Use of Groundwater Flow, Solute Transport, and Geochemical Modeling To Evaluate Long-Term Nitrate Plume Concentrations Following Phreatophyte Source Control – 17262

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ABSTRACT

The Monument Valley, Arizona, Processing Site is a former uranium mill site within the Navajo Nation in northeastern Arizona. Milling activities between 1955 and 1968 resulted in contamination of groundwater in the shallow alluvium at the site. Remedial action was completed under Title I of the Uranium Mill Tailings Radiation Control Act of 1978. Site remediation activities between 1992 and 1994 removed surficial source material and other site-related contamination, but contamination of deeper soil, primarily by nitrate, remained between the excavation depth and the water table. Residual nitrate in these soils, from uranium ore processing at the mill, has continued to be a source of groundwater contamination. To evaluate the potential for native phreatophytes to control remaining source material, fourwing saltbush and black greasewood were planted in 2000 and 2005 within the footprints of the former tailings piles. The objectives of the plantings were to increase nitrate removal from soil water through root uptake and, because phreatophyte water usage is expected to equal or exceed annual precipitation, to halt nitrate loading to groundwater. Recent evaluation showed more than an 80% decrease in soil nitrate concentrations and no effective groundwater recharge in the planting area.

Numerical groundwater flow, solute transport, and geochemical modeling were performed to evaluate the long-term response of the existing nitrate plume to the phreatophyte source control measures. This modeling will help determine if 100-year natural flushing is a viable compliance strategy for the nitrate plume. Results showed that nitrate concentrations in the alluvial aquifer are expected to drop below the standard of 10 mg/L as N in approximately 70 years as a result of the phreatophyte planting. Companion sensitivity analysis was also performed to better understand how uncertainty in groundwater flow model and solute transport model inputs would impact cleanup times. Even considering input uncertainty, nitrate concentrations are expected to reach the standard in the alluvial aquifer within 100 years.

Recognizing that model predictions are not absolute, but represent the general potential for an event to occur, the model was used to identify key sampling locations to verify that the nitrate plume will attenuate as predicted. This evaluation identified locations that can be used to assess the viability of the modeling predictions within the next 50 years. If the source diminishes or no longer exists, modeling predicts that concentrations of nitrate and ammonium in these wells

should show significant declines over the next 10–55 years. If downward concentration trends do not occur as predicted, other remedial strategies may need to be evaluated to meet groundwater standards within the specified 100-year duration.

INTRODUCTION

Monument Valley, Arizona, Processing Site

The Monument Valley Processing site is in northeastern Arizona in the Navajo Nation, approximately 24 kilometers south of Mexican Hat, Utah (Fig. 1). The site is the location of a former uranium mill. The former mill site is on the west side of Cane Valley, which drains to the north via Cane Valley Wash (Fig. 2).

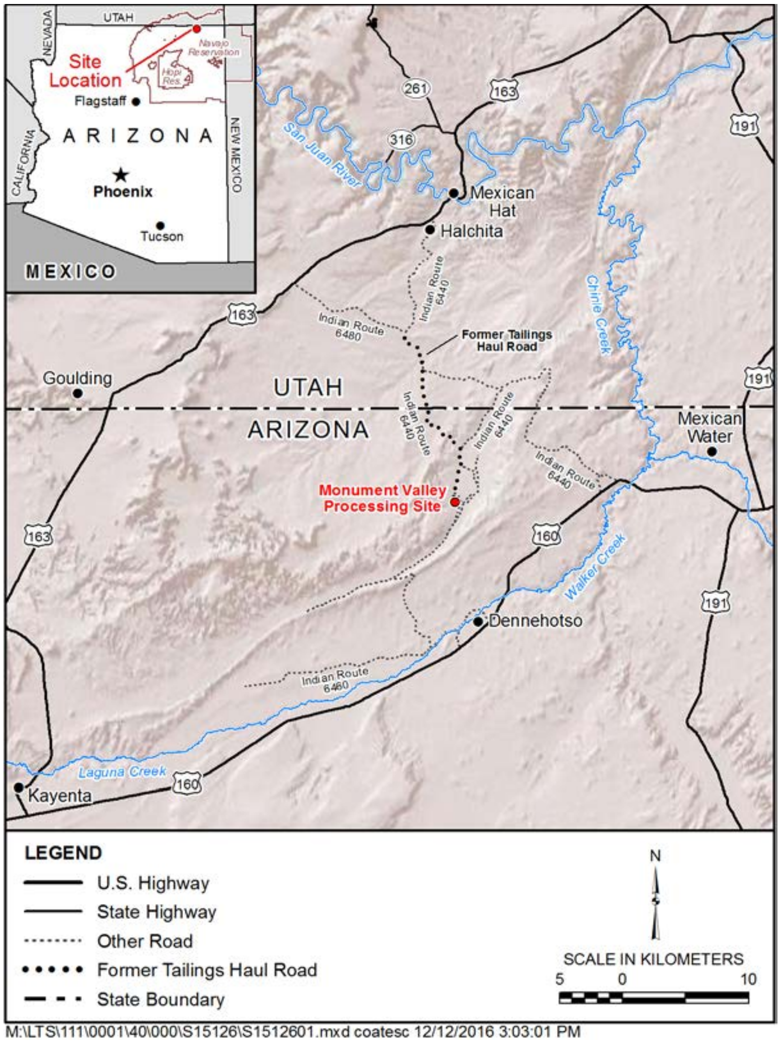

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Fig. 1. Location of the Monument Valley, Arizona, Processing Site

The elevation along Cane Valley Wash (Fig. 2) is approximately 1460 m above mean sea level. Comb Ridge, a 183 m high escarpment of sandstones of the Navajo, Kayenta, and Wingate Formations, borders the valley on the east. On the west side of the valley near the former mill site, the bedrock dips to the east at approximately 5 degrees and rises up to Yazzie Mesa (Fig. 2) at an elevation of over 1620 m. Cane Valley between Comb Ridge and Yazzie Mesa is filled with a reddish-yellow eolian sand and minor amounts of water-transported sand, gravel, and bedrock fragments.

