outward to the next closest grid points. 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 4).

All samples were analyzed a second time at ESL using a variation of the "Standard Batch Leaching" procedure (Stoller 2006). Samples were air-dried and sieved through a #10 mesh (<2 mm). Twenty gram samples of <2mm material were mixed with 50 mL 1M KCl in 125 mL Nalgene bottles, stirred at 8 RPM for 2 hours, and centrifuged 20 minutes at 3500 RPM. The KCl solutions were decanted and centrifuge bottles were again filled with 50 mL 1M KCl, stir for 30 minutes, and decanted. Samples were again centrifuged 20 minutes at 3500 RPM and decanted. Decanted KCl solutions were then filtered (0.45 υm). KCl extractions were analyzed by ion chromatography for NO_3^-, and with Hach spectrophotometry for NH_3. All analyses were performed the same day that extraction took place.

3.1.2 Results and Discussion

Soil concentrations of nitrate as N (NO_3^--N) and ammonia as N (NH_3-N) in the source areas are shown in Figure 5 and Figure 6, respectively. Sampling inside the existing subpile planting occurred October 2004 as part of routine annual monitoring (DOE, 2004b). All other data are from the current grid sampling. These figures were created by importing data and shape files to Environmental Visualization System (EVS) software and running a krigging 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 highest values within the vertical profile at each sampling location are shown. Concentrations of NO_3^--N ranged from less than 5 mg/kg to 977 mg/kg in the New Tailings Pile footprint. Areas with greater than 100 mg/kg NO_3^--N extended both north and south of the existing subpile planting. A hot spot with NO_3^--N concentrations ≥100 mg/kg and approximately 200 ft wide was detected at the southern end of the Evaporation Pond and extending east of the footprint. Concentrations of NH_3-N ranged from less than 5 mg/kg to 650 mg/kg in the New Tailings Pile footprint; the highest levels were within the boundaries of the existing subpile planting. NO_3^--N concentrations exceeded 100 mg/kg at only one sampling location in the Evaporation Pond footprint.

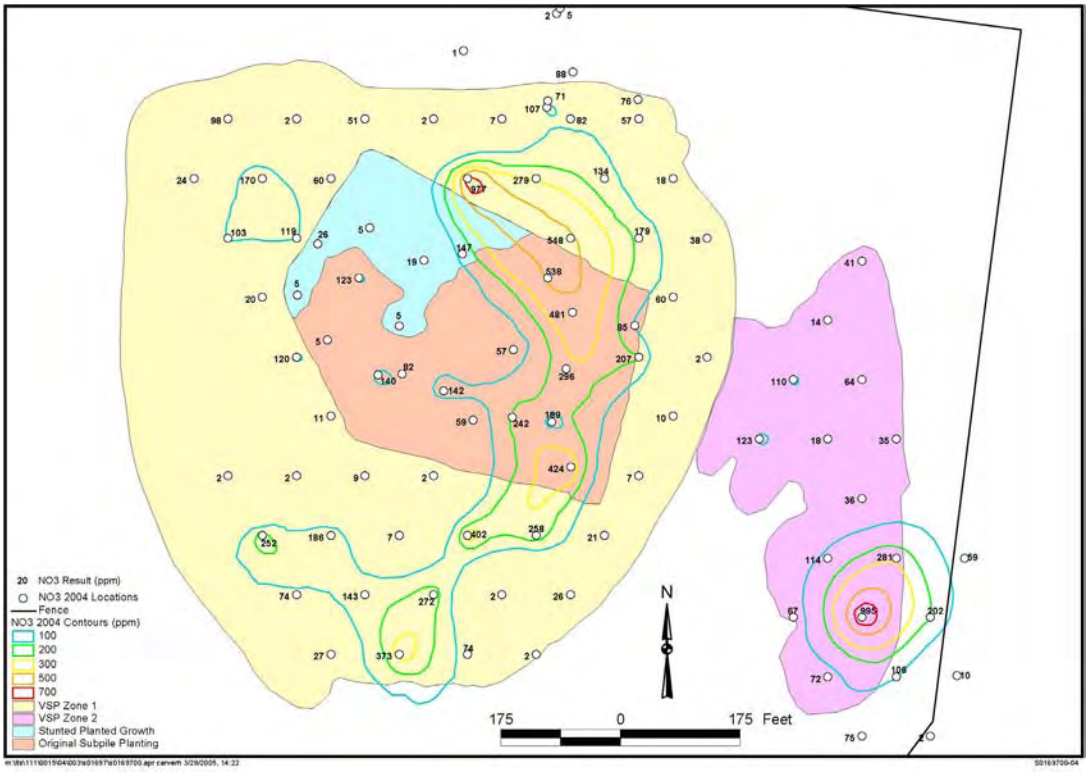

Figure 5. Map of nitrate (NO_3^--N) concentrations within the New Tailings Pile and Evaporation Pond source areas created from 2004 sampling results.

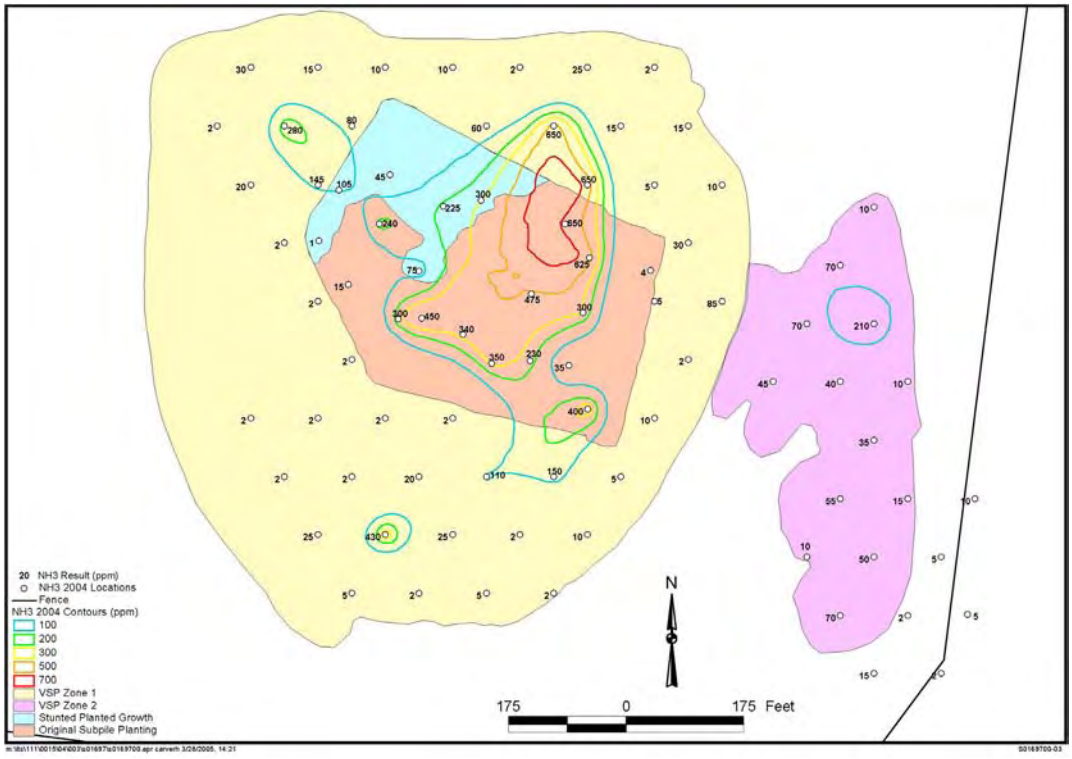

Figure 6. Map of ammonia (NH_3-N) concentrations within the New Tailings Pile and Evaporation Pond source areas created from 2004 sampling results.

The results of this task (extent of soil nitrate and ammonium in footprints of the New Tailings Pile and Evaporation Pond) was used to plan an expansion of the source area phytoremediation planting and irrigation system (see Section 3.4). These data will also be used as baseline for future evaluation of the capacity of source area phytoremediation and bioremediation efforts. Sampling will be repeated annually to monitor changes in nitrate and ammonium and compared with this baseline.

3.2 Investigate Natural Sources of Nitrate and Sulfate

Southwestern deserts are known to naturally accumulate nitrate and sulfate in soil horizons, in the vadose zone, and in ground water. Natural sources may be contributing to nitrate and sulfate in the alluvial aquifer at Monument Valley. The purpose of this 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 is needed to establish reasonable cleanup goals for the alluvial plume.

3.2.1 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 when geologic parent materials are high in gypsum, as is the case at Monument Valley. Soils and vadose-zone sediments were sampled at varying

depths from locations overlying the alluvial nitrate and sulfate plumes. Samples were analyzed at the Environmental Sciences Laboratory in Grand Junction.

3.2.1.1 Methods

Samples were collected using a hand auger on January 17-18, 2005, near wells 606, 656, 679 and 765, every half-meter from the surface down to a depth of 7 meters. Because of depth limitations with the use of a hand auger, field personnel returned on June 27-28, 2005, and collected samples at four additional locations using a Geoprobe. Two locations, 606-A and 606-B, were selected near well 606, and two locations, 677-A and 677-B, were selected near well 677. The four locations were sampled every 3 feet from the surface to 30 feet (33 feet at 606-A). All sampling locations are shown in Figure 7. On both occasions, grab samples taken at each depth were placed in double Ziploc bags, labeled with location, depth and date, and stored in coolers for transportation back to the Environmental Sciences Laboratory for analysis. Samples were analyzed using laboratory methods described in
Section 3.1.

3.2.1.2 Results

Table 1 and Table 2 show results for the two vadose zone sampling dates. Figure 8 and Figure 9 are "fence diagrams" created from the combined data sets using a modeling software program called Environmental Visualization System (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 concentrations (NO_3^--N) in the vadose zone range from < 5.6 (detection limit of the analytical procedure) to 119.6 ug/g. NH_3-N was not detected in the vadose zone. Detectable nitrate concentrations occurred primarily between 24 feet below the surface and ground water, which varied between 30 and 35 feet below the surface. For the January sampling, we were unable to sample below about 21 feet with hand augers. Using a Geoprobe for the June sampling, we were able to retrieve samples from the surface down to ground water.

Elevated nitrate concentrations were encountered 3 ft to 6 ft above the aquifer in all four June borings. These results are inconclusive with respect to origin of the nitrate. Walvoord et al. (2003) found natural reservoirs of nitrate at depths ranging from approximately 3 ft to 15 ft in areas with healthy native vegetation. Where deserts had been irrigated or where evapotranspiration rates are low, the nitrate zone occurs from 25 ft to 30 ft below the surface, as we found at Monument Valley. However, at this depth, the high nitrate layer is just above and continuous with the alluvial plume, hence vadose zone nitrate at Monument Valley may be attributable to the capillary fringe of the plume. Even if the nitrate layer is naturally occurring, concentrations are relatively low, and we can conclude that the mill site is the major 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 2975 ug/g. Concentrations greater than 100 ug/g occurred in all borings except near well 679. The elevated concentrations likely represent naturally occurring zones of gypsum ($CaSO_4^{2-}$) accumulation.

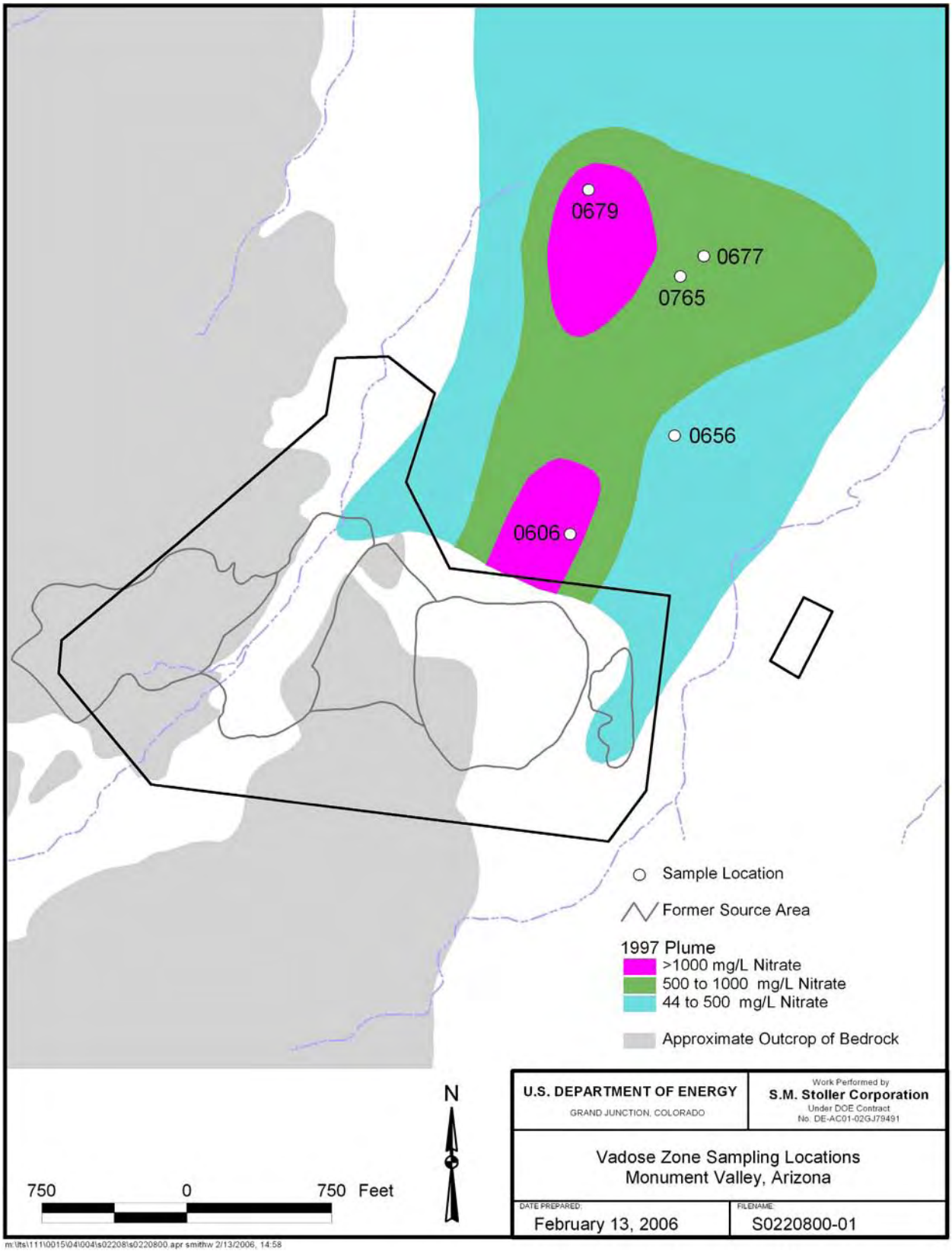

Figure 7. Map of Monument Valley site showing vadose zone sampling locations from both the January and June 2005, sampling events.

Table 1. January 2005, Vadose Zone Soil Sample Results from Monument Valley, Arizona Site

Location	Depth (m)	Moisture Content (%)	NO3-N (ug/g)	SO4 (ug/g)
Well 606	0.5	1.85%	<5.6	<25
	1.0	3.90%	<5.6	<25
	1.5	4.56%	<5.6	<25
	2.0	1.69%	<5.6	<25
	2.5	1.98%	<5.6	145
	3.0	-1.43%	<5.6	160
	3.5	-0.16%	<5.6	695
	4.0	0.24%	<5.6	780
	5.0	4.73%	<5.6	1565
	5.0	8.91%	<5.6	1995
	5.0		<5.6	2020
	5.5	8.74%	<5.6	2110
	5.8	8.73%	<5.6	1935
	6.0	4.79%	<5.6	870
	6.5	1.97%	<5.6	350
	7.0	3.71%	<5.6	100
Well 656	0.5	6.61%	<5.6	<25
	1.0	0.96%	<5.6	<25
	1.5	0.81%	<5.6	<25
	2.0	0.93%	<5.6	170
	2.5	1.56%	<5.6	890
	3.0	1.43%	<5.6	835
	3.5	1.83%	<5.6	825
	4.0	2.09%	<5.6	345
	4.5	2.20%	<5.6	1445
	5.0	3.51%	<5.6	700
	5.5	2.18%	<5.6	645
	6.0	2.54%	<5.6	695
	6.5	2.91%	<5.6	490
	7.0	5.44%	<5.6	945
	7.0		<5.6	970
Well 679	0.5	7.16%	<5.6	<25
	1.0	1.33%	<5.6	<25
	1.5	0.66%	<5.6	<25
	2.0	1.46%	<5.6	<25
	2.5	0.96%	<5.6	<25
	3.0	0.76%	<5.6	<25
	3.5	1.59%	<5.6	<25
	4.0	1.02%	<5.6	<25
	4.5	1.06%	<5.6	<25
	5.0	1.63%	<5.6	<25
	5.5	1.11%	<5.6	<25
	6.0	1.49%	<5.6	<25
	6.5	1.27%	<5.6	<25
	7.0	1.53%	<5.6	<25
Well 765	0.5	4.75%	<5.6	<25
	1.0	6.98%	51.9	540
	1.5	2.33%	9.0	70
	2.0	0.99%	<5.6	55
	2.5	0.94%	<5.6	<25
	3.0	0.90%	<5.6	45
	4.0	1.57%	<5.6	65
	5.0	3.08%	<5.6	255
	6.0	2.37%	<5.6	150
	7.0	3.02%	<5.6	205

Table 2. June 2005, Vadose Zone Soil Sample Results from Monument Valley, Arizona Site

Location	Depth (ft)	Moisture Content	NO3-N (ug/g)	SO4 (ug/g)	NH3-N (ug/g)
Well 606-A	3	1.12%	<5.6	<25	<5
	6	2.62%	<5.6	25	<5
	9	0.89%	<5.6	<25	<5
	12	0.92%	<5.6	135	<5
	15	2.40%	<5.6	1085	<5
	18	8.93%	<5.6	2975	<5
	21	11.70%	<5.6	2075	<5
	24	4.18%	7.9	105	<5
	27	3.12%	22.6	130	<5
	30	11.66%	30.5	120	<5
	33	17.90%	39.5	90	<5
Well 606-B	3	0.50%	<5.6	<25	<5
	6	2.69%	<5.6	<25	5
	9	0.93%	<5.6	30	5
	12	1.52%	<5.6	85	5
	15	8.05%	<5.6	1385	5
	18	7.86%	<5.6	1435	5
	21	1.91%	<5.6	95	<5
	24	7.10%	115.1	475	<5
	24		119.6	485	5
	27	7.59%	65.5	325	5
	30	18.92%	37.2	110	105
Well 677-A	3	0.85%	<5.6	<25	<5
	6	2.15%	<5.6	190	<5
	9	0.56%	<5.6	<25	5
	12	0.69%	<5.6	25	<5
	15	0.63%	<5.6	50	<5
	18	2.04%	<5.6	45	<5
	21	0.77%	<5.6	80	<5
	24	2.00%	<5.6	335	<5
	27	4.88%	20.3	335	5
	30	16.46%	45.1	330	<5
Well 677-B	3	0.65%	6.8	40	<5
	6	1.05%	<5.6	<25	<5
	9	1.39%	<5.6	50	<5
	12	1.19%	<5.6	<25	<5
	15	1.08%	<5.6	30	10
	18	1.45%	<5.6	55	<5
	21	1.71%	<5.6	65	<5
	24	2.25%	<5.6	85	<5
	27	3.71%	11.3	290	<5
	30 red	21.35%	64.3	490	<5
	30 white	22.49%	95.9	550	<5
	30 white		80.1	480	<5

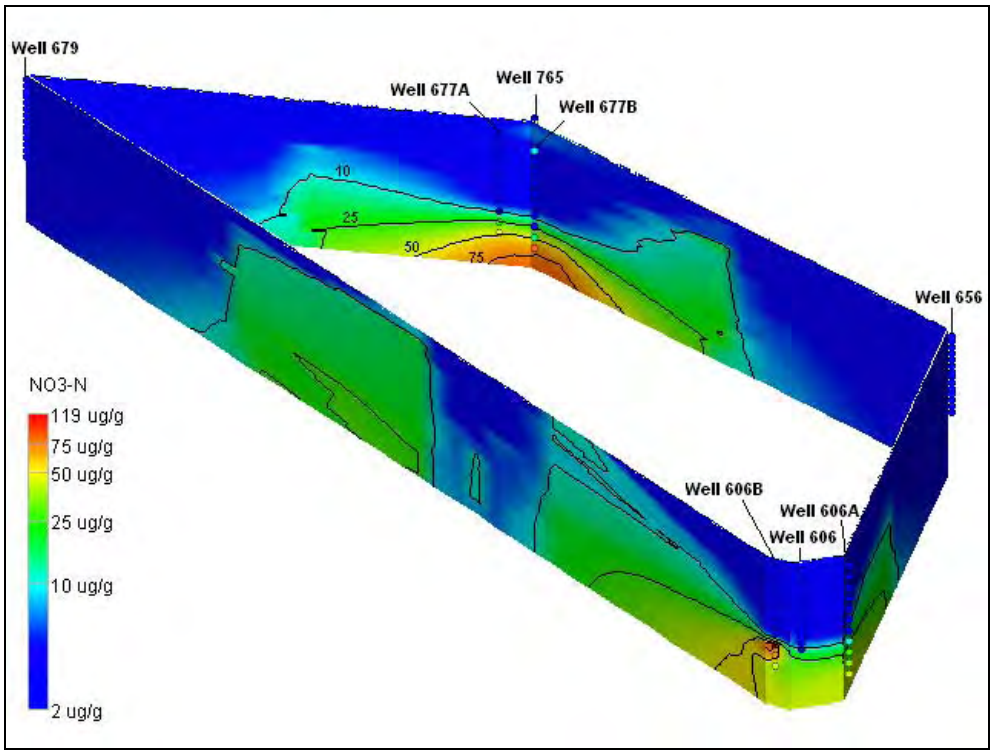

Figure 8. Monument Valley, Arizona, site view of EVS-generated solid-phase NO_3 fence diagram. View perspective is from the southwest looking to the northeast.

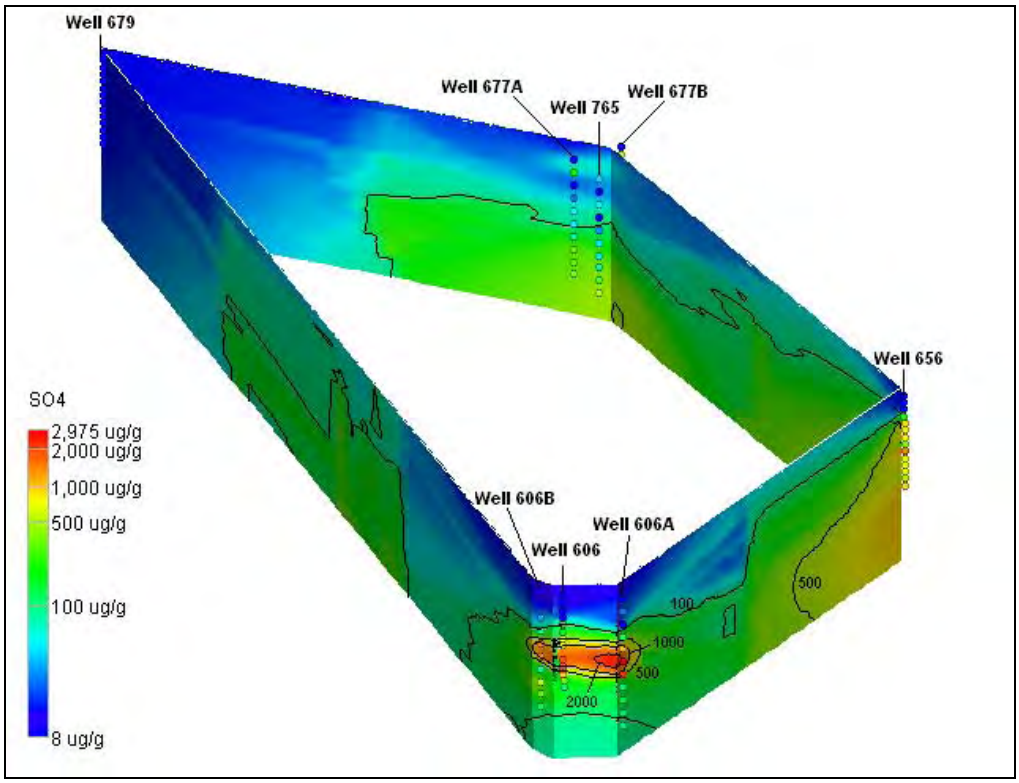

Figure 9. Monument Valley, Arizona, site view of EVS-generated solid-phase SO_4 fence diagram. View perspective is from the South-Southwest looking to the North-Northeast.

The highest SO_4^{2-} levels were found in a distinct layer in borings near well 606 between about 15 ft and 20 ft below the surface. More diffuse zones of SO_4^{2-} accumulation occurred throughout the vadose zone profile in borings 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 evapotranspiration, resulting in greater infiltration and leaching of gypsum salts. The next step is to estimate the mass contribution of natural vadose zone sulfate as a plume source.

3.2.2 Up-Gradient Alluvial Ground Water

Background concentrations of sulfate (SO_4^{2-}) and nitrate (NO_3^-) in the alluvium up gradient of the plume at the Monument Valley Site were measured. In Figure 5-14 of the *Site Observational Workplan for the Monument Valley Site* (DOE, 1998), eight locations are shown which were used to monitor background in the alluvium. The mean SO_4^{2-} and nitrate as N (NO_3^--N) concentrations at these locations are 240 and 1.8 mg/L, respectively (Table 3). The results indicated highly variable concentrations of these dissolved ions, particularly SO_4^{2-}.

