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SUBJECT: First-Order Decay Attenuation Analysis for Grants **(Final)**

Background

Grants (Site) operated from 1958 until 1990 as a milling and process facility to produce yellow cake. Uranium ore from mines in the San Mateo district, north of the Site, as well as from Homestake's Pitch property in Colorado fed the mill. At its peak, the Site reportedly processed 3,400 tons of ore per day. Tailings were disposed of in two unlined impoundments – the Large Tailings Pile (LTP) and Small Tailings Pile (STP). The LTP contains approximately 21 million tons of tailings and covers approximately 234 acres at a height of 90 feet. The STP contains approximately 1.2 million tons of tailings and covers approximately 40 acres at a height of 25 feet. In 1990, an evaporation pond (EP1) was constructed within the footprint of the STP to assist in the site water management.

The primary source of contamination at the site is draindown from the LTP. This tailings pore water contains high concentrations of molybdenum, uranium and other constituents of concern. This impacted water moves from the bottom of the LTP into the partially saturated zone of the alluvial aquifer directly beneath the LTP. By the mid-1970s, seepage from the impoundments was found to be contaminating off-site wells. Investigations confirmed that the alluvial aquifer underlying the Site was heavily impacted and bifurcated plumes reaching west and south of the Site were delineated.

Beginning in 1978, the Site has used a combination of extraction and injection wells to capture seepage and maintain a hydraulic barrier between the Site and the residential subdivisions located south of the Site. Initially, the primary means of treatment for contaminated water was through uranium removal in the mill circuit and evaporation of the brine. Over time, in response to regulatory demands, additional evaporation ponds, a reverse osmosis treatment plant, and zeolite systems were added to the Site.

Source control began in 1995, when Site initiated a tailings dewatering program in the LTP to remove tailings pore water, thereby reducing the potential for further contamination. In 2000, this extraction effort was coupled with water injection in a pilot test. The full-scale implementation of the flushing program began in 2002. The flushing program involves the injection of unimpacted to slightly impacted water into the LTP and the subsequent extraction of tailings pore water using a network of extraction wells screened through the entire thickness of the LTP. A significant portion of the injected water seeps out through the bottom of the LTP into the partially saturated alluvial zone directly beneath it, which pushes the water with the high concentrations of uranium in this zone to collection wells to the south and west of the LTP, where it is removed. The remainder of the injected water is captured via the collection wells and toe drains within the LTP.

The flushing program ceased in the middle of 2015 when the average uranium concentration in the LTP had decreased from an original 40 mg/l to about 5 mg/l. Since then, the mounded water in the LTP has continued to dissipate. Seepage reported to the toe drains, along the perimeter of the LTP, has also decreased from a peak of 50 gpm to less than 10 gpm.

A reverse osmosis (RO) plant was installed in 1999 to increase the restoration capacity at the site. Prior to its implementation collection of the impacted groundwater was limited by the evaporation rate from the lined ponds where the water was discharged. The RO plant allowed for the treated water to be utilized in the hydraulic barrier placed downstream of the tailings pile, while reducing the total flow to the lined evaporation ponds by 75%.

Land application was part of the Site remediation system that was approved by the New Mexico Environment Department (NMED). During the period of 2000 to 2012, approximately 9,551 acre-feet of water was used for irrigation. The Site was ordered to discontinue the irrigation program in 2012 over concerns that uranium and other constituents could be collecting in soils. Following discontinuation of the land application program, NMED withdrew regulatory support for the program. Since that time, the plume margins have been contained by the downgradient perimeter of injection wells. Contaminated groundwater upgradient of the perimeter is pumped back to the zeolite ponds for treatment.

The Site has conducted numerous studies to evaluate impacts of various mitigation scenarios. This technical memorandum discusses reduction in plume concentration solely due to natural attenuation processes.

First-order Decay Attenuation

The concentration versus time data for uranium and molybdenum were analyzed using methods established to evaluate monitored natural attenuation, to estimate the time it would take for contaminants to meet preliminary remediation goals (PRGs) under current trends. These methods are discussed in the US EPA technical paper (Newell et al., 2002), and in the U.S. EPA directive (U.S. EPA, 1999).

First-order decay rate of contaminant mass at any given time is directly proportional to the mass present at that time. Use of the first order decay coefficient is modified to fit the representative field data for calibration. Physical solute transport processes (e.g., diffusion, dispersion, sorption, and biodegradation) are “lumped” together in a “single” calibration parameter k .

First order decay is described by the ordinary differential equation (Wiedemeier, et al., 1999):

$$\frac{dC}{dt} = -kC \quad (1)$$

Where: C = concentration at time t (M/L^3), k = overall attenuation rate (first-order rate constant, $1/T$).