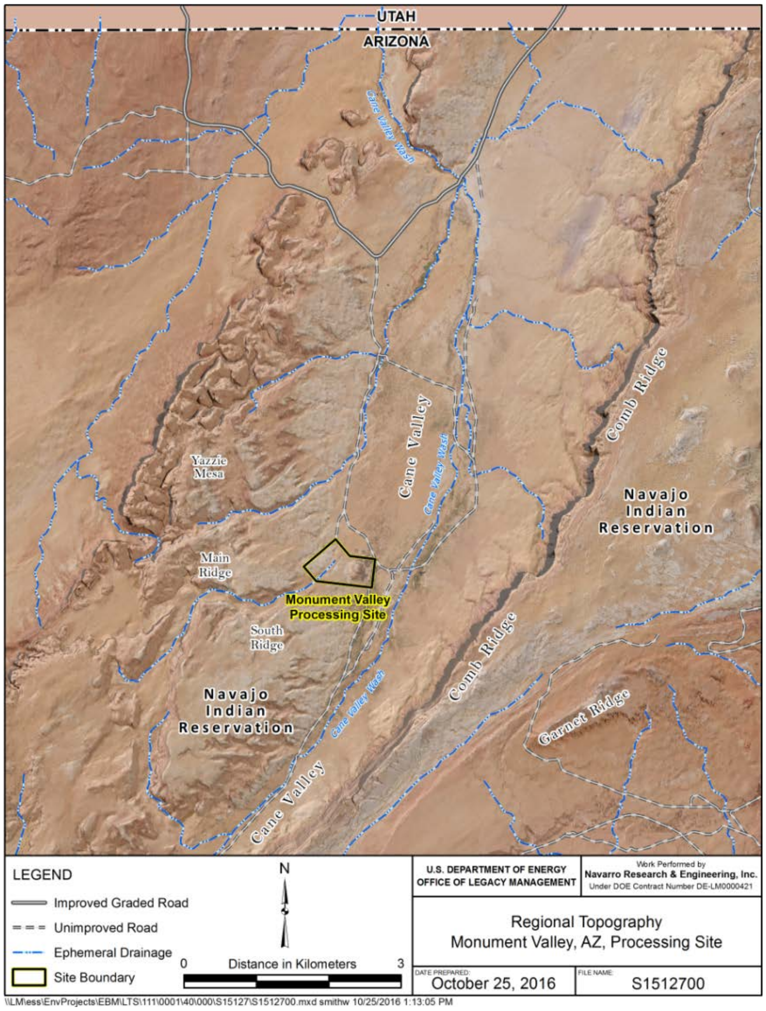

Fig. 2. Regional Topography at the Monument Valley, Arizona, Processing Site

Uranium was discovered in 1942 approximately 0.8 kilometers west of the former mill site. Vanadium Corporation of America (VCA) acquired mining rights for the deposit from the Office of Indian Affairs in 1943 and named the lease property Monument No. 2 (Fig. 2). VCA mined the property from 1943 to 1968 with a total production of 695,958 metric tons of ore. The Monument No. 2 mine produced more uranium than any other mine in Arizona [1].

An upgrader was constructed at the Monument Valley site in 1955 and operated until 1964. Before 1955, ore was either shipped to Metal Reserve at Monticello, Utah, or mechanically upgraded at a small plant near Mexican Hat. Fine-grained material was shipped offsite for chemical concentration at the Durango, Colorado, mill before March 1963 and later at the VCA mill at Shiprock, New Mexico. Coarse-grained material remained on the site and was placed in the areas identified as the former mill and old tailings pile (Fig. 3). The mechanical milling operations at the Monument Valley site continued from 1955 to 1964. A batch-leach process was used from 1964 until 1968. This leaching process included the use of sulfuric acid, ammonia, and calcium oxide with discharge of liquid waste to the evaporation pond and solid material to the new tailings pile (Fig. 3). Control of the site, structures, and materials reverted to the Navajo Nation at that time [2].

The mill buildings and milling equipment were removed after 1968 [2]. The US Department of Energy (DOE) began surface remediation in 1992. The tailings piles, windblown tailings, concrete foundations, debris, and other materials contaminated with low-level radioactivity were removed and placed in the Mexican Hat Uranium Mill Tailings Remedial Action (UMTRA) Project disposal cell, approximately 16 kilometers north of the former mill site. Relocation of these materials was completed in January 1994.