Table 3. Alluvial Sulfate and Nitrate Concentrations Measured in Background Wells Prior to this Study

Well ID	Ownership	Depth (ft)	Sulfate (mg/L)	Nitrate as N (mg/L)
0200	Private (Ben Stanley)	Unknown	543	2.37
0400	Private (Tribal Well)	12	96	0.23
0402, 0403, and 0404	DOE	8 - 10	~30	~0.02
0602	Private	35	125	0.45
0603	DOE	55	112	0.45
0616	Private	Unknown	183	1.6
0617	Private	Unknown	160	6.8
0640	Private	Unknown	668	2.5
Mean Sulfate Concentration = 240 mg/L; Standard Deviation = 233mg/L Mean Nitrate-N Concentration = 1.8 mg/L				

The high degree of variability in alluvial ground-water sulfate concentrations could be due to many factors. Many of the wells are private and completion depths are largely unknown. Production rates (which are also unknown) likely affect concentrations. Some of the wells are located on the axis of Cane Creek and are probably affected by the occurrence and quality of surface water. Some of the wells are very shallow (8 ft to 10 ft) and are likely tapping perched ground water that may not be representative of the deeper alluvial aquifer. Chemistry of the wells (0402, 0403, and 0404) in the Frog Ponds area (taken collectively as one sampling location in Table 3) indicate that the ground water at this location is influenced by artesian ground water from the DeChelly Sandstone (DOE 1998).

Another factor affecting ground water composition is the variability in geologic strata it contacts. For example, the Moenkopi Formation contains gypsum which would contribute SO_4^{2-} to ground water contacting it. The geologic beds are steeply dipping in the Cane Creek area; thus, the alluvial ground water makes contact with a variety of strata within and upgradient of the project site (see Plate 2 in DOE 1998).

In summary, there are large uncertainties in the concentrations of SO_4^{2-} and NO_3^--N in upgradient background wells that could only be properly evaluated by placing and sampling additional monitoring wells. To meet this need, 19 new borings were drilled. Three of the borings were dry and were abandoned; the other 16 were made into monitoring wells.

3.2.2.1 Methods

Wells were drilled between September 7 and 11, 2005, with a Geoprobe using direct push methodology. Borings were 2-inch diameter and the wells were 1-inch diameter. Each well has a 5-ft long interval screened at the bottom of the well. A bentonite seal was placed in the annulus from about 6 ft to the surface. Beneath the bentonite is about 15 ft of well sand and below the well sand, the alluvium was allowed to collapse around the well pipe. Wells were completed with about a 2-ft stickup, protected by a 4-inch diameter PVC casing cemented in place. Wells were capped and locked. Table 4 contains information about the wells. Well locations were surveyed using GPS. Well data were entered into the SeePRO database. More details on well installations are provided in DOE (2006).

Table 4. Information on Wells Installed for this Project

Well Number	Total Depth (ft)	Depth to Water (ft from TOC)	Screened Interval (ft)
0711	32.50	12.79	27.50–32.50
0712	31.01	10.03	26.01–31.01
0713	37.41	13.60	32.41–37.41
0714	27.36	15.90	22.36–27.36
0715	23.00	11.26	18.00–23.00
0716	29.00	10.51	24.00–29.00
0717	32.75	18.77	27.75–32.75
0718	35.91	10.97	30.91–35.91
0719	26.35	12.73	21.35–26.35
0720	41.55	13.20	36.55–41.55
0721	34.00	9.95	29.00–34.00
0722	36.00	8.92	31.00–36.00
0724	31.19	14.96	26.19–31.19
0725	40.79	15.11	35.79–40.79
0726	32.22	11.87	27.22–32.22
0727	30.73	14.44	25.73–30.73

Ground water samples were collected September 7 - 11, 2005, by using a peristaltic pump. Samples were analyzed in the ESL mobile laboratory generally within a few hours of collection. Analysis of SO_4^{2-} and NO_3^--N were made spectrophotometrically using procedures AP(SO_4-3) and AP(NO_3-3), respectively (Stoller 2006).

3.2.2.2 Results and Discussion

Ground water concentrations of SO_4^{2-} and NO_3^--N in background wells are shown on Figure 10 and Figure 11, respectively. The 700-series wells were sampled and analyzed in September 2005; whereas the most recent data (mostly from 2000 to 2002) were used for all other wells. Symbols on the figures are proportional to concentration.

Sulfate concentrations in the background area range from less than 1 mg/L to 580 mg/L and are highly variable with a mean concentration of 152 mg/L and a standard deviation of 157 mg/L (Figure 10). Two wells (0718 and 0640) located near each other between the drainages had the two highest SO_4^{2-} concentrations (300 and 550 mg/L). A well (0712) located about 700 ft downgradient from these also had a high SO_4^{2-} concentration (292 mg/L) suggesting that the highest concentrations occur is this area between the drainages. However, ground water in two nearby wells (0717 and 0724) had low SO_4^{2-} concentrations (35 and 78 mg/L, respectively).

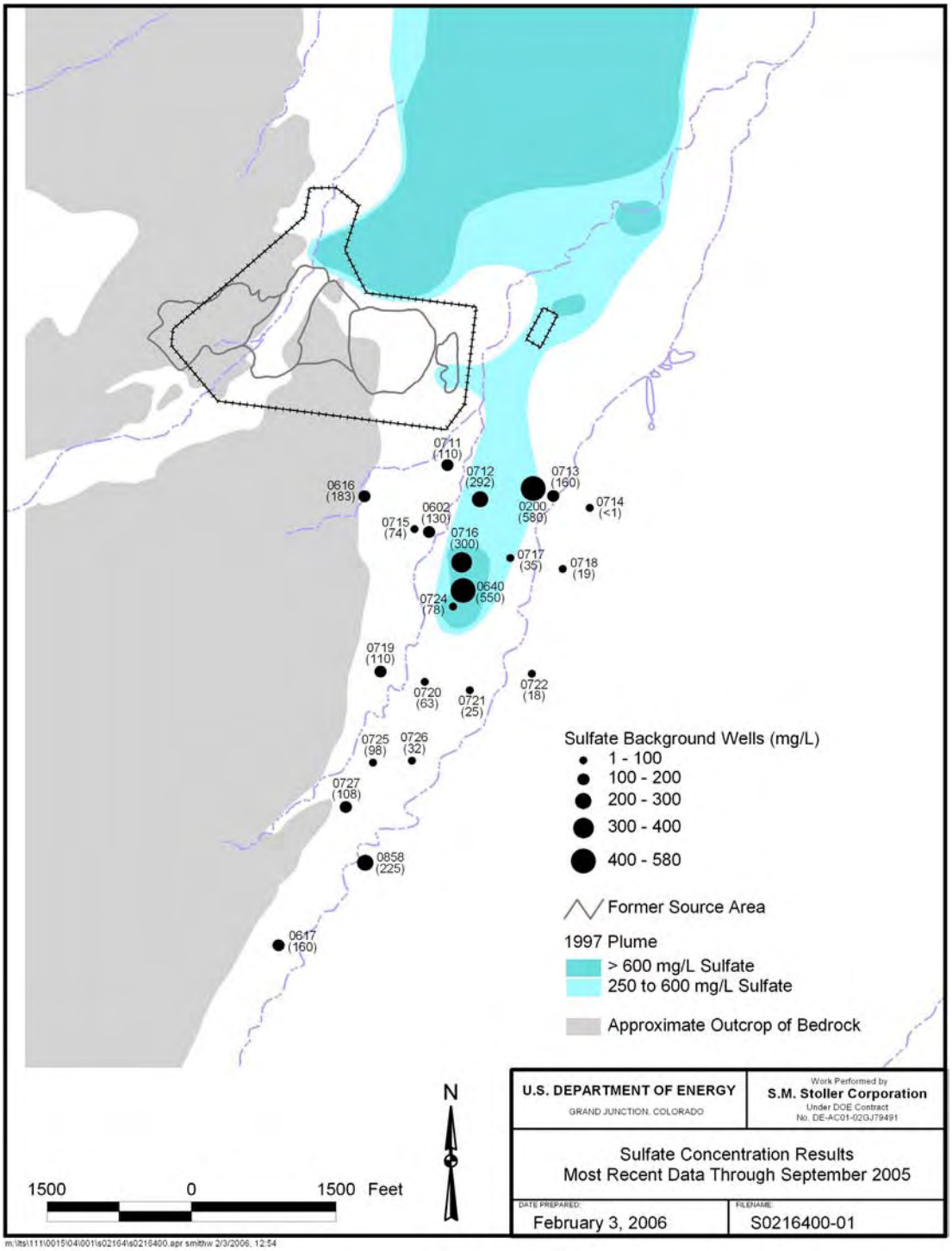

Figure 10. Sulfate concentrations in alluvial background wells.

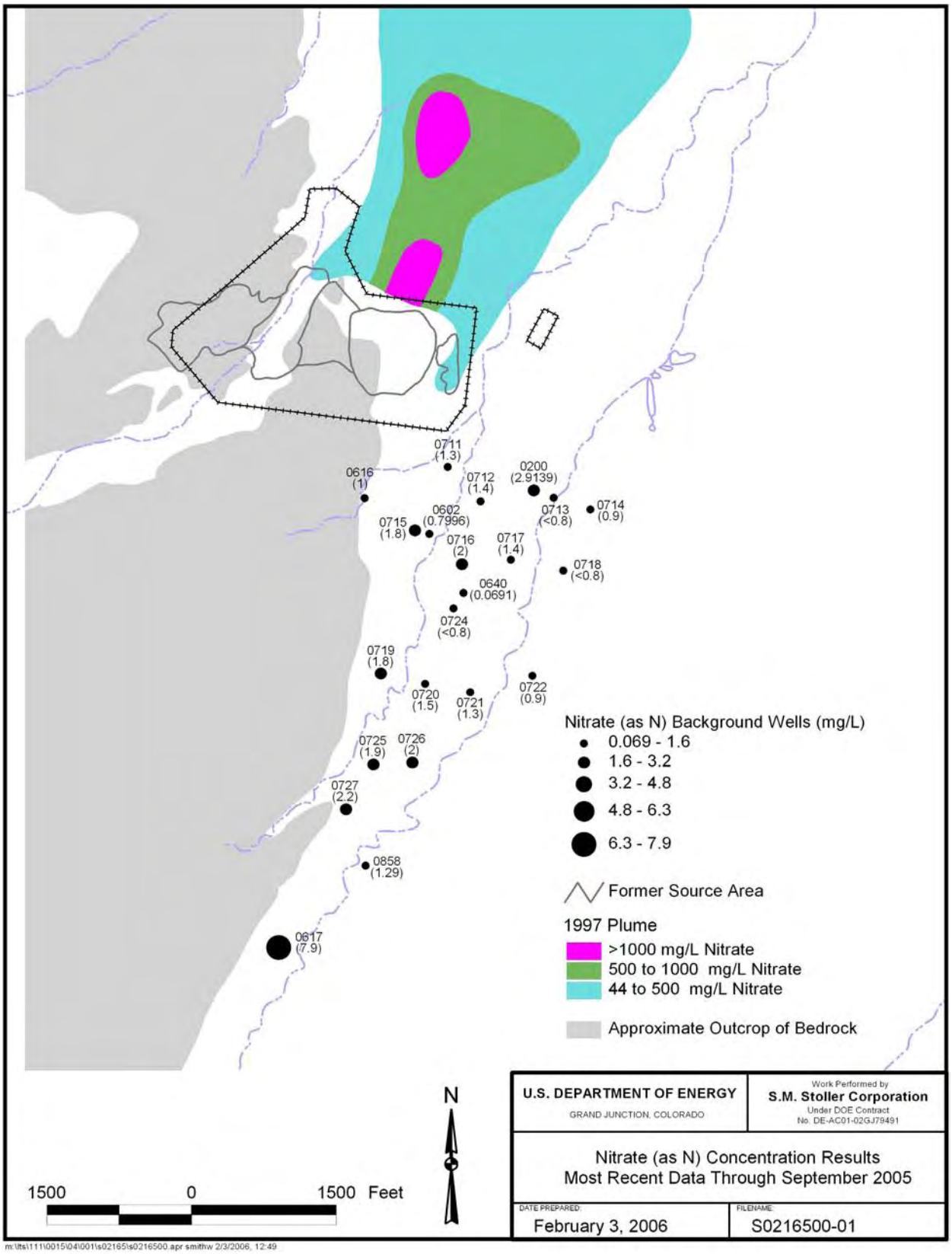

Figure 11. Nitrate (as N) concentrations in alluvial background wells.

Ground water in three wells (0714, 0718, and 0722) east of Cane Wash had relatively low concentrations of SO_4^{2-} (<1, 19, and 18 mg/L, respectively). Two of these wells (0714 and 0718) produced so little water that well development was not possible. The low SO_4^{2-} concentrations in these wells may be related to the low ground water production. Perhaps the small volume of water is from recent rainfall and not representative of ground water.

The highly variable concentrations of SO_4^{2-} are suggestive of a ground water 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 ground water samples may be reflecting this variation. Another explanation for the variability is the presence of a mixing zone where upwelling ground water from the DeChelly Sandstone mixes with ground water originating from local recharge. DeChelly ground water is low in SO_4^{2-} whereas local recharge is likely a source of higher concentrations resulting from evaporation. Upwelling DeChelly ground water is thought to be responsible for the low chemical concentration signature observed in the Frog Pond area located along Cane Wash about 1,000 feet downstream of the background area (DOE 1998).

Nitrate concentrations are relatively low throughout the background area. Nitrate (as N) concentrations range from less than 0.8 mg/L to 7.9 mg/L (Figure 11). The highest value was observed in a sample of ground water collected from the furthest south background well (0617). These low concentrations are typical of many ground waters and could result from natural or anthropogenic sources. The low NO_3^- concentrations in the background area, coupled with relatively low nitrate levels in the vadose zone overlying the plume (Section 3.2.1), indicate that essentially all of the NO_3^- in the plume is due to contamination from the mill site.

3.3 Determine Causes and Recourses for Stunted Plant Growth

An area of poor plant growth occurs in the western third of the existing subpile planting. Previous analyses of soil samples from areas with both poor and good growth show that nitrate, sulfate, calcium, magnesium, strontium, and vanadium were higher in the poor-growth area. Conversely, concentrations of iron, manganese, phosphate, potassium, sodium, and uranium concentrations were significantly lower in the poor-growth area. The stunted growth of the *Atriplex* 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 the 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 agent(s) of poor growth. High soil compaction is another possible cause of poor plant growth. Soil was sampled both inside and outside the area of suppressed growth to determine bulk density as a measure of compaction.

The soil in the poor-growth area appears white in aerial photos. The white stain in the photos also appears to coincide with a subsurface, black-mottled layer. Further analyses were conducted to attempt to identify the cause of stunted growth so that amendments or different planting methods can be used in the expanded planting. At the Tsalie, Arizona campus of Dine' College, students conducted greenhouse studies, using bulk soil from the poor-growth area, to measure the response of plants to soil amendments.

3.3.1 Soil and Plant Sampling in the Poor Growth Area

On April 13, 2005, plant tissue, plant canopy volume measurements, soil samples were obtained from randomly selected plants (Figure 12) to compare the nutrient status of plants and soil in the poor-growth area with other areas of the field. Fresh growth (up to 10 cm, > 5 g wet wt.) was clipped from each plant and stored in brown bags. Complete plant tissue tests and complete soil tests were performed on all plant material and for 12 soil samples (at ~ 0.5 m depth) obtained from either inside (7 samples) or outside (5 samples) the poor-growth area. Nutritional analytes including N, P, K, S and trace elements were measured at IAS Laboratories in Phoenix, Arizona following standard procedures. Bulk density measurements were obtained using a volume sampler to a depth of 1 m at 0.1m intervals (wherever possible) for five randomly selected locations inside and five locations outside the poor-growth area (Figure 12). Samples were dried at 85 °C for 6 days prior to obtaining a constant final weight. In addition, the presence or absence of the black mottled layer in the soil profile was noted.

No difference in plant volume inside versus outside the poor-growth area was observed when all plants were included in the statistical analysis. However, when data for the two largest plants within the poor growth area were omitted, plant volume was significantly lower in the poor-growth area with $P = 0.004$ by ANOVA (Analysis of Variance). Two plant size classes are obvious in the poor-growth area: stunted plants, and a small number of much larger plants that appear to have overcome the negative effects. Perhaps these larger plants have rooted through the growth-limiting layer.

ANOVA identified significant differences ($P < 0.05$) in total K, Fe, SO_4 and Cu concentration between plants growing inside and outside the poor-growth area. In some cases these differences were also correlated with plant canopy volume measurements. Both Cu and SO_4 were lower for plants growing in the poor-growth soil and levels were positively correlated with plant volume. Conversely, Mg and K had no correlation with plant growth but were significantly higher outside the poor-growth area. Fe concentrations were significantly lower in poor-growth plants and were positively correlated with plant volume. Soil concentrations of Ca, Mg and free lime were found to be significantly higher in the poor-growth area, while Cu and % ESP were lower (Table 6). These data substantiate previous findings.

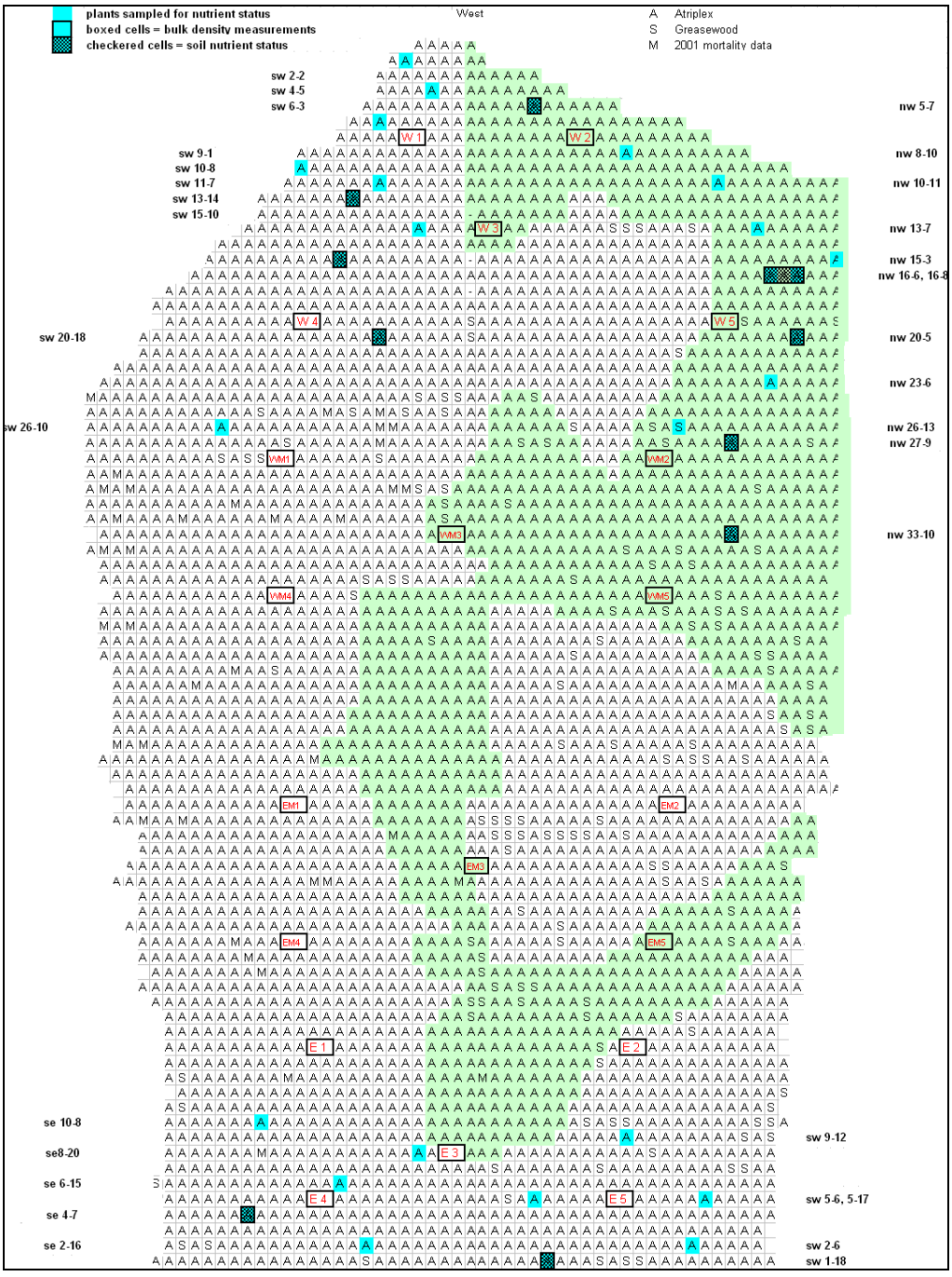

Figure 12. Map of the original 4-acre subpile planting with sample locations for plant tissue, soil analysis, and bulk density. The green shading shows the original distribution of the poor-growth area depicted from an aerial photograph taken in 2001.

Table 5. Plant Tissue Sample Analysis and Volume Measurements. Only Significant P-Values are Reported Comparing Plants Inside and Outside the Poor-Growth (Stain) Area.

row	plant #	quad	stain	Total N %	Total P %	K %	Ca %	Mg %	S %	Na %	Fe (ppm)	Zn (ppm)	Mn (ppm)	Cu (ppm)	B (ppm)	Volume (m^3)
8	10	NW	Y	0.9	0.1	1.6	2.6	0.43	0.25	0.13	160	43	62	4	31	0.008
5	7	NW	Y	1.3	0.1	1.9	2	0.46	0.29	0.08	130	68	58	6	29	0.030
10	11	NW	Y	1.5	0.09	0.6	2.2	0.52	0.25	0.61	150	10	47	3	30	0.069
13	7	NW	Y	1.4	0.1	1.7	2.6	0.55	0.21	0.06	190	41	57	4	44	0.012
15	3	NW	Y	1.1	0.11	1.7	2.3	0.42	0.31	0.27	220	22	48	4	30	0.028
16	6	NW	Y	1.5	0.11	1	2.9	0.63	0.29	0.31	150	25	59	4	32	0.117
16	8	NW	Y	4.1	0.34	1.6	1.2	0.9	0.45	0.28	110	33	730	11	34	7.215
20	5	NW	Y	1.6	0.14	1.8	3.2	0.49	0.34	0.15	190	28	67	4	39	0.010
23	6	NW	Y	0.9	0.1	1.4	2.6	0.43	0.25	0.13	160	43	62	4	31	0.001
27	9	NW	Y	4.6	0.62	1.6	1.3	0.92	0.39	0.06	69	58	59	12	59	1.108
33	10	NW	Y	5.2	0.39	1.5	1.8	1.3	0.47	0.17	130	65	460	15	60	0.155
26	13	NW	Y	4.8	0.29	1.1	2.4	1	0.49	0.47	130	41	270	8	61	9.333
2	2	SW	N	1.5	0.1	1.7	3	0.54	0.27	0.71	210	78	150	7	48	0.028
4	5	SW	N	1.5	0.13	2.8	3.4	0.73	0.27	0.23	150	49	110	4	41	0.056
6	3	SW	N	3.4	0.18	2.1	1.5	0.86	0.41	0.14	110	29	110	9	18	1.004
9	1	SW	N	3.9	0.31	2.7	1.6	1	0.48	0.19	140	43	56	13	38	0.997
10	8	SW	N	4.1	0.3	1.4	1.7	0.95	0.42	0.86	120	37	78	12	31	0.937
11	7	SW	N	3.5	0.17	1.5	2.4	1.3	0.33	0.51	130	21	110	9	46	1.803
13	15	SW	N	3.4	0.25	1.6	2.4	1.1	0.55	0.36	150	23	150	11	65	3.130
15	10	SW	N	3.1	0.25	1.3	2.4	0.98	0.39	0.63	99	43	130	8	45	0.576
20	18	SW	N	4.2	0.46	0.9	1.3	0.83	0.52	0.7	130	71	110	10	45	5.641
26	10	SW	N	4.2	0.25	2.4	1.5	0.82	0.32	0.04	80	39	130	11	39	3.658
2	16	SE	N	3.5	0.39	1.8	1.9	1.2	0.53	0.26	160	94	440	10	52	0.348
4	7	SE	N	3.5	0.23	1.5	1.3	0.56	0.41	0.06	91	34	140	12	31	2.125
6	15	SE	N	4.3	0.45	1.8	1.5	0.83	0.54	0.07	110	170	440	15	38	0.839
8	20	SE	N	4.4	0.64	1.6	1.9	0.94	0.4	0.06	110	72	610	17	52	2.797
10	8	SE	N	3.5	0.51	1.4	2.6	1.1	0.4	0.08	130	69	860	16	83	1.234
1	18	NE	N	3.3	0.31	2.4	1.3	1.1	0.39	0.1	80	35	66	12	43	5.787
2	6	NE	N	3.9	0.3	3	1.6	0.83	0.59	0.03	74	30	150	16	74	7.852
5	6	NE	N	3.9	0.27	2.2	2	0.74	0.63	0.18	68	32	71	17	57	2.937
5	17	NE	N	3.8	0.28	1.9	2.2	0.95	0.75	0.14	94	35	190	15	54	2.400
9	12	NE	N	4.6	0.35	1.8	1.7	0.93	0.72	0.38	110	18	88	9	47	1.624
Stained area (high or low)						low		low	low		High			low		
Stained area ANOVA P-values:						0.03		0.01	0.01		0.04			0.001		
with plant volume as covariate							0.02		0.02		0.01			0.04		
Relationship with plant volume							Neg.		Pos.		Neg.			Pos.		

Table 6. Relationship Between Plant Volume and Specific Soil Analytes. Pearsons Correlation Coefficients for Samples with ≥ 0.05 and P-values ≤ 0.1. ANOVA Comparing Soils Inside (Stained) versus Outside Poor-Growth Area.

