

**Natural and Enhanced Attenuation of Soil and Groundwater  
at the Monument Valley, Arizona, DOE Legacy Waste Site—10281**

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**ABSTRACT**

The U.S. Department of Energy (DOE), the Navajo Nation, and the University of Arizona are exploring natural and enhanced attenuation remedies for groundwater contamination at a former uranium-ore processing site near Monument Valley, Arizona. DOE removed radioactive tailings from the Monument Valley site in 1994. Nitrate and ammonium, waste products of the milling process, remain in an alluvial groundwater plume spreading from the soil source where tailings were removed. Planting and irrigating two native shrubs, fourwing saltbush and black greasewood, markedly reduced both nitrate and ammonium in the source area over an 8-year period. Total nitrogen dropped from 350 mg/kg in 2000 to less than 200 mg/kg in 2008. Most of the reduction is attributable to irrigation-enhanced microbial denitrification rather than plant uptake. However, soil moisture and percolation flux monitoring show that the plantings control the soil water balance in the source area, preventing additional leaching of nitrogen compounds.

Enhanced denitrification and phytoremediation also look promising for plume remediation. Microcosm experiments, nitrogen isotopic fractionation analysis, and solute transport modeling results suggest that (1) up to 70 percent of nitrate in the plume has been lost through natural denitrification since the mill was closed in 1968, and (2) injection of ethanol may accelerate microbial denitrification in plume hot spots. A field-scale ethanol injection pilot study is underway. Landscape-scale remote sensing methods developed for the project suggest that transpiration from restored native phreatophyte populations rooted in the aquifer could limit further expansion of the plume. An evaluation of landfarm phytoremediation, the irrigation of native shrub plantings with high nitrate water pumped from the alluvial aquifer, is also underway.

**INTRODUCTION**

The U.S. Department of Energy (DOE), the Navajo Nation, and the University of Arizona are conducting pilot studies of enhanced attenuation remedies for contaminated groundwater at a former uranium-ore processing site at Cane Valley, east of Monument Valley, Arizona. Nitrate, ammonium, and sulfate levels are elevated in an alluvial aquifer, and the contaminant plume is spreading away from a source area where uranium mill tailings were removed. The pilot studies at Monument Valley were mandated by a DOE Environmental Assessment that also gives direction for an evaluation of alternative remedies before a final strategy is selected [1]. Preliminary studies suggested that natural and enhanced attenuation, including phytoremediation, may be viable options for reducing nitrate, ammonium, and sulfate levels in the alluvial aquifer and at the plume source [2,3]. Phytoremediation is also in harmony with revegetation and range management goals for the site.

Pilot studies were designed to answer two questions: (1) what is the capacity of natural processes to remove nitrogen and sulfate and slow plume dispersion, and (2) can we efficiently enhance natural attenuation if necessary? This paper presents background information and highlights of natural and enhanced phytoremediation and microbial denitrification studies, conducted over a nine year period, for containment and removal of contaminants from the source area and from the groundwater plume at the site. Enhanced attenuation can be defined as initiating and/or augmenting natural and sustainable attenuation processes. The goal is to increase the magnitude of attenuation by natural processes beyond that which occurs without intervention.

## SITE HISTORY

The Monument Valley Processing Site is located on the Navajo Nation in northeastern Arizona, 26 km south of Mexican Hat, Utah (Figure 1). Uranium was first discovered in 1942 approximately 1 km west of the site. An estimated 696,000 metric tons of uranium and vanadium ore were mined from the deposit between 1943 and 1968. From 1955 until 1964, ore was processed by mechanical milling followed by chemical flocculation. The finer-grained material, higher in uranium content, was shipped to other mills for chemical processing. Coarser-grained materials were stored on site.

