

# **Mission Research Corporation**

Analysis of Natural Attenuation as a Possible Groundwater Remedial Alternative at the DOE UMTRA Old Rifle Site at Rifle, CO

Prepared by:

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Prepared for:

**MACTEC-ERS, LLC** 

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# **Table of Contents**

1. Introduction		:
1.1 Natural Attenuation Processes	,	
1.2 Evaluation Model	•	
2. Modeling Objectives		•
3. Model Function		, , ,
4. General Setting		•
5. Conceptual Model		
5.1 Aquifer System	•	
5.2 Hydrologic Boundaries		
5.3 Hydraulic Properties		
5.4 Sources and Sinks		
5.5 Water Budget		
5.6 Contaminant Source Term		
5.7 Fate and Transport Properties		
6. Computer Code Description	• • •	
6.1 Assumptions	•	·
6.2 Limitations		
6.3 Solution Techniques		
6.4 Effects on Model	•	
7. Model Construction	•	
7.1 Model Domain	•"	• •
7.2 Hydraulic Parameters		
7.3 Sources and Sinks		
7.4 Boundary Conditions		•
7.5 Selection of Calibration Targets and	l Goals	
7.6 Numerical Parameters		
8. Calibration		
8.1 Qualitative/Quantitative Analysis		
8.2 Sensitivity Analysis	•	•
8.3 Model Application Verification		
9. Predictive Simulations	•	
10. Summary and Conclusions		. •
11. References		
Appendix A - Groundwater Quality Data		
Annendix R - Computer Simulation Results	· · · · · · · · · · · · · · · · · · ·	•

# List of Tables

	Page
7.1 Source Term Parameters	32
7.2 Unsaturated Zone Parameters	33
7.3 Saturated Zone Parameters	34
	,
List of Figures	
4.1 Rifle, Colorado Site Location Map	15
4.2 Old Rifle Site Layout	16
4.3 Surficial Geology of the Old Rifle Site Area	17
7.1 Finite-difference grid depiction for the Old Rifle Site Area	.35
8.1 Residuals between observed and calculated water level data	38
passing the RMSE conditioning criteria	
8.2 Residuals between observed and calculated uranium concentration data	39
passing the RMSE conditioning criteria	,
8.3 Residuals between observed and calculated vanadium concentration data	40
passing the RMSE conditioning criteria	
8.4 Residuals between observed and calculated selenium concentration data	41
passing the RMSE conditioning criteria	•
9.1 Mean Concentration Distribution for Uranium at Conditioning Time (1998)	45
9.2 Mean Concentration Distribution for Uranium 20 Years after	46
Conditioning Time	,
9.3 Probability of Concentrations Being Less Than the MCL for Uranium at	47
Conditioning Time (1998)	
9.4 Probability of Concentrations Being Less Than the MCL for Uranium	48
20 Years after Conditioning Time	
9.5 Probability of Concentrations Being Less Than the MCL for Uranium	49
50 Years after Conditioning Time	

# List of Figures (continued)

		Page
9.6 N	Mean Concentration Distribution for Vanadium at Conditioning Time (1998)	50
9.7 N	Mean Concentration Distribution for Vanadium 100 Years after	51
	Conditioning Time	
9.8 P	robability of Concentrations Being Less Than the MCL for Vanadium at	52
	Conditioning Time (1998)	. · · · · ·
9.9 P	robability of Concentrations Being Less Than the MCL for Vanadium	53
	100 Years after Conditioning Time	
9.10	Mean Concentration Distribution for Selenium at Conditioning Time (1998)	54
9.11	Mean Concentration Distribution for Selenium 100 Years after	55
	Conditioning Time	
9.12	Probability of Concentrations Being Less Than the MCL for Selenium at	56
	Conditioning Time (1998)	
9.13	Probability of Concentrations Being Less Than the MCL for Selenium	57
	100 Years after Conditioning Time	
9.14	Uranium Concentrations Through Time at Monitor Well 654	58
9.15	Vanadium Concentrations Through Time at Monitor Well 654	59
9.16	Selenium Concentrations Through Time at Monitor Well 654	60

#### 1. Introduction

The Department of Energy (DOE) has responsibility for regulatory compliance at 24 formerly used uranium mill tailings sites around the country. The regulatory requirements are dictated by the Uranium Mill Tailings Radiation Control Act and the U.S. Environmental Protection Agency's Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings (40 CFR Part 192; 60 FR 2854). The DOE's Uranium Mill Tailings Remedial Action (UMTRA) Project has been divided into a Surface Program and a Groundwater Program. Most of the 24 UMTRA sites have been addressed under the Surface Program, with the majority of the sites having completed major tailings removal, relocation and/or disposal actions. The Groundwater Program was begun in earnest some years after the Surface Program to allow for source term removal prior to addressing the potential for adverse groundwater impacts.

The Groundwater Program has identified at least one third of the UMTRA sites as potential candidates for a natural attenuation strategy for compliance with the applicable regulations. This compliance strategy has been discussed in the Programmatic Environmental Impact Statement (PEIS) (U.S. DOE, 1996a). A natural attenuation strategy requires that, within a one-hundred year period, concentrations of the contaminants of concern be reduced below regulatory limits, or Maximum Contaminant Levels (MCLs), by natural processes. Several potential natural attenuation processes can be considered:

- hydrodynamic dispersion of the contaminants (e.g., mass spreading and concentration reduction);
- degradation and/or decay (e.g., mass reduction);
- dilution from recharge or infiltration (e.g., areal recharge, stream/irrigation leakage); and/or
- flushing (e.g., discharge to a gaining stream).

For the UMTRA sites, the degradation or decay of contaminants of concern (e.g., uranium) probably has a minimal attenuation effect because the constituents are inorganics and/or radionuclides with relatively long half-lives. Dilution, dispersion, and especially flushing, are the main processes of interest.

#### 1.1 Natural Attenuation Processes

Further discussion of each of the previously mentioned natural attenuation mechanisms and their effects on plume behavior is warranted because of the puzzle that is frequently encountered in attempting to identify the attenuation processes that are occurring and assessing the degree to which each is reducing contaminant concentrations. Stated another way, what one model and its set of parameters may provide as a logical explanation for an observed plume's movement is often totally different from another model's explanation. Because the exact fate and transport processes at a site cannot be determined uniquely, it does help to understand the relative effect that each attenuation mechanism will have on plume behavior, as well as their combined effects. With this understanding it may be possible to eliminate unrealistic or improbable mechanisms from further consideration. The following paragraphs provide a summary of the attenuation processes and their effects on contaminant levels.

Hydrodynamic dispersion is a phenomenon in which dissolved contaminant mass is spread beyond the space it would normally occupy due to average subsurface water movement alone. Transport by average water movement alone is typically referred to as advection, but it is improbable that contaminant transport in the subsurface can occur solely by advection without dispersion occurring as well. Dispersion affects a plume by smearing the contaminant levels along the leading edge of the plume as well as along its side and base edges. Dispersion occurs in contaminant transport in both the unsaturated and saturated zones.

Hydrodynamic dispersion is defined as having two separate components: (1) mechanical dispersion and (2) molecular diffusion. Mechanical dispersion in porous media flow is mixing that occurs as a consequence of local variations in velocity around some mean value of flow velocity, whereas diffusive transport occurs in response to variations in dissolved concentration of a contaminant. Although both processes cause spreading of a plume, the mixing effects of mechanical dispersion usually dominate those of diffusion. Mechanical dispersion can also be

characterized as either being longitudinal or transverse dispersion. Longitudinal dispersion is the mixing that occurs along the direction of flow, whereas transverse dispersion is the mixing that occurs in directions normal to the flow path. On a microscopic scale, transverse spreading of water flow occurs because individual flow paths within the porous medium diverge.

In solute transport, the release of a contaminant for a finite length of time is commonly referred to as a slug release. After a slug release, hydrodynamic dispersion will cause the concentrations within the plume to be less than they were initially during the release.

Sorption is the process in which contaminants leave the dissolved state in water to fixate on the solid particles comprising a porous medium. Several relationships can be used to mathematically describe the relative distribution of a contaminant between dissolved and sorbed states. The most common relationship used in transport modeling assumes linear equilibrium sorption. This relationship allows the propensity for a chemical to adsorb onto solid materials to be described in terms of a soil-water distribution coefficient, or  $K_d$ . The larger the  $K_d$  value, the greater the tendency is for the contaminant to sorb to subsurface media. Sorption retards the movement of a contaminant in groundwater, causing its bulk transport to take place at a rate that is slower than the average groundwater flow velocity. A retardation factor, which measures the ratio of the average groundwater velocity to the average velocity of a sorbing contaminant, can be determined from the contaminant's  $K_d$ .

Soil-water distribution coefficients are dependent on the dissolved form of the chemical involved in the reaction as well as the materials comprising the porous medium. For certain organic compounds the distribution coefficient is a function of the organic content in the porous materials. Inorganic chemical  $K_d$ s are strongly affected by soil makeup, particularly clay content, and can be measured in laboratory experiments or determined through field tracer studies.

Use of a soil-water distribution coefficient and retardation factor implies that sorption is reversible, indicating that the porous material eventually releases the contaminant and allows it to

go back into solution. As a consequence, sorption serves not only to delay the arrival of the contaminant, but the temporary storage of the contaminant mass in solid form also causes the peak dissolved concentrations from a slug release to be less than equivalent concentrations without sorption.

Decay refers to the degradation of a contaminant in the environment. There are numerous causes of decay including chemical reactions with water, known as hydrolysis, or the solid materials comprising a porous medium. Organic chemicals may undergo a form of decay called biotransformation. Radionuclides undergo a form of decay wherein mass is converted into radiation. Decay of a radionuclide is characterized by its half-life, which is a constant value. This in turn allows the degradation to be expressed as a first order decay process. Other types of contaminants may also decay in accordance with a first-order process, but, unlike radionuclides, the half-life of one these constituents may vary, depending on pH, oxidizing conditions, or temperature. Decay influences transport by reducing the total mass of the contaminant, thereby decreasing both its dissolved and sorbed concentration.

Dilution of a dissolved contaminant occurs when clean water mixes with contaminated water. A given quantity of contaminant mass in a larger volume of water causes a decrease in the contaminant's dissolved concentration. One form of dilution occurs when infiltrating water from a source that is widespread areally, such as precipitation or flood irrigation water, mixes with shallow contaminated groundwater. Dilution from areal recharge is manifested in much the same way that decay affects contaminant concentrations.

Water infiltrating from the base of a surface waterway and recharging an aquifer can also cause dilution. Examples of waterways that tend to lose water in this manner include irrigation canals or a stream on the margin of an alluvial basin whose bed lies above local groundwater levels. Dilution brought about by this phenomenon differs from areally distributed recharge because the mixing of waters occurs generally beneath the waterway and not uniformly over the entire aquifer.

Natural flushing from a contaminated aquifer occurs when the contaminated groundwater discharges in whole or in part to a surface waterway such as a river or agricultural drain. Because the flow in a river is generally much larger than the contribution of locally contaminated groundwater, the contaminant levels in the river are highly diluted, often to non-threatening levels. Through this process, the aquifer can eventually purge its contamination to the point where residual contaminant concentrations no longer pose a threat to human health or the environment.

#### 1.2 Evaluation Model

The UMTRA Groundwater Program has previously utilized Sandia National Laboratories (SNL) to develop an approach and associated computer tool to address groundwater issues at UMTRA sites. This approach is more robust than previous attempts to address natural attenuation concepts in that it explicitly accounts for uncertainty through the use of Monte Carlo simulation techniques. Therefore, the likelihood of success of the natural attenuation strategy can be evaluated with this approach. In contrast, conventional modeling approaches utilize discrete estimates of contaminant fate and transport behavior, which do not address uncertainty. The methodology and associated computer code developed by SNL is embodied in the Groundwater Analysis and Network Design Tool, or GANDT. This tool was used to perform the analyses presented in this report.

As mentioned, the methodology employed within GANDT to explicitly address uncertainty is the stochastic Monte Carlo technique. With Monte Carlo simulation, the modeler benefits from evaluating the relative influence of model input parameters on model predictions. Parameters that have a profound effect on model results, as identified and evaluated with sensitivity analysis techniques, are often quite uncertain. The uncertainties associated with input parameters may be due to spatial variability, measurement error, an imperfect knowledge base, or other factors. One can statistically estimate the uncertainties associated with key input parameters by collecting data during a site characterization effort. Alternatively, parameter uncertainty may be estimated using literature sources, or with the use of expert judgment. Once the critical input parameters have

been approximated by statistical distributions, the Monte Carlo method invokes sampling schemes to combine the suite of input parameters into multiple data sets. Model simulations are performed with all of these sets of input parameters. The combined results of the model runs are then statistically analyzed to form a probabilistic description of the uncertainty in model predictions.

An aspect of the GANDT code that enhances its ability to address uncertainties is the use of an efficient, stratified sampling technique to assemble the input parameter sets that fully describe the stochastic nature of the problem. This method is called Latin Hypercube Sampling (Iman and Shortencarrier, 1984), or LHS. By invoking the LHS method, the number of Monte Carlo model runs required to capture the full behavior of model uncertainty is generally many times smaller than the number needed using pure random sampling (Peck et al., 1988). A recommended minimum number of model simulations when using LHS is 4/3 the number of uncertain parameters, whereas pure random sampling may require as many as ten or more times the number of stochastic variables. Thus LHS has a significant advantage over the conventional sampling approach, making Monte Carlo analysis of groundwater flow and transport problems relatively efficient.

Another advantageous feature of the LHS methodology is its ability to specify correlations between parameters. If two or more input parameters can be demonstrated as having some degree of correlation with one another, such as through a regression analysis, accounting for it within LHS, as compared to allowing a totally random association of the parameters, may help to reduce uncertainty in model predictions.

Other functional aspects of the GANDT code, such as the flow and transport models incorporated in it, are discussed in subsequent sections. More detailed explanations of algorithms within it can be found in several publications regarding the tool and its applications (Knowlton et al., in press; Walker et al., 1996; Metzler et al., 1997).

This report provides a summary of analyses performed by Mission Research Corporation (MRC) to evaluate the potential success of a natural attenuation strategy at the DOE UMTRA Old Rifle site at Rifle, Colorado. The format of this report is based on the American Society for Testing Materials (ASTM) "Standard Guide for Documenting a Ground-Water Flow Model Application" (ASTM, 1995), with some added sections discussing groundwater flow and contaminant transport aspects of the GANDT methodology. The natural attenuation modeling discussed herein has been performed for three constituents of concern: uranium, vanadium, and selenium.

# 2. Modeling Objectives

The main objective of this modeling effort is to evaluate the likelihood of success of a natural attenuation remedial option at the UMTRA Old Rifle site at Rifle, Colorado. To help meet this objective, a probabilistic modeling approach has been applied, using Monte Carlo methods to quantify uncertainties. Specific objectives include:

- model the transport of constituents within and from a mill tailings source zone, using a pulsed leaching algorithm due to the fact that the tailings have been removed from the site;
- model the fate and transport of constituents through the vadose zone beneath the former tailings area;
- model the fate and transport of constituents in groundwater in the uppermost surficial aquifer at the site;
- perform Monte Carlo analyses to quantify the uncertainty in the distribution of contaminants in the aquifer over a 100-year period;
- condition the Monte Carlo simulation results on known water level and water quality data, i.e., automated calibration based on the water level and groundwater concentration data collected from local monitoring wells;
- develop average concentration distributions for the constituents of concern, based on the probabilistic analyses;
- develop probability distributions for MCL exceedance to visually illustrate the likelihood of meeting groundwater standards over a 100-year period;
- develop statistical ranges of water quality data at key monitor well locations over the next 100 years to be used to verify the progress of the natural attenuation processes; and
- develop conclusions/recommendations regarding the likelihood of success for natural attenuation.

#### 3. Model Function

Several years ago, the UMTRA Groundwater Program commissioned SNL to develop the Groundwater Analysis and Network Design Tool (GANDT). GANDT provides DOE Environmental Restoration programs with a comprehensive system for analyzing groundwater flow and associated contaminant transport, while directly accounting for transport uncertainty and providing decision analysis capabilities for monitor well network design. As a point of reference, GANDT began its development under the name Borehole Optimization Support System, or BOSS, but was changed due to copyright considerations. A draft report (Knowlton et al., in press) detailing the technical attributes of the GANDT code is under development and available for review. A draft user's manual has also been developed and is available upon request.

