Appendix C

Natural and Enhanced Attenuation of Groundwater

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

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

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

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

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

C.1 Groundwater Phytoremediation

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

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

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

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

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

C.1.1 Plant Communities and Depth to Groundwater

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

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

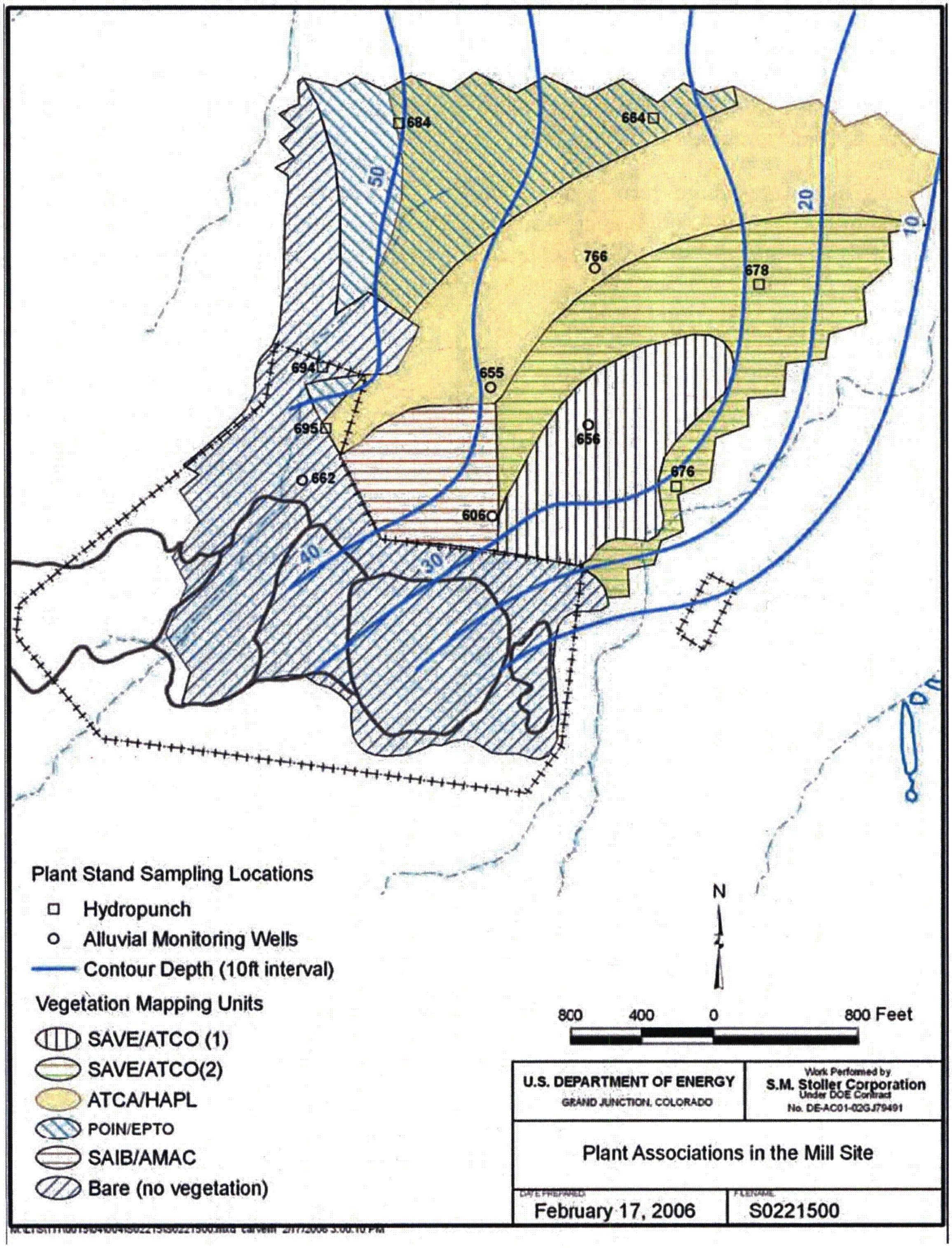

Figure C–1. Contour map of depths to groundwater superimposed on a map of plant associations. Plant acronyms are as follows: SAVE = Sarcobatus vermiculatus *(black greasewood), ATCO =* Atriplex confertifolia *(shadscale), ATCA =* Atriplex canescens *(fourwing saltbush), HAPL =* Haplopappus pluriflorus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

Production of a vegetation map involved (1) mapping stand locations on the 1995 aerial photograph; (2) identifying vegetation patterns in the photograph, under magnification, that were consistent with the plant associations; (3) outlining mapping unit boundaries using a combination of stand locations and vegetation patterns; and (4) returning to the field to check the reliability of the photograph interpretation (DOE 2004b).

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

C.1.2 Phreatophyte Rooting Depth

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

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

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

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

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

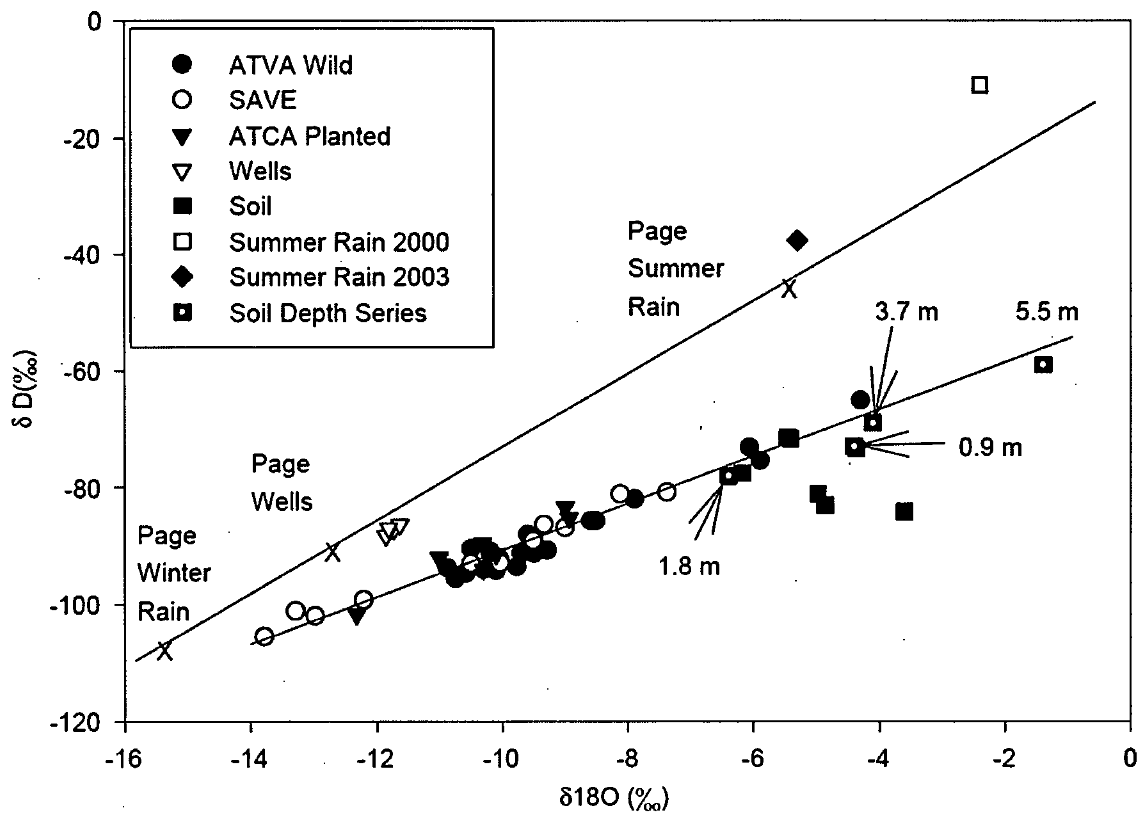

Figure C–2. $\delta^{18}O$ and δD values for soil, water, and plant tissues collected in 2000 and 2003 at the Monument Valley UMTRA site. Reference data for wells and rainwater for Page, Arizona (Lin et al. 1996), are shown plotted along the Page local meteoric water line. Plant stem water and soil pore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

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

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

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

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

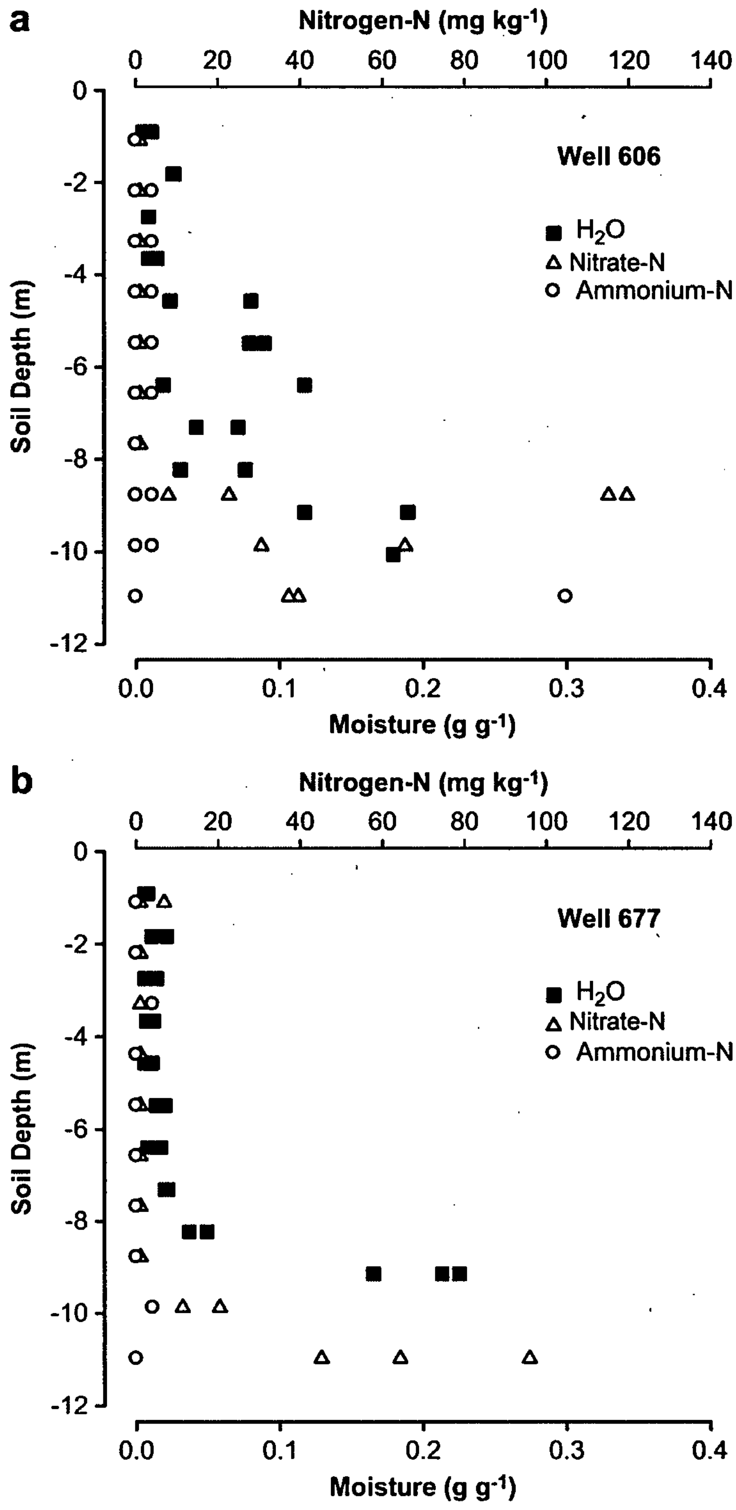

Figure C–3. Relationship between moisture content, nitrate concentrations, and ammonium concentrations as a function of soil depth at sites near well 606 (a) and well 677 (b) over the Monument Valley contamination plume (see Jordan et al. 2008).

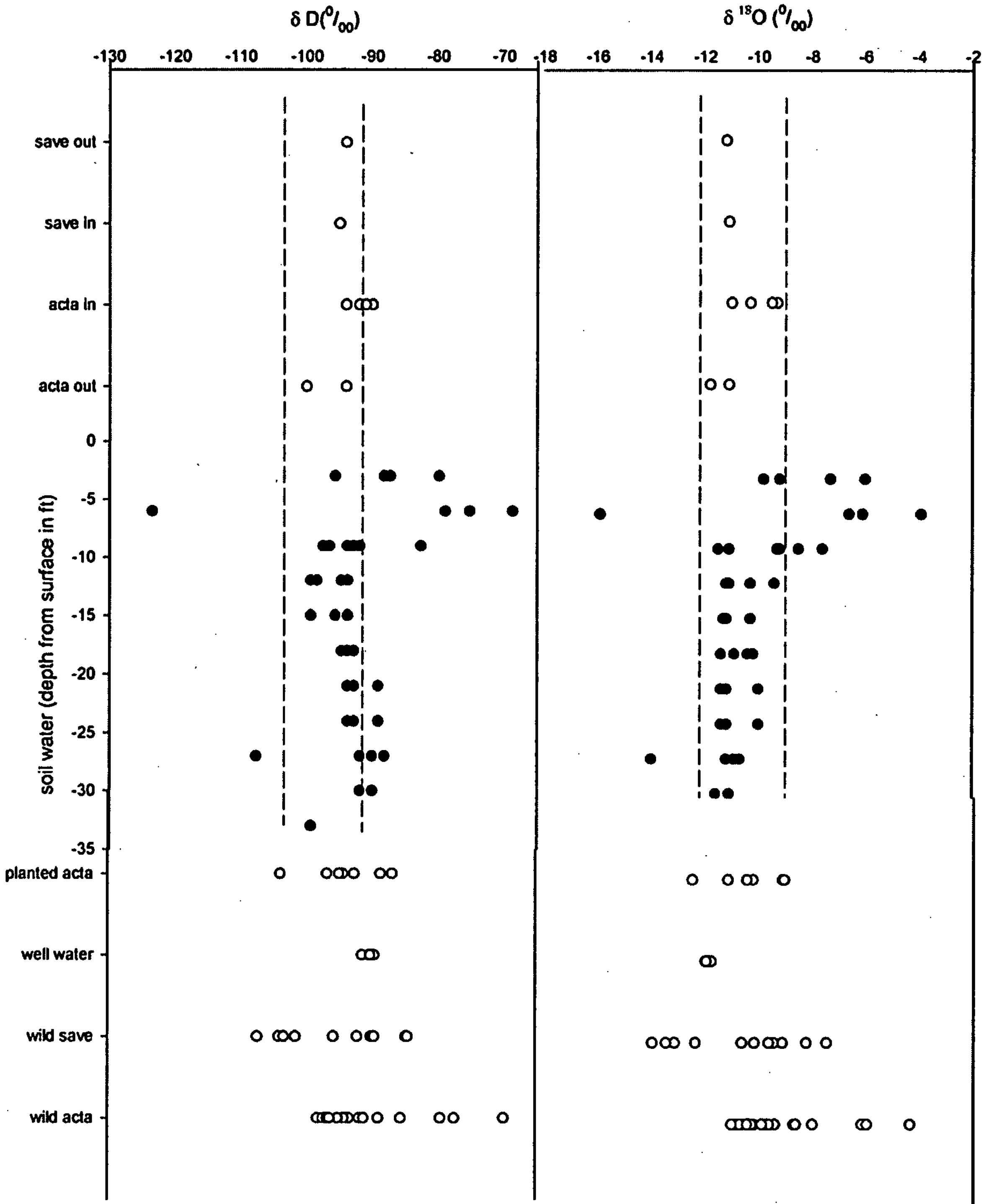

Figure C–4. $\delta^{18}O$ and δD isotope enrichment values in water extracted from soil samples collected at different depths over the alluvial plume near well 606 and well 677. The graph also shows the isotope values in water extracted from stem sample of black greasewood (SAVE) and fourwing saltbush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

C.1.3 Enhanced Plume Phytoremediation: Grazing Management and Revegetation

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

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

C.1.3.1 Early Studies

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

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

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

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

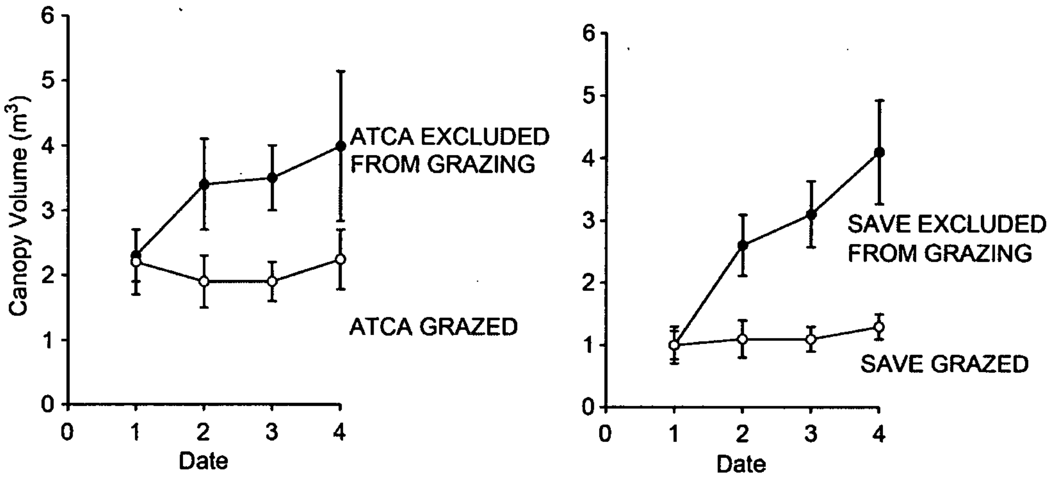

Figure C–5. Canopy volumes for fourwing saltbush (ATCA) and black greasewood (SAVE) plants either grazed or protected from grazing during 3 growing seasons at the Monument Valley site. Each data point is the mean of 12 plants; error bars show standard errors of the mean. Date 1 is June 1998, Date 2 is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

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

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

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

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

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

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

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

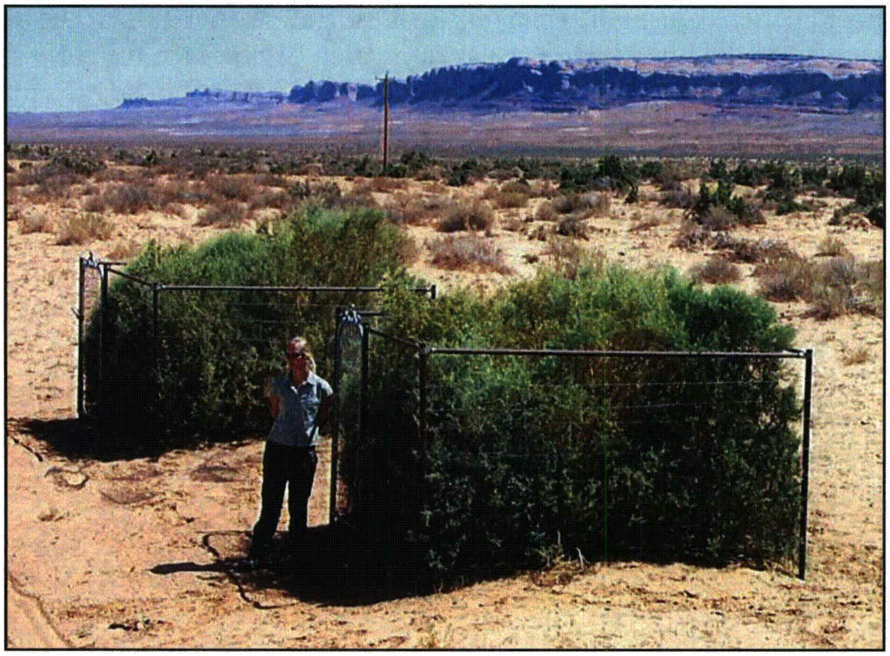

Figure C–6. Exclosure plots near well 606 planted with fourwing saltbush and black greasewood in June 1998 and irrigated from June to October 1998. This photo was taken in July 2002 during an extended drought, providing anecdotal evidence that transplants had rooted in groundwater.

