

**MONITORED NATURAL AND ENHANCED ATTENUATION OF THE  
ALLUVIAL AQUIFER AND SUBPILE SOILS AT THE MONUMENT VALLEY,  
ARIZONA, PROCESSING SITE: REVIEW OF FINAL STUDY REPORT**

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# 1 SUMMARY OF ENVIRONMENTAL ASSESSMENT COMPLIANCE GOALS AND COMPLIANCE STRATEGY

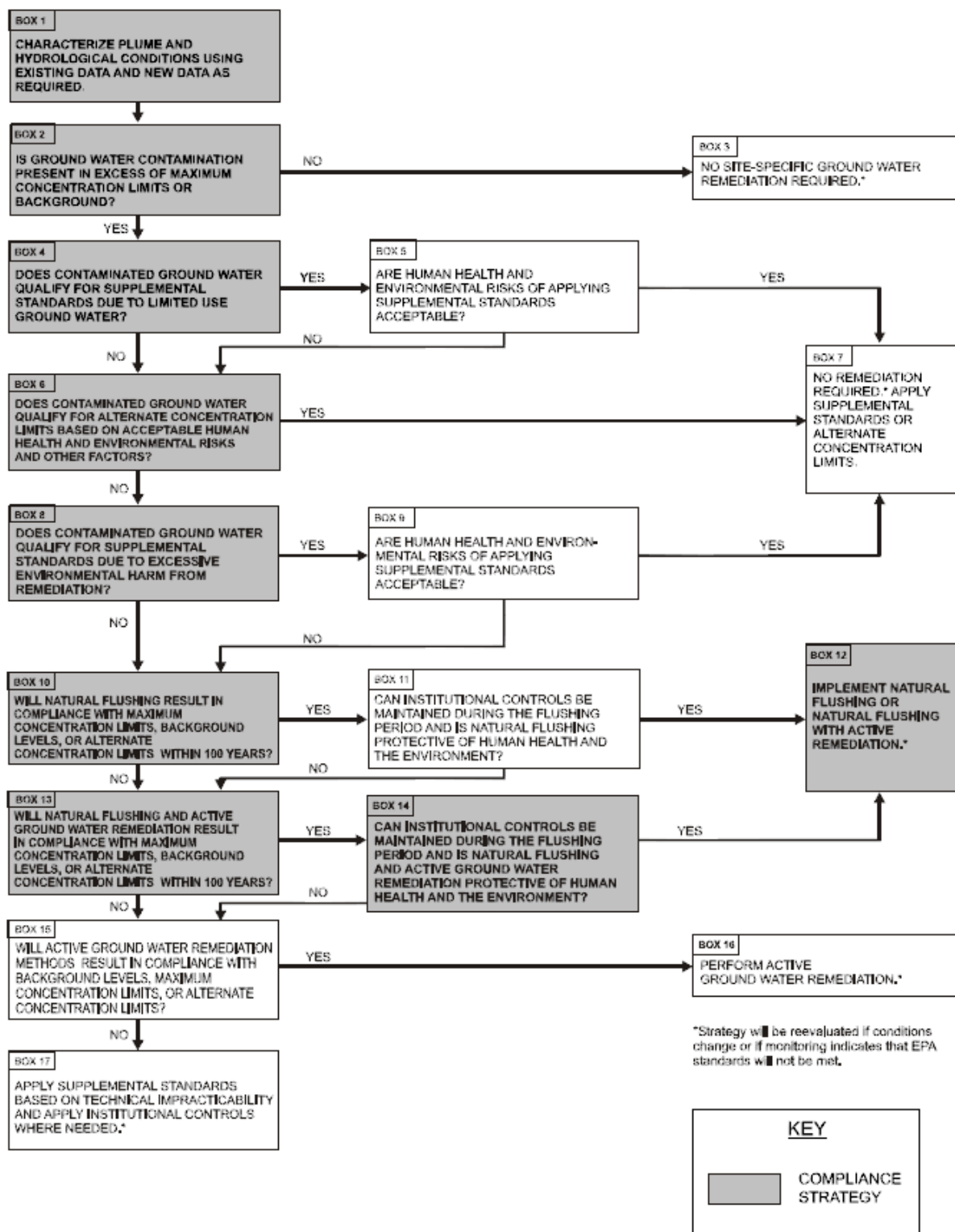
Congress passed the Uranium Mill Tailings Radiation Control Act (UMTRCA) in 1978 to control and mitigate risks to the environment and human health from sites involved in processing uranium ore. The U.S. Department of Energy (DOE) was directed to conduct remedial actions at 24 inactive uranium-ore processing sites. The selection and performance of the remedial actions required full participation by states, in consultation with affected American Indian Tribes, and with the concurrence of the U.S. Nuclear Regulatory Commission (NRC). This report reviews the results of pilot studies by DOE's Office of Legacy Management performed at the uranium-ore processing site at Monument Valley, Arizona. The site is within the Navajo Nation and was included in UMTRCA as one of the 24 inactive uranium-ore processing sites. The pilot studies evaluated several approaches to remediating ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) remaining at the site following removal of tailings and other residual radioactive materials on or near the ground surface. Uranium is present in small quantities deeper in the alluvial aquifer but was not included in the pilot studies. DOE may use the results of the pilot studies to evaluate and propose final compliance strategies and remedial actions for contamination in the soils and alluvial aquifer at the site. According to DOE (2013), which we will hereafter call the Pilot Study Report, the pilot studies were carried out pursuant to the following objectives and scope for pilot studies presented in DOE (2004), which we will hereafter call the Work Plan, and the associated environmental assessment (DOE, 2005):

- Delineate extent of nitrate, ammonium, and sulfate in subpile soils
- Investigate presence and mobility of natural nitrate and sulfate sources
- Determine causes of stunted plant growth and recourse
- Expand irrigated planting of *Atriplex canescens*
- Quantify effects of irrigation on microbial denitrification processes and rates
- Investigate nitrification processes, rates, and possible enhancements

The objectives of the pilot studies were restated in the Work Plan and DOE (2005):

- Estimate the total capacity of natural chemical and biological processes that are reducing concentrations of groundwater contaminants at the site.
- Investigate methods to enhance and sustain attenuation processes that could be implemented if the total capacity of natural processes is inadequate.
- Demonstrate methods for (i) characterizing attenuation rates, (ii) verifying short-term results, and (iii) monitoring performance of natural attenuation processes and enhancements.
- Evaluate land farming as an active remediation option if natural and enhanced attenuation processes are both inadequate.

The objectives of the Pilot Study Report differ somewhat from those stated in the Work Plan, possibly because DOE's understanding of the environmental processes at the site has evolved since the Work Plan was written. The results of the pilot studies are intended to support the decision points in the decision framework for compliance strategies presented in DOE (2005) and reproduced in Figure 1-1. The maximum concentration limits (MCLs) mentioned in



**Figure 1-1. Compliance Selection Framework for the Alluvial Aquifer at the Monument Valley Site (Reproduced From DOE, 2005)**

Figure 1-1, Boxes 10 and 13, are the U.S. Environmental Protection Agency (EPA) MCLs for nitrate as  $\text{NO}_3^{-1}$  [44 milligrams per liter (mg/L) ][44 parts per million (ppm)] and uranium (0.044 mg/L) [0.044 ppm]. According to DOE, “DOE will use best efforts to comply with the Navajo Nation remediation goal of 250 mg/L for sulfate” (DOE, 2005). DOE’s proposed actions for ammonium, nitrate, and sulfate at the Monument Valley Site are summarized in Figure 1-2. In its studies, DOE considered three zones: subpile soils, shallow alluvial aquifer, and deep alluvial aquifer. The pilot studies reviewed in this report pertain only to remediation of ammonium, nitrate, and sulfate. Ammonium in subpile soils is a potential source of nitrate in the alluvial aquifer. The pilot studies are summarized in Figure 1-3.

Aquifer	Area	Contaminants To Be Monitored	Compliance Strategy	Rationale
Alluvial	Subpile soils	Ammonium, Nitrate	Passive remediation (natural flushing and phytoremediation)	Reduce concentrations of ammonium that could be a continuing source of nitrate contamination in the alluvial aquifer
	Shallow portions of aquifer	Nitrate, sulfate	Passive remediation (natural flushing and phytoremediation)	Reduce concentrations of nitrate and sulfate
	Deeper portions of aquifer	Nitrate, sulfate	Passive remediation (combination of natural flushing and land farming)	Reduce concentrations of nitrate and sulfate
		Uranium	Passive remediation (natural flushing)	Uranium contamination does not appear to be widespread, although anomalous elevated concentrations have recently been detected.
De Chelly	Isolated area	Uranium	Passive remediation (natural flushing)	Uranium concentration only slightly exceeds the MCL in an isolated area and is decreasing with time. There is no current human health or ecological risk.