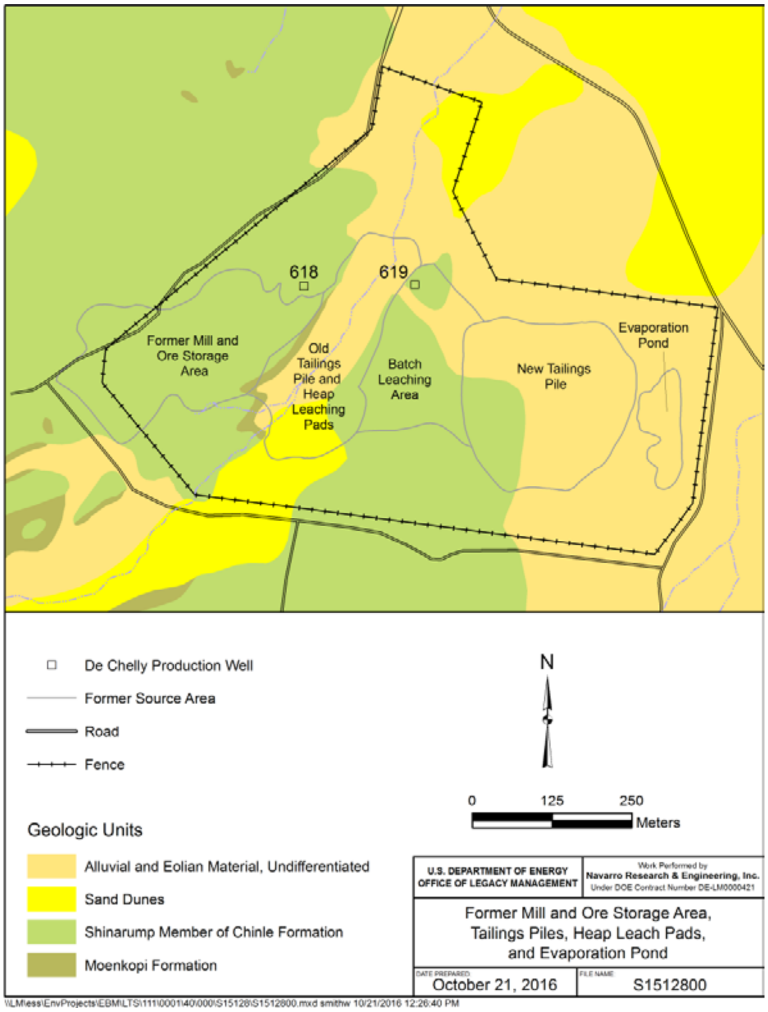

Fig. 3. Former Mill and Ore-Storage Area, Tailings Piles, Heap Leaching Pads, and Evaporation Pond with Surface Geology

Groundwater Conditions and Nitrate Contamination

Three former onsite areas that may be sources of groundwater contamination have been identified (Fig. 3): (1) the old tailings pile and heap leaching pads, (2) the new tailings pile, and (3) the evaporation pond. Fluids moving through these source areas contributed to nitrate contamination in the groundwater and may have contributed to the sulfate and uranium groundwater contamination in the past. Elevated concentrations of nitrate and sulfate are attributed to mill-related processes, and their plumes cover a significant area downgradient of the site. Uranium exceedances are generally limited to the groundwater in the alluvial aquifer in the vicinity of the old tailings pile and heap leaching pads (Fig. 3). Surficial source material was removed during site remediation between 1992 and 1994, but soil contamination, primarily nitrate, remained between the excavation depth and the water table. This residual nitrate continued to contaminate groundwater and is the focus of this paper.

Nitrate is especially useful as an indicator of the extent of mill-related contamination. Nitrate is present in relatively low concentrations in background groundwater, is associated with relatively high concentrations in the former tailings pore fluids, and is highly mobile in shallow groundwater at the site under almost all conditions. However, nitrate does degrade to nitrogen gas (denitrification) under reducing conditions. The maximum contaminant limit under the Uranium Mill Tailings Radiation Control Act for nitrate contamination is 10 mg/L (as N). Nitrate levels of 10 mg/L or greater are considered to be representative of the limit of site-related contamination in the alluvial aquifer, as discussed in the Monument Valley Site Observational Work Plan [2].

Nitrate contamination at the Monument Valley site occurs primarily in the alluvial aquifer (Figs. 4 and 5). The alluvial aquifer consists mainly of Quaternary age windblown fine- to medium-grained sand deposits, which vary in thickness from 0 m near the former mill site to 36.6 m approximately 3.2 km downgradient of the site. Additional geologic details and cross section can be found in Reference [2]. The depth to groundwater in the alluvium varies widely across the site, ranging from 3 m near the site to 12 m below ground surface at the downgradient leading edge of the nitrate plume.

Groundwater in the alluvial aquifer generally flows north. Since 1985, the horizontal gradient has been 0.01. Hydraulic conductivity in the alluvial aquifer ranges from 0.09 to 5.8 m/day. Assuming an effective porosity of 0.25 and a hydraulic gradient range of 0.007 to 0.012, the average groundwater flow velocity ranges from 0.18 to 0.31 m/day.

Recharge to the alluvial aquifer is the result of infiltration of precipitation and of upward leakage from the underlying aquifers. This area receives approximately 16.5 cm of precipitation annually, with the majority of the precipitation resulting from isolated thunderstorms during the late summer and early fall. Only a fraction of the annual precipitation actually enters the aquifer due to loss from evaporation and plant uptake; discharge from the alluvial aquifer is primarily the result of evapotranspiration and evaporation.

Figure 4 shows concentrations of nitrate in groundwater that were used as initial conditions in the modeling efforts. These concentrations are average values measured from January 1, 2010, through December 31, 2015, which can be considered as an initial simulation time of 2012. Because the highest concentrations of nitrate are observed immediately downgradient of the former evaporation pond and new tailings areas, concentrations in wells in this vicinity are typically 10 to 20 times background. Well 0606, just north of the site boundary, had the highest concentration of 630 mg/L. On the basis of nitrate distribution, the primary source of nitrate contamination in the alluvial aquifer appears to be related to process fluids draining from the former new tailings pile and the evaporation pond (Fig. 3). Concentrations in the vicinity of the ore storage area and old tailings pile are below the nitrate standard.