C.1.3.2 Landscape-Scale Studies

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

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

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

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

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

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

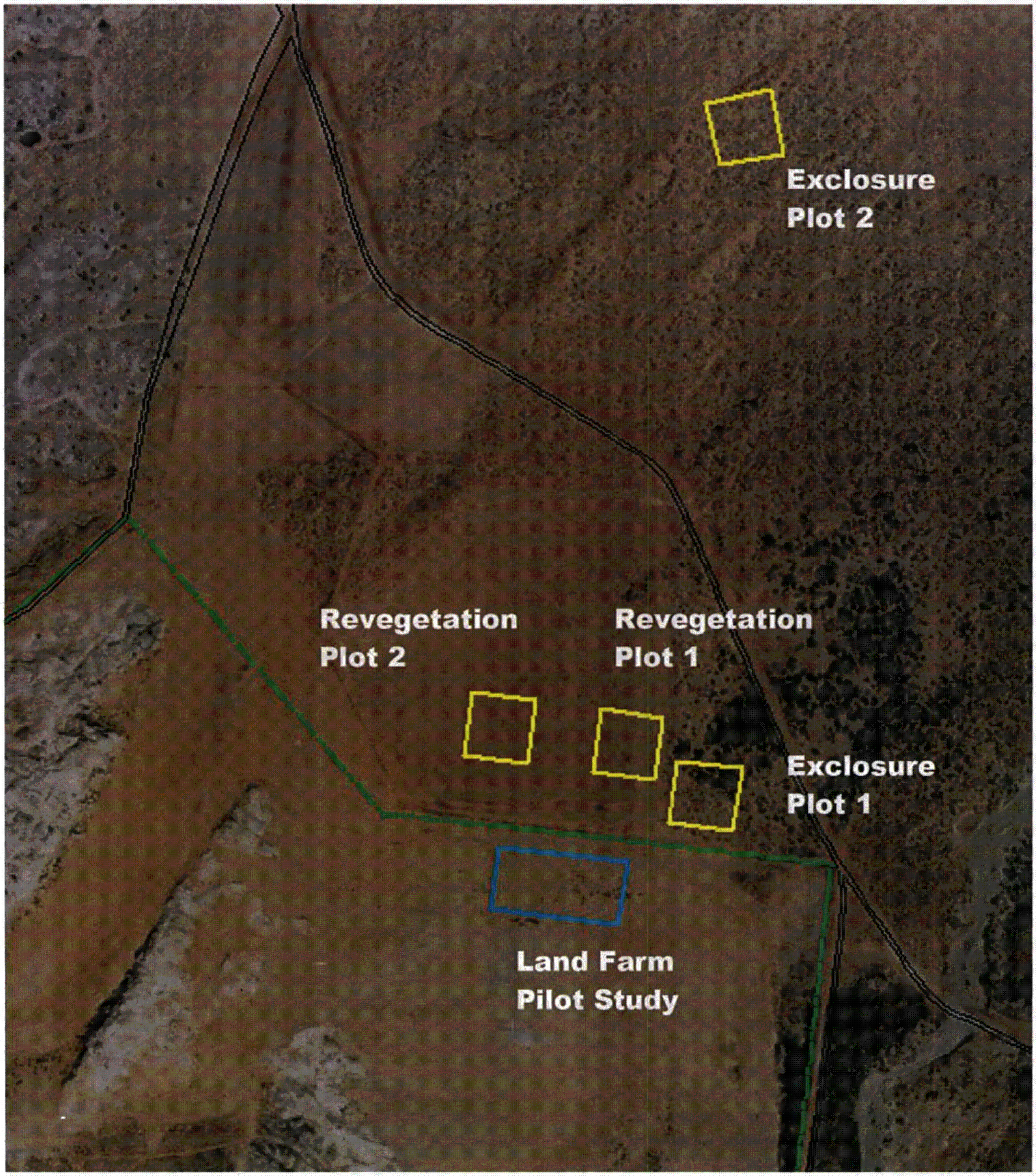

Figure C–7. Aerial photograph of plume area taken prior to installation of the pilot studies showing GPS boundaries of grazing Exclosure Plot 1 (black greasewood) and Exclosure Plot 2 (fourwing saltbush), Revegetation Plots 1 (East) and 2 (West) (all in yellow), the land-farm pilot study plot (blue;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

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

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

C.1.4 Plant Uptake of Nitrogen and Sulfur

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

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

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

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

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

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

C.1.5 Groundwater Extraction: Phreatophyte Transpiration

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

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

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

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

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

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

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

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

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

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

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

Notes:
In = inside livestock exclosures
Out = outside livestock exclosures
SE = standard error of the mean
N = sample size

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

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

C.2 Natural and Enhanced Plume Denitrification

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

C.2.1 Natural Plume Denitrification

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

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

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

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

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

First-order Rate Description	k (hr^{-1})	k (yr^{-1})	Half-life (yr)
2006-natural	2.00E-05	0.2	3.96
2007-natural	8.33E-05	0.7	0.95
2006-with ethanol	3.30E-03	28.9	0.02
2007-with ethanol	2.00E-03	17.5	0.04
2007-with methanol	1.95E-03	17.1	0.04

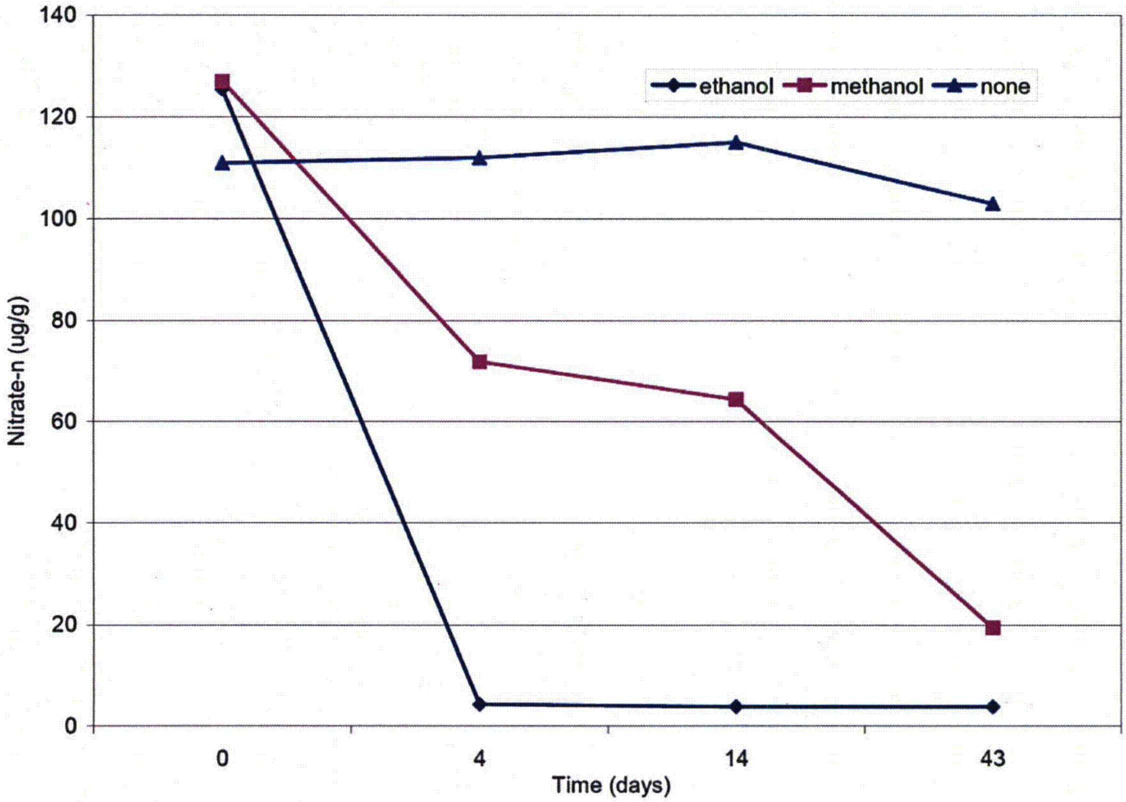

Figure C–10. Microcosm nitrate depletion in soil slurries with or without methanol or ethanol amendment (DOE 2008, Jordan et al. 2008).

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

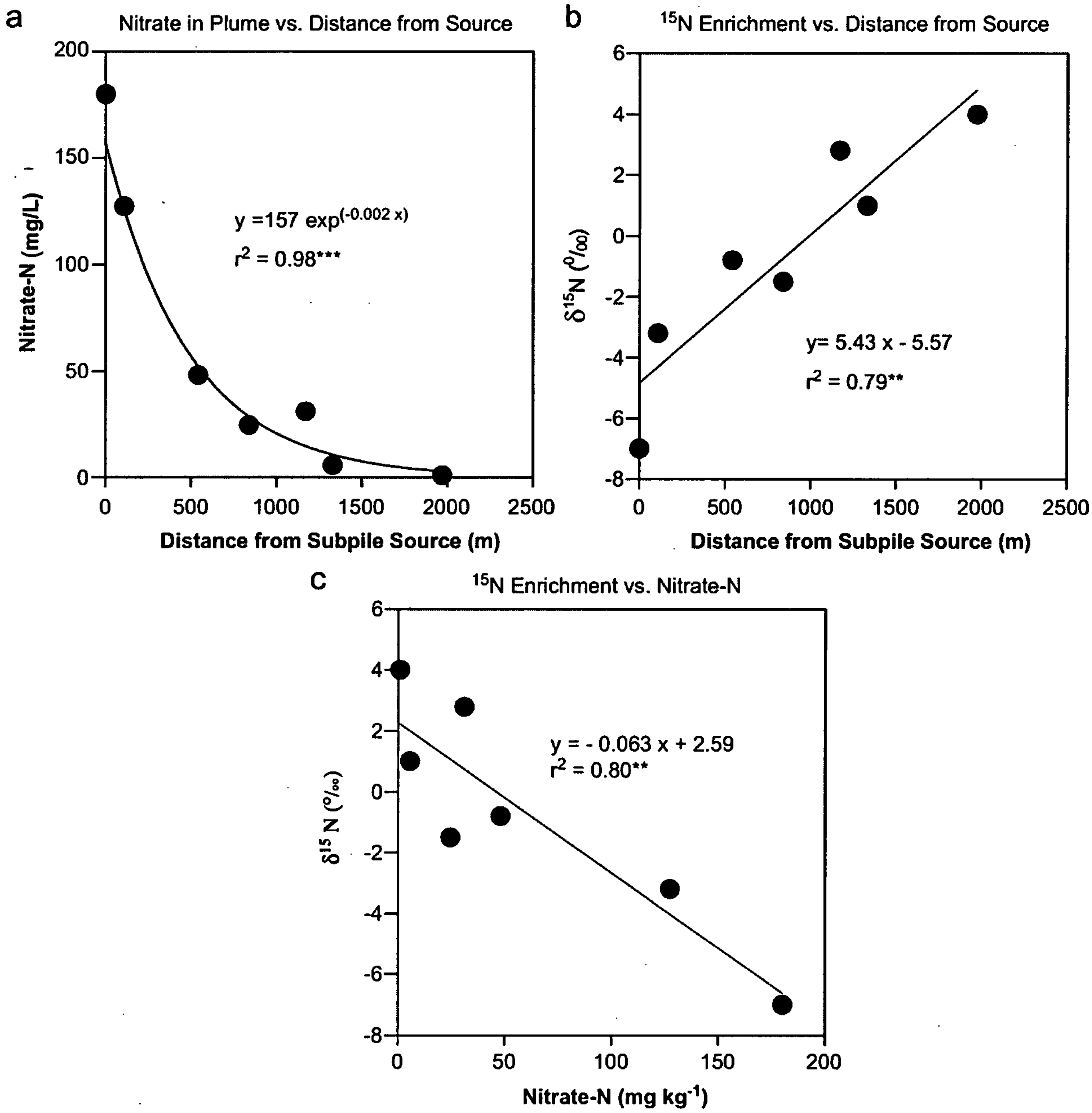

*Figure C–11. Nitrate (a) and 15N isotope enrichment (b) in the Monument Valley contamination plume as a function of distance from the source area, and ^{15}N-nitrate enrichment as a function of nitrate concentration in the same samples (c). Significance levels are denoted as ** ($P < 0.01$) and ***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

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

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

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

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

C.2.2 Enhanced Plume Denitrification and Sulfate Reduction

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

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

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

These results support the premise that it would be feasible to enhance denitrification by injecting ethanol into hot-spot areas of the plume. The plume currently has two hot spots of high-nitrate concentrations, each apparently with a footprint area of about 2 ha (Appendix D, Section D.2). Using the rate of movement of 0.1 m d^{-1}, a single injection well could treat an area of roughly 0.4 ha yr^{-1}. Therefore, it may be possible to treat the hot-spot areas with 5 injection wells each.

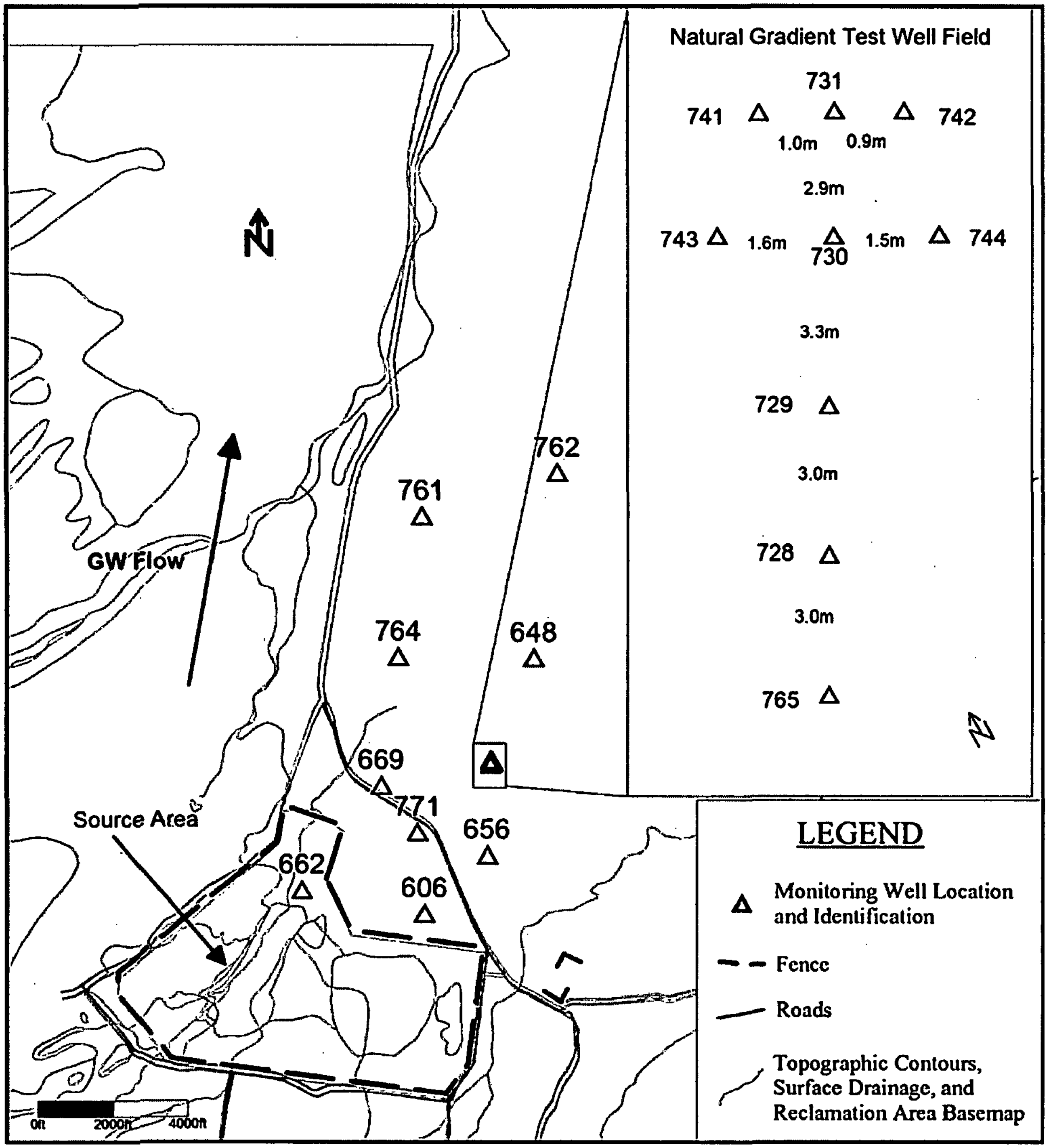

Figure C–12. Illustration of the Monument Valley site showing the source area and selected monitoring wells. The inset shows the arrangement of injection and monitoring wells used for the push-pull and single well gradient test. Ethanol was first injected into well 765 in the push-pull experiment. Ethanol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

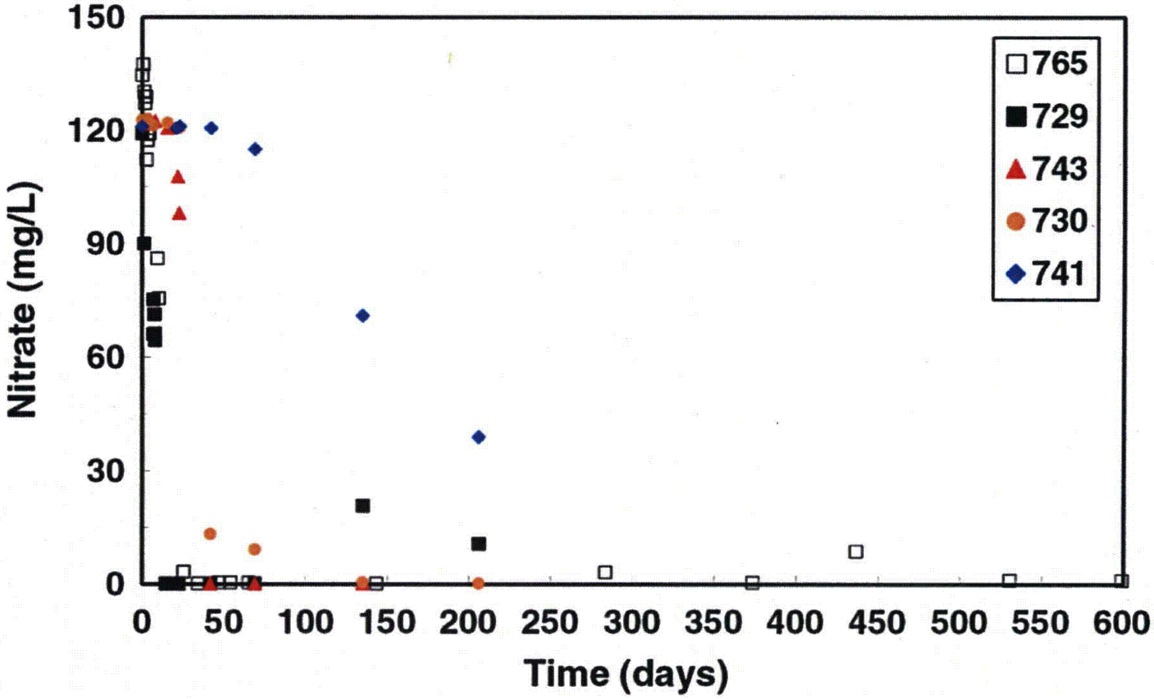

Figure C–13. Long-term nitrate concentrations measured for the push-pull test (injection well 765) and for the single-well injection test (injection well 729 and monitoring wells 743, 730, and 741). Time 0 corresponds to the start of ethanol injection.