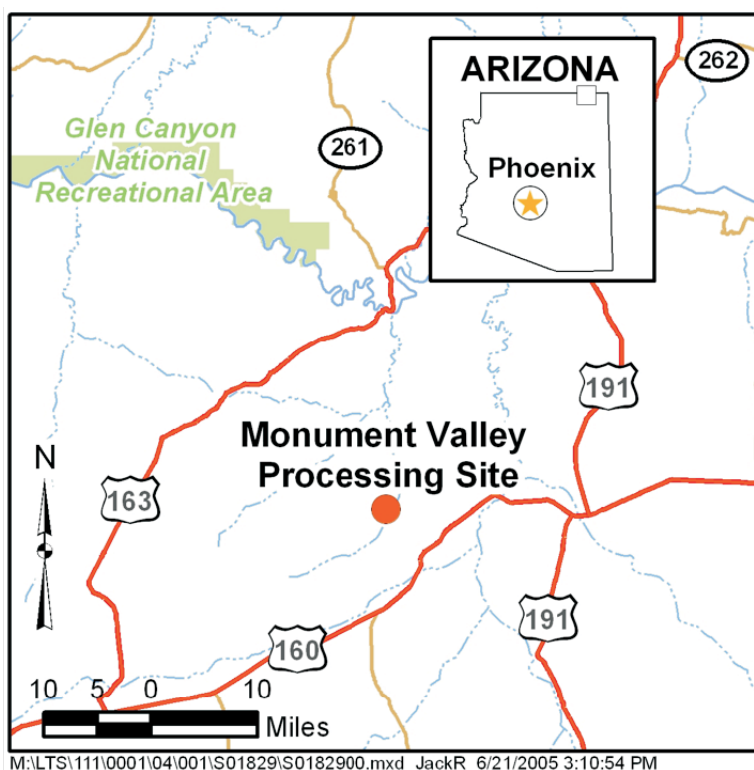


Fig. 1. Location of the Monument Valley Site in northeastern Arizona.

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

The mill closed in 1968, and most of the mill buildings were removed shortly thereafter. Surface remediation of the site, from 1992 through 1994, included excavation and hauling of tailings and other site-related contamination to the Mexican Hat Disposal Cell about 16 km to the north. Analysis of soil within the footprint of the tailings piles indicated that residual ammonium and nitrate may be contributing to nitrogen contamination in groundwater.

## **REGULATORY COMPLIANCE**

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

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 soil, buildings, and groundwater. 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* in 1989 before conducting surface remediation of the land and mill tailings in 1992 [4]. The Environmental Assessment described the affected environment, including surface water and groundwater, and the removal of tailings and debris from the Monument Valley site to the Mexican Hat disposal cell. After the source of groundwater contamination (i.e., the tailings pile) is removed, EPA regulations require that the site be evaluated to determine if groundwater quality beneath and downgradient from the site complies with EPA standards in 40 CFR 192. To comply with these standards, DOE completed the *Final Site Observational Work Plan for the UMTRA Project Site at Monument Valley, Arizona* (SOWP) [5], a site evaluation and findings, and an update of the original Baseline Risk Assessment [6]. The Baseline Risk Assessment evaluated potential human health and ecological risks that could result from exposure to residual radioactive materials. The recommended compliance strategies became the basis for the proposed remedial action in a second Environmental Assessment [7].

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 Uranium Mill Tailings Remedial Action (UMTRA) Project, Navajo EPA, Navajo Water Code Administration, and Navajo Department of Justice to address concerns at the Monument Valley site. To minimize risks to potential water users near the site in the short term, DOE and the Navajo Nation installed a water supply system to serve the Cane Valley area. A new well, water line, and infrastructure were completed in September 2003. The Navajo Tribal Utility Authority, in cooperation with the Bureau of Indian Affairs, prepared the necessary National Environmental Policy Act (NEPA) documentation for the alternate water supply.

## **NATURAL AND ENHANCED ATTENUATION STRATEGIES**

The compliance strategy for the alluvial aquifer addresses three areas of concern: subpile soils (soils within the footprint of the tailings pile), shallow alluvial groundwater, and deep alluvial groundwater. Natural attenuation was proposed for the deeper portions of the aquifer. The proposed compliance

strategies for subpile soils and shallow portions of the aquifer are a combination of natural and enhanced attenuation.

Conventional remedies for contaminated soil and groundwater focus on engineered systems such as excavating and hauling large volumes of soil to engineered landfills, and on drilling wells to pump large volumes of groundwater to the surface for treatment. In contrast, reliance on natural processes to clean up contamination, referred to as monitored natural attenuation (MNA), has increased in response to greater awareness of the limitations of engineered remedies for achieving groundwater and soil remediation goals [8]. However, the capacity of natural processes alone may not be adequate to attain remediation goals in a timely manner. At sites with uranium mill tailings contamination, natural attenuation can be used to manage groundwater contamination remaining after engineering approaches have removed or isolated the source of contamination [9].

Enhanced attenuation is a strategy that bridges the gap between active, engineered solutions, and passive MNA [10]. Enhanced attenuation involves human intervention to enhance or accelerate natural processes. Successful enhancements should increase the magnitude of natural attenuation processes beyond what would occur without intervention. A successful enhancement is also a sustainable manipulation—it does not require continuous, long-term intervention. In many cases, sustainable enhancements of natural processes are needed to achieve a favorable mass balance between the release of contaminants from a source (contaminant loading) and processes that degrade or retard migration of contaminants downgradient in the plume.

In June 2000, DOE and the Navajo Nation agreed to conduct pilot studies to evaluate natural and enhanced attenuation as the primary components of a final remedy for the alluvial aquifer at the Monument Valley site. Results of the proposed pilot studies would be the basis for remediation of the alluvial aquifer and subpile soils. 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.