MCL = maximum concentration limit established in 40 CFR 192.

**Figure 1-2. Summary of DOE’s Proposed Actions in the Alluvial Aquifer (Reproduced From DOE, 2005)**

Title	Objective	Scope (Tasks Completed as Authorized in the EA, Work Plan, and Status Reports <sup>a</sup> )
1. Control Subpile Soil Water Balance and Percolation	Enhance native vegetation establishment and evapotranspiration (ET) on source area soils to control the soil water balance, limit deep percolation, and prevent continued leaching of nitrate and ammonium into the alluvial aquifer.	<ol style="list-style-type: none"> <li>1. Determined extent of subpile ammonium and nitrate.</li> <li>2. Expanded subpile phytoremediation planting and irrigation system.</li> <li>3. Investigated natural sources of vadose zone nitrate.</li> <li>4. Monitored soil water content and percolation flux.</li> <li>5. Monitored plant growth and related evapotranspiration.</li> <li>6. Investigated causes and recourses for area of stunted plant growth.</li> </ol>
2. Enhance Natural Attenuation in the Subpile Soils	Remove nitrate and ammonium from subpile soils by enhancing natural phytoremediation and bioremediation.	<ol style="list-style-type: none"> <li>1. Monitored plant growth and related nitrogen uptake.</li> <li>2. Sampled plant root abundance and distribution.</li> <li>3. Sampled soil organic carbon.</li> <li>4. Monitored changes in subpile soil ammonium and nitrate.</li> <li>5. Evaluated natural and enhanced microbial denitrification.</li> <li>6. Evaluated soil nitrification processes.</li> </ol>
3. Evaluate Natural and Enhanced Phytoremediation of the Alluvial Aquifer	Evaluate and enhance natural phytoremediation by native phreatophytes rooted in the plume to remove plume nitrogen and, by increasing transpiration, to hydraulically limit the continued spread of the plume.	<ol style="list-style-type: none"> <li>1. Evaluated historical modeling and monitoring of nitrate, ammonia, and sulfate in the alluvial aquifer.</li> <li>2. Investigated rooting depths of native phreatophytes.</li> <li>3. Evaluated phreatophyte transpiration and hydraulic control.</li> <li>4. Evaluated effects of grazing management and revegetation on phytoremediation capacity for nitrogen uptake and transpiration.</li> <li>5. Developed a remote sensing protocol to monitor natural and enhanced phytoremediation.</li> </ol>
4. Evaluate Natural and Enhanced Denitrification in the Alluvial Aquifer	Characterize natural attenuation processes acting to reduce contaminant levels in the alluvial aquifer and investigate options for enhancing denitrification.	<ol style="list-style-type: none"> <li>1. Investigated natural concentrations of alluvial nitrogen.</li> <li>2. Modeled plume dynamics and natural attenuation processes.</li> <li>3. Estimated natural denitrification in the alluvial aquifer based on nitrate concentrations and nitrogen isotope fractionation.</li> <li>4. Evaluated carbon sources to enhance aquifer denitrification using laboratory microcosm assays.</li> <li>5. Conducted field tests of the denitrification capacity and dispersion of ethanol injected into the alluvial aquifer.</li> </ol>
5. Evaluate Land-Farm Phytoremediation	Evaluate land-farm phytoremediation, an active remedy alternative that involves pumping and irrigating a crop of native plants with nitrate-contaminated groundwater.	<ol style="list-style-type: none"> <li>1. Conducted a feasibility study of land-farm phytoremediation.</li> <li>2. Designed and constructed a land farm experiment to evaluate effects of different native shrub crops and irrigation nitrate levels on plant health, soil water, and soil nitrogen.</li> <li>3. Characterized baseline physical and chemical properties of land-farm soils.</li> <li>4. Monitored soil water content profiles using neutron hydroprobes.</li> <li>5. Sampled for changes in soil nitrate and ammonium profiles.</li> <li>6. Monitored crop health and growth using remote sensing.</li> </ol>

Title	Objective	Scope (Tasks Completed as Authorized in the EA, Work Plan, and Status Reports <sup>a</sup> )
6. Reduce Sulfate Levels as Possible	To the extent that is practical, reduce sulfate concentrations in the alluvial aquifer and sequester as soil sulfate in concert with remedies developed for groundwater nitrogen contamination.	<ol style="list-style-type: none"> <li>1. Evaluated natural sources of sulfate in the alluvial aquifer.</li> <li>2. Evaluated plant uptake of sulfate in subpile soils and alluvial aquifer.</li> <li>3. Monitored changes in subpile soil sulfate profiles.</li> <li>4. Monitored effects of ethanol injection into the alluvial aquifer on sulfate reduction.</li> <li>5. Investigated gypsiferous soils as an analog of sulfate sequestration in a phytoremediation land farm.</li> <li>6. Measured sequestration of sulfate in land farm soils.</li> </ol>
Evaluate Potential Risks	Evaluate potential risks to human health and the environment related to the pilot studies and possible remedies.	<ol style="list-style-type: none"> <li>1. Evaluated risks of plant uptake and livestock grazing for chemicals of potential concern in the subpile soil and groundwater.</li> <li>2. Evaluated potential phytotoxicity of stained or colored subpile soils.</li> <li>3. Investigated the potential health effects of manganese concretions in the subpile soils.</li> <li>4. Conducted a radiological investigation of yellow crusts on the soil surface for the phytoremediation planting in the Evaporation Pond.</li> </ol>

**Figure 1-3. Pilot Studies Titles, Objectives, and Scope (Reproduced From the Pilot Study Report, Table 1-3)**



## **2 SUMMARY OF SIGNIFICANT CLAIMS IN THE FINAL STUDY REPORT RELATED TO COMPLIANCE GOALS**

### **2.1 Subpile Soils**

The subpile soils at the Monument Valley processing site were assumed by DOE to be sources of ammonium, nitrate, and sulfate that could contaminate the alluvial aquifer at the site. Because nitrate and sulfate are anions, they can be readily transported downward through soils to underlying aquifers by meteoric water. Ammonium is a cation and tends to be less mobile because it is retarded by the electrical field around net negatively charged soil particles. Ammonium in soils, however, can be converted to nitrate by a process called nitrification in which ammonium cations are converted to nitrate anions by microorganisms. The aerobic process commonly occurs in soils because the microorganisms that cause the nitrification are ubiquitous in most soils. Hence, the ammonium in soils can be a source of nitrate contamination in underlying aquifers.

DOE investigated passive remediation approaches (natural and enhanced phytoremediation) to minimize additional nitrate and sulfate contamination of the alluvial aquifer from the subpile soils as compliance strategies for meeting EPA standards and the Navajo Nation remediation goals. DOE conducted preliminary phytoremediation feasibility studies (DOE, 2002) to evaluate whether natural and enhanced phytoremediation would be viable options for reducing nitrate concentrations in the alluvial aquifer at the Monument Valley Site. The results indicated that natural and enhanced phytoremediation would be viable options and would be consistent with the revegetation and land management goals of the site. DOE defined natural phytoremediation as relying on existing plants on the site for the alluvial aquifer remediation and defined enhanced phytoremediation as actions that include planting of additional plants, supplying irrigation, or providing fertilization, or other activities that would increase the health and number of plants that would contribute to the alluvial aquifer remediation. In general, DOE uses enhanced phytoremediation and enhanced denitrification to mean that natural processes at the Monument Valley site are being manipulated by human intervention to increase or accelerate contaminant attenuation beyond what occurs without the intervention (page A-16 of Appendix A of the Pilot Study Report).

Additional pilot studies were conducted pursuant to the Work Plan and the associated environmental assessment (DOE, 2005). The studies were conducted to evaluate the proposed compliance strategies in greater detail than the preliminary feasibility studies. For subpile soils, the focus was on (i) using phytoremediation to control the downward movement of water, (ii) enhancing natural nitrate attenuation by microorganisms, and (iii) reducing sulfate concentrations. In addition, the studies were designed to assess the distribution of ammonium, nitrate, and sulfate in the subpile soils as well as the soil water content. The Pilot Study Report makes the following conclusions regarding the effectiveness of the potential compliance strategies.

#### **2.1.1 Water Balance Using Enhanced Phytoremediation**

An established mixture of native plants can transpire sufficient water from the subpile soils to prevent the downward migration of water, which would prevent leaching of ammonium, nitrate, and sulfate into the alluvial aquifer. To establish mature native plants [fourwing saltbush (*Atriplex canescens*) and black greasewood (*Sarcobatus vermiculatus*)], transplanting and irrigation was necessary. Irrigation was supplied at a rate less than plants could transpire

(i.e., deficit irrigation). Fencing was used to restrict grazing animals from the plots. However, grazing was simulated by periodic cutting of the plants. DOE concluded that the resulting healthy community of vegetation was able to utilize available water in the subpile soils and prevent downward water movement to the alluvial aquifer. Measurements of water content and flux were used to support their conclusion.