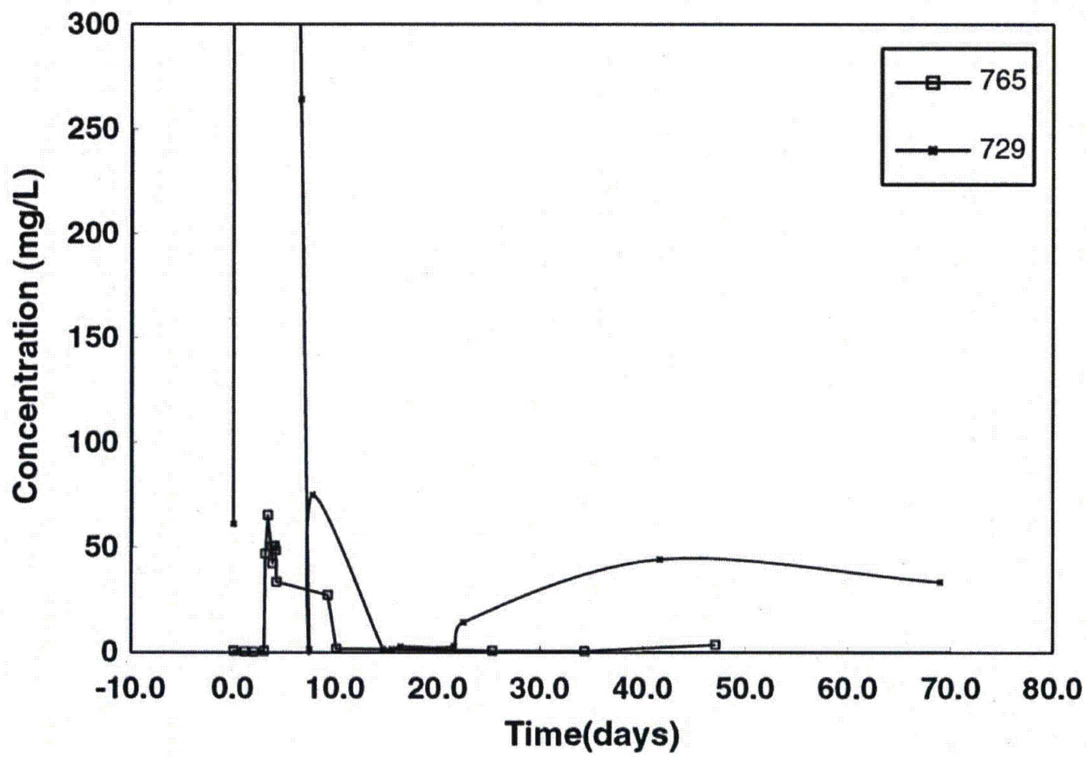

Figure C–14. Nitrous oxide concentrations measured for the push-pull test (injection well 765) and for the single-well injection test (injection well 729). Time 0 corresponds to the start of ethanol injection.

Appendix D

Review of Groundwater Modeling and Monitoring

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Contents

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

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

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

D.1 Modeling

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

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

D.1.1 Steady-State Flow

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

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

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

The selected model produced a steady-state flow field with an average horizontal, north-northeast gradient of about 0.0085 (dimensionless) and average linear velocities that generally averaged between 60 and 70 feet per year (ft/yr). Though the model performed well (DOE 2000b) in matching observed groundwater levels at numerous monitoring wells, observed lengths of the nitrate and sulfate plumes (approximately 4,500 feet [ft]) at the site in 1997 and 1998 indicated that the model-generated velocities were not large enough to have produced the plumes apparently caused by discharged process chemicals at the former mill site in the mid-1960s. A subsequent modeling effort conducted by Carroll and others (2009) that attempted to match observed nitrate concentrations in the alluvium at several different times between 1993 and 2007 showed results that inferred groundwater velocities on the order of 250 to 280 ft/yr occur in the aquifer. This in turn suggested that the hydraulic conductivity of 5.44 ft/day used throughout the DOE flow model was probably too low. The Carroll model (Carroll et al. 2009), which was based on aquifer testing results summarized in the SOWP, used a hydraulic conductivity of about 16 ft/day in the initial 2,000 ft of aquifer located downgradient of assumed nitrate sources in the vicinity of the New Tailings Pile, and a conductivity of about 25 ft/day beyond the 2,000-ft distance.

D.1.2 Early Groundwater Remedy Simulations

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

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

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

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

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

D.2 Monitoring

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

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

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

D.2.1 Ammonia

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

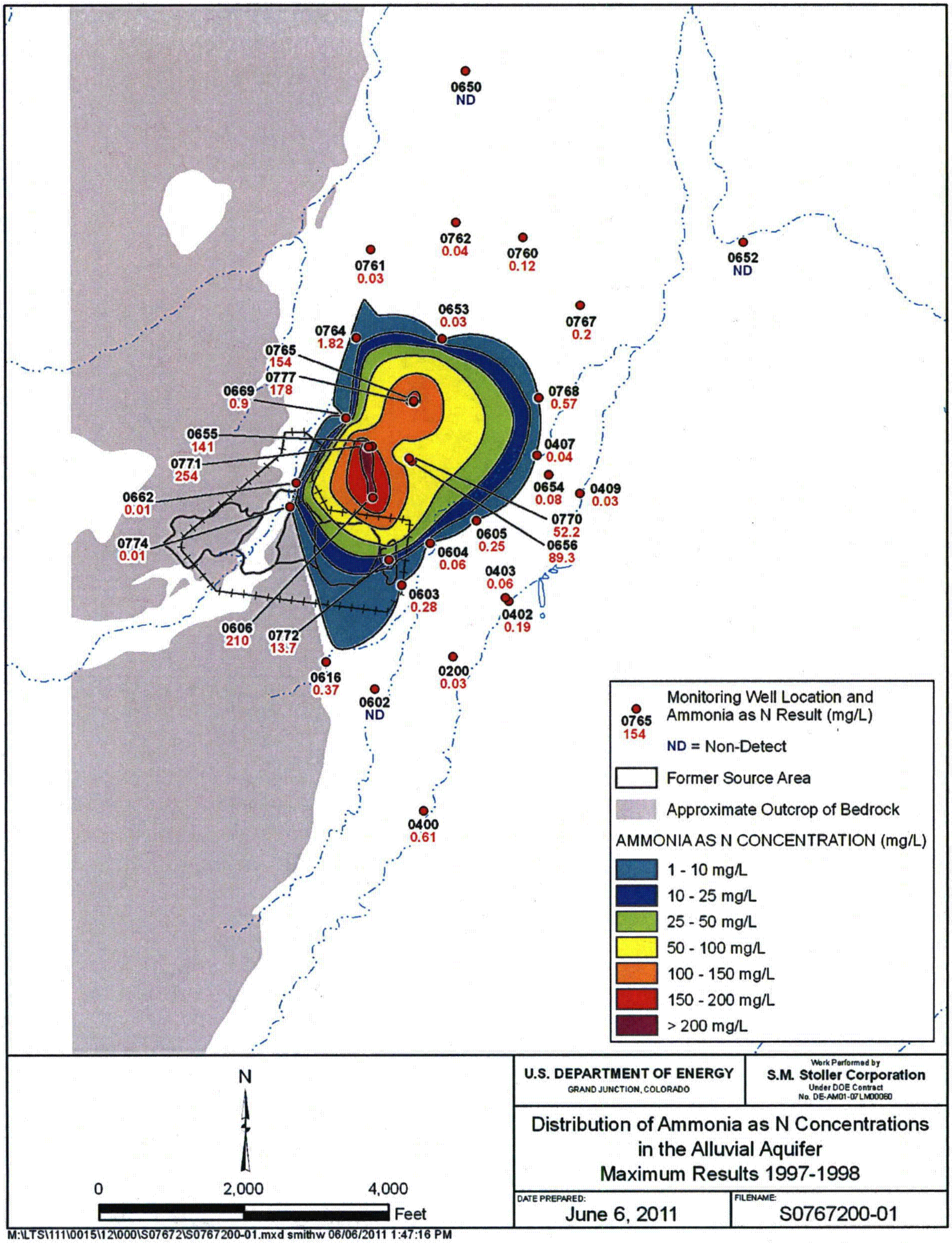


Figure D–1. Distribution of maximum ammonia (as N) concentrations during 1997 and 1998.

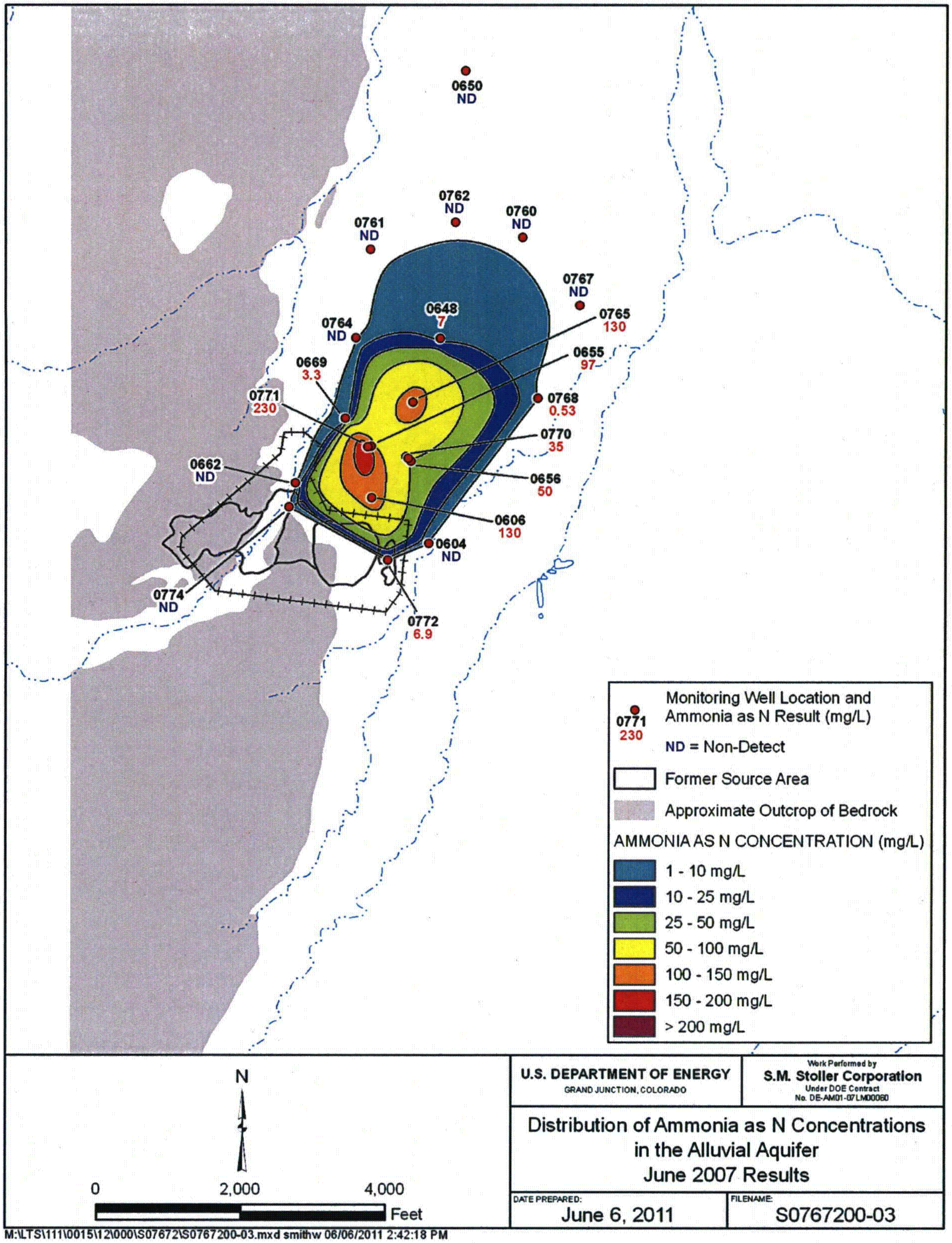


Figure D–2. Distribution of ammonia (as N) concentrations in June 2007.

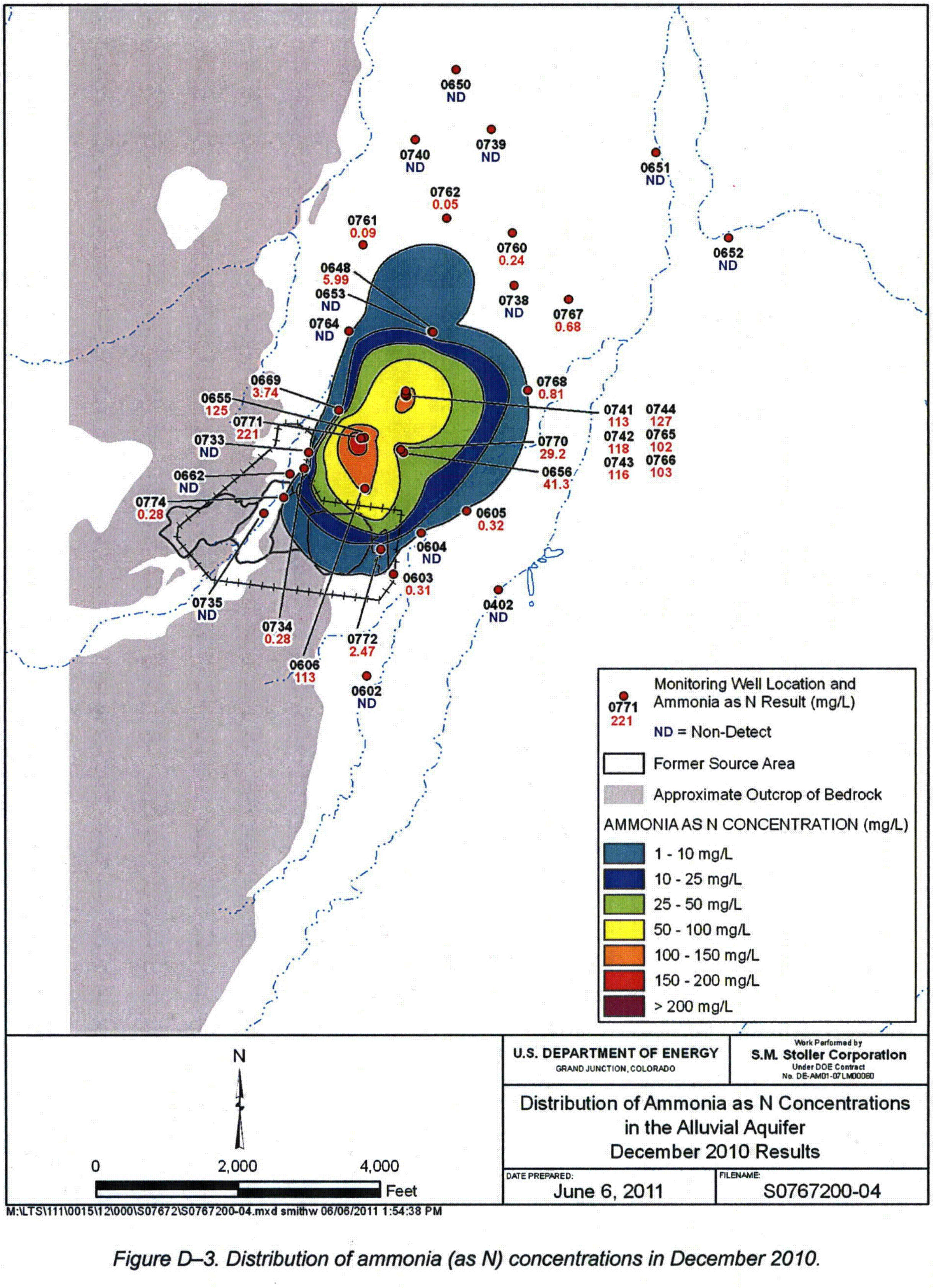


Figure D–3. Distribution of ammonia (as N) concentrations in December 2010.

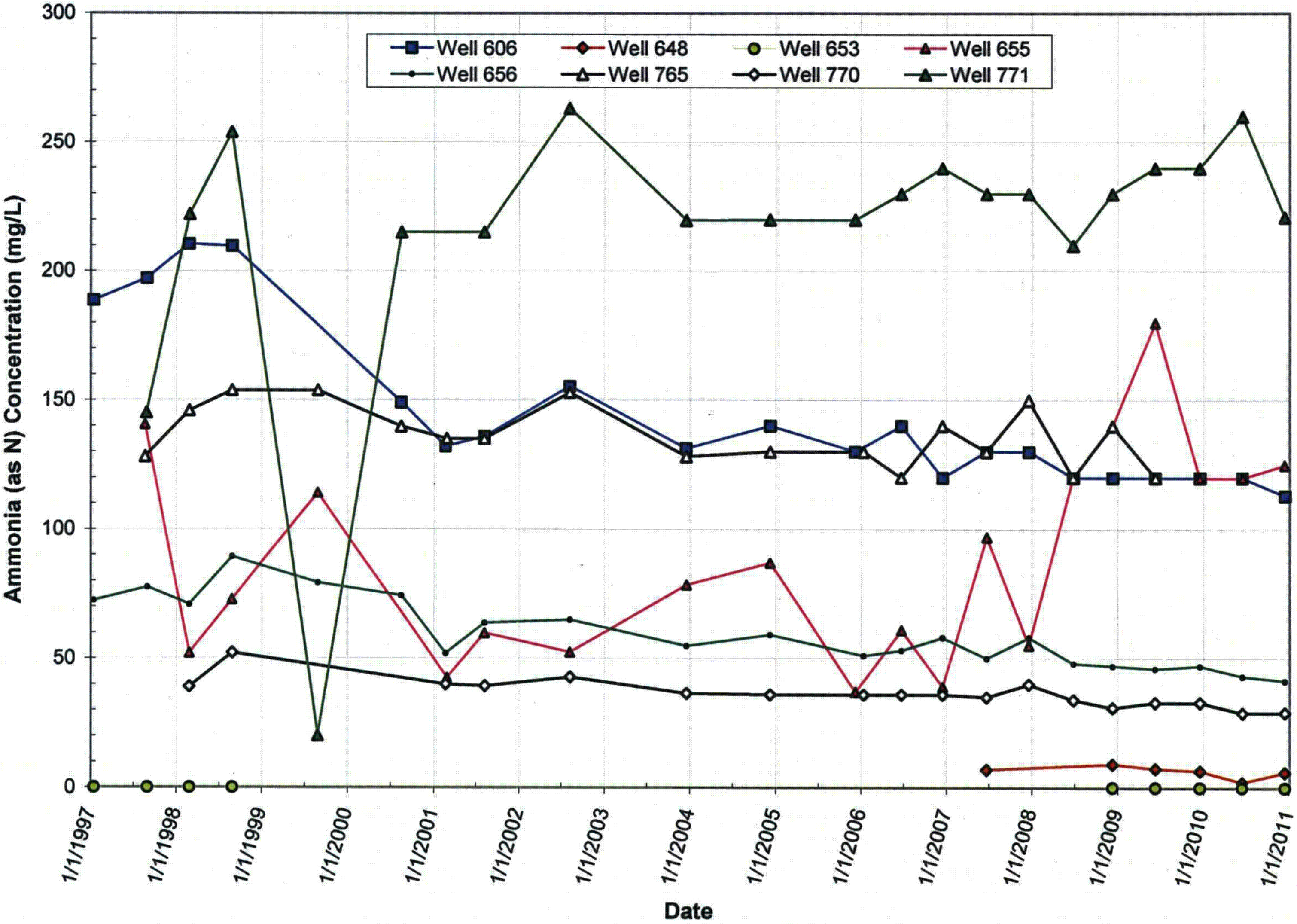


Figure D–4. Ammonia (as N) concentrations along and near the plume axis from 1997 to 2010.

