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Monument Valley Ground Water Remediation: Pilot Study Work Plan

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1.0 Introduction

The U.S. Department of Energy (DOE) is proposing ground water compliance strategies for the Monument Valley, Arizona, Uranium Mill Tailings Radiation Control Act (UMTRCA) site. An environmental assessment (EA) prepared for the site focuses on the compliance strategy for the alluvial aquifer (DOE 2004). The EA states that a series of pilot studies must be completed first. Pilot studies are trial studies or experiments carried out to evaluate and demonstrate alternative remedies before the final remedial action is selected and implemented. The pilot studies for Monument Valley are evaluating passive remedies and combinations of passive and active remedies for reducing contaminant concentrations in the alluvial aquifer.

Pilot studies conducted at Monument Valley in the past were preliminary evaluations of natural and enhanced phytoremediation options for contamination in the alluvial aquifer. Phytoremediation relies on the roots of plants to remove and slow migration of contaminants. DOE published results of the initial pilot studies in 2002: Phytoremediation of Nitrogen Contamination in Subpile Soils and in the Alluvial Aquifer at the Monument Valley, Arizona, Uranium Mill Tailings Site (DOE 2002). The overall conclusion: phytoremediation is a viable option for reducing contaminant levels in the alluvial aquifer and at the plume source, and is consistent with revegetation and land management goals for the site.

This work plan addresses the final phase of pilot studies needed to select a final ground water remediation strategy for Monument Valley. The purpose of this final phase is to demonstrate methods to verify and estimate the capacity of natural and sustainable processes that degrade and attenuate contaminants in the alluvial aquifer and at their source. Phytoremediation is but one of the natural and sustainable processes that may be contributing to the degradation and attenuation of contaminants. Other processes that may contribute to the total attenuation capacity at the site are biodegradation, abiotic chemical stabilization, and dispersion.

Background information including site history, regulatory compliance, and stakeholder interactions are presented in Section 2.0. The environmental setting including climate, soils, hydrogeology and plant ecology are reviewed in Section 3.0. A decision-making framework in Section 4.0 steps through a process for using pilot study results to select a final compliance strategy that will attain remediation goals. Sections 5.0 through 8.0 review the status of completed and ongoing studies at the Monument Valley site, and present the objectives and planned tasks for studies of source containment and removal, natural attenuation of ground water, enhanced passive remediation of ground water, and active ground water remedies. Section 9.0 is a schedule for timely completion of the pilot studies leading to selection and implementation of the final compliance strategy.
End of current text
2.0  Background Information

2.1  Location and Directions

The Monument Valley site is within the Navajo Nation in northeastern Arizona, about 26 kilometers (km) (16 miles) south of Mexican Hat, Utah (Figure 2–1). To reach the site from Mexican Hat, travel southwest on US163 to the Halchita turnoff. Turn south into the community of Halchita, past the Mexican Hat Elementary School, and then proceed south on Road 6440, a wide gravel road DOE used to haul tailings from the Monument Valley site to the uranium mill tailings disposal cell at Mexican Hat. Continue south on Road 6440 for approximately 12 miles into Cane Valley and to the point where the wide gravel road narrows to a single-track dirt road. The former mill site is within the fenced area to the south. The site is on the west side of Cane Valley Wash at an elevation of approximately 4,800 feet (ft) and is bordered on the west by Yazzie Mesa and on the east by Comb Ridge (Figure 2–2).

2.2  Site History

Uranium was first discovered in the Monument Valley area in 1942 approximately one-half mile west of the former millsite. A total of 767,166 tons of uranium and vanadium ore was mined from the original deposit between 1943 and 1968 when the mill closed and the lease with the Navajo Nation expired. Most structures were removed shortly thereafter.

From 1955 until 1964, ore at the site was processed by mechanical milling using an upgrader to crush the ore and separate it by grain size. The only chemicals used during that time period were minor amounts of flocculent, a substance used to aggregate particles within a liquid. The finer-grained material, which was higher in uranium, was shipped to other mills for chemical processing. Coarser-grained materials were stored on site in the “old tailings pile.” Some ground water contamination may have resulted from water draining through the tailings piles during that period.

From 1964 until 1968, batch leaching and heap leaching were used to process an estimated 1.1 million tons of tailings and low-grade ore at the site. In the batch-leaching process, sandy tailings were placed in lined steel tanks, and uranium and vanadium were leached by an upward flow of sulfuric acid solution. Heap leaching consisted of placing crushed, low-grade ore on polyethylene sheeting and percolating a sulfuric acid solution through the ore. Both heap-leaching and batch-leaching operations used ammonia, ammonium nitrate, and quicklime (calcium oxide) to produce a bulk precipitate of concentrated uranium and vanadium. Chemical solutions used in ore processing are believed to have been discharged to the “new tailings pile.” The new tailings pile contained both sandy tailings and processing solutions. An evaporation pond was on the east side of the new tailings pile. The purpose of the evaporation pond is unknown, but it may have been used to retain seepage from the new tailings pile.
Figure 2–1. Location of the Monument Valley Site
Figure 2–2. Regional Setting of the Monument Valley Site

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

Explanation

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- Improved Graded Road
- Unimproved Road
- Fenced Site Boundary
The former sources of ground water contamination at the site (Figure 2–3) include (1) the old tailings pile and heap-leach area, (2) the new tailings pile, and (3) the evaporation pond. Some ground water contamination originated as relatively soluble components of the ore such as calcium and sulfate from gypsum. Surface remediation at the site took place from 1992 through 1994 and resulted in the removal of most of the source materials and other site-related contamination. Tailings and soils with radium-226 concentrations exceeding 15 picocuries per gram were removed. However, analysis of subpile soil samples (samples collected from within the footprint of the former new tailings piles) indicated that site-related nonradioactive constituents in these soils may be a continuing source of ground water contamination. Ammonium and nitrate in the subpile soil appear to be contributing to nitrate contamination in ground water.

2.3 Regulatory Compliance

The UMTRCA of 1978 was enacted to control and mitigate risks to human health and the environment from residual radioactive materials that resulted from processing uranium ore. UMTRCA authorized DOE to perform remedial action at 24 inactive uranium-ore processing sites. The Monument Valley site is one of four former processing sites located within the Navajo Nation.

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

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

After the source of ground water contamination (i.e., the tailings pile) is removed, EPA regulations require that the site be evaluated to determine if contaminant concentrations in ground water comply with EPA ground water standards in 40 CFR 192. The Final Programmatic Environmental Impact Statement for the Uranium Mill Tailings Remedial Action Ground Water Project (PEIS) (DOE 1996a) provides a general discussion of ground water contamination at the 24 former processing sites. The PEIS also provides a framework for selecting site-specific ground water compliance strategies that comply with EPA regulations.
Figure 2–3. Likely Sources of Ground Water Contamination
The regulations outline several criteria for determining compliance with ground water standards:

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

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

2.3 Stakeholder Interactions

To comply with EPA regulatory requirements concerning consultation with tribes, DOE entered into a cooperative agreement with the Navajo Nation and has held numerous meetings over the past several years with representatives of the Navajo Nation, including Navajo Uranium Mill Tailings Remedial Action (UMTRA) Project, Navajo EPA, and Navajo Water Code Administration, to address concerns at the Monument Valley site. In addition, data, documents and work plans, including the SOWP, were provided to the Navajo Nation for their review and comment. In June 1998, DOE received comments from the Navajo Nation and completed the SOWP. The Navajo Nation provided DOE additional comments on the final SOWP on October 7, 1999.

To minimize risks to potential water users in the short term, DOE met with Navajo Nation representatives on September 21, 1999, and agreed to install a water supply system to serve the Monument Valley area. The Navajo Tribal Utility Authority, in cooperation with the Bureau of Indian Affairs, prepared the appropriate National Environmental Policy Act (NEPA) documentation for the alternate water supply. The water line and infrastructure were completed in September 2003.

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

In June 2000, DOE and the Navajo Nation agreed to conduct additional pilot studies for the alluvial aquifer prior to completing the EA. Pilot studies for the De Chelly aquifer were not deemed necessary. DOE and Navajo UMTRA representatives held field meetings on September 17, 2000, and May 8, 2003, at Monument Valley with local residents, stakeholders, Navajo Nation agency officials, and Indian Health Services to discuss the pilot study and potential related actions. These actions could include a grazing management plan, rights-of-way, land withdrawal, and institutional controls.

At a meeting between DOE and the Navajo Nation on November 12, 2003, in Durango, Colorado, the Navajo Nation agreed to move forward with the pilot studies. Results of the proposed pilot studies would be the basis for remediation of the alluvial aquifer and subpile soils.

In accordance with DOE’s NEPA policy and regulations, pilot studies would normally be completed before an EA is begun. However, the Navajo Nation has requested that the EA be completed to address the entire scope of DOE’s proposal, including the pilot studies and proposed compliance strategies. This would allow the Navajo Nation to consider rights-of-way, land withdrawal, institutional controls, and other actions comprehensively and simultaneously. The Navajo Nation agreed that if the pilot studies indicate that the proposed remedies for the alluvial aquifer would not comply with EPA standards and remediation goals, additional NEPA assessment and documentation may be necessary.

The final remedial action at the Monument Valley site will be selected and performed in compliance with EPA and Navajo Nation regulations, the cooperative agreement, and with the concurrence of the U.S. Nuclear Regulatory Commission.
End of current text
3.0 Environmental Setting

3.1 Climate

The Monument Valley site is semiarid. The weather station closest to the Monument Valley site is at Mexican Hat, Utah, about 26 km (16 miles) to the north. Precipitation averages approximately 16.3 centimeters (cm) (6.4 inches) annually. The wetter months on average are July through August and December through February; the driest months are May and June. Summer precipitation usually occurs as high-intensity, short-duration storms. Winter precipitation usually occurs as low-intensity, longer-duration storms (Cooley et al. 1969). Winters are cold with the daily low temperature often below freezing from November through March. Summers are warm with daily high temperature readings from 32 to over 37 °C (90 to over 100 °F). The annual pan evaporation averages 214.1 cm (84.4 inches). Average pan evaporation rates exceed precipitation every month except January. The highest pan evaporation rates, greater than 25 cm (10 inches) per month, occur from May through August.

3.2 Soils

Thick Quaternary alluvial, eolian, and some lacustrine deposits fill Cane Valley at the site (DOE 1999). The more common and widespread eolian deposits are well sorted, fine- to very fine-grained quartz sand. Less common fluvial materials, deposited in minor stream channels and in alluvial fans that occasionally spread into Cane Valley, consist of coarser sands and pebbles as large as 1 inch. Coarse deposits up to several feet thick occur at the base of the Quaternary deposits. Elsewhere, coarse layers are thin, sporadic, and discontinuous. Finer layers consisting of silt and clay fractions are also thin and sporadic. These fine layers were deposited in ponded water environments such as in a shallow lake or an abandoned stream channel. No thick or extensive layers of clay continuing more than a few hundred feet occur. Clay layers may locally perch or channel water.

Gypsiferous and calcareous layers have formed in these desert soils. Large areas along the floor of Cane Valley are covered with a thin white crust composed of gypsum (hydrous calcium sulfate) and gypsite (gypsum containing sand and silt). The crust is evidence of natural gypsiferous soils, a natural source of sulfate. The crust forms as an efflorescent deposit by evaporation of the shallow ground water causing precipitation of gypsum salts. Calcareous horizons occur as white layers within a couple of feet of the soil surface. In some exposed streamcuts, the calcareous layer occurs as an indurated calcic horizon about 3 ft thick.

The surface soil is reddish-yellow sand (mesic, arid, typic torripsamment) with about 15 percent silt and clay overlying limestone bedrock (Table 3–1). Soils have a relatively high EC value in surface samples, with Ca as the principal cation (Table 3–1). Organic matter content is only 0.6 percent (ca. 0.24 percent C) and pH is neutral to slightly alkaline.
### 3.3 Alluvial Aquifer Contamination

The hydrogeology of the site and the nature and extent of contamination are discussed in detail in DOE (1999a). This section focuses on the hydrogeology and contamination of the alluvial aquifer. The alluvial aquifer consists mainly of windblown and some water-deposited, fine- to medium-grained sands that vary in thickness from 0 to 120 ft. The thickest deposits occur in a paleovalley area north of the Old Tailings Pile and Heap Leach Pads (Figure 2–3). Outside the paleovalley area, the alluvial deposits are generally thicker near the axis of Cane Valley, and taper off adjacent to bedrock exposures near the western and eastern boundaries of the site.

Depth to ground water in the alluvial aquifer varies across the site from 8 ft along Cane Wash to 50 ft below the ground surface. In the area of the alluvial nitrate plume, the depth to ground water is between 30 and 40 ft.

The following information on the hydrology of the alluvial aquifer is based on 1997 data (DOE 1999). In 1997, the average hydraulic conductivity of the portion of the alluvial aquifer containing the nitrate plume was estimated to be 21.5 feet per day (ft/day). Assuming an effective porosity of 0.25 and a hydraulic gradient of 0.007 to 0.012, the ground water velocity ranged from 0.6 to 1.0 ft/day. At these velocities, the nitrate plume would have taken 15 to 25 years to reach its furthest extent in 1997 (5,600 ft downgradient). In the centroid of the plume, the average gradient was estimated at 0.0095 with a ground water velocity of 0.82 ft/day. Using these values, it would have taken approximately 22 years for the portion of the nitrate plume that is above background to reach its 1997 extent.

Summarized below are water quality data presented in DOE (1999) from the 1997 characterization. Section 6.1 presents trends in nitrate and sulfate concentrations ending in 2003. Ammonium, calcium, nitrate, sulfate, and manganese were the site-related constituents most prevalent in the alluvial aquifer in 1997. Less prevalent but also exceeding background in several wells were sulfate, magnesium, potassium, iron, uranium, and strontium. Nitrate, sulfate, and uranium were the constituents of concern in alluvial ground water because concentrations of these constituents exceeded either EPA ground water standards or the Navajo Nation remediation goal. The EPA standards in 40 CFR 192 establish numerical MCLs for nitrate and uranium. The MCL for nitrate (as NO₃⁻) is 44 milligrams per liter (mg/L), and the MCL for uranium is...
0.044 mg/L. Because an EPA standard has not been established under 40 CFR 192 for sulfate, DOE agreed to use best efforts to comply with the Navajo Nation remediation goal of 250 mg/L, background, or an agreed-upon risk-based benchmark (DOE 2004). Figure 3–1 and Figure 3–2 depict the area extent of the nitrate and sulfate plumes in 1997. The hydrology of the nitrate plume within the alluvial aquifer will be re-evaluated as part of the pilot study using more recent monitoring data (Section 6.6.6).

3.4 Plant Ecology

The plant ecology of the former mill site, the tailings areas, and the area overlying the nitrate plume, were first characterized in 1997 (DOE 1999; Section 4.7). Characterization included 1) identifying plant species, 2) mapping plant associations, and 3) estimating the abundance, distribution, and structure of plant populations. The 1997 characterization was repeated for shrub species using more quantitative methods in summer 2000. In the 2000 survey, percent shrub cover on the subpile soil and plume areas was estimated and plant cover and canopy volume were determined along line transects. An aerial survey of the area was completed to update the 1995 survey with respect to vegetation cover. The aerial survey data, combined with the ground data, provide a baseline assessment of current species composition, vegetation cover, and vegetation vigor for latter comparison as remediation of the site progresses.

3.4.1 Plant Species, Associations, and Vegetation Mapping

Table 3–2 lists plant species identified at the site. The occurrence and relative abundance of species, coupled with knowledge of their physiological and ecological tolerances, provide measures of the health of the ecosystem and provide evidence of environmental conditions that are of importance for planning phytoremediation and land farming options. A plant association is a vegetation classification unit. An association generally has a consistent floristic composition, a uniform appearance, and a distribution that reflects a certain mix of environmental factors that can be shown to be different from other associations. The association is a synthesis of local examples of vegetation called stands. Associations are named for their dominant species.

For the purpose of mapping vegetation at Monument Valley, a modified releve’ method was used to characterize plant cover in stands near monitoring wells, and then stands were grouped into associations using simple ordination and gradient analysis techniques (e.g., Barbour et al. 1987). Associations were identified by first grouping stands with similar species composition and cover. Because species composition and cover vary across the site as a continuum rather than as discrete units, no clear breaks between groups of stands were apparent. Therefore, a simple gradient analysis of dominant species was used to group stands. Figure 3–3 illustrates how the abundance of dominant species varies along a gradient from stand to stand.
Figure 3–1. Distribution of Nitrate Concentrations in the Alluvial Aquifer – Data Through September 1997
Figure 3–2. Distribution of Sulfate Concentrations in the Alluvial Aquifer – Data through September 1997
<table>
<thead>
<tr>
<th>Scientific Name</th>
<th>Acronym</th>
<th>Common Names</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shrubs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Artemisia filifolia Torr.</td>
<td>ARFI</td>
<td>sand sagebrush, old-man sagebrush</td>
</tr>
<tr>
<td>Atriplex canescens (Pursh) Nutt.</td>
<td>ATCA</td>
<td>Diwózhii_beii, fourwing saltbush, cenizo, chamizo</td>
</tr>
<tr>
<td>Atriplex confertifolia (Torr. &amp; Frem.) Wats.</td>
<td>ATCO</td>
<td>Dá’ák’óózh deenini, shadscale, spiny saltbush</td>
</tr>
<tr>
<td>Chrysothamnus nauseosus (Pall.) Britt.</td>
<td>CHNA</td>
<td>rubber rabbitbrush, chamisa</td>
</tr>
<tr>
<td>Ephedra torreyana S. Wats.</td>
<td>EPTO</td>
<td>T_’oh azihii_jbahíígií, joint fir, Brigham tea</td>
</tr>
<tr>
<td>Gutierrezia sarothrae (Pursh) Britt. &amp; Rusby</td>
<td>GUSA</td>
<td>Ch’il diilyésíítoh, broom snakeweed,</td>
</tr>
<tr>
<td>Haplopappus pluriflorus (Gray) Hall</td>
<td>HAPL</td>
<td>jimmyweed, jimmy goldenbush</td>
</tr>
<tr>
<td>Lycium pallidium Miers</td>
<td>LYPA</td>
<td>tomatillo, desert wolfberry</td>
</tr>
<tr>
<td>Opuntia phaeacantha Engelm.</td>
<td>OPPH</td>
<td>prickly pear, many-spined cactus</td>
</tr>
<tr>
<td>Poliomintha incana (Torr.) Gray</td>
<td>POIN</td>
<td>bush mint, rosemary-mint, purple sage</td>
</tr>
<tr>
<td>Sarcobatus vermiculatus (Hook.) Torr.</td>
<td>SAVE</td>
<td>Diwózhishzihi, black greasewood, chicobush</td>
</tr>
<tr>
<td>Senecio douglasii DC.</td>
<td>SEDO</td>
<td>threadleaf groundsel, creek senecio</td>
</tr>
<tr>
<td>Tamarix ramosissima Ledeb.</td>
<td>TARA</td>
<td>Gad n’ee_i biláhtah_i _ichí’ígií, tamarisk, salt cedar</td>
</tr>
<tr>
<td>Yucca angustissima Engelm.</td>
<td>YUAN</td>
<td>Tsá’ázi’ts’óóz, narrowleaf yucca, fineleaf yucca</td>
</tr>
<tr>
<td><strong>Grasses</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aristida purpurea Nutt.</td>
<td>ARPU</td>
<td>Dlóóbibé’ézhóó’, Purple threeawn, wiregrass</td>
</tr>
<tr>
<td>Bromus tectorum L.</td>
<td>BRTE</td>
<td>Zé’ëiilwo’ii, cheatgrass brome, downy brome</td>
</tr>
<tr>
<td>Festuca microstacys Nutt.</td>
<td>FEMI</td>
<td>small fescue, vulpia</td>
</tr>
<tr>
<td>Hilaria jamesii (Torr.) Benth.</td>
<td>HIJA</td>
<td>T_’oh _ichí’í, galleta, curly grass</td>
</tr>
<tr>
<td>Oryzopsis hymenoides (R. &amp; S.) Ricker</td>
<td>ORHY</td>
<td>Nididlídii, Indian ricegrass, sand bunchgrass</td>
</tr>
<tr>
<td>Sporabolis airoides (Torr.) Torr.</td>
<td>SPAI</td>
<td>alkali saccaton</td>
</tr>
<tr>
<td>Sporabolis cryptandrus (Torr.) Gray</td>
<td>SPCR</td>
<td>sand dropseed</td>
</tr>
<tr>
<td>Sporabolus contractus A.S. Hitchc.</td>
<td>SPCO</td>
<td>spike dropseed</td>
</tr>
<tr>
<td>Sporabolus giganteus Nash</td>
<td>SPGI</td>
<td>giant dropseed</td>
</tr>
<tr>
<td><strong>Forbs</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tripterocalyx carneus (Greene) Galloway</td>
<td>TRCA</td>
<td>wooton sandverberna</td>
</tr>
<tr>
<td>Chenopodium album L.</td>
<td>CHAL</td>
<td>common lambsquarter, goosefoot</td>
</tr>
<tr>
<td>Ambrosia acanthacarpa Hook.</td>
<td>AMAC</td>
<td>bur ragweed</td>
</tr>
<tr>
<td>Amsinkia tessellata Gray</td>
<td>AMTE</td>
<td>rough fiddleneck</td>
</tr>
<tr>
<td>Arabis L. species</td>
<td>AR sp.</td>
<td>rockcress mustard</td>
</tr>
<tr>
<td>Astragalus L. species</td>
<td>AS sp.</td>
<td>Dibéha’ich’iidii, milkvetch, locoweed</td>
</tr>
<tr>
<td>Datura wrighti Regel</td>
<td>DAWR</td>
<td>sacred datura, angels trumpet</td>
</tr>
<tr>
<td>Descurainia pinnata (Walter) Britt.</td>
<td>DEPI</td>
<td>pinnate tansey-mustard</td>
</tr>
<tr>
<td>Erigeron L. species</td>
<td>ER sp1.</td>
<td>daisy</td>
</tr>
<tr>
<td>Eriogonum Michx. Species</td>
<td>ER sp2.</td>
<td>wild buckwheat, skeletonweed</td>
</tr>
<tr>
<td>Kochia scoparia (L.) Schrader</td>
<td>KOSC</td>
<td>kochia, summer cypress</td>
</tr>
<tr>
<td>Lepidium L. species</td>
<td>LE sp.</td>
<td>pepperweed, peppergrass</td>
</tr>
<tr>
<td>Lupinus L. species</td>
<td>LU sp.</td>
<td>lupine</td>
</tr>
<tr>
<td>Machaeranthera Nees. Species</td>
<td>MA sp.</td>
<td>aster</td>
</tr>
<tr>
<td>Oenothera albicaulis Pursh</td>
<td>OEAR</td>
<td>white-stemmed evening primrose</td>
</tr>
<tr>
<td>Plantago patagonica Jacq.</td>
<td>PLPA</td>
<td>woolly plantain</td>
</tr>
<tr>
<td>Salsola iberica Sennen &amp; Pau</td>
<td>SAIB</td>
<td>Ch’il deenini, Russian thistle, tumbleweed</td>
</tr>
<tr>
<td>Sphaeralcea coccinea (Pursh) Rydb.</td>
<td>SPCO</td>
<td>Azée’ nt_’ini, scarlet globemallow, falsemallow</td>
</tr>
<tr>
<td>Sphaeralcea parvifolia A. Nels</td>
<td>SPPA</td>
<td>Nelson globemallow</td>
</tr>
</tbody>
</table>

The scientific nomenclature and authorities is consistent with Voss (1983) and the choices of Welsh et al. (1987).