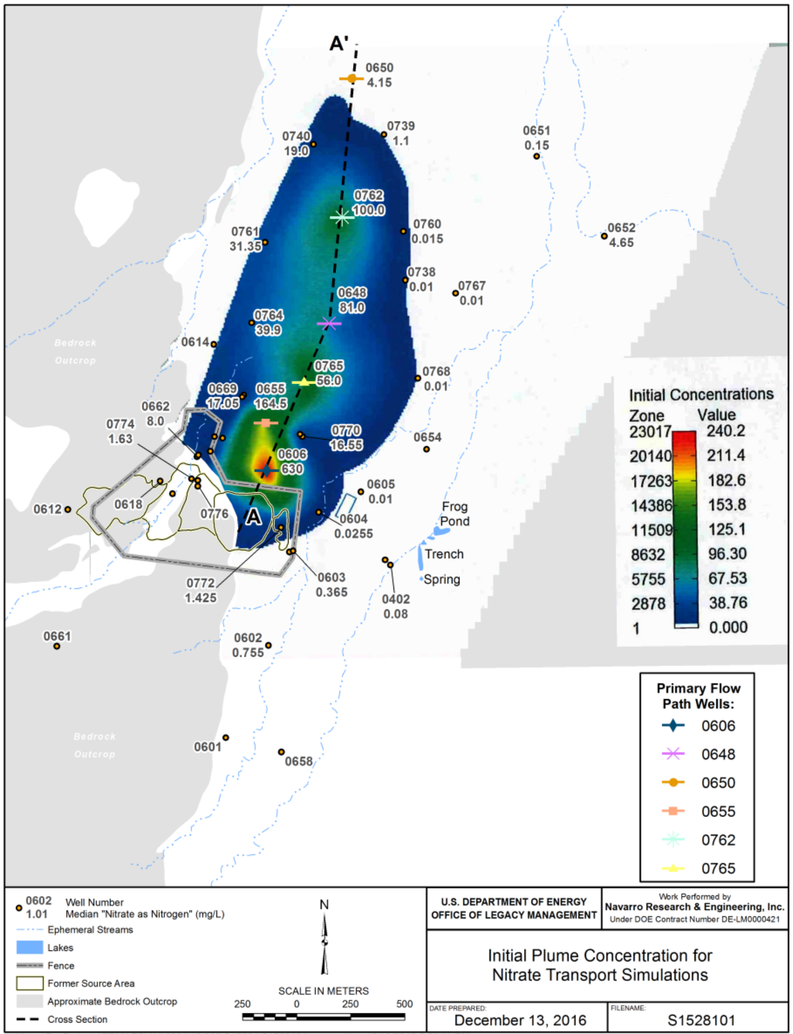

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Fig. 4. Nitrate Concentrations in Groundwater at the Monument Valley, Arizona, Processing Site, Year 2012 for Initial Plume Concentrations (mg/L)

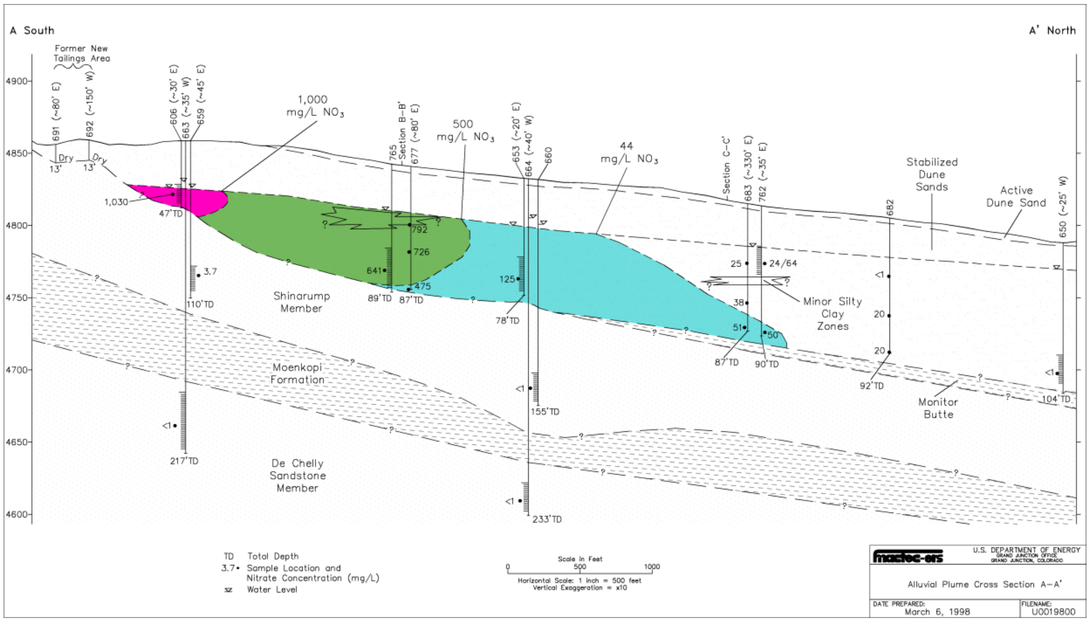

Fig. 5. Geologic Cross Section Along the Axis of the Nitrate Plume (A–A' Located in Fig. 4) with Nitrate Concentrations from 1997; source: US DOE, 1999 [2]

Concentrations of nitrate in groundwater over time are affected by a number of processes—nitrification of ammonia, denitrification of nitrate, and attenuation due to transport processes (e.g., dispersion, diffusion). Because nitrification of ammonia causes increases in nitrate, many plots for wells near the source areas do not show well-defined trends but show increases and decreases for different time periods (Fig. 6). The highest concentrations of nitrate have been consistently observed at location 0606; recently, concentrations here appear to be increasing (Fig. 6). This increase is thought to be due, at least in part, to irrigation of plants in this area with high nitrate groundwater [3]. Eventually, depletion of ammonia in subpile soils, which is nearly complete, should lead to more regular, declining trends in nitrate in the high-concentration areas of the plume. Denitrification of nitrate should also result in declining concentrations throughout the plume.

Nitrate concentrations were reduced to background levels for well 0765 in 2009. This well was used for ethanol injection during pilot studies that same year to test the potential for enhancing the denitrification of nitrate. According to the pilot study report [3], the decreases in nitrate were attributed to biological processes as a result of ethanol introduction; changes in redox conditions were also noted. Denitrification rates were estimated to be 50 times more rapid than those under natural conditions. Nitrate concentrations eventually rebounded at well 0765 with a return to oxic conditions, but to levels lower than previously observed.