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

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

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

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

The potential for contaminant concentrations to vary noticeably over short distances in the aquifer can be further analyzed by examining NH_3-N levels in co-located wells 656 and 770 between 1997–1998 and 2010 (Figure D–4). These two latter wells are also located about 50 ft from each other and the screened interval in well 770 is deeper than that in well 656. Vertical separation between the screened intervals for the wells is less dramatic than at the well 655/771 pair, as the midpoint elevations for the respective screens differ by 11 ft and screen overlap is 4 ft. In addition, neither of the geologic logs for the two locations indicates the presence of clayey material. The ammonia concentrations in the two wells tend to be close in magnitude, with the shallower well (656) during recent years consistently exhibiting NH_3-N concentrations that are about 30 percent larger than equivalent concentrations in the deeper well (770). Obviously, the larger concentrations observed in the shallower well contradicts the notion that concentrations tend to increase with depth. As previously discussed, wells 656 and 770 are located in a phytoremediation test plot, but it is unclear whether apparent root uptake of ammonia associated with the testing played a role in creating larger NH_3-N levels at the shallower vertical interval in the aquifer.

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

D.2.2 Nitrate

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

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

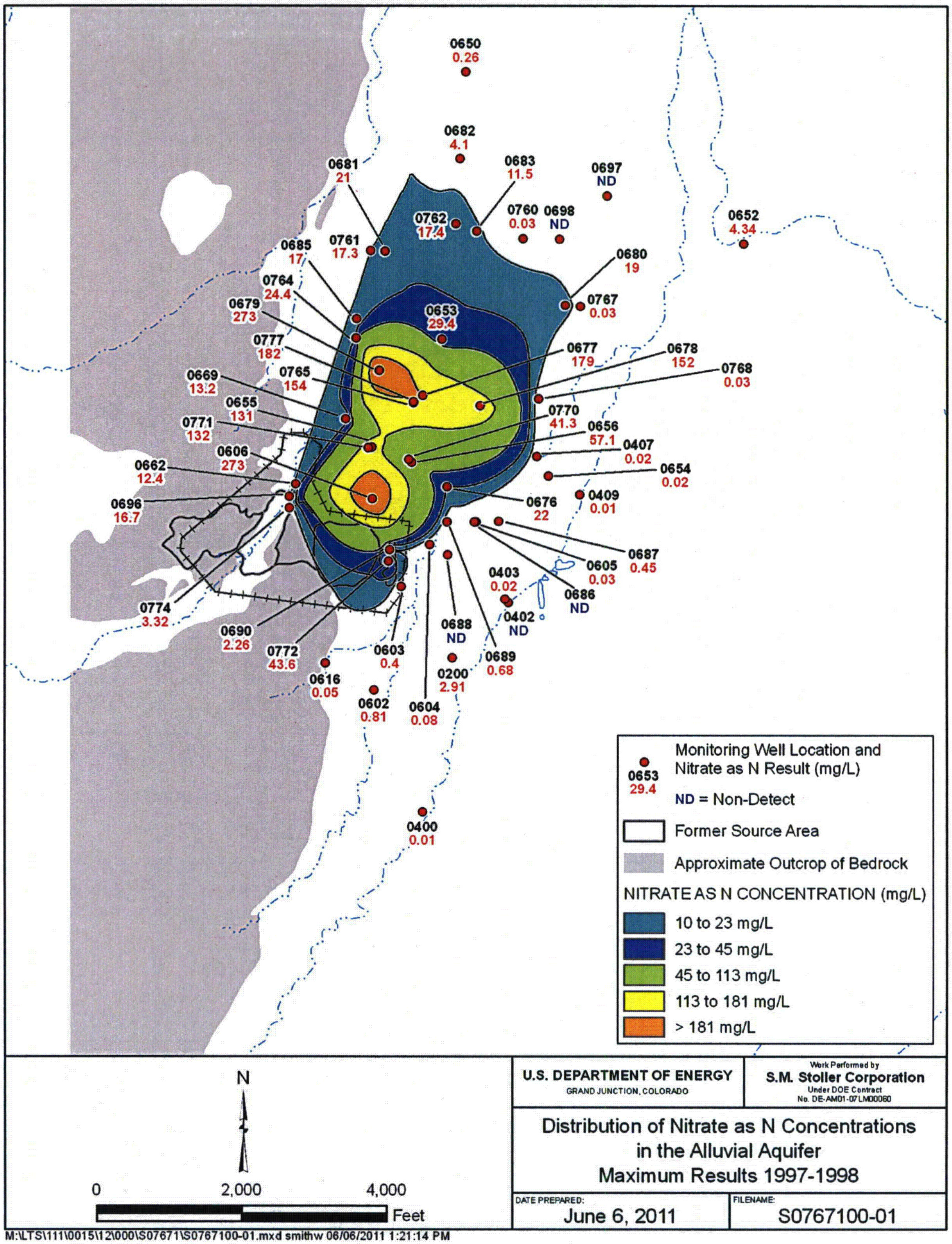
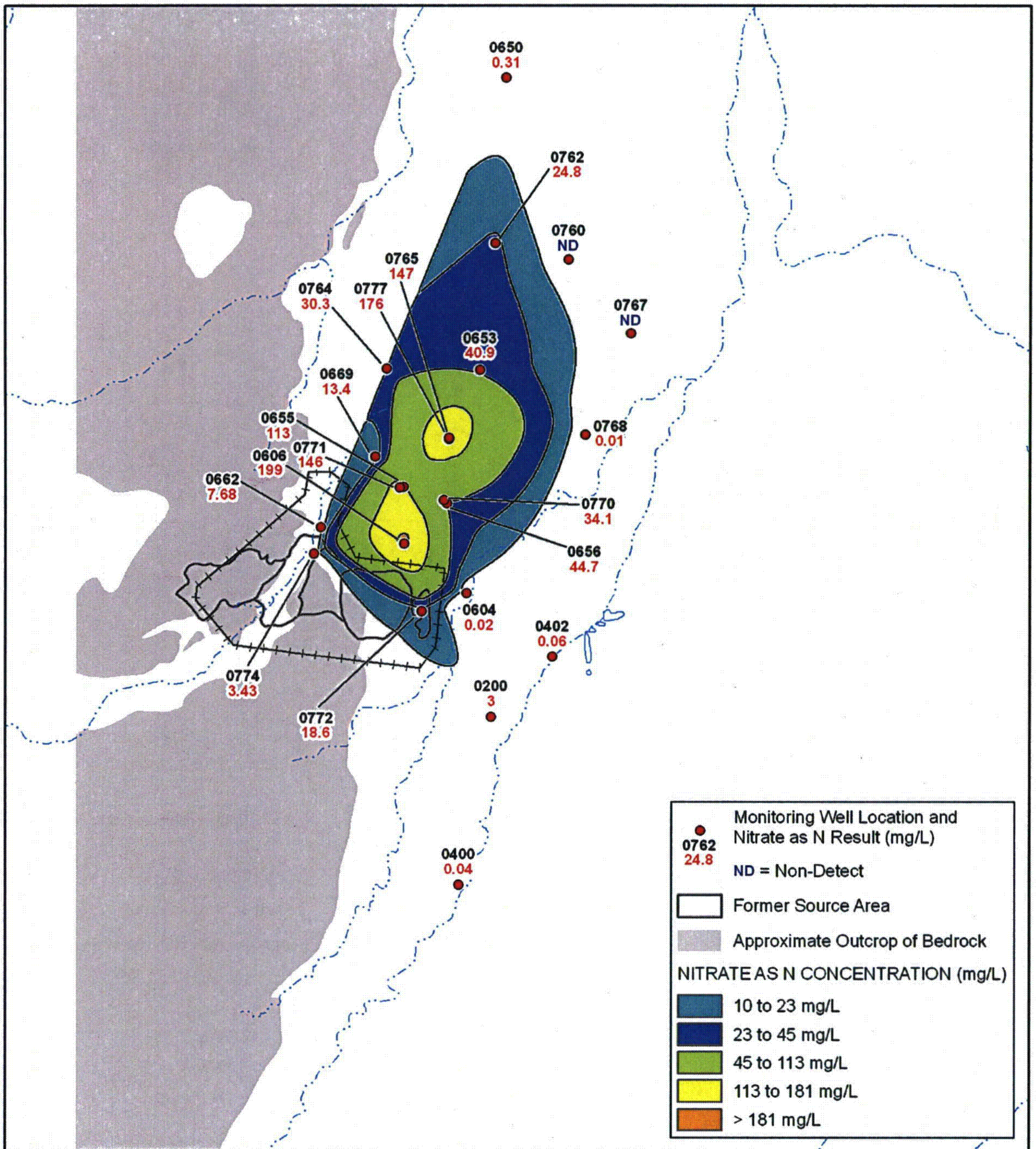


Figure D–5. Distribution of maximum nitrate (as N) concentrations in the alluvial aquifer during 1997 and 1998.



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U.S. DEPARTMENT OF ENERGY
GRAND JUNCTION, COLORADO

Work Performed by
S.M. Stoller Corporation
Under DOE Contract
No. DE-AM01-07LM00060

Distribution of Nitrate as N Concentrations in the Alluvial Aquifer August 2000 Results

DATE PREPARED: June 3, 2011
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Figure D–6. Distribution of nitrate (as N) concentrations in the alluvial aquifer in August 2000.

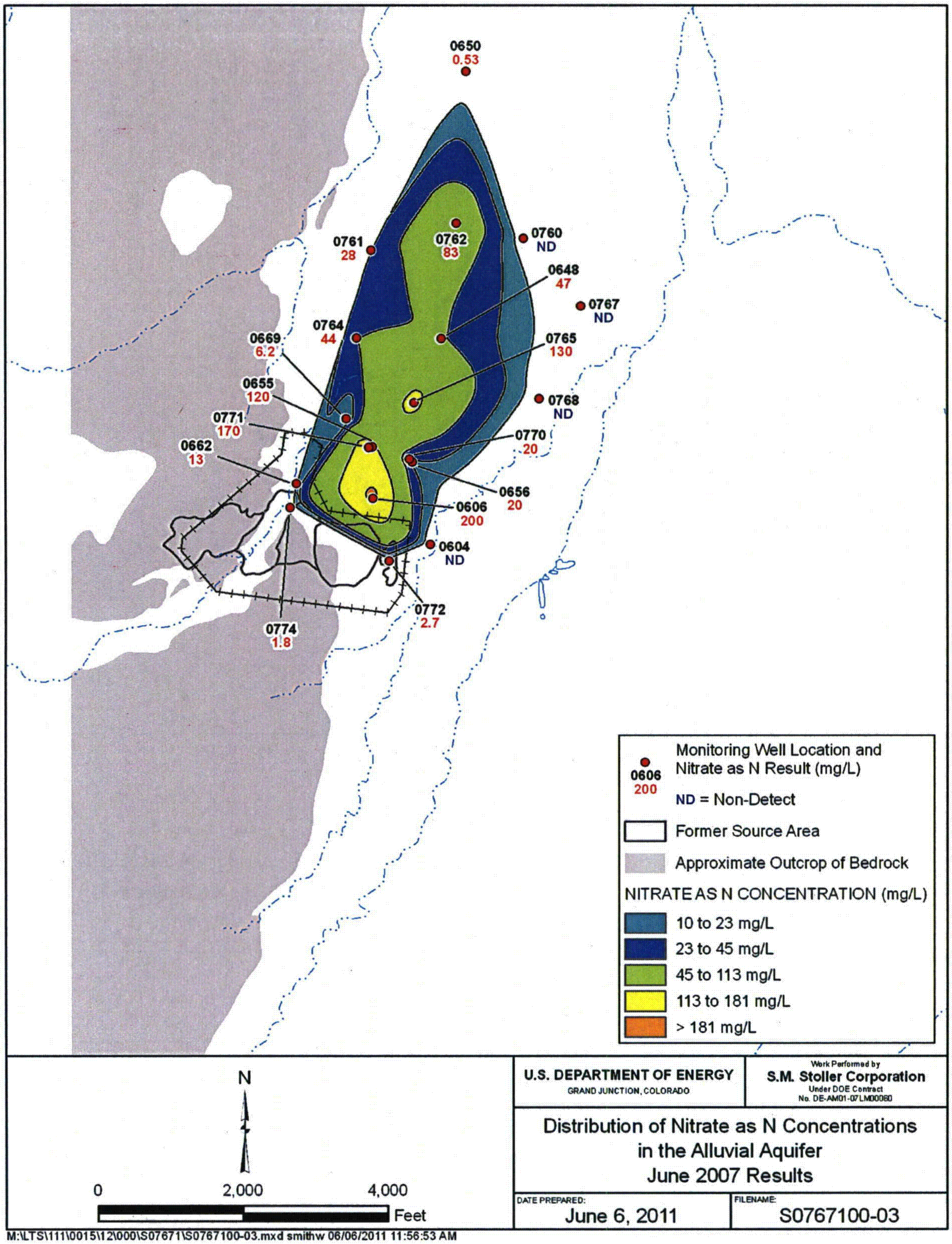

Figure D–7. Distribution of nitrate (as N) concentrations in June 2007.

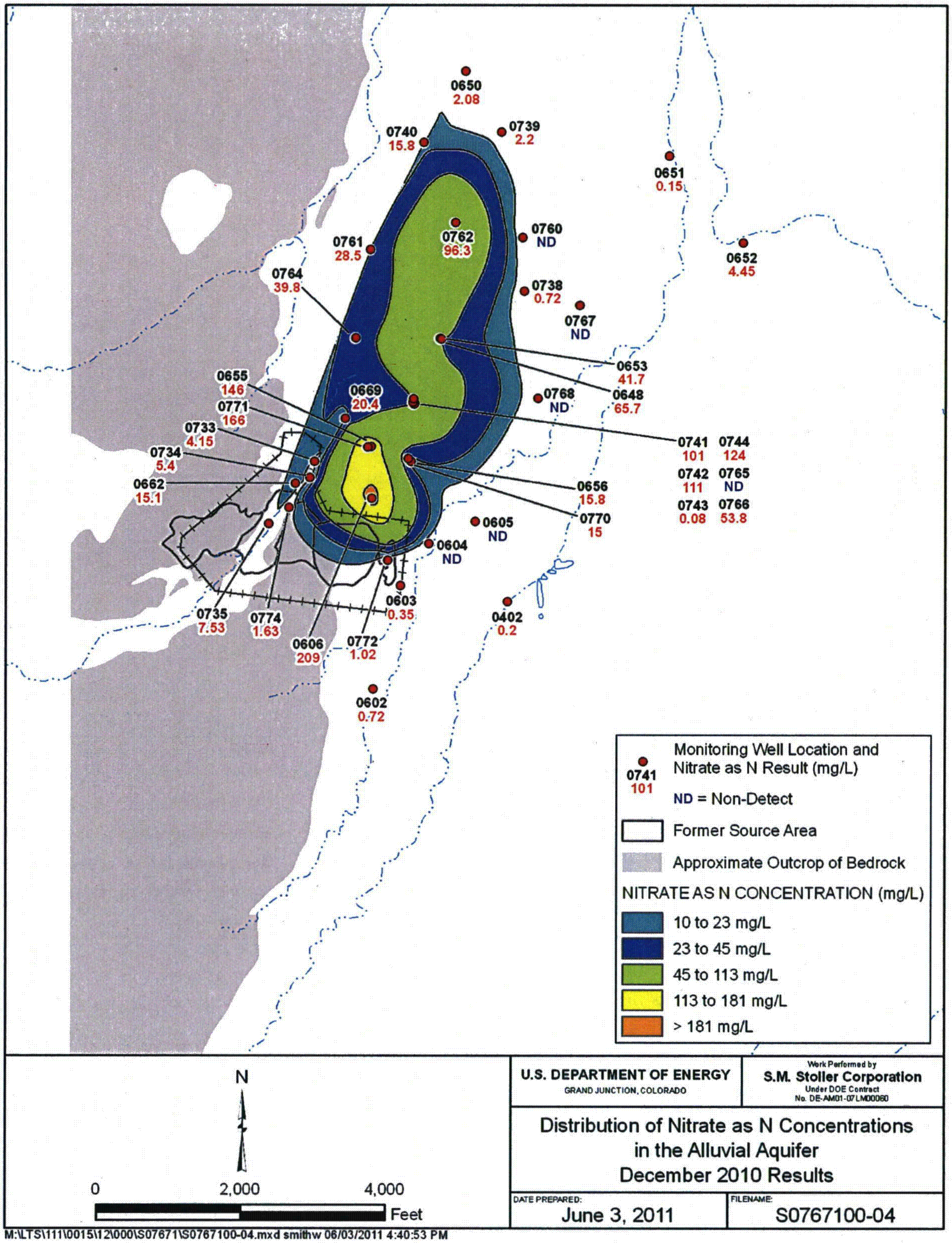

Figure D–8. Distribution of nitrate (as N) concentrations in December 2010.

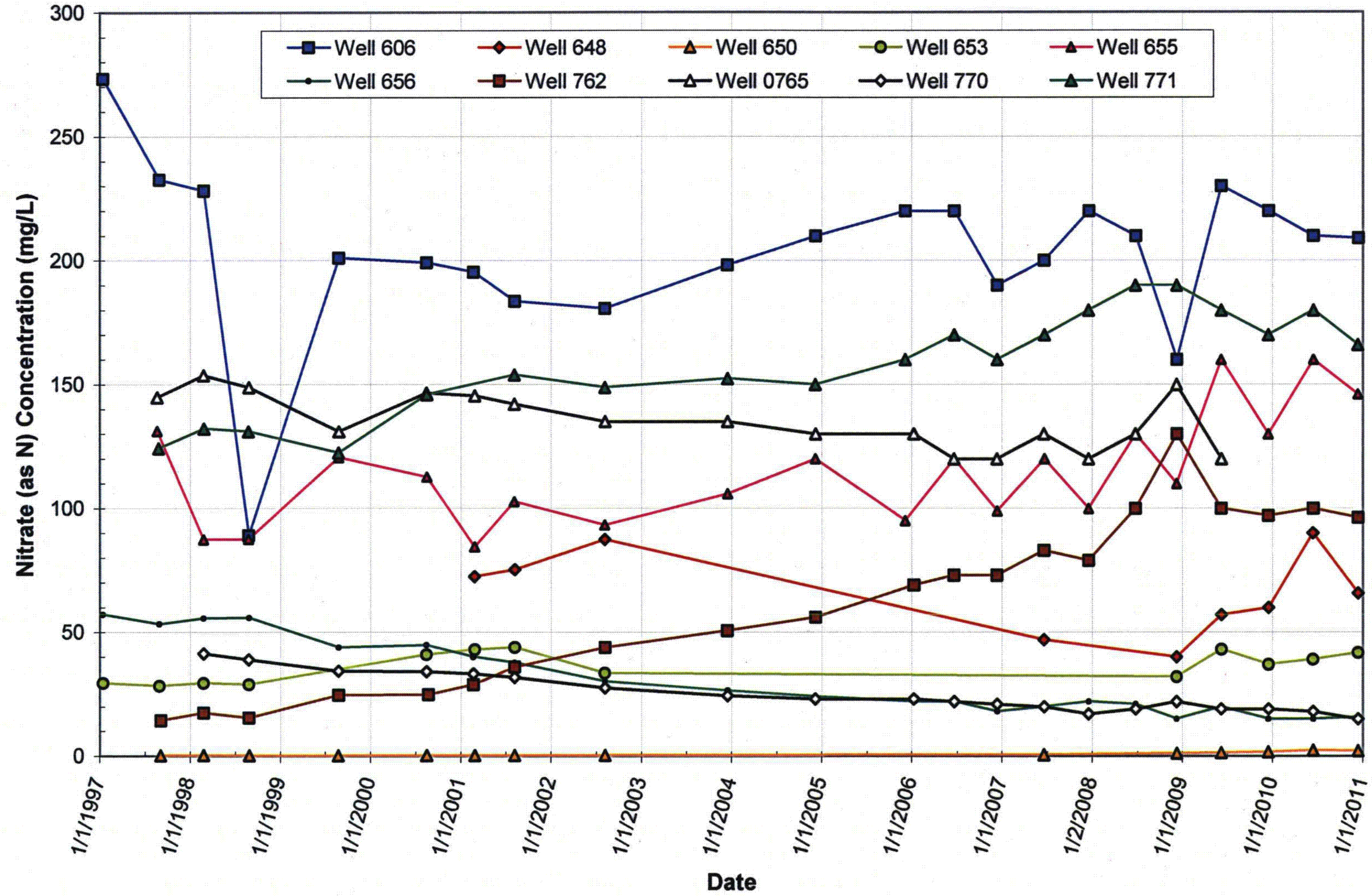

Figure D–9. Nitrate (as N) concentrations along and near the plume axis from 1997 to 2010.