Acronyms combine the first two letters of the genus and species names.

Navajo, English and Spanish common names are from a variety of sources (Mayes and Lacy 1989; Dodge 1985; Elmore and Janish 1976; Dunmire and Tierney 1995; Whitson 1992).
Figure 3–3. Indirect gradient analysis of dominant plant species for stands adjacent to monitoring well and hydropunch locations. Wells are roughly ordered as shallower to deeper depths to ground water from left to right. Plant acronyms are defined in Table 3–2.

Results of the gradient analysis suggest that some dominant species are associated and that associations overlap—a given stand may occur in more than one association. Four associations occur, named for their two most abundant shrubs:

- Sarcobatus vermiculatus (black greasewood) and Atriplex confertifolia (shadscale),
- Atriplex canescens (fourwing saltbush) and Haplopappus pluriflorus (jimmyweed),
- Poliomitha inicana (bush mint) and Ephedra torreyana (joint fir), and
- Salsola iberica (Russian thistle) and Ambrosia acanthacarpa (bur ragweed).

Production of a vegetation map (Figure 3–4) involved (1) mapping stand locations on the 1995 aerial photograph; (2) identifying vegetation patterns in the photograph, under magnification, that were consistent with the plant associations; (3) outlining mapping unit boundaries using a combination of stand locations and vegetation patterns; and (4) returning to the field to check the reliability of the photograph interpretation. Acronyms of dominant plants in associations are used for mapping unit titles in Figure 3–4.
Figure 3–4. Plant Associations Overlying the Plume at the Monument Valley Mill Site
3.4.2 Native Phreatophyte Populations

Phreatophytes (literally “well plants”) at the Monument Valley site may act, in essence, as passive, solar-powered, pump-and-treat systems for nitrates in the alluvial aquifer. Two phreatophyte populations grow over the plume area: *Sarcobatus vermiculatus* (black greasewood) and *Atriplex canescens* (fourwing saltbush). *Sarcobatus* is an obligate phreatophyte requiring a permanent ground water supply, and can transpire water from aquifers as deep as 18 meters (m) below the land surface (Nichols 1993, 1994). *Atriplex* is a facultative phreatophyte; it takes advantage of ground water when present but can tolerate periods of low water availability. The rooting depth of *Atriplex* may exceed 12 m (Foxx et al. 1984; McKeon et al. 2004a).

A line intercept method (Bonham 1989) and high-resolution aerial photography were used to estimate *Sarcobatus* cover in the SAVE/ATCO(1) mapping unit. The potential *Sarcobatus* cover was estimated using the February 1995 photograph (before the site was sprayed with herbicides), and not the current cover (DOE 1999; Section 4.7.2). The results show 37 percent *Sarcobatus* cover (95 percent C.I. = ±5.8 percent) in 1995. The percent cover of *Atriplex* in the ATCA/HAPL mapping unit (Figure 3–4), estimated using a releve’ method (Bonham 1989), was about 5 percent. *Atriplex* is a highly palatable browse species for livestock in the area and, therefore, a grazing decreaser. After 1995, the phreatophyte community was apparently sprayed with herbicide, damaging or killing many of the plants.

In June 2000, line-intercept and plot methods (Bonham 1989) were used in the field to estimate percent cover and shrub density, respectively, over an area of the plume (Table 3–3). A sparse *A. canescens* zone covers most of the plume with less than 5 percent cover. The *S. vermiculatus* zone had the highest percentage of cover, approaching 15 percent and was over the shallowest depth to the plume, approximately 7.6 m. The *S. vermiculatus* zone also had the highest density of *Atriplex confertifolia*, a co-dominant shrub over some of the plume. Shrub density ranged from 0 to 200 plants per ha over most of the plume, but reached as high as 1,500 per ha in the *Sarcobatus* zone. We examined aerial photographs (1:4200) taken in September 2000, to determine the extent of the *Atriplex* zone. It appears to extend beyond the 10 mg l⁻¹ nitrate-N isoline over the plume.

An area inside the fence that surrounds the former tailings pile, where cattle and sheep have been excluded for the past 10 years, was surveyed to determine the amount of cover that can develop in an *S. vermiculatus* zone over time if grazing is restricted. Two 50 square meter (m²) plots that had appreciable natural regrowth were selected for a line intercept survey. The plant cover was mostly *S. vermiculatus*, ranging from 1 to 2 m in height. Plant cover in these plots was 50.9 percent (S.E. = 5.1 percent) and 37.5 percent (S.E. = 2.5 percent). No protected area dominated by *A. canescens* was available for comparison at the site.
Table 3–3. Percent plant cover and plant density of four different zones overlying the contaminated alluvial aquifer. See Figure 3–4 for locations of different zones.

<table>
<thead>
<tr>
<th>Plant Type</th>
<th>Bare Zone n = 9</th>
<th>SAVE Zone n = 8</th>
<th>Sparse ACTA Zone n = 30</th>
<th>SAVE-ACTA Zone n = 7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cover</td>
<td>density</td>
<td>cover</td>
<td>Density</td>
</tr>
<tr>
<td>ATCA</td>
<td>0</td>
<td>37 (25)</td>
<td>1.4 (0.9)</td>
<td>147 (67)</td>
</tr>
<tr>
<td>ATCO</td>
<td>0</td>
<td>0</td>
<td>2.5 (1.6)</td>
<td>399 (208)</td>
</tr>
<tr>
<td>SAVE</td>
<td>0</td>
<td>0</td>
<td>11.8 (4.4)</td>
<td>672 (174)</td>
</tr>
<tr>
<td>Total:</td>
<td>0</td>
<td>37</td>
<td>15.8</td>
<td>1218</td>
</tr>
</tbody>
</table>
4.0 Decision Framework

This section presents a framework for using results of pilot studies to choose methods to remediate nitrate and sulfate in subpile soils and in alluvial ground water at Monument Valley (Figure 4–1). 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 degrade, disperse, or immobilize contaminants and thus to remediate subpile soils and the alluvial aquifer in an acceptable time frame. Monitored natural attenuation (MNA) and enhanced passive remediation (EPR) are both key components of the framework.

EPA defines MNA as “the reliance on natural processes to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods.” “Natural attenuation processes include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or ground water” (EPA 1999). For MNA to be a viable approach at Monument Valley, contaminant removal from ground water by natural processes must exceed contaminant loading from the subpile source and from natural sources. Therefore, MNA will be considered only in combination with source control. EPA includes the word “monitored” to emphasize the reliance of MNA on a comprehensive monitoring program to provide reasonable assurance that “the remedy is performing as expected and is capable of attaining remediation objectives” (EPA 1999).

EPR can be defined as managing all or part of contaminated soil or ground water by initiating and/or augmenting natural and sustainable attenuation processes (NTWG 2004). EPR alternatives are considered if the natural attenuation capacity is estimated to be incapable of attaining remediation objectives. If enhancement technologies are implemented, an additional monitoring objective is to seek ways to improve implementation of the enhancements. EPR is different from either MNA or active remediation in that human intervention is allowed, but only to enhance natural and sustainable processes. By contrast, active remediation, such as pump-and-treat technologies, require active or frequent intervention to attain remediation objectives.

A brief introduction of steps in the decision process follows.

**Characterize Natural Attenuation Processes**

The characterization step is necessary to identify and estimate the contribution of significant natural processes acting to degrade and attenuate nitrate and sulfate in the shallow aquifer and subpile soils. DOE has already shown that phytoremediation is a significant process. The pilot studies will also characterize biological processes including biodegradation and denitrification, physical processes such as dispersion, advection, and dilution (natural flushing), and chemical processes that transform or sequester nitrate and sulfate. First, a screening characterization will use a revision of the conceptual model to identify likely processes acting at the site. Additional characterization, as needed, will confirm the presence and significance of processes at the site and estimate rates of attenuation.
Figure 4–1. Framework for Applying Pilot Study Results to Choose A Remediation Strategy for the Alluvial Aquifer at Monument Valley
**Estimate Natural Attenuation Capacity**

The next step is to estimate the capacity of key attenuation processes at the site. Attenuation capacity can be thought of as the capacity of all natural processes that act to lower contaminant mass as the shallow ground water moves away from the subpile soil source. The capacity can be estimated as the sum of all of the principal biological, physical, and chemical processes that biodegrade, disperse, transform, or immobilize nitrate and sulfate in the aquifer. Monitor well sampling data provide an indirect indication of the total attenuation capacity. Characterization data give estimates of the contributions of principal processes.

**Characterize Sources and Estimate Contaminant Loading**

Contaminant loading is the rate of nitrate, ammonium, and sulfate movement from the subpile soils into shallow ground water. DOE characterized the distribution of ammonium and nitrate in part of the subpile source as the basis for the subpile phytoremediation pilot study (DOE 2002). The results of that study suggest that contaminant loading has been curtailed within the fourwing saltbush planting. The follow-up pilot studies will characterize the full extent of the subpile source and also characterize natural nitrate and sulfate sources (Nettleton 1991; Boettinger and Norton 1994; Walvoord et al. 2003) as the basis for estimating the total mass of nitrate and sulfate entering the shallow aquifer.

**Assess MNA Adequacy**

The adequacy of MNA is evaluated as the mass balance of the delivery or loading of nitrate, ammonium, and sulfate from the subpile source and from natural sources to the shallow aquifer, and the capacity or sum of natural processes to remove or disperse nitrate and sulfate. 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. If confidence is low, or conversely, if the evaluation indicates that loading rates are equal to or greater than removal/dispersal rates, then natural attenuation enhancements (EPR) will be considered.

**Evaluate Attenuation Enhancements**

The natural attenuation capacity may not be sufficient to reduce nitrate and sulfate concentrations in shallow ground water to acceptable levels. If this is the case, then the next step is to determine whether enhancing natural attenuation processes can raise the attenuation capacity beyond what is occurring naturally. The pilot studies will investigate a range of enhancements. A key goal of EPR pilot studies is to demonstrate enhancements that, once implemented, will be sustainable with little or no further intervention. For example, the pilot studies will evaluate additional plantings of native desert phreatophytes combined with grazing management as a means of (1) increasing plant uptake of nitrogen and sulfur from the shallow aquifer and (2) increasing transpiration so as to slow the movement of or hydrologically isolate the plume. Pilot studies will investigate other enhancements, as appropriate, such as stimulating or augmenting biodegradation in the shallow aquifer. This step will also evaluate an expanded subpile planting and microbial enhancements to further reduce contaminant loading.
Assess EPR Adequacy

The assessment of EPR adequacy seeks to answer two 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 EPR will be recommended as the final remedy. If the answers are maybe or no, then a more active remedy will be required.

Evaluate Land Farming

DOE proposed land farming as an active remedy for the alluvial aquifer if more passive methods are shown to be inadequate (DOE 2002). Land farming is a form of active phytoremediation. Shallow contaminated ground water would be pumped and used to fertilize crops such as native plant seed that could be marketed for mine land reclamation or other uses. The land farm pilot study will address several issues: land suitability for irrigation, cropping system selection, nitrate uptake and toxicity, fate and toxicity of sulfate, irrigation management, farm operation requirements, and ecological and land-use impacts.

Propose Compliance Strategy for Alluvial Aquifer

The pilot studies will provide the information DOE and the Navajo Nation need to step through this decision framework to arrive at a compliance strategy for the alluvial aquifer. A combination of MNA, EPR, and/or land farming will likely be proposed, including an expanded subpile planting to reduce contaminant loading. If the pilot studies conclude that a combination of these remedies are inadequate to achieve remediation objectives for Monument Valley, then other remedies will be considered.

Monitor Final Remedy

DOE will monitor the performance of the final remedy. The monitoring program will specify the location, frequency, and types of samples and measurements to evaluate whether the remedy is performing as expected and is capable of attaining remediation objectives (EPA 1999). For MNA/EPR remedies, the goal is to verify that the attenuation capacity remains adequate and that if site conditions change, the attenuation capacity will be maintained until remediation objectives are achieved.

Evaluate Other Alternatives

If pilot studies indicate that a combination of MNA, EPR, and active land farming will not achieve remediation objectives, then other active remediation alternatives may be evaluated. While not addressed in the current studies, one possible alternative is a denitrifying bioreactor. Denitrifying bioreactors are a type of pump-and-treat method that may be more efficient and less costly than physical methods of nitrate removal. Plume water would be passed through sand-bed reactors inoculated with denitrifying bacteria and supplemented with a carbon source such as ethanol, glucose or acetate. The treated water could then be reinjected into the aquifer. Other infiltration beds contain sawdust, wood mulch, or leaf compost to donate electrons promoting heterotrophic denitrification (Robertson and Cherry 1995). The infiltration beds are simple to build and resulted in 60 to 100 percent attenuation of input nitrate concentrations of up to 125 mg/L. Field test results over a 6 to 7 year period indicate that the infiltration beds should last at least a decade with little maintenance (Robertson et al. 2000).
5.0 Source Containment and Removal

Any strategy for remediation of the alluvial aquifer must account for the flux of contaminants from the source. Evaluations must determine if the capacity of the ground water remedy, whether passive or active, is sufficient to balance or off-set contaminant loading from the source. Previous characterization of the source, and pilot studies for containing and removing the source, have focused on the subpile soils as the source of contaminants in the alluvial aquifer. Natural sources of nitrate and sulfate may also occur at Monument Valley. This section presents the status of ongoing efforts to remediate contaminants in the subpile soils. This section also states the objectives and describes tasks for follow-up work to more fully characterize, contain, and remove contaminants from the subpile soils, and to characterize natural sources.

5.1 Status of Subpile Soil Remediation

Results of an ongoing demonstration of phytoremediation of the source of nitrate, the subpile soils, indicate that an irrigated planting of fourwing saltbush (*Atriplex canescens*) is extracting nitrate from the subpile soil and preventing recharge and leaching of nitrate and sulfate into the alluvial aquifer (McKeon et al. 2004b). Results also indicate that nitrate removal from the subpile soil is faster than can be attributed to plant uptake alone. Our hypothesis is that much of the nitrate removal can be attributed to microbial denitrification processes. This section summarizes work to date on efforts to remediate the subpile soil, considered the major source for contaminants in the alluvial aquifer.

5.1.1 Characterization of Subpile Contaminants

Initial soil sampling in 1997 discovered a potential hot-spot of ammonium contamination in the New Tailings Pile (otherwise known as the subpile) area. This finding was based on a sample at location 866 (Figure 5–1). A more detailed survey conducted in June 1997 included analysis of both nitrate and ammonium levels from subpile soils sampled in a radial pattern away from location 866 (DOE 2002). These initial soil samples were determined to contain elevated levels of nitrate ranging from 45–1,060 parts per million (ppm) (Figure 5–2). Ammonium levels were significantly less, ranging from zero to 163 ppm (Figure 5–3). The phytoremediation pilot study plot was delineated, irrigation lines installed and > 4,000 phreatophytic plants were sown based on these initial results.

An unexpected finding during the first 3 years of operation of the subpile plot was the rapid removal of nitrate from the soil. NO$_3^-$-N decreased substantially during the four measurement periods ($P < 0.001$), from an average of 180 mg kg$^{-1}$ at the start of irrigation to just 80 mg kg$^{-1}$ by the end of the third full growing season, whereas NH$_4$-N levels did not change ($P > 0.05$) (McKeon et al. 2004b) (Figure 5–4). Both NO$_3^-$ ($P < 0.05$) and NH$_4$ ($P < 0.001$) concentrations were significantly higher with soil depth for all sampling periods (Figure 5–4). However, the interaction term (Depth x Year) was not significant ($P > 0.05$) for either contaminant, indicating that no net downward movement of contaminants (NO$_3^-$ and NH$_4$) occurred during the study. Total losses of NO$_3^-$-N were estimated to be 1,360 kg ha$^{-1}$ yr$^{-1}$ over a 4.6 m depth (equivalent to 0.031 mg-N kg$^{-1}$ day$^{-1}$ on a soil weight basis). This was much more than could be accounted for by plant uptake alone. In fact the plants consumed only a small fraction of the total ($< 7$ percent) if we assume that all the nitrogen taken up by the plants was NO$_3^-$-N.
Figure 5–2. Map of nitrate concentrations radiating from sample location 866 taken in June 1997. Nitrate plume was generated by kriging the highest nitrate concentrations in each sample hole using Environmental Visualization System (EVS).
Figure 5–3. Map of ammonia concentrations radiating from sample location 866 taken in June 1997. Ammonia plume was generated by kriging the highest ammonia concentrations in each sample hole using Environmental Visualization System (EVS).
Figure 5–4. Average soil NO$_3$-N (open circle) and NH$_4$-N (closed circle) concentrations from four sample dates (A) and with soil depth (B) in the Monument Valley phytoremediation plot. Data for April 2000 are means across four different sample locations and five depths; data for the other dates are for 20 sample locations and 6 depths. Depth data are mean values across the different sample locations and dates. Both NO$_3$-N and NH$_4$-N were significantly different by depth ($P < 0.05$) but not by sample date. Error bars show standard errors of the mean.
5.1.2 Phytoremediation: Plant Establishment, Growth, and Nitrogen Uptake

The original remediation strategy relied on phytoremediation 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, irrigated plot approximately 160 m × 100 m was installed the summer of 1999. The irrigation system consisted of a series of drip irrigation lines placed on the soil surface spaced 2 m apart and with 2 m spacing between emitters. The plot was divided into four irrigation zones each containing approximately 970 plants. Each plant was irrigated at rates of 2–4 liters per hour for 2 hours per day, 5 days per week during the growing season (April through September). Water pumped from an uncontaminated well containing 380 mg/L total dissolved solids (DOE 1999) was monitored through a flow meter placed in the main line. The irrigation system was designed to apply approximately 720 liters per plant, or 0.36 m over the plot each year.

Approximately 4,000 small (10 to 20 cm tall) fourwing saltbush seedlings grown from seed collected from the Navajo Nation land and raised in a greenhouse at the University of Arizona Environmental Research Laboratory in Tucson, Arizona, were transplanted on site. Planting methods were consistent with Glenn et al. (2001). The seed mixture included large-fruited (var. *angustifolia*) and small-fruited (var. *occidentalis*) types of fourwing (Glenn et al. 1998). Fourwing saltbush has been grown successfully for revegetation of other UMTRA Project sites (Glenn et al. 2001). Planting was completed in August 1999. The irrigation pump failed during the first season, resulting in approximately 20 percent mortality of transplants by April 2000. The irrigation system was repaired and the dead plants were replaced.

In September for 3 consecutive years, 2000 to 2002, plant survival, canopy volume, ground cover area, and biomass were monitored. Plant height and width were measured for every other plant in 2000 (n = ca. 2000) and every fifth plant in 2001 and 2002 (n = ca. 800). Plant canopy volume was calculated from the mean length of two cross-sectional widths and the height of each plant by using the formula for a hemisphere (2/3 πr³). Projected area of a canopy on the ground was calculated using the area of a circle (πr²), with the average width as an estimate of r. Above ground biomass data were estimated by destructive harvesting of 20 *A. canescens* plants each year; the relationship between dry weight and canopy volume was determined and used to extrapolate biomass production of the entire plot. Total plant N was measured in ground samples according to the Kjeldahl method (Maynard and Kalra 1993).

From 2000 to 2002, the annual plant survival rate improved considerably and was greater than 97 percent. Each year, new seedlings were transplanted to replace dead ones. Plant growth was initially slow especially in the northwest portion of the plot (see Section 5.1.3). Apparently, the contamination in this zone is confined to a shallow layer just beneath the soil surface, and once the plant roots penetrate through to deeper soil, they began to grow rapidly. At the end of the fourth growing season, plant cover over the entire plot approximated 45 percent, and the standing crop of biomass was estimated to be approximately 1,800 kg ha⁻¹ (Figure 5–5). This vigorous and prolific plant growth facilitated a deficit water balance over the field preventing further leaching of nitrates during irrigation (see Section 5.1.5).

The N content of the above-ground plant biomass averaged 1.75 percent (n = 20 plants). Therefore, extrapolating based on year-end standing biomass, the total N uptake from the soil profile by the plants was approximately 30 kilograms (kg). Below ground samples were not
taken, but it is reasonable to assume that there was twice as much biomass below ground than above ground. The *Atriplex* (predominantly) and *Sacrobatus* plants could have potentially taken up 60 kg of nitrogen from the subpile soil. This only accounts, however, for one tenth of the total loss in NO₃-N, alone, over the field (see Section 5.1.4).

![Graph showing growth of fourwing saltbush plants at the Monument Valley phytoremediation plot, 2000 to 2002.](image)

*Figure 5–5. Growth of fourwing saltbush plants at the Monument Valley phytoremediation plot, 2000 to 2002, on the basis of plant canopy cover projected on the ground (A) and dry biomass per plant (B). Error bars show standard errors of the mean.*

### 5.1.3 Stunted Plant Growth

An area of poor plant growth was identified on the irrigated field that corresponds approximately to the area where a white-colored, chemical stain is visible on the soil on aerial photographs (Figure 5–6). Growth measurements (represented as the log mean volume) of 30 randomly
selected plants from each zone were significantly less \((P < 0.0001)\) for plants growing in stained areas compared to plants growing in unstained areas (DOE 2002).

![Aerial photograph of the Monument Valley Subpile Soil Phytoremediation Plot taken September 2000, showing the outline of the planting. Areas of an apparent chemical stain appear white. Number 866 was the location of the initial ammonia sampling in 1997.](image)

In another study (DOE 2001), soil samples from both the stained and unstained area were collected at two depths and analyzed to determine their chemical composition. The concentration of a variety of analytes including nitrate, sulfate, calcium, magnesium, strontium, and vanadium were higher in samples obtained from the stained area than from the unstained area. Conversely, the concentrations of iron, manganese, phosphate, potassium, sodium, and uranium
concentrations are consistently and significantly lower in the stunted-growth (stained) soil than in the thriving-growth (unstained) soil. 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 separate greenhouse study (DOE 2002), growth of Sudan grass in soil obtained from the stained area was significantly ($P < 0.0001$) 27.8 times less than growth in a soil sample taken from outside the fenced area. Chemical analysis of Sudan grass tissue samples were inconclusive as to the causative agent(s) of poor growth in the stained soil.

Further inspection of the soil shows that the area of poor growth and the white stain in the aerial photo also appears to coincide to an area of soil that has a shallow, black-mottled layer beneath the soil surface. In either case, it is apparent that possible chemicals of concern have been left behind in the subpile soil. Further analysis is necessary to identify the cause of stunted plant growth.

5.1.4 Denitrification

An unexpected result of monitoring subpile soils was a more rapid removal of nitrate between 1999 and 2002 than can be attributed to uptake by Atriplex (Section 5.1.1). Denitrification, or the biologically mediated reduction of NO$_3^-$ to N$_2$ gas, could account for this loss. Denitrification typically occurs when soils undergo wetting events and become anaerobic (Peterjohn 1991; Tiedje 1994). Peterjohn (1991) reports that the production of denitrifying enzymes in desert soils is highly correlated to changes in water content as well as N and C availability. Also, given the relative persistence of ammonium in the irrigated soil over time, we presume that the subpile soil has anaerobic microsites available for denitrification to occur. However, the exact pathways or microorganisms involved in catalyzing denitrification in this system remain undefined.