Nitrate has been measured at concentrations exceeding the standard as far downgradient as well 0740 (just to the side of the primary flow path wells, see Fig. 4); nitrate has been detected at location 0650, but at concentrations below the standard (Fig. 4). Nitrate has been increasing at both of these locations, indicating that the plume is still migrating downgradient.

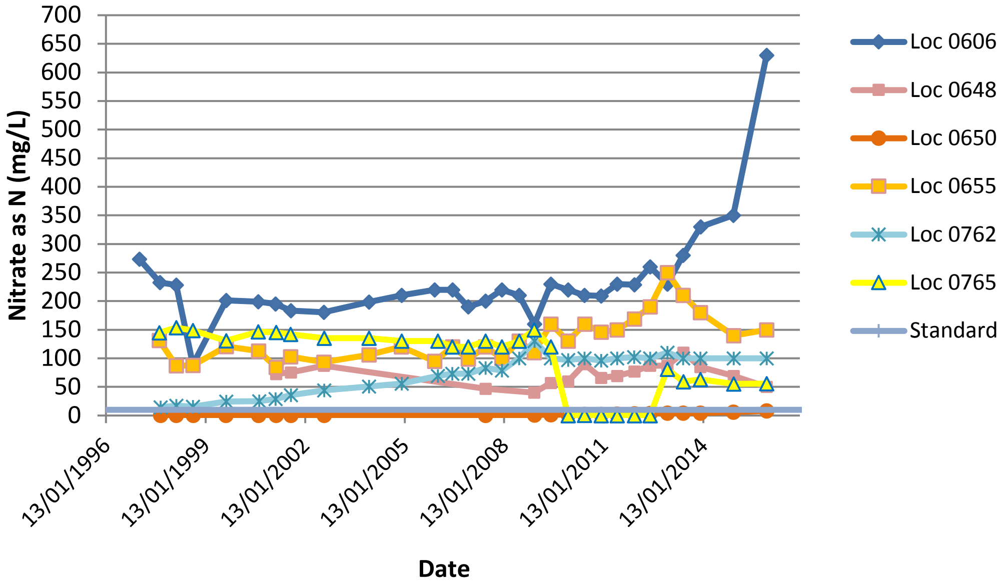

Fig. 6. Nitrate Concentration (as N) Along Primary Flow Path

Phreatophyte Pilot Studies

DOE’s Office of Legacy Management has completed a suite of pilot studies designed to evaluate, on a landscape scale, proposed passive and active remedies for ammonium, nitrate, and sulfate in the alluvial aquifer and in source area soils at the Monument Valley site [3]. Two native phreatophytes, fourwing saltbush and black greasewood, were planted in 2000 and 2005 within the footprints of the former tailings piles to control the remaining source material. Natural and enhanced phytoremediation using native desert plants and natural and enhanced microbial nitrification and denitrification were evaluated as potential passive remedies for both the shallow portions of the alluvial aquifer and for subpile soils. The objectives of the plantings were to increase nitrate removal from soil water through root uptake and, because phreatophyte water usage is expected to equal or exceed annual precipitation, to halt nitrate loading to groundwater.

Key results of the pilot study [3] are as follows:

- The source of nitrate contamination in subpile soils has been reduced by at least 80%. Phytoremediation has been successful at controlling further leaching of the remaining source to the groundwater. The source of nitrate contamination to groundwater has been effectively eliminated.
- Laboratory microcosm studies and field geochemical data indicate that natural microbial action in site groundwater is effective at denitrifying dissolved nitrate and attenuating the groundwater plume. First-order denitrification-rate coefficients were calculated by different methods and were comparable. These results suggest that natural flushing alone may be able to achieve nitrate remediation goals.

- If natural flushing alone is not sufficient to meet cleanup goals, enhancement of attenuation can be achieved through ethanol injection.

Long-Term Nitrate Plume Evaluation

Numerical groundwater flow, solute transport, and geochemical modeling were performed to evaluate the long-term response of the existing nitrate plume following the phreatophyte source control measures. The objective of these modeling efforts is to evaluate natural flushing as a viable compliance strategy for Monument Valley site groundwater. As a regulatory compliance approach, natural flushing calls for nitrate levels in all wells at the site to decline to less than the standard of 10 mg/L nitrate as N within 100 years. This paper focuses on the descriptions and results of these modeling efforts.

DESCRIPTION

Groundwater Flow and Solute Transport

Numerical groundwater flow modeling was performed using MODFLOW-2000 [4] and MT3DMS [5] was used to simulate solute transport.

Groundwater flow model configuration involves translating the site groundwater flow conceptual model onto a two- or three-dimensional grid and locating boundary conditions and individual aquifer parameter zones within the model domain. Boundary conditions represent hydraulic features such as inflow/outflow boundaries. Parameter zones represent areas of recharge and hydraulic conductivity within the model domain having the same numerical value.

Details on the groundwater flow model design, including grid dimensions, the model domain, boundary conditions, and parameter zones are detailed in a recent Monument Valley site modeling report [6]. This report also provides the parameter values used for recharge, evapotranspiration, porosity, and hydraulic conductivities.

Model calibration was performed using PEST coupled with pilot points [7]. PEST is a parameter estimation code that automatically determines the best parameter values for a model as configured. Parameters are model input values that are adjusted during model calibration. Common examples are recharge and evapotranspiration rates. Pilot point usage takes auto calibration a step further and determines the best spatially continuous parameter distributions for the model given specific boundary configurations and target values. For this application, pilot points were used to determine the “best” hydraulic conductivity distribution.