Solving this differential equation yields:

$$C = C_0 e^{-kt} \quad (2)$$

If the plume concentrations adhere to the first-order decay constant then plots of concentration over time can be expected to be exponential on a linear concentration scale, or linear on a logarithmic concentration scale.

The advantage of graphing the natural log of concentration is that stable or decreasing trends can be more clearly differentiated from random concentration fluctuations. A negative slope of concentration with time is indicative of a shrinking plume.

The attenuation rate constant is applicable to shrinking plumes only and is derived from the slope k of the natural log concentration versus time curve measured (Figure 1). The k represents mass

loss from all processes rather than true degradation rate and has units of inverse time (e.g. per day). In first-order decay attenuation analysis, the rate constant (k) does not account for any future changes in attenuation processes.

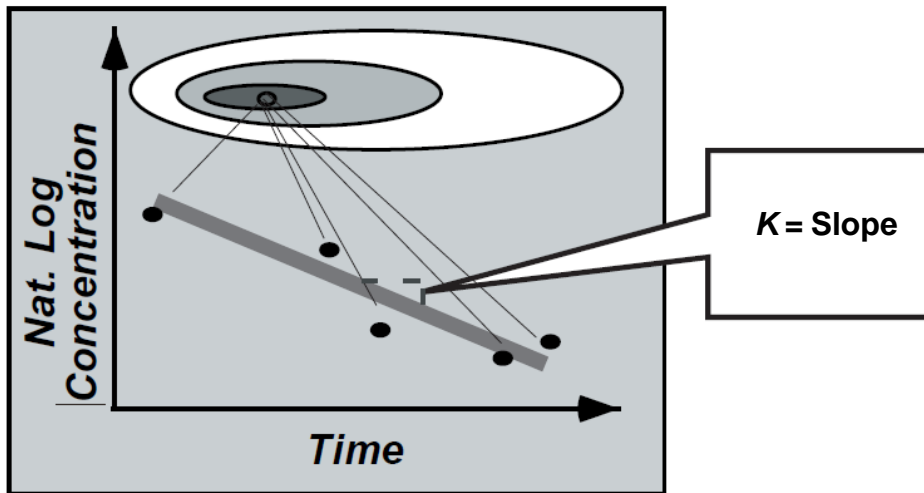


Figure 1. Determining Concentration vs. Time Rate Constant K (modified from Newell et al., 2002)

Mahalanobis Distance Multivariate Outlier Analysis

First-order decay attenuation analysis, like other statistical analyses, is highly sensitive to outliers in the data which can distort results. This is especially true for small datasets with slowly-decreasing concentration. Therefore, outliers were identified and removed prior to the analysis.

A univariate outlier is a data point that has an extreme value for one variable. A multivariate outlier is a combination of unusual values for two or more variables. Both types of outliers can influence the outcome of statistical analyses. In many cases multivariable observations cannot be detected as outliers when each variable is considered independently. A simple example can be seen on Figure 2, which presents data points having two measures on a two-dimensional space. The lower left observation is clearly a multivariate outlier but not a univariate one.

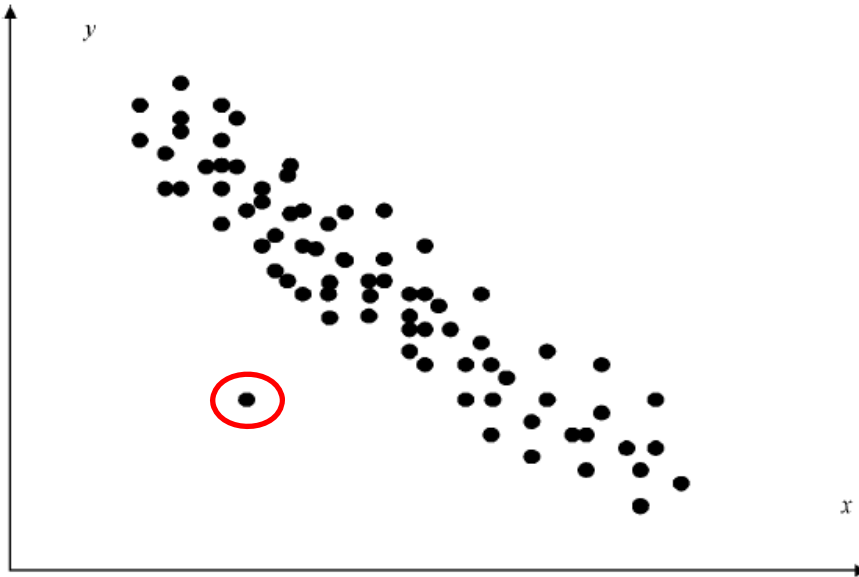


Figure 2. A Two-Dimensional Space with One Outlying Observation (Lower Left Corner in Red Circle).