## **ENVIRONMENTAL SETTING**

### **Climate**

The Monument Valley Site is semiarid with 163 mm average annual precipitation. Wetter months are July through August and December through February. May and June are generally drier. Summer precipitation typically occurs as high-intensity, short-duration storms, and winter precipitation occurs as low-intensity, longer-duration storms. Average daily low temperatures are below freezing from November through March. Summers are warm with daily high temperatures of 32 to over 37 °C. The annual pan evaporation averages 2141 mm. Average pan evaporation rates exceed precipitation every month except January. The highest pan evaporation rates, greater than 250 mm per month, occur from May through August.

### **Soils and Hydrogeology**

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

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

The hydrogeology of the site and the nature and extent of contamination are discussed in detail in DOE's Site Observational Work Plan [5]. The alluvial aquifer underlying the site consists mainly of windblown and some water-deposited, fine- to medium-grained sands. In the area of the alluvial nitrate plume, the depth to groundwater is between 9 and 12 m. The average hydraulic conductivity of the portion of the alluvial aquifer containing the nitrate plume was estimated to be 6.5 m/day. Assuming an effective porosity of 0.25 and a hydraulic gradient of 0.007 to 0.012, the groundwater velocity ranged from 0.2 to 0.3 m/day. At these velocities, the nitrate plume would have taken 15 to 25 years to reach its farthest extent in 1997 (about 1700 m downgradient). In the centroid of the plume, the average hydraulic gradient was estimated at 0.0095 with a groundwater velocity of 0.25 m/day. These values indicate it would have taken approximately 22 years for the portion of the nitrate plume that is above background to reach its 1997 extent.

Ammonium, calcium, nitrate, sulfate, and manganese were the site-related constituents most prevalent in the alluvial aquifer in 1997. Nitrate is the constituent of greatest concern in alluvial groundwater because concentrations exceeded the EPA groundwater standard of 44 milligrams per liter for nitrate as NO<sub>3</sub>. Since the completion of uranium mill tailings removal in 1994, nitrate concentrations have decreased from about 1,200 mg/L in 1994 to about 800 mg/L in 2003 in a well at the centroid of the plume. In contrast, nitrate concentrations have increased in outer plume wells, although no significant increases in nitrate concentration have yet been detected in downgradient wells. The increase of nitrate in the outer plume is likely due to more highly contaminated groundwater from the centroid of the plume making its way downgradient.

### **Plant Ecology**

The occurrence and relative abundance of plant species, coupled with knowledge of their physiological and ecological tolerances, provided measures of the health of the ecosystem and evidence of environmental conditions that are of importance for phytoremediation planning. Plant cover in stands near monitoring wells was characterized, and stands were then grouped into associations using simple ordination and gradient analysis techniques [11]. Because species composition and cover vary across the site as a continuum rather than as discrete units, a simple gradient analysis of dominant species was used to group stands. Results of the gradient analysis suggested that some dominant species are associated and that associations overlap—a given stand may occur in more than one association. Four associations occur, named for their two most abundant shrubs:

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

Phreatophytes (literally “well plants”) at the Monument Valley site may act, in essence, as passive, solar-powered, pump-and-treat systems for nitrate and ammonium in the alluvial aquifer. Two phreatophyte populations grow over the plume area: *Sarcobatus vermiculatus* and *Atriplex canescens* (dívózhii\_beii

and *díwózhiiishzhiin* in Navajo, and fourwing saltbush and black greasewood in English). *S. vermiculatus* is considered an obligate phreatophyte requiring a permanent groundwater supply, and can transpire water from aquifers as deep as 18 m below the land surface [12]. *A. canescens* is a facultative phreatophyte; it takes advantage of groundwater when present but can tolerate periods of low water availability. The rooting depth of *A. canescens* may exceed 12 m [13].

## **SOURCE CONTAINMENT AND REMOVAL**

About 1.7 ha of the source area for the nitrate plume, soils remaining after tailings were removed, was planted in 1999, mainly with the native desert shrub *A. canescens*, to function as a phytoremediation cover. Phytoremediation relies on the roots of plants to remove, degrade, and slow the migration of contaminants. The purposes of the planting were (1) to control the soil water balance through evapotranspiration, limiting deep percolation and contaminant seepage, and (2) to extract and convert ammonium and nitrate into plant tissue. A rectangular irrigated plot was planted with approximately 4,000 *A. canescens* seedlings grown from seed collected on Navajo Nation land and raised in a greenhouse at the University of Arizona. A drip irrigation system was installed to accelerate growth and enhance denitrification. In March 2006, the remaining 1.6 ha of the source area was planted and irrigated. A total of 3.3 ha of the source has now been planted with a phytoremediation cover, and over 7,300 plants are now growing in the irrigated planting.

### **Nitrogen Uptake in Plants**

*A. canescens* shrub growth and nitrogen uptake have been monitored since 2000. A relatively small number of dead or missing plants have been replaced. Plant cover, estimated in 2007 using an October QuickBird satellite image, ranged from 27 percent in sparse areas to 71 percent in areas of greatest growth [14]. At the end of the 2007 growing season, mean plant canopy cover was 45 percent for the 1999 planting and 16 percent for the 2006 planting. Plant canopy cover and growth rates have varied across the plantings in response to the age of the planting, irrigation rates, and soil fertility.