The transport model grid is the same as the flow model grid because the transport simulation uses the calibrated groundwater flow field to migrate contamination through the model domain. Nitrate transport parameters used in the model are the same as the parameters used by Carroll et al. (2009) [8]. Porosity, dispersivity, distribution coefficient (K_d), bulk density, diffusion, and degradation half-life are assumed homogeneous across the model domain. Figure 4 shows the initial nitrate plume concentrations in 2012 from wells that are then interpolated across the plume for the nitrate transport simulations. Chemical reactions (nitrification) change ammonium to nitrate. The ammonium plume (not shown) has a smaller footprint than the nitrate plume, suggesting that nitrification is occurring faster than denitrification (nitrate changing to nitrogen gas). For transport modeling, it is assumed that nitrification is an instantaneous process, and all ammonium is converted to nitrate prior to initiating the transport simulation, because these reactions are not simulated by MT3DMS. However, these reactions are considered in the geochemical modeling. Nitrate source concentrations were assumed to be zero throughout the 100-year transport simulation because phreatophytes planted at the former mill site have significantly reduced nitrate source concentrations, and plant water usage exceeds precipitation infiltration, effectively halting infiltration (and source loading) through the source area. This assumption will be monitored with new monitoring wells in this area.

Geochemical Modeling

Geochemical modeling using PHREEQC [9] was conducted to verify the MT3DMS nitrate natural flushing duration predictions. Geochemical models simulate chemical interactions between individual contaminants and the porous media, which is not handled directly in numerical transport models. For example, PHREEQC can simulate the transformation of ammonium to nitrate, while the MT3DMS numerical simulations assumed that all ammonium was instantaneously transformed into nitrate. In PHREEQC, the degradation rates can vary based on changes in groundwater geochemistry. These changes are more representative of actual groundwater conditions that can evolve as the plume contacts downgradient porous media. Processes that were modeled in PHREEQC include physical processes such as advection, diffusion, and dispersion and chemical processes such as cation exchange (ammonium), nitrification, and denitrification. Sorption processes (retardation factor) were not included in the PHREEQC simulations.

The PHREEQC geochemical simulation evaluated nitrate migration between well 0606 and well 0650, the farthest downgradient well. A one-dimensional model was divided into segments having fixed lengths corresponding to the distance groundwater is expected to travel in a single year. Similar to the numerical transport model, the geochemical model used the physical transport parameters reported in Carroll et al. (2009) [8] (such as dispersivity and diffusion) and initial solute concentrations corresponding to individual well concentrations. The geochemical simulation also assumed that the nitrate source was no longer active.

DISCUSSION

Groundwater Flow and Solute Transport

The results of the groundwater flow and solute transport modeling show that nitrate concentrations in the alluvial aquifer are expected to drop below the standard of 10 mg/L as N in approximately 70 years (Fig. 7) due to natural flushing and the source zone reduction from phreatophyte planting. An example of the model output with a shrinking nitrate plume in the year 2050 (35 years) is shown in Fig. 8.

Companion sensitivity analysis was performed to better understand how uncertainty in groundwater flow and solute transport model inputs would impact cleanup times. The sensitivity analysis included an evaluation of the transport advection solver, retardation, dispersivity, diffusion, degradation half-life, initial concentration, and recharge [6]. Only the results from the recharge sensitivity, which show the variations in maximum nitrate concentrations due to small changes in the recharge values, are shown here (Fig. 9). Even considering input uncertainty on all the different parameters, nitrate concentrations are expected to reach the standard everywhere in the alluvial aquifer within 100 years [6] after the year 2012.

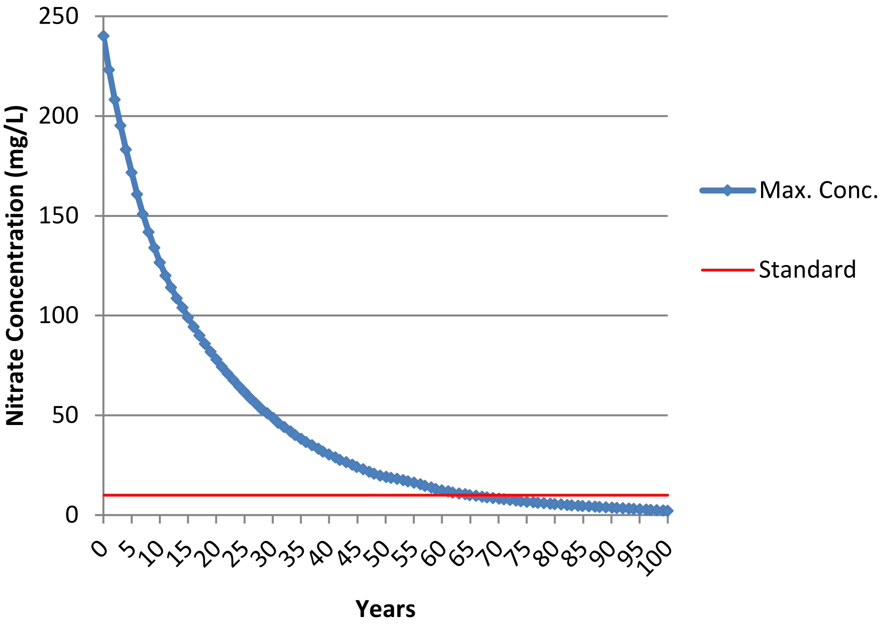

Fig. 7. Maximum Simulated Nitrate Concentrations (as N) Within the Model Domain

Geochemical Modeling

The 100-year forward simulation results predict a natural flushing duration of 53 years (Fig. 10), which is similar to the numerical transport model prediction of 66 years. The agreement between the PHREEQC and MT3DMS predictions suggests that natural flushing is a viable remedial alternative for the Monument Valley site. The curves in Fig. 10 do not show a smooth decline in individual well concentrations because the variations in the original nitrate plume configuration were based on individual well concentrations in 2012 compared to the contoured plume (Fig. 4) used in the MT3DMS simulations.