One method for multivariate outlier detection is use of the Mahalanobis distance (Mahalanobis, 1936) and the comparison with a critical value of the χ^2 distribution (Rousseeuw & van Zomeren, 1990).

Mahalanobis distance (MD) is a statistical measure of the extent to which cases are multivariate outliers, based on a chi-square (χ^2) distribution, assessed using $p < .001$. The shape and size of multivariate data distributions are measured by the covariance matrix.

Mahalanobis distance for each observation point X_i (2-dimensional vector in this study for time and concentration) is defined as:

$$V = \frac{1}{n-1} \sum_{i=1}^n (X_i - \bar{X})(X_i - \bar{X})^T \quad (3)$$

$$MD_i = \sqrt{(X_i - \bar{X})^T V^{-1} (X_i - \bar{X})} \quad (4)$$

Where n is the number of data pairs, and \bar{X} is the center of all observation points.

Figure 3 explains the idea of Mahalanobis distance for a 2-D case. The Mahalanobis distances from points 1 and 2 to the “center of the cluster” are equal to each other, but are smaller than the Mahalanobis distance from point 3 to the center of the cluster.

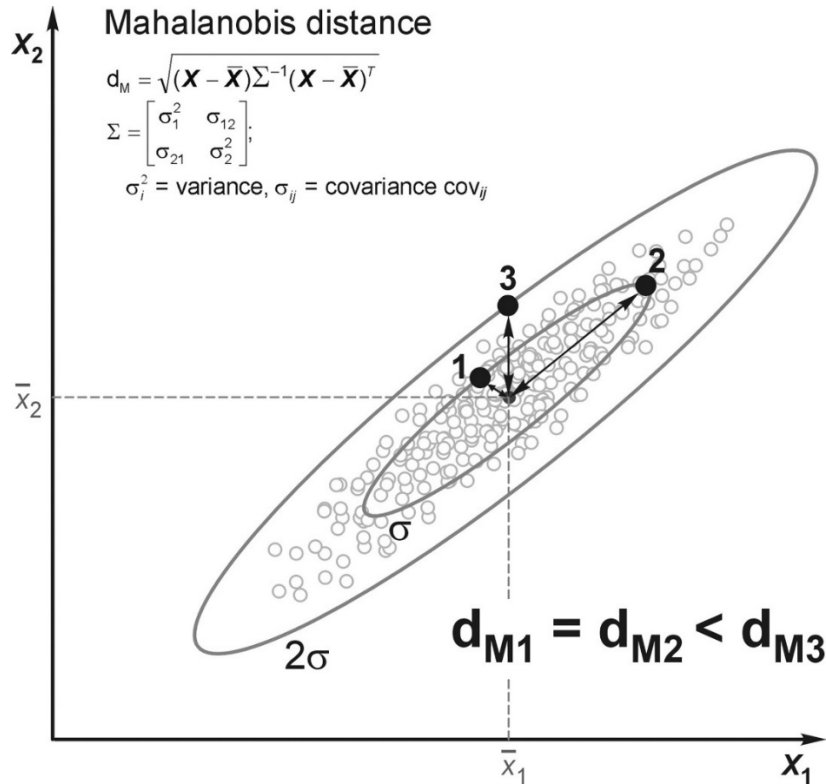


Figure 3. Mahalanobis Distance (MD) Illustration

Linear Regression with Confidence Level

Instead of estimating the time it would take for contaminants to meet PRGs, it is desirable to create the upper and lower bands around the regression line at a certain level of confidence (such as 95%, presented in this study) given uncertainty of first-order decay curve fitting.

The upper and lower bounds around the regression line are calculated as follow:

$$\hat{y} \pm t_{\alpha/2, n-2}(s.e.)_y \quad (5)$$

Where \hat{y} ($\ln(C)$) is the fitted concentration in natural logarithm at time t , $t_{\alpha/2, n-2}$ is the critical t-value with $n-2$ degree of freedom. $(s.e.)_y$ is defined as standard error of the regression line multiplied by the standard error of the estimate at t :

$$(s.e.)_y = \sqrt{\frac{\sum_{i=1}^n (y_i - \bar{y})^2}{n-2}} \sqrt{\frac{1}{n} + \frac{(t - \bar{t})^2}{\sum_{i=1}^n (t_i - \bar{t})^2}} \quad (6)$$

First-order Decay Attenuation of Grants Data

A spreadsheet model tool was developed in-house to carry out the analysis. The tool requires the time series of measured concentration as input. The tool also shows the quality of the regression fit using statistics such as Nash-Sutcliffe Efficiency (NSE), Coefficient of Determination (r^2) and index of agreement (IA). Detailed information about these evaluation statistics can be found in other sources (e.g. Moriasi et al., 2007).