### **2.1.2 Enhanced Denitrification in the Vadose Zone**

The increased soil water content as a result of deficit irrigation yielded enhanced denitrification in the subpile soils. Approximately half of the soil nitrogen was removed during 2000–2010. Because only a small quantity of nitrogen and sulfur was in the plants and the soil nitrogen was enriched with  $^{15}\text{N}$ , it was hypothesized that soil microorganisms were mainly responsible for the reduction in nitrogen content. It was noted that soil bacteria preferentially utilize  $^{14}\text{N}$  versus  $^{15}\text{N}$  in their metabolism during denitrification. Therefore, an enrichment of  $^{15}\text{N}$  suggests that denitrification is ongoing. This also was supported by nitrous oxide production that was 10 to 20 times higher in assay chambers placed over irrigated versus nonirrigated soils. Nitrous oxide is a product from denitrification. To further enhance denitrification, a carbon source (ethanol) was added to the irrigation water to support microbial growth.

### **2.1.3 Treatment of Sulfate in Vadose Zone**

Phytoremediation in the subpile soils is reducing the sulfate transport to the alluvial aquifer because of the induced water balance. In addition, the plants will take up sulfate into their tissues and retard the downward migration of sulfate. Furthermore, sulfate may precipitate as gypsum (hydrated calcium sulfate) and remain in the subpile soils.

## **2.2 Alluvial Aquifer**

The Pilot Study Report describes potential remediation actions for the shallow alluvial aquifer {water table less than approximately 15 meters (m) [50 feet (ft)] below land surface} and deep alluvial aquifer {water table greater than approximately 15 m [50 ft] below land surface}. Some of the remedial actions addressed by the pilot studies pertain to just the shallow portion of the aquifers, while others would apply to both portions. The basis for distinguishing the shallow and deep portions of the alluvial aquifer is the assumed maximum root depth of phreatophytes being approximately 15 m [50 ft]. DOE's claims and conclusions based on the results of the pilot studies are contained in the Pilot Study Report, Table 4.

### **2.2.1 Hydraulic Control of Plume by Phreatophyte Evapotranspiration**

Native phreatophytes transpired water from the shallow alluvial aquifer and “hydraulically slowed plume dispersion” (Pilot Study Report, Table 4, p. 26]. DOE appears to base this interpretation on the conclusion that phreatophytes are removing water from the shallow aquifer. DOE also concluded that “[...] vegetation of denuded areas and management of grazing in other areas overlying the plume would greatly increase transpiration, enhancing hydraulic control.” The conclusion that phreatophytes are removing water from the aquifer is based on

- The physiology of the native vegetation consisting of phreatophytic shrubs, fourwing saltbush, and black greasewood (Pilot Study Report, Appendix C, Section C.1)

- The stable hydrogen and oxygen isotopic signatures of phreatophyte plant matter being similar to that in the deep vadose zone and top of the water table (Pilot Study Report, Appendix C, Section C.1.2)
- The measured evapotranspiration rates of phreatophytes at the site (Pilot Study Report, Appendix C, Section C.1.5)

### **2.2.2 Phytoremediation of the Nitrate and Sulfate**

The rate of direct uptake by phreatophytes of nitrate and sulfate from the alluvial aquifer was very small compared to the mass of these contaminants in the plume (Pilot Study Report, Appendix C, Section C.1.4). Thus "...scientists turned to the enhancement of microbial denitrification as a second option for plume nitrate (Pilot Study Report, p. 17)."

### **2.2.3 Natural Denitrification in the Alluvial Aquifer**

Natural attenuation of nitrate in the alluvial aquifer was primarily controlled by microbial denitrification. This conclusion was based on the similarity of first-order denitrification rates in laboratory microcosms and those inferred from modeling of nitrate concentration trends in the alluvial aquifer (p. 27). The data and analyses on which this conclusion is based are reported in Carroll, et al. (2009) and summarized in the Pilot Study Report, Appendix C, Section C.2. This process would presumably apply to both the shallow and deep portions of the aquifer.

### **2.2.4 Enhanced Denitrification in the Alluvial Aquifer**

Denitrification rates could be substantially increased by injecting a biodegradable organic substrate, such as ethanol, into the aquifer. This conclusion is based on the results of ethanol injection push-pull and natural gradient tests performed in the 2010 and 2011 pilot-scale field tests in the alluvial aquifer and on independent studies at other sites. This process would presumably apply to both the shallow and deep portions of the aquifer.

### **2.2.5 Remediation of Sulfate in Alluvial Aquifer**

The rate of uptake of sulfate by phreatophytes was very small with respect to the (i) mass of sulfate in the plume, (ii) injection of ethanol into the aquifer reduced sulfate concentrations by producing hydrogen sulfide, and (iii) sulfate that would be sequestered in the soil using active phytoremediation. The latter two processes would presumably apply to both the shallow and deep portions of the aquifer.

### **2.2.6 Land-Farming Phytoremediation**

Land-farming phytoremediation (pump and treat) would involve pumping water from the alluvial aquifer and applying it to plots of actively managed native phreatophytes. This remedial action could be applied to both the shallow and deep portions of the alluvial aquifer. DOE conducted field studies of the uptake of water, nitrate, and sulfate in irrigated plots of native phreatophytes (Pilot Study Report, Appendix E). Based on these studies, the Pilot Study Report concluded that the results "demonstrated that a land farm with a crop of native fourwing saltbush shrubs may work well as a backup remedy for the plume if other remedies prove to be insufficient." This conclusion assumes that plant transpiration and soil evaporation would be sufficient to consume the water pumped and that nitrate and sulfate would not be returned to the aquifer.

The rate at which water would need to be pumped from the alluvial aquifer to remove 90 percent of the plume mass in 30 years was estimated to be between 5.7 and 10.9 cubic meters per hour ( $\text{m}^3/\text{hr}$ ) [21 and 40 gallons per minute (gpm)] in DOE (2000, Table 5-2). The Pilot Study Report also concludes that “Plant uptake and soil denitrification kept nitrate levels from building up in the land-farming soil; plant transpiration limited recharge and leaching of nitrate and ammonia back into the aquifer; sulfate pumped from the plume was sequestered in the soil profile, most likely as gypsum (calcium sulfate)...” (p. 28).

### 3 EVALUATION OF PILOT STUDY CONCLUSIONS

#### 3.1 Subpile Soils

Based on the results of the preliminary and pilot studies, DOE made several conclusions about the likely success of remediation strategies for limiting future movement of ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) into the alluvial aquifer. DOE primarily concluded that (i) phytoremediation would consume water in the subpile soils, which would limit downward migration of ammonium, nitrate, and sulfate and (ii) natural and enhanced denitrification would reduce the nitrate content in the subpile soils by conversion of nitrate to either nitrous oxide ( $\text{N}_2\text{O}$ ) or nitrogen gas ( $\text{N}_2$ ). The following sections discuss the DOE conclusions in the Pilot Study Report.

##### 3.1.1 Water Balance Using Enhanced Phytoremediation

DOE's conclusion that establishing healthy plants in subpile soils will reduce the downward migration of ammonium, nitrate, and sulfate in water during the growing season is valid based on the information evaluated in the Pilot Study Report. Establishing healthy vegetation will utilize available water in soils during the growing season, which will reduce the water content. The lower water content will significantly slow the downward water movement from the subpile soils toward the alluvial aquifer and slow the downward migration of ammonium, nitrate, and sulfate during the growing season. To establish healthy vegetative cover over the subpile soils, DOE transplanted fourwing saltbush and black greasewood, both native phreatophytes, to all fields. To support the transplants, drip irrigation was supplied as they grew. The amount of irrigation supplied was less than the amount that the plants could transpire. Because human involvement was needed for the transplanting and irrigation, DOE called these activities enhanced phytoremediation.

However during the nongrowing season, the water content of the subpile soils may increase to an amount that may induce flushing of ions (i.e., nitrate and sulfate) out of the subpile soils and downward toward the alluvial aquifer. For semi-arid sites, like the Monument Valley Site, water movement from soils to an underlying aquifer may occur from an unusually wet winter or quick and abundant snowmelt in the spring (Winograd, et al., 1998; Spangler and Johnson, 1999). During these events, the uptake of water by plants is significantly less than the amount of water being supplied. Consequently, the water content of the subpile soils may increase and result in downward water movement to the alluvial aquifer. Ions, such as nitrate and sulfate, will be transported with the water to the alluvial aquifer. Although a healthy vegetative community may utilize available water in soils during the growing season under average conditions (Scanlon, et al., 2005), nongrowing season precipitation may occur in which the plants cannot utilize all of the moisture and subsequent downward water movement may occur to underlying aquifers. In addition, cases may exist that groundwater recharge may occur at locations where the mean annual precipitation (i.e., water addition) is much less than the mean annual potential evapotranspiration as shown by Small (2005). Furthermore, Small (2005) states that mean annual precipitation and mean annual potential evapotranspiration alone are not good indicators to predict where groundwater recharge may occur. For a long-term remediation strategy, DOE needs to consider factors other than that the amount of water being supplied by precipitation and irrigation is less than the potential evapotranspiration. Potential effects of nongrowing season precipitation, and possibly episodic precipitation events, on the downward migration of ammonium, nitrate, and sulfate should be considered.