Several isotopic approaches are regularly used to identify the presence or extent of denitrification in soils and ground water systems. Typically, if denitrification is occurring, the $^{15}$N/$^{14}$N stable isotopic signature ($\delta^{15}$N) of NO$_3^-$-N will increase as nitrate concentrations decrease with time. On the other hand, if the loss is due to a physiochemical process, the shift in the $\delta^{15}$N value over time is not as noticeable. In order to evaluate if denitrification may explain the loss in NO$_3^-$N over time, we conducted duplicate extractions of soluble salts from 96 archived samples (24 per year) pooled across depths and locations for each sample date and then measured total N, NO$_3^-$, NH$_4^+$ and $\delta^{15}$N in the pooled soil samples and the water-soluble extracted salts. An enrichment of $\delta^{15}$N was observed in the soluble salts over the study period indicating active denitrification (Figure 5–7). The concentration of total N and NO$_3^-$-N in the soluble fraction also decreased with time (Figure 5–7).

Control experiments show that the archived soil samples contained 85–120 percent of the original NO$_3^-$-N obtained upon sampling, and 75–90 percent of this was recovered in the dried residue of the aqueous extraction. On the other hand, NH$_4^+$-N accounted for less than 10 percent of the N in the final aqueous extract residue. NH$_4^+$ was lost from the dried soil samples as a result of storage for a prolonged period of time at room temperature (ca. 85 percent of initial activity lost [Maynard et al. 1993]) and during the extraction and drying procedure which proceeded under alkaline conditions (pH ca. 8.5 during drying) (ca. 60 percent of activity in aqueous extract lost after drying). Therefore, NO$_3^-$-N accounted for nearly all of the total-N recovered in the soluble salts fraction across sample dates (Figure 5–7).
Although total N decreased significantly over time in proportion to NO₃⁻-N losses (Figure 5–8) the δ¹⁵N values in soil samples were not significantly different among sampling dates, with a mean δ¹⁵N value of 2.7 percent (range = 1.6 percent to 3.6 percent). NO₃⁻-N accounted for about 40 percent of total N in the soil in the earliest soil samples and only half of this was lost over time, hence, only 20 percent of total soil N was lost over the study. A shift in the total soil

\[ y = 8.9 - 6.2 \ln(x) \]
\[ r^2 = 0.78^{**} \]
\( \delta^{15}N \) values due to this amount of depletion would be small and difficult to discern in the total soil N fraction.

![Figure 5–8. Total-N (closed diamonds) and NO\(_3^–\)-N (open circles) over time in pooled soil samples from the Monument Valley subpile planting. The samples were pooled across depth and location for the four sampling dates.](image-url)

Preliminary studies were initiated to further characterize the denitrification potential of the irrigated Monument Valley subsoil pile. In soil slurries supplemented with NO\(_3^–\) and dextrose, the rate of N\(_2\)O gas generated in samples taken from the irrigated plot (Table 5–1) was roughly eight times greater than for soil samples taken from an adjacent non-irrigated area \((P < 0.5)\). On the other hand, N\(_2\)O generated in samples at field moisture incubated without acetylene, glucose, or NO\(_3^–\) addition was considerably less than that observed for supplemented soils (Table 5–1). The average N\(_2\)O evolution rate observed in the incubation of unsupplemented, irrigated soils was 10 times less than the rate projected for the entire field over time where as DEA measurements more closely approximated the rate of nitrate loss.

Table 5–1. The mean rate of N evolved as N\(_2\)O in soil microcosms studies of the denitrification activity on and off the irrigated plot. DEA measurements were determined by supplementing soil slurries with dextrose and NO\(_3^–\) and incubating the samples under 10 percent acetylene. The rate of N\(_2\)O gas evolution was also determined for unamended soil microcosms at field moisture. Values in parentheses show standard errors of the mean.

<table>
<thead>
<tr>
<th>Soil Sample Location</th>
<th>Denitrification Potential ( \text{(Kg N evolved as N}_2\text{O ha}^{-1} \text{y}^{-1}) )</th>
<th>At Field Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off plot ((n = 8))</td>
<td>95 (19)</td>
<td>6.8 (1.6)</td>
</tr>
<tr>
<td>On plot ((n = 8))</td>
<td>715 (286)</td>
<td>117 (38)</td>
</tr>
</tbody>
</table>
In summary, our preliminary findings suggest that the microbially-mediated process of denitrification is most likely responsible for the loss of NO$_3^-$-N from the irrigated subpile soil. First, very little if any nitrate was lost due to leaching. Second, a considerable shift in the $\delta^{15}$N-NO$_3^-$ signature was observed in archived samples as nitrate concentrations decreased over time. Third, the potential to reduce NO$_3^-$ to a gas in samples taken from the irrigated soil was significantly greater than from soil samples that never received irrigation. Finally, nitrous emissions from disturbed soil samples taken on the irrigated field were significantly greater ($P<0.05$) than samples taken from an adjacent non-irrigated area.

5.1.5 Soil Water Measurement and Recharge Management

Another purpose of the Atriplex planting is to control recharge and leaching of contaminants from the subpile soil into the alluvial aquifer. The strategy is based on the concept of deficit irrigation whereby sufficient water is applied for good plant growth but the amount is less than the potential evapotranspiration (PET); hence, little or no water discharges past the rooting zone. This strategy works well at Monument Valley because PET is high and the desert shrubs planted in the subpile soil can rapidly extract the available water yet persist under conditions of water deficit. Monitoring was necessary to confirm that irrigation water was not moving below the root zone and potentially leaching contaminants. Soil water profiles were monitored using neutron hydroprobes, water flux in the root zone was measured directly, and PET was estimated from local meteorological data. The combination of these monitoring data indicate that a deficit irrigation was maintained and recharge was not occurring below the root zone.

In August 1999, four, thin-walled polyvinyl chloride (PVC) hydroprobe ports were installed to monitor soil water profiles, one in the center of each irrigation zone. Each port extended from the soil surface to either 4.6 m depth or to bedrock where the soil was shallow. Monthly soil moisture measurements were obtained at 0.17 m intervals. It was assumed that no changes in water content at depth would indicate that water was not moving below the root zone. Soil moisture was measured with a 503 DR Campbell Nuclear Neutron Hydroprobe (Campbell Pacific Nuclear International, Inc).

The hydroprobe was calibrated using soil obtained from the site. PVC ports identical to the ports on the plot were centered in a 200 liter drums filled with soil compacted to 1.59 g cm$^{-3}$ (the bulk density of soil measured at the site). Hydroprobe measurements and soil samples were obtained for air-dried soil, saturated soil, and soil drained to near field capacity (saturated then allowed to drain for 24 hours). Neutron counts and volumetric soil moisture content of soil samples taken from the calibration barrel were used to develop the calibration curve. Complete saturation of this sandy soil occurred at a moisture content of approximately 0.24 to 0.30 g cm$^{-3}$.

In April 2000, 16 more ports were added to the plot to obtain more representative soil moisture measurements. These were spaced equally within the plot (five per irrigation zone for a total of 20). From April 2000 to the end of the experiment (October 2002), soil moisture was measured monthly each year. Each year from 1999 to 2002, the entire plot was irrigated from April through September with a total depth of 0.32 to 0.36 m of water. Results of a June 2000 test indicated that water application rates ranged from 2.5 to 4.6 L hr$^{-1}$ per plant. When the hydroprobe ports were installed in September 1999, most of the soil profile was relatively dry, with moisture contents ranging from 0.02 to 0.10 g cm$^{-3}$; although in one port, samples taken at depths of 3 to 4 m were nearly saturated (0.20 to 0.23 g cm$^{-3}$). From 2000 to 2003, moisture
levels throughout the profiles were essentially static even during months without irrigation. Over the course of the study, mean moisture content values increased only slightly to approximately 0.11 g cm\(^{-3}\) (42 percent saturation) (Figure 5–9). In general, the plot was driest within the top 1 m of soil and wettest near the bottom of the profile. After 3 years of irrigation, a few ports were saturated at the 4 m depth, ports located in the vicinity of the port that was saturated initially.

In March 2001, prototype water flux meters designed by Pacific Northwest National Laboratory (Gee et al. 2002) were installed to demonstrate a method for direct measurement of recharge below the root zone. Water flux meters were placed at a depth of approximately 3 m at three locations: two within the subpile plot adjacent to hydroprobe ports and a third in a denuded area outside the planting. Three and a half meter deep holes, 25 cm in diameter, were augured at each location. Extensions 1 m in length were attached to the top of each flux meter to prevent lateral divergence of moisture. Data were collected using a CR23X data logger (Campbell Scientific). The two water flux meters placed within the planting registered zero recharge between March 2001 and October 2002. By contrast, a cumulative drainage of 3.75 cm was recorded with the flux meter placed in the denuded area outside the irrigated planting. The difference is attributed to transpiration from the Atriplex planting.

PET was estimated using data from a meteorological station mounted 3 m above ground level within the subpile planting. Wind speed, wind direction, solar radiation, air temperature, relative humidity, and precipitation were recorded hourly. These data were used to calculate PET with the Penman-Monteith equation (Pearcy et al. 1991). PET values ranged from 2.2 millimeters per day (mm/day) in March to 9.0 mm/day in July, for a total PET of 1,400 millimeters (mm) from March 2001 to November 2001. The sum of irrigation (325 mm) plus precipitation (105 mm) was only 30 percent of PET for this period.

5.2 Natural Sources of Nitrate and Sulfate

Nitrate and sulfate likely occur naturally in Monument Valley soils and may be a source of nitrate and sulfate in the alluvial aquifer. Natural sources of nitrate and sulfate will be factored into estimates of source loading (movement of nitrate and sulfate into the alluvial aquifer) along with the subpile source.

5.2.1 Natural Nitrate Sources

In a recent study published in the journal Science, Walvoord et al. (2003) provide evidence for a potentially vast, natural pool of nitrogen, as nitrate, in the vadose zone beneath many southwestern U.S. desert soils. The source of nitrates is mainly from atmospheric deposition and litter decay during the Holocene. Nitrogen fixation by soil microorganisms is another possible natural source of soil nitrate. Walvoord et al. (2003) hypothesize that nitrates have leached from and accumulated below the soil zone in response to episodic wetting events followed by surface evaporation of water and extraction of water by plants.
Figure 5–9. Soil moisture levels by soil depth in the Monument Valley phytoremediation plot, 2000 to 2002. Each datum is the mean value for 12 months for each depth in each of the 20 hydroprobe ports.
The occurrence of such large quantities of natural nitrate in the subsurface of desert soils raises questions regarding the sources of nitrate in the alluvial aquifer at Monument Valley. Nitrates other than those from the mill site may be contributing to the plume. Limited data from the site are highly variable. A set of presumably uncontaminated reference soil samples collected upgradient from the former mill site contained 26–800 mg kg$^{-1}$ nitrate in the top 30–150 cm of the soil profile (mean = 170 mg kg$^{-1}$, n = 6). These values are consistent with the findings of Walvoord et al. (2003) for this location. In contrast, nitrate concentrations for samples taken from vadose zone soils within the top 100–200 cm directly over the plume were considerably lower (c.a. 1 mg kg$^{-1}$).

For comparison, samples taken in what is considered the source zone or fenced area are considerably higher in both nitrate and sulfate than in control areas (Table 5–2) but the data are quite variable. High concentrations of nitrate and sulfate, compared to crustal average values, occur within the fenced source zone (DOE 2001). High nitrate concentrations were documented for samples taken near the former evaporation ponds to the southeast while high sulfate concentrations were found along the northwest border of the fence. The nitrate values for these samples were not higher than the upgradient samples.

Table 5–2. A comparison of average natural or background concentrations of nitrate and sulfate (mg kg$^{-1}$) in soil samples from outside the fenced area with samples from inside the fenced area.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Upgradient Soil$^a$</th>
<th>Vadose Zone Over Plume$^b$</th>
<th>Fenced Zone$^d$</th>
<th>DOE Report$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mg kg$^{-1}$)</td>
<td>(mg kg$^{-1}$)</td>
<td>(mg kg$^{-1}$)</td>
<td>(mg kg$^{-1}$)</td>
</tr>
<tr>
<td>Ammonium</td>
<td>2.56</td>
<td>n.d.$^c$</td>
<td>50</td>
<td>n.d.</td>
</tr>
<tr>
<td>Nitrate</td>
<td>170</td>
<td>1.22</td>
<td>508</td>
<td>81</td>
</tr>
<tr>
<td>Sulfate</td>
<td>202</td>
<td>n.d.$^c$</td>
<td>1686</td>
<td>4203</td>
</tr>
</tbody>
</table>

$^a$Data obtained from Table 4-4 in the Final Site Observational Work Plan (DOE 1999) from upgradient wells 869 and 870 (n = 6).

$^b$Deionized water-extractable nitrate concentrations determined for soil samples taken directly over the plume in December of 2003 from wells 664, 606, 663, and 779 (n = 8; two depths per location).

$^c$n.d. = not determined.

$^d$Data obtained from Table 4-4 in DOE (1999) from locations 851, 863-868 within the fenced area otherwise known as the source zone (n = 20).

$^e$Mean concentrations obtained from data in Table 3 of DOE (2001). All samples were taken within the fenced area, but not directly within the existing subpile soil planting.

5.2.2 Natural Sulfate Sources

Gypsiferous soils (soils high in calcium sulfate; gypsum) form naturally in arid and semiarid landscapes of the Southwest and in other deserts of the world (Birkland 1984). Natural gypsum in soils at Monument Valley, if they exist, may be a source of sulfate in the alluvial aquifer. Soils in arid and semiarid regions of the Southwest often have a carbonate rich horizon below the surface called caliche or a calcrete soil layer. In areas receiving < 300 millimeters per year (mm/yr) (12 inches/yr) precipitation, salts more soluble than carbonates, commonly gypsum, can accumulate at greater depths (Nettleton 1991). Taxonomic gypsic horizons occur where the gypsum concentration in a soil layer is more than 5 percent greater than horizons above or below the layer of gypsum accumulation.

Gypsiferous soil horizons can be composed of pedogenic as well as detrital gypsum (Buck and Van Hosen 2000). Four potential origins for gypsum accumulation in soils have been
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established: 1) in situ weathering of existing parent material (Carter and Inskeep 1988), 2) sulfate enriched precipitation usually from an oceanic source (Podwojewski and Arnold 1994), 3) eolian or fluvial input of gypsum or sulfate-rich sediment (Taimeh 1992), and 4) in situ oxidation of sulfate minerals (Toulkeridis et al. 1998).

Geologic strata in the Monument Valley area likely contains significant quantity of the mineral gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). In particular, the Triassic Moenkopi Formation contains gypsum over most of its depositional area including the Monument Valley area. At some localities, gypsum comprises at least 15 percent of the formation (Stewart et al. 1972). The gypsum occurs in the form of nodules, veinlets, sandstone cements, and beds. It results from evaporite deposition in shallow restricted seas common to the Moenkopi (Stewart et al. 1972). The nearest location to the Monument Valley site at which the presence of gypsum has been confirmed is about 22 miles away at a stratigraphic section measured by Stewart (Stewart et al. 1972). Stewart describes “rectangular white gypsum fragments” as large as 1 inch in maximum dimension, found in the upper part of the Moenkopi. It is likely that the Moenkopi contains gypsum in the immediate vicinity of the Monument Valley site as well.

The sedimentary gypsum can be eroded, transported by wind or water as solid matter or dissolved in precipitation, and then redeposited where percolating water moves it down in a soil profile. Gypsum has a solubility of about 1.7 grams per liter of which 950 mg/L is sulfate. Sulfate concentrations, due to gypsum dissolution, can be much higher if there is a sink (such as a calcium carbonate mineral) for calcium. In 301 analyses of alluvium ground water on the Hopi and Navajo Indian Reservation, Cooley et al. (1969), measured a range of 2.5 to 8,890 mg/L of sulfate.

5.3 Goals and Objectives

The overall goals for remediation of subpile soils are to contain and remove nitrate and ammonium, and to prevent leaching of nitrate into the alluvial aquifer. Specific objectives follow.

Delineate extent of nitrate, ammonium, and sulfate in subpile soils.

The location and layout of the original irrigated planting installed in 1999 was based on the distribution of ammonium in the subpile soils. Ammonium is more toxic and was of greater concern, so the planting was designed to contain and remove ammonium. However, the results of follow-up subpile sampling indicated that nitrate may be more widespread. Since nitrate is also more mobile than ammonium, it may represent a more immediate source of nitrogen in the alluvial aquifer. Therefore, the extent of nitrate contamination (and also ammonium and sulfate) in the subpile soil will be further delineated in order to increase confidence in efforts to contain and remove these potential sources of ground water contamination.

Investigate presence and mobility of natural nitrate and sulfate sources.

Southwestern deserts are known to naturally accumulate nitrate and sulfate in soil horizons and in the vadose zone. Given the environmental setting of the site and some early characterization data, we should not ignore possible natural sources of nitrate and sulfate contributing to the alluvial aquifer plumes. The occurrence and mobility of natural sources of nitrate and sulfate in
soils and in the vadose zone both overlying the plume and upgradient of the plume will be investigated.

**Determine Causes of Stunted Plant Growth and Recourses**

Poor growth of *Atriplex* shrubs in portions of the subpile planting where surface stains and subsurface mottling were observed led to studies of the composition and toxicity of these materials (Section 5.1.3). Poor plant growth could hinder efforts to remove and contain subpile contaminants. Because results to date are inconclusive, a more comprehensive investigation of the causes of stunted plant growth and possible recourses will be conducted.

**Expand Irrigated Planting of *Atriplex canescens***

Results of the subpile soil characterization will become the basis for expanding the irrigated planting of *Atriplex canescens* (fourwing saltbush). The objective is to continue the deficit irrigation strategy for phytoremediation; to apply enough water to stimulate plant growth and take up nitrate, but not enough to cause recharge and leaching of nitrate and sulfate into the aquifer. Soil water balance monitoring and periodic sampling of contaminant levels will also be conducted in the expanded irrigated plantings as measures of remediation success.

**Quantify Effects of Irrigation on Microbial Denitrification Processes and Rates**

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. Effects of irrigation and planting will be determined by comparing microbial populations and measuring denitrification activity at various depths both in the irrigated soil and in adjacent non-irrigated soil.

**Investigate Nitrification Processes, Rates, and Possible Enhancements**

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 presence and rates of nitrification in subpile soil will be evaluated first. Methods to enhance nitrification will then be investigated if warranted and feasible.

### 5.4 Task Descriptions

This section presents the pilot study tasks and methods that address source characterization, containment, and removal.

#### 5.4.1 Delineate Extent of Subpile Contaminants

A sampling program will be designed to better delineate ammonium, nitrate, and sulfate in mill-related source areas including the new tailings pile area, and evaporation pond area, and the batch leaching area (see Figure 2–3.). Sampling will be conducted using a combination of stratified sampling and “hot spot” sampling (Gilbert 1987) extending beyond the present subpile
soil plot into these areas. A stratified sampling design will put greater weight on areas where higher contaminant concentrations are more likely such as within the footprint of the evaporation pond (Figure 2–3), possible extensions of “hot spots beyond the current subpile planting (Figure 5–2 and Figure 5–3), and areas with altered surface or subsurface coloration (Section 5.1). A minimum of 25 sample sites will be taken using hand augers at 1, 3 and 5 m depths. Samples will be analyzed for nitrate, ammonium and sulfate, for a total of 25 locations \( \times 3 \) depths = 75 samples. Results will be plotted and the new areas for the expanded planting and irrigation system will be mapped. If the sampling is not sufficient to delineate the boundaries of contaminants, additional sampling will be conducted.

Analyses of soil samples will be made by extracting with potassium chloride (KCl) solution [STO 210; procedure CB(BT-2)]. This procedure, adapted from Page et al. (1982), involves agitation of the disaggregated soil sample for 2 hours in a 1 N KCl solution. Analysis of nitrate and sulfate are made by ion chromatography [STO 210; procedures AP(NO3-4) and AP(SO4-4)] after dilution to avoid interference with the chloride peak. Analysis for ammonia is made by spectrophotometric methods [STO 210; procedure AP(NH3-1)]. A more aggressive digestion using nitric acid [STO 210; procedure SE(MD-1)] will be used on some samples to assure that all sulfate minerals are being digested.

5.4.2 Investigate Natural Sources of Nitrate and Sulfate

Soils and vadose-zone sediments overlying the plume and the alluvial aquifer upgradient of the plume will be investigated as potential natural sources of nitrate and sulfate. If applicable, recent literature on likely environmental settings where nitrate accumulates will be the basis for stratifying sampling locations and depths in the soil profile and vadose zone. If the literature is inadequate as a basis for stratified sampling, then a sampling grid with a minimum of 20 sampling locations will be set up over the portion of the plume with \( > 500 \text{ mg/L} \) nitrate. Samples would be taken at 3 depths (0–1, 2–3 and 4–5 m) at each location. The soil survey for Monument Valley will be reviewed, if one exists, to determine the presence and likely settings for soil horizons with calcium sulfate accumulation (Gypsic horizons). If a soil survey has not been prepared for the area, then soil pits will be excavated over the plume to determine whether gypsiferous soil is present.

The alluvial aquifer upgradient from the plume is likely a greater source of nitrate and sulfate. Data on background concentrations of sulfate in the alluvium at the Monument Valley Site are inconclusive, but are needed in order to establish reasonable cleanup goals for ground water remediation. Table 5–3 lists sulfate data for eight well locations presented in DOE (1999) as background for sulfate in the alluvium. The mean sulfate concentration at these locations is 240 mg/L. The results are highly variable as indicated by a standard deviation of 233 mg/L.
Table 5–3. Background Alluvial Sulfate Concentrations, Monument Valley DOE (1999)

<table>
<thead>
<tr>
<th>Well ID</th>
<th>Ownership</th>
<th>Depth (ft)</th>
<th>Sulfate (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0200</td>
<td>Private (Ben Stanley)</td>
<td>Unknown</td>
<td>543</td>
</tr>
<tr>
<td>0400</td>
<td>Private (Tribal Well)</td>
<td>12</td>
<td>96</td>
</tr>
<tr>
<td>0402, 0403, and 0404</td>
<td>DOE</td>
<td>8 - 10</td>
<td>~30</td>
</tr>
<tr>
<td>0602</td>
<td>Private</td>
<td>35</td>
<td>125</td>
</tr>
<tr>
<td>0603</td>
<td>DOE</td>
<td>55</td>
<td>112</td>
</tr>
<tr>
<td>0616</td>
<td>Private</td>
<td>Unknown</td>
<td>183</td>
</tr>
<tr>
<td>0617</td>
<td>Private</td>
<td>Unknown</td>
<td>160</td>
</tr>
<tr>
<td>0640</td>
<td>Private</td>
<td>Unknown</td>
<td>668</td>
</tr>
</tbody>
</table>

Mean Sulfate Concentration = 240 mg/L  
Standard Deviation = 233 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 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 5–3) indicates that the ground water at this location is influenced by artesian ground water from the DeChelly Sandstone (DOE 1999).

Another factor affecting ground water composition is the variability in geologic strata it contacts. For example, the Moenkopi Formation contains gypsum (see Section 5.2.2) which would contribute sulfate 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 1999).