GANDT is a comprehensive groundwater analysis package, providing the following features:

- Utilizes flow and transport models in a probabilistic framework to account for uncertainty in contaminant movement and fate; and
- Simplifies the analysis of natural attenuation potential, providing an estimate of the likelihood of success of this option, thereby possibly avoiding costly and time-consuming pump-and-treat options for groundwater remediation.

The GANDT code contains a number of tools that, when combined, make it a unique modeling system. Some of these items are:

- Simulates leaching from contaminant source terms, including a pulsed leaching time to account for source removal;
- Simulates either aqueous- or vapor-phase movement of contaminants in the unsaturated zone, and accounts for contaminant transfer into the underlying aquifer;
- Analytical and numerical solutions for the saturated zone (including FTWORK, a 3-D numerical finite difference code for flow and advective/dispersive transport [Faust et al., 1994]);

- An automatic grid generation module to simplify the numerical model input (and also automatically account for grid orientation when the user specifies uncertainty in the groundwater flow direction);
- Monte Carlo technique employed to propagate input parameter uncertainties into flow and transport uncertainties;
- Latin Hypercube Sampling (LHS) technique (Iman and Shortencarrier, 1984) employed to minimize computational burden by reducing the number of simulation runs required for the Monte Carlo analysis;
- Spatial variability explicitly accounted for using a geostatistical simulator (e.g., Sequential Gaussian simulator), which honors observed hydraulic conductivity estimates;
- Conditioning of simulation results on observed water quality data using statistical methods (e.g., essentially a built-in calibration method to honor water level and water quality data); and
- An intuitive graphical user interface and graphical display of results for ease of use on PC
   Windows and Macintosh platforms.

GANDT currently has the capability to simulate flushing, dilution, and radioactive decay. The numerical simulation option in the GANDT code is currently set up to perform steady-state flow simulations and transient fate and transport analyses.

In conventional flow and transport simulations a calibration procedure is manually performed to "match" model results with observed site data, such as measured water levels and water quality data. One of the model parameters that is commonly adjusted to achieve a better match between observed and computed values is aquifer hydraulic conductivity. The calibration process can be quite tedious and time consuming. SNL has built an automated calibration capability in GANDT that effectively conditions, or honors, observed water levels and concentrations in the saturated zone through use of statistical analysis techniques. Any Monte Carlo simulation with a cumulative measure of the differences between observed and computed water levels and concentrations, which are commonly called residuals, that does not meet a specified statistical

tolerance is omitted from the probabilistic analysis. This feature is extremely important when the user is interested in probabilistic (i.e., Monte Carlo) analyses, where many simulations are performed to get a statistical representation of the uncertainty in model results. The user has the ability to choose from a chi-square test (Haan, 1977) for acceptance of a run or a root mean squared error (RMSE) analysis (Anderson and Woessner, 1992). To apply the chi-square method, the residuals must be normally or log-normally distributed. GANDT can graphically display data distributions to evaluate normality, giving the user great flexibility in selecting conditioning criteria.

GANDT currently has the ability to condition model inputs and results on hydraulic conductivity information, water level data, and water quality data. In order to condition on hydraulic conductivity data with the available geostatistical simulator, there needs to be a minimum of 20 data points to honor the data appropriately. The technique was not employed in this particular analysis of the Old Rifle site due to the limited hydraulic conductivity sampling. Of the three possible types of data used for model calibration in groundwater contamination investigations, water quality information is most effective in reducing transport uncertainty. This phenomenon was illustrated by Van Rooy and Rosbjerg (1988), who compared the relative ability of three different parameter estimation approaches - geostatistical conditional simulations of transmissivity, selection of groundwater flow model runs based on observed hydraulic heads, and selection of transport model runs based on measured concentrations - to produce a model that best approximated actual site conditions in a case study. Similar results were reported by McLaughlin et al. (1993), who used three comparable parameter estimation techniques to clearly show that the greatest reduction in model uncertainty was achieved by conditioning on water quality measurements. Though the current analysis of the Old Rifle site does not utilize hydraulic conductivity as calibration targets, it is being used to condition on water level and water quality data.

GANDT has the ability to display the results of probabilistic analyses in a variety of ways. Twodimensional visualization graphics that the user can observe include hydraulic conductivity distribution plots, contaminant distribution plots, and probability of exceedance plots.

Contaminant distributions can be displayed for all user-specified time steps, and for each of as many as six layers in a numerical simulation. The types of contaminant plots available are:

- Plume concentrations from each Monte Carlo simulation, with user-specified color mapping of the contaminant concentrations, and an optional player mode that cycles the Monte Carlo simulation output in an "animation" format;
- Average plume distribution from all Monte Carlo runs;
- Standard deviation plot;
- Variance plot;
- Coefficient of variation plot; and
- Probability plots, wherein the user specifies a threshold contaminant concentration (e.g., MCL), and the resulting plot displays the probability of exceeding that concentration, or it could be plotted as the likelihood of being less than a specified concentration.

The last plotting option mentioned is extremely important in evaluating the likelihood of success of a natural attenuation approach to remediation.

# 4. General Setting

The UMTRA Project has responsibility for two former uranium mill processing sites in the vicinity of the city of Rifle, Colorado (Figure 4.1). The Old Rifle site is located approximately 0.3 miles east of the center of Rifle. The New Rifle site is located approximately 2 miles southwest of the center of Rifle. The Colorado River is just south of both sites.

The Old Rifle processing site was operated by Union Carbide sporadically from 1924 to 1958. From 1924 to 1932 the mill was used to process vanadium. From 1932 to 1942 the mill was not in use. From 1942 to 1958 the mill processed both vanadium and uranium. After 1958, most of the tailings at the Old Rifle site were reprocessed and brought to the New Rifle site. The New Rifle site was in operation from 1958 through 1984. The New Rifle site was used to process uranium and vanadium. Surface remedial action took place at both sites from 1992 through 1996. Tailings from both sites were relocated to the Estes Gulch disposal site approximately 9 miles north of the New Rifle site. Groundwater issues are currently under investigation at both sites. This report is focused strictly on groundwater conditions at the Old Rifle site, and more specifically aimed at evaluating the potential for natural attenuation as a no further action remedy at the site.

The Old Rifle site encompasses about 22 acres adjacent to the Colorado River. Approximately 13 acres of tailings were left at the site between 1958 and the time of surface cleanup (Figure 4.2). In 1967, the tailings pile was partially stabilized in accordance with state of Colorado regulations. As mentioned above, the surface soils and tailings were remediated between 1992 and 1996.

Groundwater occurs principally in three units at the site: an unconfined surficial aquifer; an underlying intermediate zone of colluvium (e.g., derived from the weathered Wasatch Formation); and the deeper semiconfined Wasatch Formation aquifer. The surficial aquifer consists of sands and gravels (up to 25 feet [ft] thick) deposited by fluvial processes associated mainly with the Colorado River. The Wasatch Formation is over 5000 feet thick in the Rifle area. It consists of

variegated claystone, siltstone, and fine-grained sandstone. Figure 4.3 depicts the surficial geology of the area around the Old Rifle site. Additional information on the general setting for the Old Rifle site, including more detailed discussions of the site hydrogeology, is presented in reports prepared by the U.S. Department of Energy (DOE) (1995; 1996b).

A DOE Baseline Risk Assessment report (DOE, 1995) indicated that several constituents in the surficial aquifer comprise the greatest concern for groundwater contamination at the Old Rifle site. This and other previous investigations have suggested that contaminants in this aquifer are flushed out into the Colorado River by natural groundwater flow.

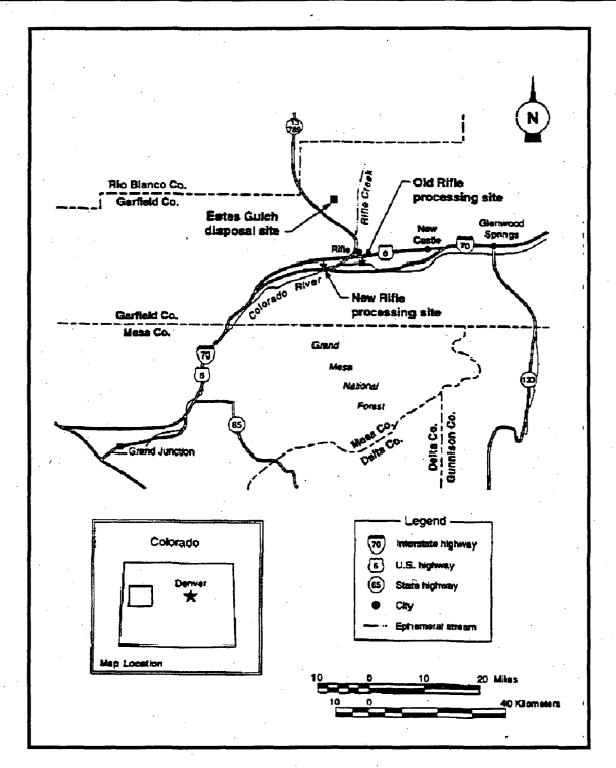


Figure 4.1 - Location Map of Old and New Rifle Sites Near Rifle, Colorado (After DOE, 1996b)

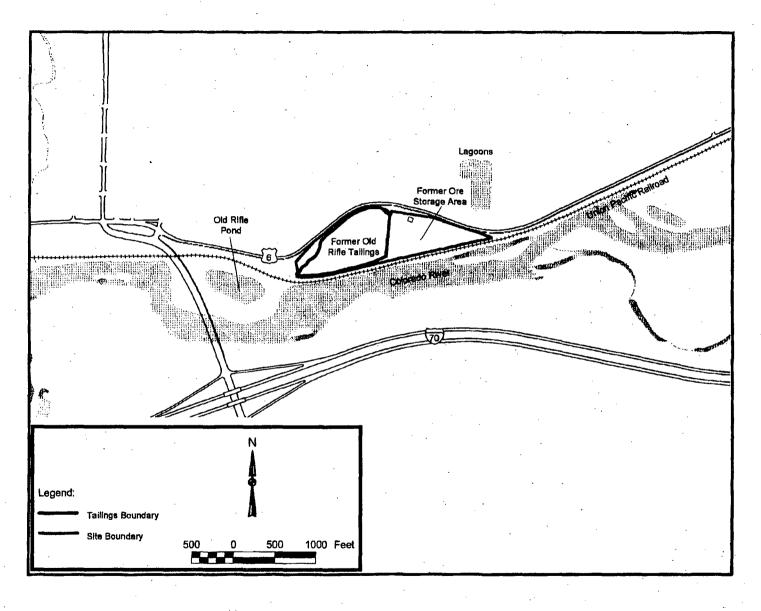


Figure 4.2 - Old Rifle Site Layout (after DOE, 1995)

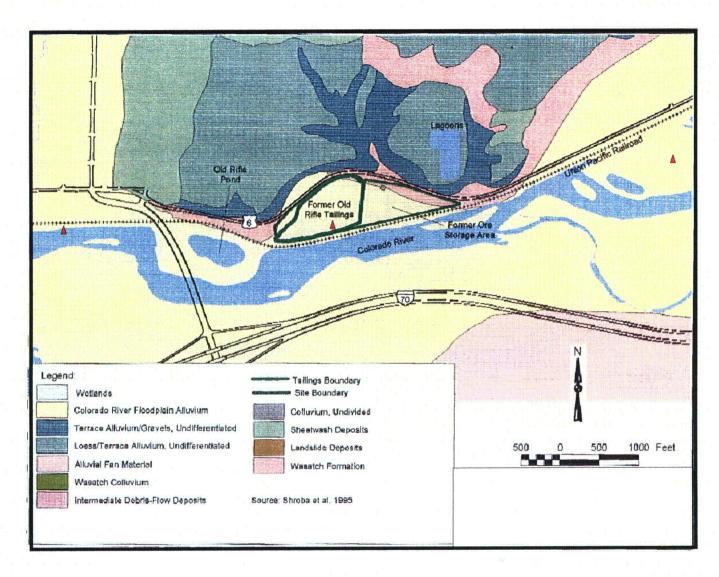


Figure 4.3 - Surficial Geology of the Old Rifle Site (after DOE, 1996b)

### 5. Conceptual Model

Because this investigation focuses on natural attenuation processes, development of a conceptual model for the Old Rifle site should focus on both general hydrogeologic processes and the phenomena that more specifically help to attenuate contaminant concentrations, including:

- dilution from areal recharge;
- dispersion as part of the transport process; and
- natural flushing to the Colorado River (i.e., aquifer discharge to the gaining river).

The groundwater system at the site is hydraulically connected to the unsaturated zone, which, at one time, contained the contaminant source in the form of a tailings pile. The GANDT code simulates the leaching of contaminants from the source zone, subsequent transport through the unsaturated zone, and mass flux into and within underlying aquifers. Thus, each of these zones must be examined in the conceptual model. In addition, the time frame of interest is approximately 100 years into the future (i.e., the time allowed under the regulations for natural flushing to occur). Given a 100-year time frame of interest, it is assumed that the seasonal, transient behavior of the hydrologic system will be dampened, allowing the system to approximate some average form of behavior. Accordingly, steady-state flow conditions are assumed to be appropriate. Uncertainty associated with the long-term average flow conditions, such as the magnitude of the hydraulic gradient and the hydraulic characteristics of the aquifer, is taken into account by establishing statistical distributions for these parameters in the Monte Carlo analysis.

#### 5.1 Aquifer System

The aquifer system at the Old Rifle site consists of a surficial, unconfined unit, a colluvium unit, and a deeper semiconfined aquifer. The main aquifer of interest for groundwater compliance is the surficial unit. Some testing has been performed on this uppermost aquifer and has been

documented by DOE (1996b). Additional characterization activities took place at the site during 1998, and the data were provided by MACTEC-ERS, the UMTRA support contractor.

The depth to groundwater is relatively shallow, and ranges from 10 to 17 feet in the mill tailings area. The surficial materials are up to 25 feet thick and assumed to be hydraulically connected to the Colorado River, located downgradient of the tailings. This hydraulic connection is assumed to be one in which the Colorado River is a gaining stream, with the aquifer discharging to it. Downgradient of the tailings area is an outcropping of the Wasatch formation. This outcrop has an effect on the groundwater flow direction, forcing groundwater in the alluvium to move to the Colorado River. The hydraulic gradient of the alluvial aquifer is in a west-southwest direction with a magnitude of about 0.0045 feet per foot. Aquifer slug tests previously performed at the site suggest a range of hydraulic conductivity of 0.13 to 2.1 feet per day [ft/d], and are considered low for the type of alluvial materials present at the site. Slug tests do not stress a substantial volume of the aquifer and may not be representative of larger scale behavior of the system. Aquifer pumping tests are better indicators of larger scale hydraulic conductivity behavior. An aquifer pump test was recently performed at the site. The mean hydraulic conductivity determined from observation well analyses was 117 ft/d, and ranging from 110 to 125 ft/d.

### 5.2 Hydrologic Boundaries

For the purposes of this natural attenuation analysis, a steady-state flow system is assumed. This approach is taken on the premise that, though hydraulic heads change with both sporadic and periodic stresses (e.g., recharge from precipitation, high river conditions, flooding, irrigation, conveyance of water in irrigation canals, pumping), the average, long-term groundwater flow conditions (i.e., flow direction, flow rate) remain generally the same. This assumption corresponds with a state of "dynamic equilibrium" (Freeze, 1969), in which there are no long-term (several years) changes, or trends, in regional and local groundwater levels.

Though there are clear indications of short-term changes in hydraulic head at and near the Old Rifle site, there is little to no evidence collected thus far to clearly demonstrate that the regional groundwater flow system is undergoing major, lasting alterations.