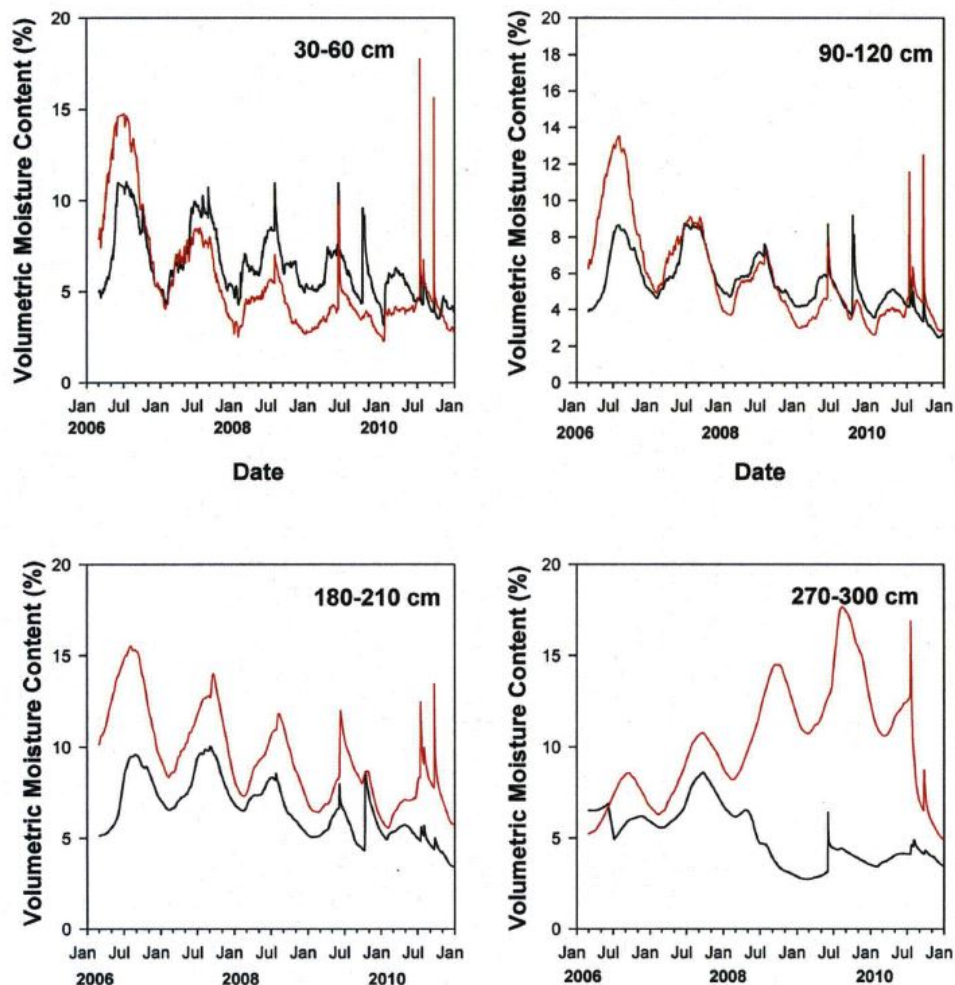
To monitor water content and potential downward water movement of the subpile soils in the pilot studies, DOE used a hydroprobe, water content reflectometers, and water flux meters. The hydroprobe measures soil water content by neutron thermalization. The water content reflectometers measure soil water content by electrical conductivity. The water flux meters measure water movement using a funnel, wick, and tipping bucket system where the collected water is weighed. Based on measurements of subpile soil water content and water flux, DOE concluded that enhanced phytoremediation successfully controlled the water balance of the subpile soils to limit downward water movement and the transport of ammonium, nitrate, and sulfate.

Questions remain regarding the conclusion by DOE of no downward water movement in the subpile soils including: (i) the water content deeper in the subpile soils for the Old Field appears to have an increasing trend, which may potentially result in downward water movement, especially if the trend continues; and (ii) only 4 water flux meters were used for the 3.3 ha [8.2 ac] of planted fields where enhanced phytoremediation was tested. For the former concern, Figure 3-1 shows an increasing trend of the soil water content at the 270–300 cm [106–118 inches (in)] depth. During the growing season of 2009 and 2010, it appears as if the volumetric water content exceeded the field capacity of  $0.15 \text{ cm}^3/\text{cm}^3$  [15 percent] (Pilot Study Report, p. B–25). It is not clear why this increasing trend is only found in the Old Field. In a Groundwater Compliance Action Plan, DOE will need to give more detail on how irrigation will be managed to prevent an increase in water content deeper in the soil profile as shown in Figure 3-1. For the latter concern, data based on only 4 water flux meters for 3.3 ha [8.3 ac] may be insufficient to draw conclusions for all of the area. Only a single water flux meter was used on the Old Field. Because soils have heterogeneities in their structure, as do most natural porous media, downward water flux may be occurring at locations other than where the water flux meters are positioned.

It is reasonable to assume that during the growing season, established healthy plants can utilize available soil moisture and lower the water content of the soil. The result may be negligible downward water movement, or there may be no downward water movement to the underlying aquifer. However, there may be downward water movement to an aquifer if the amount of water being added to the soil is greater than the amount plants use during the nongrowing season or episodic precipitation events. Even if the average amount of water plants use is greater than the average amount of water being introduced to the soil, downward water movement may occur from nongrowing season precipitation, episodic precipitation events, and heterogeneities in soil properties and the distribution of roots. In a Groundwater Compliance Action Plan, DOE will need to address effects of nongrowing season precipitation and episodic precipitation events.

### **3.1.2 Enhanced Denitrification in the Vadose Zone**

Based on measurements of nitrogen levels in the subpile soils early in the pilot studies, the decrease in nitrogen levels was significantly greater than what could be accounted for by the transplanted native phreatophytes extracting and metabolizing nitrogen and sulfur. DOE estimated that the transplanted shrubs in the Old Field removed only about 1 percent per year of nitrogen from the subpile soils over the 10-year period of the pilot studies. DOE concluded that denitrification by microorganisms was the likely cause for the measured reduction in nitrogen levels. It was assumed that the irrigation stimulated the microorganisms. Denitrification in soils is the biological reduction of nitrate to molecular nitrogen or nitrous oxide, which are both gases that can be released to the atmosphere. The microorganisms (bacteria)



**Figure 3-1. Soil Moisture Content at Four Soil Depths in Enhanced Phytoremediation Plots, Measured by Water Content Reflectometers. Results Are Daily Means of Water Content for Three Monitoring Stations in New Fields (Black Line) and One in the Old Field (Red Line). (Reproduced From the Pilot Study Report, Appendix B, Figure B-20).**

generally responsible for denitrification obtain their energy by oxidizing a carbon source. It is generally reported that denitrification occurs under anaerobic conditions (Brady, 1974, p. 431; Hausenbuiller, 1972, p. 255). However, there have been published papers in which aerobic denitrification has been reported (Meiklejohn, 1940).