				Select Soil Analytes (ppm)							
			depth								
plant	*quad*	*stain*	*(cm)*	*pH*	*Ca*	*Mg*	*Fe*	*Cu*	*% ESP*	*free lime*	*Vol m^2*
5-7	nw	y	51	8.6	6600	170	4.2	0.21	1.2	High	0.03
16-6-7	nw	y	35	8.1	8400	170	4.3	0.16	0.2	High	0.12
33-10	nw	y	35	8	13000	230	5	0.21	1.3	High	0.16
27-9	nw	y	49	8.2	10000	240	4.4	0.22	0.7	High	1.11
16-6-7	nw	y	57	8.2	7900	230	3.9	0.18	0.4	High	0.12
20-5	nw	y	60	8.2	9100	450	2.5	0.18	0.9	High	0.01
5-7	nw	y	96	8.2	8000	230	2.8	0.18	0.5	High	0.03
4-7	se	n	48	6.8	6500	170	3.9	0.4	1.4	None	2.12
1-18	ne	n	52	8.6	3300	130	3.2	0.28	1.9	Med	5.79
20-18	sw	n	62	5.3	2200	89	41	0.52	4.2	None	5.64
15-10	sw	n	49	7.2	4000	100	5.7	0.19	3.2	Low	0.58
11-7	sw	n	44	8.3	5400	150	5.1	0.18	1.1	Med	1.80
				-0.5	-0.7	-0.5	0.6	0.8	0.7		Pearson correlation coefficient (r)
				0.10	0.01	0.09	0.04	0.004	0.02		P-value for r
				0.08	0.04			0.009			MSW regression (overall P = 0.003)
				high	high	high		low	low		stained area (high or low)
				0.08	0.002	0.03		0.05	0.01		ANOVA P-value

Multiple step-wise linear regression analysis shows significant ($P < 0.05$) positive and negative correlations between plant canopy volume and Ca and Cu, respectively. These data suggest strong nutrient interactions between Cu and Ca; high soil concentrations of Ca may be impeding Cu and perhaps Fe uptake. Unfortunately, there are no definitive visual symptoms of Ca excess in plant tissues. In general, Ca, particularly in the form of calcium carbonate, is known to decrease plant uptake of other nutrients such as, Cu, Zn, Fe and P.

The area of poor *Atriplex* growth was coincident with the distribution of the black-mottled layer and with the white surface stain (Table 7). The black mottled soil layer was prevalent throughout most of the soil profile from roughly 10 cm beneath the surface to at least 1 m in the poor-growth area. The black-mottled layer was encountered deeper outside the poor-growth area, from ~ 0.5 m to at least 1 m beneath the surface. The surface soil is also considerably lighter in the poor-growth area; the light color may be attributed to its higher Ca content. A composite soil sample from the stained area is currently being analyzed by IAS laboratories for a suite of heavy metals including vanadium to determine the chemistry of the black-mottled layer.

Table 7. Bulk Density for Soil Inside and Outside the Poor-Growth (Stained) Area. Presence or Absence of the Black Mottled Material is noted for Each Sample.

				Dist. port (m)						
Plant row-#	*area*	*stain*	*port*	*N*	*S*	*E*	*W*	*depth (cm)*	*Stain**	*bulk density (g/cm^{-3})*
33-10	nw	y	WM5	11			4.3	20	None	1.44
33-10	nw	y	WM5	11			4.3	35	B	1.41
33-10	nw	y	WM5	11			4.3	45	B	1.35
27-9	nw	y	W5			20		5	B	1.61
27-9	nw	y	W5					49	None	1.64
20-5	nw	y	W5	9.8		6.4		10	B	1.64
20-5	nw	y	W5	9.8		6.4		60	none	1.57
20-5	nw	y	W5	9.8		6.4		80	B	1.44
16-6-7	nw	y	W5	87			25	10	B	1.6
16-6-7	nw	y	W5	87			25	35	B	1.71
16-6-7	nw	y	W5	87			25	57	B	1.58
16-6-7	nw	y	W5	87			25	88	B	1.55
5-7	nw	y	W2	7.4				10	B	1.67
5-7	nw	y	W2	7.4				30	B &W	1.64
5-7	nw	y	W2	7.4				51	B	1.61
5-7	nw	y	W2	7.4				76	B &W	1.57
5-7	nw	y	W2	7.4				96	B	1.56
11-7	sw	n	W1		9.3	8.4		10	none	1.73
11-7	sw	n	W1		9.3	8.4		26	little**	1.7
11-7	sw	n	W1		9.3	8.4		44	little	1.69
11-7	sw	n	W1		9.3	8.4		76	little	1.68
11-7	sw	n	W1		9.3	8.4		91	B	1.7
15-10	sw	n	W4	4.2			6.7	10	none	1.7
15-10	sw	n	W4	4.2			6.7	29	little	1.74
15-10	sw	n	W4	4.2			6.7	49	little	1.75
20-18	sw	n	W4					14	little	1.55
20-18	sw	n	W4	15		2.2		41	none	1.71
20-18	sw	n	W4	15		2.2		62	none	1.63
20-18	sw	n	W4	15		2.2		95	none	1.59
1-18	ne	n	E3	14		19		10	none	1.69
1-18	ne	n	E3	14		19		31	none	1.72
1-18	ne	n	E3	14		19		52	none	1.71
1-18	ne	n	E3	14		19		77	B &W	1.71
1-18	ne	n	E3	14		19		100	B	1.71
4-7	se	n	E4		8	1.7		10	none	1.73
4-7	se	n	E4		8	1.7		26	none	1.78
4-7	se	n	E4		8	1.7		48	B &W	1.65
4-7	se	n	E4		8	1.7		73	B	1.78
4-7	se	n	E4		8	1.7		100	B	1.73

* occurrence of black (B) or white (W) material in the sample

** black material was noticeable in small amounts

3.3.2 Soil Compaction

High soil compaction was investigated as a possible explanation for the area of poor *Atriplex* growth. Bulk density measurements show that soils are significantly ($P < 0.05$) less compacted inside than outside the poor-growth area. The mean bulk density for all depths sampled outside was 1.56 ± (0.02) compared to 1.70 (0.01) inside the poor-growth area. (Values in parentheses are the standard error of the mean.) Bulk density measurements were mostly uniform throughout the soil profile Figure 13 and Table 7).

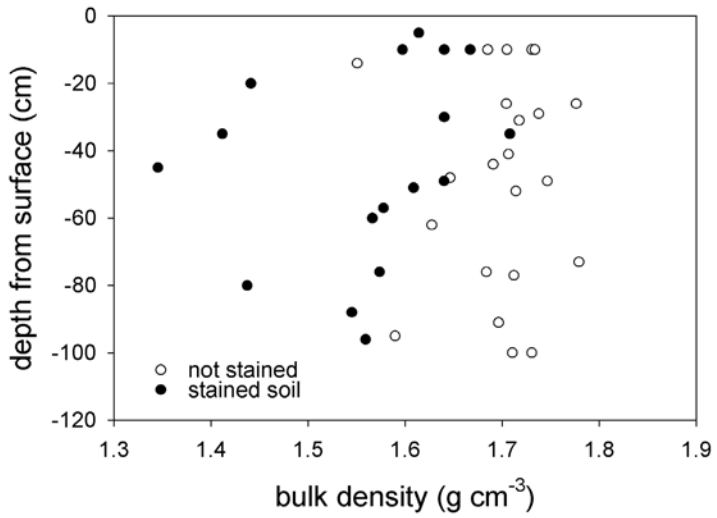

Figure 13. Soil bulk density with depth inside and outside poor-growth (stained) area.

3.3.3 Greenhouse Growth Trials

The soil and plant analyses suggest that high soil calcium levels may be interfering with the ability of plants to absorb Cu and Fe to meet nutritional needs. If true, it might be possible to reverse the growth inhibition by supplying additional Cu and Fe to the plants. In collaboration with faculty and students at the Tsalie campus of Dine College, a greenhouse experiment was set up to test this hypothesis. The experiment used a randomized complete block design with four replicate pots per treatment to test the following levels of supplemental Cu and Fe:

- Cu added to pots with stained soil at levels of 0, 5, 10, 20, 40 and 80 ppm.
- Fe added to pots with stained soil at levels of 0, 5, 10, 20, 40 and 80 ppm.
- Cu + Fe added to pots with stained soil at levels of 0, 5, 10, 20, 40 and 80 ppm.

All treatments pots contained potting soil mixed with poor-growth soil from Monument valley in a 1:3 (volume:volume) ratio. Negative controls (4 pots) had plants grown in poor-growth soil with no potting soil and no metal additions. Positive controls (4 pots) were plants grown in and pots containing 1 kg of washed river sand + compost. Pots were irrigated twice weekly with 250 ml of solutions containing the metal additions corresponding to each treatment, plus

Grow-More soluble fertilizer supplying 25 ppm of N, P and K. Each irrigation produced approximately 200 ml of drainage, ensuring that concentrations of nutrients in the pots were similar to those added in the irrigation supply. The experiment was conducted from October to December 2006. Unfortunately, the Tsaile greenhouse was not heated during the trials, and all plants grew poorly. The experiment will continue in spring, 2006, as it has the potential to improve growth in the subpile phytoremediation plantings.

3.4 Expand Source Area Planting and Irrigation System

Planting and irrigating a 4-acre field in the subpile source area has been exceptionally effective in removing nitrate from the soil (principally through microbial denitrification; Section 3.7) and, using a deficit irrigation schedule, limiting deep percolation and leaching of nitrate to the alluvial aquifer (Section 3.5). The purpose of this task was to expand the source area planting and irrigation system with the goal of isolating and eventually removing all mill-related sources of nitrate and ammonia. This section addresses methods to delineate an area for the expanded source area phytoremediation. Section 6.2 describes the combined irrigation system for all pilot study plots, including the irrigation design for the source area planting.

3.4.1 Methods

Several factors were considered in the development of a map for the expanded source area planting: (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 *Atriplex canescens*, and (4) depth to bedrock. Maps of source area nitrate and ammonia were derived from a 2005 systematic sampling within the historical footprints of the New Tailings Pile (subpile) and Evaporation Pond (Section 3.1). These 2005 data were combined with annual monitoring data from within the original subpile planting for the years 2001-2005 to produce comprehensive source area nitrate and ammonia distribution maps (Figure 14 and Figure 15).

A surface map of vegetation, denuded areas and rock outcrops was created by subjectively defining mapping unit boundaries in the field with using GPS (Figure 16). Mapping units were chosen with respect to their relevance in isolating and removing the source. For example, mature stands of greasewood (*Sarcobatus vermiculatus*; SAVE) and fourwing saltbush (*Atriplex canescens*, ATCA) have established over the past few years within the millsite fence line. Given earlier studies at Monument Valley (DOE 2002, 2004bc, McKeon et al. 2005), we can infer that evapotranspiration is controlling the soil water balance and preventing percolation and leaching of contaminants within these stands, and that plants are also removing nitrate. Therefore, rather than disturb these stands by preparing the soil for planting, we choose to let natural phytoremediation (attenuation) progress without intervention. A contour map showing depth to bedrock (Figure 17) was created using data from Section 3.1 where bedrock was encountered during the systematic grid sampling.

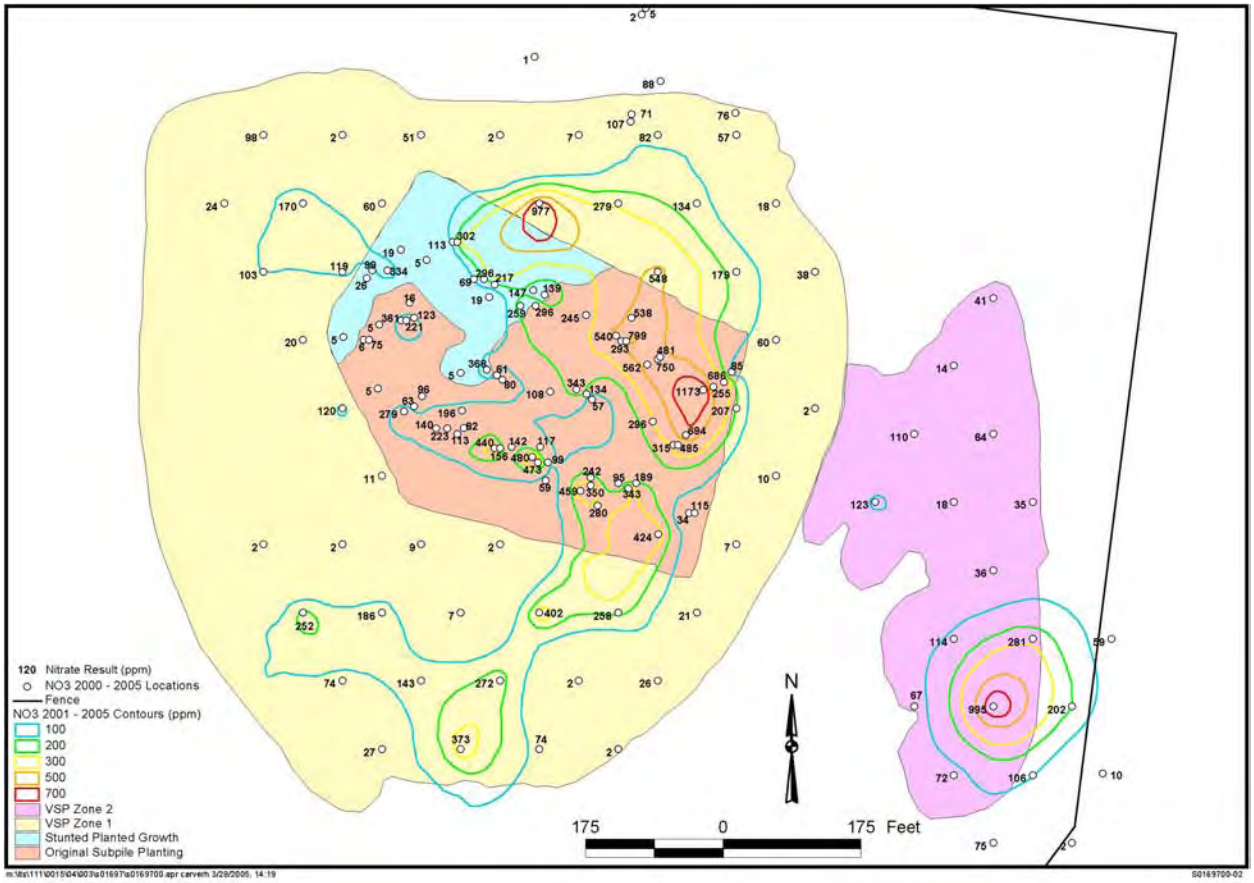

Figure 14. Map of nitrate (NO_3^--N) concentrations within the New Tailings Pile and Evaporation Pond source areas created from a combination of 2004 systematic sampling (Section 3.1) and annual monitoring within the original subpile phytoremediation planting for the years 2001-2005. The highest value at each sample location is shown.

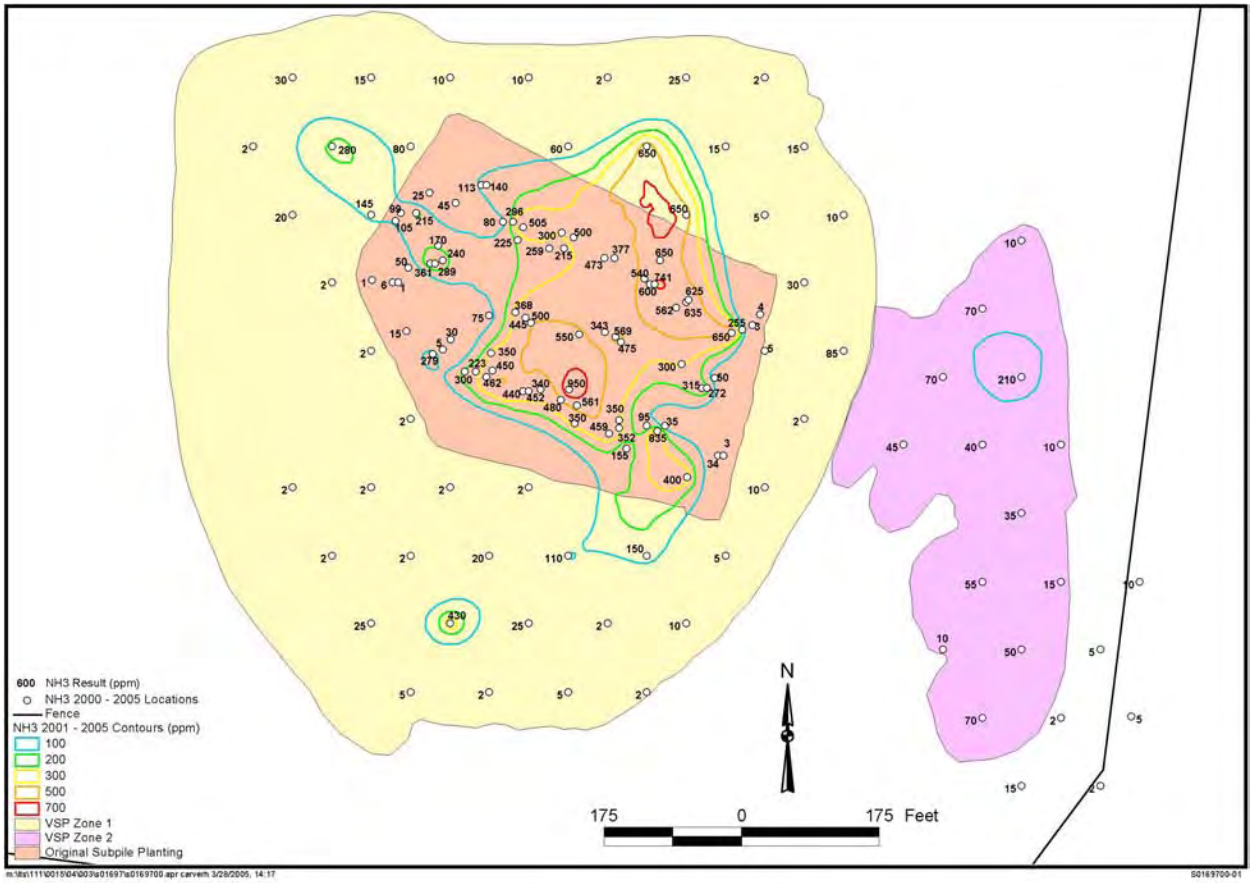

Figure 15. Map of ammonia (NH_3-N) concentrations within the New Tailings Pile and Evaporation Pond source areas created from a combination of 2004 systematic sampling (Section 3.1) and annual monitoring within the original subpile phytoremediation planting for the years 2001-2005. The highest value at each sample location is shown.

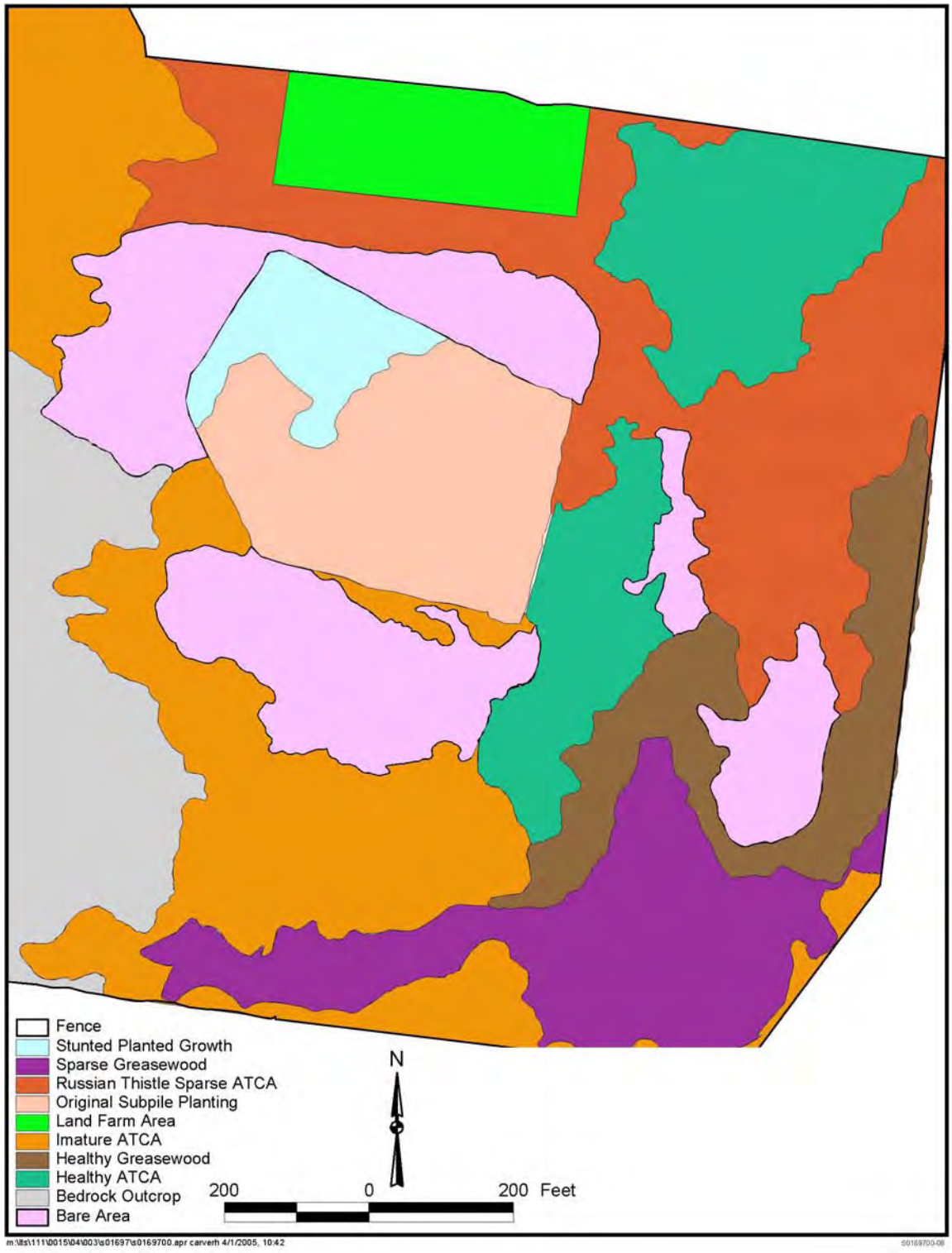

Figure 16. Map of vegetation types, bare areas, rock outcrops, and the existing subpile phytoremediation planting (including the stunted growth area). The map was created by subjectively delineating relevant mapping units using GPS.

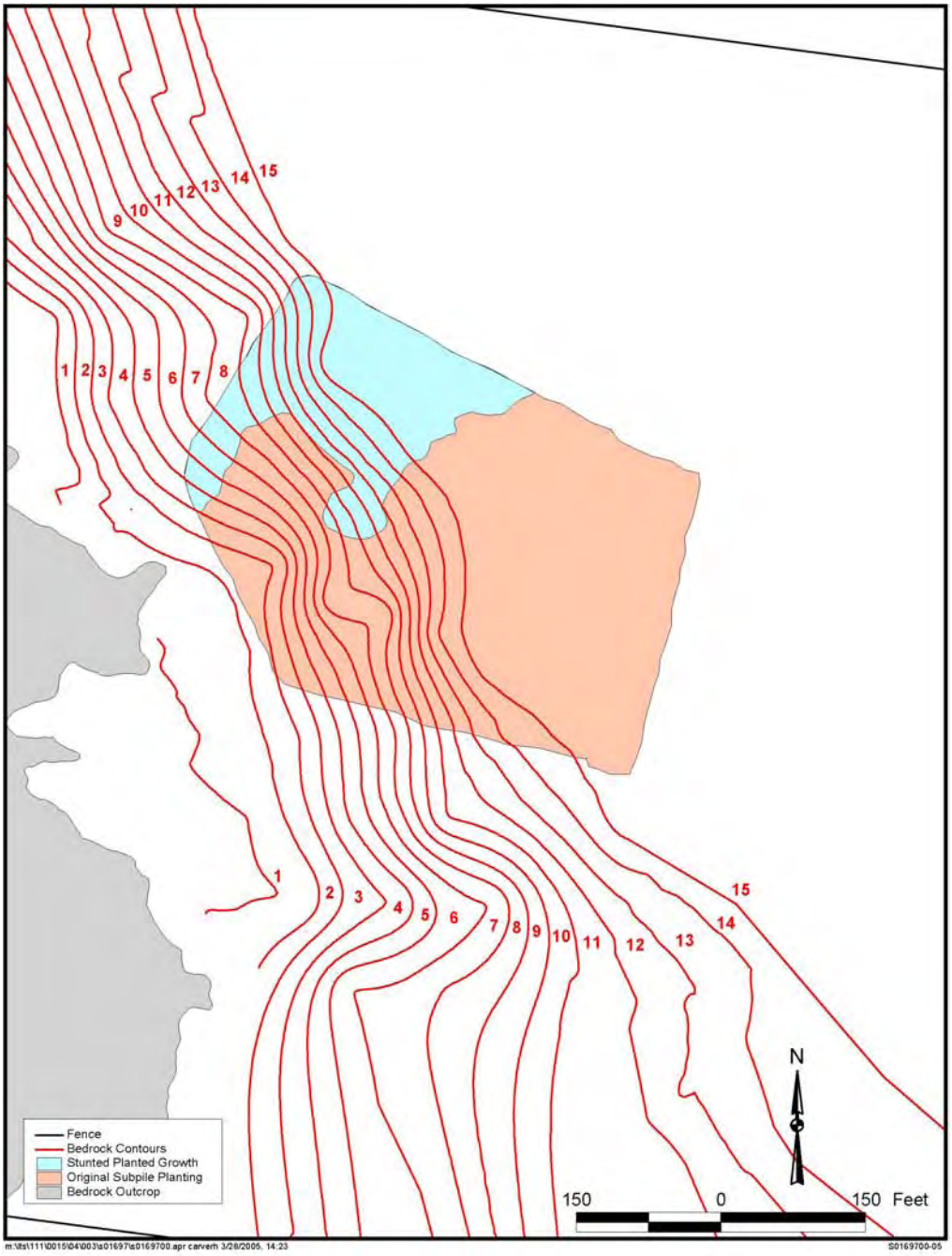

Figure 17. Rock outcrops and depth-to-ground water contour map in proximity of the original phytoremediation planting.

3.4.2 Results and Discussion

The area chosen for the expanded phytoremediation planting is shown in Figure 18. The planting will encompass the majority of the original subpile phytoremediation, areas within the New Tailings Pile footprint both north and south of the original planting, and an area within the Evaporation Pond footprint. Delineation of the expanded planting relied on nitrate and ammonia distribution maps (Figure 14 and Figure 15), vegetation (Figure 16), and depth to bedrock (Figure 17). 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 ppm, (2) bare or sparsely vegetated soils, and (3) depth to bedrock exceeding 5 feet.