The assumption of steady-state flow conditions is made not only with respect to the time period between the mill startup and recent years, but also with respect to future conditions, extending as much as 100 years hence. It is true that it may not be possible to assure that such a system will continue for this length of time, as future land use and other regional trends may influence local groundwater flow. However, without direct knowledge of land-use plans for this area, the focus of this study was on the potential for natural flushing of site contaminants with conditions as they exist today.

In GANDT, steady-state flow is assumed and established by controlling boundary conditions in the code's flow simulator. Two options exist in the code to control boundary and initial conditions. The first, an autogrid generator option, has been used extensively in the past to streamline the process of model setup within the Monte Carlo framework. This option has the ability to generate a new finite difference grid for each simulation in the Monte Carlo suite, oriented along the axis of flow in the aquifer. The orientation of the grid is important if the direction of the groundwater gradient is uncertain. A user-specified gradient is used to establish prescribed head conditions at the up-gradient and down-gradient boundaries of the model. The lateral side boundaries within the modeled area are assigned a no-flow condition. If a gaining stream is located downgradient of the contaminant source, the river trace is used to establish and replace the model's downgradient boundary condition. In such a case, the river is assigned constant heads, which are based on the prescribed gradient and an estimate of the head loss attributed to phenomena such as convergent flow, vertical flow across alluvial strata, and flow across semipermeable streambed materials (Peterson and Wilson, 1988).

For a more user-controlled set of boundary and initial conditions, GANDT offers an option for user-specified input. In this option the user has the ability to construct a single representation of

the finite-difference grid. This gives the user more flexibility in grid construction but precludes any significant evaluation of the uncertainty in the direction of groundwater flow. In the case of Old Rifle, the uncertainty in the direction of groundwater flow is considered negligible. In addition, this option lets the user explicitly specify boundary conditions and initial conditions throughout the modeled domain. Much more flexibility is granted to the user in this second option of the code at the expense of model setup time.

Because the Colorado River is assumed to be a gaining stream downgradient of the tailings area, the river is treated essentially as a sink, with flow from the aquifer entering the river. The user must specify the elevation of the river bottom, the head in the river, and the river-bed conductance as input to the model. The model then calculates the actually flows and mass loading of the contaminants to the river.

The assumption that the Colorado River downgradient of the site is a gaining stream may be questioned due to the lack of conclusive evidence demonstrating such a phenomenon. There are reasons to believe that the river is indeed gaining in the subject area. In particular, it is typical of perennial streams like the rivers in this region to benefit from groundwater inflows due to topography effects (Freeze and Cherry, 1979). Groundwater typically flows from higher areas, where recharge is relatively significant and water levels are elevated by the recharge, to lower areas, where streams are commonly found. Consequently, surface water bodies in the form of streams, rivers, lakes, and wetlands tend to act as discharge sites for the upland recharge. For this natural recharge-discharge mechanism to be upset, in which a river begins losing its water to the subsurface rather than gaining from it, very large withdrawals of groundwater on a regional scale are quite often necessary (Peterson and Wilson, 1988). On the basis of data presented in the DOE reports (1995; 1996b), there is no indication that such a reversal in flow has occurred at the Old Rifle site, especially not within the surficial aquifer.

# 5.3 Hydraulic Properties

Several slug tests have been performed at the Old Rifle site to estimate hydraulic properties for the surficial, unconfined aquifer. An aquifer pumping test was recently performed, as well. The range of estimated hydraulic conductivity values from the aquifer pumping test for the alluvium is 110 to 125 ft/d, with an average of 117 ft/d. The aquifer pump test data are considered more representative of large-scale behavior of the aquifer properties than the slug test data due to the type of test performed. This is mostly due to the fact that slug tests provide measures of material properties over relatively small zones of influence (e.g., Domenico and Robbins, 1998), whereas long-term pump tests gauge aquifer response over distances spanning as much as hundreds of feet. The spatial variability of the aquifer has not been addressed in a rigorous fashion. Therefore, considerable uncertainty exists regarding the true nature of the hydraulic properties of the alluvial aquifer. GANDT has the capability to address spatial variability in hydraulic conductivity explicitly through the use of a geostatistical technique. However, more hydraulic conductivity data are needed to justify this type of approach than exist for the Old Rifle site. Therefore, just uncertainty is addressed in these simulations through the use of the Monte Carlo approach rather than a spatial variability analysis. The hydraulic gradient in the alluvial aquifer is approximately 0.0045 feet per foot.

#### 5.4 Sources and Sinks

There are no major pumping wells or other sinks in the vicinity of the Old Rifle site. There are, however, sources of water being supplied to the aquifer. The first source of water is associated with leakage from the tailings source materials during the operation of the mill and subsequent drainage after closure. The second source of water is the irrigation canals upgradient of the site. The infiltration associated with these irrigation canals can impart a seasonal fluctuation to the water table in the vicinity of the tailings. The simulations performed for this analysis span over many years and an assumption of steady state is made. Therefore, an average hydraulic head

distribution is used to represent the water table configuration, and not a seasonally variable water table. The hydraulic effects of the irrigation canals are then considered only in terms of their average behavior on the system and controlled by the upgradient prescribed head boundary condition.

# 5.5 Water Budget

Water budget considerations for the steady-state model used to simulate the surficial aquifer flow include (1) infiltration of water through the mill tailings source area, (2) groundwater discharge to the Colorado River, and (3) areally-distributed recharge throughout the site. The first of these is assumed in GANDT to influence contaminant transport from the tailings but have no appreciable effect on the general hydraulic gradients and flow directions currently occurring in the model area. Reasons for this latter assumption were discussed previously as part of the rationale for adopting steady-state flow conditions (see Section 5.2). The second component, groundwater discharge, is determined in GANDT as a result of the stream-aquifer option in the model. The third, areal recharge, comprises an input parameter for the Monte Carlo simulations. It has been assumed in this investigation that this latter component, like water seepage through mill tailings, is not substantial enough to influence general groundwater flow conditions and velocities. However, GANDT does account for the effects of areal recharge on contaminant dilution. This is accomplished through a version of the numerical groundwater model in the code that specifically addresses water-mass conservation in the solute transport equation (Voss, 1984; Knowlton et al., in press).

Water budget results will vary with each Monte Carlo run conducted with the GANDT code. Because each simulation makes use of varying hydraulic properties, total cumulative flow volumes cannot be predicted a priori. What can be estimated prior to the Monte Carlo analysis, however, is the range of flows per unit width of the model. On the basis of reported hydraulic conductivities, hydraulic gradients, and aquifer thicknesses (see Chapter 4 and Section 7.2), these

per-unit-width flows are expected to range from 7.9  $\rm ft^2/day$  to 9  $\rm ft^2/day$  (2900  $\rm ft^2/yr$  to 3300  $\rm ft^2/yr$ ).

#### 5.6 Contaminant Source Term

As previously mentioned, several contaminants of concern have been identified for the Old Rifle site. The basis for concern depends on whether the contaminants are elevated in concentration relative to background, relative to the MCLs, or if they pose a possible threat to human health and the environment. The contaminants of concern were identified in the Site Observational Workplan (DOE, 1996b) and the Baseline Risk Assessment for the site (DOE, 1995). A subset of these contaminants of concern was analyzed for this study: uranium, vanadium, and selenium. Arsenic was evaluated as a possible contaminant of concern, but current monitor well water quality data suggest that concentrations are under the regulatory limit.

Concentrations of the contaminants of concern in the mill tailings source area when the tailings were present are very uncertain. The concentration distribution is generally established on the basis of expert judgment and trial-and-error in the modeling process. The source term dimensions are established on the basis of measurements of the site layout and from information in the SOWP (DOE, 1996b). Each of these types of source-term variables are treated as uncertain in the GANDT analyses.

# 5.7 Fate and Transport Properties

Model fate and transport properties are derived from field and laboratory testing (e.g., sorption tests), as well as literature values. Experimental data are available, for instance, on sorption coefficients for uranium and molybdenum (e.g., Yu et al., 1993; DOE, 1993). There is a fairly wide range of sorption coefficient values reported for each of these contaminants.

### 6. Computer Code Description

The GANDT code can be used to analyze flow and transport of contaminants from a source area in the unsaturated zone, through the unsaturated soils underlying the source material, and subsequently into and within the saturated zone. Uncertainty analyses are directly addressed in GANDT through probabilistic simulations based on the Monte Carlo method in conjunction with Latin Hypercube Sampling (LHS) of stochastic model parameters. Probabilistic results from the code can help to provide estimates of the likelihood of occurrence of specific transport scenarios. GANDT contains options for simulating subsurface contaminant movement using screening level, analytical solutions of advective-dispersive transport. A numerical, three-dimensional, finitedifference groundwater flow and transport solution based on the public-domain code FTWORK (Faust et al., 1994) can also be employed. The numerical simulator is used for this study because of its ability to account for groundwater discharge to a river, including a sinuous waterway. Spatial variability of hydraulic conductivity is accounted for through the use of geostatistical conditional simulation (Peck et al., 1988), the algorithms for which are taken from the GSLIB system of codes (Deutsch and Journel, 1992). GANDT is relatively unique because of its ability to automatically condition model runs on observed hydraulic head and water quality data, which essentially provides the model user with a built-in calibration technique. The code has an option to employ an automatic grid generator for ease of use in setting up a finite-difference grid when employing FTWORK. Data input and the examination of results from probabilistic analyses are handled easily through an intuitive user interface.

Versions of GANDT exist for both on PC-Windows and PowerPC Macintosh platforms. A draft reference report detailing the algorithms used in GANDT is available upon request (Knowlton et al., in press). A draft user's manual for GANDT is also available.

# 6.1 Assumptions

The reader is referred to the draft reference manual for GANDT (Knowlton et al., in press) for a complete description of the flow and transport models and geostatistical algorithms employed in the software. Many of the assumptions upon which both the analytical and numerical simulators in the code have been developed are also provided in the reference manual. More detailed explanations of the FTWORK model are presented in Faust et al. (1994).

#### **6.2 Limitations**

Potential limitations of the modeling software that may be relevant to this natural attenuation evaluation include:

- <u>Steady-state flow conditions</u> The current version of the code does not simulate transient groundwater flow.
- <u>Single time frame for conditioning</u> At this time, the user can only specify one time to be used for conditioning of model results on measured hydraulic head values and groundwater concentrations.

#### 6.3 Solution Techniques

As mentioned above, both analytical and numerical models of subsurface flow and transport are provided in GANDT, discussion of which is presented in the draft reference manual (Knowlton et al., in press).

#### 6.4 Effects on Model

Perhaps the biggest concern regarding the application of GANDT to this evaluation of natural attenuation is the model's utilization of steady-state flow solutions. However, as discussed in

earlier report sections, utilization of steady-state conditions in the current study appears to be a legitimate approach to assessing the long-term prospects for natural attenuation at the Old Rifle site.

#### 7. Model Construction

The GANDT system is designed to be user friendly and minimize work associated with data input. As a consequence, many of the groundwater flow and transport modeling steps that are necessary for conventional model construction have been simplified or automated. Some of these features are identified in the next few sections.

#### 7.1 Model Domain

A model domain was constructed which was large enough that internal processes (e.g., source term loading to the aquifer) did not impact boundary conditions. The finite-difference grid established for the model was created with the manual problem definition option of the code. A variably spaced grid was established, 71 nodes by 101 nodes (totalling 7171 cells), and grid spacing varying from 23 feet to 164 feet. The grid was oriented along the main axis of flow, in a west-southwesterly direction. The grid domain was somewhat centered on the mill tailings area. Figure 7.1 shows a depiction of the finite-difference grid for the site.

#### 7.2 Hydraulic Parameters

Hydraulic parameters used in this study were derived primarily from the Site Observational Work Plan (SOWP) (DOE, 1996b). Additional model parameters were selected from publications that specifically discuss site characteristics (DOE, 1995) and from other literature sources of a more general nature. Site information obtained after the publication of the original SOWP was supplied directly by MACTEC-ERS personnel. The resulting parameter values, including the distribution descriptors for uncertain parameters, are listed for the contaminant source term, the unsaturated zone, and the saturated zone in Tables 7.1, 7.2, and 7.3, respectively. These tables also list the data sources used to justify the parameter values selected.

#### 7.3 Sources and Sinks

As stated previously, no point sources or sinks (e.g. pumping wells) are considered in the Old Rifle analysis. It is recognized that the irrigation canals influence seasonal water level changes at the site, but an average water table condition was assumed appropriate for the length of the simulation suites. This is also consistent with the assumption of steady state flow conditions over the time frame of interest. Water infiltrating from the mill tailings through the unsaturated zone and into the alluvial aquifer was considered as input. Areal recharge was also considered. The Colorado River represents the sole discharge feature within the groundwater flow model.

#### 7.4 Boundary Conditions

As stated above, the flow model in GANDT is set up for steady-state conditions. The upgradient and downgradient boundaries are set as prescribed head conditions, to honor the estimated gradient of 0.0045 and the relative head levels of the wells within the modeled domain. Lateral model boundaries are treated as no-flow boundaries. The stream-aquifer leakage option within the code is invoked for flow to the Colorado River. The distribution of head values, bottom river elevations, and streambed conductance values are prescribed along the length of the river. The head and conductance values of the river are treated as uncertain within the Monte Carlo framework.

#### 7.5 Selection of Calibration Targets and Goals

As discussed in Section 5.2, the GANDT methodology relies on conditioning, or honoring, water level and water quality data. This is accomplished through what is termed a post-conditioning exercise, which occurs after the Monte Carlo simulations have completed. The conditioning is performed in a two-step process. First, the water level data are analyzed for honoring the existing data. Second, the accepted runs from the water level conditioning are queried for honoring the

water quality data. In this way, only acceptable flow conditions are considered within the broader framework of water quality conditioning.

The current GANDT code is capable of performing a conditioning analysis only on the basis of one time period. Thus, groundwater levels and water quality data from a single point in time are desired to perform the calibration. The year chosen for the data conditioning in this investigation was 1998. As mentioned previously, the irrigation canals at the site have a seasonal influence on water levels in the vicinity of the site. The GANDT code is set up to perform a steady state flow simulation. Therefore, the two sets of water level measurements taken during 1998, in May and September, were averaged to estimate a steady state flow condition. Concentration data from 1998 were used as calibration targets for water quality conditioning. Appendix A shows a listing of the groundwater water quality data utilized as calibration targets. These data were supplied by MACTEC-ERS, as extracted from the SEE.UMTRA database.

Two types of tests are available in the GANDT code for honoring water level and water quality data through a post-conditioning statistical test. The first is a chi-square distribution test (Haan, 1977) on the transport model residuals (i.e., differences between measured and simulated concentrations). For a chi-square test to be valid, the residuals must be either normally or log-normally distributed. Such a requirement was not met in the preliminary model runs made with GANDT. Consequently, a second method of assessing the differences between simulated and measured concentrations, the root mean squared error (RMSE) approach (Anderson and Woessner, 1992), was employed. A trial-and-error methodology, in which various parameter choices are tested to determine their effect on model residuals, was required to establish an appropriate RMSE value. Generally, an RMSE value on the order of the observed calibration targets (e.g., water quality concentrations) is typical. The RMSE criteria ultimately selected for the water level conditioning was 0.93 feet. The RMSE criteria selected for the uranium, vanadium, and selenium simulations were 0.065 mg/l, 0.175 mg/l, and 0.025 mg/l, respectively.

### 7.6 Numerical Parameters

The input parameters and distributions used in these simulations are shown in Tables 7.1, 7.2, and 7.3, for source term, unsaturated zone, and saturated zone parameters, respectively. A parameter not included in the tables is the half-life of uranium, which is assumed to be  $1 \times 10^9$  years. The data presented in these tables was derived from several sources: 1) site specific data and analyses, when available; 2) literature information; and 3) expert judgment, including trial and error in the modeling runs. Tables 7.1, 7.2, and 7.3 contain an annotation on the source of the information used for each of the parameters.