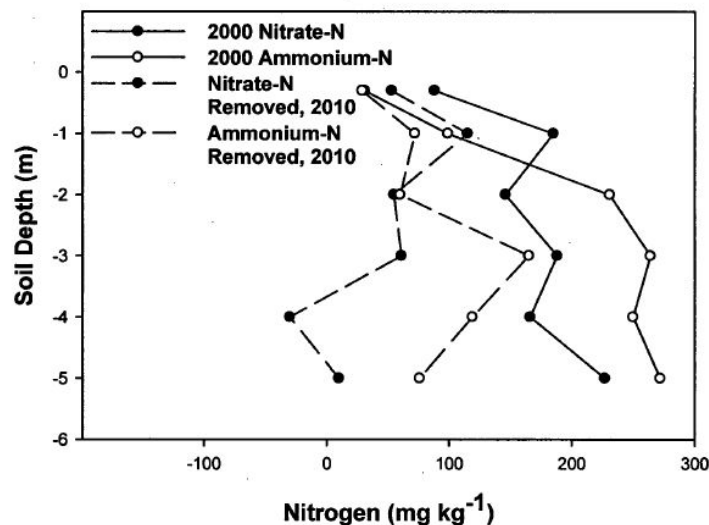
To verify that denitrification was contributing to the reduction in the measured nitrogen levels, assay chambers were placed over irrigated and nonirrigated subpile soils. The measured production of nitrous oxide was 10 to 20 times higher in assay chambers over the irrigated soils, indicating that (i) denitrification is occurring in subpile soils under aerobic conditions and (ii) the irrigation was enhancing the denitrification. In additional investigations, the ratio of  $^{15}\text{N}$  to  $^{14}\text{N}$  isotopes was measured because microorganisms are reported to prefer the  $^{14}\text{N}$  isotope in their metabolism. It was found that the ratio increased over time, which supported the conclusion that denitrification was occurring because of an enrichment of  $^{15}\text{N}$ . To further enhance denitrification, a carbon source (ethanol) was added to the irrigation water to support microbial

growth. Whereas denitrification in laboratory studies increased when ethanol was added, denitrification was not further enhanced in the field investigation. Only under wet soil conditions did ethanol addition significantly enhance denitrification. It was concluded that irrigation would enhance denitrification, but the irrigation should be limited so as not to induce the downward migration of water (i.e., wet conditions). Over the 10 years of the pilot studies, DOE stated that irrigation-enhanced denitrification reduced the nitrogen levels in the subpile soils by approximately one half. It was noted that there was an initial rapid decrease in the early years with removal rates decreasing over time.

It is unclear whether the denitrification was occurring aerobically or occurring in small pockets or films with induced anaerobic conditions. Nevertheless, there was measured production of nitrous oxides, which indicates that denitrification was occurring in the subpile soils. For the water contents of the subpile soils during irrigation, well-aerated conditions should exist in most of the pore spaces. Any denitrification will lower the nitrate content of the subpile soils, provided that nitrification, which is the conversion of ammonium to nitrate by microorganisms, is not producing nitrate at a faster rate than is being reduced by denitrification. In the Pilot Study Report, DOE claimed that the nitrate produced from nitrification was then subject to denitrification, which resulted in a net loss of nitrogen from the subpile soils. However, Figure 3-2 shows that the loss of ammonium from the Old Field was greater than the loss of nitrate for the 10-year period of the pilot studies, except for the upper meter of the soil. The increase (negative loss in Figure 3-2) in nitrate at around the 4-m [13-ft] depth suggests that nitrate was added over time to this depth, which could have occurred from either (i) the downward movement of water and nitrate from above or (ii) by nitrification exceeding denitrification at this depth. The Pilot Study Report states that the irrigation enhanced denitrification. It is reasonable to assume that nitrification would not be similarly enhanced, but the Pilot Study Report does not explicitly address any enhancement of nitrification. The results shown in Figure 3-2 appear to contradict the results shown in Tables 3-1 and 3-2. The tables show that there was a greater reduction in nitrate than ammonium, but Figure 3-2 shows a greater reduction in ammonium. In Figure 3-3, the averages nitrate values for 2004 for each of the soil depths in Table 3-1 are plotted (broken lines). The results show that the nitrate levels in the upper part of the soil profile remain relatively unchanged between 2004 and 2010, but the nitrate levels in the lower part of the soil profile increase from 2004 to 2010. Further explanation from DOE may be required to clarify the overall effects of denitrification and nitrification on the nitrate and ammonium levels in the subpile soils and possible downward migration of nitrate in the subpile soil with time.

Denitrification and nitrification are components of the nitrogen cycle in soils. The biochemical conversion of nitrate to gaseous nitrous oxides and/or nitrogen gas (denitrification) is typically conducted by facultative anaerobic microorganisms (Brady, 1974, p. 431). The conversion of ammonium to nitrate (nitrification) is commonly facilitated by aerobic autotrophic bacteria that are ubiquitous in soils (Brady, 1974, p. 428). Only denitrification results in a loss of nitrogen (nitrate) from soils. Therefore, any enhancement of denitrification will result in a greater loss of nitrate than what would occur without the enhancement. Because nitrate is very mobile in soils, reduction in nitrate levels also will reduce the amount of nitrate that may potentially move downward toward an unconfined aquifer. In the Pilot Study Report, irrigation to enhance plant growth also serves to enhance microbial activity and consequently to increase the rate of denitrification. However, DOE has not demonstrated whether the enhancement of denitrification also enhances nitrification, which may result in more nitrate being created than is lost through denitrification. Furthermore, DOE has not demonstrated whether denitrification is a short term phenomenon or will continue for long periods. Data in Table 3-1 indicates that the reduction in nitrate occurred rapidly followed much slower reductions or even increases.





**Figure 3-2. Initial Concentrations of Nitrate and Ammonium in the Old Field, 200, and the Amount of Nitrate and Ammonium Removed by 2010, As a Function of Soil Depth (Reproduced From the Pilot Study Report, Appendix B, Figure B-27).**

### 3.1.3 Treatment of Sulfate in the Vadose Zone

In the Pilot Study Report, there were no investigations of processes minimizing the downward movement of sulfate to the alluvial aquifer other than controlling the water balance as discussed in Section 3.1.1. In fact, irrigating the subpile soils resulted in an increase of the sulfate content of the surface subpile soils, as shown in Figure 3-4, because the irrigation water contained sulfate. DOE did not address likely consequences of sulfate addition to the subpile soils if irrigation is used to enhance phytoremediation and denitrification. DOE indicated the possible formation of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), but the process was not supported by measurements or analyses. Gypsum commonly develops in semi-arid soils, but this process typically occurs naturally over very long time periods (Hausenbuiller, 1972, p. 301). Gypsum may precipitate in soils when the solubility of the mineral is exceeded (Dixon and Weed, 1977, p. 84). In a Groundwater Compliance Action Plan, DOE may need to address the effects of any likely addition of sulfate to the subpile soils and support its assertions for the pH conditions that may prevail.

## 3.2 Alluvial Aquifer

### 3.2.1 Hydraulic Control Plume by Phreatophyte Evapotranspiration

The results of the pilot studies do not provide a sound basis for determining the rate at which or extent to which either existing or enhanced phreatophyte communities would remove water from the alluvial aquifer or slow the movement of the nitrate and sulfate plume. Based on the following considerations, the phreatophytes may be primarily removing water from the vadose zone before it reaches the alluvial aquifer rather than directly extracting it from the aquifer. First, the hydrogen and oxygen isotope analyses do not unambiguously support the conclusion

**Table 3-1. Nitrate-N Concentrations (mg/kg) in Soil Samples From the Old Field, 2000 to 2004. The Field Is Divided Into Four Irrigation Zones That Were Each Samples at 2–5 Locations Near Neutron Hydroprobe Ports. Values Are Means With Standard Errors of Means in Parentheses. (Reproduced From the Pilot Study Report, Appendix B, Table B–2).**

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

that the phreatophytes are directly transpiring water from the shallow aquifer. Figure 3-5 shows the correlation of enrichment of Hydrogen-2 ( $\delta D$ ) versus Oxygen-18 ( $\delta^{18}O$ ) in groundwater, phreatophyte stem moisture, and the vadose zone water. The phreatophyte stem moisture isotopic ratios all fall on the evaporated water line, as do the soil water ratios, indicating the stem water could be derived either from the vadose zone or locally recharged water.

Second, the evapotranspiration rates measured for both protected and unprotected stands of saltbush and black greasewood increase with annual precipitation, as illustrated in Figure 3-6. This suggests that the phreatophytes may be primarily removing infiltrating water before it recharges that aquifer. If the phreatophytes are primarily removing water from the saturated zone the evapotranspiration rates would not vary with annual precipitation. (Note: according to DOE, the water flux meters measured no downward water flux.)

To the extent that phreatophytes are removing water before it reaches the water table, they would be slowing groundwater flow and the movement of the plume. On the other hand, less uncontaminated water would infiltrate and reach the aquifer in areas outside of the subpile

Table 3-2. Ammonium-N Concentrations (mg/kg) in Soil Samples From the Old Field, 2000 to 2004. The Field Is Divided Into Four Irrigation Zones That Were Each Samples at 2–5 Locations Near Neutron Hydroprobe Ports. Values Are Means With Standard Errors of Means in Parentheses. (Reproduced From the Pilot Study Report, Appendix B, Table B–2).