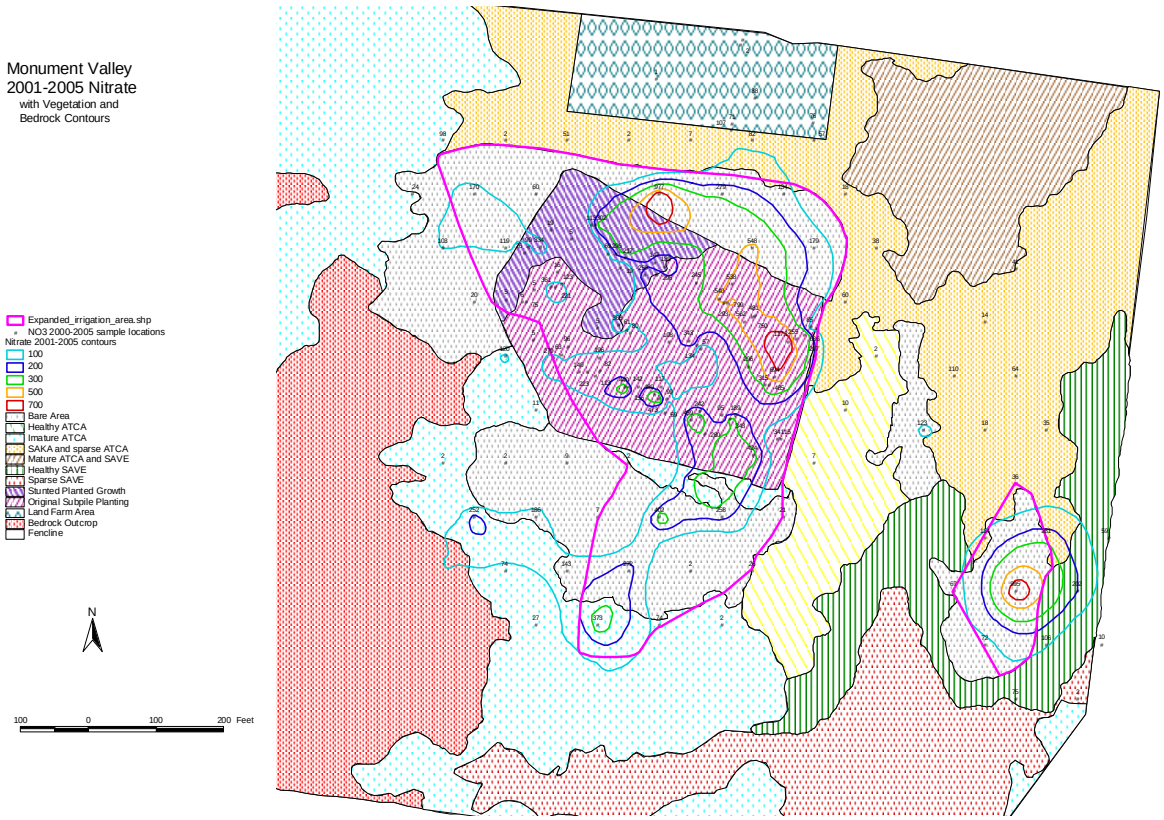

Figure 18. Outline of the expanded source area phytoremediation planting superimposed on maps of soil nitrate distribution and vegetation.

Most bare areas with elevated NO_3^-N or NH_3-N were included in the expansion. The large, bare, nitrate hot spot within the Evaporation Pond footprint is an example. However, not all areas with elevated NO_3^-N or NH_3-N concentrations were included. Some areas already support 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 is an exception. The nitrate hot spot is in a sparse, immature stand of saltbush. This area was not ripped, but the stand will be 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 is shallow. Because of relatively low contaminant mass and the likelihood that irrigation would cause leaching rather than prevent it, this area was omitted from the new 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. Planting these areas will reduce deep percolation and may help control contaminant movement into the alluvial plume.

The infrastructure for the expanded source-area irrigation system is in place (Section 6.2). The old irrigation system has become ineffective, has outlived its design life, and has been replaced. The more compacted portions of the new planting areas were ripped in preparation for planting, which is scheduled to take place in spring 2006.

3.5 Monitor Soil Water and Recharge

The original subpile (source area) phytoremediation plot has been irrigated each year since it was installed in 2000, with the exception of 2003. The plants are purposely under-irrigated to prevent leaching of nitrate from the subpile into the aquifer. Irrigation volumes have ranged from 0.16 m/yr to 0.36 m/yr during years with irrigation, with water provided daily through drip emitters from March to October. Soil moisture levels have been measured monthly at 1' to 15' depths at 20 neutron hydroprobe stations arrayed within the field.

Figure 19 shows soil moisture levels as a function of soil depth from 2000 to 2005. In 2004 and 2005, additional soil moisture data was collected in probe ports off the field (in unirrigated soil). These ports were located in the between the irrigated field and the beginning of the plume to the north.

Moisture levels in the irrigated field were below saturation (ca. 0.25 g/cm^3) at all times. Moisture levels in the middle depths decreased by about 20 percent between 2001 and 2004, due to lack of irrigation and the continued growth of the plants. The decrease in soil moisture coincided with an apparent drop in denitrification activity, documented in out gassing measurements, in vitro assays of soil samples, and soil core samples measured for nitrate (see Section 3.7). Therefore, the irrigation schedule could possibly be adjusted to increase the soil moisture levels to stimulate the continued removal of nitrate from the profile. To stimulate microbial activity, consideration will be given to loading the soil profile with moisture by irrigating the plot in winter when the plants are not active. In the summer, plants would use stored water plus summer irrigation water. Previous work has shown that a mature stand of saltbush can use 2-3 m of water per year. In 2006 wicking lysimeters will be installed in the source area to detect any leaching of nitrate.

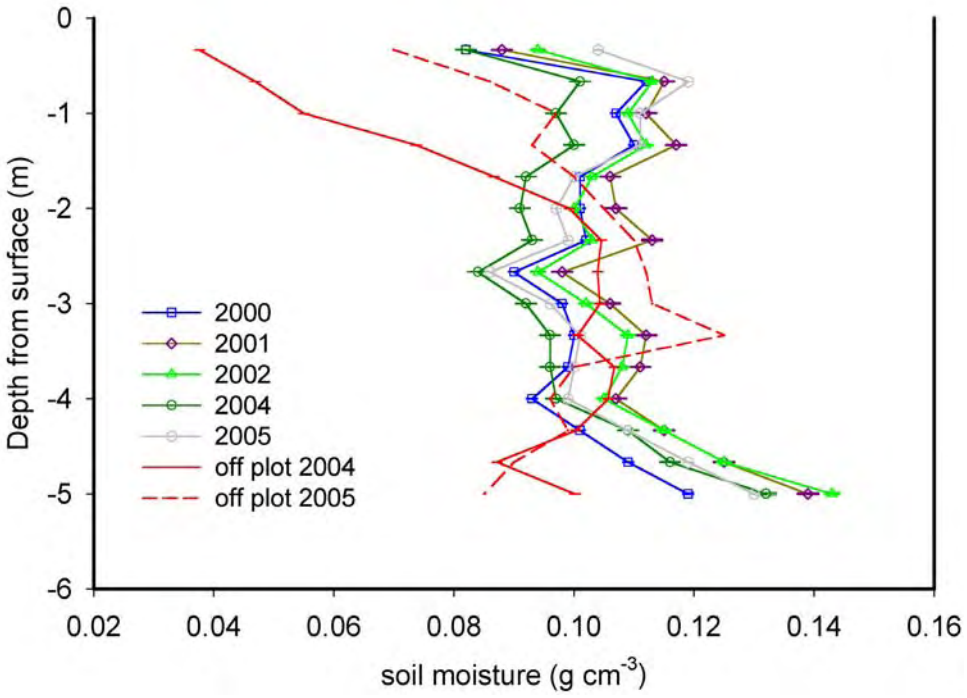

Figure 19. Mean annual soil moisture levels in the irrigated subpile farm, and in ports located outside the irrigated area but within the subpile soil. The on-field values are from 20 ports measured monthly; March - October of each year except 2003. The off-field values are from 4 ports measured monthly; March - October, in 2004 and 2005.

3.6 Monitor Canopy Growth and Total Nitrogen

The original subpile phytoremediation was planted to remove the source of nitrogen entering the alluvial aquifer. Native desert shrubs, mainly *Atriplex canescens* (fourwing saltbush), were planted over the subpile soils to take up nitrogen into plant tissues where it is converted to organic nitrogen compounds. A rectangular, 4-acre irrigated plot was installed the summer of 1999. Approximately 4,000 small (10 to 20 cm tall) *Atriplex* seedlings grown from seed collected from Navajo Nation land and raised in a greenhouse at the University of Arizona were transplanted on site. The seed mixture included large-fruited (var. *angustifolia*) and small-fruited (var. *occidentalis*) types of *Atriplex*. Planting was completed in August 1999. *Atriplex* growth and N uptake have been monitored since 2000.

3.6.1 Methods

Survival, canopy volume, canopy cover, and dry-weight biomass of *Atriplex canescens* shrubs were monitored annually for the subpile soil planting. Canopy cover and canopy volume were estimated for approximately 200 plants (50 plants per zone) at the end of the growing season, September 2005. Of the 200 plants measured, 8 were dead giving a mortality rate of 4 percent for the 2005-growing season. Plant height (a) and cross-sectional radii (b,c) of plants were measured to estimate canopy volume using the formula for a hemispheroid ($2/3\ \pi abc$). Plant canopy cover (m^2) was estimated using the formula for an ellipsoid (πbc). Canopy cover was also estimated by obtaining an aerial photograph of the 4-acre field. The percent plant cover was calculated by placing a grid over the image and dividing the number of grid-point intercepts of plant biomass (green/dark pigment) by the total number of intercepts for the entire field.

The above ground biomass and total N were estimated based on the canopy volume-biomass relationship shown in Figure 20 using a subset of *Atriplex* shrubs ranging from small to large volume. Shrubs were harvested and dry weights of current-year productivity and total dry-weight biomass was determined for the 200 plants measured and used to calculate total N uptake by the plants. The average plant N content (percent) was determined for a subsample of 5 *Atriplex* shrubs by IAS Laboratory in Phoenix, AZ using the Kjeldahl method.

3.6.2 Results and Discussion

Table 8 shows plant growth and N-uptake results, respectively. In 2005, plant cover and N-uptake increased only slightly by c.a. 8 percent over the 2004-growing season. Plant area measurements indicate that the mean ground cover is 56 percent over the whole field, but inspection of the aerial photograph (Figure 21) taken of the 4 acre field in early October, 2005, shows that nearly complete cover has been achieved over about a third of the field, and that patches of good plant growth are occurring even in the heavily stained areas of the field.

As in previous years, when separated into the four irrigation zones, Zone 4 (east end of the field) has the most prolific growth with the plant cover approaching 100 percent and Zone 1 (west end of the field) has the least plant cover (< 50 percent) due in part to the stunted growth observed for the white stained soil (see Task 3.3). Future goals are to promote plant growth over the subpile soil in areas that are high in nitrate and ammonium.

As plant volume and plant cover increase in the field, water demand rises. Hence, the irrigation rate should be increased to meet crop water demand and promote denitrification in the soil profile.

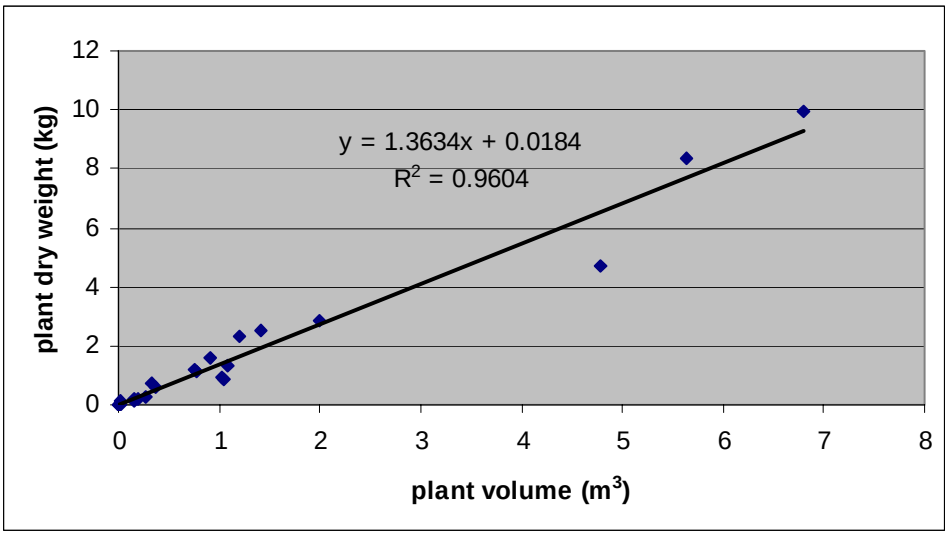

Figure 20. The relationship between plant volume (m^3) and plant dry weight for a subset of Atriplex shrubs collected from the subpile soil.

Figure 21. Ariel photograph of the 4-acre irrigated field taken October 10, 2006.

Table 8. Average plant growth and N uptake over the 2000-2005 growing season. Values in parentheses represent the standard deviation of the mean. N-uptake was calculated by determining the total biomass of plants growing in on the 4-acre subpile planting and multiplying it to the average % plant-N content.

Growing Season	Plant Cover (m^2)	Plant-N content (%)	Cumulative N-uptake (Kg)
2000	0.238 (± 0.003)	1.24 (± 0.10)	
2001	0.732 (± 0.017)	1.99 (± 0.62)	
2002	1.14 (± 0.018)	n. d.	
2004	2.08 (± 0.022)	2.17 (±0.22)	190
2005	2.24 (± 0.009)	2.05 (±0.39)	206

3.7 Evaluate Denitrificiation and Nitrification in the Subpile Soil

Planting and irrigating the subpile area has been exceptionally effective in removing nitrate from the soil. Preliminary data suggest that irrigating and planting the subpile soil has enhanced the microbial process know as denitrification, the conversion of nitrate to nitrogen gas (DOE 2004b,c). Nitrification is the conversion or oxidation of ammonium to nitrate which can be brought about by nitrifying bacteria. Nitrification activity in the subpile soil, whether natural or induced, could increase the remediation of ammonium. The resulting nitrate would potentially be more rapidly removed by denitrification. The purpose of this task is to confirm that denitrification is a likely mechanism of nitrate loss in the irrigated subpile planting, and to evaluate the presence and rates of nitrification.

Figure 22 shows changes in soil moisture, nitrate-N, ammonium-N, and nitrate + ammonium (labeled Total N) from 2000 - 2005. (Note that the y-axis for moisture content does not start at zero.) Differences in moisture, nitrate and total N are significant over years ($P<0.05$ by 1-Way ANOVA), but ammonium differences are not significant. The loss of nitrate between 2000 and 2002 coincided with peak soil moisture levels. As the soil became drier due to lack of irrigation and presumed increased plant uptake of water, the loss of nitrate ceased.

Previously, we conducted a salt balance on the plot, to see if leaching of nitrates could be responsible for the nitrate losses. The salt balance study showed that the small decrease in soluble salts detected on the plot could be attributed to loss of nitrate. On the other hand, there was no decrease in other soluble salts, and if leaching were the mechanism for nitrate loss, all soluble salts should have declined equally. In 2006 we will measure leaching directly using water flux meters (wicking lysimeters).

We also showed that nitrate loss was accompanied by enrichment of the residual nitrate in ^{15}N, a characteristic of biological nitrification (Figure 23). Enrichment was a negative function of soil concentration for both irrigated and unirrigated portions of the subpile source area. We attempted to understand the nitrate trends in terms of the microbiology of the soil-water system.

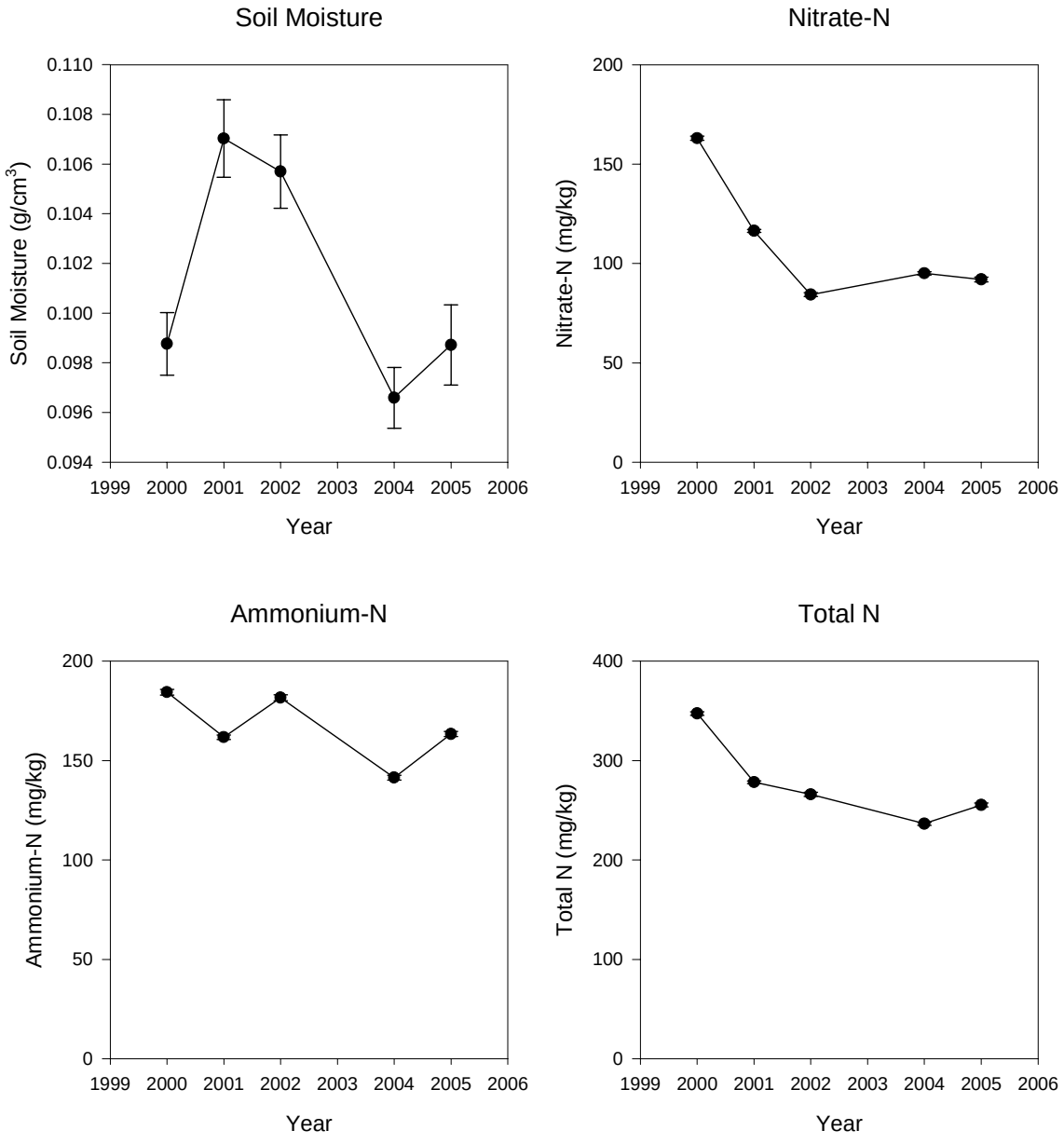

Figure 22. Changes in soil moisture, nitrate-N, ammonium N, and nitrate + ammonium in the subpile soil source plot, 2000-2005. Note that the y-axis scale does not start at zero.

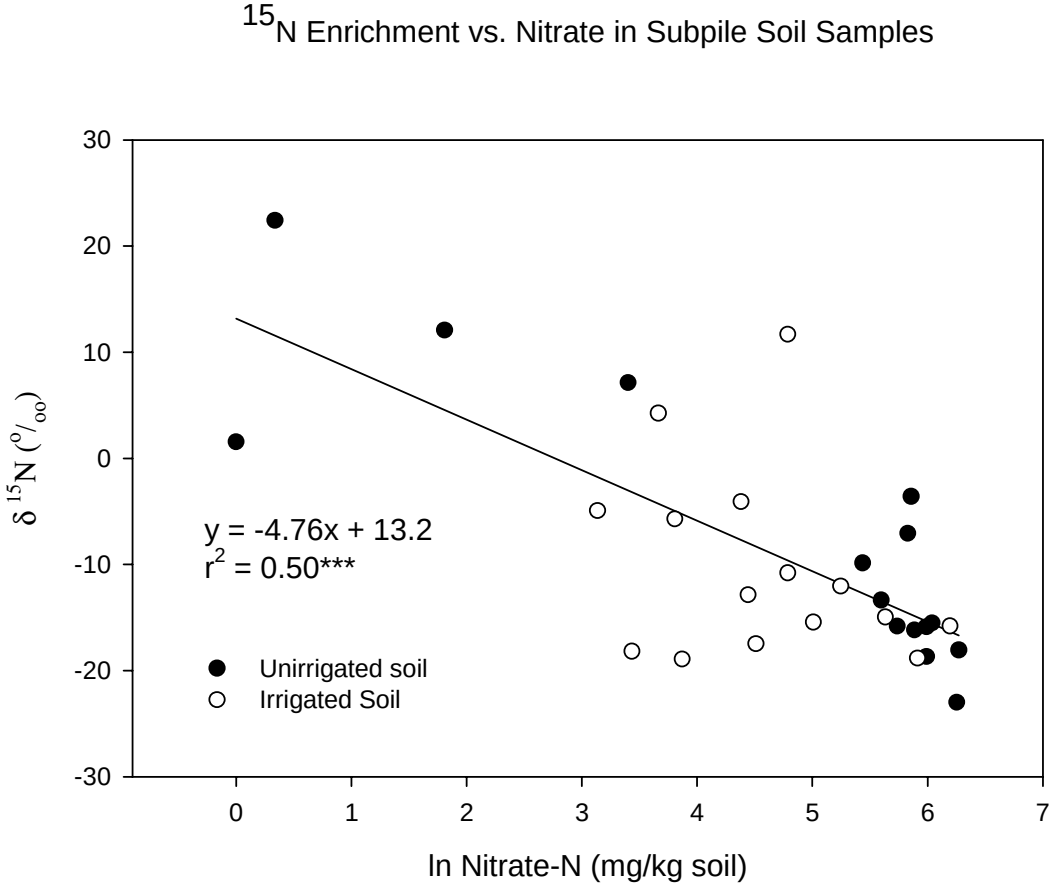

Figure 23. ^{15}N enrichment as a function of the log of nitrate concentration in soil samples from the irrigated and unirrigated portions of the subpile soil source area.

Figure 24 shows the transformations that take place in the microbial soil nitrogen cycle. Nitrate can be reduced to N_2 and N_2O gasses that leave the soil (denitrification). Ammonium can be oxidized to nitrate (nitrification), which can then be denitrified. Finally, nitrogen can be incorporated into organic compounds in the bacteria (assimilation). We incubated soil samples from the irrigated and unirrigated portions of the subpile soil in microcosms and measured their rate of N_2O production (Table 9). We incubated the samples with and without the gas acetylene added to the headspace. Acetylene inhibits the conversion of N_2O to N_2; hence, by comparing N_2O production with and without acetylene, we can estimate the proportion of each compound that is produced under natural conditions (N_2 cannot be easily measured directly, so this indirect approach is necessary).

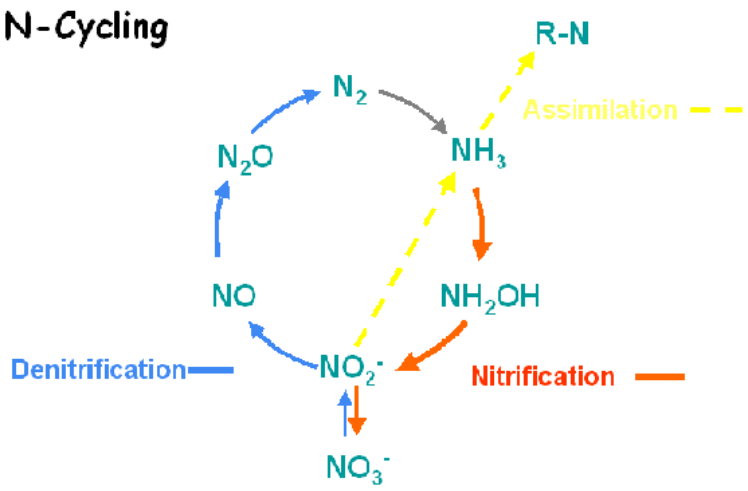

Figure 24. Main elements of the microbial nitrogen cycle.

At the low levels of denitrification measured in soil samples from the plume in 2004, we found that acetylene addition actually inhibited, rather than stimulated, N_2O production. This can be interpreted as a sign that nitrification is occurring. When ammonium is oxidized to nitrate, a portion of the nitrogen is not completely oxidized, but escapes from the system as N_2O gas (analogous to a "leaky pipe"). Nitrification is inhibited by acetylene, and at much lower levels than is required to inhibit denitrification. Table 9 indicates that coupled nitrification-denitrificaiton could be occurring at low levels in the soil, accounting for the apparent slow loss of ammonium from the soil. However, the rate of N_2O production in the soil samples were several hundred fold lower than the rates that would account for the soil nitrate losses observed from 2000 to 2002.

Table 9. Microcosm rates of N_2O production at field moisture content (µg/Kg/day) with and without acetylene (n= 7 or 8). Data are an average of samples (50-100 g sieved soil; n = 8) collected at two different soil depths (0-1 m and 3-4 m). Values in parentheses are the SEM.