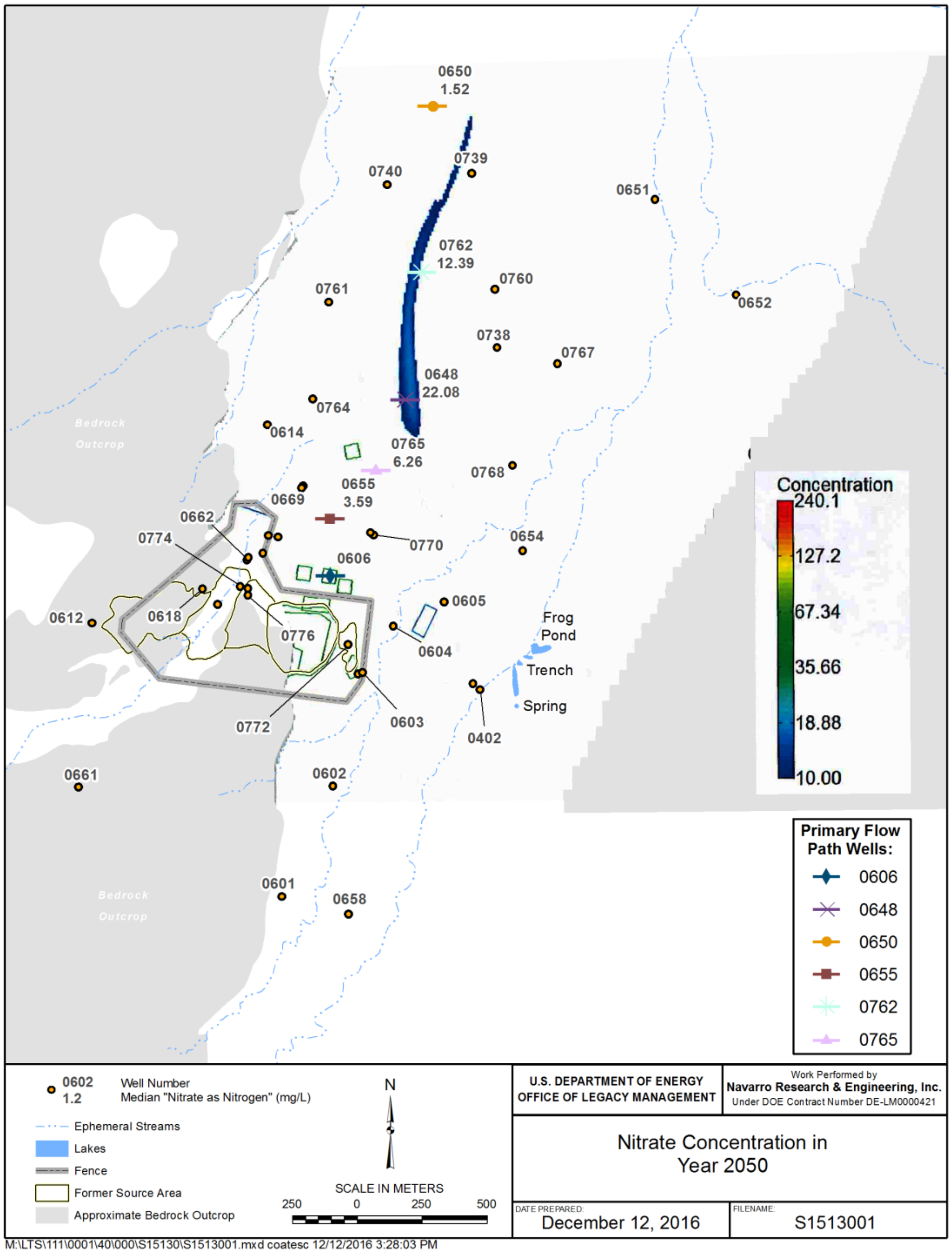

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Figure 8. Simulated Nitrate Concentration in Year 2050 (mg/L)

PROPOSED MONITORING LOCATIONS

Models are a simplification of the real world and as such do not exactly replicate reality. Thus, the reported model predictions are not absolute; rather, the predictions represent the potential for natural flushing to occur. Sensitivity analysis suggests that the potential for natural flushing to occur within 100 years at the Monument Valley site is likely. The only way to verify the model predictions is through groundwater monitoring. TABLE I lists proposed monitoring locations to verify that natural flushing is progressing as predicted. These wells are the primary flow paths wells shown in Figs. 4 and 8, with the addition of well 656 (which is next to well 770, so the well label for 656 does not show up on Figs. 4 and 8).

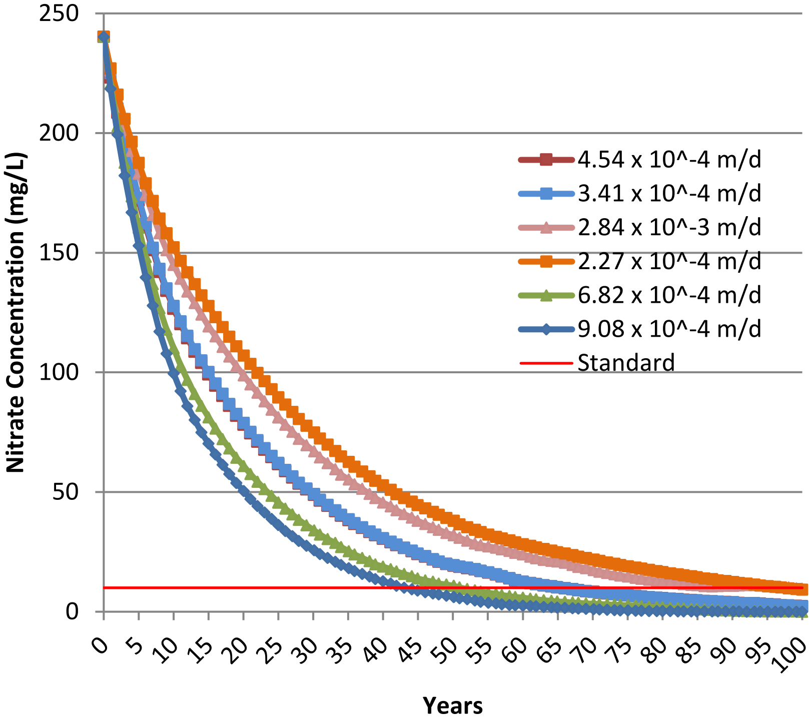

Fig. 9. Maximum Simulated Nitrate (as N) Concentrations due to Recharge Variations