Annual nitrogen uptake was estimated using a double sampling routine. Plant canopy volume was estimated from measurements of plant canopy widths and height. Plant biomass was estimated using a regression with plant canopy volume. Subsamples of leaves and stems are analyzed to estimate nitrogen content on the basis of biomass. By the end of the 2007 growing season, the estimated total annual nitrogen uptake by *A. canescens* was 204 kg in the 1999 planting and 42 kg in the 2006 planting [14].

### **Denitrification and Nitrification**

Soil cores were collected in the source area soils every year since 2000 from both the 1999 planting and later from the 2006 planting, and analyzed for nitrate as N, ammonium as N, and sulfate as S. Figure 2 shows mean soil nitrate and ammonium results from the 1999 planting for the period 2000–2008 [15]. Both nitrate and ammonium levels have decreased significantly ( $P < 0.001$ ) since 2000. The decrease in nitrate appears to have slowed, as expected for a substrate-dependent, exponential decay process. On the other hand, ammonium levels are still decreasing. Nitrification (of ammonium) is a likely reason for the slow decrease in nitrate. Overall, total nitrogen has been reduced from 350 mg/kg to 200 mg/kg. Nitrate and ammonium concentrations in the 2006 plantings may have decreased between 2007 and 2008, but results were not significant ( $P > 0.05$ ), and levels remain elevated.

These data show that planting and irrigating the source area has been exceptionally effective in removing nitrate from the soil. However, the data also show that nitrogen removal far exceeds what can be attributed to plant uptake. A salt-balance evaluation and a study of  $^{15}\text{N}$  enrichment in the residual nitrate show that the nitrate loss can be attributed to microbiological processes and not leaching [15]. Soil

samples taken throughout the 1999 planting show that  $^{15}\text{N}$  enrichment ( $\delta^{15}\text{N}$ ) is linearly related to the log of nitrate and ammonium concentrations, and that slopes of enrichment curves are the same. Denitrification favors  $^{14}\text{N}$  over  $^{15}\text{N}$ , so residual nitrate in the soil becomes enriched in  $^{15}\text{N}$  as nitrate becomes depleted. This is evidence that loss of nitrogen is due to denitrification in the case of nitrate, and of nitrification followed by denitrification in the case of ammonium.

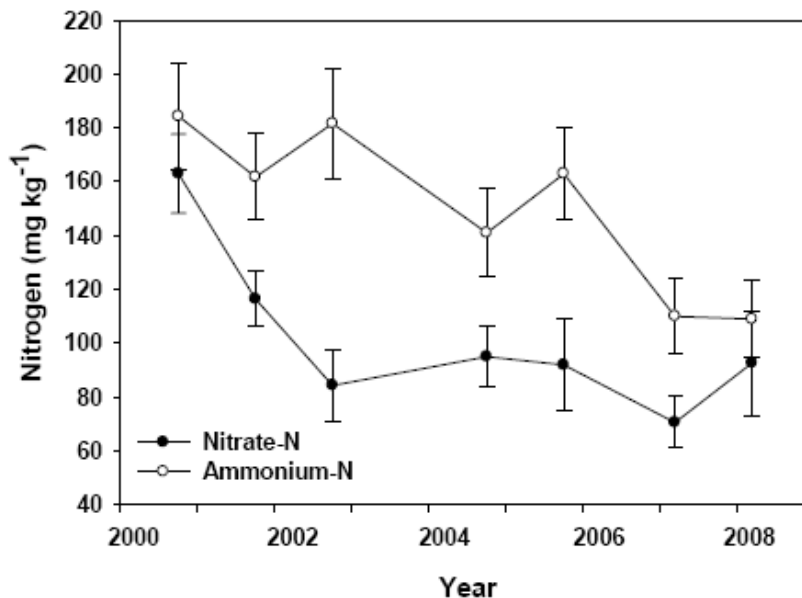


Fig 2. Nitrate and ammonium concentrations in the 1999 planting from 2000 to 2008.

Results depicted in Fig. 2 are from the analysis of 100 auger holes sampled at 3–5 soil depths at each sample interval. Error bars are standard errors of means. Data were analyzed by one-way analysis of variance with sample interval as the independent variable; both nitrate and ammonium have decreased ( $P < 0.001$ ).

Nitrate and ammonium both increased in concentration with soil depth, whereas sulfate is most concentrated at shallow depths. Most nitrate losses have come from the middle of the soil profile, whereas most ammonium losses have come from shallow soil depths. Nitrification of ammonium to nitrate is an oxidative process that is more likely to occur in shallow, aerated soil, whereas denitrification is an anaerobic process more likely to occur in deeper, less-aerated soil.