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

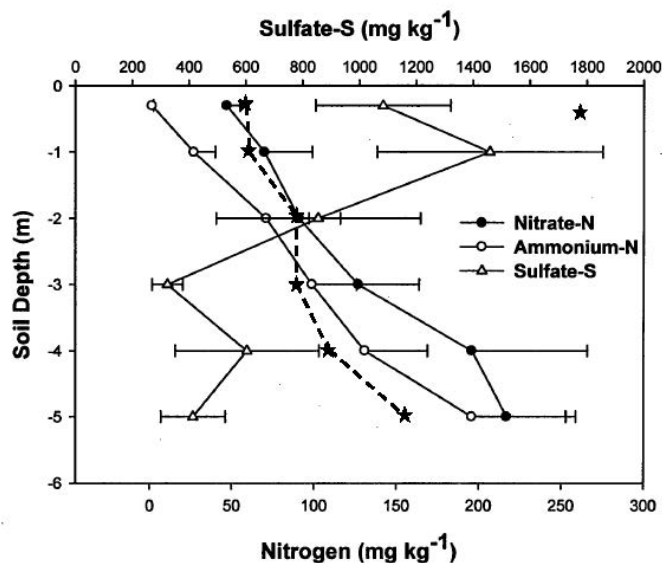


Figure 3-3. Distribution of Nitrate, Ammonium, and Sulfate as a Function of Soil Depth in Source Area Soil Samples From the Old Field in 2010 (Modified From the Pilot Study Report, Appendix B, Figure B–26)

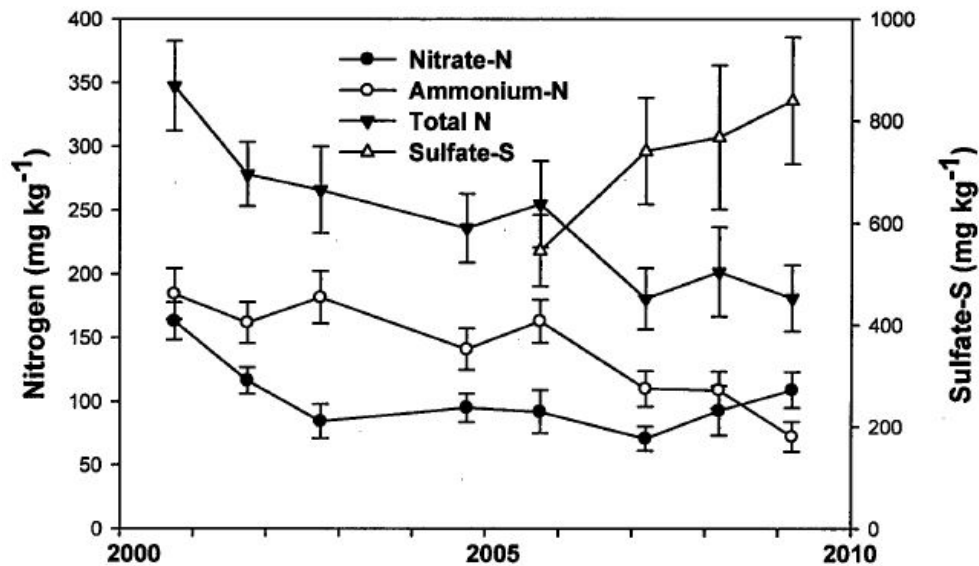


Figure 3-4. Concentrations of Nitrate, Ammonium, Nitrate + Ammonium (Total N), and Sulfate in Soil Samples From the Old Field, 2000 to 2010. Error Bars Are Standard Errors of Means. Sulfate Was First Measured in 2005. (Reproduced From the Pilot Study Report, Appendix B, Figure B-24)

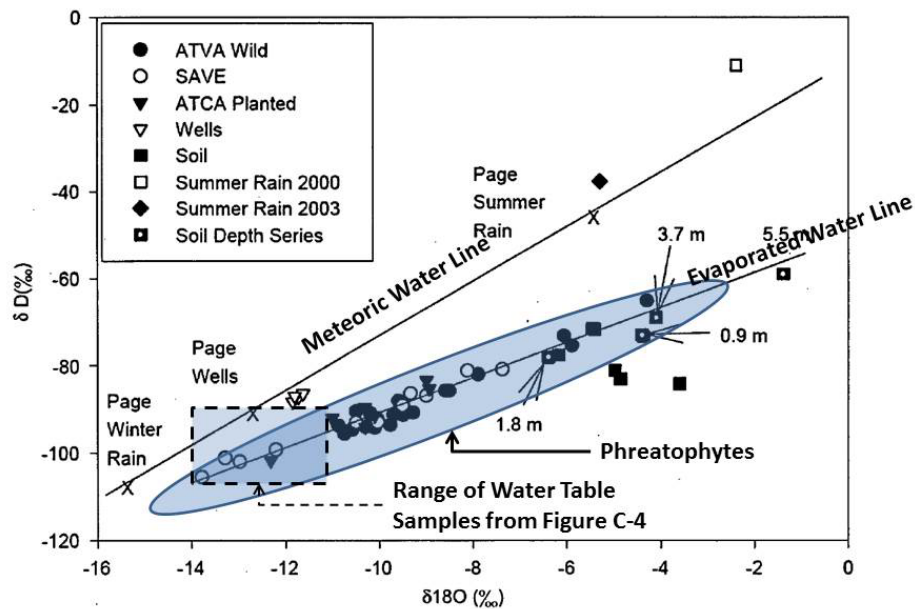
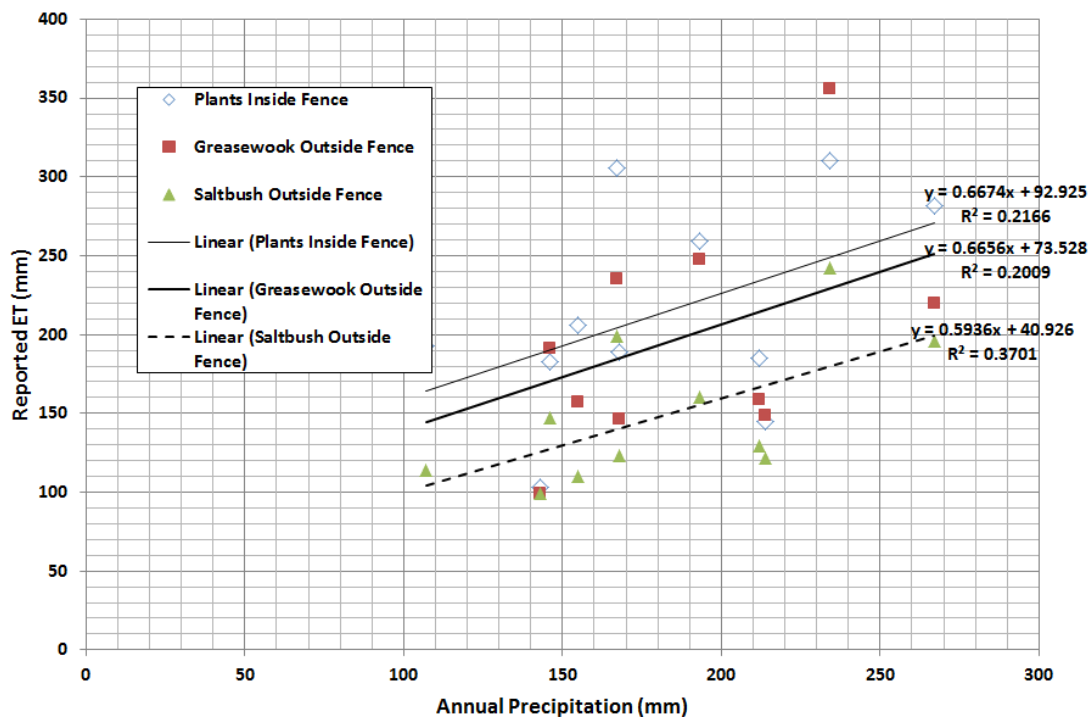


Figure 3-5. Correlation Between Hydrogen-2 ( $\delta^2\text{H}$ ) Versus Oxygen-18 ( $\delta^{18}\text{O}$ ) Enrichment in Phreatophyte Stem Moisture, Vadose Zone Soil Water, Rain Water at Page, Arizona and Well Water at Page, Arizona (Modified From Pilot Study Report, Figure C-2). The Phreatophyte Stem Moisture Isotopic Ratios All Fall on the Evaporated Water Line, as Do the Soil Water Ratios, Indicating the Stem Water Could Be Derived Either From the Vadose Zone or Locally Recharged Water. The Box Showing the Range of Water Table Samples Is Based on the Isotopic Data in the Pilot Study Report, Figure C-4 and the Water Table Elevations for Wells 607 and 677 (Reproduced From the Pilot Study Report, Appendix C, Figure C-2).