**Table 7.1 - Source Term Parameters** 

TYPE OF PARAMETER	NAME OF PARAMETER [UNITS]	VALUE OR DISTRIBUTION	JUSTIFICATION FOR DATA
Geometry	Thickness [ft]	6.5	Based on measurements at site, DOE (1996b).
Flow	Infiltration rate [ft/yr]	Uniform, $min = 0.01$ , $max = 0.33$	Expert judgment; model trials.
	Saturated hydraulic conductivity [ft/d]	Lognormal, min = 11.7, max = 125.	Based on information in DOE (1996b) and data from MACTEC-ERS.
	Porosity	Uniform, min = 0.35, max = 0.4	Based on information in DOE (1996b) and general literature.
	Residual water content	0.09	General literature.
	van Genuchten n factor	Uniform, $min = 1.8$ , $max = 2.6$	General literature.
Fate & Transport	Initial Soil Concentration [ppm]	Uranium: Uniform, min = 0.008, max = 0.03; Vanadium: Uniform, min = 0.008, max = 0.03; Selenium: Uniform, min = 0.001, max = 0.008.	Expert judgment; model trials.
	Solubility of contaminant [ppm]	Uranium: 100; Vanadium: 100; Selenium: 100;	General literature.
	Distribution coefficient [cc/g] <sup>1</sup>	Uranium: Uniform, min = 0.1, max = 0.2; Vanadium: Uniform, min = 0.3, max = 0.9; Selenium: Uniform, min = 0.1, max = 1.5	DOE (1983), information from MACTEC-ERS, and general literature.
	Dry bulk density [g/cc] <sup>1</sup>	1.7	General literature.
	Time since waste release [y]	56	DOE (1996b).
	Pulse duration [y]	16	DOE (1996b).

<sup>1 –</sup> Common unit of expression

**Table 7.2 - Unsaturated Zone Parameters** 

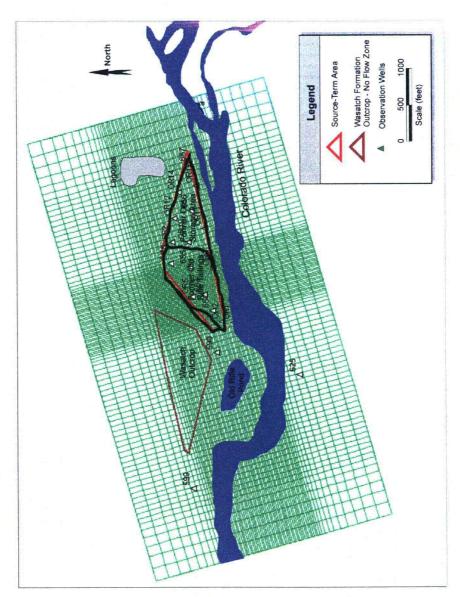
TYPE OF	NAME OF PARAMETER	VALUE OR DISTRIBUTION	JUSTIFICATION FOR
PARAMETER	[UNITS]		DATA
Geometry	Thickness [ft]	10	DOE (1996b).
Flow	Saturated hydraulic	Lognormal, min = 11.7, max =	DOE (1996b) and data from
	conductivity [ft/d]	125.	MACTEC-ERS.
	Porosity	Uniform, $min = 0.30$ , $max = 0.34$	Based on information in
			DOE (1996b) and general
			literature.
	Residual water content	0.09	General literature.
	van Genuchten α coefficient	Uniform, min = $0.61$ , max = $4.27$	General literature.
	[1/ft]		
,	van Genuchten n factor	Uniform, min = 1.8, max = 2.6	General literature.
Fate &	Longitudinal dispersivity	3.3	Expert judgment and
Transport	[ft]		general literature.
	Distribution coefficient	Uranium: Uniform, min = 0.1,	DOE (1983) and general
	[cc/g] 1	max = 0.2; Vanadium: Uniform,	literature.
		min = 0.3, max = 3.0; Selenium:	
		Uniform, min = 0.1, max = 1.5	
	Dry bulk density [g/cc]	1.8	General literature.

<sup>-</sup> Common unit of expression

**Table 7.3 - Saturated Zone Parameters** 

TYPE OF	NAME OF PARAMETER	VALUE OR DISTRIBUTION	JUSTIFICATION FOR
PARAMETER	[UNITS]		DATA
Geometry	Thickness [ft]	16	DOE (1996b).
Flow	Down gradient flow	196	DOE (1996b) and expert
	direction (counterclockwise		judgment.
	from due east) [degrees]		
	Hydraulic gradient	0.0045	DOE (1996b) and expert
:	(horizontal)		judgment.
	Recharge rate [ft/y]	Uniform, min = 0.0033, max =	Expert judgment and
		0.033	general literature.
	Saturated hydraulic	Lognormal, min = 72, max = 125	DOE (1996b), data from
	conductivity [ft/d]		MACTEC-ERS, and model
			trials.
	Hydraulic conductivity	100	Expert judgment and
	anisotropy (H/V)		general literature.
	Porosity	Uniform, $min = 0.30$ , $max = 0.34$	DOE (1996b) and general
			literature.
Fate &	Longitudinal dispersivity	Uniform: min = 65, max = 100	Expert judgment and
Transport	[ft]		general literature.
	Dispersion anisotropy	Uniform: min = 33, max = 100	Expert judgment and
•	[long./trans]		general literature.
	Distribution coefficient	Uranium: Uniform, min = 0.1,	DOE (1983), data from
	[cc/g] 1	max = 0.2; Vanadium: Uniform,	MACTEC-ERS, and
		min = 0.3, $max = 3.0$ ; Selenium:	general literature.
	,	Uniform, $min = 0.1$ , $max = 1.5$ .	
	Dry bulk density [g/cc]	1.8	General literature.
	Tortuosity	0.39	General literature.

<sup>&</sup>lt;sup>1</sup> – Common unit of expression



'.1 - Finite Difference Grid Used in the Uncertainty Analysis for the UMTRA Old Rifle Site

#### 8. Calibration

As mentioned above, the procedures used in GANDT to assume that model runs perform reasonably well in matching site conditions is quite different from traditional flow model calibration techniques based on manipulating various input constructs in the hope of matching observed hydraulic heads and water quality data. Specifically, GANDT employs a post-conditioning algorithm that is based on the comparison of observed and simulated water level and water quality data. The post-conditioning exercise is automated in the Monte Carlo simulation framework.

#### 8.1 Qualitative/Quantitative Analysis

Post-conditioning results are somewhat a reflection of the appropriateness of available water level and water quality data. Occasionally, when limited field data or inappropriate data (e.g., laboratory data that does not reflect field conditions) are used, few, if any, simulations meet the conditioning criteria. If the observed water level and concentration data are representative of site contamination, one would expect a greater number of model runs to honor these data and pass the conditioning tests.

In a Monte Carlo analysis that incorporates LHS, it is theoretically possible to quantify uncertainties in the modeling results with as little runs as 4/3 times the number of uncertain variables. In practice a factor of 2 to 4 is recommended. There are about 19 uncertain parameters in the analyses performed here for the Old Rifle site. Therefore, a minimum of 38 runs passing the conditioning test is desired. A total of 800 simulations were specified for the Monte Carlo suite. For the steady-state flow regime, 266 out of the 800 runs passed the RMSE conditioning criteria of 0.93 feet for honoring observed water levels. Figure 8.1 shows a plot of the residuals between observed and calculated head data passing the RMSE conditioning criteria. For the uranium simulations, 43 runs passed the RMSE conditioning criteria of 0.065 mg/l. Figure

8.2 shows a plot of the residuals between observed and calculated uranium concentration data passing the RMSE conditioning criteria. For vanadium, 44 runs passed the RMSE conditioning criteria of 0.173 mg/l. Figure 8.3 shows a plot of the residuals between observed and calculated selenium concentration data passing the RMSE conditioning criteria. For selenium, 62 runs passed the RMSE conditioning criteria of 0.0255 mg/l. Figure 8.4 shows a plot of the residuals between observed and calculated selenium concentration data passing the RMSE conditioning criteria. The results of these analyses are presented in a subsequent section.

### **8.2 Sensitivity Analysis**

A formal sensitivity analysis with the Old Rifle simulations was not performed. The GANDT analysis resulted in a quantitative expression of the flow and transport uncertainty, which is a higher order step than intended by a conventional sensitivity analysis in terms of addressing variability or reliability in the results.

# **8.3 Model Application Verification**

No additional time steps were evaluated against observed data for a verification analysis. The built-in conditioning/calibration step is considered adequate in defending the representativeness of the simulations.

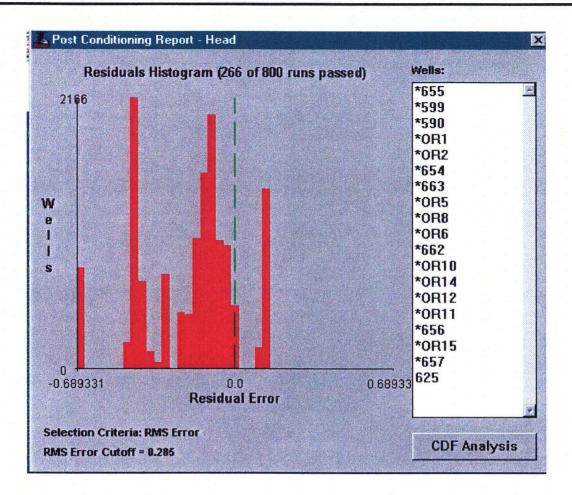


Figure 8.1 - Residuals between observed and calculated water level data passing the RMSE conditioning criteria, set to 0.93 feet (0.285 meters)

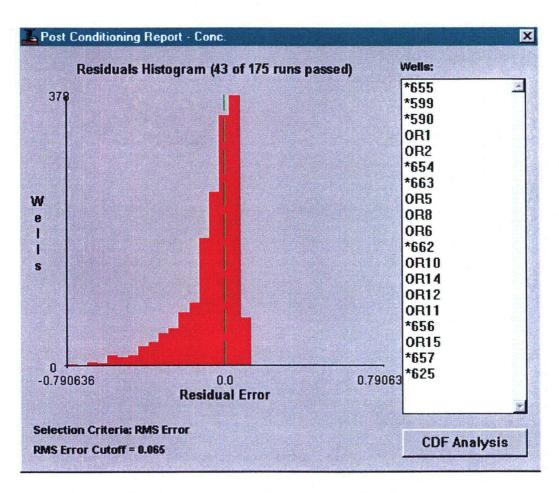


Figure 8.2 - Residuals between observed and calculated uranium concentration data passing the RMSE conditioning criteria, set at 0.065 mg/l

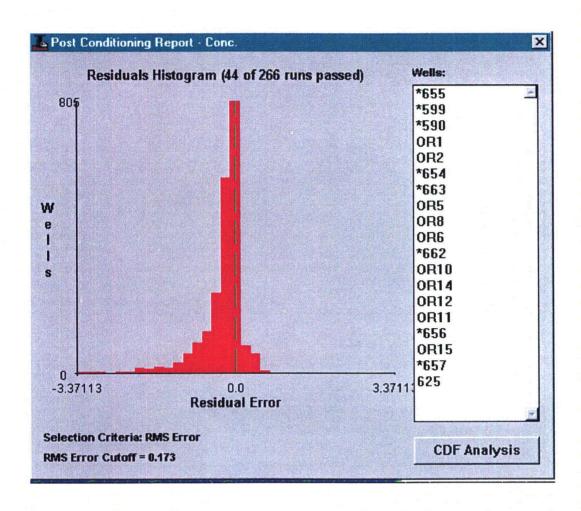


Figure 8.3 - Residuals between observed and calculated vanadium concentration data passing the RMSE conditioning criteria, set at 0.173 mg/l

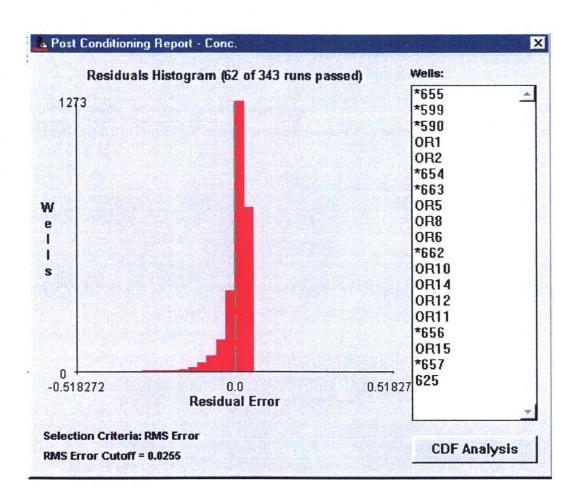


Figure 8.4 - Residuals between observed and calculated selenium concentration data passing the RMSE conditioning criteria, set at 0.0255 mg/l

# 9. Predictive Simulations

Results of the predictive modeling simulations are quite encouraging with regard to the potential for natural attenuation as a possible groundwater remedial alternative at the Old Rifle site. The modeling effort in this study yields a tremendous amount of information, both in the form of graphical and quantitative results. Most of the predictive modeling results are graphically presented for the purpose of showing the likelihood of natural attenuation. As part of this exercise, two types of plots have been selected for inclusion in the report.

The first type of plot contains the mean, or average, concentration distribution from all Monte Carlo runs that have met the conditioning criteria. The average concentration distribution can be interpreted as the expected case. The transient nature of the plume is visualized by displaying several time steps for each of the three contaminants of concern: uranium, vanadium, and selenium.

The second type of graphic comprises a probability plot illustrating the spatial distribution of the probability that the plume concentration will be less than a specified concentration threshold, preferably the contaminant's MCL. Such results are very useful in evaluating the likelihood of success of the proposed alternative. A plot indicating a very high probability that the concentrations will be less than the MCL within a 100-year time frame is interpreted as a high likelihood of success for natural attenuation.

MCLs are used as the concentration thresholds in the uranium, vanadium, and selenium simulations. The MCLs for uranium, vanadium, and selenium are 0.044 mg/l, 0.33 mg/l, and 0.05 mg/l, respectively.

Appendix B contains graphical results for all contaminants investigated, for all output times, in the form of average concentration distributions and probability distribution plots. Several of these plots are presented here for purposes of discussion. Figures 9.1 and 9.2 show the mean contaminant plume distributions for uranium in 1998 and 40 years into the future, respectively

Figures 9.3 and 9.4 show the results of the spatial distribution of the probability that the concentrations are greater than the MCL for uranium of 0.044 ppm. As in the case of the mean concentration plots, Figures 9.3 and 9.4 show simulated probability distributions in 1998 and 40 years in the future, respectively. It can be seen from these plots that the average concentration of uranium falls below the MCL of 0.044 mg/l after 40 years into the future. However, significant probability exists that the MCL's will not be met during at the 40-year time frame, as evidenced in Figure 9.4 Figure 9.5 depicts the probability distribution after 50 years in the future. At this time there is a greater than 95% probability that the concentrations are less than the MCL. After 75 years a 100% probability of flushing below the MCL is predicted. Additional plots of concentration and probability distributions are shown in Appendix B for other time frames of interest.

The transport behavior of vanadium is markedly different from that of uranium. Vanadium has a higher sorptive potential than uranium, and therefore is not likely to flush from the sediments as quickly as uranium. The average vanadium concentration distribution results are shown in Figures 9.6 and 9.7, for 1998 conditions and 100 years into the future, respectively. Figures 9.8 and 9.9 display the distribution of the probability that the groundwater concentrations are greater than the vanadium MCL of 0.33 mg/l. Additional transient plots are displayed in Appendix B. From these plots it is apparent that the average concentration distribution falls below the regulatory limit within 75 years. However, at 100 years in the future there is still a greater than 10% likelihood that the concentration may be above the limit. Monitoring the groundwater conditions through time will be important to determine whether the system behaves more like the average behavior, and therefore be acceptable, or be relatively slow in flushing the vanadium.

The transport behavior of selenium is also markedly different from that of uranium. Selenium has a higher sorptive potential than uranium, and therefore is not likely to flush from the sediments as quickly as uranium. The average selenium concentration distribution results are shown in Figures 9.10 and 9.11, for 1998 conditions and 100 years into the future, respectively. Figures 9.12 and 9.13 display the distribution of the probability that the groundwater concentrations exceed the selenium MCL of 0.05 ppm. Additional transient output times are depicted in Appendix B. On

average the selenium concentrations are below the MCL within ten years from the conditioning time. However, it takes approximately 75 years for the concentrations to decrease to the point where there is less than a 5% probability of exceeding the MCL. Another way to interpret this information is that there is a 95% likelihood that the concentrations will be below the MCL's in 75 years. Monitoring the groundwater conditions through time will be important to determine whether the system behaves more like the average behavior, and therefore be acceptable, or be relatively slow in flushing the selenium.