A soil microcosm study supported the hypothesis that nitrification occurs when source area soils are drier, and denitrification occurs at higher moisture contents [16]. The microcosm denitrification results were similar to values observed in the field plot during times when soils were wet. In the field, denitrification rates rose when soils were wettest and dropped when plantings matured and dried the soil. Batch and column studies have shown that ethanol, a carbon source, can also greatly enhance denitrification of source area soils [16]. However, in a 2007 field study that supplied ethanol through the irrigation system, the ethanol did not enhance denitrification rates [14]. Denitrification rates are usually highest in wet, anaerobic soils. Average soil moisture content remained well below field capacity, suggesting that in the source area, soil moisture (not carbon) is the limiting factor for denitrification.

### Soil Moisture and Percolation Flux Monitoring

One objective of planting phreatophytes in the source area is to control the soil water balance and limit percolation and leaching of nitrate, much like an evapotranspiration disposal cell cover. Plantings are

purposefully under-irrigated to prevent recharge. Annual irrigation rates have been decreased or increased over the course of the study, from zero in 2003 up to 490 mm in 2007, to enhance nitrification and denitrification, respectively. Soil moisture profiles are monitored with neutron hydroprobes and time-domain reflectometry, and percolation flux is monitored with water fluxmeters to evaluate the dynamic soil water balance.

Soil moisture levels are measured monthly during the irrigation season (March through October) at approximately 0.3 m intervals in a series of 60 neutron hydroprobe ports distributed in the 1999 planting, the 2006 planting, and in control (not irrigated) areas. The variability in soil moisture was evaluated using a three-way analysis of variance in which year, month, and location were independent variables and volumetric soil moisture averaged over all depths was the dependent variable [15]. The results indicated that yearly changes were only marginally significant ( $P = 0.051$ ), while monthly changes and variation among locations were highly significant ( $P < 0.001$ ). The interaction term, year  $\times$  site, was also highly significant ( $P < 0.001$ ), showing that the locations responded differently to altered irrigation schedules. Overall, the results suggest that soil water content is highest in the irrigated plots where plants are not well established and in denuded control plots.

Real-time monitoring with water content reflectometers (WCRs) and soil water fluxmeters (WFMs), installed in 2006 at four locations within source area plantings, provided additional understanding of the variability in moisture content and also a direct measure of recharge [15]. Results from WCRs indicated that water content was consistently higher in the 1999 planting of mature senescent plants, most likely because of a low productivity and low transpiration rates. WCRs located in 2006 planting, where productivity is highest, have recorded yearly declines in water content at all depths, a likely response to increasing leaf area and transpiration.

The four WFMs monitor percolation of water that could potentially leach contaminants. WFMs were installed near the bottom of the root zone and are capable of directly monitoring saturated and unsaturated water fluxes ranging from 0.02 mm/year to more than 1,000 mm/year [17]. WFMs are passive wick lysimeters that monitor percolation flux from a soil-filled funnel. The soil captures flow from a predetermined area where it drains into the funnel neck occupied by a conductive material capable of applying a capillary pressure to the overlying soil. Water flux is measured directly with a miniature tipping bucket placed below the lower end of the wick. Prototype WFMs were first field-tested at Monument Valley in 2003.

The four WFMs recorded zero percolation since 2006 in all locations; areas with small immature plants, with mature senescent plants, and with large productive plants. These results and the soil moisture data show that the phytoremediation planting has cut off the plume from its source. Precipitation and irrigation are stored in the fine sand until seasonally removed by evapotranspiration and are not percolating and leaching nitrate.

### **Natural Sources of Soil Nitrate and Sulfate**

Because Southwestern desert soils are known to naturally accumulate nitrate and sulfate [18], possible natural sources of nitrate and sulfate in the plume were evaluated at the Monument Valley site. The vadose zone overlying the plume and in the alluvial aquifer upgradient of the plume were both sampled as possible sources [19].

In the vadose zone, nitrate levels were below detection limits in most samples but sometimes exceeded 100 mg/kg in the capillary fringe of the plume. Sulfate concentrations greater than 100 mg/kg occurred in almost all borings; hence, the elevated concentrations likely represent naturally occurring zones or horizons of gypsum accumulation. Wells were drilled into the alluvial aquifer using a Geoprobe to better



characterize nitrate and sulfate upgradient of the plume. Nitrate levels were low, typical of desert groundwater. These results and the relatively low levels in the vadose zone indicate that essentially all of the nitrate plume can be attributed to the mill site source. The upgradient sulfate levels, however, were highly variable. This may be a response to localized recharge through sediments high in gypsum, or perhaps to upwelling and mixing of deep groundwater that is low in sulfate with localized recharge that is higher in sulfate.

## NATURAL AND ENHANCED ATTENUATION OF GROUNDWATER CONTAMINANTS

The pilot studies are evaluating natural and enhanced attenuation remedies for groundwater contamination in the alluvial aquifer at Monument Valley with a focus on two attenuation processes: phytoremediation to remove nitrate and sulfate and to slow plume dispersion, and microbial denitrification.