**Figure 3-6. Correlation Between Reported Annual Evapotranspiration (ET) and Annual Precipitation for Protected Phreatophytes (Plants Inside Fence) and Unprotected Phreatophytes (Outside Fence)**

source area to dilute contaminant concentrations outside of the subpile soil source area. With respect to the effects of revegetation and improved land management on hydraulic control of the plume, an increase in the total rate of evapotranspiration, whether taken from the vadose zone or the saturated zone, would undoubtedly slow the movement of the plume. However, as already stated, these effects would reduce dilution of nitrate and sulfate concentrations in the aquifer. If the phreatophytes are primarily removing water from the vadose zone, these effects will occur in both the shallow and deep aquifer zones. That the native phreatophytes are transpiring a substantial amount of water from the vadose zone is also implied by the results reported from land-farming pilot studies in the Pilot Study Report, Appendix E.

### 3.2.2 Phytoremediation of the Nitrate and Sulfate

The data on nitrate and sulfate uptake by phreatophytes from the alluvial aquifer in Section C.1.4 of the Pilot Study Report support DOE's conclusion that this mode of phytoremediation would not play a significant role in remediation of the alluvial aquifer.

### 3.2.3 Natural Denitrification in the Alluvial Aquifer

The Pilot Study Report relies on the close correspondence between denitrification rates measured in laboratory microcosms and those estimated from field nitrate concentration trends. The report concludes that microbial denitrification is the primary natural attenuation process in the alluvial aquifer. This conclusion is based on data from Carroll, et al. (2009). These data indicate that the denitrification rates estimated from field data only agree with the laboratory rates for the portion of the aquifer distal from the source area in which the dissolved oxygen

concentrations are low (0.1 to 1.0 mg/L) [0.1 to 1 ppm] but denitrification rates are much lower closer to the source area where dissolved oxygen concentrations are higher. The decrease in dissolved oxygen concentrations is attributed to consumption of ammonia by microbial oxidation. Although the correspondence between the laboratory and field denitrification rates supports DOE's conclusion regarding the importance of microbial denitrification in the alluvial aquifer, sustaining the inferred denitrification rates is contingent on maintaining relatively low dissolved oxygen concentrations in the alluvial aquifer. This raises a question as to whether reducing or eliminating the source of ammonia to the alluvial aquifer in the subpile soil source area would increase the dissolved oxygen concentration in the aquifer and reduce the effectiveness of microbial denitrification in the pre-existing plume in the future.

### **3.2.4 Enhanced Denitrification in Alluvial Aquifer**

The conclusion that denitrification rates can be increased by injecting a biodegradable, organic substrate into the aquifer is reasonable and consistent with findings from other sites. Enhanced denitrification occurs because microbial oxidation of the substrate reduces dissolved oxygen concentration to levels where microbial reduction of nitrate to reduced nitrogen species can occur. Enhanced denitrification also provides an organic nutrient to increase the microbial population. It remains to be determined whether enhanced denitrification of a large portion of the alluvial aquifer would be feasible due to the cost of adding an organic substrate and the complexity of controlling the movement and distribution of the organic substrate in the aquifer.

### **3.2.5 Remediation of Sulfate in Alluvial Aquifer**

Except for the possibility of reducing sulfate concentrations by establishing reducing conditions through the injection of an organic substrate, as would be done for enhanced denitrification, the Pilot Study Report does not present any clear path forward for remediation of the sulfate plume, other than by reducing contributions from the subpile soils and land-farming phytoremediation. Normally, one would expect some natural attenuation of the plume as the result of physical dilution and mechanical dispersion in the aquifer if the source is eliminated. These processes would affect both the nitrate and sulfate plumes. If DOE's conclusion that microbial denitrification is the primary attenuation process for the nitrate plume, meaning that dilution and dispersion have negligible effects, then these physical attenuation processes would likewise have little effect on the sulfate plume.

### **3.2.6 Land-Farming Phytoremediation**

The feasibility of using land-farming pump and treat to treat either the shallow or deep portions of the alluvial aquifer would depend on the ability of soil evaporation and phreatophyte transpiration to consume the water pumped from the aquifer and prevent nitrate and sulfate from leaching back into the aquifer. Nitrate leaching could also be prevented by the plants taking up the nitrate or by denitrification processes in the soil. Sulfate leaching could be prevented if the sulfate is sequestered in the soil in the form of a low solubility mineral, such as gypsum. The results of pilot studies presented in the Pilot Study Report, Appendix E found little or no nitrate accumulation in irrigated test plot soils, which DOE attributed to either plant uptake or leaching back into the aquifer [Note: DOE claims that there is no downward water movement in the subpile soils (Pilot Study Report, Appendix E, p. E-9)]. The black greasewood plots were found to have lower evapotranspiration rates than the fourwing saltbush plots because nitrate and sulfate leaching occurred in these plots (Pilot Study Report, Appendix E, p. E-0).

An important question that the Pilot Study Report leaves unanswered is the area of land farming that would be required to evapotranspire the pumped water. DOE (2000) estimated that the pump and treat alternative would require pumping 4.8 to 9.2 m<sup>3</sup>/hr [21 to 40 gpm] of water from the alluvial aquifer. These rates imply that between  $4.2 \times 10^4$  and  $7.9 \times 10^4$  m<sup>3</sup> [ $1.5 \times 10^6$  and  $2.8 \times 10^6$  cubic feet (ft<sup>3</sup>)] per year of water would need to be evapotranspired. Based on data presented in the Pilot Study Report, Appendix C, the average actual evapotranspiration rate for phreatophytes at the site was approximately 200 millimeters (mm) per year [0.66 ft/year]. This evapotranspiration rate implies that a minimum of 21.4 to 25.9 ha [53 to 64 ac] would be required to consume all of the pumped water, ignoring natural precipitation. As discussed previously, estimated annual evapotranspiration rates on test plots were comparable to annual precipitation, so the area needed to evapotranspire both the pumped water and precipitation would likely be greater. The Pilot Study Report does not analyze whether the area available for land farming is sufficient to consume the water from the pumping system.

### 3.3 Contribution of the Final Pilot Study Report to Obtaining the Objectives As Stated in the Work Plan

Table 3-3 lists the extent to which the Pilot Study Report addresses the objectives and scope for pilot studies presented in the Work Plan (DOE, 2005).

<b>Table 3-3. Objectives and Scope for Pilot Studies in the Work Plan</b>	
<b>Work Plan Objective</b>	<b>Extent Addressed in Pilot Study Report</b>
Delineate extent of nitrate, ammonium, and sulfate in subpile soils	DOE delineated the extent of these contaminants (Appendix B)
Investigate presence and mobility of natural nitrate and sulfate sources	DOE found natural nitrate to be indistinguishable from plume nitrate, and natural sulfate to be present, but not significant, with respect to sulfate from the milling process (Appendix B)
Determine causes of stunted plant growth and recourse	Results of soil sampling and greenhouse studies provided clues as to the causes of stunted growth, but an effective remedy was not found.
Expand irrigated planting of <i>Atriplex canescens</i> [four-wing saltbush]	DOE established irrigated test plots, but these plots are of limited extent
Quantify effects of irrigation on microbial denitrification processes and rates	DOE found that increasing the water content of the vadose zone soils increases the denitrification rate. Adding an organic substrate (ethanol) to the irrigation water of the field test plots did not substantially increase denitrification rates. Assessing nitrate concentrations with time in irrigated and non-irrigated plots provided a measure of effects of irrigation on microbial denitrification in subpile soils.
Investigate nitrification processes, rates, and possible enhancements.	DOE focused primarily on denitrification. No attempts were made to directly enhance nitrification. The loss of ammonium was attributed to nitrification, and the nitrate produced was subject to denitrification.

### 3.4 Contribution of the Final Pilot Study Report to Achieving the Objectives As Stated in the Pilot Study Report

Table 3-4 lists the extent to which the pilot studies contribute to achieving the objectives as stated in the Pilot Study Report.

<b>Table 3-4. Contributions to Achieving Objectives of the Final Pilot Study</b>	
<b>Pilot Study Objective</b>	<b>Extent Achieved</b>
Estimate the total capacity of natural chemical and biological processes that are reducing concentrations of groundwater contaminants at the site	Although the investigation results reported in the Pilot Study Report provide information on the processes and rates of natural attenuation of nitrate, ammonium, and sulfate, the Pilot Study Report does not quantify the total attenuation capacity of the processes.
Investigate methods to enhance and sustain attenuation processes that could be implemented if the total capacity of natural processes is inadequate	The pilot studies found that conversion of ammonium to nitrate and denitrification in the vadose zone could be enhanced by increasing the water content of the vadose zone and adding an organic substrate. The pilot study found that denitrification rates in the aquifer could be increased and sulfate concentrations decreased by adding an organic substrate.
Demonstrate methods for (i) characterizing attenuation rates, (ii) verifying short-term results, and (iii) monitoring performance of natural attenuation processes and enhancements.	The pilot studies demonstrated that denitrification rates could be characterized through a combination of field and laboratory studies, the use of stable nitrogen isotope ratios, and field monitoring of concentrations.
Evaluate land farming as an active remediation option if natural and enhanced attenuation processes are both inadequate	The pilot study report evaluated evapotranspiration rates of protected and unprotected plots of phreatophytes and the effects of irrigation on phreatophyte growth and soil moisture profiles. The pilot study report did not quantify the irrigated area that would be required for land farming water pumped from the aquifer or extent to which contaminants in the irrigation water would be removed or sequestered.