Date	N_2O production (µg/Kg/day)			
	Irrigated [a]	Non-irrigated	Irr. + acetylene	Non-Irr. + acetylene
06-04	5.13 (±1.66)	0.29 (±0.07)	0.20 (±0.02)	0.17 (±0.02)
07-04	0.18 (±0.08)	-0.001 (±0.003)	0.08 (±0.04)	-0.01 (±0.01)
08-04	1.15 (±0.50)	0.02 (±0.007)	0.05 (±0.02)	0.01 (±0.01)
09-04	0.04 (±0.02)	-0.03 (±0.01)	0.01(±0.01)	0.15 (±0.14)

[a] ANOVA; values are significant across location and treatment ($P < 0.05$)

We then investigated the sensitivity of denitrification to soil moisture content (Figure 25). Soils from the site had moisture levels in the range of 0.05-0.07 g/cm^3 and denitrification rates were generally under 1 µg/kg/day. Addition of moisture stimulated all the samples tested, and one of the samples achieved a rate of 15 ug/kg/day. This extrapolates to a value of approximately 370 kg/ha/yr, approaching the value observed over the field during the period 2000-2002 (about 1100 kg/ha/yr). Furthermore, in the moistened soil, N_2O production was enhanced by acetylene

(Figure 26), indicating that under moist soil conditions N_2 gas is probably the main end product. This is important, because N_2O is a greenhouse gas, whereas N_2 is inert.

These studies also support the conclusion that irrigation of the soil should be increased in order to stimulate denitrification. Now that a mature plant community has been produced in the original subpile plot, conservative irrigation practices are no longer necessary, because the plants can evapotranspire 2-3 m of water per year. Winter irrigation would be a good option for keeping the soil moist, as the plants will not be active during this period.

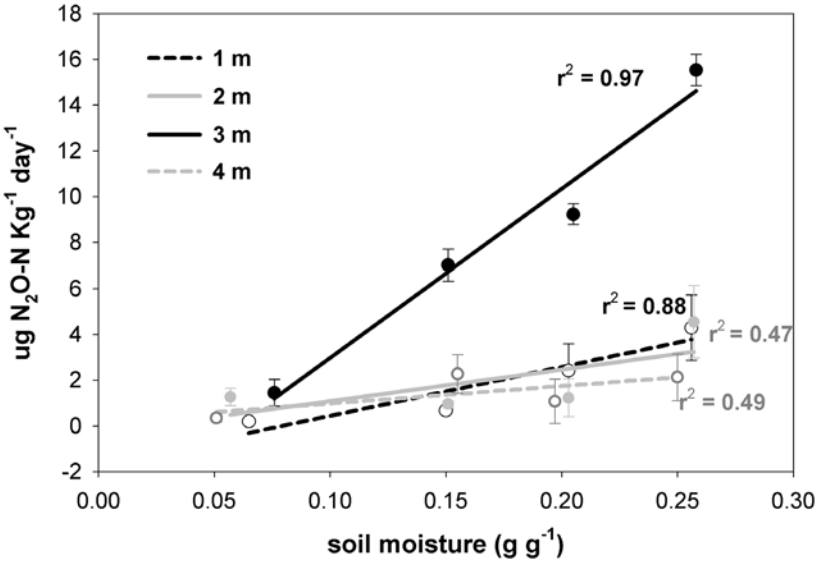

Figure 25. Rates of N_2O production in soil samples from the irrigated portion of the subpile soil, with natural or enhanced levels of moisture. Samples taken at several stations in the field were composited by soil depth. Error bars represent the SEM, n = 3 for each moisture regime.

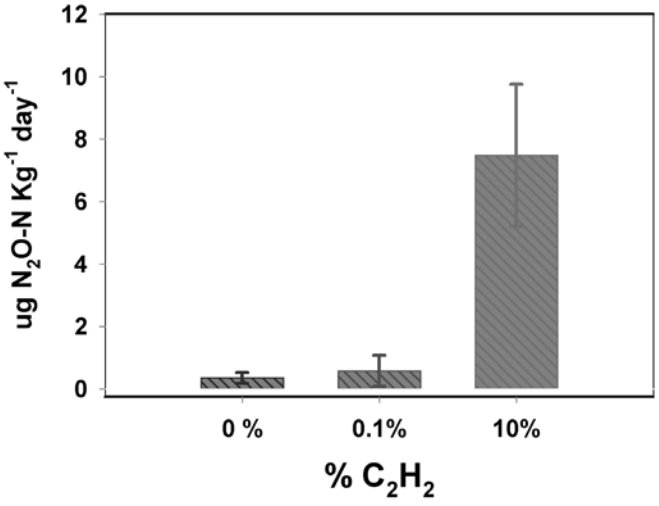

Figure 26. Effect of acetylene on N2O production by soil samples from the irrigated portion of the subpile soil. The sample was moistened to 0.2 g/cm3 prior to incubation. Error bars represent the SEM, n = 3 for each acetylene treatment.

3.8 Measure Root Distribution and Abundance

Measurements of root depth and abundance will show the depths at which *Atriplex* shrubs are extracting water, relative amounts of annual root growth and productivity, and spatial variability in root distribution related to plant spacing and areas of stunted growth in the planting. These data are needed to evaluate the subsurface component of phytoremediation and fine-tune the irrigation system.

Root distribution will be characterized using a minirhizotron video microscope (Bartz Technology Corporation). The system consists of a high-resolution video and still camera designed to view and record root abundance and growth at varying depths below ground. The camera slides down clear tubes installed in the ground and records digital video through the walls of the tube. Clear tubes will be installed in at least 20 locations with a specialized low-impact auger system.

The camera can take pictures at 1 cm intervals along the tube, and can be returned to the same position time after time in order to record progressive changes in root density and size. The highly detailed images focus down to root hairs while still providing an image large enough for efficient quantification. The system provides real-time viewing and image capture and storage on a laptop. Once images have been stored, WinRHIZO Tron software will be used to measure root diameter, length, and living status, and then to compute the average values for key parameters including living and dead root surface area and root volume. Images taken at different locations and at different times from the same location will be used to estimate mean root characteristics for the entire planting as well as seasonal and annual changes.

This task will begin in spring 2006 after planting of the expanded source area is complete.

3.9 Measure soil organic carbon

Most often microbial denitrification in soils and organic carbon content of soils are tightly correlated. Total organic carbon (TOC) can be used as an indicator of denitrification activity. The purpose of this task was to measure TOC directly beneath the plant canopy on the irrigated subpile soils that corresponded to samples taken for denitrification analysis (Section 3.7).

Random soil samples obtained from the irrigated 4-acre field were composited for 4 depths at 1 M intervals and extracted for total organic carbon (TOC) (Table 10). TOC content was determined by a wet oxidation method (Neilson and Sommers in the Methods of Soil Analysis, Part 2 (1986). As expected, TOC decreases with depth. The first meter of soil contains the most organic material (0.07 percent) which is likely attributable to plant root material and leaf litter. As expected, there appears to be a negative correlation between N-containing species (NO_3^- and NH_3-N) and organic matter.

The TOC levels were low and it is likely that denitrification is carbon-limited in this soil. Batch studies of denitrification from plume samples show that ethanol greatly stimulates denitrificiation (Section 5.5); hence it might be possible to enhance denitrification in the subpile field through ethanol injection. Also, it is possible that the decrease in nitrate loss over 2004 - 2005 could be due to carbon depletion as well as lower soil moisture levels. This possibility will be explored in 2006.

Table 10. Total Organic Carbon (TOC), Ammonium, and Nitrate from Composite Samples of Subpile Soils Taken in June 2005

Depth (m)	TOC (%)	NH3-N	NO3
1.0	0.07	117.03	160.00
2.0	0.03	182.11	238.19
3.0	0.02	175.11	957.67
4.0	0.02	210.81	636.88

4.0 Natural Attenuation of Ground Water

The pilot studies are evaluating natural attenuation as the primary remedy for ground water contamination at Monument Valley. Several natural processes may be acting to decrease nitrate and sulfate levels in the alluvial aquifer. The pilot studies are designed to acquire field data needed to estimate the capacity of natural attenuation processes. The goals for evaluating natural attenuation are to determine if the capacity of all natural processes acting to lower nitrate and sulfate levels in the alluvial aquifer 1) exceed rates of contaminant loading from sources, and 2) will achieve remediation requirements in a reasonable time. The pilot study work plan (DOE 2004c, Section 6.0) contains background information on natural attenuation at Monument Valley and detailed descriptions of tasks.

4.1 Determine Depth to Ground Water within Phreatophyte Populations

This task produced a simple map of depths to ground water in areas of existing phreatophyte populations (Figure 27). This map, coupled with isotope information showing where plants are extracting water and nitrogen from the plume (Section 4.2), was used to select areas for the enhanced plume phytoremediation studies (Section 5.1). Figure 27 shows contour lines of depth to ground water at the southern end of the plume superimposed over a map of plant associations (DOE 2004c, Section 3.4). Depths to ground water range from 30 to 40 feet within the ATCA (*Atriplex canescens* or fourwing saltbush) association and from 20 to 30 feet within the SAVE (*Sarcobatus vermiculatus* or black greasewood) association. Revegetation plots were installed within the denuded or bare area along a depth gradient from east to west and overlying nitrate "hot spots" so as to span ranges of depth to ground water (Section 5.1).

4.2 Partition Plant Water and Nitrate Sources Using Stable Isotopes

The plant community overlying the plume is dominated by two phreatophytic shrubs, fourwing saltbush and black greasewood. If rooted into the plume, these shrubs could be contributing in two ways to natural attenuation. First, they could be extracting water from the plume, slowing its movement away from the site. Second, they could be extracting nitrate from the plume to support plant growth. If the shrub community is extracting water and nitrate from the plume, their contribution to remediation could potentially be increased through a program to enhance shrub populations and control grazing over the plume (see Task 5.1). At present, plant cover is only 5 percent over the plume, due to heavy grazing by livestock. On the other hand, plant cover in

protected (fenced) areas is as high as 25 percent. Furthermore, canopy volume of plants protected from grazing by exclosure fences increased 2-3 fold over four years, whereas grazed plants did not show net growth over the same period (McKeon, 2006).

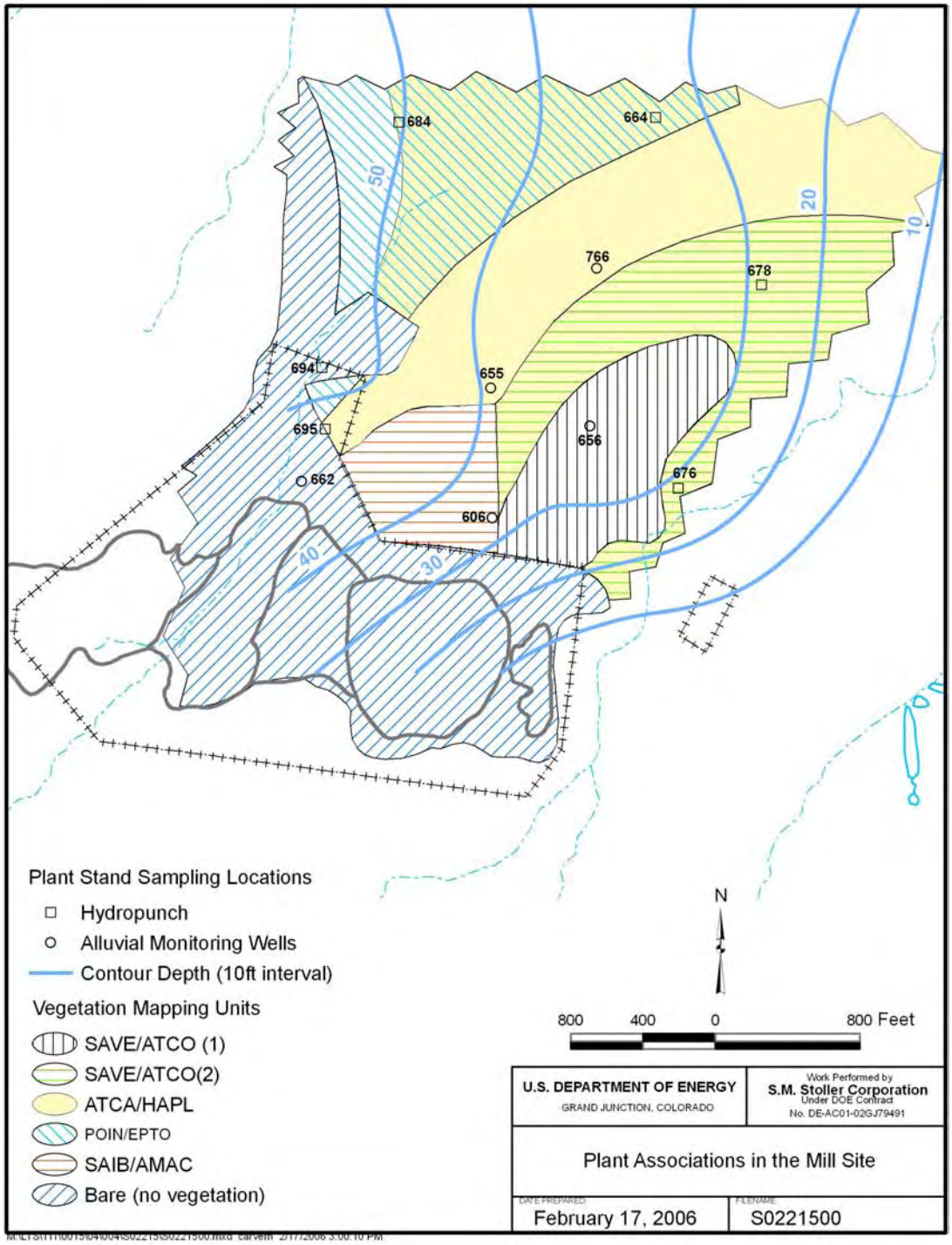

Figure 27. Plant associations in the mill site.

Stable isotope methods were used to determine whether plants are extracting water and nitrate from the plume. Water contains a small proportion of the heavy isotopes, ^{18}O and D (Deuterium),

in addition to the more common ^{16}O and H. Natural nitrogen sources also contain a small proportion of ^{15}N in addition to ^{14}N. The content of heavy isotopes is expressed as δ values in units of $^{o}/_{oo}$ relative to a seawater standard for oxygen and hydrogen isotopes and relative to atmospheric nitrogen for nitrogen isotopes. Positive values indicate that the heavy isotope is enriched in the sample relative to the standard and negative numbers indicate that the heavy isotope is depleted relative to the standard. Past pilot studies show that summer and winter rains at Monument Valley have distinctly different signatures, and that water in the plume has isotope values intermediate between summer and winter rains (DOE 2004c.) Water from stem samples of plants growing over the plume should have the same isotope composition as the source of water accessed by the roots. Hence, comparisons of samples of stem tissues, soil at different depths, and the top of the plume can indicate the source of water used by the plants. Similarly, comparisons of the nitrogen isotope composition of nitrate in the ground water and in the plant tissues can indicate if the plants are extracting nitrate from the plume.

4.2.1 Methods

Soil samples were extracted with augers from locations near Well 606 and Well 677. The auger holes extended from the surface to the phreatic zone (top of the aquifer) at 24' - 30' depths. Samples were analyzed for nitrate, ammonium, and moisture contents (Figure 28) and oxygen and hydrogen isotopes (Figure 29). Stem tissues from fourwing saltbush and black greasewood growing over the plume near each well were also sampled (Figure 29). Well 606 samples had very low nitrate levels down to the 24' depth, then values increased to >100 ppm (as nitrate-N). Moisture contents were very low down to the 15' depth, and then rose to approximately 10% between 15' and 22', decreased at the 24' to 27' depth interval, then rose again to 20% at 30'. Well 677 samples had very low moisture and nitrate levels down to 27', and then values increased to approximately 20% and 100 ppm, respectively, at 30'. These data show that the top of the contamination plume occurred at about 24' for Well 606 and at about 30' for Well 677. The bulge in soil moisture at 15' to 22' for Well 606 samples might represent rainwater perched above the contamination plume, because it was low in nitrogen. No such bulge was seen above the aquifer for Well 677 samples.

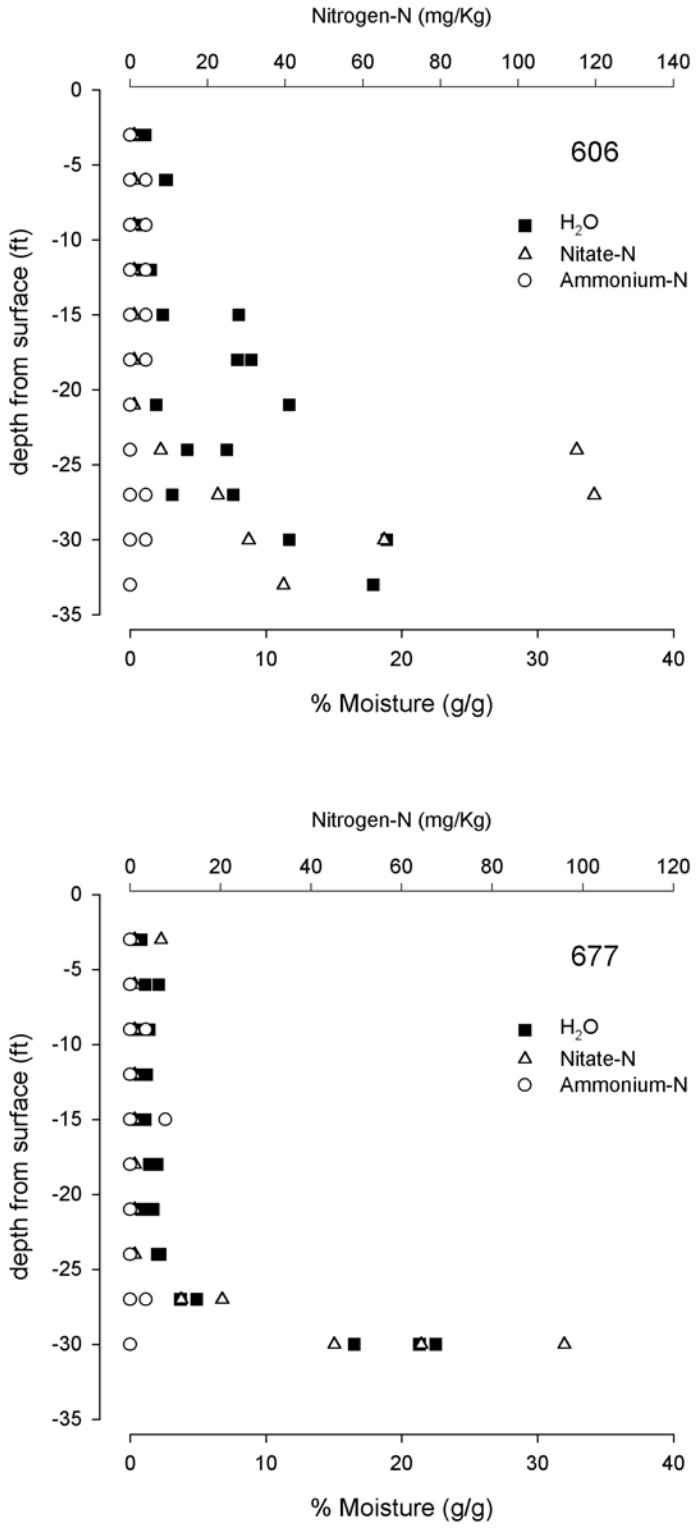

Figure 28. Soil moisture, nitrate and ammonium concentrations in soil samples at two well locations over the contamination plume at the Monument Valley UMTRA site.

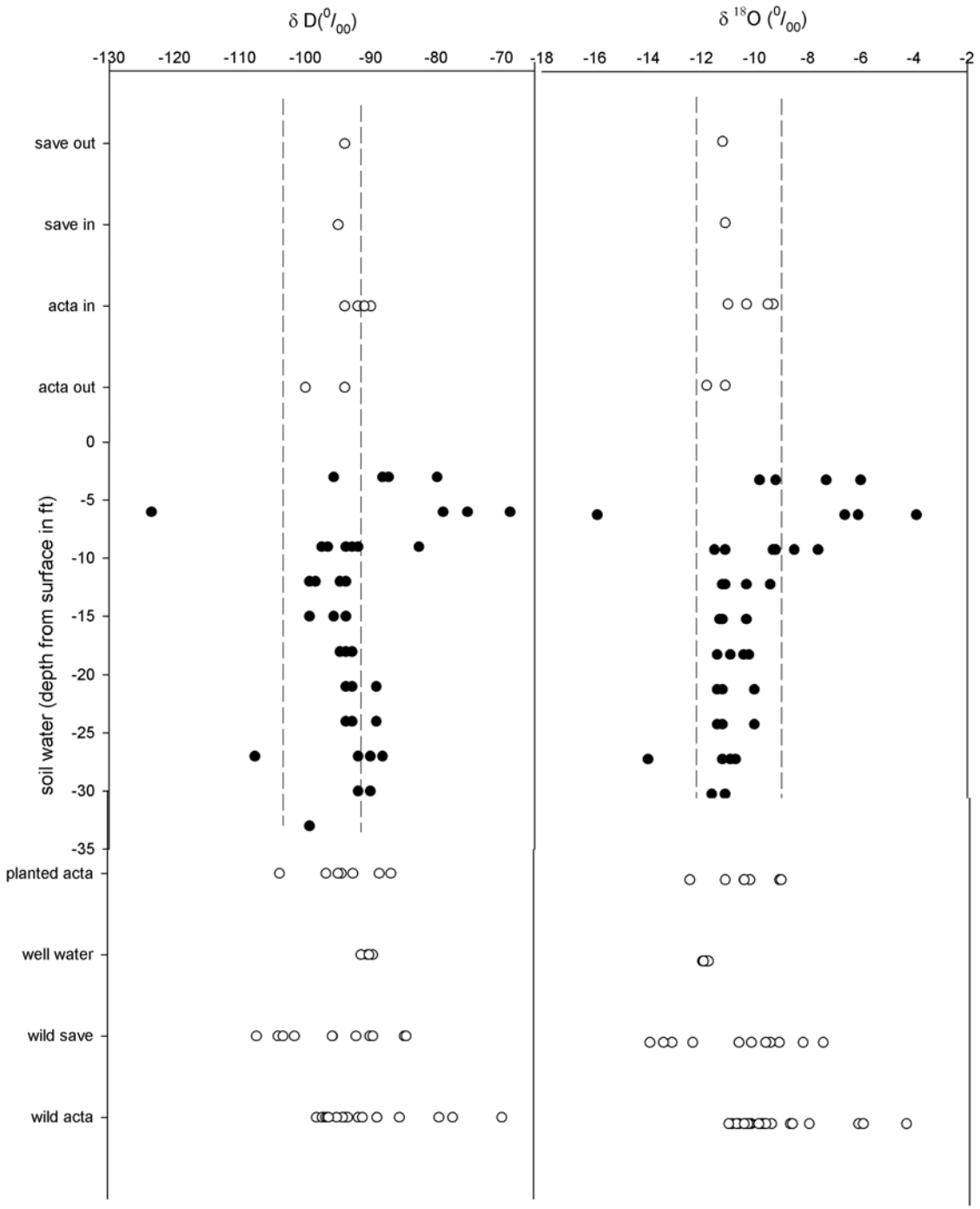

Figure 29. D and ^{18}O enrichment values in water extracted from soil samples collected at different depths over the alluvial plume near Well 606 and Well 677. The graph also shows the isotope values in water extracted from stem sample of black greasewood (SAVE) and fourwing saltbush (ATCA) plants growing 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).

4.2.2 Results

Soil moisture samples had higher (less negative) δ values for oxygen and hydrogen isotopes from the surface to the 10' soil depth, compared to values from 12' depth down to the top of the plume (Figure 28). Plants in and out of exclosures near the wells had enrichment values within the range measured in well water and in deep soil samples. Fourwing saltbush planted as seedlings inside exclosures over the plume also had isotope signatures typical of plume water. Wild black greasewood plants growing at other locations over the plume also had signatures typical of plume water, whereas wild fourwing saltbush plants had signatures typical of plume as well as more shallow vadose zone water. This supports the conclusion that black greasewood is an obligate phreatophyte rooted into the plume whereas fourwing saltbush is a facultative phreatophyte that can use vadose zone water if it is available.

^{15}N enrichment values in nitrate extracted from soil samples in the 24' to 30' depths over Wells 606 and 677 ranged from 5.2 to 8.7 (mean = 6.6 $^{o}/_{oo}$, n = 6). These values did not differ significantly (P = 0.67 by t-test) from values for nitrogen extracted from leaf tissue in plants growing over the plume, which ranged from 2.21 to 9.7 (mean = 5.8 $^{o}/_{oo}$). There was not enough extractable nitrate in the soil samples from the surface down to 22'.

The results indicate the following: At well 677, the plants are clearly rooted into the plume, as the soil above the plume has insufficient moisture to support plant growth (<5% moisture). Similarly, there is very little nitrate or ammonium in the shallow soil layers so the shrubs are likely using nitrogen from the plume, and ^{15}N enrichment values support this conclusion. At Well 606, there was a source of vadose zone water at the 15' to 22' depth, in addition to the plume water. It is likely that plants at this location utilized both sources. The vadose zone soil had low nitrate levels, hence it is likely that plants used nitrate from the plume to support growth. In conclusion, the shrub community clearly has potential for mitigating plume movement and extracting nitrate.

4.3 Estimate Sulfate Uptake Rates in Phreatophytes

The primary treatment goal for the alluvial aquifer is to restore water quality to a condition such that contaminant levels are below EPA ground water standards in 40 CFR 192 (DOE 2004a). An additional goal is reduce sulfate levels in the alluvial aquifer. Although sulfate standards are not addressed in 40 CFR 192, the former mill is assumed to be the primary source for the sulfate plume and treatment of sulfate will be a component of the final remedy. These pilot studies are helping to establish reasonable treatment goals and attenuation processes for sulfate. An evaluation of background concentrations in the plume and input to the plume from natural sources are two of the tasks underway to address these issues (Section 3.2).