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

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

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

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

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

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

D.2.3 Sulfate

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

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

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

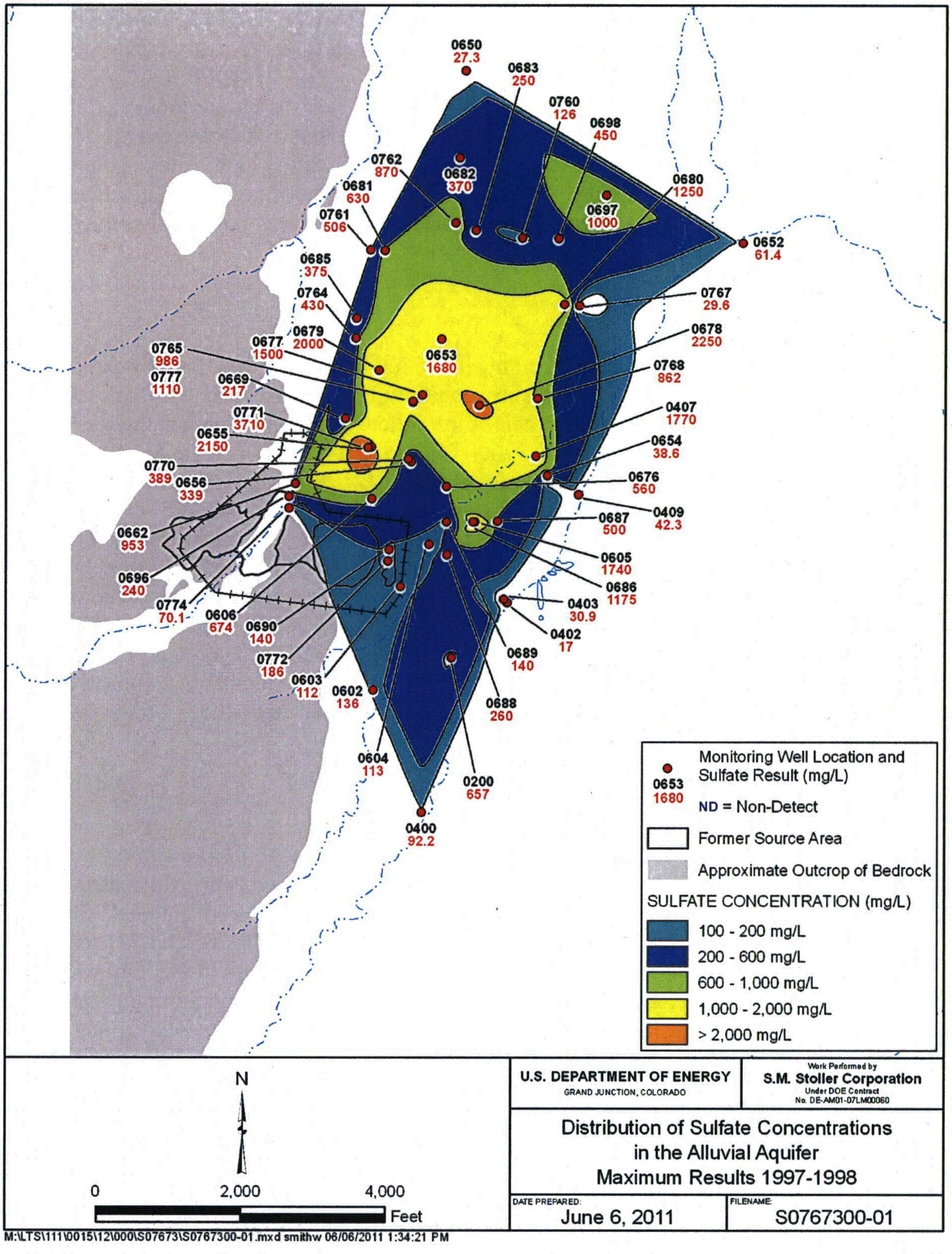

Figure D–10. Distribution of maximum sulfate concentrations during 1997 and 1998.

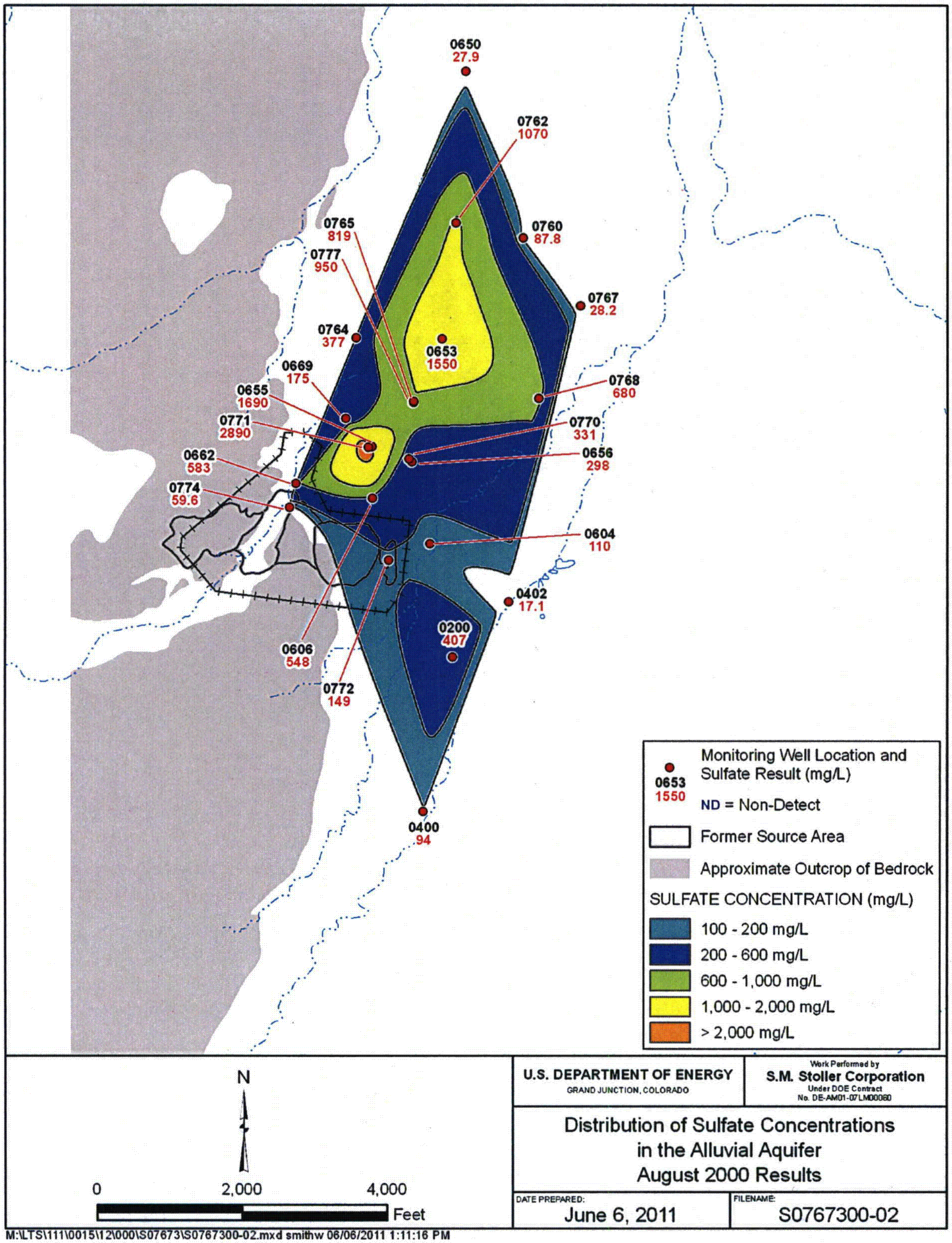

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Figure D–11. Distribution of sulfate concentrations in August 2000.

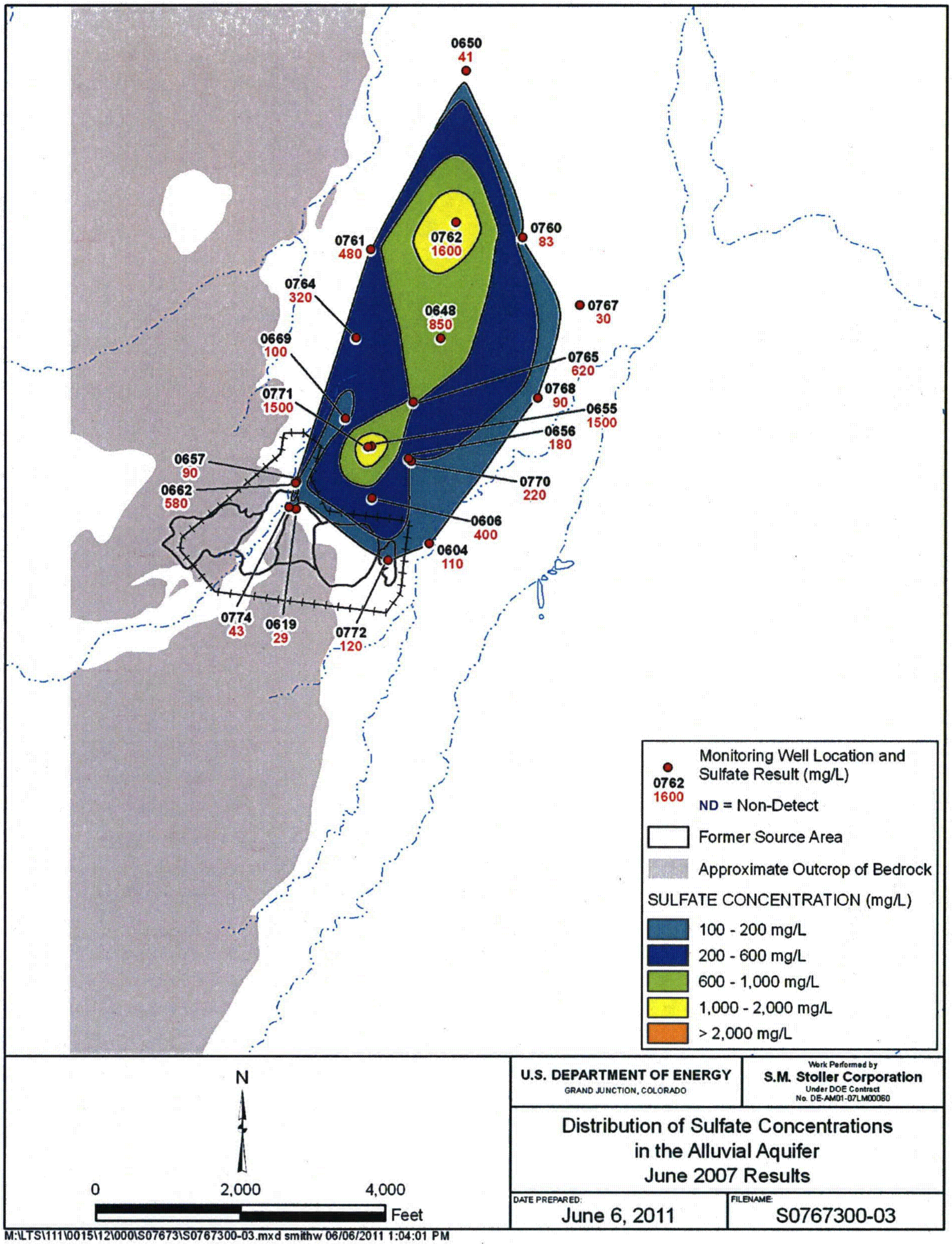

Figure D–12. Distribution of sulfate concentrations in June 2007.

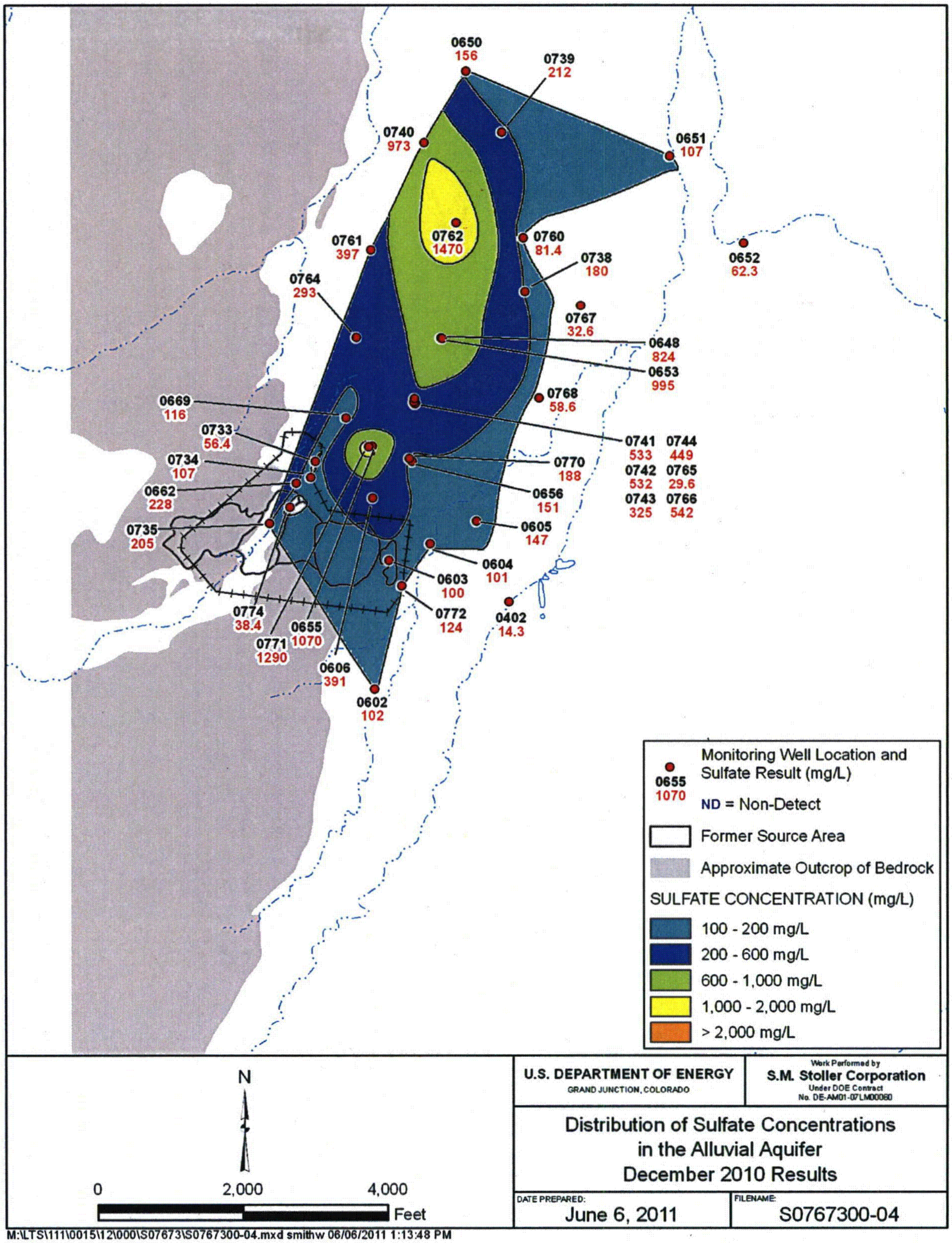

Figure D–13. Distribution of sulfate concentrations in December 2010.

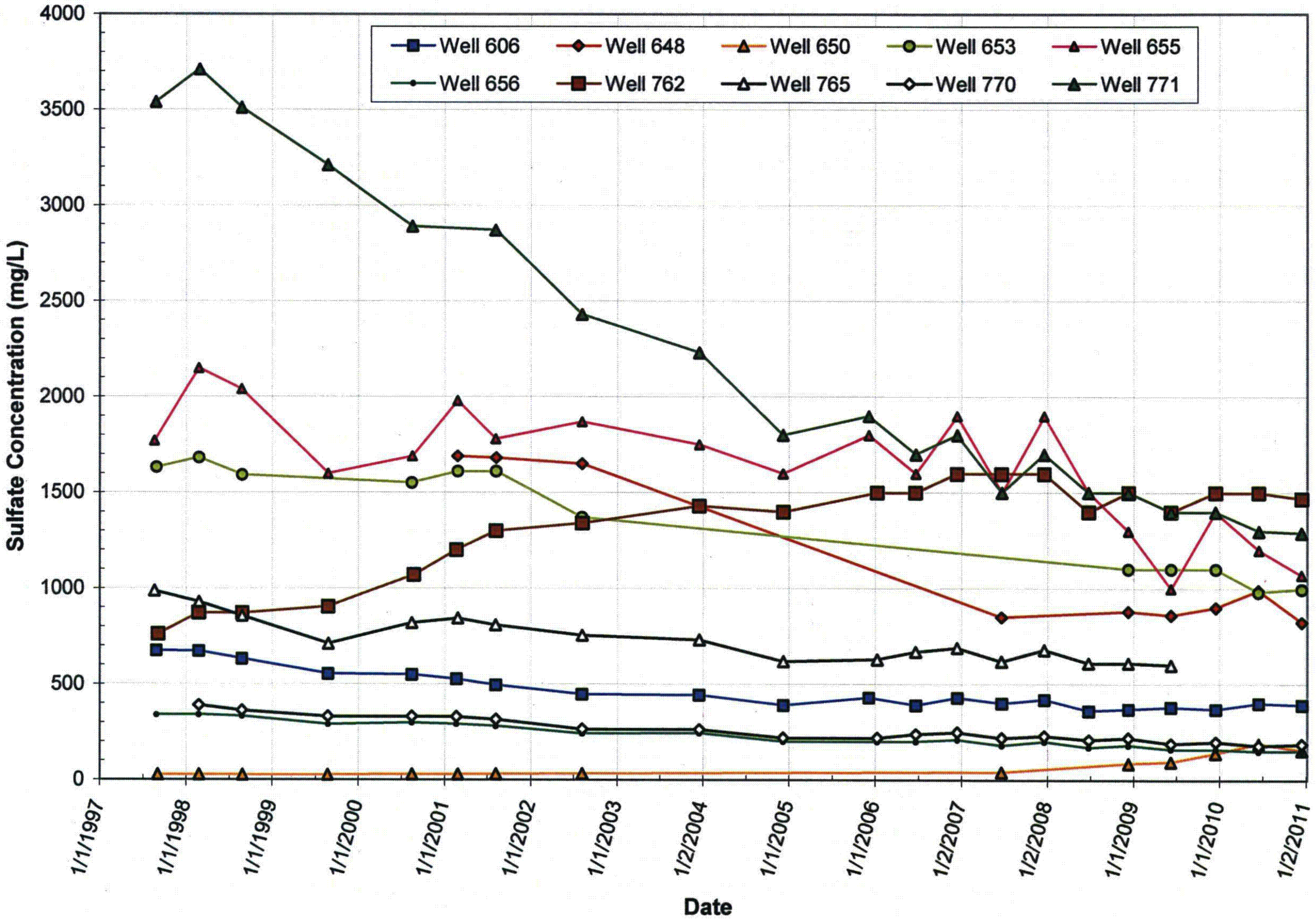

Figure D–14. Sulfate concentrations along and near the plume axis from 1997 to 2010.