In summary, there is large uncertainty in the concentration of sulfate in upgradient background wells which can only be properly evaluated by placing and sampling additional monitoring wells. A geohydrologic investigation will be needed to determine the most appropriate locations and depth for new background monitoring wells. The investigation will include: (1) extending geologic cross sections into the background area, (2) gathering all available information on private wells, (3) more thoroughly evaluating of stratigraphic control on water production and water quality, and (4) projecting water table elevations from the site into the background area. Wells should be located in areas that are representative of the variability of water producing zones in the upgradient aquifer.

5.4.3 Determine Causes and Recourses for Stunted Plant Growth

Poor plant growth in the northwest portion of the subpile planting coincides with surface stains and a black mottled layer in the subsurface. The occurrence and depth of the black layer were documented during the 2002 sampling for ammonium and nitrate. These data, and additional samples, if necessary, will be used to determine if the distribution of the black layer is coincident with the white surface stain and the area where *Atriplex* growth has been suppressed. Sampling will consist of digging a shallow pit with a shovel, and using a hand auger to go deeper if
necessary, to determine the presence or absence and depth of the black layer. A subsample of soil containing the black material will be saved and analyzed for heavy metals and other constituents that might interfere with plant growth. High soil compaction is another possible cause of poor plant growth. Soil will be sampled both inside and outside the area of suppressed growth to determine bulk density as a measure of compaction. If the cause of poor growth is ascertained, methods to improve plant growth such as installing planting wells that extend below the black mottled layer and the use of organic amendments, fertilizers, or soil chemical amendments will be considered.

### 5.4.4 Expand Subpile Planting and Irrigation System

After an expanded area for remediation is identified, approximately 6,000 *A. canescens* plants will be raised in a greenhouse for transplanting. Plants will be spaced 2 m by 2 m, which is comparable to the existing subpile soil plants. Each plant will receive 4 liters of water per day from April through September.

The irrigation system for the existing subpile planting will be removed. The existing system has out-lived it’s design life and has become ineffective. Water is distributed unevenly or not at all from emitters along several lines. Also, the source of irrigation water will be changed from well 625 east of the site to well 618 west of the site. This will require installation of new plumbing.

The extent of subpile contamination and a map of the expanded subpile sampling will be required before the irrigation system can be designed. Information on the well output, plant species, plant spacing, irrigation rate and watering frequency will also be needed to design irrigation zones, water distribution piping an valves, emitter flow rates, and emitter types. Controllers will be used to automate irrigation zones from a central location. A topographic survey of the new expanded planting area and a profile of the alignment and elevation differences from the supply well to the expanded subpile planting will be required for an efficient hydraulic design for the distribution system.

### 5.4.5 Monitor Soil Water and Recharge

Soil moisture and flux will be monitored in both the existing and expanded subpile plantings in order to ensure that no net leaching of nitrate and or sulfate occurs.

#### Soil Moisture Content and Storage

Soil moisture will be monitored using a combination of neutron thermalization (NT) hydroprobes (Gardner 1986) and water content reflectometers. Volumetric water content will continue to be monitored monthly both in the existing array of 20 NT hydroprobe ports and in new ports installed in the expanded planting, to show the seasonal wetting front—the distribution of soil moisture over the site as a function of soil depth. Readings will be taken at 30-cm depth increments to the bottom of the ports (about 5 m unless bedrock occurs shallower).

Soil water content will also be measured using water content reflectometers (Campbell Scientific Incorporated). Water content reflectometers (WCRs) consist of two parallel rods attached to an electronic signal generator. A pulsed wavelength traveling down a coax or waveguide is influenced by the type of material surrounding the conductors. If the dielectric constant of the
material is high, the signal propagates slower. Because the dielectric constant of water is much higher than most other materials, a signal within a wet or moist medium propagates slower than in the same medium when dry. The reflectometer measures the effective dielectric as a pulse transit time, which in turn is calibrated against water content. A manufacturer’s calibration is supplied with the sensor but will be checked against specific site soil conditions since salinity and other soil properties such as mineralogy can affect the calibration. Changes in soil moisture will be determined by reading the WCR probes hourly.

Soil water storage ($S$) will be calculated from both the NT probe at many locations and WCR measurements of water content ($\theta$) using a modification (Waugh et al. 1994) of the trapezoidal approximation by Green et al. (1986) as follows:

$$S \approx \theta_1 z_1 + \sum_{i=2}^{n} \left[ \frac{(\theta_{i-1} + \theta_i)}{2} (z_i - z_{i-1}) \right]$$

where $\theta_i$ and $z_i$ are the water content and depth for the uppermost measurement, $\theta_1$ is the volumetric water content measurement at the $i$th point in the soil profile, $z_i$ is the depth of the $i$th point in the profile, and $n$ is the total number of points.

**Soil Drainage**

Drainage or recharge from the subpile planting will be monitored using two approaches. The first is an interpretation of the soil moisture content data monitored with NT and WCR methods. If moisture content values in the lower depths of the profile remain well below saturation and remain relatively constant, it can be inferred that saturated flow is not occurring and water flux occurs as unsaturated flow if at all. This type of inference is possible because the homogeneity of the fine sandy soil profile allows us to assume a unit gradient.

An instrument was recently developed, a small lysimeter or water flux meter (WMF), that will be installed near the bottom of the root zone and is capable of directly monitoring unsaturated water fluxes ranging from 0.02 mm/yr to more than 1,000 mm/yr (Gee et al. 2002). The WMF features a funnel to direct water from the soil into a passive wick for moisture tension control, a miniature tipping bucket for real-time flux measurements that can be calibrated from the surface, and a pipe or chimney extending above the funnel to minimize divergent flow. The more accurate WMFs with the WCRs above them will be installed directly next to a subset of the less accurate hydroprobe ports, and data obtained will be correlated to hydroprobe port data using a double sampling protocol (Gilbert 1987).

Sources of uncertainty in monitoring percolation flux with the new water flux meter will be evaluated. Given that soils materials, layer construction, or vegetation will vary from one location to another on the cover, then it must be shown that the number and placement of WMFs is representative of that variability. WMFs will be installed by augering holes in the soil, and then the continuity of soil conditions will be reconstructed as well as possible. Preferential flow within or divergence of flow away from the backfilled hole above the flux meter due to installation could cause either overestimation or underestimation of soil recharge.
5.4.6 Monitor *Atriplex* Canopy Growth and Total N

Survival, canopy volume, canopy cover, and dry-weight biomass of *Atriplex canescens* shrubs will be monitored in the existing and in the expanded subpile soil planting. Survival will be evaluated by census. Canopy cover and canopy volume will be estimated using stratified sampling and productivity will be estimated using a double sampling routine (Gilbert 1987). The subpile planting will be stratified (subdivided) either by irrigation zone or post-stratified if stunted growth continues to be observed. An adequate sample size (number of plants) for 10 percent accuracy and precision will be statistically estimated using 2001–2003 data. 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 \((\pi bc)\).

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 *Atriplex* shrubs are measured, a subset of 20 shrubs ranging from small to large volume 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. 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 20 shrubs. 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).

5.4.7 Evaluate Natural Denitrification Processes

Rates of denitrification in the subpile soil will be measured 1) to confirm that the estimated rapid loss of nitrate is due to microbial denitrification, 2) to identify possible soil denitrification enhancements, and 3) to identify the end product of denitrification for purposes of enhancing microbial activity and to limit the production of a harmful greenhouse N2O while promoting denitrification. Denitrification activity in soil samples will be assessed following the protocol of Tiedje (1994). Twenty soil samples taken on the irrigated field will be composited, and 20 samples taken off of the field will be composited. Six replicate 1:1 slurries from each composite will each be added to septum sealed flasks along with a solution of 1 mM KNO3, glucose and 1 g L-1 chloramphenicol. Following the protocol, the air in the flask is evacuated and replaced with helium to obtain an anoxic environment. Ten percent of the headspace is replaced with purified acetylene to prevent the conversion of N2O to N2. Headspace samples are taken at 0, 3, 6 and 24 h for N2O analysis using a gas chromatograph equipped with an electron capture detector (GC-ECD). The rate of N2O production in the headspace is used to calculate the potential denitrification activity of the sample. This sampling and analytical protocol will be repeated every two months throughout the growing season to gain an accurate measurement of the spatial and temporal variability in denitrifying activity at the site.

For N2O out-gassing or flux measurements in the field, a PVC soil cover similar to that described by Hutchinson and Mosier (1981) will be used. With this method, 20 PVC covers are placed over the soil at discrete locations and 20 ml headspace samples are collected intermittently over a 3 hour period using air-tight syringes. Samples are stored in evacuated containers sealed with boiled rubber septum until N2O is analyzed on the GC-ECD. Denitrifying activity in soils incubated with and without acetylene will be compared. To do so, 3–6 grams of calcium carbide would be added to the incubation system to react with available oxygen and produce acetylene.
is incorporated over four, 3 square centimeter areas next to the placement of each soil cover (Mosier and Klemedtsson 1994). Acetylene specifically inhibits the conversion of N$_2$O to N$_2$ allowing us to distinguish between the different denitrification processes. Due to the high spatial and temporal variability associated with this measurement, samples will be taken monthly and acetylene treatments conducted quarterly.

The number of denitrifiers in the soil profile (to a 5 m depth) will be enumerated via two methods: the classical cultivation method, Most Probable Number (MPN), described by Tiedje (1994), and a molecular-based approach using Polymerase Chain Reaction (PCR) primers and protocols developed to enumerate the cultivation-independent fraction of denitrifying microorganisms (Hallin and Lindgren 1999, and Yan et al. 2003). The primers are conserved to genes encoding the enzymes responsible for nitrate reduction by a variety of microorganisms including those that are difficult to cultivate using the more traditional MPN method (Yan et al. 2003). Soil samples will be taken from on and off the irrigated field at three depths (0, 2, and 5 m) for a total of 36 samples per each sampling event. Samples will be kept on ice upon collection in sterile whirlpack bags until further processing. In addition, nitrate measurements will be taken for each soil sample collected. Denitrifiers will be enumerated monthly using the traditional MPN approach and every three months using the molecular approach.

If necessary, further delineation of microbial processes related to complete nitrogen turnover in this soil using stable isotope dilution studies (Mosier and Klemedtsson 1994, Pendersen et al. 1999, Tiedje et al. 1989) will be considered (see Section 5.4.7). These analyses would be conducted in laboratory microcosms representing replicates of composite samples taken from on and off the irrigated field.

### 5.4.8 Evaluate Nitrification Processes

Similar to denitrification, nitrification (or the oxidation of ammonia to nitrate) will be evaluated as the likelihood or the potential that the soil microbial consortia will nitrify. If nitrification activity is either naturally present or can be induced, it represents a possible pathway by which soil ammonium can be remediated, as the nitrate produced would potentially be rapidly denitrified. To test for the nitrification potential of the soil, samples are diluted 1:10 in a 1 mM phosphate buffered solution of 1.5 mM ammonium and the rate of nitrate accumulation is measured over time colorimetrically using the Schezochrome Reagents from Polyscientific (Mintie et al. 2003). Sample collection and analysis will proceed concurrently with the denitrification evaluation studies.

If there is adequate potential nitrification and denitrification activity, it may be necessary to obtain more direct measurements of these processes in-situ using stable isotope methods. Gross rates of N-mineralization, nitrification and denitrification can also be determined using the $^{15}$N ammonium and nitrate isotopic pool dilution technique (Pendersen et al. 1999). Here, soil samples are incubated for various times with stable isotopic solutions of $^{15}$N-ammonium or $^{15}$N-nitrate. The ammonium or nitrate is extracted from the soil solution and the difference (or dilution) in $^{15}$N remaining in the pool as ammonium or nitrate is used to calculate the gross nitrification, or denitrification rate, respectively (Pendersen et al. 1999). If nitrification proves to be of importance in this soil, similar to denitrification, estimates of the soil microbial nitrifying population will be obtained using molecular techniques (Hesselsoe et al. 2001, Okana et al. 2004).
5.4.9 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 (see Section 5.4.3). 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 that have been 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.

5.4.10 Measure Soil Organic Carbon

Because of the tight correlation between microbial denitrification and organic carbon content of soils, Total Soil Organic Carbon (SOC) measurements will be obtained for soil samples taken directly underneath plant canopy and the bare soil on both the irrigated and un-irrigated soils that correspond to samples taken for denitrification analysis (see Section 5.4.6). The SOC content of the soil is determined either by dry combustion or by a wet oxidation method, both of which are well documented by Neilson and Sommers in the Methods of Soil Analysis, Part 2 (1986). Initially, SOC will be analyzed by both methods but the method providing a more sensitive measurement will be used for future sampling. If a relationship is found between SOC and denitrification, it will be worthwhile to explore methods of artificially increasing the available carbon supply; for example, a carbon source could be added in the irrigation supply.
6.0 Natural Attenuation of Ground Water

MNA will be evaluated 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 MNA pilot studies will acquire field data needed to estimate the capacity of natural attenuation processes. Monitoring data on plume concentrations, distributions, and dispersion in the alluvial aquifer may provide historical evidence of the total capacity of natural attenuation processes and the effectiveness of the effort thus far to contain the subpile source. A small-scale research project conducted at Monument Valley between 1998 and 2001 investigated phytoremediation as a component of natural attenuation. The results show that populations of native desert shrubs rooted in the aquifer are removing significant amounts of nitrate.

This chapter provides 1) a summary of monitoring data acquired to date on spatial and temporal patterns in nitrate and sulfate concentrations in the alluvial aquifer, 2) the status of passive ground water phytoremediation studies, 3) background information on potential natural geochemical and microbiological attenuation processes at the site, and 4) objectives and tasks for an expanded pilot study of natural attenuation processes and capacities. The expanded pilot study includes a large-scale passive phytoremediation planting, an investigation of passive bioremediation and geochemical attenuation processes, and the application of monitoring and predictive tools to assess MNA adequacy.

6.1 Status of Ground Water Monitoring and Modeling

6.1.1 Monitoring

Ground water characterization methods used to collect data in the SOWP (DOE 1998) include: (1) surface geophysics, (2) direct-push ground water sampling and analysis, (3) installation of monitoring wells, sampling and analysis, (4) aquifer pump tests, and (5) surface infiltration tests. Surface geophysical surveys, including seismic refraction, transient electromagnetic soundings, induced polarization and resistivity soundings, were used to better define the geometry of the alluvial aquifer, the position of the ground water table, and to some extent, locations of contamination. Direct-push sampling at 28 locations was used to better define ground water concentrations of nitrate and sulfate in 1997. At many of these locations, depth-discrete concentration information was obtained and indicated a significant stratification of the contaminants. The direct push locations were not made into wells and thus were sampled only once.

One hundred two wells have been used to monitor ground water chemistry and water elevations at the Monument Valley site over time (See_Pro Monitor Well Report). Of these, 75 still exist and the remainder have been decommissioned. Wells were completed in the alluvium (52 existing wells), the Shinarump Member of the Chinle Formation (10 existing wells), and the DeChelly Member of the Cutler Formation (13 existing wells). The existing alluvial wells are located within the contaminant plume area and also upgradient, cross gradient, and downgradient of the plume. Seventeen alluvial wells and one DeChelly well are currently being routinely monitored for ground water chemistry and water elevations. These wells are strategically located to determine changes in the plume geometry over time.
6.1.2 Recent Trends of Ground Water Nitrate and Sulfate Concentrations

Nitrate concentrations in the inner plume (near the source area) are plotted against time in Figure 6–1. Since the completion of uranium mill tailings removal in 1994, nitrate concentrations appear to be decreasing in most inner plume wells (inner plume wells are those closest to the source area). Well 0606 shows the greatest decrease, from about 1,200 mg/L in 1994 to about 800 mg/L in 2003. In contrast, nitrate concentrations are increasing in all outer plume wells (Figure 6–2). No significant increases in nitrate concentration have yet been encountered in downgradient wells (Figure 6–3).

The decreasing nitrate concentrations in the inner plume are probably related to the recharge of fresh water following mill tailings removal. Sulfate concentrations have also decreased significantly in the inner plume area (Figure 6–4), supporting the notion that contaminants are being diluted by decreasing concentrations in the recharge rather than by biochemical degradation. The increase of nitrate in the outer plume is likely due to more highly contaminated ground water from the centroid of the plume making its way downgradient. Oxidation-reduction potential (ORP) values in the inner plume decreased from about 400 millivolts (mV) to about 180 mV shortly after removal of the tailings (data not shown). The decrease in ORP may signal a decreasing connection between the oxidized surface environment during milling and construction at the former mill site and the ground water system.

Figure 6–1. Nitrate Concentrations in Inner Plume
Figure 6–2. Nitrate Concentrations in Outer Plume

Figure 6–3. Nitrate Concentrations in Downgradient Area
6.1.3 Modeling

A ground water flow model using the modeling code MODFLOW (MacDonald and Harbaugh 1988) was developed to better predict the ground water flow velocity through the alluvial aquifer. The model was calibrated against measured water levels but has not yet been used to make predictions of cleanup times. This model will be enhanced and used in the current work scope to evaluate alternative remediation methods.

6.2 Status of Passive Ground Water Phytoremediation

The capacity of existing populations of two native desert shrubs, *Sarcobatus vermiculatus* and *Atriplex canescens*, to root into and extract water and nitrate from the alluvial aquifer was evaluated (McKeon et al. 2004a). *S. vermiculatus* (black greasewood) and *A. canescens* (fourwing saltbush), both in the family Chenopodiaceae, are obligate and facultative phreatophytes, respectively, that dominate the natural plant community overlying much of the plume. A long history of heavy grazing by livestock has greatly reduced the capacity of these populations to remove water and nitrate from the aquifer. Effects of fencing these populations and manage grazing on the phytoremediation capacity are discussed in Section 7.1.

A small-scale research project was conducted between 1998 and 2001 to determine if the existing, grazed populations of black greasewood and fourwing saltbush are making a significant contribution to natural attenuation of the nitrate plume. The study had two specific objectives:

- Determine if *S. vermiculatus* and *A. canescens* are rooted into and are removing water and nitrate from the alluvial aquifer.
- Estimate water and nitrate extraction rates for the existing rangeland use and ecological conditions.

The most obvious evidence that black greasewood and fourwing saltbush plants were rooted in and removing nitrogen from the nitrate plume was the size and appearance of plants that had been transplanted in exclosure (fenced) plots (see Figure 7–3). Even after multiple years of
drought when all other shallower-rooted plants became desiccated during the summer, the
exclosure plants were unusually dark green and unusually large for these species (see
Section 7.1.1). Examination of isotopes as tracers of water sources in plants, and nitrate-N and
total-N levels in plants, provided objective evidence that this was indeed the case.

6.2.1 Stable Isotope Evidence for Rooting Depths

The ratios of stable isotopes of hydrogen and oxygen in water can be used as a tracer or
“signature” for sources of water in plants (Dodd et al. 1998; Dawson 1993; Dawson et al. 2002;
Lin et al. 1996). Ratios of heavy isotopes to lighter isotopes of hydrogen (²H/¹H or
deuterium[D]/protium[H]) and oxygen (¹⁸O/¹⁶O), designated as δD and δ¹⁸O, are expressed in
units of parts per thousand (‰) as compared to a seawater standard. Values are positive if water
is enriched in heavy isotopes and are negative if depleted in heavy isotopes (Coplen et al. 1999).
Water samples extracted from stem sections of plants generally have isotope signatures similar to
the source of water tapped by the plant roots, hence it is possible to infer the source of water used
by a plant by comparing isotope signatures in the plant to those of potential water sources in the
environment (Coplen et al. 1999). Isotope signatures from water in black greasewood and
fourwing saltbush growing over the alluvial nitrate plume were compared to signatures for well
water samples, soil samples, and precipitation samples (McKeon et al. 2004a).

The heavy isotopes ratios δD and δ¹⁸O were analyzed in soil water, rainwater, the aquifer and
plant samples collected in September 2000 and July 2003. Samples were taken after a summer
rainfall event. Rainfall data were obtained in 2000 from Mexican Hat, Utah, samples, and in
2003 from collection gauges placed on site. Stem samples of black greasewood and fourwing saltbush were collected on site and aquifer samples were obtained concurrently with collection of
rain and plant stem samples from wells 606, 653, 765, and 770. Soil water was also sampled
concurrently at depths of 50 cm to 90 cm close to the drip line of sampled plants near wells 606
and 765. All soil, water, and plant samples were sealed and stored in 50 cubic centimeter glass
vials. A cryogenic vacuum distillation process was used to extract the water from the soil and
plant samples (Ehleringer and Osmond 1991). Water analysis for calculating δD and δ¹⁸O was
performed with a dual-inlet mass spectrometer.

δD and δ¹⁸O values in water from rain, soils, wells, and plant stems were subjected to one-way
analysis of variance (ANOVA) across years, with water source as the categorical variable. Water
samples from wells and plant tissues at Monument Valley did not differ significantly (P>0.05)
for either δ¹⁸O or δD but they were distinctly different (P<0.05) from values for soil moisture or
rainwater (Figure 6–5). Furthermore, δ¹⁸O or δD values for samples taken from the planted
fourwing saltbush shrubs did not differ from values for natural plants (P>0.05). Values for the
two plant species did not differ significantly (P>0.05) for either isotope, nor did samples taken
before or after the onset of the summer monsoon season (P>0.05). These δ¹⁸O and δD isotope
signatures from water in stems of plants growing over the alluvial nitrate plume suggest that both
species are rooted into and obtaining much of their moisture requirements from the plume at
depths of 10 m to 18 m.
6.2.2 Evidence of Nitrogen (N) Sources for Uptake by Plants

Ratios of nitrogen isotopes $^{15}\text{N}$ to $^{14}\text{N}$ in plant tissues, designated $\delta^{15}\text{N}$, can be useful in detecting the source of nitrogen used by plants, although the results are more difficult to interpret than $\delta^{18}\text{O}$ and $\delta D$ isotope signatures for water (Dawson et al. 2002). Fractionation (plants may biochemically discriminate against heavier isotopes) is one confounding factor. It is also difficult to isolate the many different pools of N in soils that may be available for plant uptake.

In an effort to determine the source of N in plants, $\delta^{15}\text{N}$ values were measured in leaf samples from fourwing saltbush growing in an area over the plume and in an area adjacent to the plume (McKeon et al. 2004a). $\delta^{15}\text{N}$ values were also measured in aqueous extracts from soil sampled at a 1.5 m depth over the plume and from plume water taken from wells. Different $\delta^{15}\text{N}$ values would be an indication that plants were accessing different N pools in soil or ground water. Nitrate-N and total N levels in leaf tissue samples from fourwing saltbush growing in the area over the plume and in the area adjacent to the plume were also compared. Since plants rooted in soil or water high in N can accumulate high levels of N and nitrate in leaf tissues, the plants growing in plume water would be expected to have higher leaf nitrate-N and total-N levels that plants not rooted in the nitrate plume. McKeon et al. (2004a) provide details of sampling and analytical methods.
The δ15N results were inconclusive with regard to source of nitrogen. δ15N values were similar for the water, soil and *A. canescens* leaf tissues on and off the plume, and values were within the range expected for nitrate in desert soils and nitrate derived from the industrial fixation of atmospheric nitrogen (Kendall and Aravena 1999). However, plants on the plume accumulated higher levels of nitrate-N and total nitrogen in their leaf tissues than plants off of the plume, a possible indication of nitrate enrichment in the soil or ground water (Missaoui et al. 2002; Strickland et al. 1995; Lawrence et al. 1968). In the summer, plants on the plume had five-fold higher leaf nitrate-N levels and 50 percent higher total leaf nitrogen than plants off the plume (Figure 6–6). Plants did not differ in nitrate or nitrogen content in winter, presumably because they were not active in either water or nitrate uptake during the cold months.