The purpose of this task is to estimate sulfate uptake rates by phreatophytes currently rooted in the alluvial aquifer. The evaluation will require a combination of literature on sulfate utilization by halophytic phreatophytes, sampling to determine sulfur concentrations in plant tissue, and using estimates of plant productivity (biomass produced per acre per year) to calculate sulfur uptake on a landscape scale. Sulfate concentration in plant tissue will be estimated for subsamples of biomass for various plant parts (e.g., current-year and total twig and leaf biomass). Sulfate analysis will be performed using ion chromatography according to Kouno and Ogata (1988) on aqueous extracts of plant tissue. This task is scheduled to begin in 2006.

4.4 Evaluate Denitrification in the Plume Using Stable Isotopes

Nitrate levels in alluvial aquifer monitoring wells have decreased over time. The hot spots near the subpile source area, formerly as high as 1,000 ppm, are now under 800 ppm. Part of the decrease is likely due to dilution of nitrate in the aquifer. However, it is also possible that part of the nitrate has been lost to biological denitrification. High rates of biological denitrification were induced in the subpile soil source area when the soil was planted and irrigated. Furthermore, laboratory tests have shown the occurrence of denitrification activity in samples of saturated soil taken from the top of the aquifer (see Task 5.5). Determining rates of denitrification in the plume is important in selecting a remediation strategy. If the loss rate due to denitrification is sufficiently high, a plume remediation method that depends on monitored natural attenuation might be feasible.

The amount of nitrate that has been lost to denitrfication over time was estimated using the ratio of the natural isotopes of N (^{15}N and ^{14}N) in the subpile soil and in the plume at increasing distances from the source. The process of dilution will not affect the ratio of ^{15}N and ^{14}N in the plume. On the other hand, biological denitrification favors ^{14}N over ^{15}N. As denitrification proceeds, the residual nitrate remaining in the plume will become enriched in ^{15}N relative to the starting material. A simple model for denitrification in the plume assumes that nitrate in the source area, which has been partially protected from denitrification due to low soil moisture levels, will have isotope ratios similar to the starting nitrate materials. On the other hand, nitrate in the plume is in saturated soil and can undergo dentrification. If nitrate at the leading edge of the plume has been subject to denitrification for a longer time than nitrate near the source area, a gradient in isotope ratios from the source area to the leading edge of the plume would be expected. This gradient in isotope ratios can be used to estimate the fraction of nitrate that has been lost to denitrification rather than dilution.

4.4.1 Methods

The source values for ^{15}N and ^{14}N were determined by extracting nitrate from soil samples taken over the unirrigated portion of the subpile soil. Samples were also collected from 6 wells ranging from 348’ to 6404’ north of the source area (Table 11). Nitrate was chemically extracted and analyzed for ^{15}N and ^{14}N by a commercial laboratory. Nitrate levels were determined analytically at ERL. Isotope ratios were expressed as δ values in $^{o}/_{oo}$:

$$\delta = (R_s - R_{std})/(R_{std})1000 \qquad (1)$$

where R_s is the ratio $^{15}N/^{14}N$ in the sample and R_{std} is the same ratio in an atmospheric standard. The fraction (*f*) of nitrate or ammonium left in the plume at each well sample point was calculated as,

$$f = e^{(\delta - \delta o)/\varepsilon} \qquad (2)$$

where δo is the value at the source and ε is the enrichment factor for pure biological denitrification; -17 was the value chosen for ε based on a compilation of laboratory studies. Actual values of ε can vary because different bacteria have different isotope discrimination values. Actual values of ε will be determined in the future using laboratory analyses of samples taken from the nitrate plume.

4.4.2 Results

Table 11 and Figure 30 present the findings. Nitrate in the plume decreased as an exponential function with distance from the source. Using a best-fit curve for the data, the estimated value at the source was 682 ppm while the value at the leading edge of the plume at 6000' was 19 ppm. The actual value of nitrate at 6404' from the source (Well 650) was 3.8 ppm. Residual nitrate in the plume became increasingly enriched in ^{15}N with distance from the plume, fitting a linear equation ($P<0.05$). δ values increased from -5.6 at the source to a projected value of +4.5 at the leading edge of the plume at 6000'. From equation (2), and assuming a value of -17 for ε, the fraction of nitrate remaining at 6000' calculates to be 0.54. Using this relationship, at the leading edge of the plume, an estimated 46% of nitrate originally present has been lost to denitrification. As mentioned, the value of ε varies among studies, and the range of values for the 13 studies that produced the mean value used here was -12 to -30, so the true value of *f* might range between 0.4 and 0.7.

Table 11. Results of Nitrate and Stable Isotope Analyses

Source (well #)	Distance from Source (feet)	Nitrate (ppm)	$\delta^{15}N$ ‰ Nitrate
Subpile Soil	0	-	–8.9
606	348	554	–3.2
765	1761	209	–0.8
648	2724	107	–1.5
761	3800	135	2.8
762	4321	24	1.0
650	6404	3.9	4.0*

*This value is total N; there was not enough nitrate for extraction method employed.

4.5 Monitor and Model Plume Dynamics

The purposes of this task are to update well monitoring data, document recent changes in nitrate and sulfate plumes, construct relatively simple models of the capacity of natural attenuation processes, and model responses of plumes to attenuation enhancements. The most recent nitrate and sulfate plume maps were created with 1997 monitoring data.

Monitoring data from 2003 indicate that nitrate (Figure 31) and sulfate (Figure 32) concentrations in the proximal portion of the plume appear to have decreased since 1994. Well 606 shows the greatest decrease, from about 1,200 mg/L in 1994 to about 800 mg/L in 2003. Decreases in nitrate and sulfate could be related to several factors: (1) removal of the tailings source in 1994, (2) an increase in fresh water recharge after large areas were denuded (less ET) following removal of tailings, (3) an increase in phytoextraction as health improved for wild phreatophyte stands rooted in the aquifer, and (4) establishment of saltbush plantings in the subpile source to control recharge and leaching. In contrast, nitrate concentrations have increased in distal plume wells (Figure 33). These increases are likely due to migration of more contaminated water from the centroid of the plume (DOE 2004c, Section 6.1.2).

Updated plume maps will be created in 2006.

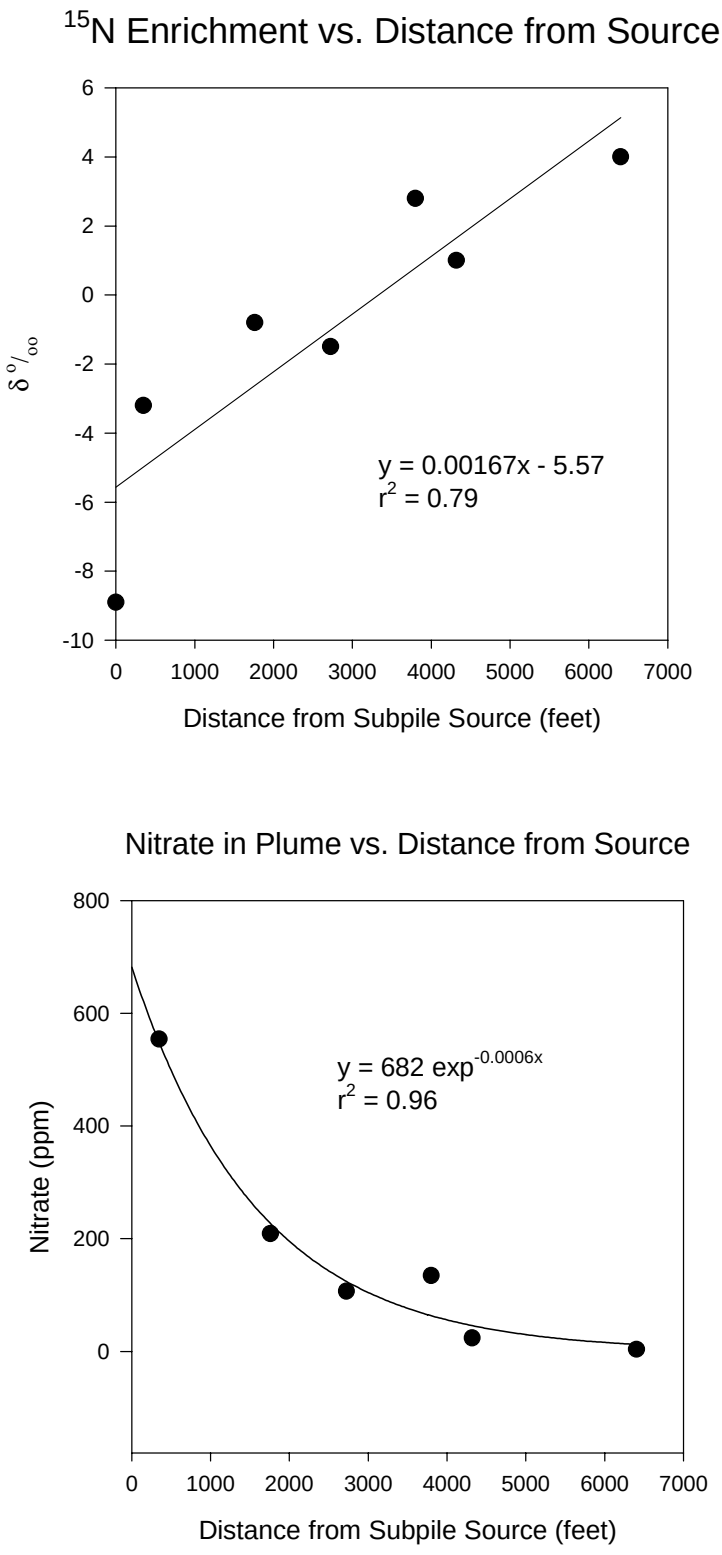

Figure 30. Plots of data.

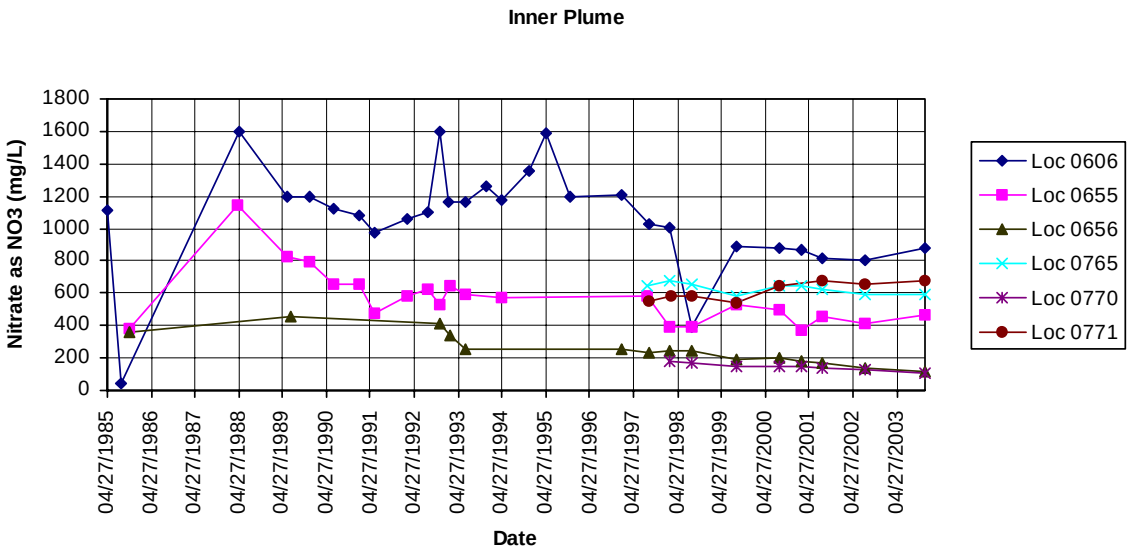

Figure 31. Nitrate concentrations in proximal portions of the plume.

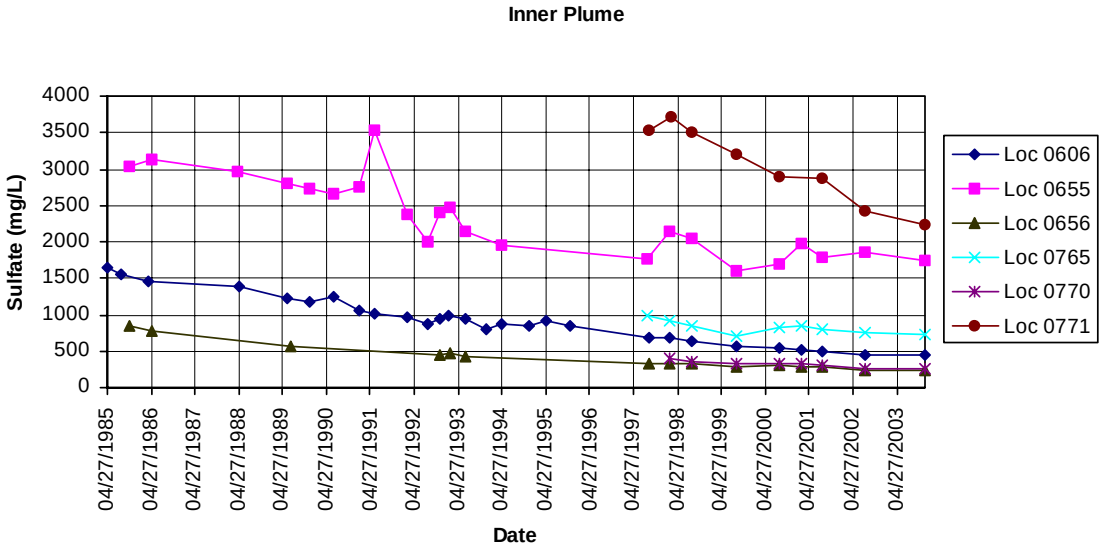

Figure 32. Sulfate concentrations in proximal portions of the plume.

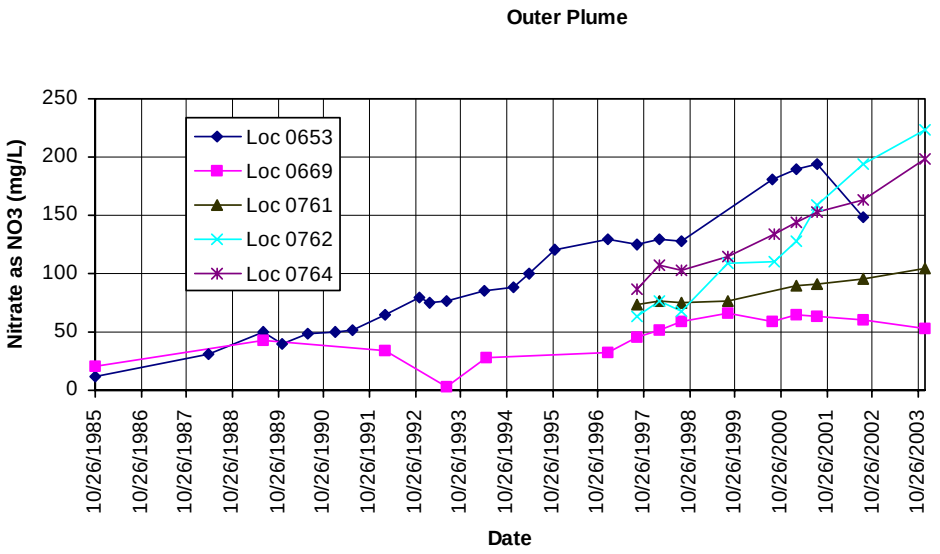

Figure 33. Nitrate concentrations in distal portions of the plume.

5.0 Enhanced Attenuation

Enhanced attenuation (EA) can be defined as initiating and/or augmenting natural and sustainable attenuation processes. The goal is to increase the magnitude of attenuation by natural processes beyond that which occurs without intervention. EA approaches may be implemented if it cannot be shown with a high level of certainty that total capacity of *natural* attenuation processes (Section 4.0) are capable of attaining ground water remediation objectives. The pilot studies are focusing on enhancements that are sustainable—that do not require long-term, continuous intervention—particularly measures to enhance growth of native phreatophytes overlying the plume (enhanced phytoremediation). The goals are to slow plume movement and extract nitrate and sulfate.

5.1 Install Landscape-Scale Grazing Protection and Revegetation Plots

Preliminary studies found that protecting native *A. canescens* and *S. vermiculatus* plants from grazing can double biomass productivity, transpiration rates (water extraction from the aquifer), and N-uptake rates (DOE 2004c, McKeon et al. 2006). Preliminary studies also found that transplants could be successfully established, grow vigorously for several years in small exclosure plots, and with managed irrigation, send roots 30 feet into the nitrate and sulfate plume. The purpose of this task is to determine if comparable results are attainable with a large-scale grazing protection (exclosure) plots and irrigated plantings (revegetation plots) over a range of depths to ground water.

Two 50 m by 50 m plots within existing *A. canescens* and *S. vermiculatus* stands overlying the plume were fenced to protect plants from grazing (Exclosure Plots in Figure 34). The goal is to promote an increase in nitrate and plume water extraction. Fenced plots were constructed where

the potential benefits of grazing protection were considered to be the greatest. Plot location criteria included:

1) Relatively high-density *A. canescens* and *S. vermiculatus* stands as delineated in the preliminary studies (DOE 2004c, Section 3.4),
2) Stands with ongoing recruitment and with a high proportion of young plants,
3) Locations spanning a range of depths to the aquifer (Section 4.1), and
4) Locations where nitrate concentrations in the alluvial aquifer are relatively high.

Grazing Exclosure Plot 1 contains a mature *S. vermiculatus* (black greasewood) stand to the north and a mixed stand of immature greasewood and *A. canescens* (fourwing saltbush) to the south. The plot was placed just east of a high nitrate area in the plume. Exclosure Plot 2 overlays a high nitrate area farther to the north. It contains a stand of fourwing saltbush ranging in maturity from new seedlings to mature, overgrazed plants.

Two 50 m by 50 m fenced plots were also installed for a large-scale transplanting demonstration (Revegetation Plots in Figure 34). The two fenced plots are located in a denuded area overlying the proximal region of the plume with the highest nitrate conctrations (Section 3.2). The plots also span a broad range of depths to ground water (Section 4.1). Depths to ground water are about 30 feet for Revegetation Plot 1 and 40 feet for Revegetation Plot 2.

Planting will begin in spring 2006. Plant materials will consist of a 3:1 ratio of *A. canescens* ssp. *Angustifolia* (DOE 2004c, Section 7.1.2) and *S. vermiculatus* planted in three spacing patterns to determine the best spacing for maximum vegetative cover and plant survival. In each plot plants will be spaced at 0.5m, 1 m, and 2 m, for approximately 1,000 total plants. The plants were grown at the University of Arizona Environmental Research Laboratory over the winter. Irrigation will be delivered only through the first growing season (April through September). Each plant will be irrigated at a rate of 4 liters per day.

5.2 Design and Install an Irrigation System for Revegetation Plots

An automated irrigation system was designed for the revegetation plots and partially installed in September 2005. Well 618 is the clean water source that will be used to irrigate the plants until their roots contact ground water, a 1-2 year period. A schematic of the irrigation design is included in Section 6.2.

5.3 Monitor Plant Growth and Nitrate and Sulfate Uptake Rates

Monitoring of exclosure and revegetation plots will begin in spring 2005. Plant survival, canopy volume, canopy cover, and dry-weight biomass of each species present will be measured. Changes in plant abundance will be monitored annually at the end of each growing season. Survival of shrubs will be evaluated by census. Canopy volume and cover of shrubs, both existing plants and transplants, will be measured individually. As with the subpile planting (Section 3.0) and the land farm planting (Section 6.0), at the end of the growing season, plant height (a) and cross-sectional radii (b,c) of plants will be measured, canopy volume will be estimated using the formula for a hemispheroid ($2/3\ \pi abc$), and canopy area will be estimated using the formula for an ellipsoid (πbc). Rooting depth will be monitored with a small borehole camera (see Section 3.8).

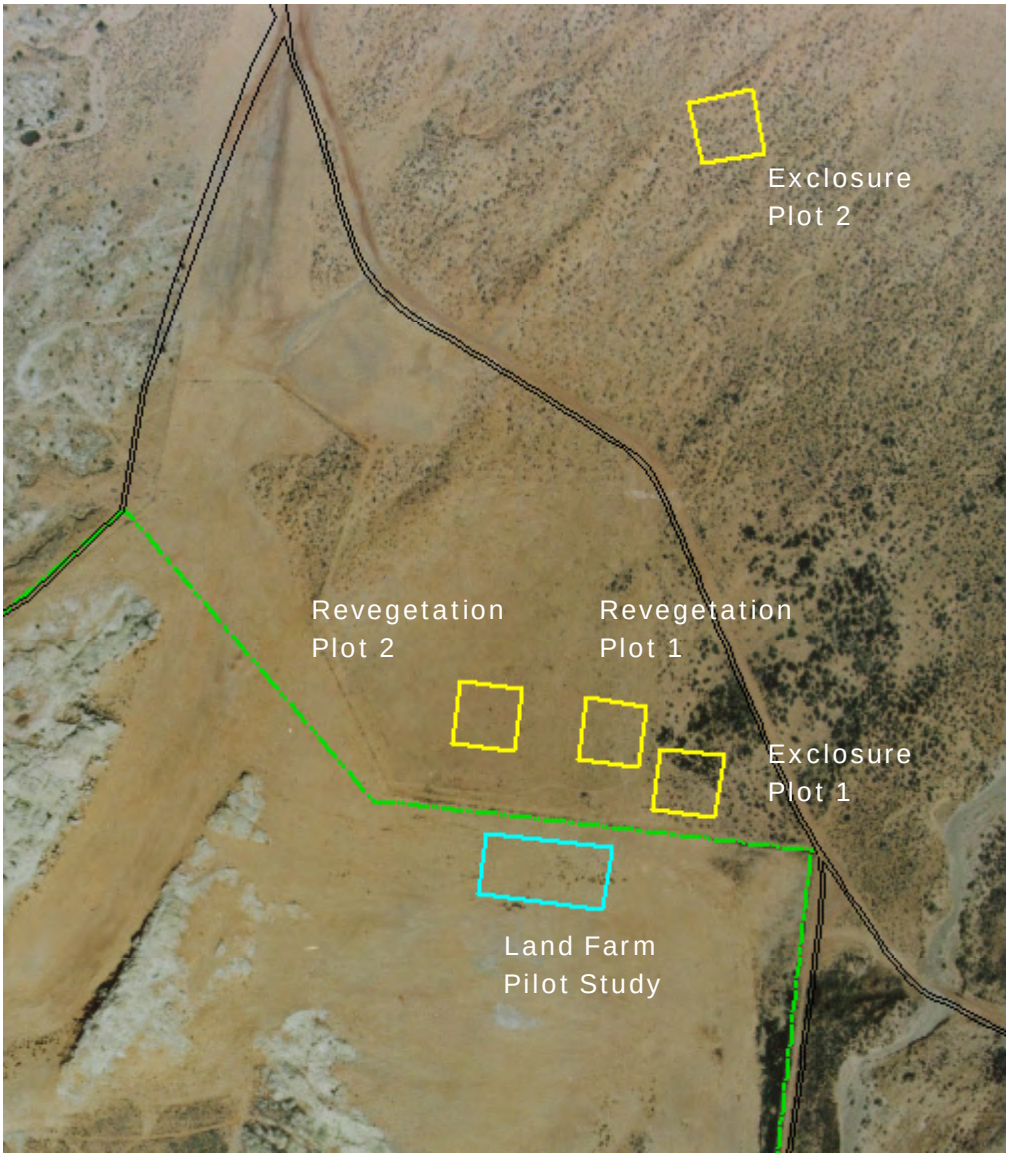

Figure 34. Aerial photograph of plume area showing GPS boundaries of grazing exclosures and revegetation plots (yellow), the land farm pilot study plot (blue; see Section 6.0), and the millsite remediation fence line (green).

Above ground biomass and total N will be estimated based on the canopy volume-weight relationship (Bonham 1989). After canopy volume of *Atriplex* shrubs are measured, a subset of will be sampled to establish the canopy volume-weight relationship. These shrubs will be harvested and dry weights of current-year productivity and total dry-weight biomass will be determined. Total N will be estimated for subsamples of biomass for various plant parts (current-year and total twig and leaf biomass) using the Kjeldahl method (Maynard and Kalra 1993). Sulfate concentration in plant tissue will be estimated for subsamples of biomass for various plant parts (current-year, total twig and leaf biomass). Sulfate analysis will be performed using ion chromatography according to Kouno and Ogata (1988) on aqueous extracts of plant tissue.

5.4 Estimate Phreatophyte Evapotranspiration (ET) under Current and Possible Future Land Use Scenarios

Stable nitrogen isotope measurements (Section 4.5) show that natural attenuation of nitrate through denitrification occurs in the plume as well as the source area, and that approximately half of the original source nitrogen may have been lost to this process already. Furthermore, stable oxygen and hydrogen isotope measurements (Section 4.2) support the conclusion that fourwing saltbush and black greasewood plants growing over the plume access water from the phreatic layer at the top of the plume, and may also access nitrate from the plume. Hence, the plant community over the plume can play an important role in natural and enhanced attenuation by controlling the movement of the plume away from the site (hydraulic control) during the years required for natural attenuation to reduce nitrate to safe levels. Unfortunately, in the past the site was overgrazed and plant cover is only approximately 5 percent, although it is as high as 25 percent in protected (fenced) areas.

Navajo Nation has now approved installation of exclosure plots for grazing protection, and revegetation plots to accelerate natural succession of phreatophyte communities (Section 5.1), both to test the feasibility of enhancing plant growth and ET. It will important to measure actual rates of ET in these plots and in adjacent grazed areas to develop a simple water balance model to estimate how well these enhanced plant communities can control hydraulic gradients (Section 4.5). The main component of ET in this system will be plant transpiration (T) as the soil surface is normally dry and the water originates in the plume. Sap flow sensors can be used to determine T. This method was formerly limited in scope due to the expense of the individual sensors and other components available through commercial sources. However, a University of Arizona group is now making and deploying sensors at relatively low cost, hence it will be possible to collect data on as many as 50 individual plants at a time. Combined with growth measurements, ET measurements will provide data from which an accurate nitrogen and water balance for the plant community can be constructed. This information will be used to determine future remediation scenarios with respect to land use over the plume area.

This task will begin in exclosure plots in 2006 and in revegetation plots once plants have matured.