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

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

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Appendix E

Active Groundwater Phytoremediation: Native Plant Land Farming

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Contents

Figures

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

Results show that a land farm with a crop of native fourwing saltbush shrubs should work well as a backup remedy for the plume if other remedies are found to be insufficient. Fourwing saltbush thrived when irrigated with plume water. Plant uptake and soil denitrification kept nitrate levels from building up in the land-farm soil; plant transpiration limited recharge and leaching of nitrate and ammonia back into the aquifer; sulfate pumped from the plume remained in the soil profile, perhaps sequestered as gypsum (calcium sulfate); and the land farm produced both forage that is safe for livestock and a native seed crop that could be used by the Navajo Nation for rangeland or mine land reclamation.

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

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

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

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

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

E.1 Land Farming Feasibility

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

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

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

E.2 Methods

E.2.1 Experimental Design

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

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

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

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

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

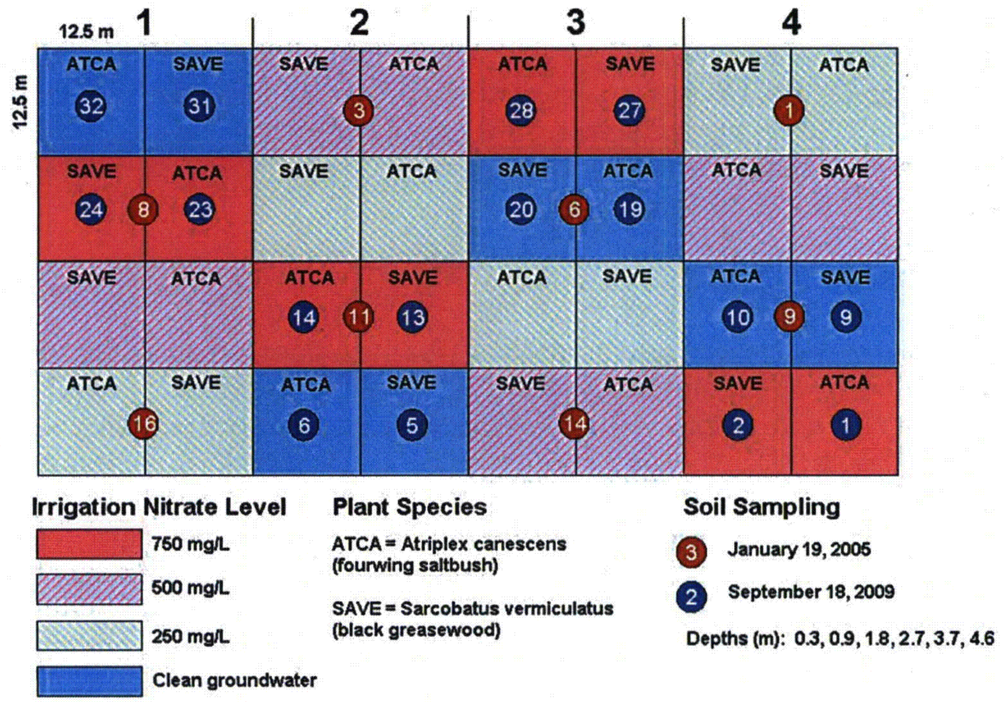


Figure E–1. Illustration of randomized split-block experimental design showing plots for nitrate treatment levels and shrubs species, and soil sampling locations and times.

E.2.2 Irrigation System

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

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

E.3 Results

E.3.1 Crop Growth, Transpiration, and Nitrogen Uptake

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

E.3.1.1 2006 Results

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

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

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

E.3.1.2 2010 Results

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

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

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

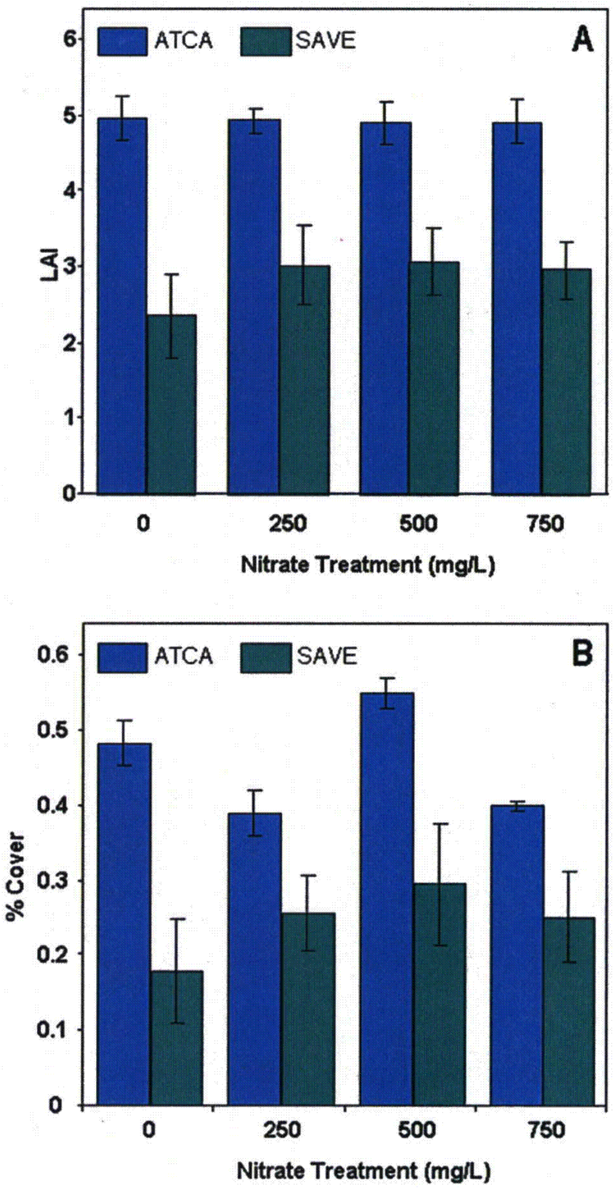
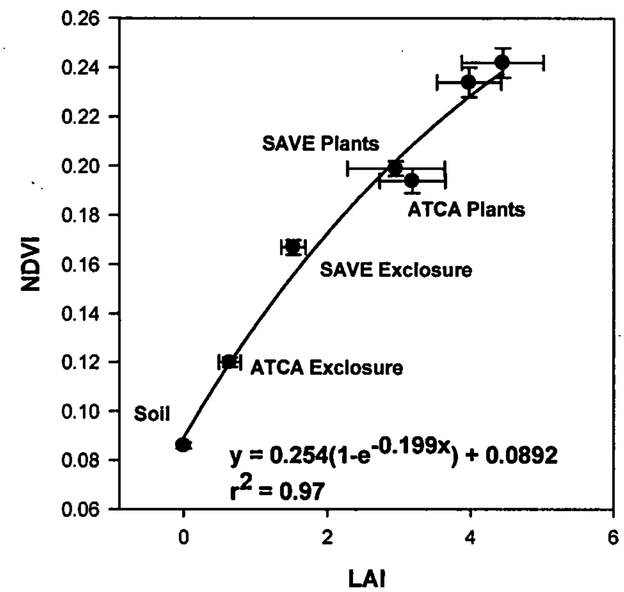


*Figure E–3. (A) Leaf area index (LAI) and (B) percent cover of fourwing saltbush (*Atriplex canescens, *or ATCA) and black greasewood (*Sarcobatus vermiculatus, *or SAVE) for irrigation water nitrate treatments. Bars are one standard error of the mean. Analysis of variance (ANOVA) results show that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

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

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



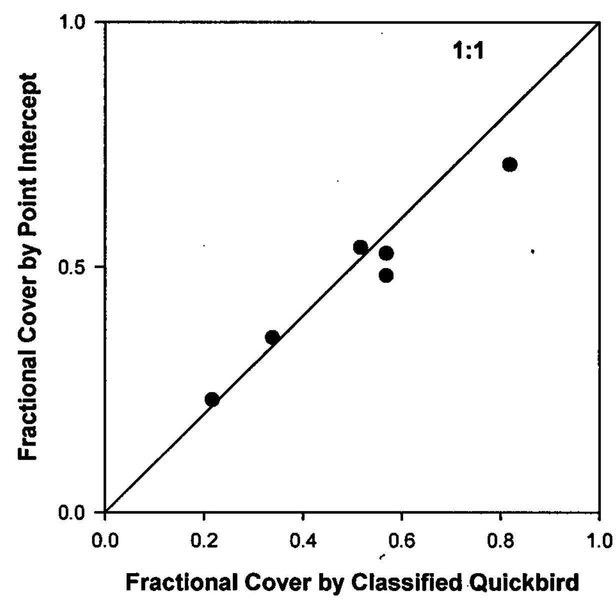


Figure E–4. Top: LAI measured on the ground by leaf harvesting versus NDVI using Quickbird. Bottom: Fractional cover estimated visually on Quickbird using a point intercept method versus an automated method using a pixel classification program in ERDAS.

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

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

E.3.2 Soil Water Monitoring

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

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

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

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

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

where:

θ_1 and Z_1 are the water content and depth for the uppermost measurement

θ_i is the volumetric water content measured at the ith point in the profile

Z_i is the depth of the ith point in the profile

n is the total number of points.

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

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

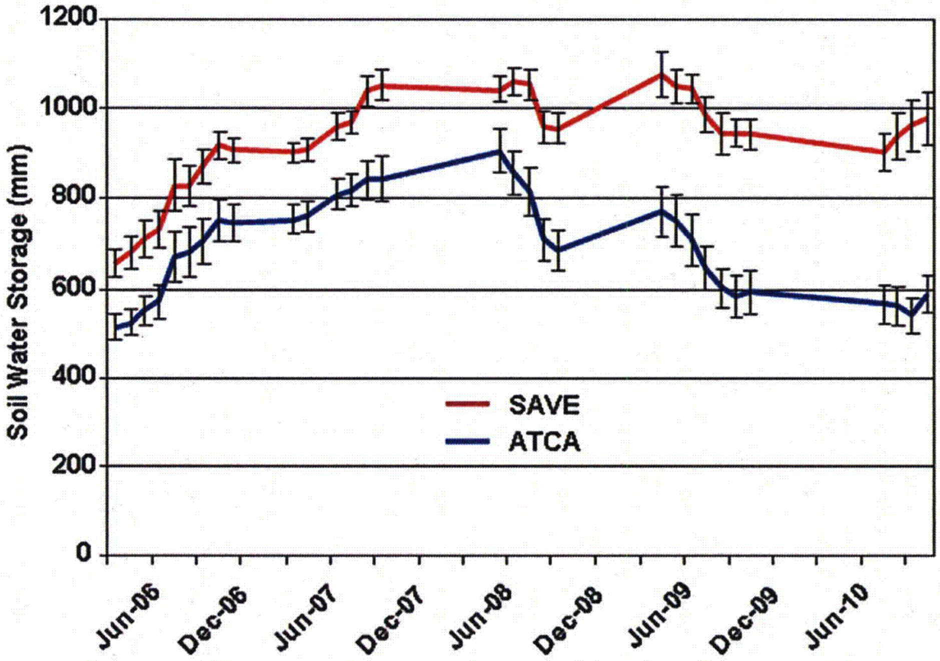


Figure E–5. Changes in soil water storage in Sarcobatus vermiculatus *(SAVE) and* Atriplex canescens *(ATCA) land-farm plots monitored monthly during the growing season using a neutron hydroprobe. Error bars = standard error of the mean.*

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

E.3.3 Soil Nitrogen and Sulfur

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

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

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

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

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

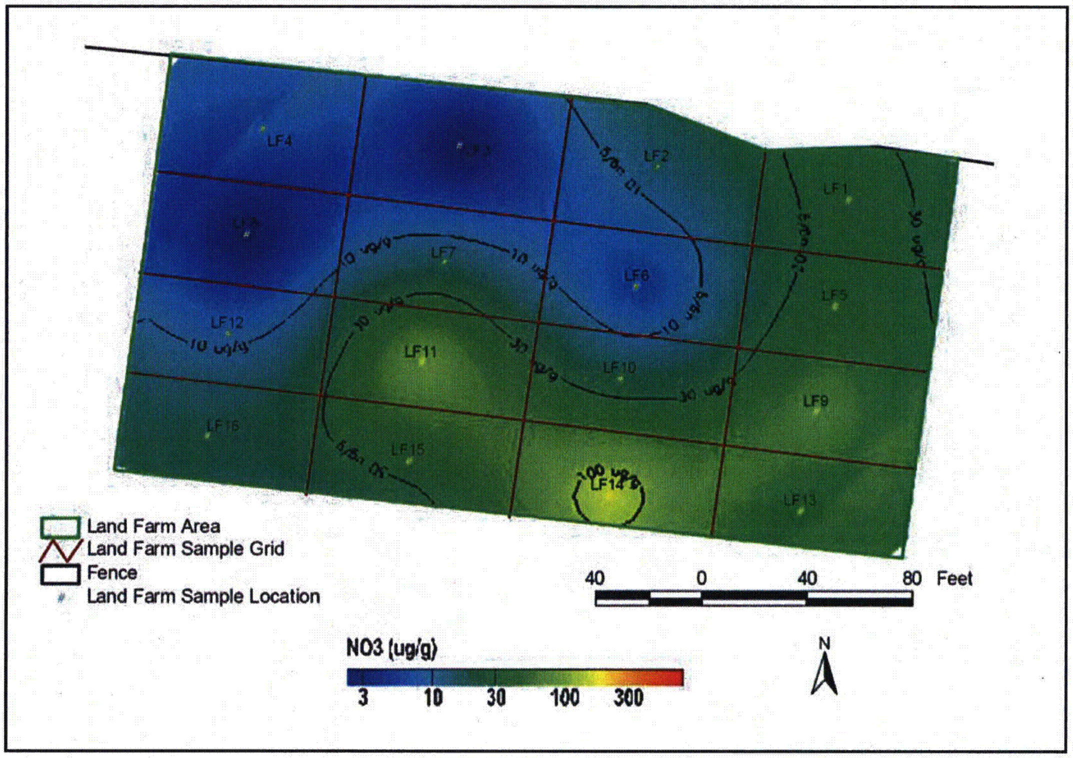


Figure E–6. Map of baseline soil nitrate distribution in the land farm created using mean concentrations at each sampling location.

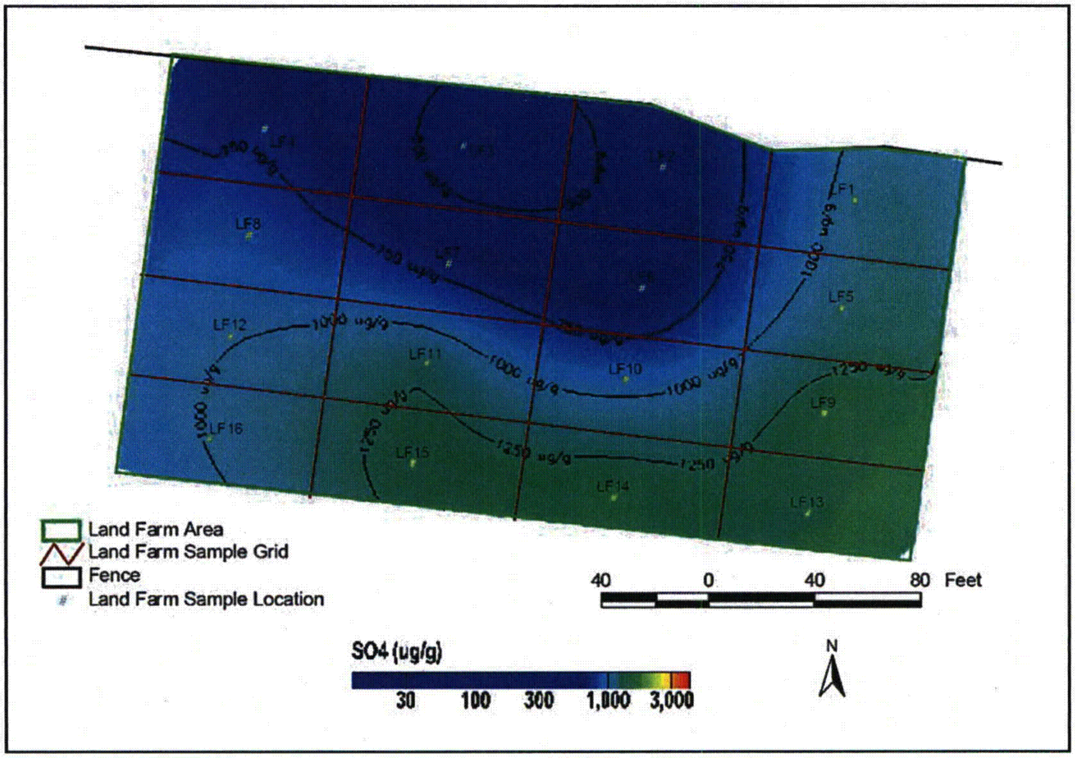


Figure E–7. Map of baseline soil sulfate distribution in the land farm created using mean concentrations at each sampling location.

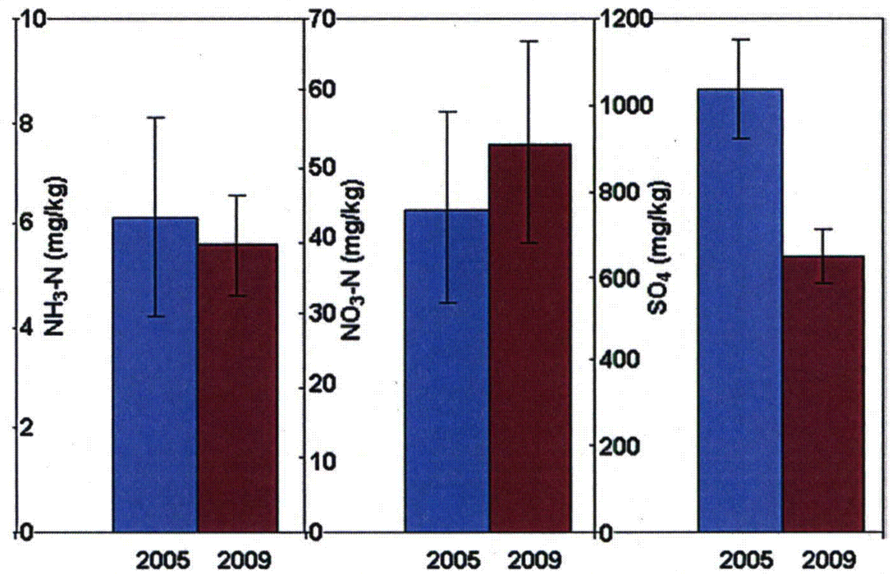


Figure E–8. Comparison of mean soil ammonia-N, nitrate-N, and sulfate concentrations for combined treatments in the land farm study in 2005 and 2009.