In a follow up greenhouse experiment (DOE 2002), *A. canescens* plants were grown on water from three Monument Valley wells over the contamination plume, with nitrate-N contents of 20, 125, and 250 mg kg⁻¹. Leaf nitrate-N levels increased in proportion to the concentration in the well water, supporting the conclusion that high leaf nitrate-N is an indication that field plants are rooted into the plume. At other desert locations both nitrate and total nitrogen contents vary considerably over an annual cycle in *Atriplex spp.*, as in the present study, and nitrate tends to increase in response to increased soil nitrate availability associated with rainfall events (Islam and Adams 2000).

### 6.2.3 Preliminary Estimate of Existing Phytoremediation Capacity

Many factors can influence rates of water, nitrogen, and sulfur extraction by plants. Estimates of potential uptake rates are needed to determine if natural phytoremediation (uptake by the existing phreatophyte populations without intervention) is making a significant contribution to the natural attenuation of the nitrate plume.

In preliminary studies (DOE 2002, McKeon et al. 2004a), nitrogen levels in soils and in the aquifer were measured, and rates of uptake into plant tissues were extrapolated to develop mass balance calculations. The alluvial aquifer plume contains approximately $2 \times 10^6$ cubic meters of water and $3.5 \times 10^5$ kg of nitrate-N (DOE 1999). These quantities were divided by annual nitrogen and water extraction rates estimated for the current range condition (no planting or fencing to exclude grazing). Annual uptake rates of nitrate were calculated based on the nitrogen content of annual biomass increment as measured for the existing grazed rangeland. The 130 ha site was divided into two parcels: a 100 ha parcel dominated by *A. canescens* at 5 percent cover; and a 30 ha parcel dominated by *S. vermiculatus* at 15 percent cover (McKeon et al. 2004a). Water extraction rates by plants were estimated on the basis of regression equations in Steinwand et al. (2001) relating evapotranspiration (ET) and percent cover. Tissues of *A. canescens* and *S. vermiculatus* growing over the plume were also examined for sulfate and total sulfur content. For current range condition, *A. canescens* leaves contained about 374 ppm sulfate and 0.27 percent sulfur. *S. vermiculatus* values were similar.

Under current range conditions, a preliminary estimate of nitrogen extraction rates by plants is 25 kg ha⁻¹ yr⁻¹. If it is assumed that the nitrogen in plant tissues originates from nitrate in the contamination plume, then a removal time of 108 years can be extrapolated. ET by *Atriplex* at 5 percent cover is approximately 50 mm yr⁻¹ and ET by *S. vermiculatus* at 15 percent cover is 270 mm yr⁻¹, according to data in Steinwand et al. (2001). Hence, over the 130 ha of plume area, the preliminary estimated time for ET of one plume volume of water is approximately 15 years.
for current range condition. These preliminary estimates assume no source loading from the subpile soils or from natural sources of nitrate.

![Leaf Nitrate](image1)

![Leaf Total Nitrogen](image2)

Figure 6–6. Means and standard deviations of nitrate-N contents (top) and total N contents (bottom) of leaves of Atriplex canescens plants harvested at Monument Valley in summer (July 2002) or winter (December 2002) either On or Off the nitrate contamination plume. Different letters above bars denote significant differences among means ($P<0.05$).
6.3 Abiotic Geochemical Attenuation

Nitrate does not sorb readily to sediment and is not controlled by the solubility of nitrate-containing minerals; thus, nitrate moves rather freely through the subsurface unless attenuated by biotic processes (Freeze and Cherry 1979; Hem 1985). In some aquifers, nitrate is transformed to more reduced compounds such as ammonium, nitrite nitrogen, (dissolved gas) and nitrous oxide (dissolved gas) by biologic activity (Section 6.4). Unlike nitrate, ammonium sorbs strongly to subsurface solids often as an interlayer cation in clay minerals. Thus, sorbed ammonium could provide a source of subsurface nitrogen that could be oxidized to nitrate. Ammonium (as uncharged ammonia) can also volatilize although significant volatilization is not expected at the pH values of the Monument Valley ground water system. Nitrogen in the form of dissolved gasses can be released from ground water to the vapor phase in the vadose zone. Nitrite also sorbs to sediment but not as strongly as ammonium. In summary, natural geochemical attenuation of nitrate at Monument Valley is not expected to be significant without biotic reduction to other compounds.

Sulfate is a strongly bonded anion that does not readily breakdown except under chemically reducing conditions in the presence of sulfate-reducing microorganisms. In most ground water systems, sulfate migrates freely through the subsurface and is not attenuated by adsorption to the sediment. Calcium sulfate minerals (gypsum or anhydrite) can form if the concentration of sulfate is relatively high and a source of calcium is present. Calcium sulfate minerals often precipitate in arid soils as calcium and sulfate become concentrated by evaporation. If ground water sulfate concentrations are high and carbonate concentrations are low, gypsum can form in the subsurface by the replacement of calcium carbonate minerals. If ground water encounters a zone of strong chemical reduction (e.g., as produced by a carbon source being utilized by reducing bacteria), sulfate will transform to sulfide. The ultimate fate of sulfide is commonly an iron sulfide mineral; however, sulfide can also exist as dissolved hydrogen bisulfide or hydrogen sulfide gas. Sulfide does not commonly persist long in desert environments.

6.4 Passive Bioremediation of Ground Water

Preliminary evidence presented in Section 5.1.4 indicates that bioremediation (denitrification) is likely occurring in subpile soils. Denitrification is the biologically mediated reduction of nitrate (NO$_3^-$) to N$_2$ gas. Bioremediation may also be occurring in the alluvial aquifer. Bioremediation is a term used to describe the transformation of contaminants by biological processes in contaminated soil or water. It involves exploiting the activity of indigenous (those that are native to the site) microorganisms (e.g., yeast, fungi, or bacteria), to transform contaminants into less toxic forms (Jordan et al. in press). The capacity for microbial transformation of a given contaminant is highly dependent on the contaminant itself and the immediate and surrounding environment.

One approach for isolating the occurrence of natural bioremediation of nitrate in the alluvial aquifer is to evaluate stable isotopes of N as a means for partitioning microbiological processes for reducing nitrate to N$_2$ gas from aquifer dispersion and dilution processes or possible geochemical attenuation processes. Similar to the investigation of N uptake sources in plants (see Section 6.2.2), partitioning of microbiological attenuation in ground water is possible because N is comprised of two stable isotopes with atomic masses of 14 and 15. $^{14}$N makes up the majority (c.a. 99.6 percent) of the N found on earth while the reminder (c.a. 0.4 percent) of the N exists as
Hence, all N-containing compounds will have an $^{14}$N:$^{15}$N ratio of roughly 272. The natural abundance of $^{15}$N in any compound is commonly expressed as delta $\delta^{15}$N in ‰ relative to an atmospheric standard.

$\delta^{15}$N measurements can be used to examine the source, flow and fate of N in the alluvial system because the signature of the N-containing substrate and the N-containing product of different processes (biological, physical or chemical) differ when $^{14}$N and $^{15}$N react at different rates (Kendall and Ramon 2000; Lund et al. 2000). This is called an isotope effect or isotopic fractionation. For biologically mediated processes, the kinetic isotope effect for $^{14}$N is considerably greater than $^{15}$N because there is generally an enzymatic preference for binding the lighter N isotope. For example, denitrification and volatilization have particularly strong fractionation. Hence, the fractionation of $^{15}$N via these processes can contribute to large differences in the $\delta^{15}$N signature of the N-compounds undergoing transformation (Fryar et al. 2000; Hoffman et al. 2000). A combination of isotope signatures from oxygen ($\delta^{18}$O) and $^{15}$N have been also used to infer sources nitrate contamination in ground and surface water systems (Burns and Kendall 2002; Coplen et al. 2004; Fukada et al. 2003; Perez et al. 2000; Perez et al. 2001).

By using both $\delta^{18}$O and $\delta^{15}$N measurements, it may be possible to trace and quantify the flow of nitrate through the plume. In the subsurface, volatilization of nitrate would be at a minimum and any isotopic fractionation of nitrate-N as it flows through the plume away from the source would suggest a biological rather than a geochemical or physical process.

6.5 Goals and Objectives

The goals for evaluating natural attenuation processes 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 (Section 5.0), and 2) will achieve remediation requirements in a reasonable time. If not, then enhanced remediation (Section 7.0) and/or active remediation (Section 8.0) may be necessary. Preliminary studies indicate that phytoremediation is likely making a significant contribution to natural attenuation. This pilot study will determine the rates of and extent of phytoremediation, and evaluate the contributions of natural bioremediation and natural flushing (dispersion and dilution) processes.

Specific objectives follow:

**Determine Maximum Depth of Plume Water Extraction by Plants**

Preliminary studies of natural phytoremediation provided persuasive evidence that *A. canescens* and *S. vermiculatus* are rooted into and extracting water from the alluvial aquifer (McKeon et al. 2004, DOE 2002). The current study will determine the maximum depths these native phreatophytes can extract ground water and, therefore, the extent of the plume from which plants are capable of extracting water and nitrate.

**Confirm and Determine Rates of Plant Utilization of Plume Nitrate**

Preliminary data also indicate that plants are removing nitrate from the plume; however, the evaluation of the rates of nitrate extraction was inconclusive because stable N isotope ratios vary
greatly both seasonally and with depth in the root zone (preliminary data were inadequate to isolate sources of N in plant tissues). The follow-up objective is to refine and extend the evaluation of stable N isotope ratios to better determine nitrate-N uptake rates by phreatophytes.

Evaluate Plant Utilization of Plume Sulfate

Preliminary studies did not address plant uptake rates for sulfate. The current pilot study will extrapolate sulfate uptake rates from a combination of literature on sulfate uptake, sulfur in tissues of phreatophytes growing in the plume, and plant productivity data.

Evaluate Occurrence of Natural Microbiological Attenuation

Microbiological denitrification may be contributing to natural attenuation of the ground water nitrate similar to denitrification processes in subpile soils (see Section 5.1.4). If so, enhancement of microbial denitrification could be an efficient means for accelerating nitrate plume remediation (Section 7.0). Similar to the approach used to evaluate water and nitrate extraction by plants (see Section 6.2.1), ratios of stable isotopes of N and O will be used to estimate partitioning of microbial denitrification from geochemical attenuation (if any) and physical dispersion and dilution.

6.6 Task Descriptions

This section presents specific pilot study tasks designed to acquire information needed to evaluate the capacity of natural attenuation processes at the site; to determine 1) maximum plume water extraction depths by phreatophytes, 2) the extent and rates of nitrate phytoremediation, 3) rates of sulfate uptake by plants, and 4) the role of microbial denitrification as a natural attenuation process in the nitrate plume.

6.6.1 Determine Depths to Ground Water Within Phreatophyte Populations

The purpose of this task is simply to map the depths to ground water in areas of existing phreatophyte populations. This baseline information will be used to select areas for the enhanced phytoremediation tests. Figure 3–4 is a map of plant associations overlying the plume. This map will be superimposed on a map of depth to ground water based on recent well monitoring data. The maximum depths to ground water within the ATCA (Atriplex canescens or fourwing saltbush) and SAVE (Sarcobatus vermiculatus or black greasewood) associations will be determined. Revegetation plots (Section 7.1.2) will be installed within the denuded or bare area along a depth gradient from east to west and overlying nitrate “hot spots” so as to span this maximum depth.

6.6.2 Partition Plant Water and Nitrate Sources Using Stable Isotopes

The maximum rooting depth of phreatophytes will be inferred by comparing the signatures of naturally occurring heavy isotopes of oxygen and hydrogen in stem samples of plants, and in their possible sources of water, growing in areas of the plume with the greatest depth to ground water. Isotope ratios of $^{15}\text{N}:{^{14}\text{N}}$ in ground water, soil, and plant tissue will be evaluated to determine if the plume water is the source of nitrogen for plant growth.
Soil samples will be taken from four locations near monitoring wells within the existing populations of *A. canescens* and *S. vermiculatus* during the most active growing season (June–August). Wells will be selected that represent a range of depths to ground water. Samples will be taken at 1 m intervals within the soil profile and vadose zone from the surface to the phreatic water surface using a geoprobe bore hole sampler. Samples will also be obtained at this time for the soil column studies (Section 7.4.5). Concurrently, plant stem samples will be taken from five *A. canescens* and five *S. vermiculatus* plants near each of the monitoring wells. Samples will be extracted and measured for nitrogen, oxygen and hydrogen isotopes and nitrate, total nitrogen, and moisture content (see Section 6.1.3 for analytical methods). Nitrate will be purified for isotope analysis from the soil and water samples according to Fukada et al. (2003) and Silva et al. (2000) using anion exchange chromatography (see Section 6.6.5).

**6.6.3 Estimate Phreatophyte Evapotranspiration**

Estimates of plant ET can be made using eddy covariance ET towers and correlated to potential ET determined by a micrometeorological station on site (see Section 7.2). Methods described in Section 7.6.4 will be used for estimating evapotranspiration rates for both natural and enhanced phytoremediation including hydraulic control of ground water flow with plants.

**6.6.4 Estimate Sulfate Uptake Rates in Phreatophytes**

Sulfate concentration in plant tissue will be estimated for subsamples of biomass for various plant parts (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.

**6.6.5 Discriminate Plume Attenuation Processes Using Stable Isotopes**

Nitrate attenuation in the plume both in time and space can be due to a combination of denitrification and physical dilution. $^{15}\text{N}$ and $^{18}\text{O}$ analyses can distinguish between these two processes (see Section 6.4), and then the results can be incorporated separately into models of nitrate attenuation in the plume. $^{14}\text{N}$ and $^{15}\text{N}$ are naturally present in environmental nitrogen sources. The lighter isotope, $^{14}\text{N}$ is used preferentially over $^{15}\text{N}$ in biological conversions. In contrast, physical process such as dilution and dispersion do not distinguish between isotopes. Therefore, changes in $^{15}\text{N}$/$^{14}\text{N}$ ratios can be used to detect the extent of biological conversion of nitrogen sources. With denitrification, $\text{N}_2$ or $\text{N}_2\text{O}$ are gasses leave the system so the remaining soil or aquifer pools of nitrate become progressively enriched in $^{15}\text{N}$. The $^{15}\text{N}$ enrichment factor ($\delta^{15}\text{N}$, measured in /$\text{oo}$) can be used to quantify the extent of denitrification that has occurred in a pool of nitrate over time, and to distinguish between dilution effects, which do not result in altered $\delta^{15}\text{N}$ values. Similarly, the fractionation of oxygen during denitrification also causes the $\delta^{18}\text{O}$ concentrations in the residual NO$_3^-$ pool to increase as NO$_3^-$ concentrations decrease. The dual isotope approach produces a more distinctive signature overcoming any ambiguity associated with values derived using $\delta^{15}\text{N}$ data, alone.

Water samples will be obtained from existing alluvial monitoring wells located throughout the plume. At least 2 L of water will be pumped from each well to obtain 6 to 12 milligrams of nitrate required for accurate measurements of $\delta^{18}\text{O}$-NO$_3^-$ and $\delta^{15}\text{N}$-NO$_3^-$. Nitrate concentrations in plume water samples will be verified prior to isotope analysis using either an ion
chromatograph or a colorimetric method such as the HACH NitraVer 5 Kits, or using Schezchrome reagents (Mintie et al. 2003).

A summary of the analytical procedure follows. The water is filtered through a 0.45 micron filter and kept on ice (or refrigerated) until further processing. Nitrate is extracted from the sample in an anion exchange resin and eluted using HCl. The solution is neutralized with Ag₂O to form AgNO₃ following the detailed procedure described by Fukada et al. (2003). The AgNO₃ solution is then oven-dried overnight. N and O isotope analysis will be achieved by combustion and cryogenic separation on an isotope-ratio mass spectrophotometer in the Geosciences Department at the University of Arizona. This sampling will be done quarterly for 2 years.

The results will be used to calculate 1) nitrate decrease as a function of migration distance of the plume front; 2) the rate of decrease that can be attributed to denitrification, using the δ¹⁸O-NO₃ and δ¹⁵N-NO₃ values; and 3) the amount of the decrease that can be attributed to dilution (the difference between 1 and 2).

### 6.6.6 Monitor and Model Plume Dynamics

Work under this task will focus mostly on the collection of data that can be used to both confirm and gauge the significance of natural attenuation processes at the site. These data will be used to construct relatively simple models for the purpose of approximately quantifying contaminant loading and attenuation capacity. The largest natural attenuation impact is likely to be observed with nitrate because this constituent can not only exhibit decreases in concentration due to physical processes, but can also undergo biologically mediated mass reduction via denitrification and phytoremediation. In contrast, any observed decreases in concentration of sulfate downgradient of the disposal cell will probably reflect the effects primarily of dilution and dispersion.

The local ground water system’s capacity for denitrification will be evaluated by tracking several biochemical indicators both upgradient and downgradient of the disposal cell. Several locations downgradient of the cell will be sampled so that the variation of denitrification processes with plume length can be deciphered. In addition to measuring dissolved nitrate levels, the following will be monitored: (1) concentrations of dissolved nitrogen (N₂), nitrite (NO₂⁻), total Kjeldahl nitrogen (TKN), and ammonium (NH₄⁺); (2) dissolved organic carbon (DOC), chemical oxygen demand (COD), and biochemical oxygen demand (BOD); (3) dissolved oxygen (DO), and oxidation-reduction potential (ORP); and (4) the presence and relative abundance of denitrifying bacteria (denitrifiers).

Indicators considered optimal for denitrification include the presence of dissolved organic carbon sources (e.g., humic acid), anaerobic aquifer conditions (DO concentrations < 1 mg/L), and the presence of denitrifiers. If denitrifiers are identified upgradient of the disposal cell, it is possible that biological transformation of nitrate has evolved in the local ground water system as a result of natural processes. Observation of dissolved NO₂⁻, regardless of location, could be indicative of a system in which denitrifying microbial populations readily transform nitrate into the intermediate product nitrite but are less efficient in mediating the subsequent breakdown of nitrite to nitrogen gas.
As with nitrate, dissolved sulfate concentrations will be measured in wells upgradient of the disposal cell and at multiple downgradient locations. In the event that relatively large concentrations of this constituent are measured at upgradient locations, the potential for natural dissolution of sulfate from gypsiferous formations in the region will be examined.

Both analytical transport solutions and relatively simple numerical models will be considered so that rates of mass loading and attenuation can be approximated. The analytical simulator developed by Domenico (1985) will be applied to match observed concentrations of those constituents whose attenuation is virtually all attributed to dispersion and dilution. If organic carbon sources capable of driving denitrification are identified, the U.S. Geological Survey numerical code BIOMOC (Essaid and Bekins 1997) will be used to develop a vertical section model of nitrate transport along the plume centerline. In addition to allowing for multiple dissolved species, including dissolved organic carbon, this finite difference simulator has the capacity to account for vertical heterogeneity and the effects of phreatophyte uptake of nitrate downgradient of the disposal cell. More detailed models capable of simulating three-dimensional flow, transport, and biodegradation (e.g., RT3D [Clement 1995]; SEAM3D [Waddill and Widdowson 2000]) will only be used if continued monitoring indicates that denitrification processes cannot be adequately quantified using a vertical section representation of the site.
7.0 Enhanced Passive Remediation of Ground Water

Enhanced passive remediation (EPR), also called enhanced natural attenuation, will be implemented if it cannot be shown with a high level of certainty that total capacity of natural attenuation processes (Section 6.0) is capable of attaining ground water remediation objectives. EPR pilot studies will focus on enhancements that are sustainable; that do not require long-term, continuous intervention. The goal of these studies is to acquire the data necessary to quantify at a field scale how much the enhancements—interventions—will raise the attenuation capacity above what occurs naturally (without intervention). For example, small-scale preliminary investigation conducted at Monument Valley between 1998 and 2001 suggests that phytoremediation, removal of water and nitrate from the alluvial aquifer by native desert phreatophytes, can be increased significantly by planting denuded areas and managing grazing over the nitrate plume.

This chapter provides 1) a summary of the status of enhanced ground water phytoremediation studies at Monument Valley, 2) background information on bioremediation enhancements, 3) a discussion of enhanced chemical stabilization, 4) objectives and tasks for a large-scale pilot study of enhanced phytoremediation, and 5) sequential studies to first screen and then demonstrate bioremediation enhancements.

7.1 Status of Enhanced Phytoremediation

Section 6.1 summarized a small-scale study showing that existing populations of two native, phreatophytic shrubs, Sarcobatus vermiculatus (black greasewood) and Atriplex canescens (fourwing saltbush), are most likely rooted into and extracting water and nitrate from the alluvial aquifer. A companion study, summarized below, evaluated the capacity of enhancements to increase water and nitrate extraction rates. Rangeland vegetation in the region, including S. vermiculatus and A. canescens populations overlying the plume, is in poor condition as a consequence of decades of heavy grazing by livestock (DOE 2002). Furthermore, native phreatophyte populations overlying an area of the plume with the highest nitrate levels were bladed in the early 1990s as part of the cleanup of tailings piles and other residual radioactive materials (Section 2.2).

The objectives of the enhancement study were as follows:

- Evaluate effects of protecting individual S. vermiculatus and A. canescens shrubs from grazing on rates of water and nitrate uptake from the alluvial aquifer.
- Determine if S. vermiculatus and A. canescens transplants can be rapidly established with irrigation in denuded areas, and then survive and flourish without further intervention.
- Estimate water and nitrate extraction rates for transplanted S. vermiculatus and A. canescens.

7.1.1 Restricting Grazing to Enhance Phytoremediation

A preliminary study of the effects of restricting grazing on phytoremediation of the nitrate plume (McKeon et al. 2004a) was conducted using grazing exclosures constructed around 24 plant pairs (12 A. canescens and 12 S. vermiculatus) of similar initial size (1–3 m$^3$ per plant). One plant of each pair was enclosed within a 2 by 2 by 1.5 m chain link fence for protection from grazing while the other plant was left unprotected. Canopy volume, ground cover area, and biomass...
density were measured for each shrub in the study when exclosures were constructed in June 1998, and then annually in September or October for 3 consecutive years. Plants were subsampled for biomass harvesting. Tissue samples were collected of all new, annual growth of leaves, small stems, and often seeds. The dry weights of the samples were measured, and representative portions of the samples were analyzed for total nitrogen content using the Kjeldahl method (Tabatai 1996). An ammonia ion selective electrode was used to determine ammonia nitrogen values, and a nitrate ion electrode was used to determine nitrate nitrogen values (American Public Health Association 1998).

Initially the canopy volumes of shrubs inside and outside grazing exclosures were similar. During the three growing seasons, canopy volumes of shrubs inside exclosures increased by 2–4 times the starting values, whereas the size of grazed plants outside the exclosures remained unchanged (Figure 7–1). Differences in biomass per m² of canopy ground cover were not significant between grazed and ungrazed plants of either species, however, the net annual productivity of ungrazed plants was approximately 1.5 times that of the grazed plants. Grazed plants had significantly ($P<0.05$) lower total N content than ungrazed plants, and *S. vermiculatus* had higher total N content than *A. canescens* (Figure 7–1). Ungrazed plants had higher levels of nitrate-N than grazed plants ($P<0.05$). Plants that were excluded from grazing also contained significantly higher ($P<0.05$) concentrations of total sulfur than grazed plants (Table 7–2).