5.5 Conduct Soil Column Study of Carbon Sources

DOE is evaluating monitored natural attenuation (MNA) as the primary remedy for ground water contamination at Monument Valley. Several natural processes including denitrification and advection may be acting to decrease nitrate levels in the alluvial aquifer. Bench-top soil column studies were conducted to help estimate the capacity of bioremediation as well as natural flushing (dispersion and dilution) processes in the alluvial aquifer. The objective was to evaluate natural attenuation processes and to determine if the capacity of all natural processes acting to lower nitrate levels in the alluvial aquifer exceed rates of contaminant loading from sources and will achieve remediation requirements in a reasonable time.

The column studies also evaluated enhanced bioremediation. Enhanced bioremediation generally refers to optimizing environmental conditions such that the appropriate microorganism(s) will flourish and transform the maximum amount of contaminant in a shorter amount of time. Enhanced bioremediation usually involves the addition of nutrients (e.g. oxygen, carbon and /or nitrogen) to the soil or subsurface environment to accelerate natural processes conferred by the

indigenous microbial population. For example, nutrients are fed to contaminated ground water and soil via wells to encourage the natural population of microorganisms. In the case of nitrates and/or sulfates, it is commonplace to inject an electron donor, such as acetate, ethanol or glucose. The objective of this activity was to acquire the data necessary to quantify if enhancements (intervention) will raise the attenuation capacity above what occurs naturally (without intervention) and whether they are sustainable—do not require long-term, continuous intervention.

5.5.1 Methods and Materials

Soil samples were taken near wells 606 and 677 at an approximate depth of 12 m in the saturated zone. Samples were bagged and kept in coolers upon transport to the lab. Samples were air-dried and sieved with a 200-mesh sieve and stored at 4 °C until further processing.

A preliminary batch study was conducted using a 1:1 slurry of saturated evaporation pond soil and a 200 mm solution of different carbon sources to determine initial denitrification kinetics for aquifer materials by measuring the loss of nitrate and nitrous oxide production over time. In this study, it was determined that acetate and ethanol may stimulate denitrification (data not shown) in the Monument Valley soil. A second soil slurry study was conducted using well 677 soil. The production of nitrous oxide in the headspace of vials supplemented either with or without 10 percent acetylene measured with a gas chromatograph (Shimadzu, MD) and the loss of nitrate was monitored periodically over the course of 2 weeks with Szechrome Reagent (PolySciences, State) at an absorbance of 540 nanometers (nm).

Sterile glass columns (dimensions: inner diameter of 2.5 cm by 14.5 cm, volume = 71.177 cm^3) were packed with well 606 soil to achieve a bulk density between 1.60 g/cm^3 to 1.70 g/cm^3. Artificial ground water (AGW) was pumped into the column for 24 h against gravity at an approximate flow rate of 0.3 milliliters per minute (ml/min.) to saturate the soil. Upon saturation, the flow rate was adjusted to approximate the velocity of the alluvial aquifer (0.003 ml/min) and the reservoir was switched to a reservoir containing AGW and 300 parts per million (ppm) or milligrams per liter (mg/L) nitrate. This concentration was selected to represent the average concentration of nitrate found in the Monument Valley plume. A fraction collector was set up with test tubes filled with 100 microliters (µl) of 0.3 Molar (M) Sodium Hydroxide (NaOH) to catch and preserve samples. After 4 pore volumes (PV), the reservoir was switched back to AGW and ran for an additional 3 PV. At this time the reservoir was switched again to one containing AGW, nitrate (300 mg/L) and one of the following carbon sources (200 mM each): acetate, ethanol, or formate. Samples were analyzed for nitrate using Szechrome Reagent (PolySciences, State) to generate nitrate breakthrough curves (BTC) for AGW + Nitrate and AGW+nitrate + carbon source.

Moment analysis of the BTC was used to obtain a mass balance of nitrate for each treatment. The amount of nitrate recovered during each treatment was calculated by determining the area beneath each break through curve and compared to known input concentrations of nitrate.

5.5.2 Results

In all cases when nitrate + AGW was pumped into the columns, moment analysis of the BTCs indicated complete recovery of nitrate pumped into the columns (Table 12), compared total mass injected to 0^{th} moment). As expected, nitrate was not significantly retarded when traveling through the Monument Valley soil, having an average retardation factor of 1.01. In Column 2,

nitrate actually moved faster than AGW (R = 0.619). This may also have been due to the fact that a considerable amount (~ 5 g) of soil was lost from the column during the experiment, changing the transport characteristics of the column.

Table 12. Moment Analysis of Nitrate Breakthrough Curves BTCs Generated During Nitrate Transport Through Soil Columns Packed with Monument Valley Well 606 Soil.

Column	Solute	Total mass injected (mg)	Coeff. Of variation (+/-)	0th Mmt (mg)	0th Mmt -CV (mg)	CV+Oth Mmt (mg)	Retardation Factor
1	Nitrate	61.668	2.709	63.525	60.816	66.234	1.174
	Nitrate + Acetate	57.776	4.449	55.228	50.779	59.677	0.942
2	Nitrate	68.034	7.276	74.398	67.122	81.674	0.619
	Nitrate + Ethanol	79.390	1.413	74.954	73.541	76.367	1.082
3	Nitrate	85.191	6.456	81.969	75.513	88.425	1.073
	Nitrate + Formate	79.967	8.611	70.874	62.263	79.486	1.161

Enhanced natural attenuation was monitored in columns supplemented with different carbon sources. In a preliminary batch study, 1:1 soil slurries of well 677 saturated soil and 200 mM carbon source, ethanol stimulated denitrification activity (Figure 35) measured as a function of N2O-N in the headspace of vials incubated with or without acetylene.

Similar positive, yet minimal, enhanced attenuation was observed in well 606 soil columns supplemented with ethanol as a carbon source. Moment analysis of nitrate BTCs (Figure 36) indicated a loss of ca. 3 mg of nitrate when nitrate + ethanol + AGW was pumped into the soil. The other carbon sources tested (Table 12 and Figure 37 and Figure 38) were not successful in stimulating denitrification during transport (ie. all the mass of nitrate pumped into the column was recovered in the elluant) in the well 606 soil. Greater mass loss is anticipated in well 677 soil.

5.5.3 Discussion

The batch study showed that organic carbon sources could stimulate the rate of denitrification in the plume. The column studies are, so far, inconclusive with regards to the actual rates of denitrification that could be achieved. Unamended artificial ground water plus plume soil did have a positive rate of denitrification, amounting to 0.035 μg/kg/hr (std. Error = 0.02). This seemly low rate needs to be compared with the volume of water and nitrate content in the plume. The plume volume is estimated at 2×10^6 m^3 and the nitrate-N content is approximately 10^5 kg (assuming 175 mg/kg mean N concentration in 0.3 plume volumes of water). The mass of soil in the plume is approximately 2.8×10^9 kg (assuming 1400 kg/m^3). The denitrification rate measured in the batch study would support a denitrification rate of approximately 860 kg/yr over the plume volume, for an estimated removal time of 120 years. This very approximate calculation is in agreement the isotope enrichment data, that denitrification could be a significant factor in removing nitrate from the plume over time (Section 4.5). The rates might be enhanced by addition of carbon sources; however, injection and dispersion methods in the plume would need to be investigated.

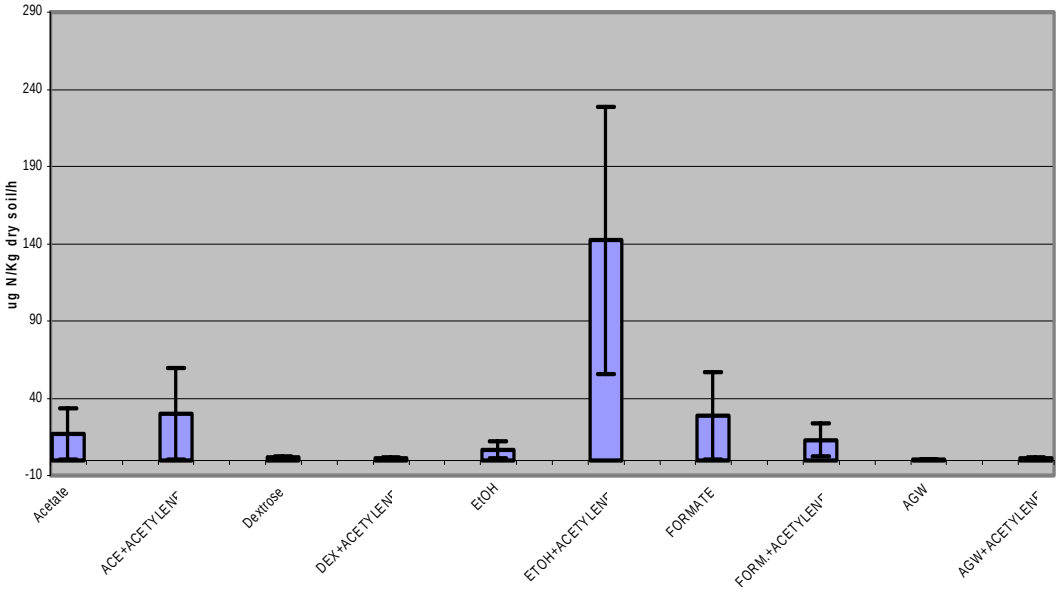

Figure 35. Nitrous oxide production (ug N kg dry soil^{-1} h^{-1}) in 1:1 Monument Valley well 677 soil and carbon source + artificial ground water (AGW) slurries. Carbon sources tested were acetate (ACE), dextrose (DEX), ethanol (ETOH) and formate (FORM) at 200 mM each. Acetylene, an inhibitor of dinitrogen production, was added to the headspace of septa sealed, evacuated vials at 10 % to assist in measuring complete denitrification using a gas chromatograph. Error bars represent the standard error of the mean with n = 3.

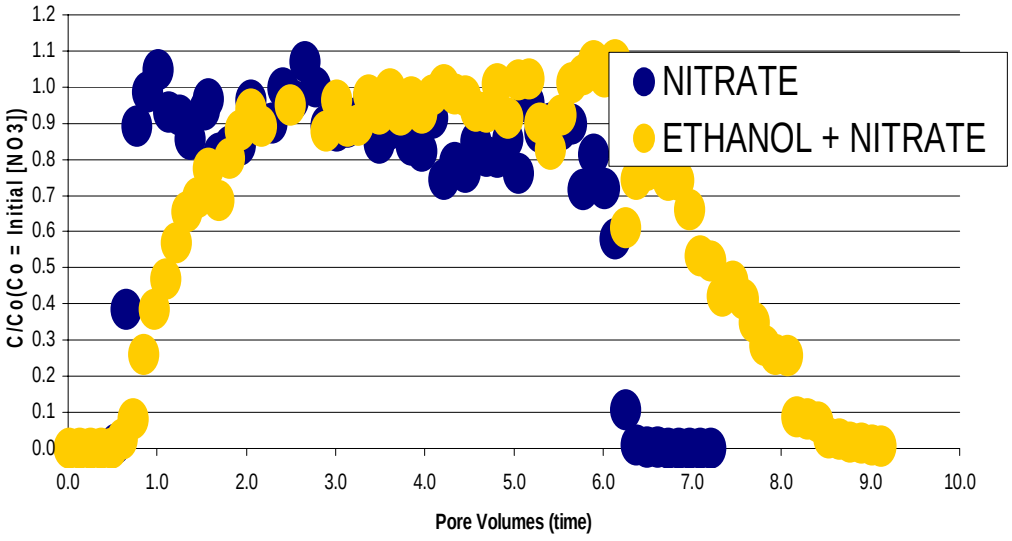

Figure 36. Nitrate breakthrough curves for Monument Valley well 606 soil when supplemented with or without a carbon source (200 mM ethanol).

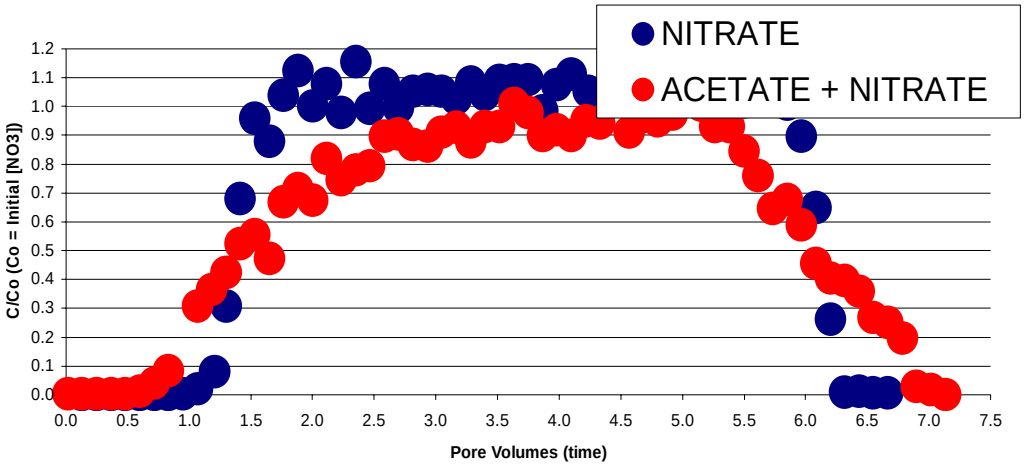

Figure 37. Nitrate breakthrough curves for Monument Valley well 606 soil when supplemented with or without a carbon source (200 mM acetate).

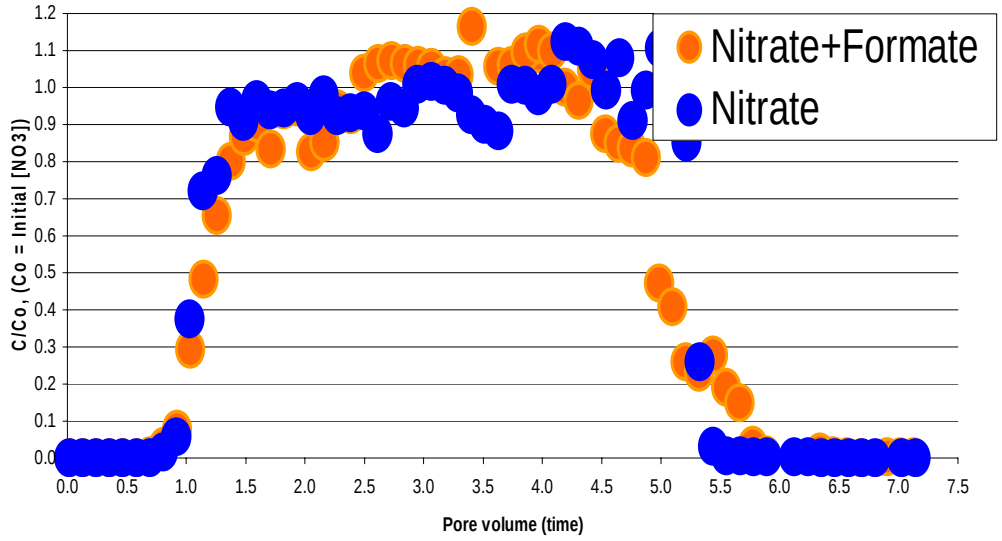

Figure 38. Nitrate breakthrough curves for Monument Valley well 606 soil when supplemented with or without a carbon source (200 mM formate).

6.0 Active Ground Water Remediation: Land Farming

Land farming was selected as the most feasible and efficient *active* remedy for the nitrate and sulfate plumes (DOE 2004c, Section 8.0). Land farming will be considered only if the more passive alternatives are found to be inadequate. The farm would serve several functions: (1) extract nitrates in irrigation water pumped from the plume; (2) convert nitrates into useful plant biomass; (3) reduce sulfate levels in the alluvial aquifer, (4) minimize water infiltration and leaching of contaminants back into the aquifer; and (5) enhance restoration of the disturbed ecosystem. Land farming would consist of pumping the contaminated alluvial aquifer to irrigate and fertilize a farming operation on areas disturbed during the surface remediation. The land farm would produce a crop such as native plant seed for mine land reclamation. Pumping would

continue until nitrate concentrations in the alluvial aquifer drop below the 44 mg/L MCL for nitrate.

6.1 Develop Experimental Design

The land farm pilot study is more than a field-scale demonstration. It is a factorial field experiment designed to address specific uncertainties. Developing an experimental design ensures that the right type of data, and enough of it, will be available at the end of the experiment to answer specific questions with confidence:

- Which cropping systems are most efficient in using nitrate?
- What is the optimum irrigation rate?
- What are the optimum nitrate concentrations in irrigation water?
- Will residual sulfate and nitrate accumulate in the field?
- How productive are the crops?
- Are the crops safe for livestock?

The experimental design consists of treatment and design structures. The terms treatment structure and design structure refer to the factors that will be compared and controlled in the field experiment and how field plots will be arranged (Milliken and Johnson 1992). Treatments are defined by factors and levels of each factor. The design structure consists of the arrangement of experimental units into groups or blocks in the field. Dependent variables are the environmental parameters that will be measured to compare treatments during the course of the study.

The treatment structure for the land farm pilot study consists of two main factors: nitrate concentration in irrigation water and crops in the cropping system. The four nitrate levels span a range derived from the results of greenhouse studies: 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. Water pumped from the DeChelley aquifer will be used as the clean water control level. The irrigation rate may be changed over the course of the study until an optimum deficit irrigation rate is achieved, but irrigation rates will not be compared within the treatment structure.

The design structure is a randomized split plot. A 50 x 100 m area will be planted and then split into 32 equal-size plots (Figure 39) receiving four replications of 8 different treatment combinations (nitrate level x crop). Cropping systems using fourwing saltbush and black greasewood will be planted initially. Later, Indian ricegrass or other grasses may be planted in strips separating the rows of shrubs in an alley crop configuration. Both will be grown primarily for seed production. Seed will be harvested annually, and after the harvest, livestock will be allowed to graze plants in fall and winter only if plant tissues do not exceed established toxicity levels. Saltbush and greasewood roots, penetrating deeper in the soil profile than Indian ricegrass roots, will likely intercept water and nitrate that passes below the Indian ricegrass rooting zone. Land farm plots will be planted in spring 2006.

6.2 Design Irrigation System

The irrigation system for the land farm, source area phytoremediation, and revegetation plots is illustrated in Figure 40. A detailed as-built design and drawing were submitted to Stoller Engineering in fall 2005.

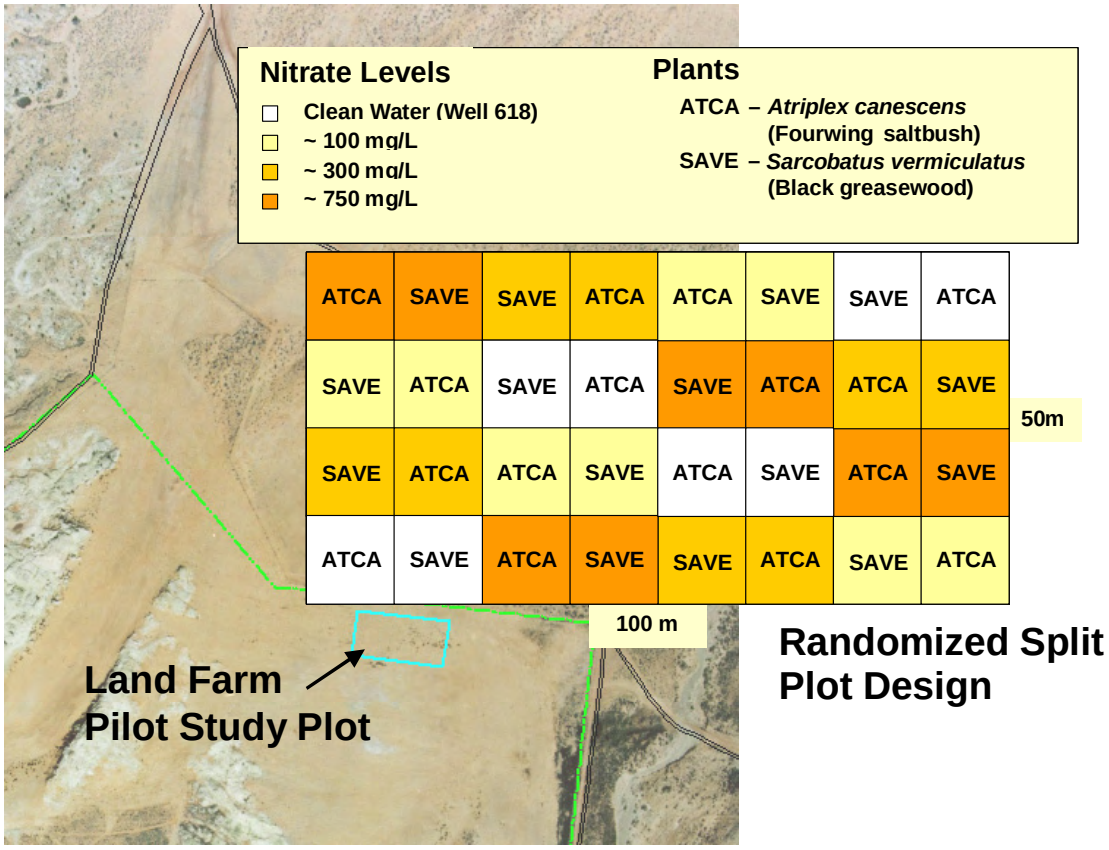

Figure 39. Land farm pilot study experimental design.

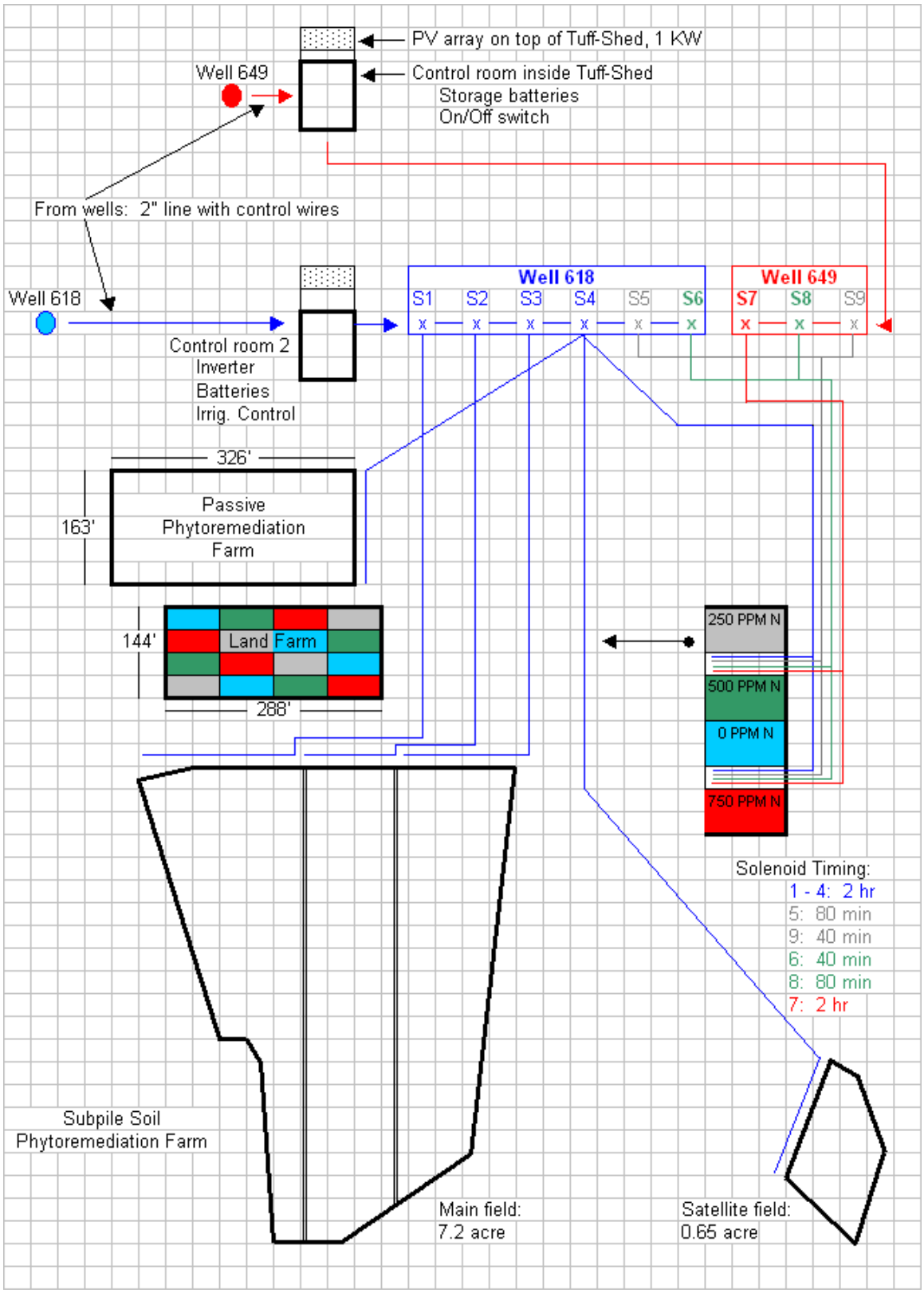

Figure 40. Schematic of irrigation system for the source area phytoremediation plantings, plume phytoremediation plots, and the land farm plots.

6.3 Characterize and Monitor Soil Chemical Properties

Soil samples were taken at eight locations within the land farm to establish baseline concentrations of nitrate, ammonium, and sulfate. The area was separated into a grid of 4 blocks wide by 4 blocks long, each block approximately 75 ft long by 40 ft wide (see Figure 41). Sample points were flagged in the approximate center of each block. Coordinates were later taken for each sample location using a GPS unit. Sampling of the land farm occurred on January 19, 2005, at every other flagged sample location (LF1, LF3, LF6, LF8, LF9, LF11, LF14 and LF16). Soil samples were collected at depths of 1, 3, 6, 9, 12 and 15 ft using a hand auger. Soil samples were also collected at other depths if changes in soil color or texture were observed. Grab samples at each sample depth were placed in double zip-lock bags, labeled with location, depth and date, and stored in coolers for transportation back to the Environmental Sciences Laboratory for analysis using the procedures described in Section 3.2.