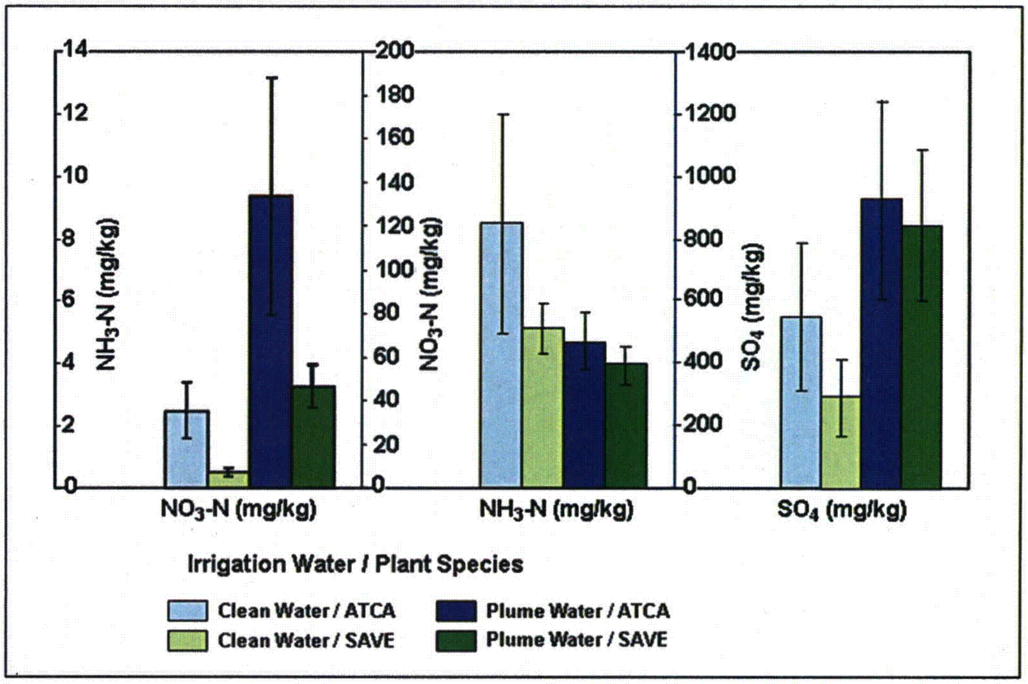


Figure E–9. Comparisons of soil ammonia-N, nitrate-N and sulfate levels in 2009 for the different irrigation water and plant treatments in the land farm study.

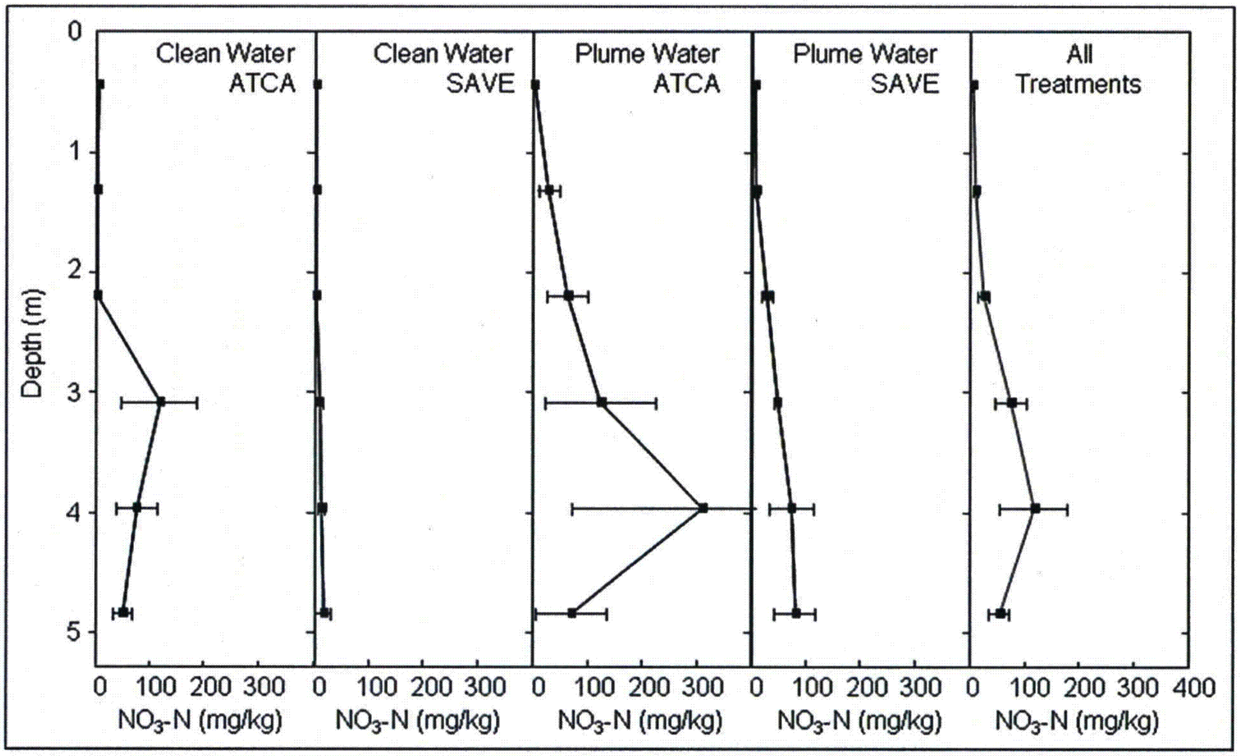


Figure E–10. Mean soil nitrate-N with depth for irrigation water and plant treatments in the Monument Valley land farm study.

Appendix F

Remote Sensing Monitoring of Phytoremediation

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

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

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

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

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

F.1 Land Areas Monitored

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

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

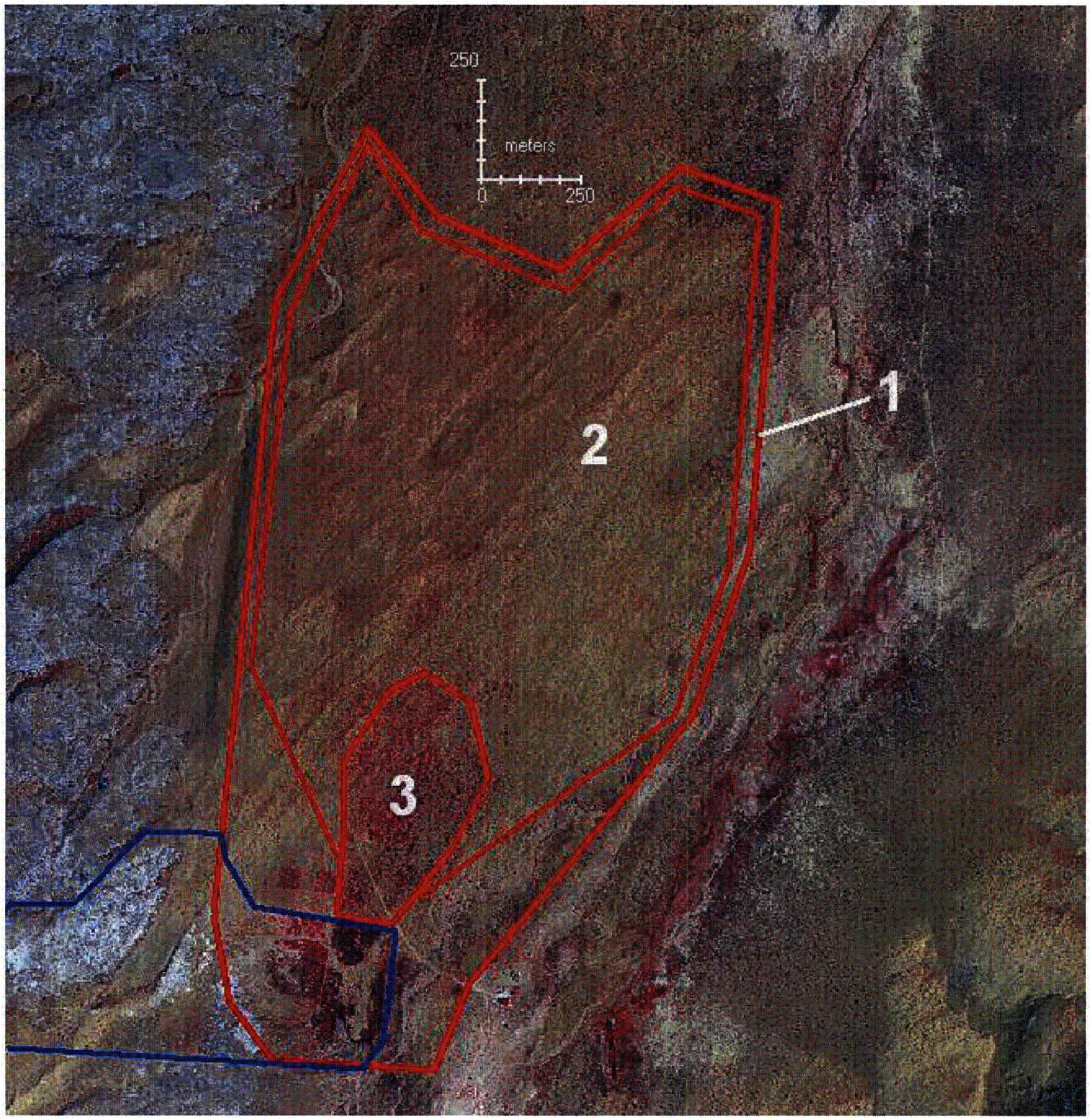


Figure F–1. Areas of interest at the Monument Valley site: (1) the whole site; (2) the Outside ATCA zone; and (3) the Outside SAVE zone. The blue line shows the fence line around the source area.

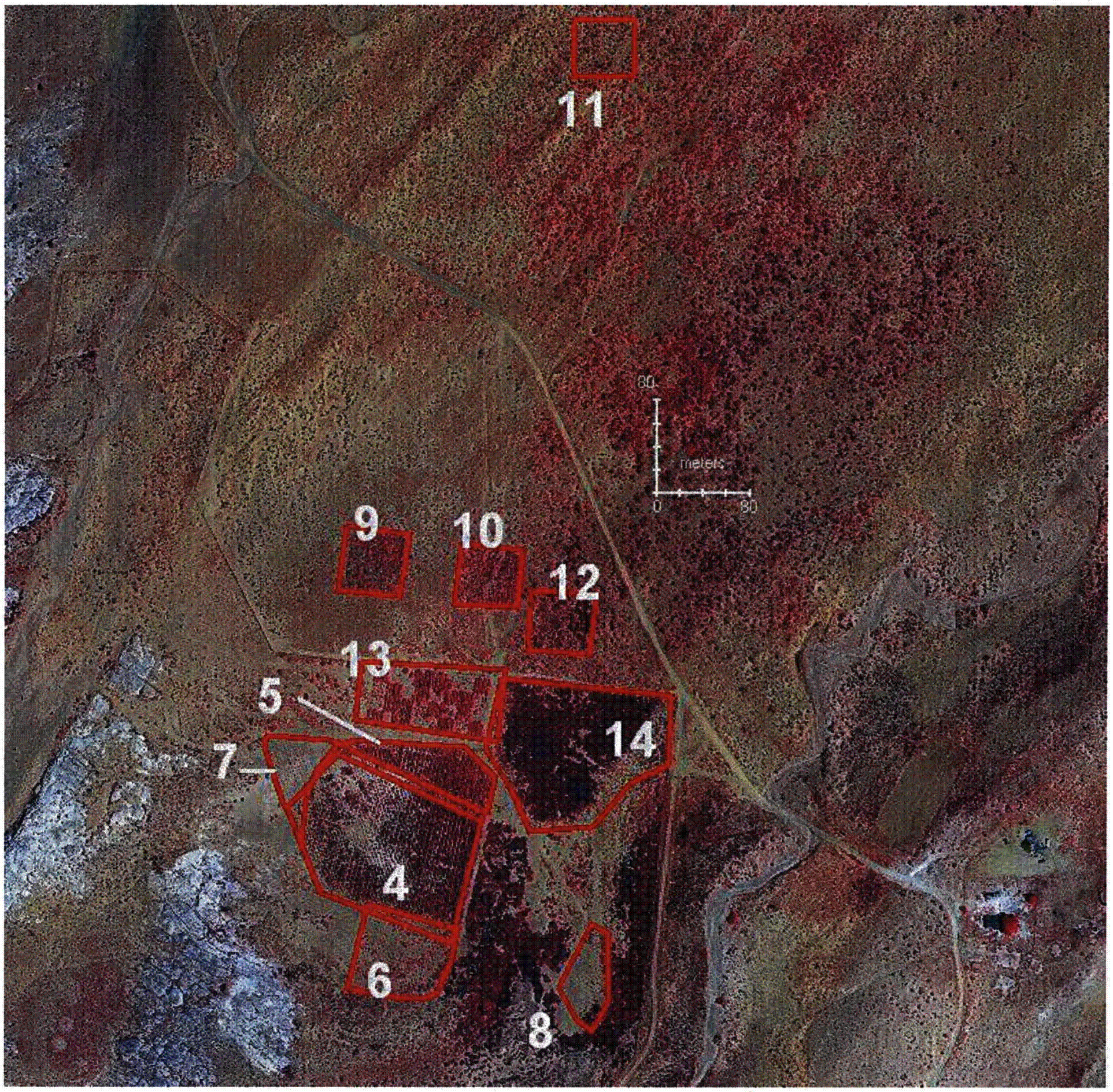


Figure F–2. Areas of interest at the Monument Valley UMTRA site: (4) the Old Field; the New North (5), New South (6), New West (7), and Evaporation Pond Fields (8); irrigated and planted West (9) and East (10) livestock exclosures; unirrigated exclosures in natural stands of ATCA (11) and SAVE (12);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

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

F.2 Ground Vegetation Surveys

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

F.3 Remote Sensing Methods

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

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

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

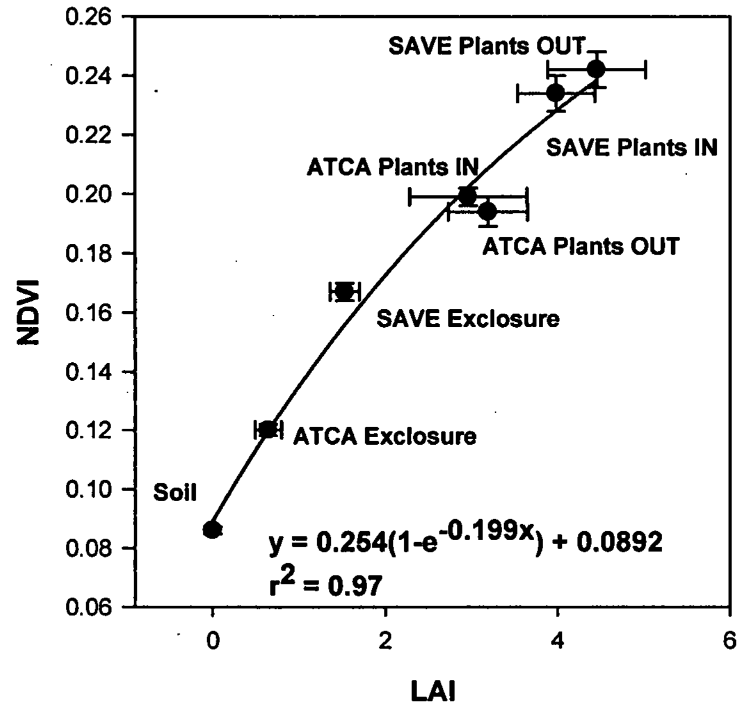
F.4 Vegetation Monitoring Results

F.4.1 Site Conditions in 2010 by Quickbird

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

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

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



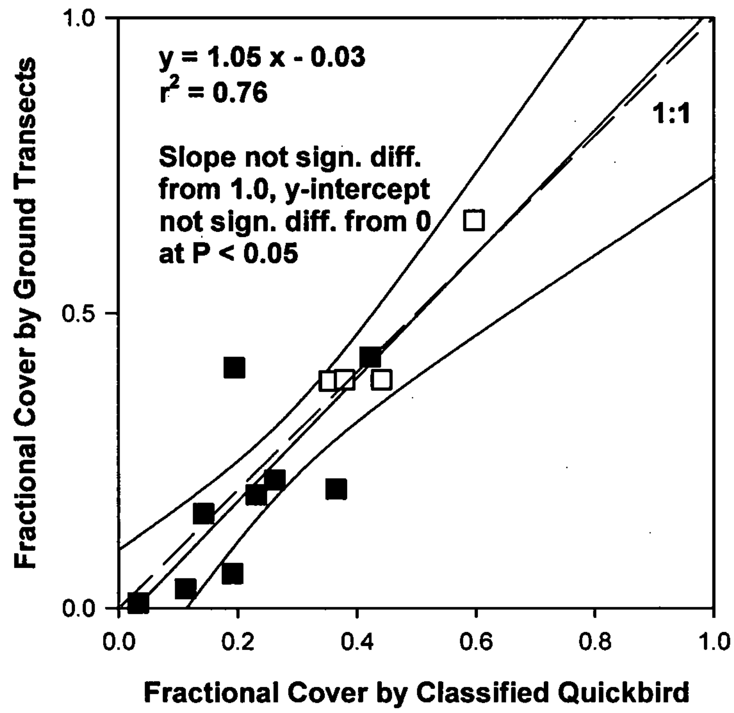


Figure F–3. (Above) Relationship between leaf area index (LAI) measured by leaf-harvesting and fractional ground cover measurements inside and outside exclosure plots and NDVI values on 2007 and 2010 Quickbird images. (Below) Relationship between fractional cover measured inside and outside exclosure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

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

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

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

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

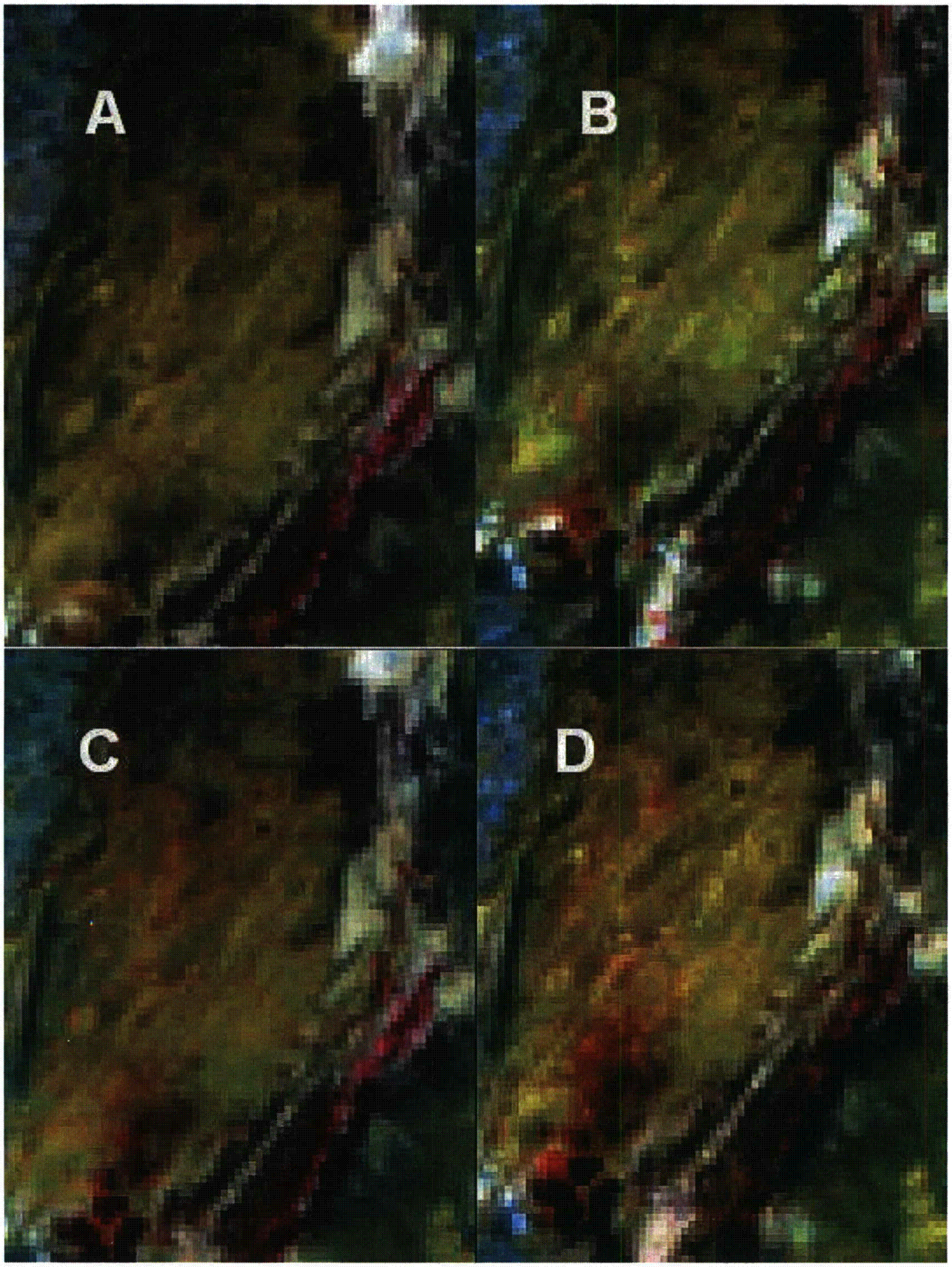


Figure F–4. False-color Landsat Thematic Mapper 5 images of the Monument Valley site with the near infrared band denoting vegetation shown in red. Images are summer scenes for 2000 (A), 2005 (B), 2007 (C), and 2009 (D).