### Phytoremediation and Remote Sensing

*A. canescens* and *S. vermiculatus*, if rooted into the nitrate plume, could be contributing to natural attenuation in two ways: (1) transpiration of water from the plume, slowing its dispersion from the site, and (2) uptake of nitrate from the plume. Stable isotope methods were used to evaluate plant extraction of water and nitrate [15]. Water contains a small proportion of the heavy isotopes,  $^{18}\text{O}$  and deuterium (D), in addition to the more common  $^{16}\text{O}$  and H. Stem water samples from plants growing over the plume should have the same isotope composition as the source of water accessed by their roots. The  $^{18}\text{O}$  and D results support the hypothesis that *S. vermiculatus* is an obligate phreatophyte rooted into the plume, whereas *A. canescens* is a facultative phreatophyte that uses both plume water and vadose zone water. Similarly, the nitrogen isotope composition of plant tissues can indicate if plants are extracting nitrate from the plume. Natural nitrogen sources also contain a small proportion of  $^{15}\text{N}$  in addition to  $^{14}\text{N}$ . Results of  $^{15}\text{N}$  analyses support the hypothesis that both plant species extract nitrate from the plume.

Preliminary studies found that protecting existing stands of *A. canescens* and *S. vermiculatus* from grazing could double biomass production, transpiration rates (water extraction from the aquifer by plants), and nitrogen uptake rates [20]. These studies also demonstrated how, on a small scale, greenhouse-grown transplants of native shrubs could be established in denuded areas of the plume, and with managed irrigation, send roots 9 meters and deeper into the alluvial aquifer. In fall 2005, four large plots (two grazing exclosure plots and two revegetation plots) were set up to see if the preliminary studies could be repeated on a large scale. After two growing seasons, canopy cover of phreatophytic shrubs was more than 2 times greater inside than outside the grazing exclosures. However, growth of shrub transplants remained low in the revegetation plots because of herbivory by small mammals.

With managed grazing, phreatophytic shrubs growing over the nitrate plume could extract enough water to slow the spread of the plume during the time it takes for denitrification to reduce nitrate to safe levels. Currently, relatively heavy grazing is practiced at the site, and shrub cover is only about 9–10 percent over most of the plume. Annual evapotranspiration over the plume is approximately equal to annual precipitation. However, exclosure studies have shown that the ground cover could conceivably be increased to 25 percent through controlled grazing [20]. In 2006 and 2007, transpiration rates of individual *A. canescens* and *S. vermiculatus* plants were measured both inside and outside grazing exclosure plots using sap-flow instrumentation. These data were then extrapolated to a landscape scale using Quickbird and Moderate Resolution Imaging Spectrometer (MODIS) satellite estimates of shrub cover [21]. Results suggest that an increase of 30 mm/year in annual evapotranspiration over the plume through enhanced vegetation abundance could tip the water balance of the aquifer from recharge to discharge. Conversely, increased grazing pressure or loss of vegetation through climate change could tip the balance towards recharge, leading to further migration of the plume away from the source area.

## **Groundwater Denitrification**

Early pilot studies suggested that natural denitrification is occurring in the plume [20, 22]. Nitrate levels in the alluvial aquifer decrease with distance from the source area and have also decreased over time. Part of the decrease is likely due to dilution, but part of the nitrate may have been lost to microbial denitrification. A natural process called  $^{15}\text{N}$  enrichment in the plume provided a preliminary estimate of denitrification. The  $^{15}\text{N}$  enrichment study evaluated the ratio of the natural isotopes of nitrogen ( $^{15}\text{N}$  and  $^{14}\text{N}$ ) in the plume. Biological denitrification favors  $^{14}\text{N}$  over  $^{15}\text{N}$ ; therefore, as denitrification proceeds, the residual nitrate remaining in the plume becomes enriched in  $^{15}\text{N}$ . Preliminary results suggested that up to 60 percent of a drop in nitrate from the source out to the leading edge of the plume can be attributed to denitrification.

An evaluation was started in 2007 of the feasibility of enhancing natural groundwater denitrification processes as part of the final remedy [14]. The feasibility study (1) characterized the occurrence and rates of natural attenuation processes (denitrification, sorption, and dispersion), (2) completed laboratory microcosm experiments for injecting carbon sources to enhance denitrification, (3) conducted a temporal and spatial analysis of plume well data, and (4) calibrated a nitrate transport model to predict and compare natural and enhanced attenuation scenarios [23].