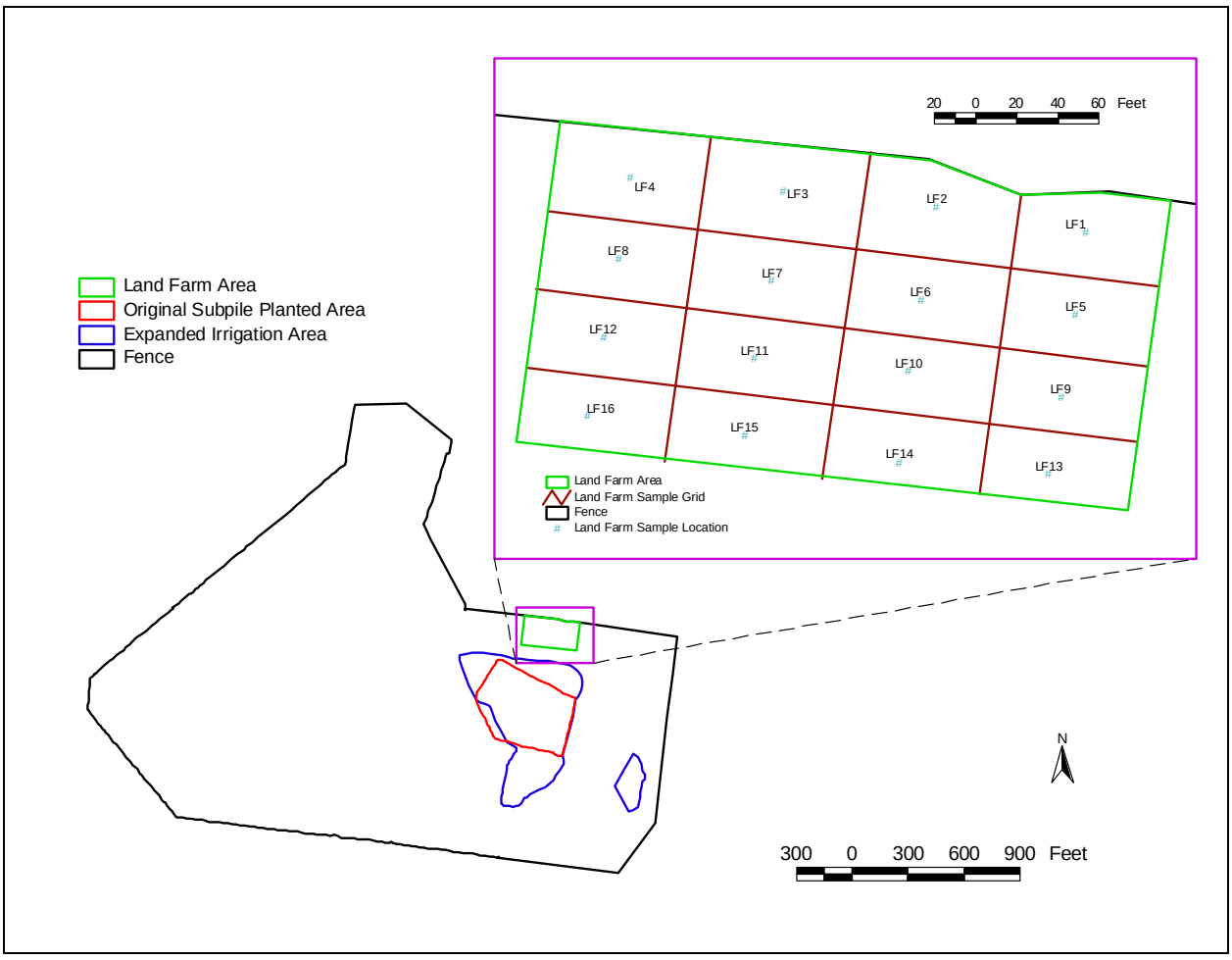

Figure 41. Map of land farm area illustrating sampling grid lines and sampling points for the baseline characterization.

Analytical results are shown in Table 13. Concentration maps were created using Environmental Visualization System (EVS) software (Figure 42 through Figure 45). Both nitrate and sulfate distributions were mapped using the average and the maximum concentration at each sample

location. Ammonia concentrations were generally below detection limits for the analytical procedure. Results show that concentrations of both nitrate and sulfate vary across the site with ranges of < 5.6 ug/g (detection limit) to 778 ug/g for NO_3^-N, and <25 ug/g (detection limit) to 4185 ug/g for SO_4^{2-}. These baseline concentration maps will be factored into evaluations of changes in soil NO_3^-N and SO_4^{2-} over time in response to treatments imposed in the land farm experiment.

Table 13. Land Farm Soil Baseline Sample Results

Location	Depth (ft)	Moisture Content	NH3-N (ug/g)	NO3-N (ug/g)	SO4 (ug/g)	Comments
LF1	1.0	5.60%	<5	<5.6	<25	
	3.0	4.47%	<5	<5.6	295	
	4.0	1.10%	<5	<5.6	30	
	6.0	11.30%	<5	30.5	95	
	7.5	5.96%	<5	182.8	4185	
	9.0	4.63%	<5	63.2	1575	
	12.0	4.43%	<5	<5.6	825	
	15.0	6.87%	<5	<5.6	1620	
LF9	1.0	4.63%	<5	<5.6	960	
	3.0	4.57%	<5	11.3	520	
	4.0	3.95%	<5	<5.6	2855	
	6.0	4.04%	5	<5.6	725	
	9.0	9.20%	<5	288.9	2745	
	12.0	6.73%	5	178.3	1330	
	15.0	3.58%	5	30.5	425	
LF11	1.0	5.26%	<5	<5.6	1645	
	3.0	5.13%	<5	7.9	680	
	4.0	4.44%	<5	84.7	2730	
	5.0	6.98%	<5	235.9	1075	
	5.0		<5	222.3	1080	duplicate
	6.0	4.17%	<5	150.1	2325	
	9.0	7.99%	<5	132.1	665	
	12.0	3.12%	<5	11.3	420	
	15.0	3.89%	<5	<5.6	375	
LF8	1.0	5.69%	<5	<5.6	<25	
	3.0	1.57%	<5	<5.6	75	
	4.0	2.85%	<5	<5.6	505	
	5.0	4.97%	65	<5.6	820	
	6.0	3.47%	<5	<5.6	1280	
	7.0	4.81%	<5	<5.6	850	
	8.0	3.21%	<5	<5.6	550	
	9.0	3.70%	<5	<5.6	725	
	12.0	1.95%	<5	<5.6	315	
	13.5	15.46%	5	<5.6	2345	high clay
	14.0	16.91%	<5	<5.6	2780	
	14.0		<5	<5.6	2610	duplicate
	15.0	4.94%	<5	<5.6	730	
	16.0	2.90%	<5	<5.6	380	
LF16	1.0	5.89%	<5	<5.6	1730	
	3.0	3.02%	<5	10.2	90	
	4.0	7.83%	<5	16.9	2100	
	6.0	2.92%	<5	<5.6	930	
	6.0		<5	<5.6	930	duplicate
	9.0	3.21%	5	<5.6	1305	
	12.0	4.07%	20	35.0	660	
	15.0	4.22%	125	91.4	325	
LF3	1.0	5.07%	5	<5.6	260	
	3.0	4.79%	5	<5.6	150	
	6.0	3.63%	5	<5.6	70	
	9.0	3.41%	10	<5.6	825	
	12.0	3.04%	10	<5.6	635	
	15.0	3.24%	5	<5.6	530	
LF14	1.0	4.46%	10	<5.6	515	
	2.0	10.55%	<5	84.7	1550	
	3.3	7.82%	<5	777.7	3360	
	6.6	6.94%	<5	199.8	3315	
	7.5	3.61%	<5	<5.6	370	
	9.8	4.98%	<5	147.9	1360	
	13.1	2.15%	<5	9.0	325	mottling
	16.4	2.88%	<5	16.9	400	
LF6	1.0	5.23%	<5	<5.6	60	
	3.3	9.66%	<5	<5.6	290	
	3.3		<5	<5.6	300	duplicate
	5.0	3.26%	<5	16.9	35	
	6.6	3.74%	<5	<5.6	535	
	7.0	5.82%	15	<5.6	1770	
	9.8	5.06%	<5	<5.6	1210	
	13.1	2.76%	<5	<5.6	625	
	15.0	2.08%	<5	16.9	480	
	16.4	1.97%	5	<5.6	455	
	17.0	2.14%	<5	<5.6	605	
LF15	1.0	6.37%	<5	<5.6	3135	

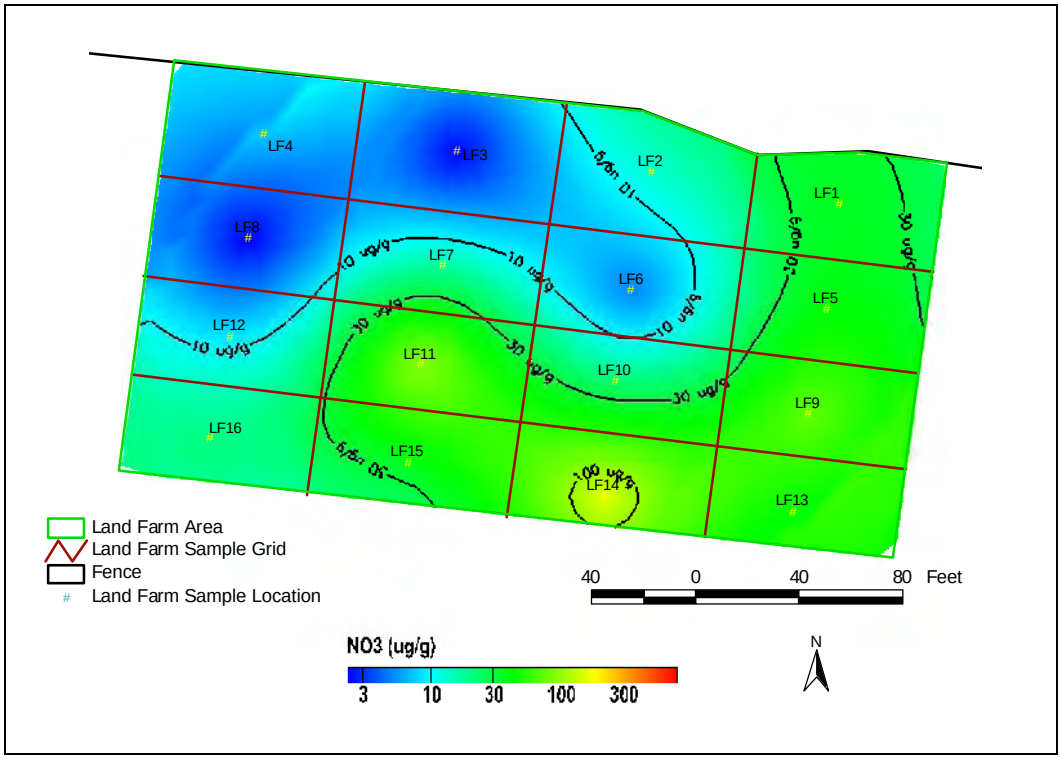

Figure 42. Map of baseline soil nitrate distributions in the land farm created using average concentrations at each location.

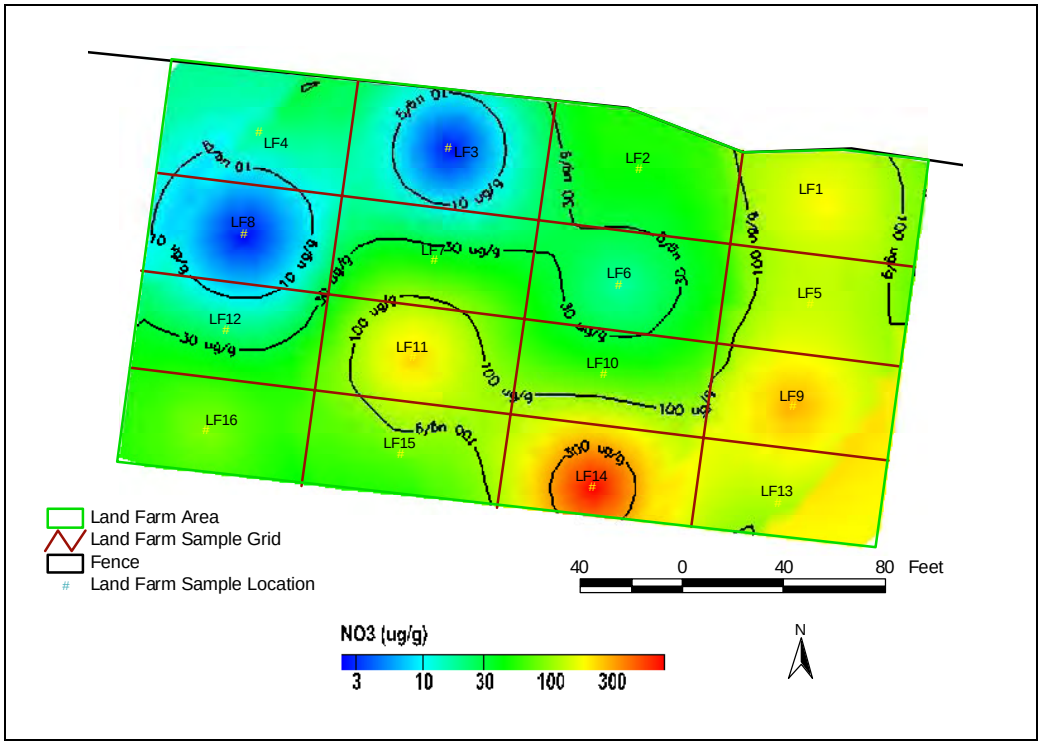

Figure 43. Map of baseline soil nitrate distributions in the land farm created using maximum concentrations at each location.

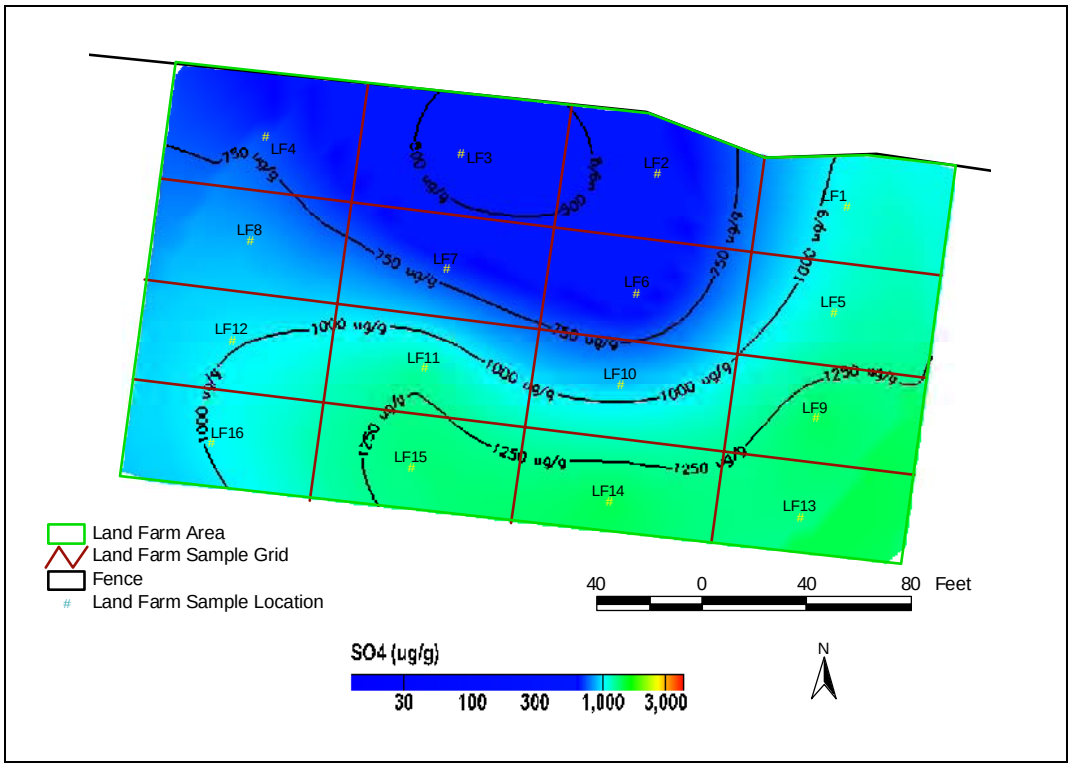

Figure 44. Map of baseline soil sulfate distributions in the land farm created using average concentrations at each location.

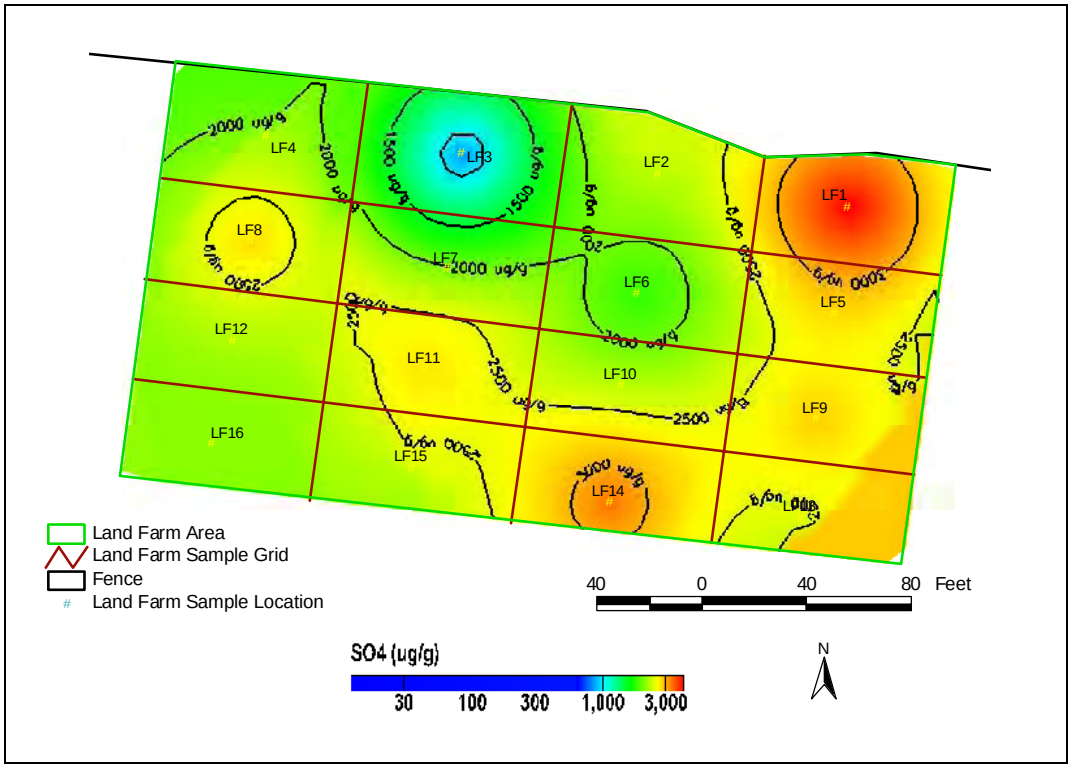

Figure 45. Map of baseline soil sulfate distributions in the land farm created using maximum concentrations at each location.

6.4 Characterize Soil Physical Properties

The purpose of this task is to determine baseline physical and hydraulic properties of the pilot farm soils. Composite soil samples will be collected from each block prior to the construction of the pilot farm and analyzed for particle-size distribution, Atterberg limits, moisture-density relationships, saturated hydraulic conductivity, specific gravity, and soil moisture retention characteristics. This task will begin in 2006.

6.5 Monitor Soil Water

The purpose of this task is to monitor soil moisture profiles within land farm plots to detect seasonal wetting fronts. Soil moisture will be monitored using neutron thermalization (NT) hydroprobes. Direct measurement of downward moisture flux will not be necessary because any minor recharge would be extracted again by the downgradient wells. However, monitoring soil water storage in the root zone and seasonal wetting fronts will be necessary for management of irrigation rates. Hydroprobe ports installed in 1999 will be used to monitor volumetric moisture content in each experimental plot (Section 6.1). Readings will be taken at 30-cm depth increments to the bottom of the ports (about 5 m). This task will begin prior to irrigation in spring 2006.

6.6 Monitor Crop Growth and Productivity

The survival, growth, productivity (including seed production) will be compared for the different crops and nitrate irrigation levels. Seed, leaf, and stem production will be monitored yearly. Seed from fourwing saltbush and other seed crops will be harvested and weighed seasonally when ripe and viable. Current year stem and leaf growth will also be monitored and the effects of simulated grazing on plant productivity will be evaluated. These activities will begin following the 2006 growing season.

For each treatment and plant species, survival will be evaluated by census. An adequate sample size for *A. canescens* canopy measurements (number of plants) for 10 percent accuracy and precision will be statistically estimated using 2001−2003 subpile soil plant data. Shrub canopy dimensions will be determined by measuring plant height (a) and cross-sectional radii (b,c) of plants. Plant volume will be estimated using the formula for a hemispheroid ($2/3\ \pi abc$), and canopy area will be estimated using the formula for an ellipsoid (πbc). If Indian ricegrass or other grasses an forbs are planted in the future, productivity for these species will be estimated by clipping and measuring dry-weights from an adequate number of 0.25 m^2 random quadrates to achieve 10 percent accuracy and precision.

Above ground biomass and total N will be estimated based on the canopy volume-weight relationship (Bonham 1989) and using a double sampling procedure. After canopy volume of the plant species is measured, a subset of 3 shrubs and 10 grasses (if applicable) ranging from small to large volume will be sampled in each treatment to establish the canopy volume-weight relationship. These plants will be harvested and dry weights of current-year productivity and total dry-weight biomass will be determined. Mean and total productivity and biomass for all measured plants will be estimated using the linear regression of canopy volume and dry-weight biomass for the 10 shrubs and 20 grasses. Total N will be estimated for subsamples of biomass

for various plant parts (current-year and total twig and leaf biomass) using the Kjeldahl method (Maynard and Kalra 1993).

Grazing simulation will be performed by manually removing leaf and stem tissue from *A. canescens*. In each of the treatments, 25 percent of the plants will be trimmed at the end of the first growing season to simulate grazing. These plants will be compared each year to determine if grazing is detrimental to plant growth.

6.7 Evaluate Nitrification and Denitrification Processes

Samples from the land-farming pilot study and the source area phytoremediation (Section 3.7) will be processed similarly. First, denitrification and nitrification potential measurements will be obtained. Second, N_2O evolution over the irrigated farm will be collected using soil covers randomly placed by nitrate treatment. Results from these measurements should generate the appropriate nitrate concentration(s) required to stimulate optimal plant yield while enhancing denitrification/nitrification. It is not necessary to modify sampling procedures for the land farm study because nitrate provided in the irrigation water serves as a substrate for plant uptake and microbial transformation. This task will begin in 2006.

6.8 Investigate Gypsiferous Soil Analogs

Preliminary calculations of the likely fate of sulfate in plume water applied to the land farm suggests that, because of relatively high calcium in the water, approximately 75 percent of the sulfate will precipitate as $CaSO_4 \cdot 2H_2O$ (gypsum) within the farm soil profile. The purpose of this task is to investigate the occurrence of natural gypsiferous soils in the Monument Valley area as an analog for sulfate accumulation in the test farm soil. This task will begin in 2007.

The occurrence, genesis, and morphology of gypsiferous soils in the Cane Valley vicinity will be investigated. Results will be compared to expected gypsum loading from the proposed phytoremediation farm. If gypsiferous soils occur, undisturbed soil the morphology of undisturbed profiles will be described and profile samples will be obtained for laboratory analysis to determine the quantity of gypsum and other salts.

Field methods discussed by Birkland (1999) will be followed and terminology developed by the USDA Soil Survey Staff (1997) will be used to describe the soil properties and horizons (DOE 2004c, Section 8.4). Characteristics of the landform and ecology associated with the soil will also be described.

6.9 Manage and Market Seed Crop

Coal mines on the Navajo Nation may be a market for native seed. Regional users of native rangeland plant seed will be contacted to determine if a market exists on the Navajo Nation. For example, Black Mesa Mine near Kayenta disturbs about 400 acres per year, and in recent years has been reclaiming about 400 to 600 acres per year. In the 1960s and early 1970s, the mine planted mostly low-diversity mixes of forage species, primarily non-native crested wheatgrass. When the Surface Mining Control and Reclamation Act of 1977 stipulated stricter reclamation requirements, and a new industry made native seeds available in bulk, Black Mesa began planting a diverse seed mix consisting of 85 percent native seed. In response to requests from the tribes, in the 1980s, Black Mesa also began seeding plants that have cultural and medicinal uses.

Black Mesa now plants many different species of culturally and medicinally important plants, including green ephedra, banana leaf yucca, fourwing saltbush, cliffrose, Gambel oak, fringed sage, Indian ricegrass, needle-and-thread grass and piñon pine.

Regional users of native rangeland plant seed will be contacted to determine if a market exists on the Navajo Nation. Species in addition to fourwing saltbush and Indian ricegrass will be considered in consultation with reclamationists and range managers and may be added to the land farm pilot study at a alter date. If appropriate, DOE will work with the Navajo Nation to assess the feasibility of establishing a local enterprise to grow and market native seed.

This task is scheduled to begin in 2006.

6.10 Test Plant Toxicity and Simulate Grazing

Another objective of the land farm is to determine if livestock and wildlife grazing is safe and if grazing as a land sue during remediation is feasible. This requires monitoring the toxicity and productivity of plant materials. Tissues of fourwing saltbush, black greasewood, and any other crops will be sampled periodically during the growing season from each treatment block in the land farm and analyzed for nutritional content including proximate analyses for crude protein, ash, fiber, fat, lignin, and energy content. Analytical procedures are described in detail in Swingle et al. 1996. Samples will also be analyzed for nitrate, hydrocyanic acid, sulfate, total sulfur, and metals of concern. At the first harvest, 20 samples will be analyzed to determine a final sample size that provides 10 percent precision and accuracy. This task will begin at the end of the 2006 growing season.

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