Remediation systems at the Site have been in operation since 1978. To evaluate system performance in meeting remediation goals, monitoring data for the combined influent concentrations were reviewed.

The combined influent to the treatment plant represents average concentrations in the groundwater collected from all of the aquifers prior to treatment. However, the alluvial aquifer is the source of most of the groundwater collected at the Site. Monitoring data for the plant influent sampling port were available from 1999, when the RO treatment plan was brought online.

The concentration-versus-time data for uranium and molybdenum were analyzed using methods established to evaluate monitored natural attenuation, to estimate the time it would take for uranium and molybdenum to meet PRGs under current trends.

- **Uranium:** Three outliers were identified and excluded from the analysis. The statistics of the fitted parameters are: NSE= 17%, r^2 =18%, IA=55%. It is projected that compliance concentration (0.16 mg/l) will be reached in approximately Year 208 (Year zero 0 = Dec 31, 1977). Under 95% confidence levels, the maximum and minimum time to compliance are Year 283 and Year 165, respectively (Figure 4). The large difference between upper and lower bounds is due to uncertain curve fitting as NSE =17% < 50% (Moriasi et al., 2007).

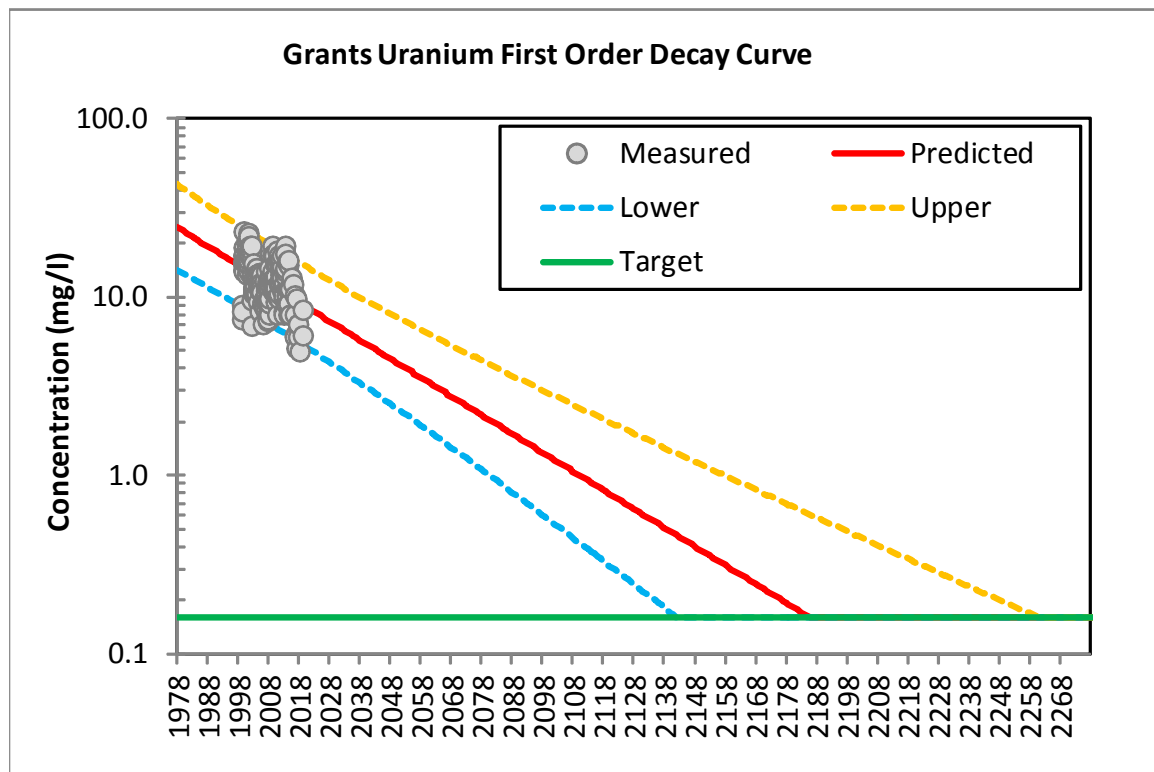


Figure 4. First-order Decay Attenuation Result - Uranium

- **Molybdenum:** Four outliers were identified and excluded from the analysis. The statistics of the fitted parameters are: NSE= 13%, r^2 =14%, IA=50%. It is projected that compliance concentration (0.10 mg/l) will be reached approximately at Year 349. Under 95% confidence levels, the maximum and minimum time to compliance are Year 529 and Year 263, respectively (Figure 5). The large difference between upper and lower bounds is due to uncertain curve fitting as NSE =13% < 50% (Moriasi et al., 2007).