As mentioned, monitoring will be an important aspect of future activities at the Old Rifle site to assure that the standards are met. To that end, this modeling effort has also predicted the statistical expectations of the monitoring program in the future. Figure 9.14 shows the predicted uranium concentration behavior at monitor well 654 through time. The error bars on the plot represent the minimum and maximum predicted concentrations from the Monte Carlo simulations, and the symbol represents the average concentration. If future monitoring conditions fall within these statistical ranges then the site should be on track for natural flushing. If the observed concentrations are above these limits then the site should be re-evaluated with regard to the potential success of the natural attenuation strategy. Similar plots for vanadium and selenium in monitor well 654 are shown in Figures 9.15 and 9.16, respectively.

The results of this analysis suggest that there is a high likelihood of success for natural attenuation processes to be effective as a possible remedial alternative for uranium at the Old Rifle site. Selenium has a relatively high probability for successful flushing but may also exhibit a potential to be above the MCL standard in a 100-year time frame.

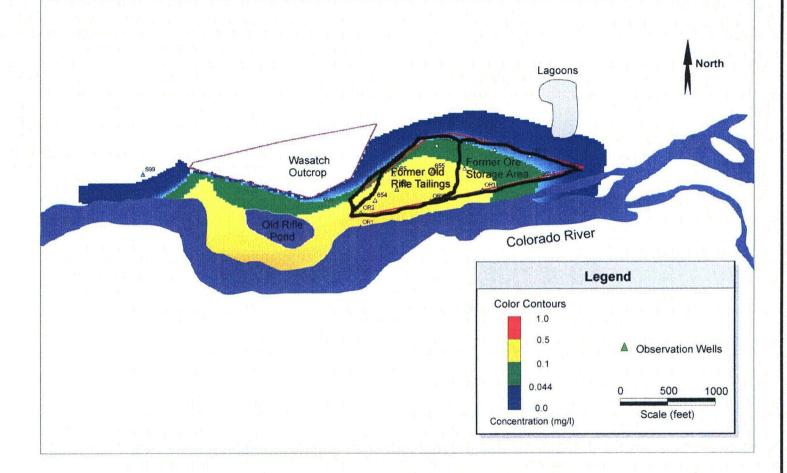


Figure 9.1 - Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - Conditioning Time, 1998

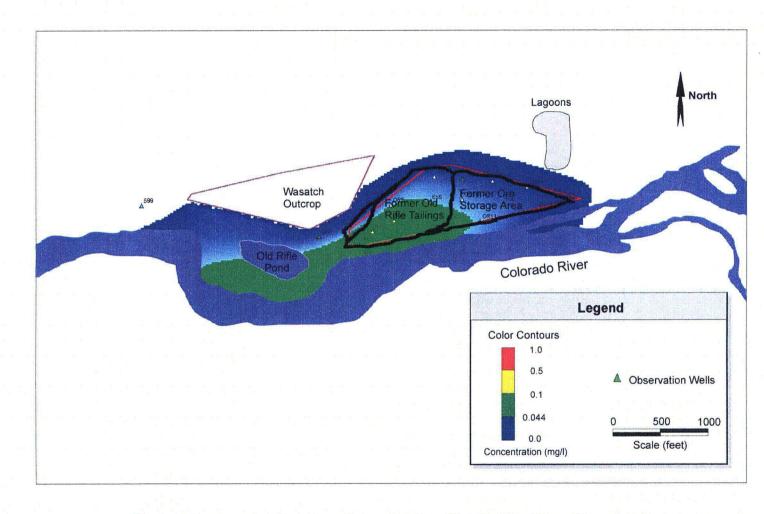


Figure 9.2 - Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 20 years after Conditioning Time, 2018

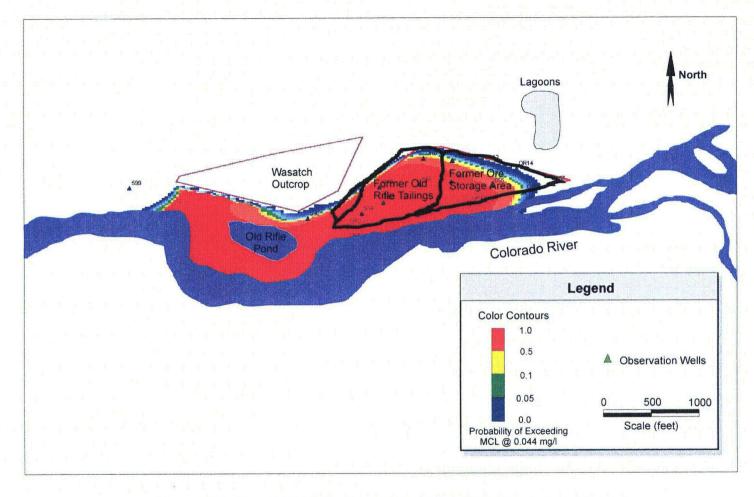


Figure 9.3 - Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Uranium (0.044 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - Conditioning Time, 1998

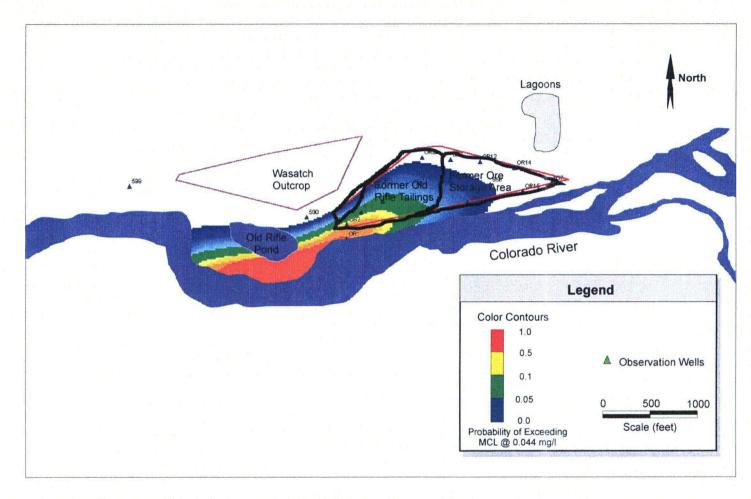


Figure 9.4 - Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Uranium (0.044 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 20 years after Conditioning Time, 2018

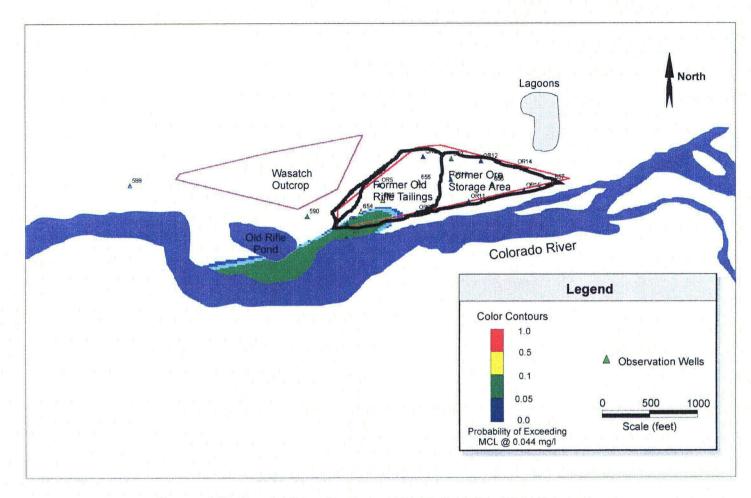


Figure 9.5 - Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Uranium (0.044 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 50 years after Conditioning Time, 2048

Figure 9.6 - Average Vanadium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - Conditioning Time, 1998

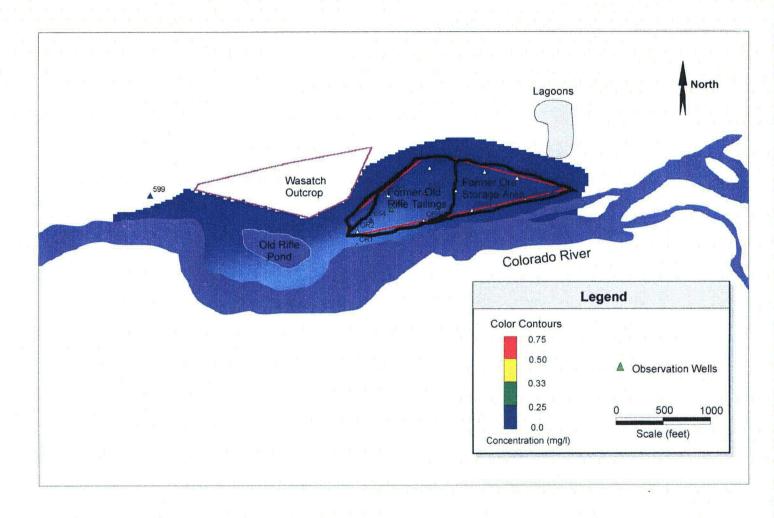


Figure 9.7 - Average Vanadium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 100 years after Conditioning Time, 2098

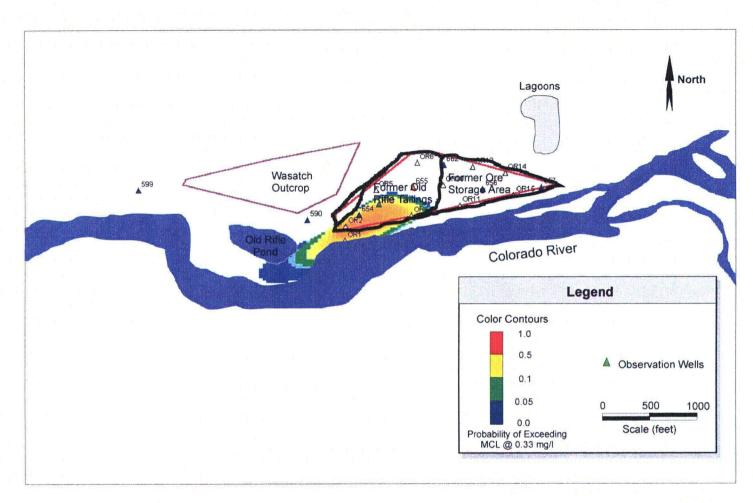


Figure 9.8 - Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Vanadium (0.33 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - At the Conditioning Time, 1998

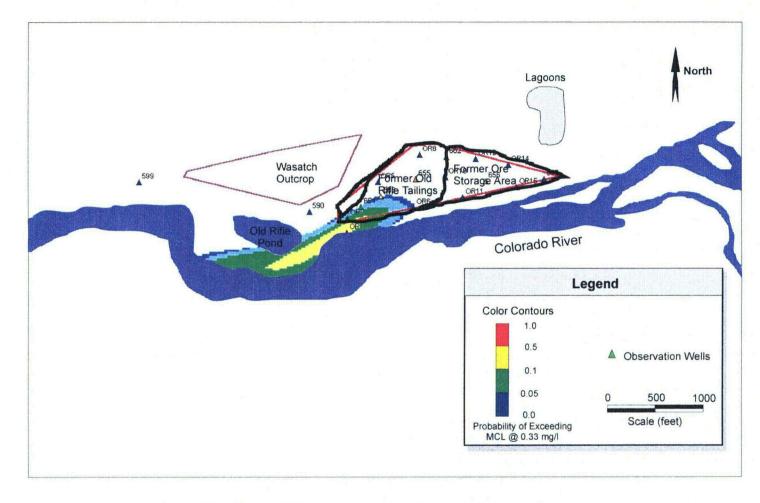


Figure 9.9 - Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Vanadium (0.33 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 100 years after Conditioning Time, 2098

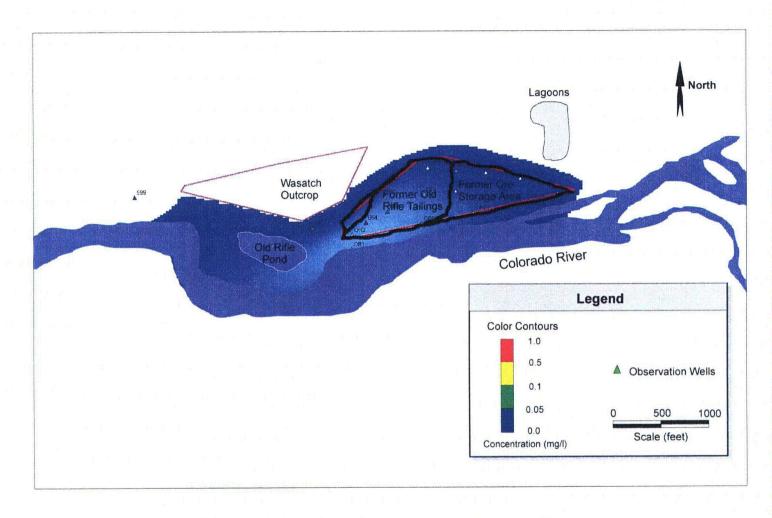


Figure 9.10 - Average Selenium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - Conditioning Time, 1998

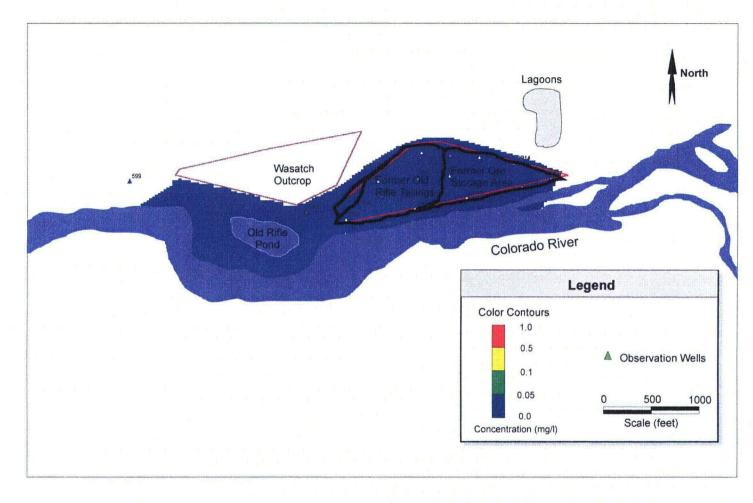


Figure 9.11 - Average Selenium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 100 years after Conditioning Time, 2098

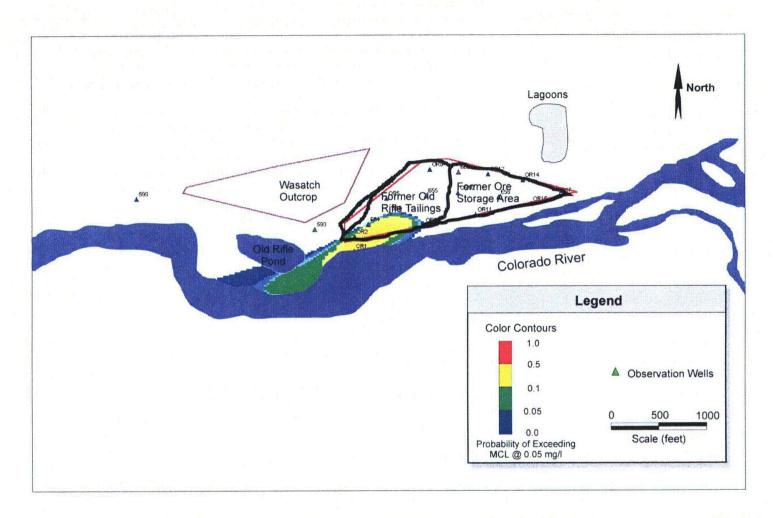


Figure 9.12 - Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Selenium (0.05 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - At the Conditioning Time, 1998

Figure 9.13 - Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Selenium (0.05 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 100 years after Conditioning Time, 2098