Results of these studies confirm that the natural attenuation of nitrate is occurring at the site. Dispersion and sorption, estimated from the laboratory microcosm experiments, had minor effects on nitrate transport. Denitrification appears to be the dominant process as determined by microcosm decay and isotopic fractionation experiments, field-scale isotopic fractionation analyses, and numerical modeling. The modeling exercise suggested that although natural attenuation is occurring, it may take more than 150 years to achieve cleanup standards without enhancements. However, the modeling exercise also suggested that the injection of ethanol as a substrate for denitrification could substantially increase groundwater denitrification rates and shorten the cleanup time by more than 100 years. A field-scale ethanol injection study is underway.

## **INTERRELATIONSHIPS OF $\text{NH}_4$ , $\text{NO}_3$ , $\text{SO}_4$**

Contamination of groundwater by nitrate, ammonium, and sulfate are the major concerns for remediation of the Monument Valley site, and there is great interest in the impact of natural attenuation on risk and management of groundwater contaminant plumes. Transport and fate processes that influence ammonium, nitrate, and sulfate concentrations were evaluated [15].

Spatial and temporal concentration data collected from a transect of monitoring wells located along the plume centerline were analyzed to evaluate the overall rates of natural attenuation. The results indicate that nitrate, ammonium, and sulfate concentrations are decreasing due to natural attenuation processes. Adsorption appears to partly control the transport and fate of ammonium in the plume. Sulfate concentrations are most likely controlled by equilibrium formation/dissolution of the solid mineral phase gypsum. Naturally formed gypsum lenses are already found in soils at the site. Excess Ca ions in the soil react with sulfate in the source area and contamination plume to produce gypsum deposits, which are relatively immobile.

Ammonium has decreased in the irrigated subpile soils in the source area through microbial processes (nitrification followed by denitrification). Ammonium biotransformation to nitrate (i.e., nitrification) may also be occurring in the upgradient part of the plume. Nitrate biotransformation occurs through reduction to atmospheric nitrogen gas (i.e., denitrification) in both the irrigated subpile soils and the downgradient region of the plume. The occurrence and rate of denitrification was evaluated through microcosm experiments, nitrogen isotopic fractionation analysis, and solute transport modeling. First-order rate

coefficients calculated with each method were comparable. The composite natural attenuation rate coefficient was slightly larger but similar to the denitrification rate coefficient, which suggests that microbially induced decay primarily controls nitrate attenuation at the site. Sulfate reductive biotransformation was not evident from the available data.

Overall, approximately half of the nitrate and ammonium originally present in the source area has been remediated since 1999 through planting and irrigating of native shrubs, and an estimated 30–70 percent of nitrate in the plume has been lost through natural denitrification since the mill was closed in 1968. Estimates of sulfate losses through gypsum formation are not yet available, but eventually an equilibrium level is expected to be established at the solubility of calcium sulfate (2,000 mg/L) in the hotspots of the plume, and lower where the plume has been diluted.

## **LAND FARMING**

Land farming is under consideration as an active remediation alternative only if more passive alternatives (natural and enhanced attenuation) are found to be inadequate. Land farming would involve pumping plume water from the alluvial aquifer to irrigate fields of native plants. This would remove nitrate and sulfate from the aquifer, convert nitrate into healthy plant tissue, and—mimicking natural gypsic soil horizons in the area—store sulfate as gypsum in the farm soil. Irrigation would be managed to prevent contaminants from leaching back into the aquifer. As with other phytoremediation alternatives, land farming would improve the rangeland ecological condition and could produce a crop such as native plant seed that the Navajo Nation could use for mine-land reclamation and rangeland restoration. A land-farm pilot study was designed and constructed in 2005 to compare different crops and different nitrate concentrations in irrigation water. Preliminary results show that plants receiving the highest nitrate concentration, 750 mg/L of nitrate, grew the largest, and *A. canescens* grew significantly larger than *S. vermiculatus*.

## **REMOTE SENSING METHODS**

Phreatophytic shrub populations at Monument Valley play a role in controlling movement of the groundwater nitrate plume and also in limiting soil percolation in the source area of the plume. The Monument Valley site will require long-term monitoring of vegetation cover and evapotranspiration if natural and enhanced attenuation methods are selected for the final remedy. Vegetation abundance over the source area helps determine the extent of recharge of water from the source area and from surrounding uplands into the plume, because water used by vegetation decreases the amount that can migrate into the aquifer. Vegetation abundance over the plume helps determine the rate of plume migration away from the site, because water used by vegetation decreases the amount available to expand the volume of the plume over time.

An unobtrusive approach for evaluating changes in phreatophytic shrub populations based on remote sensing technologies was developed from research at Monument Valley [21]. The research used a combination of field measurements and remote sensing to measure transpiration by *S. vermiculatus* and *A. canescens* growing over the nitrate plume at the site. Heat balance sap flow sensors were used to measure transpiration by the two phreatophytes, and results were scaled to larger landscape units and longer time scales using leaf area index (LAI), fractional vegetation cover, meteorological data, and the enhanced vegetation index from the MODIS sensors on the Terra satellite. Transpiration was high, depending on leaf area, and was controlled by vapor pressure deficit in the atmosphere. *S. vermiculatus* tended to have higher transpiration rates than *A. canescens* and had a steeper response to vapor pressure deficit, but both exhibited midday depression of leaf conductance. Over most of the site, fractional vegetation cover and area-wide LAI were low due to heavy grazing by cattle and sheep. However, a portion of the plume that had been protected from grazing for 10 years had higher transpiration rates.