Table 7–1. Total nitrogen and nitrate on a dry weight basis of *A. canescens* and *S. vermiculatus* leaves under ungrazed and grazed conditions for plants harvested in 2000. Two-way ANOVA with plant type and grazing condition as dependent variable showed that *S. vermiculatus* had significantly ($P<0.05$) higher nitrogen content than *A. canescens*; *S. vermiculatus* plants under ungrazed conditions had significantly higher nitrogen than under grazed conditions. Nitrate results were not different by plant type ($P>0.05$) but ungrazed plants had significantly greater nitrate-N than grazed plants. Table shows means and (standard errors).

<table>
<thead>
<tr>
<th>Plant</th>
<th>Nitrogen (%)</th>
<th>Nitrate (mg N kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>A. canescens</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ungrazed</td>
<td>2.14 (0.12)</td>
<td>727 (95)</td>
</tr>
<tr>
<td>Grazed</td>
<td>2.05 (0.15)</td>
<td>590 (69)</td>
</tr>
<tr>
<td><em>S. vermiculatus</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ungrazed</td>
<td>2.76 (0.17)</td>
<td>951 (139)</td>
</tr>
<tr>
<td>Grazed</td>
<td>2.26 (0.08)</td>
<td>558 (60)</td>
</tr>
</tbody>
</table>

The results show that productivity and canopy volume of both *A. canescens* and *S. vermiculatus* increases markedly when grazing was eliminated. This rapid growth in response to protection from grazing is further evidence that the plants are rooted into the alluvial aquifer (see Section 6.1.2), as a rapid growth response would not be expected if plants were rooted into the predominantly dry soil over the plume. Nitrogen content of the plant tissues also increased slightly and nitrate-N increased markedly in response to protection. These results corroborate other studies of grazing effects on the Navajo Nation. Brotherson et al. (1983) conducted a fence-line contrast study on the effects of grazing at the nearby Navajo National Monument.
Total plant cover was 18 percent in the grazed area and 33 percent in the ungrazed area of their site. Lash et al. (1999) compared grazed and ungrazed sites in Tuba City, Arizona, at another former uranium mill site. Grazing had been excluded for 10 years inside a fenced portion of the range. Plant cover was 25 percent in the ungrazed part of the site and 5 percent in the grazed area.

7.1.2 Revegetation to Enhance Phytoremediation

Exclosure plots were also used to determine if *S. vermiculatus* and *A. canescens* seedlings would establish and survive if transplanted in denuded areas over the plume. Seeds of both species, collected near Tuba City, Arizona, were germinated in a greenhouse. *A. canescens* ssp. *angustifolia* seed was collected. Although less common than subspecies *occidentalis* in the Tuba City and Monument Valley areas (Glenn and Brown 1998; Glenn et al. 1998), *A. canescens* ssp. *angustifolia* exhibits better survival and growth when used in revegetation projects (Glenn et al. 2001). In June 1998, ten plants of each species were transplanted into six exclosures identical to those placed around mature plants (see Section 7.1.1). The exclosures were located over the plume near well 606 (3 exclosures) and well 765 (3 exclosures; Figure 7–2). Plants were spaced 0.5 m apart in rows of five (two rows per species). Plants were irrigated once each week with 8 liters of clean ground water from June to October 1998.

![Figure 7–1. Canopy volumes for *A. canescens* (ATCA) and *S. vermiculatus* (SAVE) plants either grazed or protected from grazing during 3 growing seasons at the Monument Valley site. Each data point is the mean of 12 plants; error bars show standard errors of the mean. Date 1 is June 1998, Date 2 is October 1998, Date 3 is March 1999, and Date 4 is September 2000.](image-url)
Transplants of *A. canescens* and *S. vermiculatus* were approximately 5 to 10 cm in height when planted in exclosures in June 1998. Transplants were irrigated only to October 1998 during the first growing season. By May 1999 *A. canescens* transplants had a 90 percent survival rate and reached an average height of 65.4 cm (SE = 2.6), whereas *S. vermiculatus* had only a 45 percent survival rate and reached a mean height of only 15.4 cm (SE = 3.7). By October 2001 *A. canescens* dominated and individual plants intergrew to completely fill each exclosure (4 m²),
reaching heights exceeding 2 m (Figure 7–3). Livestock grazed the plant stems that grew out through the exclosure fencing, and plants took on the same dimensions as the exclosures. By contrast, *S. vermiculatus* transplants remained small and most did not survive to the third growing season.

![Figure 7–3. Exclosures near Well 606 planted with Atriplex canescens and Sarcobatus vermiculatus in June 1998 and irrigated from June to October 1998. This photo was taken in July 2002 during an extended drought.](image)

The *A. canescens* transplants appeared to be rooted into the plume by the end of the third growing season, based on stable isotope results (see Section 6.1.1). *S. vermiculatus*, on the other hand, proved to be more difficult to establish as transplants when irrigated for one growing season. On the basis of the results of this preliminary study, *A. canescens*ssp. *angustifolia* appears to be a good candidate for revegetation of the bare zone and for enhancing phytoremediation of the plume.

### 7.1.3 Preliminary Estimate of Enhanced Phytoremediation Capacity

Section 6.1.3 describes preliminary estimates of water and nitrate uptake rates and clean-up time projections for the *existing* vegetation overlying the plume. Native phreatophyte populations are in poor condition because of heavy grazing and the disturbance during the surface remediation. Mass balance estimates were extrapolated from measured nitrogen levels in soils and in the aquifer and from estimates of rates of uptake into plant tissues.

Similar preliminary estimates were developed for native phreatophytes protected from grazing. Plume mass data ($2 \times 10^6$ m$^3$ of water and $3.5 \times 10^5$ kg of nitrate-N; see Section 6.1.3) was divided by annual nitrogen and water extraction rates were estimated for an enhanced phytoremediation scenario (inside the grazing exclosures). In this scenario, a combination of grazing management and revegetation are expected to increase cover and productivity of phreatophyte populations overlying the plume. The 130 ha site would consist of a 100 ha parcel dominated by *A. canescens* at 25 percent cover and a 30 ha parcel dominated by *S. vermiculatus* at 40 percent. Cover values are based on Brotherson et al. (1983) and Lash et al. (1999) for these
species as measured in ungrazed populations within the DOE fenceline (McKeon et al. 2004a). As for the existing vegetation scenario (Section 6.1.3), water extraction rates by plants were estimated on the basis of regression equations between ET and percent cover in Steinwand et al. (2001).

For the enhanced phytoremediation scenario, the preliminary estimate of nitrogen extraction rate increases from 25 kg ha\(^{-1}\) yr\(^{-1}\) to 181 kg ha\(^{-1}\) yr\(^{-1}\). The extrapolated cleanup time drops to 15 years compared to 108 years for existing conditions. ET rates would increase to 250 mm yr\(^{-1}\) and 720 mm yr\(^{-1}\), for \textit{A. canescens} and \textit{S. vermiculatus}, respectively, from rates of 50 mm yr\(^{-1}\) and 270 mm yr\(^{-1}\) for existing conditions, and ET of one plume volume of water would take only 4.3 years compared to 15 years for existing conditions.

Based on the average total sulfur values for ungrazed and grazed plants (Table 7–1), the plant accumulation rate of sulfate can be determined based on the mean dry weight of ungrazed \textit{A. canescens} (849 g/m\(^2\)) and \textit{S. vermiculatus} (1,010 g/m\(^2\)) from the exclosure study. If current range conditions were enhanced to 35 percent cover, \textit{A. canescens} is estimated to extract about 32.7 kg SO\(_4\) ha\(^{-1}\) and the \textit{S. vermiculatus} estimate is 31.1 kg SO\(_4\) ha\(^{-1}\).

These preliminary calculations show that an expanded and protected phreatophyte community might have a significant effect on the site nitrate, sulfate and water balance. At present, the alluvial aquifer is receiving recharge at an unknown rate from several sources and the contamination plume is moving slowly downgradient from the site (DOE 1999). Hence, extraction of water by the current vegetation cover may not match recharge. With grazing exclusion and revegetation of denuded areas, projected ET rates are 2 to 3 times higher than annual precipitation, so it is possible that the additional water would be withdrawn from the alluvial aquifer (Steinwand et al. 2001). This could help control the further movement of the contamination plume away from the site.

There are many remaining uncertainties in these preliminary projections. For example, the maximum depth at which phreatophytes can extract water from the plume is unknown. Large portions of the plume are likely too deep for plants to access. Also, the proportion of plant nitrogen originating from the plume is still unclear. Finally, rates of water uptake and nitrogen uptake are not necessarily in balance. Water extraction may be faster than nitrate extraction, so nitrate levels in the plume could actually increase as plume water volume decreases.

### 7.2 Evapotranspiration and Enhanced Hydraulic Control

ET is the water lost from a land area due to evaporation of water from the soil surface plus the water lost from transpiring leaf surfaces. ET is an important component of the water balance of the alluvial ground water system. Modeling of the site water balance, ground water flow, and plume migration and attenuation will require estimates of ET for both current and possible future conditions. A first approximation of ET zones, developed from a reconnaissance of vegetation at the site and literature values for ET, was used for a preliminary characterization of the water balance of the alluvial aquifer system (DOE 1999). Because of the poor condition of vegetation due to heavy grazing, ET estimates were much less that the potential ET. Conversely, in deep soils in upland arid ecosystems, ET can account for almost all surface recharge when late-successional vegetation dominates and is healthy. Furthermore, discharge resulting from ET likely exceeds recharge where healthy phreatophyte populations are tapping the alluvial aquifer.
Precipitation over the plume is approximately 160 mm yr\(^{-1}\) (Cooley et al. 1969). Summer rainfall generally occurs as high-intensity, short-duration storms conducive to runoff, while winter precipitation usually occur as low-intensity, longer duration, storms with annual snowfall depths ranging between 250 and 1,000 mm (Cooley et al. 1969). Winter precipitation is more available for infiltration into the soil than summer rain. Stable isotope studies show that the plants at the Monument Valley site mainly utilize deep soil water, including stored winter rain and water from the aquifer, to support ET (McKeon et al. 2004a).

Potential ET (ET\(_{0}\)) at the site is approximately 1,400 mm (DOE 1999). A vigorous plant community of black greasewood and saltbush should be capable of utilizing all the annual precipitation as well as some of the plume water in ET. For example, results from Owens Valley, California, show that natural stands of these plants have ET rates in the range of 270 to 400 mm yr\(^{-1}\) when they have access to ground water, as at the Monument Valley site (Steinwand et al. 2001). However, due to the low plant cover at Monument Valley, an apparent result of heavy grazing pressure, DOE estimated that approximately 40 mm yr\(^{-1}\) of precipitation is available for recharge at the site. Site ET can tip the balance from recharge to discharge depending on the condition of the plant communities. Accurate estimates of ET under different management scenarios are needed to predict the future movement of the plume and to select appropriate remediation scenarios.

Hydraulic control is a remediation scenario that would involve enhancing ET. Hydraulic control can be defined as the use of plants to remove ground water through uptake and consumption in order to contain or control the migration of contaminants (EPA 2000). Growth and ET by black greasewood and saltbush growing over and upgradient of the plume might be enhanced in an effort to slow migration of the plume. Conversely, continued heavy grazing and degradation of phreatophyte stands could increase rates of migration. More accurate estimates of current and potential ET by phreatophytes, and spatial and temporal variability in ET, are needed for input to models of hydraulic control scenarios.

**7.3 Enhanced Bioremediation of Ground Water**

Background information and task descriptions for detecting the presence and possibly estimating rates of microbial denitrification in the alluvial nitrate plume, as a component of natural attenuation, were presented in Sections 6.4 and 6.6.5. This section provides background information on approaches for evaluating denitrification enhancements.

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. There are instances where exogenous microorganisms are added to a contaminated system in order to encourage the degradation of certain contaminants, but 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. Nutrients are fed to contaminated ground water and soil via wells to enhance the natural population of microorganisms.

Enhanced bioremediation techniques have been successfully used to remediate soils and ground water contaminated with fuel, volatile organic compounds (VOCs), semi-volatile organic
compounds (SVOCs), and pesticides. In the case of nitrates and/or sulfates, it is common place to inject an electron donor, such as acetate, ethanol or glucose (Istok et al. 2004; Prieme et al. 2002). Istok et al. (2004) were able to stimulate the complete reduction of nitrate upon the addition of ethanol to a similarly nitrate-contaminated plume within 600 h. Here, they injected ground water mixed with either 400 mM ethanol or glucose at different rates into a number of nitrate-contaminated wells using a siphon. Following injection, they monitored the same wells by periodic sampling over 40 days. Nitrate reduction occurred at a maximum rate of 3 mM h\(^{-1}\) when ethanol and glucose was added at a rate of 7.6 and 0.94 mM h\(^{-1}\), respectively.

7.4 Enhanced Chemical Stabilization

7.4.1 Enhancing Nitrate Removal Using Zero-Valent Iron and Other Abiotic Reductants: Summary of Current Research

Dissolved nitrate concentrations usually decrease as ground water makes contact with granular iron, sometimes referred to as zero-valent iron (ZVI). ZVI has been used extensively in the last decade in permeable reactive barriers (PRBs) to reductively dehalogenate chlorinated solvents (Gavaskar et al. 1998) or to immobilize uranium or chromium (Morrison et al. 2002a). PRBs are zones of reactive materials, such as ZVI, placed in the subsurface that decontaminate ground water flowing through them. Although most of the research and testing of reductive metals has focused on ZVI, nitrate removal has also been shown to occur via pyrite oxidation; Engesgaard and Kipp (1992) provide an example related to a redox front at a site in Denmark. Another reductant, sodium dithionite, has been used to immobilize chromium in the subsurface (Vermeul et al. 2002). Dithionite is used to reduce immobile iron in the aquifer which in turn reduces chromium and other redox-sensitive contaminants. Dithionite has not been tested for nitrate reduction. An advantage of dithionite is that it can be emplaced deep into an aquifer by injection.

Changes in nitrate concentrations contacting ZVI were monitored in a variety of PRBs installed at a uranium mill tailings disposal site near Durango, Colorado (Morrison et al. 2002b). The concentrations of nitrate in the ground water at this site are relatively low but the results indicate that nitrate concentrations often decrease in the presence of ZVI (Table 7–3). However, in one case, the nitrate concentrations increased. Ammonia concentration gradients corresponding to the samples shown in Table 7–3 were also variable with ammonia increasing across the PRB in most cases (Morrison et al. 2002b). However, the ammonia inventory was insufficient to balance the nitrogen due to nitrate decay. Nitrate concentrations in effluent from one of the Durango PRBs, decreased gradually over a period of several months, after startup suggesting that microbial processes may have been responsible for nitrate removal.

Table 7–3. Removal of Nitrate by ZVI in PRBs at Durango, Colorado. From Morrison et al. (2002b).

<table>
<thead>
<tr>
<th>Form of ZVI</th>
<th>Type of System</th>
<th>Influent (mg/L)</th>
<th>Effluent (mg/L)</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel Wool</td>
<td>Leach Field</td>
<td>1.83</td>
<td>0.123</td>
<td>-93.3</td>
</tr>
<tr>
<td>Foam Blocks</td>
<td>Baffled Tank</td>
<td>0.415</td>
<td>0.0727</td>
<td>-82.5</td>
</tr>
<tr>
<td>Steel Wool</td>
<td>Baffled Tank</td>
<td>0.232</td>
<td>0.822</td>
<td>+354</td>
</tr>
<tr>
<td>Granular</td>
<td>Baffled Tank</td>
<td>1.73</td>
<td>1.37</td>
<td>-20.8</td>
</tr>
</tbody>
</table>
In laboratory column tests using contaminated ground water from a former uranium milling site near Rifle, Colorado, nitrate concentrations decreased from 9 mg/L in the influent to about 2.5 mg/L in the effluents (DOE 2000b). In this same column test, effluent ammonia concentrations were nearly the same as influent concentration suggesting that reduction of nitrate to ammonia did not occur.

Field column tests using five different brands of ZVI were conducted at a former uranium milling site near Monticello, Utah (DOE 1998). Influent nitrate concentrations were about 16 to 18 mg/L. All five types of ZVI significantly reduced the nitrate concentrations with effluent concentrations ranging from nearly 0 to about 6 mg/L. Another column test was conducted, at the same field site, in which samples were collected from a series of sampling ports positioned at equal intervals along the column (DOE 1998). The influent nitrate concentration was 13 mg/L. Concentrations decreased to less than detection after passing through 1 ft of the ZVI.

A pilot-scale PRB using ZVI was installed at DOE’s Oak Ridge site in 1997 (Gu et al. 1998; Gu et al. 2002). In addition to the removal of uranium and technicium, the Oak Ridge PRB removed nitrate to detection limits from highly contaminated (typically 20 to 150 mg/L and up to 1,000 mg/L) ground water. Based on tests in which peat and/or denitrifying bacteria were added to the ZVI, these authors attribute some of the nitrate loss to biotic denitrification, but believe that direct abiotic reduction of nitrate may also occur. In tests including both peat and ZVI, about 25 percent of the nitrate was converted to ammonia and a large percentage may have converted to N₂ or N₂O gases.

From the examples provided in the previous paragraphs, it is apparent that ZVI will cause dissolved nitrate concentrations to decrease significantly, although the results have been variable. Ammonia appears to be a reaction product, but in some cases its concentration has been low. The mechanism of nitrate disappearance in ZVI reactors is not well understood. As suggested above, microbial denitrifiers may play a role, although some tests indicate almost immediate and rapid disappearance that is not likely to be caused by microbes. In batch-type laboratory tests of nitrate removal at various pH values and various concentrations of nitrate, Huang et al. (1998) concluded that nitrate removal is abiotic, probably caused by electron transfer directly at the ZVI surface or by hydrogen gas released during ZVI corrosion. They also determined that all nitrate was reduced to ammonia.

7.4.2 Bench-Scale Testing and Implementation

Laboratory or field-based column tests would be conducted to determine the effectiveness and reaction rates for denitrification using ZVI, dithionite, and other potential reductants (e.g., ferrous iron, sodium sulfide). Influent to the columns would be site ground water with high nitrate concentrations. Nitrate, nitrite, ammonia, and redox state would be carefully monitored throughout the tests. Short term (hours to days) tests can be used to screen the effectiveness of various reactive media. Longer term (weeks) tests are needed to evaluate the long-term performance.

For enhanced passive remediation, ZVI must be emplaced in the subsurface. Several means of emplacing ZVI have been field tested, many of which are described in Filtz and Mitchell (1995). The most common method is to excavate a trench and fill it with ZVI. Cost-effective excavation methods are probably only available for depths of less than 50 ft. The nitrate contamination at
Monument Valley is much deeper (up to about 100 ft) and therefore, excavation is probably not practical. Alternative construction methods that are capable of deeper emplacement include jet grouting (USAF 1999, 2002), micro-scale ZVI injection (personnel communication with Kirk Cantrell, Pacific Northwest National Laboratory), and hydrofracing (Hocking 1998). Other reductants, such as dithionite (Vermeul 2002) or sodium sulfide are soluble in water and can be injected into an aquifer.

7.5 Goals and Objectives

The goals of enhanced passive remediation pilot studies are to determine if phytoremediation and bioremediation enhancements are feasible and sustainable, and, if the total natural attenuation capacity (Section 6.0) is found to be inadequate, then to determine whether enhancements are likely to achieve remediation requirements in a reasonable time. If enhanced passive remediation approaches are found to be inadequate, then active remediation (Section 8.0) may be required. Specific objectives follow:

Establish Large-Scale Planting of Phreatophytes Rooted Into the Plume

Phreatophyte transplants were successfully established, rooted into the plume, and grew vigorously for several years in small exclosure plots. The current pilot study will determine if comparable results are attainable with a large-scale irrigated planting.

Estimate Water, Nitrate, and Sulfate Extraction Rates for Enhanced Phytoremediation

The small exclosure studies of ungrazed and planted phreatophytes demonstrated methods for estimating water and nitrate uptake rates; however, exclosures were too small to extrapolate water use and nitrate uptake to a large-scale phytoremediation. In the current pilot study, water use and nitrate uptake will be estimated in test plots that are large enough to be representative of the spacing and growth rates of plants as would occur in a full-scale, irrigated planting. Rates of sulfate removal from the alluvial aquifer by phreatophytes will also be evaluated.

Evaluate Hydraulic Control of Plume Migration Using Phreatophytes

Nitrate concentrations in the outer, northern reaches of the plume have gradually increased since 1985 indicating that more highly contaminated water from the centroid of the plume is moving downgradient. Results of the preliminary phytoremediation enhancement studies indicated that use of alluvial aquifer water by planted and protected phreatophyte populations could slow further downgradient movement of the plume. Improved estimates of water use by phreatophytes grown in large-scale test plots, combined with ground water modeling and monitoring (see Section 6.6.6), will be used to evaluate hydraulic controls of plume migration.

Conduct Enhanced Bioremediation Treatability Study

The role of natural microbial denitrification in the nitrate plume will be evaluated using stable isotope methods as part of the natural attenuation study (see Section 6.6.5). Enhancement of ground water denitrification by injecting carbon sources of electron donors has been successful at other sites (see Section 7.2). A bench scale treatability study will be conducted using alluvial aquifer water from the Monument Valley site to test the microbial response to different carbon sources.
Evaluate In-Situ Injection Methods for Bioremediation and Monitor Performance

If the treatability studies identify a carbon source and injection rate or mass that would likely enhance denitrification in the alluvial aquifer, the objective of the next phase would be to investigate and demonstrate in-situ injection methods, and then monitor rates and spatial scales of the microbial response.

7.6 Task Descriptions

This section presents the pilot study tasks and methods designed to 1) demonstrate and evaluate large-scale protection and planting of native phreatophytes for enhanced phytoremediation of the alluvial aquifer, 2) evaluate various bioremediation enhancements on a bench scale, and then 3) test the feasibility and monitor the performance of a large-scale in-situ bioremediation enhancement if applicable.

7.6.1 Install Large-Scale Grazing Protection and Revegetation Plots

Two 50 m by 50 m plots within existing A. canescens and S. vermiculatus stands overlying the plume will be fenced to protect plants from grazing (Figure 7–4). This will promote an increase in nitrate extraction from the plume water by these phreatophytes. Plots will be established in locations where the potential benefits of grazing protection are greatest such as 1) areas with relatively high-density A. canescens and S. vermiculatus stands as delineated in the preliminary studies, 2) areas where roots are tapping the aquifer, and 3) areas where nitrate concentrations in the alluvial aquifer are relatively high.

Two 50 m by 50 m plots will also be installed for the large-scale transplanting demonstration (Figure 7–4). One plot will be located in the denuded area where A. canescens transplanted in the small exclosures established, grew vigorously, and were shown to be rooted in the plume (see Section 7.1.2). The second transplant plot will be installed in area that spans a range of depths to ground water up to the maximum depth phreatophytes are likely to root into the alluvial aquifer (see Section 6.6.1). Candidate locations are the western parts of the denuded area and an area where existing A. canescens and S. vermiculatus stands are sparse and overgrazed. Plant materials in the plots will consist of a 3:1 ratio of A. canescens ssp. Angustifolia (see 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 will be grown at the University of Arizona Environmental Research Laboratory for 12 weeks and transplanted in April. 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.