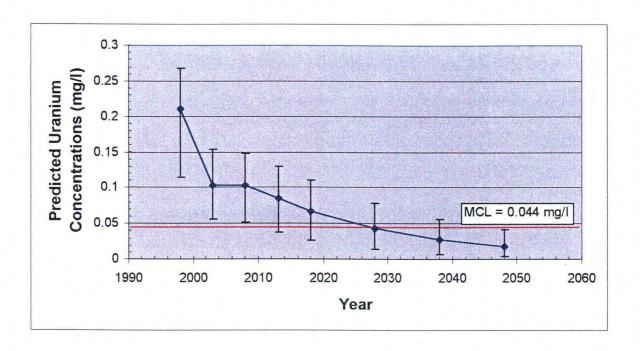


Figure 9.14 - Uranium Concentrations Through Time at Monitor Well 654

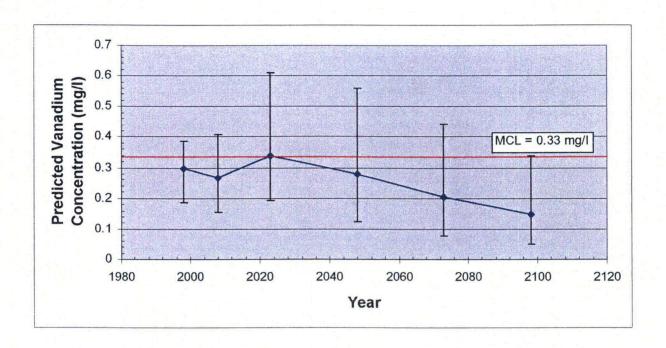


Figure 9.15 - Vanadium Concentrations Through Time at Monitor Well 654

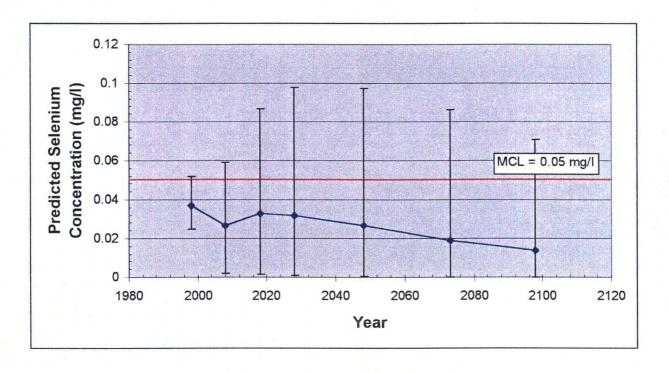


Figure 9.16 - Selenium Concentrations Through Time at Monitor Well 654

# 10. Summary and Conclusions

Probabilistic analyses of groundwater flow and transport at the Old Rifle site were performed to assess the likelihood of success in implementing a natural attenuation strategy. The GANDT methodology and code set, originally developed for the DOE at Sandia National Laboratories (SNL), were used to perform the analyses. Natural attenuation prospects were examined with respect to achieving maximum contaminant levels (MCLs) over a 100-year period, during which controls on site activities would be maintained.

The results of the probabilistic analyses were encouraging. The uranium transport simulations suggest a high probability of success for natural flushing to meet the MCL's for these contaminants within a 75-year time period. It should be noted that the analyses performed were based on existing data and information. The vanadium transport simulations suggest that it is much more persistent, due to higher sorption characteristics of the species compared to uranium. The selenium transport simulations also suggest that it is much more persistent, due to higher sorption characteristics of the species compared to uranium. On average, both the vanadium and selenium constituents would be expected to flush from the alluvial aquifer in a 100-year time frame. However, there still exists about a 10% likelihood that the concentrations could be above the MCL at the end of 100 years. For this reason, and because of regulatory requirements, the site should be monitored routinely, and predictive transport modeling, such as that reported on here, should be revisited and updated if necessary.

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# Appendix A Groundwater Quality Data

# Water Quality Data Used in Numerical Simulations as Calibration Targets for the Automated Conditioning Analysis

LOCATION	DATE		e Arthur Landers
CODE	SAMPLED	RESULT	ANALYTE
0291	21-May-98	0.05	Uranium
0292	21-May-98	0.0524	Uranium
0301	20-May-98	0.145	Uranium
0301	20-May-98	0.146	Uranium
0302	19-May-98	0.172	Uranium
0303	20-May-98	0.0623	Uranium
0304	19-May-98	0.0833	Uranium
0305	19-May-98	0.064	Uranium
0306	20-May-98	0.0466	Uranium
0307	19-May-98	0.0376	Uranium
0308	19-May-98	0.073	Uranium
0309	19-May-98	0.0367	Uranium
0310	19-May-98	0.27	Uranium
0590	22-May-98	0.0839	Uranium
0590	17-Sep-97	0.0764	Uranium
0597	21-May-98	0.0443	Uranium
0598	21-May-98	0.0216	Uranium
0599	22-May-98	0.039	Uranium
0600	22-May-98	. 0.0078	Uranium
0600	16-Sep-97	0.0056	Uranium
0604	26-May-98	0.0268	Uranium
0604	17-Sep-97	0.0225	Uranium
0605	16-Sep-97	0.0469	Uranium
0606	21-May-98	0.0429	Uranium
0606	16-Sep-97	0.0326	Uranium
0620	26-May-98	0.0244	Uranium
0621	20-May-98	0.0026	Uranium
0621	17-Sep-97	0.0021	<u>Uranium</u>
0622	26-May-98	0.0013	Uranium
0622	17-Sep-97	0.0012	Uranium

LOCATION: CODE	DATE SAMPLED	RESULT	ANALYTE
0623	26-May-98	0.001	Uranium
0646	20-May-98	0.003	Uranium
0647	20-May-98	0.0039	Uranium_
0648	19-May-98	0.003	Uranium
0649	19-May-98	0.0014	Uranium
0654	19-May-98	0.112	Uranium
0655	18-May-98	0.177	Uranium
0656	20-May-98	0.0668	Uranium
0656	20-May-98	0.0671	Uranium
0657	19-May-98	0.11	Uranium
0658	21-May-98	0.0594	Uranium
0659	21-May-98	0.0587	Uranium
0660	22-May-98	0.0055	Uranium
0662	20-May-98	0.0856	Uranium
0663	18-May-98	0.19	Uranium

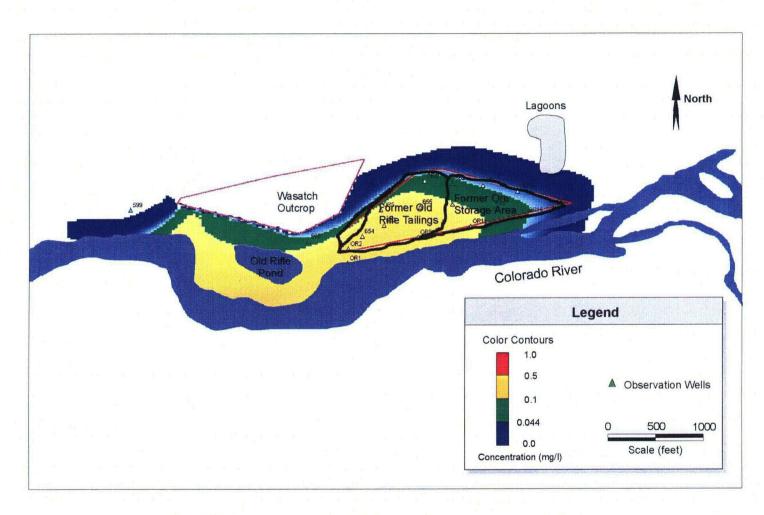
LOCATION	DATE		
The said water of water the said and	SAMPLED	RESULT	ANALYTE
0291	21-May-98	0.001	Vanadium
0292	21-May-98	0.001	Vanadium
0301	20-May-98	0.001	Vanadium
0301	20-May-98	0.001	Vanadium
0302	19-May-98	0.372	Vanadium
0303	20-May-98	0.0598	Vanadium
0304	19-May-98	0.0373	Vanadium
0305	19-May-98	0.765	Vanadium
0306	20-May-98	0.001	Vanadium
0307	19-May-98	0.0046	Vanadium
0308	19-May-98	0.0044	Vanadium
0309	19-May-98	0.001	Vanadium
0310	19-May-98	0.0142	Vanadium
0590	22-May-98	0.001	Vanadium
0590	17-Sep-97	0.01	Vanadium
0597	21-May-98	0.001	Vanadium
0598	21-May-98	0.001	Vanadium
0599	22-May-98	0.0042	Vanadium
0600	22-May-98	0.001	Vanadium
0600	16-Sep-97	0.01	Vanadium
0604	26-May-98	0.001	Vanadium
0604	17-Sep-97	0.01	Vanadium
0605	16-Sep-97	0.01	Vanadium
0606	21-May-98	0.001	Vanadium
0606	16-Sep-97	0.01	Vanadium
0620	26-May-98	0.0014	Vanadium
0621	20-May-98	0.001	Vanadium
0621	17-Sep-97	0.01	Vanadium
0622	26-May-98	0.001	Vanadium
0622	17-Sep-97	0.01	Vanadium

LOCATION	DATE		
CODE	SAMPLED	RESULT	ANALYTE
0623	26-May-98	0.001	Vanadium
0646	20-May-98	0.001	Vanadium
0647	20-May-98	0.0021	Vanadium
0648	19-May-98	0.0065	Vanadium
0649	19-May-98	0.0341	Vanadium
0654	19-May-98	0.0561	Vanadium
0655	18-May-98	0.595	Vanadium
0656	20-May-98	0.105	Vanadium
0656	20-May-98	0.106	Vanadium
0657	19-May-98	0.001	Vanadium
0658	21-May-98	0.001	Vanadium
0659	21-May-98	0.0011	Vanadium
0660	22-May-98	0.001	Vanadium
0662	20-May-98	0.0601	Vanadium
0663	18-May-98	0.254	Vanadium

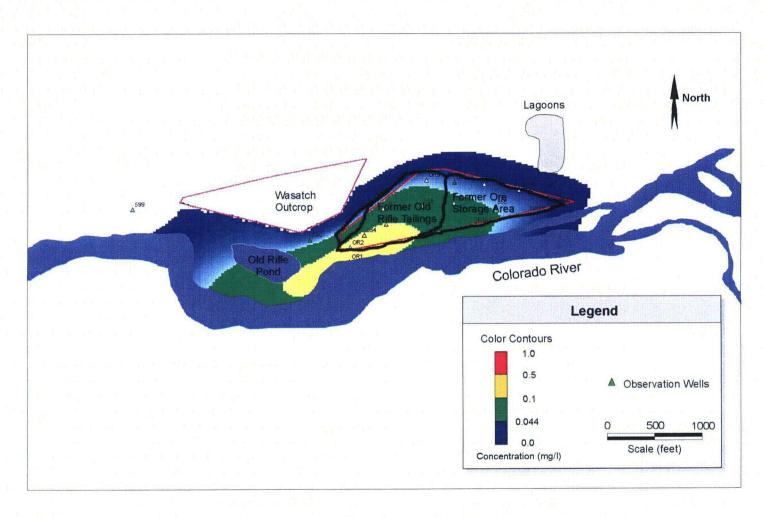
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0292	21-May-98		Selenium
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0301	20-May-98		Selenium
0302	19-May-98		Selenium
0303	20-May-98		Selenium
0304	19-May-98		Selenium
0305	19-May-98		Selenium
0306	20-May-98		Selenium
0307	19-May-98		Selenium
0308	19-May-98		Selenium
0309	19-May-98		Selenium
0310	19-May-98	0.001	Selenium
0590	22-May-98	0.0194	Selenium
0590	17-Sep-97		Selenium
0597	21-May-98		Selenium
0598	21-May-98		Selenium
0599	22-May-98		Selenium
0600	22-May-98		Selenium
0600	16-Sep-97		Selenium
0604	26-May-98		Selenium
0604	17-Sep-97	0.0122	Selenium
0605	16-Sep-97	0.0072	Selenium
0606	21-May-98	0.0086	Selenium
0606	16-Sep-97	0.0044	Selenium
0620	26-May-98		Selenium
0621	20-May-98	0.001	Selenium
0621	17-Sep-97	0.001	Selenium
0622	26-May-98	0.001	Selenium
0622	17-Sep-97	0.001	Selenium

LOCATION	DATE		
CODE	SAMPLED	RESULT	ANALYTE
0623	26-May-98	0.001	Selenium
0646	20-May-98	0.001	Selenium
0647	20-May-98	0.001	Selenium
0648	19-May-98	0.001	Selenium
0649	19-May-98	0.0017	Selenium
0654	19-May-98	0.0181	Selenium
0655	18-May-98	0.0398	Selenium
0656	20-May-98	0.0145	Selenium
0656	20-May-98	0.0144	Selenium
0657	19-May-98	0.0481	Selenium
0658	21-May-98	0.0247	Selenium
0659	21-May-98	0.0243	Selenium
0660	22-May-98	0.001	Selenium
0662	20-May-98	0.0346	Selenium
0663	18-May-98	0.028	Selenium

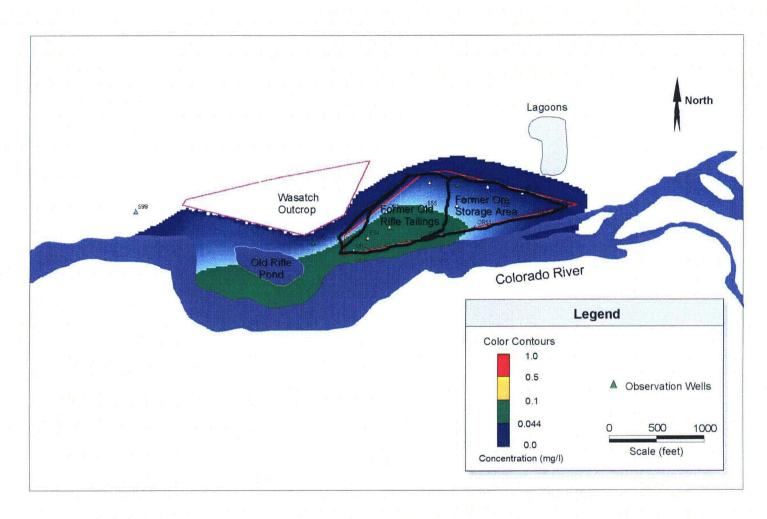
## Appendix B Computer Simulation Results



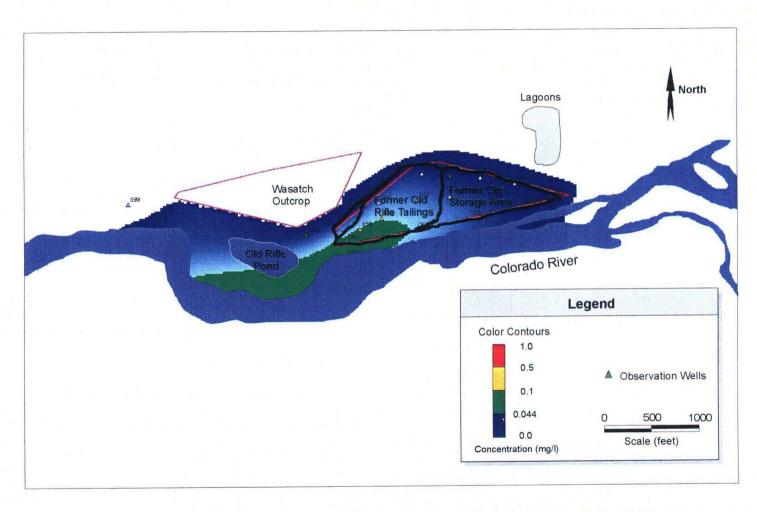
Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - Conditioning Time, 1998