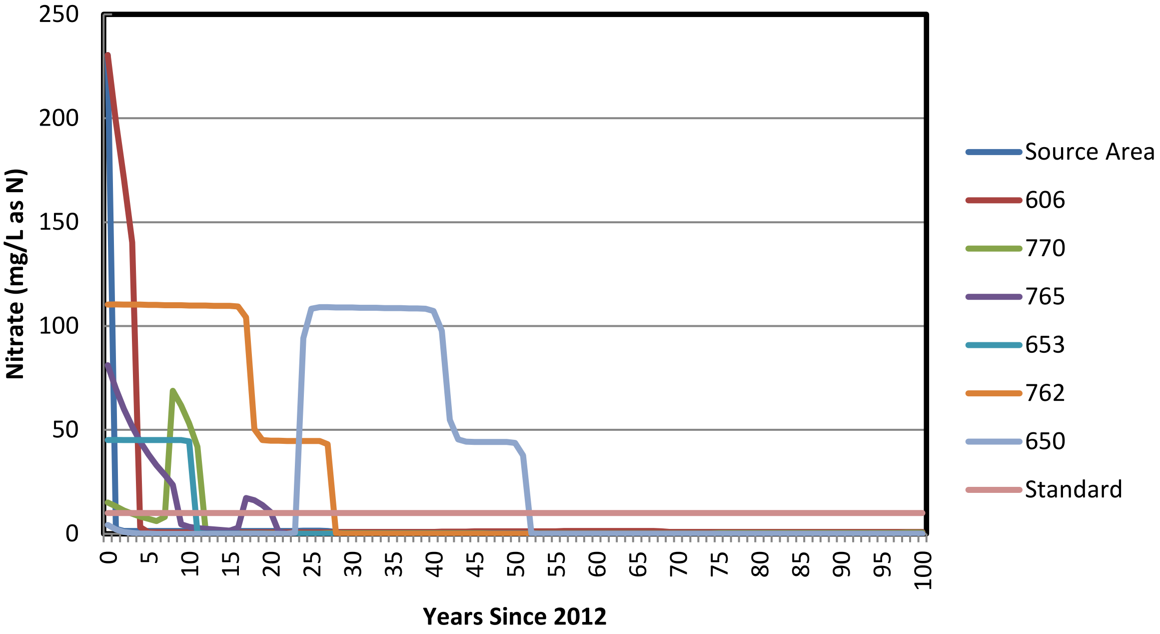

Fig. 10. Graph of PHREEQC Nitrate Temporal Results

TABLE I. Proposed Monitoring Locations To Verify the Viability of a Natural-Flushing Strategy (ordered going down the main flow path)

Well	Expected Time To Achieve 10 mg/L Nitrate (as N) Standard (Years)
0606	10–20
0656	15–25
0655	25–35
0765	30–40
0648	40–50
0762	45–55
0650	15–25

An important assumption of this modeling evaluation is that the nitrate source area is no longer active. If the source is active, even with reduced contaminant loading rates, the 100-year natural flushing duration may not be achieved. Well 0606 is located downgradient of the former mill site, and if source cleanup has been achieved, nitrate concentration in that well is expected to decrease to below the 10 mg/L (as N) standard within 10–20 years. It is recommended that well 0606 be routinely monitored to characterize nitrate groundwater trends over the next 20 years. In addition, several new monitoring wells are planned for installation in 2017 for additional monitoring of the nitrate source area.

On the basis of the solute transport simulation results, it is recommended that the wells listed in TABLE I be sampled annually (along with other Monument Valley site wells) to assess whether natural flushing is progressing as predicted. While not absolute, the times listed to achieve the nitrate groundwater standard provide guidance for evaluating the viability of natural flushing at various locations throughout the plume.

CONCLUSIONS

Groundwater flow, solute transport, and geochemical models were developed to simulate groundwater flow and nitrate transport in the alluvial aquifer beneath the Monument Valley site under ambient flow conditions. Solute transport modeling predicted that with no active source, due to phreatophyte planting, nitrate concentrations would decline everywhere within the alluvial aquifer to levels below the groundwater standard within 60–80 years. This time frame was also confirmed using geochemical modeling, which included denitrification reactions. Thus, natural flushing is a viable remedial alternative for the Monument Valley site. For natural flushing to be viable, groundwater contaminant concentrations must drop below the groundwater standard within 100 years. This time frame is indicated from the modeling results even with simulations that included multiple sensitivity analyses.

The model was used to identify key sampling locations to verify that the nitrate plume will attenuate as predicted. A series of existing monitoring wells located along the center line of the nitrate plume was selected as verification wells for natural flushing at the site. If the source diminishes or no longer exists, modeling predicts that concentrations of nitrate and ammonium in these wells should show significant declines over the next 10–55 years. If concentrations do not trend downward in these wells as predicted, DOE can conduct additional studies to determine whether active remediation will accelerate contaminated degradation so groundwater standards can be achieved within the specified 100-year duration.

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