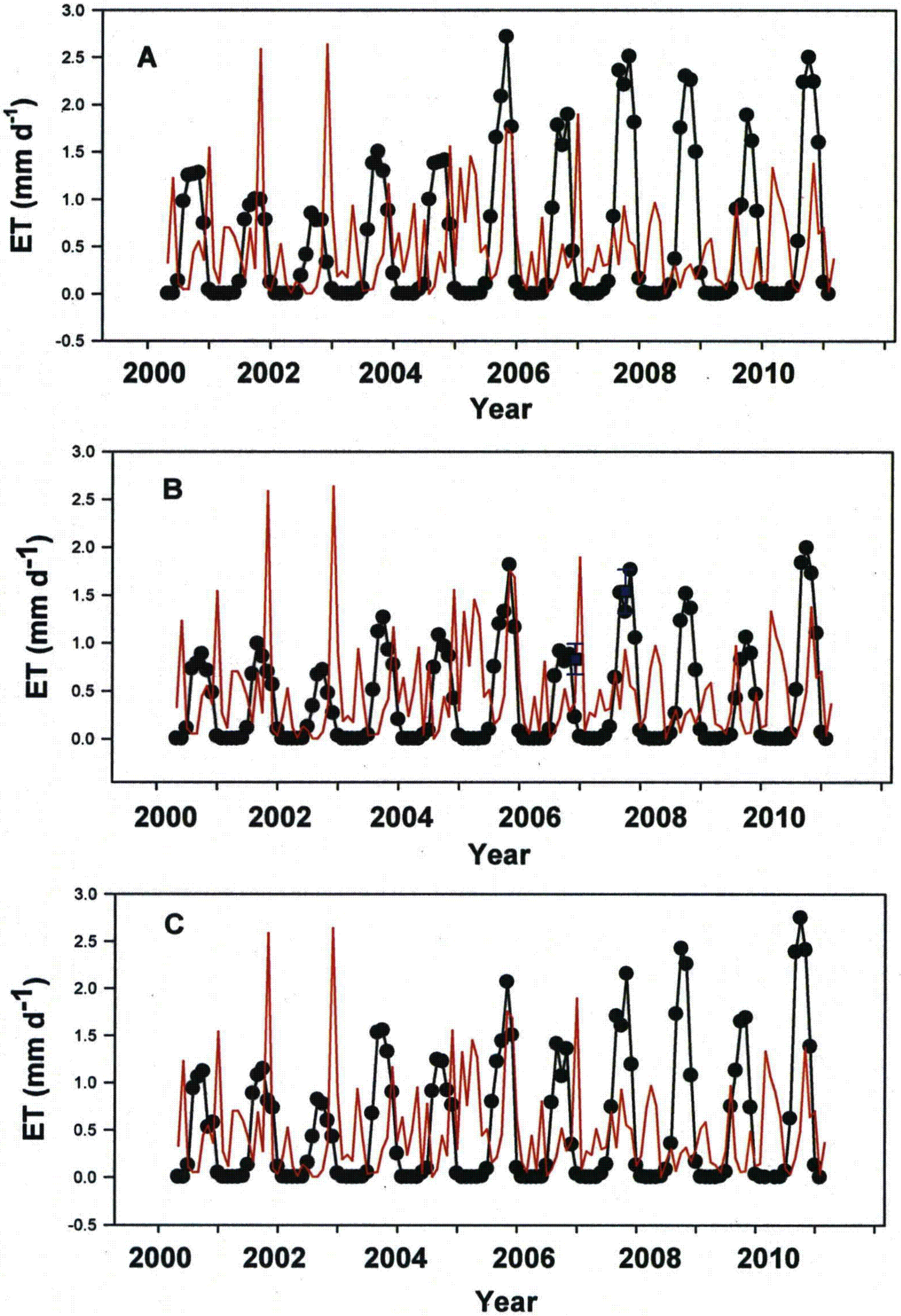


Figure F–5. ET in mm d^{-1} (black dots) estimated from MODIS Enhanced Vegetation Index and air temperature for the plants inside the source area fence (A); in the Outside ATCA zone (B); and in the Outside SAVE zone (C). The red lines are precipitation in mm d^{-1}. The inside-fence area was represented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

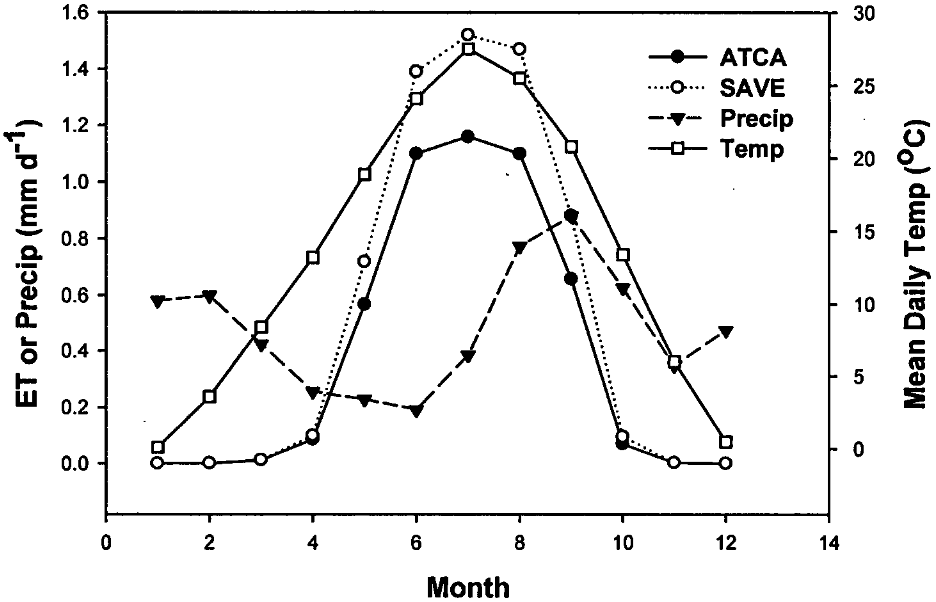


Figure F–6. Annual cycles of ET, precipitation, and air temperature in the Outside ATCA and Outside SAVE areas, averaged over years for 2000–2010.

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

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

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

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

F.5 Conclusion and Recommendations

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

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

Appendix G

Risk Evaluations

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Contents

Figures

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

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

G.1 Plant Uptake and Grazing

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

G.1.1 Chemicals of Potential Concern

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

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

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

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

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

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

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

G.1.2 Greenhouse Studies

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

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

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

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

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

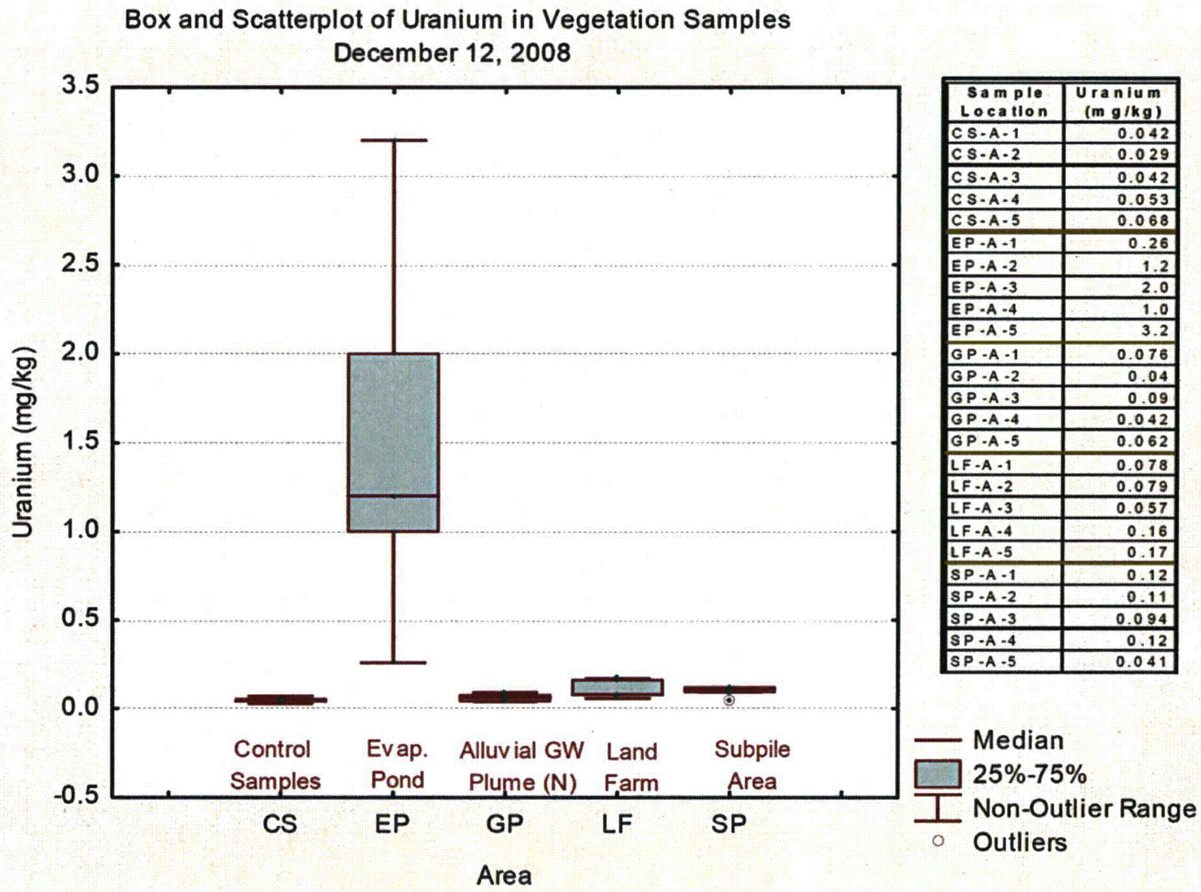
G.1.3 Field Studies of Plant Uptake

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

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

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

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



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

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

G.2 Evaluation of Stained Soils

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

G.2.1 Stained Subpile Soils

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

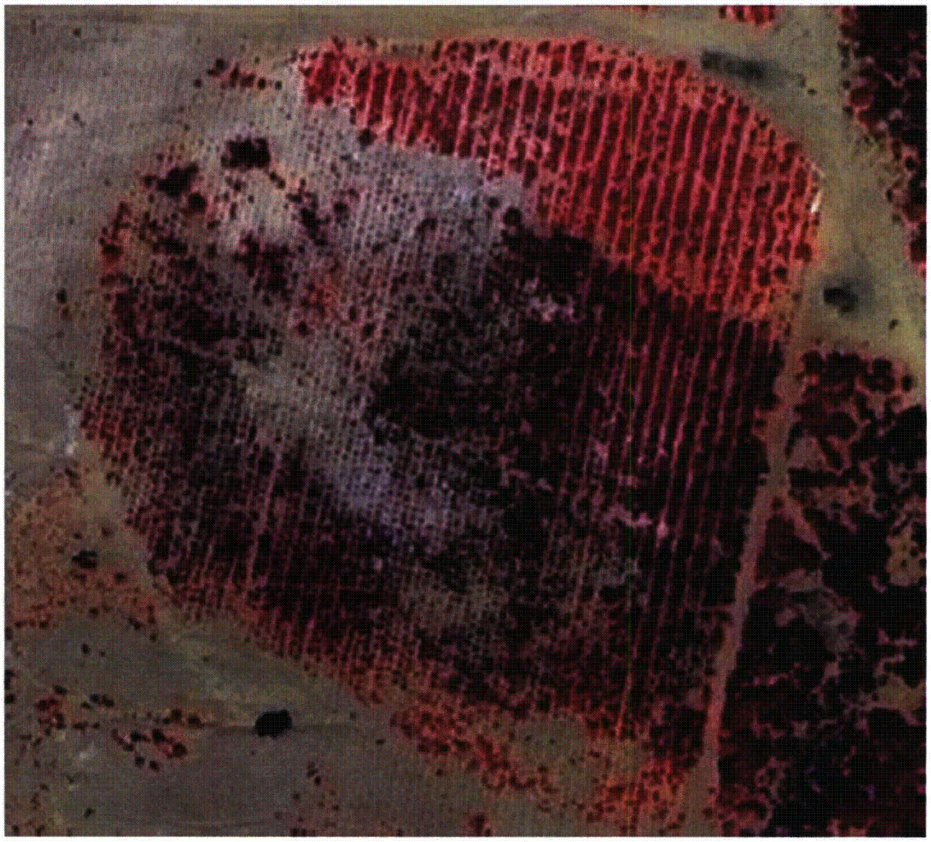


Figure G–2. False-color 2009 Quickbird images showing whitish colored soil and areas of poor plant growth in the western portion of the subpile phytoremediation planting.

G.2.2 Manganese Toxicity Investigation

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

- Chemical analyses of the concretions show that they are indeed aggregates enriched in Mn and Fe.
- Although the onset of irrigation may have mobilized Mn, and the Mn oxides may be precipitating, most of the mobilization of Mn at this site likely occurred during the leaching of uranium-rich minerals with acid.
- The levels of Mn are within values for normal soils, and they are well below any levels of concern for human health risks.

G.2.3 Evaporation Pond Crusts

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

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

Appendix H

Beneficial Land Use

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Figures

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

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

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

H.1 Ecological Importance of Nitrate and Ammonium

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

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

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

H.2 Land Reuse: Seed and Forage Crops

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

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

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

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

H.3 Ethnobotany

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

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Appendix I

List of Publications, Reports, and Presentations

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

Book Chapter

Waugh, W.J., E.P. Glenn, P.H. Charley, B. Maxwell, and M.K. O'Neill, 2011. *Helping Mother Earth Heal: Diné College and Enhanced Natural Attenuation Research at U.S. Department of Energy Uranium Processing Sites on Navajo Land*, In: Burger, J. (ed.) Stakeholders and Scientists: Achieving Implementable Solutions to Energy and Environmental Issues, Springer, New York, New York.

Journal and Proceedings Publications

Bresloff, C.J., U. Nguyen, E.P. Glenn, W.J. Waugh, and P.L. Nagler (draft), *Remote Sensing Monitoring of Site Vegetation and Evapotranspiration by a Desert Phreatophyte Community at a Former Uranium Mill Site on the Colorado Plateau.*

Borden, A.K., M.L. Brusseau, K.C. Carroll, N. H. Akyol, A. McMillan, J. Berkompas, Z. Miao, F. Jordan, G. Tick, W.J. Waugh, and E.P. Glenn, 2011. *Ethanol addition for enhancing denitrification at the uranium mill tailings site in Monument Valley, Arizona.* Water, Air, and Soil Pollution DOI 10.1007/s11270-011-0899-1.

Waugh, W.J., D.E. Miller, E.P. Glenn, D. Moore, K.C. Carroll, and R.P. Bush, 2010. Natural and Enhanced Attenuation of Soil and Groundwater at the Monument Valley, Arizona, DOE Legacy Waste Site, *Proceedings of Waste Management 2010 Symposium*, Phoenix, Arizona.

Carroll, K.C., F.L. Jordan, E.P. Glenn, W.J. Waugh, and M.L. Brusseau, 2009. Comparison of nitrate attenuation characterization methods at the uranium mill tailing site in Monument Valley, Arizona, *J. Hydrology*, 378(1-2):72-81.

Glenn, E., K. Morino, K. Didan, F. Jordan, K. Carroll, P. Nagler, K. Hultine, L. Sheader, and J. Waugh, 2008. "Scaling sap flux measurements of grazed and ungrazed shrub communities with fine and course-resolution remote sensing," *Ecohydrology*, 1(4):316–329.

Jordan, F., W.J. Waugh, E.P. Glenn, L. Sam, T Thompson, and T.L. Thompson, 2008. Natural bioremediation of a nitrate-contaminated soil-and-aquifer system in a desert environment, *Journal of Arid Environments*, 72(5):748–763.

McKeon, C., E.P. Glenn, W.J. Waugh, C. Eastoe, F. Jordan and S.G. Nelson, 2006. Growth and water and nitrate uptake patterns of grazed and ungrazed desert shrubs growing over a nitrate contamination plume, *Journal of Arid Environments*, 64(1):1–21.

McKeon, C., F.L. Jordan, E.P. Glenn, W.J. Waugh, and S.G. Nelson, 2005. Rapid nitrate and ammonium loss from a contaminated desert soil, *J. of Arid Environments*, 61(1):119–136.

Technical Conference Presentations

Waugh, W.J., and E.P. Glenn, 2012. *Land-Farm Phytoremediation of Groundwater Using Native Desert Shrubs at the Monument Valley, Arizona, DOE Legacy Waste Site*, Proceedings of Waste Management 2012.

McMillan, A.L., A.K. Borden, M.L. Brusseau, K.C. Carroll, N.H. Akyol, J.L. Berkompas, Z. Miao, F. Jordan, G.R. Tick, W.J. Waugh, and E.P. Glenn, 2011. *Long-term effects of ethanol addition on denitrification at the uranium mill tailing site in Monument Valley, Arizona,* Proceedings of the American Geophysical Union Fall Meeting, San Francisco, California, December 5–9.

Borden, A.K., J. Berkompas, Z. Miao, K.C. Carroll, W.J. Waugh, E.P. Glenn, and M.L. Brusseau, 2009. Pilot Tests of Enhanced Denitrification Using Ethanol, *Geological Society of America Annual Meeting*, Portland, Oregon, October 21.

Carroll, K.C., F.L. Jordan, E.P. Glenn, W.J. Waugh, and M.L. Brusseau, 2008. *Comparison of Nitrate Attenuation Characterization Methods for Groundwater Remediation* (poster), American Geophysical Union Annual Meeting, San Francisco, California, December 15–19.

Jordan, F., J. Waugh, and E. Glenn, 2008. *A Plant-Based Approach to Remediating a Nitrate-Contaminated Soil/Aquifer System in a Desert Environment*, 2008 Joint Meeting of The Geological Society of America and Soil Science Society of America, Houston, Texas, October 5–9.

Waugh, W.J., E.P. Glenn, and F. Jordan, 2007. *Phytoremediation: Growing Answers for Soil and Ground Water Contamination at Monument Valley, Arizona*, Navajo Nation Division of Natural Resources Conference (invited seminar), Flagstaff, Arizona, June 11–14.

Waugh, W.J., E.P. Glenn, and F. Jordan, 2007. *Ground Water Restoration at Abandoned Uranium Mills on the Navajo Nation Using Native, Desert Phreatophytes*, Ecological Society of America / Society for Ecological Restoration Joint Meeting, San Jose, California, August 5–10.

Maxwell, B., M. Carroll, J. Waugh, F. Jordan, and E. Glenn, 2007. *Remediation of Soil and Ground Water Using Native Desert Phreatophytes,* National Water Conference, USDA-Cooperative State Research, Education, and Extension Service, Savannah, Georgia, January 28–February 1.

Jordan, F.L., E.P. Glenn, J.C. Glier, C.A. McKeon, and W.J. Waugh, 2006. *Restricting Grazing to Enhance Phytoremediation of a Shallow Aquifer*, Soil Water Conservation Society Annual Meeting, Keystone, Colorado, July 22–26.

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Appendix J

Appendix References

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