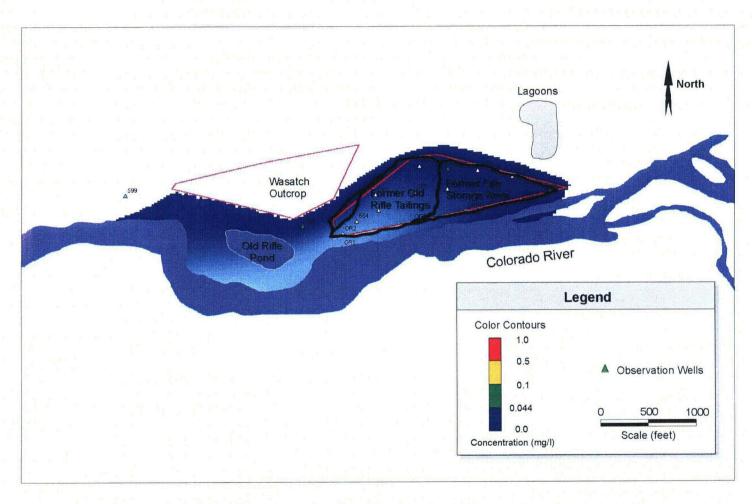
Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 10 years after Conditioning Time, 2008



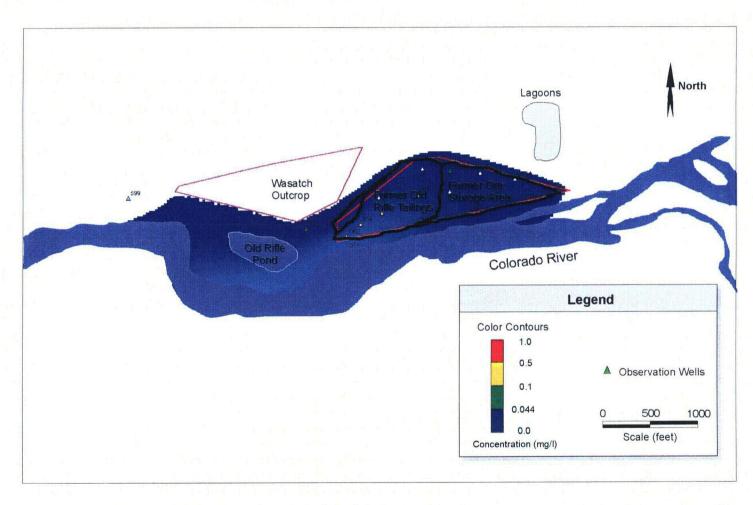
Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 20 years after Conditioning Time, 2018



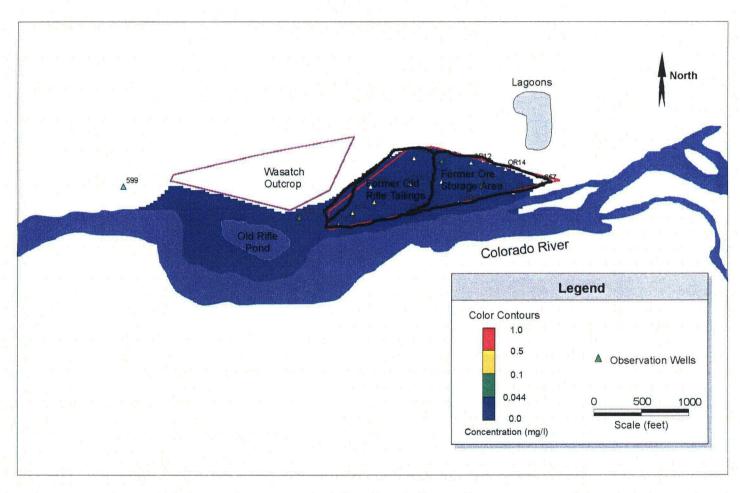
Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 30 years after Conditioning Time, 2028



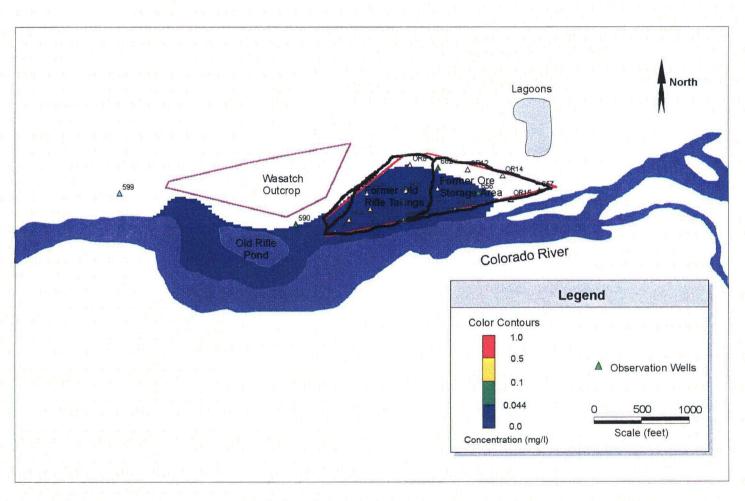
Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 40 years after Conditioning Time, 2038



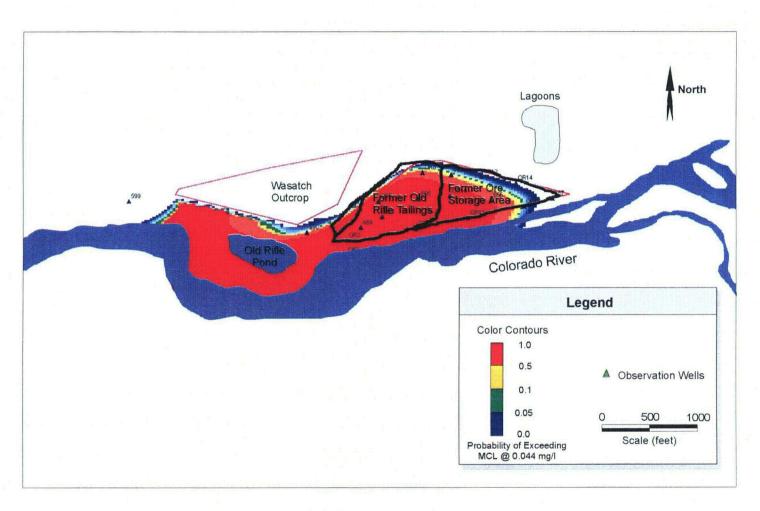
Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 50 years after Conditioning Time, 2048



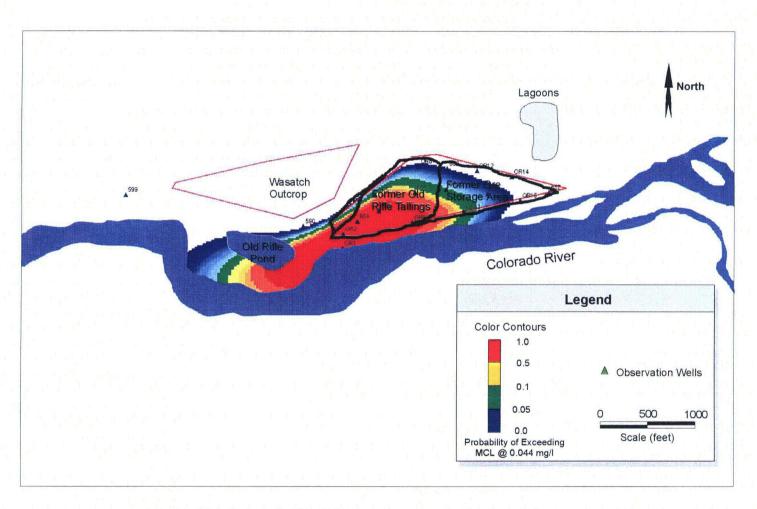
Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 75 years after Conditioning Time, 2073



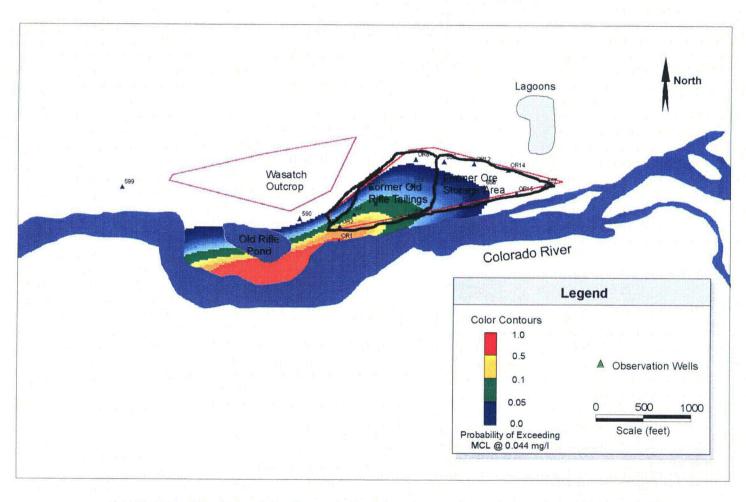
Average Uranium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 100 years after Conditioning Time, 2098



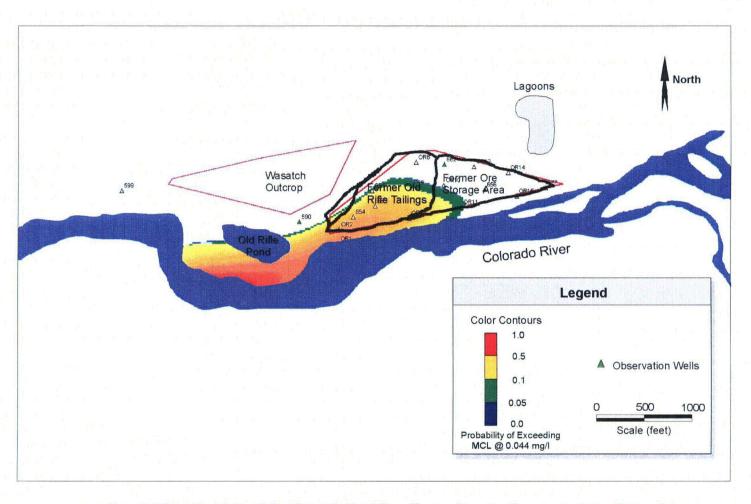
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Uranium (0.044 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - Conditioning Time, 1998



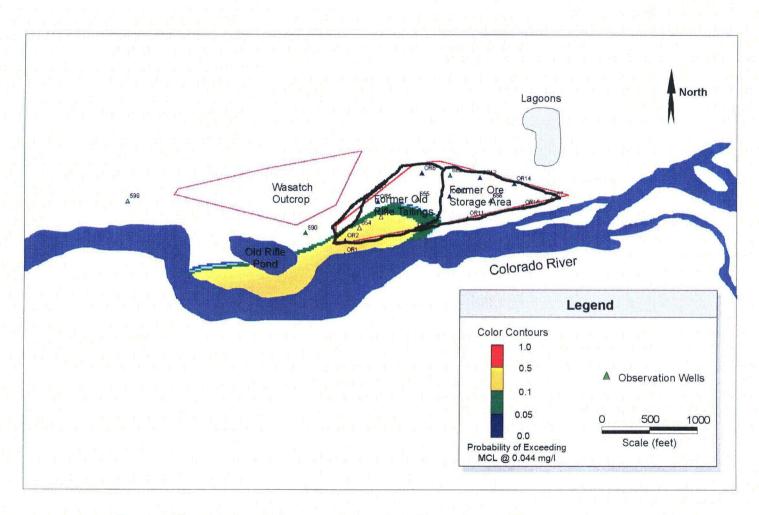
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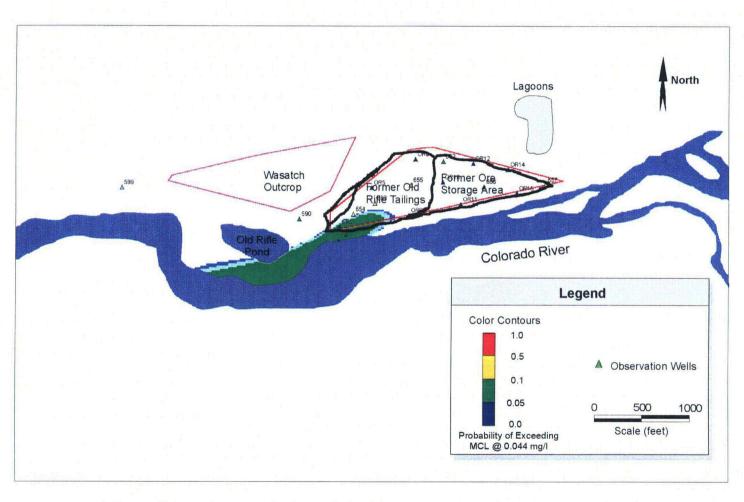
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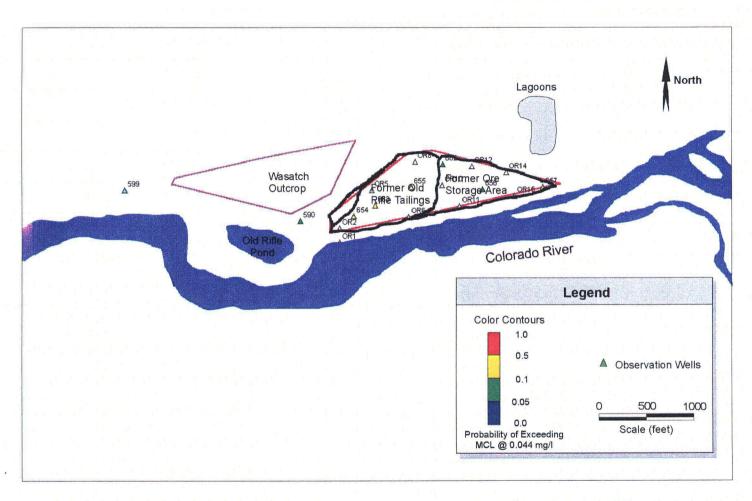
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Uranium (0.044 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 30 years after Conditioning Time, 2028



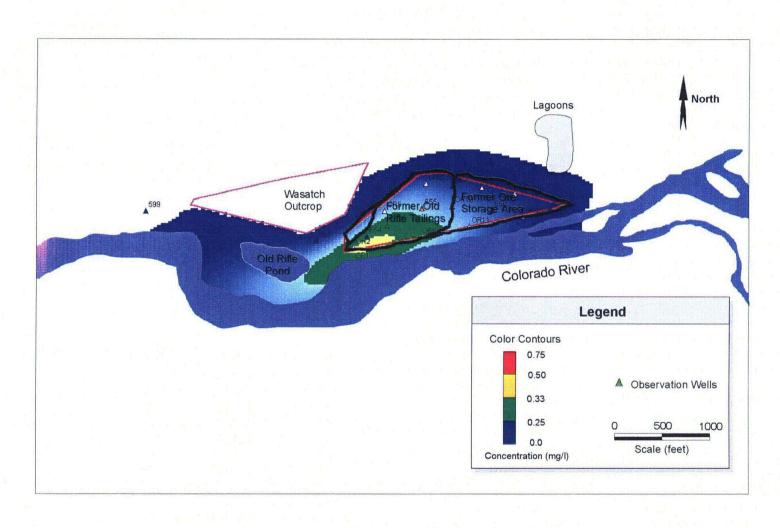
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Uranium (0.044 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 40 years after Conditioning Time, 2038



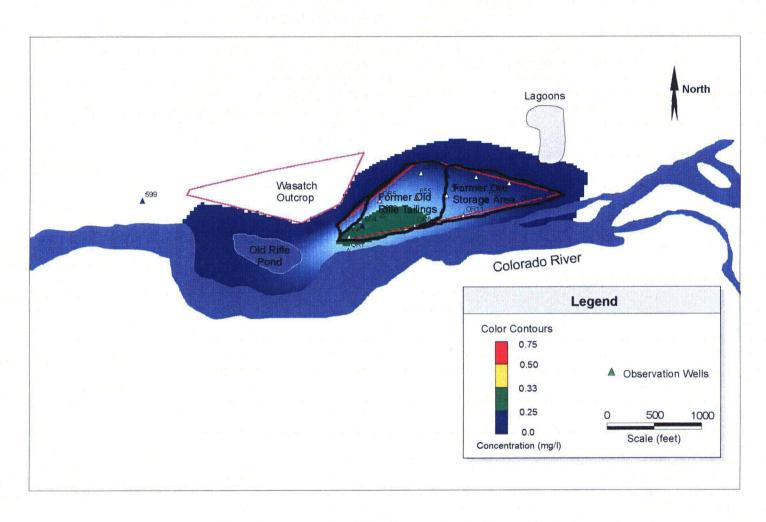
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Uranium (0.044 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 50 years after Conditioning Time, 2048