7.6.2 Design and Install an Irrigation System for Revegetation Plots

An automated irrigation system will be designed for the revegetation plots. Well 618 will be used as the water source. A topographic map and profile of the supply line alignment will be required to design the piping and valves to achieve the proper hydraulics. A layout of the planting and plant spacing, irrigation rate, irrigation frequency will be used to design irrigation zones and the controller for automation.
Figure 7–4. Proposed locations of grazing protection plots, phytoremediation transplant plots, and the land farming pilot study (see Section 8.4.1)
7.6.3 Monitor Plant Growth and Nitrate and Sulfate Uptake Rates

Within each 50 m by 50 m plot, survival, canopy volume, canopy cover, and dry-weight biomass of each species present will be measured, and then the expansion or contraction of plant abundance will be monitored annually at the end of the growing season. Plant cover will initially be measured by aerial photography, providing a complete census of the plants in each plot. A multiband digital camera with visible and near-infrared (NIR) bands will be used, so that light absorption can be compared among canopies and treatments using the Normalized Difference Vegetation Index (NDVI). NDVI is calculated from the visible and NIR light reflected by vegetation. Healthy vegetation absorbs most of the visible light that hits it, and reflects a large portion of the near-infrared light. Unhealthy or sparse vegetation reflects more visible light and less near-infrared light. Therefore, over grazed plots will likely have very little difference in the intensity of visible and near-infrared wavelengths reflected, and protected plots will likely have much more reflected radiation in near-infrared wavelengths than in visible wavelengths. See Section 7.6.4 for more information on measuring NDVI.

Survival of shrubs will be evaluated by census. Canopy volume and cover of shrubs, both existing plants and transplants in the plots, will also be individually measured. As with the subpile planting (Section 5.4.6) and the land farm planting (Section 8.4.7), 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 \( \frac{2}{3}\pi abc \), and canopy area will be estimated using the formula for an ellipsoid \( \pi bc \). 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.

7.6.4 Estimate Evapotranspiration for Current and Possible Future Remediation Scenarios

Accurate estimates of ET under different management scenarios are needed to predict the future movement of the plume and to evaluate enhanced hydraulic controls (see Section 7.2). The different scenarios include: 1) maintain the vegetation community in its current state; 2) protect some of the natural plant community from grazing; and 3) create protected plots of planted saltbush and black greasewood on currently bare soil areas. ET data will be collected under each of these scenarios. ET measurements will be carried out in natural stands of black greasewood and fourwing saltbush and in the 50 m exclosure plots described in Section 7.6.1.

A combination of two non-intrusive methods, sap flow measurements and eddy covariance measurements, will be used to estimate site ET. Measurements will be made only in natural stands of plants during the first year because the planted plots will not be sufficiently developed to have significant ET rates. ET will be measured over three 2-week periods at the beginning...
(April), middle (July) and end (September) of the growing season. Sufficient stems of black greasewood and fourwing saltbush will be gauged to determine ET with a standard error of estimate of 15 percent. An eddy covariance tower will be set up in the middle of each plot with the instrument station placed 1.5 m over the canopy. ET measurements will be made for 1 week each in a black greasewood community and in a saltbush community over the plume. During the June measurement period, aerial photography using a visible-band camera and a DyCam red-NIR camera will be conducted over the plume area, to provide data for scaling ET from single plots to the entire site.

Sap flow gauges (Rana and Katerji 2000) attach to plant stems and introduce either a pulse of heat or a steady source of heat into the stem. The rate of water flow through the stem is estimated either by the velocity of water, measured by the time needed for a heat pulse to travel between two thermocouples, or by the energy balance of a stem section to which a constant source of heat is supplied. Sap flow gauges provide accurate ET estimates for individual branches or main stems of plants (Nagler et al. 2003). Results can be scaled up to whole plants or stands of plants by the stem census method, or by relating leaf area per stem to site leaf area index (LAI). This scaling procedure is especially relevant to the Monument Valley site where plants are separated from each other and only a few species dominate the community. Steinwand et al. (2001) developed relationships between percent ground cover, LAI, daily and annual transpiration rates, and potential ET for _S. vericulatus_, _Atriplex lentiformis_ and _Chrysothamnus nauseosus_, validated by direct measurement of ET for each shrub type in Owens Valley. This approach would also be appropriate to the Monument Valley site using sap flow data.

The eddy covariance method determines λE (the latent heat of evaporation of water) and therefore ET directly (Rana and Katerji 2000). Eddies are rapidly ascending and descending currents of air above a canopy that exchange heat and water vapor between the land surface and the atmosphere. The method calculates a covariance between instantaneous fluctuations in vertical wind speed, air temperature and water vapor density, which are measured at high frequency (0.1 sec) at a point above the canopy. The net flux of dry air is zero, but there can be a net flux of sensible heat towards the surface if downward eddies carry, on average, air at higher temperature than ascending eddies. A net flux of water vapor out of the canopy is measured if ascending eddies carry more water vapor on average than descending eddies. Similarly, a flux of carbon dioxide in or out of the canopy can be demonstrated due to canopy photosynthesis or respiration. Eddy covariance towers provide data over several thousand square meters of surface, therefore they do not have to be scaled up as do the sap flow data. In practice, sap flow and eddy covariance methods are often combined to provide a complete picture of ET at a site, from the individual plant to the stand levels of measurement (Scott et al. 2003).

Once accurate ET data is obtained, it will be scaled to the entire site. This will be accomplished by surveying the site plant community with remote sensing techniques. Aerial photographs showing individual plants over the whole site will be acquired using a multiband camera that has red, blue and NIR bands. The pixels will be converted to NDVI values, which exaggerates the difference between the red and NIR reflectance properties of leaves, to provide an estimate of leaf area index (needed for modeling), absorbed photosynthetically active radiation, and fractional vegetation cover over a site (Nagler et al. 2004). Numerous studies have shown a close relationship between vegetation indices and ground estimates of ET (e.g., Kustas and Norman 1996). Once a relationship between ET and NDVI is established at a site, ET could be estimated by using seasonal satellite images such as Landsat. This would be a long-term monitoring goal for the Monument Valley site.
7.6.5 Conduct Soil Column Study of Carbon Sources

Aquifer sediment samples will be taken from wells having high (500-1,000 ppm) nitrate concentrations (see Section 6.6.2 for sample collection). The samples will be air-dried and packed into a stainless steel column (dimensions: 2 cm I.D. × 7 cm length) to achieve a bulk density approximating that of the aquifer material (1.45 g cm⁻³). The column will be connected via tubing to a peristaltic pump and a reservoir containing a sterile ground water solution. The solution in the reservoir will be pumped through the column at an approximate flow rate of 0.007 ml/min. After saturating the soil for 2 days, the reservoir containing artificial ground water will be supplemented with 500 ppm nitrate and one of three different carbon sources (glucose, acetate, and ethanol) at three different injection rates or input masses. The column will be flushed with ground water between rate treatments but repacked with fresh sediment for each carbon source.

Nitrate breakthrough will be monitored in the effluent draining from the column using a fraction collector for each of the different treatments. Each sample collected will be analyzed for nitrate and possibly the carbon source. This procedure will be duplicated for each treatment for a total of 18 breakthrough curves. Moment analysis of the breakthrough curves will generate information regarding the total mass of nitrate recovered for each treatment. These data will be used to identify the optimal carbon source and concentration to use in the in-situ, well-injection feasibility study (Section 7.6.6).

7.6.6 Demonstrate and Monitor In-Situ Carbon Source Injection

Once the electron donor or carbon source conditions have been identified using the column studies (Section 7.4.6), the feasibility of injecting an electron donor into the contaminated plume will be investigated. The predetermined carbon source will be injected into wells having a known and high (500-1,000 ppm) concentration of nitrate. Similar to the procedure outlined in Istok et al. 2004, a solution of ground water of known nitrate concentration, carbon source, and bromide will be injected into four test wells using a siphon for the length of time required to achieve the desired concentration of the carbon source. Bromide (Br⁻) is a conservative tracer and does not undergo transformation. Similarly, four other test wells will be selected as controls receiving only tracer and ground water. Immediately following the injection, samples will be collected daily from the same wells for up to a month. Samples will be analyzed for NO₃⁻ and Br⁻ and possibly the carbon source. By comparing the relative concentration of NO₃⁻ to that of Br⁻ in all wells, we can determine if the carbon source is effective at enhancing the reduction of nitrate. Because the Monument Valley plume is so expansive, it may be necessary to install additional monitoring wells in rows extending downgradient from the carbon-injection port. This strategy should allow for the determination of the true spatial extent of treatment effects.
End of current text
8.0 Active Ground Water Remediation: Land Farming

Land farming was selected as the most feasible and efficient active remedy for nitrate contamination in the alluvial aquifer (DOE 2000a, DOE 2002). Land farming will be considered if the more passive alternatives presented above, MNA and EPR, are found to be inadequate. Land farming is a phytoremediation technique that applies information that has been known for years in agriculture and range science to solving an environmental problem. Ideally, the farm will serve several functions in the disturbed Monument Valley ecosystem: (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.

As a form of active phytoremediation, 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.

8.1 Feasibility of the Land Farming Alternative

The feasibility of recovering nitrogen from the alluvial aquifer for a phytoremediation farming operation rests on several issues:

- rangeland ecology and management
- suitability of land and water for irrigation,
- choice, establishment, and value of cropping systems,
- water and cultural requirements of crops,
- nitrate uptake rates and toxicity,
- fate and toxicity of sulfate and other constituents in the irrigation water, and
- irrigation management to prevent the return of nitrate and sulfate to the aquifer.

8.1.1 Range and Revegetation Management

A phytoremediation farm could be managed to improve the condition of rangeland ecology in the area. The current poor range condition, as evidenced by the dominance of exotic grasses and forbs in the plant community and the lack of recruitment of native forage species, can be attributed to a long history of heavy grazing. The irrigated farm would be located in an area just north of the former millsite fenceline that was bladed during the surface remediation. The current vegetation consists of weedy plants with virtually no forage value. A high-yield seed, hay, or forage crop could improve the value of the disturbed land and, assuming no change in stocking rates, could provide enough fodder to reduce grazing pressures and give the plant ecology of surrounding rangelands a chance to recover. After irrigation ceases, a sparse community of native species would persist, satisfying a DOE goal to not only reclaim but to improve rangeland condition in areas disturbed by remediation activities.
8.1.2 Land Suitability for Irrigation

Classification of irrigation suitability in arid regions considers soil texture, soil depth, soil water retention, soil permeability, soil chemistry (salinity, sodicity, and alkalinity), percent coarse fragments, and topography. Soils in the remediated area at Monument Valley range from a loamy sand, with about 70 percent fine sand, 25 percent silt, and less than 5 percent clay, to a sand with greater than 90 percent fine sand, less than 5 percent silt, and virtually no clay (DOE 1998; Section 4.6.2). Given this range of soil textures, the field capacity should fall between about 7 and 15 percent volumetric water content (e.g., Brady and Weil 2001). The permeability of these soils averages about $1.0 \times 10^{-4}$ cm/s (DOE 1998; Section 4.6.1). These soils are deep, have very few coarse fragments, and slopes do not exceed 8 percent. Salinization would not be expected for these deep, coarse-textured soils under normal irrigation practices.

Overall, based on an arable land classification system used by the Navajo Nation and the U.S. Bureau of Indian Affairs (Table 8–1), the soils in the remediated areas do not fall in the highest class, primarily because of the sand texture, but are suitable for irrigation of a seed or forage crop (e.g., Glenn et al. 1998). The U.S. Department of Agriculture recommends a check for excessive concentrations of boron, heavy metals, and pH. Baseline values of these parameters will be obtained during the initial stages of the pilot study.

8.1.3 Cropping System

The goal of land farming is to convert as much nitrate in the plume water to plant nitrogen as efficiently as possible, while providing useful crop materials, restoring vegetation to the disturbed areas over the plume, and enhancing denitrification. DOE and the University of Arizona have conducted a series of greenhouse studies and field studies over the past 5 years to evaluate types of crops and cropping systems that 1) are adapted to the harsh desert environment, 2) would be a worthwhile product, 3) could be readily converted to productive rangeland once ground water remediation is complete, and 4) do not concentrate nitrogen or other ground water constituent so as to pose a risk to human health and the environment.

Harvesting, grazing, and seed production are practical and productive alternatives for removing nitrogen from a phytoremediation farm at the Monument Valley site. An alfalfa farm is an example of a harvesting alternative. Alfalfa would be cut four to five times during summer at Monument Valley, dried, and baled. The baled material would be tested by proximate analysis for nutritional content and, in addition, nitrate and sulfate levels could be determined. The baled hay would be provided to the local community in a method to be determined by the Navajo Nation and local chapter houses.

As a grazing alternative, fourwing saltbush could be allowed to grow throughout the summer, then end-of-season grazing would be permitted to remove the accumulated annual growth (thus removing plant nitrogen that originated as nitrate in the plume). Grazing rights would be determined by the Navajo Nation and local chapter houses. At a yield of 10 to 20 tons per acre, the pilot farm would provide 16 to 32 tons per year of potential fourwing saltbush browse at maturity.
Table 8-1. Irrigation Suitability Land Classification

<table>
<thead>
<tr>
<th>Land Characteristics</th>
<th>Class 1</th>
<th>Class 2</th>
<th>Class 3</th>
<th>Class 6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Soils</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Texture (Surface 10 inch)</td>
<td>MC,M,MF</td>
<td>Any</td>
<td>Any</td>
<td>Any</td>
</tr>
<tr>
<td>Moisture Retention-AWHC 0-48 inch</td>
<td>&gt;6.0 inch</td>
<td>&gt;4.5 inch</td>
<td>&gt;2.5 inch</td>
<td></td>
</tr>
<tr>
<td>Effective Depth</td>
<td>&gt;48 inch</td>
<td>&gt;30 inch</td>
<td>&gt;20 inch</td>
<td></td>
</tr>
<tr>
<td>Salinity (EC H 103), 0-48 inch</td>
<td>&lt;4</td>
<td>&lt;8</td>
<td>&lt;12</td>
<td></td>
</tr>
<tr>
<td>Permeability, 10 to 48 inch</td>
<td>0.2-6.0 in/hr</td>
<td>0.06-6.0 in/hr</td>
<td>0.06-20 in/hr</td>
<td></td>
</tr>
<tr>
<td>Coarse Fragments, 0 to 10 inch</td>
<td>&lt;15</td>
<td>&lt;35</td>
<td>&lt;55</td>
<td></td>
</tr>
<tr>
<td>Gravel (% by volume)</td>
<td>&lt;15</td>
<td>&lt;35</td>
<td>&lt;55</td>
<td></td>
</tr>
<tr>
<td>Cobble (% by volume)</td>
<td>&lt;5</td>
<td>&lt;10</td>
<td>&lt;15</td>
<td></td>
</tr>
<tr>
<td>Rock Outcrops (distance apart)</td>
<td>&gt;200 ft</td>
<td>&gt;100 ft</td>
<td>&gt;50 ft</td>
<td></td>
</tr>
<tr>
<td>Frequency of Overflow (years)</td>
<td>None (&lt;1 in 10)</td>
<td>Rare (1 in 10)</td>
<td>Occasional (2 in 10)</td>
<td></td>
</tr>
<tr>
<td>Depth to Calcic Horizon</td>
<td>&gt;20 inch</td>
<td>&gt;10 inch</td>
<td>Any</td>
<td></td>
</tr>
<tr>
<td>Depth to Water Table</td>
<td>&gt;60 inch</td>
<td>&gt;48 inch</td>
<td>&gt;30 inch</td>
<td></td>
</tr>
</tbody>
</table>

**Topography and Land Development**

| Slope (percent)                      | <5      | <8      | <15     |
| Rock Fragments for Removal (cu yds/Ac) | <10     | <35     | <70     |
| Cobble                               | <10     | <35     | <70     |
| Stone                                | <10     | <25     | <70     |
| Surface Gradingd                     | None or light | Medium | Heavy   |
| Tree Removal (% canopy)              | <10     | <40     | <70     |
| Reclamation required for Sodicity    | None    | Moderate | High    |

**Drainage**

<table>
<thead>
<tr>
<th>Surface Drainage Requirement</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth to Restrictive Layer (&lt;0.1 inch/hour H.C.) When W.A.H.C. of the 4 ft to restrictive layer, or 4 ft to 10 ft layer (whichever is least) is &gt; 0.15 inches/hour</td>
<td>&gt;6 ft</td>
<td>&gt;6 ft</td>
<td>&gt;6 ft</td>
</tr>
<tr>
<td>When W.A.H.C. of the 4 foot to restrictive layer, or 4 foot to 10 foot layer (whichever is least) is &lt; 0.15 inches/hour</td>
<td>&gt;8 ft</td>
<td>&gt;8 ft</td>
<td>&gt;8 ft</td>
</tr>
<tr>
<td>If artificial drainage is required: Hydraulic Conductivity of zone to be drained</td>
<td>&gt;0.15 in/hr</td>
<td>&gt;0.15 in/hr</td>
<td>&gt;0.15 in/hr</td>
</tr>
<tr>
<td>Depth to Drainage Barrier</td>
<td>&gt;6 ft</td>
<td>&gt;6 ft</td>
<td>&gt;6 ft</td>
</tr>
</tbody>
</table>

Notes on Specifications for Land Classes:

a Each individual factor represents a minimum requirement. Two or more interacting deficiencies may result in land being placed in lower class than single deficiencies specify.

b Specifications for the “Soil” group are representative of conditions after land is developed for irrigation.

c Less than 15% gravel for class 2 if surface texture is coarse or moderately coarse.

Less than 35% gravel for class 3 if surface texture is moderately coarse.

(1) Land is further downgraded if surface grading reduces effective depth or otherwise permanently reduces soil fertility.

(2) Degrees of leveling for hummocky areas:

- light: 0-200 cubic yards of earth work per acre.
- medium: 200-400 cubic yards of earth work per acre.
- heavy: 400-800 cubic yards of earth work per acre.
- v. heavy: over 800 cubic yards of earth work per acre.

(3) Degrees of leveling for gullied areas:

- light: 0-200 cubic yards of earth work per acre.
- medium: 200-400 cubic yards of earth work per acre.
- heavy: 400-800 cubic yards of earth work per acre.
- v. heavy: over 800 cubic yards of earth work per acre.

Surface drainage refers to the natural ability to either shed or transmit water. It is not the same as overflow (which refers to the condition of inundation) or internal drainage.

- Category 1: Surface drainage is not limiting.
- Category 2: Surface drainage is limiting, but easily corrected.
- Category 3: Surface drainage is limiting and not easily corrected.

Zone to be drained is least of the following:

1. Four feet to a restrictive layer
2. Four feet to bedrock
3. Four feet to a drainage barrier
4. Four feet to ten feet.
Fourwing saltbush and possibly other native plants could also be grown to produce seed for reclamation of strip mines, mine tailings, and abandoned mines on the Navajo Nation and elsewhere. For this alternative, fourwing saltbush would be grown as above, but seed would be harvested before livestock are permitted to graze during late fall and winter months. In fall 2001 we harvested about 50 kg of fourwing saltbush seed; about 2 kg or more of seed from mature plants. There are about 4,000 plants in the subpile phytoremediation planting, half of which are female, so 2,000 plants × 2 kg gives a potential yield of 4,000 kg of seed. The field is 1.6 ha, so the potential yield is 2,500 kg/ha. Commercial seed costs up to $66/kg ($30/lb) for seed with the wings milled off. If the seed companies pay as little as $10/kg ($4.50/lb) for bulk seed, this would be a return of $25,000/ha (about $10,000/acre).

8.1.4 Nitrate Levels in Irrigation Supply

Two simulations were performed to evaluate the maximum permissible nitrate concentrations in the irrigation water, each starting with 500 ppm (Figure 8–1). Previous research using nitrate-contaminated water (Baumgartner et al. 2000a,b) showed that saltbush grows normally up to 1,200 ppm nitrate. Therefore, 1,000 ppm was used as the maximum permissible level in the soil solution during phytoremediation. In the first simulation, it was assumed that plants removed 240 ppm nitrate and the remainder stayed in the soil, and that nitrate in the plume was diluted by an infinite supply of water containing 50 ppm nitrate as the plume was pumped (one reservoir model). In the second simulation it was assumed that the actual volume of water was diluted by the volume of water surrounding the hotspot (44 to 500 ppm nitrate) (two reservoir model). In both simulations, nitrate in the soil solution remained well below 1,000 ppm during the remediation process. It can be concluded that water initially containing 600 to 700 ppm nitrate could be used for irrigation of forage crops without yield reduction.

![Figure 8–1. Simulated Nitrate Concentrations in the Soil Solution During the Remediation Process](image-url)
8.1.5 Potential Toxicity Problems for High-Nitrate Fertilization

Even the highest levels of nitrate in the plume should not cause direct phytotoxicity (damage to plants). In general, > 9,000 ppm nitrate in plant tissues can produce toxic effects in animals (Lawrence et al. 1968). When grown on low-nitrate water, grasses like Sudan grass had 3,500 ppm nitrate, but on 1,100 ppm and 2,200 ppm nitrate, it had 6,857 ppm and 5,028 ppm nitrate in leaf tissues, respectively (Baumgartner et al. 2000a). These exceed the highest standards but are less than what is considered the maximum safe level. Saltbush did not respond to nitrate fertilization by accumulating additional nitrate in the leaves, and levels never exceeded 4,300 ppm nitrate (Baumgartner et al. 2000a). The remedies for this potential problem are: (1) do not apply nitrate in excess of what can be safely absorbed by the crops and converted to plant protein; and (2) monitor levels of nitrate and hydrocyanic acid in saltbush.

8.1.6 Sulfate Soil Chemistry and Toxicity

The feasibility of using land farming for phytoremediation of ground water must consider the fate and potential toxicity of sulfate in irrigation water. Because of the high calcium content of the water, evaporation could concentrate the liquid to the extent that CaSO₄·2H₂O (gypsum) precipitates in the soil profile. Because of the limited rainfall in Monument Valley, the gypsum would likely remain indefinitely in the soil and thus be removed from the aquifer. Gypsum is often used as a soil amendment and is not expected to harm the plants used for phytoremediation. Thompson and Glenn (1998) estimated the extent to which sulfate can be removed from the ground water through concentration by evaporation when the water is used for irrigation. As the volume of water in the soil profile is reduced to 5 percent of the starting volume through ET, approximately 78 percent of the sulfate in the solution will precipitate as gypsum. Gypsum likely occurs naturally in the geology and soils of the area. Development of a gypsiferous soil may simulate natural pedogenic processes in the area.

Plants can be irrigated with water saturated in calcium sulfate without showing growth inhibition but they can accumulate high tissue levels of sulfate, ranging from 70 to 900 ppm as sulfur. Sulfate can be toxic to animals at high levels in plant tissues (Watson et al. 1994; National Academy of Sciences 1980). Sulfate can be converted to hydrogen sulfide in animal’s rumens, resulting in loss of appetite. This problem has not been documented for animals grazing on saltbush, but it is a potential problem given the high levels of sulfate in the irrigation supply. The remedy is to monitor plant tissues for excess sulfate.