Transpiration rates on a ground-area basis varied with LAI. As discussed above, the results support the premise that managing grazing could slow or halt the movement of the contamination plume by allowing the shrub community to extract more water than is recharged in the aquifer.

## **SUMMARY**

The U.S. Department of Energy Office of Legacy Management, the Navajo Uranium Mill Tailings Remedial Action program, and the University of Arizona are exploring alternative remedies for groundwater contamination at Monument Valley, Arizona, that include natural and enhanced attenuation processes. Pilot studies are answering two questions: (1) what is the capacity of natural processes to remove nitrate and control plume dispersion, and (2) can we efficiently enhance natural attenuation if necessary?

### **Source Containment and Removal**

Phreatophytes were planted in the nitrate plume source area (soils remaining after tailings were removed) to limit percolation and leaching of nitrate by controlling the soil water balance. About 1.7 ha of the source area was planted in 1999, and the remaining 1.6 ha was planted in 2006, primarily with the native desert shrub fourwing saltbush (*Atriplex canescens*). Monitoring results show that planting and irrigating native shrubs has produced a marked reduction in both nitrate and ammonium in the source area over an 8-year period. Total nitrogen has been reduced from 350 mg/kg in 2000 to less than 200 mg/kg in 2008. Microbial processes rather than plant uptake are responsible for most of the nitrogen reduction. However, the plants help control the site water balance, preventing additional leaching of nitrogen compounds into the aquifer.

The decrease in nitrate may have slowed, as expected for a substrate-dependent, exponential decay process. On the other hand, ammonium levels are still decreasing. Nitrification (of ammonium) is a likely reason for the slow decrease in nitrate. Enrichment of  $^{15}\text{N}$  ( $\delta^{15}\text{N}$ ) provides additional evidence that loss of nitrogen is due to denitrification in the case of nitrate, and of nitrification followed by denitrification in the case of ammonium. Denitrification favors  $^{14}\text{N}$  over  $^{15}\text{N}$ , so residual nitrate in the soil becomes enriched in  $^{15}\text{N}$  as nitrate becomes depleted.

### **Natural Groundwater Attenuation**

Contamination of the alluvial aquifer by nitrate, ammonium, and sulfate is the major concern. Results from the collection of spatial and temporal concentration data from a transect of monitoring wells located along the plume centerline indicate that nitrate, ammonium, and sulfate concentrations are decreasing due to natural attenuation processes. Adsorption appears to partly control the transport and fate of ammonium in the plume. Sulfate concentrations are most likely controlled by equilibrium formation/dissolution of the solid mineral-phase gypsum. Naturally formed gypsic lenses are already found in soils at the site. Calcium ions in the soil react with sulfate in the source area and contamination plume to produce gypsum deposits, which are relatively immobile. Nitrification may be occurring in the upgradient part of the plume as well as in the source area. Nitrate biotransformation occurs through reduction to atmospheric nitrogen gas (i.e., denitrification) in both the irrigated subpile soils and the downgradient region of the plume.

The occurrence and rate of denitrification was evaluated through microcosm experiments, nitrogen isotopic fractionation analysis, and solute transport modeling. First-order rate coefficients calculated with each method were comparable. The composite natural attenuation rate coefficient was slightly larger but similar to the denitrification rate coefficient, which suggests that microbially-induced decay primarily controls nitrate attenuation at the site. Sulfate reductive biotransformation was not evident from the

available data. An estimated 30–70 percent of nitrate in the plume has been lost through natural denitrification since the mill was closed in 1968. Estimates of sulfate losses through gypsum formation are not yet available, but eventually an equilibrium level is expected to be established at the solubility of calcium sulfate in the hotspots of the plume, and lower where the plume has been diluted.

### **Enhanced Attenuation of Groundwater**

Enhanced attenuation can be defined as initiating and/or augmenting natural and sustainable attenuation processes. The goal is to increase the magnitude of attenuation by natural processes beyond that which occurs without intervention. Enhancing in situ biological denitrification through injection of amendments appears to be a promising method for remediation of nitrate-contaminated groundwater.

The Monument Valley site is considered to be an excellent candidate for in situ enhanced-attenuation denitrification. The region of high nitrate contamination in the plume is in a relatively small volume of the aquifer. Treatment of this high-concentration portion of the plume could allow natural attenuation of the remainder of the plume. Questions that remain to be addressed are the degree of enhancement that can be achieved and the optimal means of implementation. These questions will be addressed with a pilot-scale demonstration supplemented with mathematical modeling analyses.

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