## **4 RECOMMENDATIONS**

### **4.1 Subpile Soils**

#### **4.1.1 Water Balance Using Enhanced Phytoremediation**

DOE intends to use enhanced phytoremediation to control the water balance of the subpile soils so that ammonium, nitrate, and sulfate will not be a source of contamination in the alluvial aquifer. For this approach to be effective, DOE needs to consider effects of nongrowing season precipitation and episodic precipitation events on the potential downward migration of ammonium, nitrate, and sulfate. Episodic flow in arid to semi-arid climates can occur in response to a sequence of precipitation events (Scanlon, et al., 1997). Summer monsoonal rains may be a source for episodic precipitation events, as well as El Niño, Pacific decadal oscillations, and larger scale weather patterns. In its argument supporting enhanced phytoremediation, DOE neglected any effects of nongrowing season precipitation and episodic precipitation events that may supply sufficient water to the subpile soils and would result in leaching of ammonium, nitrate, and sulfate toward the alluvial aquifer. Although episodic events and abundant nongrowing season precipitation are not common, they can be a major cause for groundwater recharge from overlying soils in semi-arid climates (Spangler and Johnson, 1999). As reported by the Western Regional Climate Center in Reno, Nevada, the monthly total snowfall in December 1992 was 114 cm [45 in] (<http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?azmonu>, monthly snowfall listings), which could be considered an episodic event that could generate groundwater recharge.

In addition, DOE needs to provide further evidence that there is no downward water migration. Other than measurements of water content, there was only a single water flux meter in a 1.7-ha [4.2-ac] field (the Old Field). A single water flux meter is not sufficient to conclude that there is no downward water movement from subpile soils toward the alluvial aquifer. Further, DOE should explain why the water content at the 270–300 cm [106–118 in] depth appears to have an increasing trend, which may indicate downward water movement.

#### **4.1.2 Enhanced Denitrification in the Vadose Zone**

DOE plans to supply irrigation water to support phytoremediation as was conducted in the pilot studies. The resulting higher water content in the subpile soils may enhance denitrification over what would occur under drier conditions. In the pilot studies, there was an initial rapid decrease in nitrate levels followed by slower reductions. Based on the observed trend that there appears to be only very minor reduction in nitrate levels between 2004 and 2010 in the subpile soil (Figure 3-3), DOE needs to estimate what the consequences may be from long-term irrigation and what effect enhanced nitrification, in addition to enhanced denitrification, may have on nitrate levels in the subsoils.

In addition, DOE needs to resolve the apparent contradiction between Tables 3-1 and 3-2 and Figure 3-2. In the tables, more nitrate appears to have been removed than ammonium. In the figure, more ammonium appears to have been reduced than nitrate. The increase in nitrate deeper in the subpile soil between 2004 and 2010 also needs to be clearly explained.

### **4.1.3 Sulfate in the Vadose Zone**

In Figure 3-3, DOE shows that the sulfate concentration in the subpile soils increased because the irrigation source contained sulfate. DOE did not address directly how this increase may affect the subpile soils and potential remediation activities over a long time period. The consequence of adding sulfate to the subpile soils, especially if long-term irrigation is proposed, will need to be investigated.

## **4.2 Alluvial Aquifer**

The following sections contain recommendations specifically related to remediation of the alluvial aquifer.

### **4.2.1 Hydraulic Control of Plume by Phreatophytes**

The Pilot Study Report does not provide clear estimates of how much water an enhanced population of phreatophytes would withdraw directly from the shallow alluvial aquifer versus the amount they would withdraw from the vadose zone. DOE should provide such an estimate and supporting calculations of the rate of groundwater movement to determine how an enhanced population of phreatophytes would affect the movement of the contaminant plume in both the shallow and deep portions of the aquifer.

#### **4.2.1 Phytoremediation of the Nitrate and Sulfate**

Because the Pilot Study Report found that the rate of uptake of nitrate and sulfate by phreatophytes from the alluvial aquifer was very small with respect to the mass of these contaminants in the aquifer, no recommendations are made to further investigate this remedial process.

#### **4.2.2 Natural Denitrification of the Alluvial Aquifer**

The Pilot Study Report and supporting data indicate that natural denitrification is occurring primarily in the portion of the alluvial aquifer downgradient from the subpile soils where the dissolved oxygen concentration in the groundwater is conducive to denitrification. This zone of depleted dissolved oxygen is probably the result of aerobic nitrification of ammonium near the subpile soil source area. If phytoremediation of the subpile soil area successfully reduces the ammonium load to the aquifer, the dissolved oxygen content in the aquifer may increase and reduce the effectiveness of denitrification in the alluvial aquifer. Although reducing the ammonium load to the aquifer from the subpile soil area is desirable for reducing the contribution of nitrate to the aquifer, DOE should evaluate how this might affect natural attenuation of the downgradient portion of the nitrate plume given the relatively low importance attributed to physical attenuation processes (dilution and dispersion).

#### **4.2.3 Enhanced Denitrification of the Alluvial Aquifer**

The results of pilot studies indicate that adding a carbon substrate, such as ethanol, can increase denitrification in the alluvial aquifer. Enhanced denitrification was also found to reduce sulfate concentrations, presumably by reducing sulfate to sulfide. If this action is selected in the Groundwater Corrective Action Plan, additional studies would be required to determine the

technological and economic feasibility of large-scale injection of organic chemicals into the aquifer, as well as an evaluation of any secondary deleterious effects on water quality.

#### 4.2.4 Remediation of Sulfate in the Alluvial Aquifer

Assuming that physical natural attenuation processes play a limited role in attenuating nitrate in the alluvial aquifer, they would also play a limited role in remediation of the sulfate plume. The only actions for remediation of the sulfate plume the pilot study addressed were pumping water from the aquifer and irrigating fields of phreatophytes, or enhanced denitrification, that also reduced sulfate concentrations. Additional investigations would be required to determine the capacity of the shallow soils and vadose zone to sequester sulfate in some relatively immobile form. If, as DOE hypothesized, the sulfate applied to the land-farming area is sequestered as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), then any water infiltrating the land-farming area exceeding what is transpired will have a sulfate concentration determined by the solubility of gypsum. In the simplest case, the sulfate concentration in the infiltrating water can be estimated from the solubility of gypsum determined by

$$\frac{C_{Ca}}{M_{wCa}} \frac{C_{SO4}}{M_{wSO4}} = K_{sp} = 6.1 \times 10^{-5} \quad (4-1)$$

Where

- $C_{Ca}$  – Concentration of calcium ions in grams per liter [g/L]
- $C_{SO4}$  – Concentration of sulfate ions in [g/L]
- $M_{wCa}$  – Molecular weight of calcium in grams per mol [g/mol]
- $M_{wSO4}$  – Molecular weight of sulfate in [g/mol]
- $K_{sp}$  – Solubility product of gypsum in  $\text{mol}^2$  per liter<sup>2</sup> [ $\text{mol}^2/\text{L}^2$ ]

As indicated, the solubility product of gypsum is approximately  $6.1 \times 10^{-5} \text{ mol}^2/\text{L}^2$  (Skoog and West, 1974). Assuming that calcium concentration is approximately equal to the sulfate concentration, the solubility product equation can be rearranged to solve for the sulfate concentrations as

$$C_{SO4} = \sqrt{6.1 \times 10^{-5} \times 40 \frac{\text{g}}{\text{mol}} \times 96 \frac{\text{g}}{\text{mol}}} = 0.48 \frac{\text{gm}}{\text{L}} \equiv 480 \frac{\text{mg}}{\text{L}} [\text{ppm}] \quad (4-2)$$

Based on this calculation, the sulfate concentration in the infiltrating water could exceed the Navajo Nation goal for remediation of sulfate of 250 mg/L [250 ppm] unless it is attenuated by other mineral or ion exchange reactions. Additional studies are needed to determine the ultimate capacity of the soil and vadose zone in the potential land-farming areas to sequester sulfate so that it does not return to the aquifer at concentrations that would exceed the Navajo Nation goal for remediation of sulfate.

#### 4.2.5 Land-Farming Phytoremediation

The land-farming pump and treat alternative will require that the land-farming area be sufficient to completely evapotranspire the applied groundwater plus natural precipitation. DOE should provide an estimate of the land-farming area that would be required to manage the pumped groundwater that accounts for a limited growing period and natural precipitation at the site, including the effect of unusually wet years and extreme precipitation events.

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