8.1.7 Irrigation Management

The management strategy for the land farm is to apply sufficient water to support high yields of the phytoremediation crops, and to maximize nitrate uptake into plant tissues while minimizing percolation of water past the root zone. Water and nitrate that pass beyond the root zone will reenter the aquifer, reducing the efficiency of the phytoremediation effort. However, since the land farm will be upgradient of the contamination plume, leachate water from the farm would eventually be recovered again in the well field. Hence, some leaching past the root zone to control soil levels of salts and nitrate can be accepted as part of the irrigation management strategy. Two irrigation strategies could be used to minimize leaching of nitrates back to the aquifer: (1) deficit irrigation and (2) use of deep-rooted saltbush plants to absorb water and nitrate from deep within the soil profile.
For deficit irrigation, only part of the maximum crop water demand is applied. For example, if measurements of the soil water profile indicate that the root zone requires an application of 0.2 m of water to reach field capacity, the irrigator might apply 0.18 m of water (90 percent of crop water demand). This is sufficient to ensure good crop development as well as nearly complete uptake by the plant. Water can also be withheld at the end of the growing season, allowing the crop to absorb excess water in the soil profile as it matures. Deficit irrigation requires a good knowledge of crop water requirements and soil moisture conditions throughout the crop cycle, and it requires an efficient method of applying irrigation water. It requires a knowledge of soil chemistry as constituents in the water supply will accumulate in the root zone and may have to be controlled through a leaching fraction, natural precipitation, or uptake by more deeply rooted alley crop plants such as saltbush. The pilot farm should be designed to develop best management practices for deficit irrigation for each cropping scenario tested.

The most efficient irrigation system for saltbush is drip irrigation, using buried drip lines. Drip irrigation applies water directly to the roots of plants in controlled volumes; hence it has very high efficiency. Buried lines ensure that contaminated plume water would not be available to livestock or other animals as surface water. Therefore, buried drip lines are proposed as the irrigation method for the pilot farm. Irrigation schedules would be set monthly, based on soil-moisture depletion curves determined by measurement of soil moisture levels before and after irrigation events, using a neutron hydrometer and buried soil moisture sensors.

8.2 Phytotoxicity Evaluation

The toxicity of irrigation water to various crops under consideration for land farming, and the potential toxicity to grazing animals of forage or hay crops irrigated with plume water are of concern. This section includes a brief review of toxicity literature for potential chemicals of concern in the aquifer, and summarizes the results of a greenhouse study conducted to measure effects of plume water on plant growth and tissue concentrations of toxic substances (DOE 2002).

8.2.1 Toxicity of Chemicals of Concern

A literature search was conducted to address the concern that accumulation of NO$_3$-, SO$_4$-, hydrocyanic acid (HCN), strontium (Sr), vanadium (V), U, and Mn within the plants may have an effect on plant growth and the quality of crops as forage for livestock.

Accumulation of nitrate and HCN in plants is of concern. The accumulation of nitrate is of concern when feeding livestock. High nitrate accumulation also results in oxygen deprivation. There can be significant variability of nitrate accumulation within a field. Nitrate levels lower than 5,000 $\mu$g NO$_3$ g$^{-1}$ are considered safe for feeding to all cattle. Five thousand to 10,000 $\mu$g NO$_3$ g$^{-1}$ contain risk for pregnant cows and young calves, and above 10,000 $\mu$g NO$_3$ g$^{-1}$ can be hazardous to all cattle (Strickland et al. 1995). The lethal dose of nitrate for cattle ranges from 88 to 110 mg NO$_3$/kg body weight. Ranges of 40 to 50 mg NO$_3$/kg body weight are lethal for sheep (Knowles and Ottman 1997).

HCN can cause death in livestock by interfering with the ability of oxygen to enter body cells thus causing suffocation at the cellular level (Strickland et al. 1995). The amount produced in the
plant depends on environmental conditions. Young growth and stressed plants contain larger amounts of HCN. Leaves contain the most HCN (Knowles and Ottman 1997). Hydrocyanic acid levels at 0-500 μg HCN g⁻¹ in dried plant tissue are safe for grazing. Feeding with levels higher than 500 μg HCN g⁻¹ is not recommended and grazing should be monitored (Strickland et al. 1995).

Sulfur is an essential element for the survival of animals. It is involved in many different functions of both plant and mammalian cells. Sulfur toxicity occurs in the gastrointestinal tract where microflora convert S to hydrogen sulfide. It takes large amounts of S to start producing hydrogen sulfide. There are no established limits on S/SO₄ for cattle and sheep diets. An apparent maximum tolerable level for sheep is 0.4 percent dietary S as sodium sulfate (Subcommittee on Mineral Toxicity in Animals 1980).

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

Manganese is an essential element for both plant and animal growth. Manganese toxicity results from an interference with iron and results in the decreased production of hemoglobin. Sheep and cattle should not be fed diets containing more than 1,000 μg Mn g⁻¹ (Subcommittee on Mineral Toxicity in Animals 1980).

Vanadium (V) has been shown to be an essential element in animal diets. The bright white metal can also be toxic by inhibiting enzymes and causing the lysis of cells. Feeding studies found 20 mg V Kg⁻¹ body weight fed daily to calves produced symptoms within 3 days. Sheep fed 40 mg V Kg⁻¹ body weight had a 65 percent death rate within 80 hours of feeding. There is no established maximum tolerable limit for V (Subcommittee on Mineral Toxicity in Animals 1980).

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

### 8.2.2 Greenhouse Study of Plant Uptake

In 2001, a greenhouse study was carried out at the University of Arizona’s Environmental research Laboratory in Tucson to test the feasibility of growing crop plants of forage quality (DOE 2002). Water from the contaminated alluvial aquifer and soils from locations proposed for the land farm were used for the study.
8.2.2.1 *Plants, Soils, and Water*

Plants used in this study include Piper sudan grass (*Sorghum sudanese* (Piper) Stapf.), Sweet and Sorghum-sudan grasses (*Sorghum X drummondii* (Steud.) Millsp. and Chase), Agate and Ineffective Agate alfalfa (*Medicago sativa* L.), and the native species four-wing saltbush (*Atriplex canescens* (Pursh) Nutt). The Ineffective Agate alfalfa is a non-nodulating form of Agate Alfalfa and could require more nitrogen (Barnes et al. 1990). Four-wing saltbush seeds were collected from native plants from Monument Valley, Arizona.

Soils were collected from three locations at the Monument Valley site. The surface soil is reddish-yellow sand (mesic, arid, typic torripsamment). One soil was collected in an area where no mining or milling processes took place. It contained 58 mg V kg\(^{-1}\) concentrations. The second soil was collected from an area where a nitric and sulfuric acid evaporation pond was previously located and contained 111 mg vanadium (V) kg\(^{-1}\). The final soil was collected in the subpile planting where *Atriplex canescens* growth has been problematic. This soil contains 198 mg V kg\(^{-1}\). Only topsoil (0–20 cm) was collected in all three locations.

Water was collected from three wells that had been previously analyzed and contained three very different nitrate (NO\(_3\)) concentrations. After collection from those three wells, water was tested again for selected chemical constituents. The NO\(_3\) concentrations in the water were shown to be similar in all three wells. To simulate three different concentrations of NO\(_3\), water from one well was left at baseline level contamination and the two other wells were each spiked with KNO\(_3\) from a 1,000 times stock solution to 500 and 1,000 mg NO\(_3\) kg\(^{-1}\) as nitrate prior to each watering event. This was to simulate the range of concentrations present in the contaminated aquifer as a whole. Sulfate (SO\(_4\)) concentrations ranged from 290 to 620 mg SO\(_4\) kg\(^{-1}\), the specific electrical conductance ranged from 2.8 to 3.7 mS/cm and pH ranged from 6.59 to 7.81.

8.2.2.2 *Summary of Results and Conclusions*

The best plant growth occurred on soil from outside the former uranium milling site in Monument Valley, Arizona, at the site proposed by DOE for a pilot phyto remediation farm. Plant growth was inhibited in soils from within the fenceline around the former pile area. Growth on three soils from different areas in the vicinity of the site improved with the addition of organic matter, such as potting soil, to the soil.

One thousand mg nitrate (NO\(_3\)) kg\(^{-1}\) (measured as NO\(_3\)) concentration in water was lethal to most plants. This toxicity was alleviated by the addition of organic matter to the soil. One thousand and 500 mg NO\(_3\) kg\(^{-1}\) concentrations in water resulted in plant tissue concentrations of NO\(_3\) above recommended feeding values for cattle. At 83 mg NO\(_3\) kg\(^{-1}\) concentration in the water, alfalfa did not accumulate NO\(_3\) to excessive levels. All other plant types accumulated nitrate close to or above 5,000 mg NO\(_3\) kg\(^{-1}\), the highest amount of nitrate considered safe for feeding to all cattle. Plants grown with organic matter and watered with 1,000 mg NO\(_3\) kg\(^{-1}\) accumulated NO\(_3\) up to 20 times higher than the safe feeding level. HCN accumulation was lowest in Piper sudan grass with a mean below the lower toxic limit. Both Sweet and Sorghum-sudan grasses accumulated HCN above toxic levels. Sulfur as sulfate (SO\(_4\)) in dried plant tissues accumulated to harmful concentrations in alfalfa grown with water containing 83 mg NO\(_3\) kg\(^{-1}\) and 620 mg SO\(_4\) kg\(^{-1}\). Plants did not accumulate Sr, Mn, V or U to harmful levels.
Considering these results, the land farm pilot study will focus on growing native plant species such as fourwing saltbush that can be grown for seed for use in disturbed-land revegetation (mine land reclamation and rangeland seeding) on the Navajo Nation.

### 8.3 Goals and Objectives

The goal of the land farming pilot study is to develop best management practices for 1) pumping, irrigating, and growing a crop with contaminated water from the alluvial aquifer; 2) enhancing reclamation of areas disturbed by the remedial action; and 3) minimizing human health and ecological risks associated with the farming operation. Specific objectives of the land farming pilot study follow.

**Select suitable cropping systems.**

The crops and cropping system used for the land farm should efficiently extract and covert plume nitrate into plant nitrogen, produce a useful commodity, improve rangeland ecology, and do so without posing risk to human health or the environment. The initial emphasis was production of forage or hay crops such as Sudan grass and alfalfa (DOE 2002). Given some results of greenhouse studies indicating that these crops could accumulate toxic levels of nitrate and hydrocyanic acid, the focus has shifted to growing seed crops for use in reclaiming mine lands and other disturbed rangelands.

**Determine optimum irrigation rates.**

Deficit irrigation of subpile soils has been successful (see Section 5.1.5); sufficient clean water can be applied to maintain plant growth without causing recharge and leaching of contaminants. The objective for managing irrigation volume on the land farm is similar: apply sufficient nitrate-laden water to maximize crop yields yet minimize percolation below the root zone. Irrigation management would be less important on the land farm than on the subpile soil if the land farm is placed upgradient of extraction wells so any leachate would be recovered again.

**Determine optimum nitrate concentrations for irrigation water.**

The land farm pilot study will determine operational nitrate concentrations in irrigation water that would result in efficient rates of removal from the alluvial aquifer without accumulation to levels that are toxic to crops or to livestock and wildlife that may consume crops. Greenhouse studies (Baumgartner et al. 2000a, DOE 2002) on toxicity and accumulation of nitrogenous compounds in plant tissues produced mixed results. An objective of the land farm pilot study is to resolve this issue by monitoring the health and toxicity of crops in response to a range of nitrate levels in irrigation water.

**Monitor accumulation of residual constituents in the farm soil.**

The accumulation of nitrate and sulfate in land farm soil from irrigation water should not exceed the capacity of the system to transform or retain these constituents. The chemistry of land farm soils will be monitored to prevent excessive buildup of nitrates and to demonstrate whether sulfates are precipitating and accumulating as gypsum. The occurrence of natural gysiferous...
soils in the Monument Valley area will also be investigated as an analog for sulfate accumulation in the test farm soil.

**Monitor crop productivity and safety.**

An objective of the land farm is to produce a safe and marketable crop. The land farm pilot study will evaluate seed production rates for each crop species and investigate efficient methods for harvesting seed. The toxicity and productivity of plant materials will also be monitored to determine if winter grazing is safe and feasible.

### 8.4 Task Descriptions

The land farm pilot study will be designed to address specific questions and concerns raised during meetings with the Navajo Nation Division of Natural Resources in 2000 and 2003 (see Section 2.4). The experimental design, installation, and monitoring tasks in this section will acquire field-scale data needed to evaluate and resolve uncertainties with the use of land farming as an active remedy for the alluvial aquifer.

#### 8.4.1 Develop Experimental Design

The land farm pilot study will be more than a field-scale demonstration. It will be a field experiment designed to address specific uncertainties. The experiment will be organized to ensure that the right type of data, and enough of it, will be available at the end of the experiment to answer specific questions as clearly and efficiently as possible.

The experimental design will consist 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). The treatment structure of a factorial experiment consists of the set of treatments or treatment combinations that will be compared. Treatments are defined by factors and levels of each factor. The design structure consists of the field arrangement of the experimental units into groups or blocks. 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 will consist of two main factors: nitrate concentration in irrigation water and crops in the cropping system (Table 8–2). The four nitrate levels span a range derived from the results of greenhouse studies: 200 mg/L, a level not likely toxic to crop plants or to livestock feeding on the crop; 400 mg/L, a level not likely toxic to crops but possibly toxic to livestock; 800 mg/L, a level possibly toxic to crops (800 mg/L). Water pumped from the DeChelley aquifer will be used as the “clean water” control level. The preliminary cropping system compares a deeper-rooted native shrub (fourwing saltbush) and a shallower-rooted native grass (Indian ricegrass) planted in an alley cropping system (see Section 8.4.2). 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.
Table 8–2. Experimental Treatment Structure for the Land-Farming Pilot Study

<table>
<thead>
<tr>
<th>Factor</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate Concentration</td>
<td>Clean water&lt;br&gt;200 mg/L nitrate&lt;br&gt;400 mg/L nitrate&lt;br&gt;800 mg/L nitrate</td>
</tr>
<tr>
<td>Cropping System</td>
<td>Native deep-rooted shrub(s)&lt;br&gt;Species: <em>Atriplex canescens</em> var. <em>angustifoilia</em>&lt;br&gt;(fourwing saltbush) or other shrubs&lt;br&gt;Native grass(es) and/or forb(s)&lt;br&gt;Species: <em>Achnatherum hymenoides</em>&lt;br&gt;(Indian ricegrass) or other grasses or forbs</td>
</tr>
</tbody>
</table>

The preliminary design structure is a randomized block. A 1-acre area will be planted in an alley cropping system and then split into 4 equal-size blocks (Figure 8–2). An alley cropping system using fourwing saltbush and Indian ricegrass would have rows of saltbush grown at 3 m spacing, separated by strips of Indian ricegrass. Both would be grown primarily for seed production. Seed would be harvested annually, and after the harvest, livestock would be allowed to graze plants in fall and winter only if plant tissues do not exceed established toxicity levels. Saltbush roots, penetrating deeper in the soil profile than Indian ricegrass roots, would intercept water and nitrate that passes below the Indian ricegrass rooting zone.

8.4.2 Select Crops

Crops will be selected based on several criteria:

- Adapted to sandy soil and harsh climate of Monument Valley.
- Can be rapidly established from seed or transplants.
- Deep rooted to extract water and nitrate from a large volume of soil.
- Produce seed that will be of value for revegetation of mine lands and disturbed rangelands on the Navajo Nation.
- Indigenous species that will persist given good range management practices once irrigation ceases.

Fourwing saltbush and Indian ricegrass appear to satisfy these criteria. Both are major components of the potential natural vegetation in the area (see Section 3.4). Both are widely used for mine land and rangeland revegetation ([www.nativeseeditnetwork.org](http://www.nativeseeditnetwork.org)).

Fourwing saltbush is found at elevations from 3,000 to 6,000 ft on sites that receive 8 to 15 inches of annual precipitation. It grows in a wide variety of soil types from valley bottoms and plains to mountainous areas. Fourwing saltbush is well suited to deep, well drained sandy soil, sand dunes, gravelly mesas, and grassy uplands, and frequently grows intermixed with numerous other shrub and grass species. The presence of fourwing saltbush often enhances the growth of grasses that benefit from the presence of nitrogen and other minerals that concentrate under the canopy.
Fourwing saltbush is highly palatable browse for most livestock and big game. It is used primarily in the winter when it is high in carotene and averages about four percent digestible protein. The leaves may be as high as 18 percent total protein. Proper grazing use on this shrub should be no more than 40 percent of the total annual growth during the growing period and no
more than 50 percent during the plant dormancy period. Although fourwing saltbush is well adapted to winter grazing, careful management is needed due to the brittle nature of the twigs. A rotation, deferred system of grazing may result in the highest productivity.

Indian ricegrass is a cool-season perennial bunchgrass. It is native to the arid and semiarid regions of the western United States. Indian ricegrass prefers soils that contain up to 75 percent sand and receive at least 7 inches of average annual precipitation. It does not tolerate shade but does tolerate moderately alkaline soils. As with fourwing saltbush, Indian ricegrass is also considered to be a valuable winter forage species. As a grazing decreaser, overgrazing by livestock has greatly reduced the occurrence of this species on native sites. Indian ricegrass is widely recommended for mine land reclamation projects. Its major limitation is its high seed dormancy which results in poor first year germination. As a result of high seed dormancy, most attempts to establish it on sites with less than 12 inches of annual precipitation have been unsuccessful. Plantings are more likely to succeed on sites with 12 or more inches of annual precipitation or irrigation. Without managed grazing, stands may begin to decline by the fifth year.

8.4.3 Design Pumping and Irrigation System

An irrigation system will be designed to efficiently deliver four different concentrations of nitrate plume water (0, 200, 400, and 800 ppm nitrate) as proposed for the experimental design (Section 8.4.1). Drip emitters and sprinklers may both be needed to irrigate woody and herbaceous plants, respectively, if an alley crop planting is used (Section 8.4.2). The information that will be needed to design the irrigation system includes ground water nitrate concentrations in extraction wells, a topographic survey of the proposed land farm area, and the planting layout.

Submersible pumps will be installed in selected wells with varying concentrations of nitrate. Plume water will be piped to tanks adjacent to the pilot farm where is may be mixed to achieve the treatment concentrations of nitrate. Tank capacities will be determined based on pumping rates from the extraction wells and crop irrigation requirements. After a preliminary design is complete, electrical power needs will be estimated and the power system infrastructure will be designed.

8.4.4 Characterize Soil Physical Properties

The physical and hydraulic properties of the pilot farm soils will be evaluated with a combination of laboratory measurements. 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. Table 8–3 lists the standard analytical methods and citations for each soil parameter.

8.4.5 Characterize and Monitor Soil Chemical Properties

Prior to planting, baseline soil samples will be taken from each block and analyzed for nitrate, ammonium, and sulfate. Samples will be taken from three depths (surface, 1.5 m, and 3.0 m) at three random locations in each block. Random sampling will be repeated at the end of each growing season to monitor rates of nitrate and sulfate accumulation in the land farm soil profile.
### Table 8–3. Analytical Measurements for Soil Physical and Hydraulic Properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Method Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated hydraulic conductivity of Granular Soils</td>
<td>ASTM D2434</td>
<td>Constant head permeameter</td>
</tr>
<tr>
<td>Moisture-Density Relationships</td>
<td>ASTM D698</td>
<td>Physical compaction</td>
</tr>
<tr>
<td>Atterberg Limits</td>
<td>ASTM D4318</td>
<td>Liquid limit, plastic, water content</td>
</tr>
<tr>
<td>Particle Size Distribution</td>
<td>ASTM D422</td>
<td>Sieve and hydrometer</td>
</tr>
<tr>
<td>Soil Moisture Retention Curve</td>
<td>Klute (1986)</td>
<td>Hanging column, pressure plate, and chilled mirror hygrometer</td>
</tr>
<tr>
<td>Minimum / Maximum Density</td>
<td>ASTM D 4253</td>
<td>Vibration</td>
</tr>
<tr>
<td>Percent Moisture</td>
<td>ASTM D 2216</td>
<td>Oven-Drying</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>ASTM D 854</td>
<td>Gravimetric</td>
</tr>
</tbody>
</table>

Analyses of soil samples will be made by extracting with potassium chloride (KCl) solution [STO 210; procedure CB(BT-2)]. This procedure, adapted from a widely used soil-extraction method described in Page et al. 1982, involves agitation of the disaggregated soil sample for 2 hours in a 1 N KCl solution. Analysis of nitrate and sulfate are made by ion chromatography [STO 210; procedures AP(NO3-4) and AP(SO4-4)] after dilution to avoid interference with the chloride peak. Analysis for ammonia is made by spectrophotometric methods [STO 210; procedure AP(NH3-1)]. A more aggressive digestion using nitric acid [STO 210; procedure SE(MD-1)] will be used on some samples to assure that all sulfate minerals are being digested.

#### 8.4.6 Monitor Soil Water

Soil moisture will be monitored using neutron thermalization (NT) hydroprobes (see Section 5.4.5). 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 monitored in order to better manage irrigation rates. One NT hydroprobe port will be installed to monitor volumetric moisture content in each block in the pilot farm experimental design. Readings will be taken at 30-cm depth increments to the bottom of the ports (about 5 m).

#### 8.4.7 Monitor Crop Growth and Productivity

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. 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. Grass productivity will be estimated by clipping and measuring dry-weights from an adequate number of 0.25 m$^2$ random quadrats to achieve 10 percent accuracy and precision. 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 ($\pi$bc).

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 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.

### 8.4.8 Evaluate Nitrification and Denitrification Processes

Samples from the land farming pilot study will be processed similarly to the procedures outline for subpile soil samples (see Sections 5.4.7 and 5.4.8). First, denitrification and nitrification potential measurements will be obtained. Second, N$_2$O 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.

### 8.4.9 Investigate Gypsiferous Soil Analogs

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$_4$.2H$_2$O (gypsum) within the farm soil profile. Gypsiferous soils also form naturally in arid and semiarid landscapes of the Southwest and other deserts of the world Birkland (1999). Natural gypsiferous soils at Monument Valley may provide an analog for the genesis of the land farm soils.

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. Characteristics of the landform and ecology associated with the soil will also be described.

The following key soil profile characteristics will be recorded:

- Depth to the upper-most mineral horizon.
- Percentage by volume of various soil features (e.g., gravel, carbonate and gypsum development stage, mottles).
• Color, both moist and dry in accordance with the Munsell Soil Color Charts.
• Structure description of the type, grade, and structure size.
• Consistence, which measures the adherence of the soil, will be observed in dry, moist, and wet conditions.
• Texture, which is used to classify the soil in accordance with USDA nomenclature.
• pH.
• Stages of carbonate morphology will be described using methods from Gile et al. (1966).
• Stages of gypsum accumulation will be described in a fashion similar to that developed for carbonate accumulation.

Soil will be sampled from each horizon. Samples obtained from a road cut or sidewall of an arroyo will be taken by initially scraping the outer most ten centimeters of soil from the face. This assures that influence from salt accumulation at the surface will not bias the sample. Samples obtained from an excavated test pit will be taken directly from the sidewall. Physical properties will be determined in accordance with procedures in Klute (1986). Analysis of gypsum will follow Nelson (1982).

8.4.10 Manage and Market Seed Crop

Coal mines on the Navajo Nation may be a market for native seed. 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 other than fourwing saltbush and Indian ricegrass will be considered in consultation with reclamationists and range managers prior to final selection of crops for the land farm pilot study. If appropriate, DOE will work with the Navajo Nation to assess the feasibility of establishing a local enterprise to grow and market native seed.

8.4.11 Test Plant Toxicity and Simulate Grazing

Tissues of fourwing saltbush, Indian ricegrass, and all other crop species will be sampled periodically from each block in the land farm during the growing season and analyzed for nutritional content including proximate analyses for crude protein, ash, fiber, fat, lignin, and energy content. The 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.
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