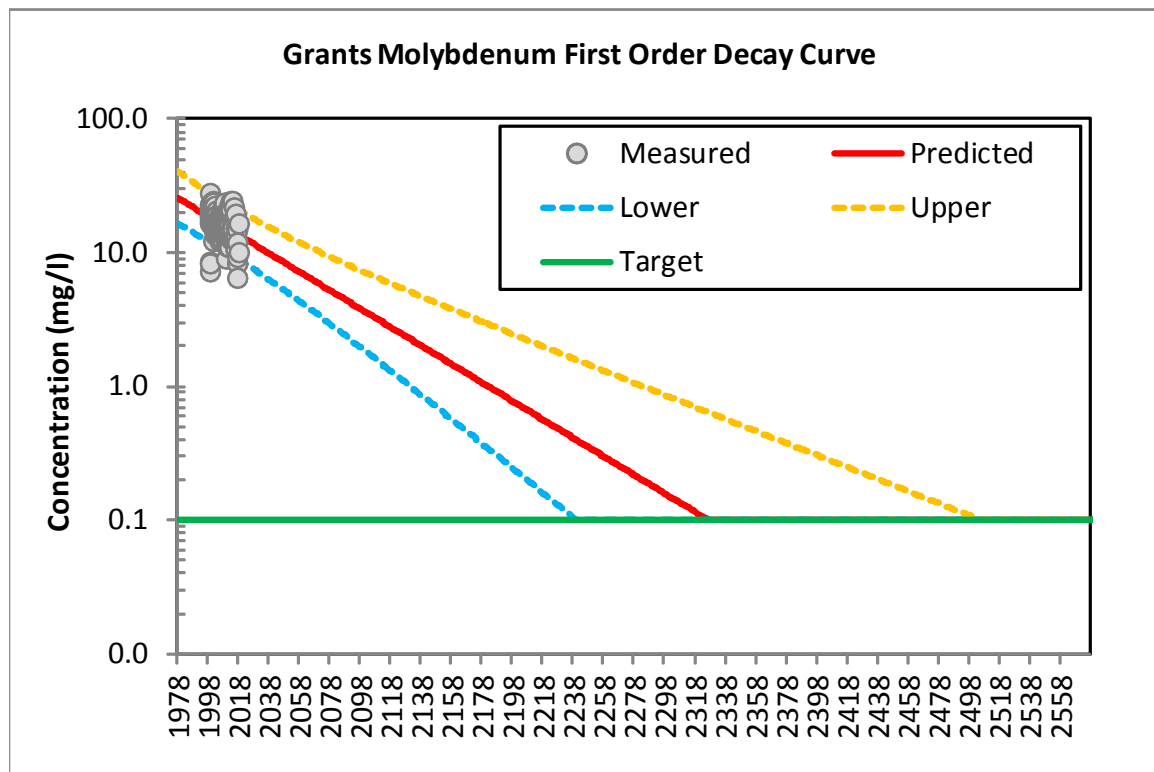


Figure 5. First-order Decay Attenuation Result - Molybdenum

References

- Rousseeuw, P.J. and van Zomeren, B.C., 1990, Unmasking multivariate outliers and leverage points, *Journal of the American Statistical Association*, Vol: 85:411, 633-639, DOI: 10.1080/01621459.1990.10474920
- Moriasi, D.N., Arnold, J.G., van Liew, M.W., Bingner, R.L., Harmel, R.D. and Veith, T.L., 2007, Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. *Trans. ASABE*, Vol. 50, 885-900
- Mahalanobis, P. C., 1936, On the generalized distance in statistics. *Proceedings of the National Institute of Sciences of India* Vol 2:49-55
- Newell, C., Rifai, H., Wilson, J., Connor, J., Aziz, J. and Suarez, M., 2002, Calculation and use of first-order rate constants for monitored natural attenuation studies, US EPA technical paper.
- U.S. Environmental Protection Agency, 1999, Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Office of Solid Waste and Emergency Response (OSWER), Directive 9200.4-17P, Washington, D.C., April 21, 1999
- Wiedemeier, Y.H., Wilson, J. T, Kampbell, D. H, Miller, R.N. and Hansen, J.E., 1999, Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. Volume 1. Air Force Centre for Environmental Excellence (AFCEE)