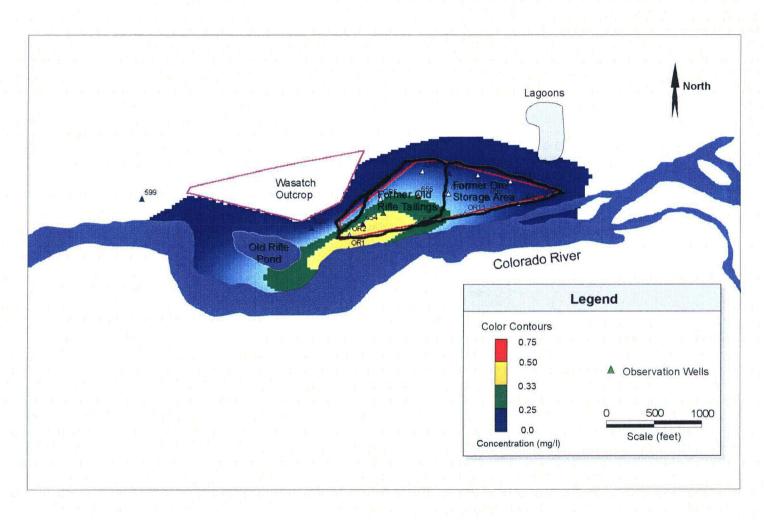
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Uranium (0.044 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 75 years after Conditioning Time, 2073



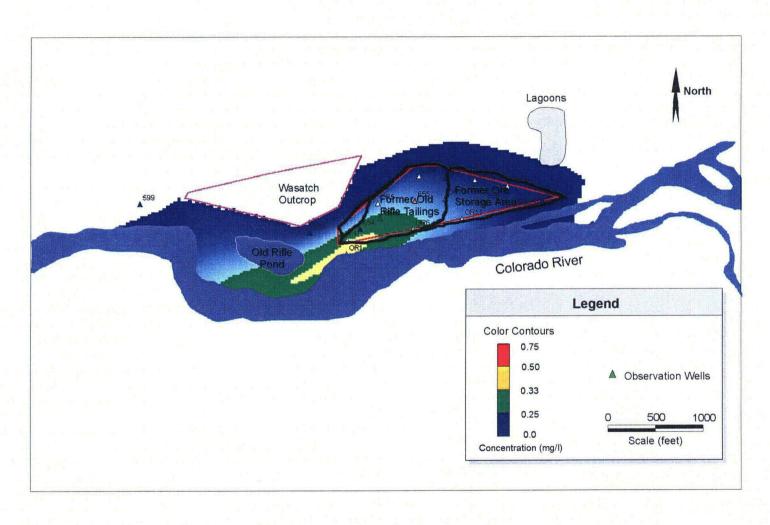
Average Vanadium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - Conditioning Time, 1998



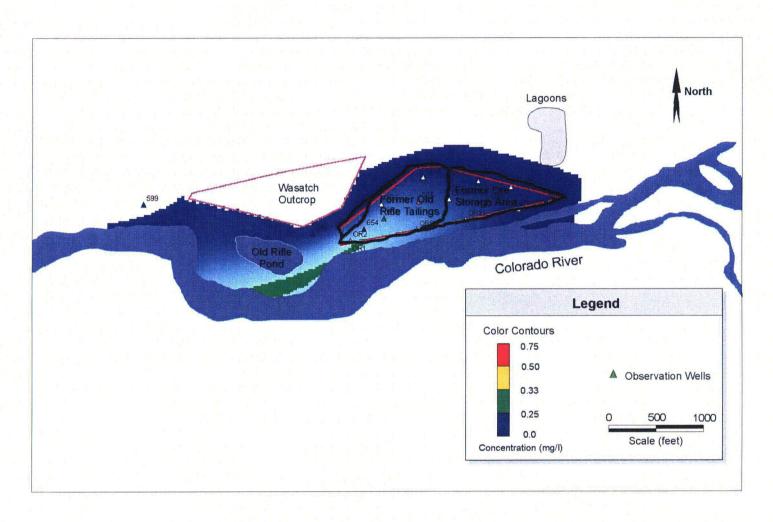
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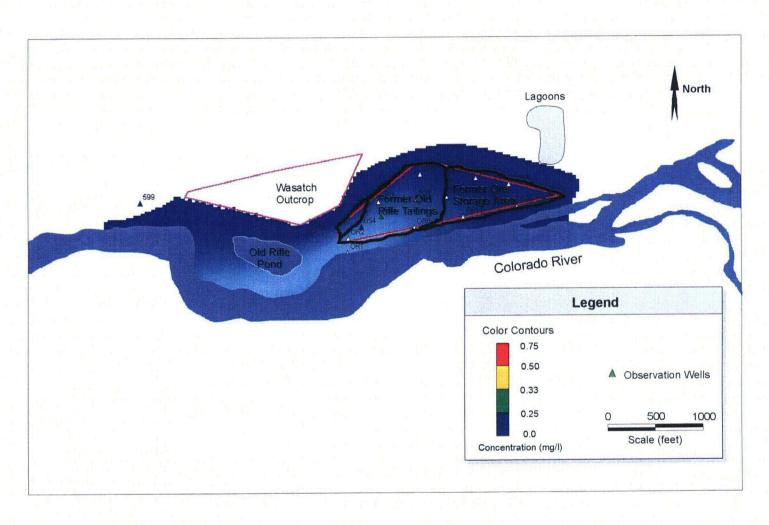
Average Vanadium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 25 years after Conditioning Time, 2023



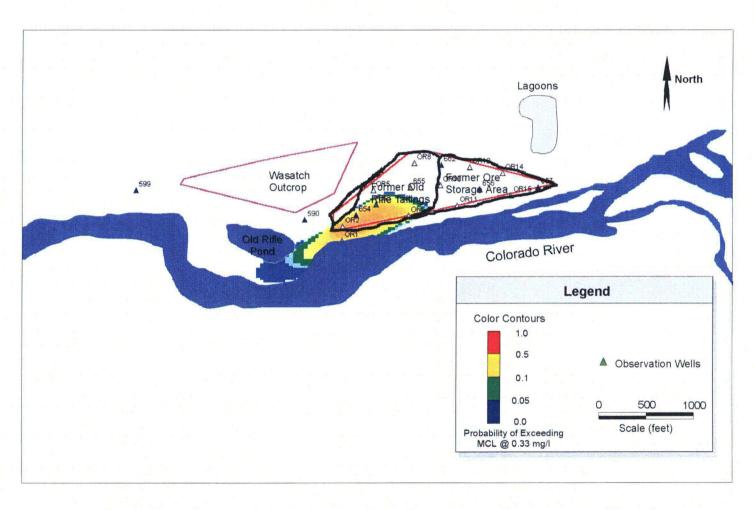
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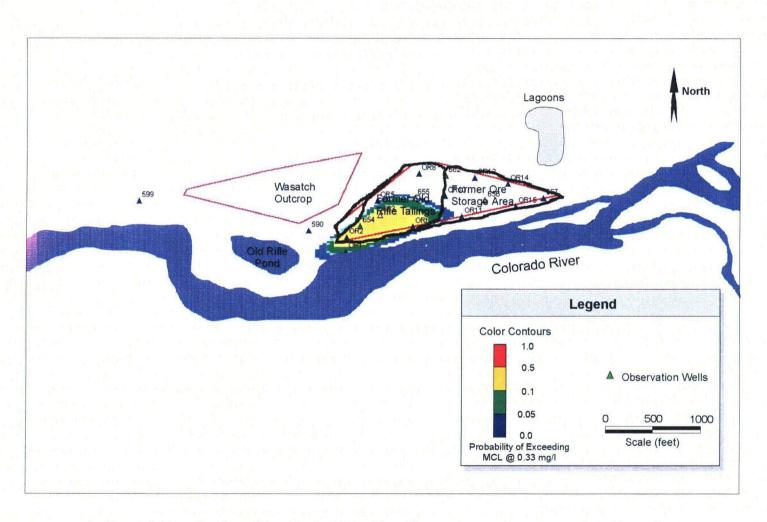
Average Vanadium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 75 years after Conditioning Time, 2073



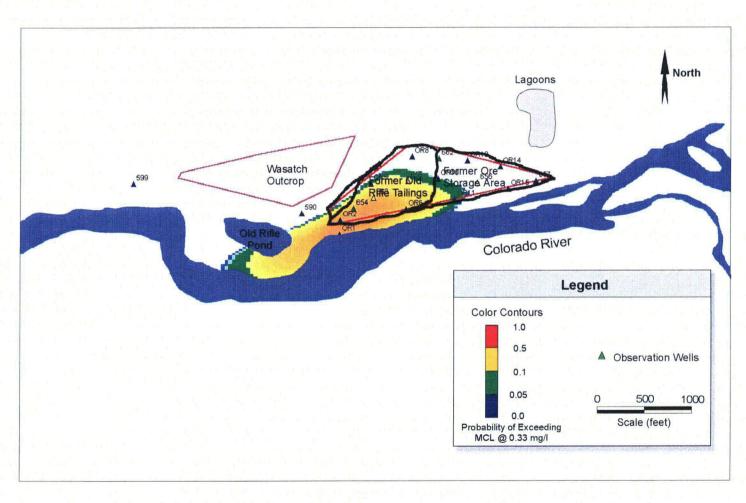
Average Vanadium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 100 years after Conditioning Time, 2098



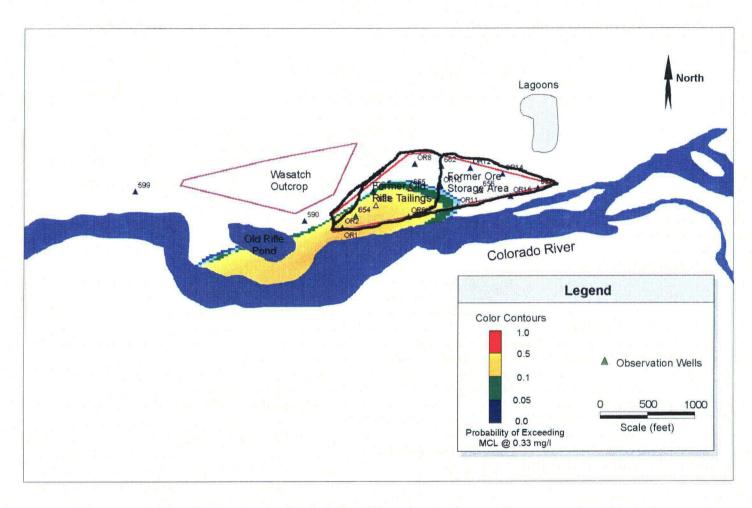
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Vanadium (0.33 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - At the Conditioning Time, 1998



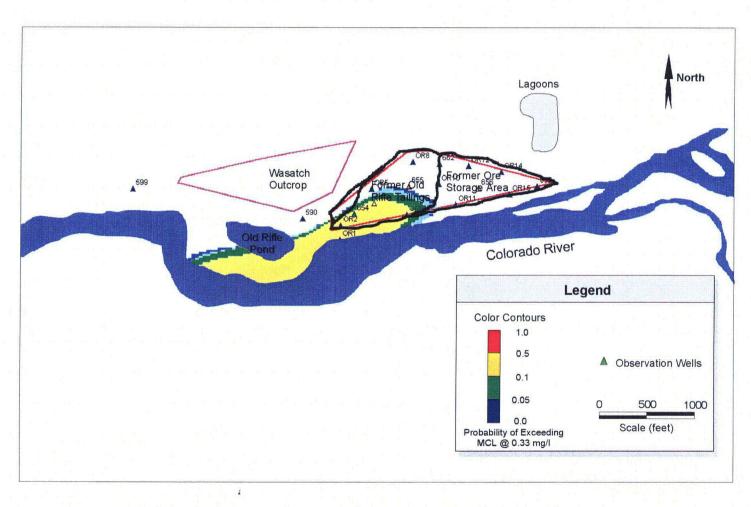
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Vanadium (0.33 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 10 years after Conditioning Time, 2008



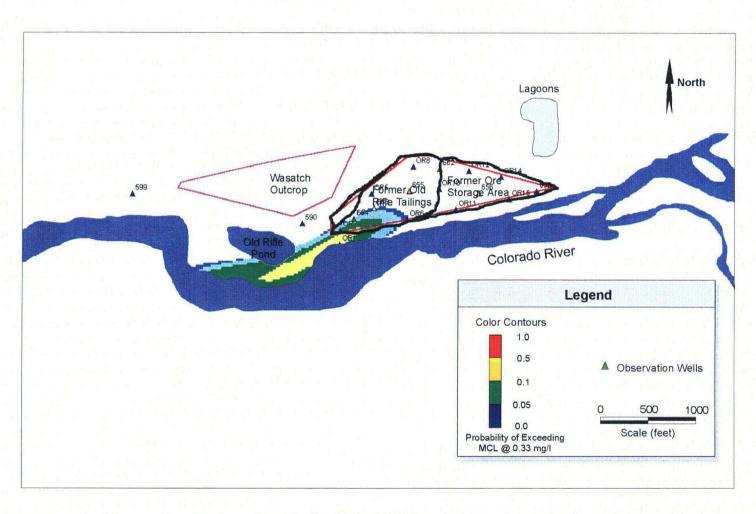
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Vanadium (0.33 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 25 years after Conditioning Time, 2023



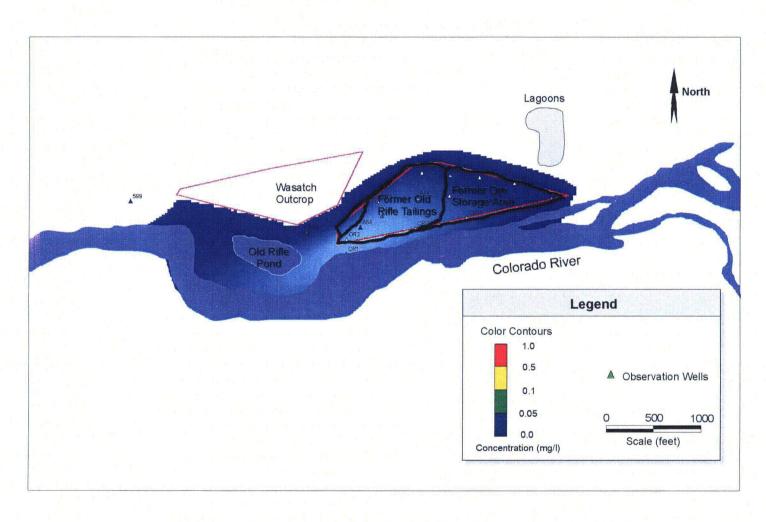
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Vanadium (0.33 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 50 years after Conditioning Time, 2048



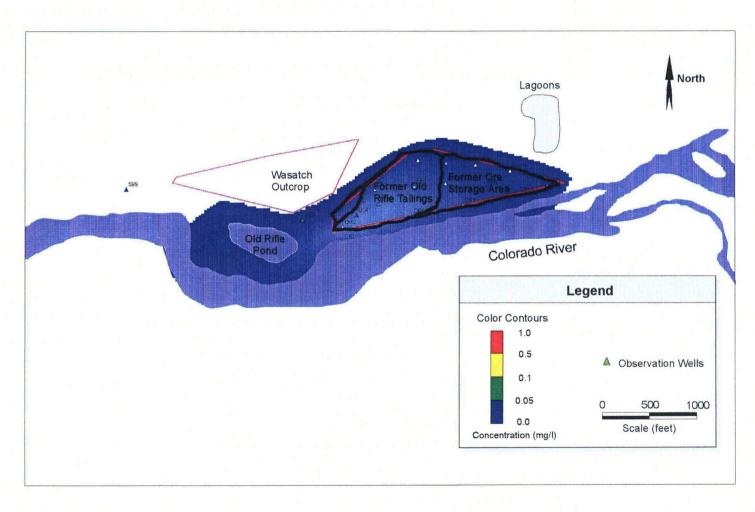
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Vanadium (0.33 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 75 years after Conditioning Time, 2073



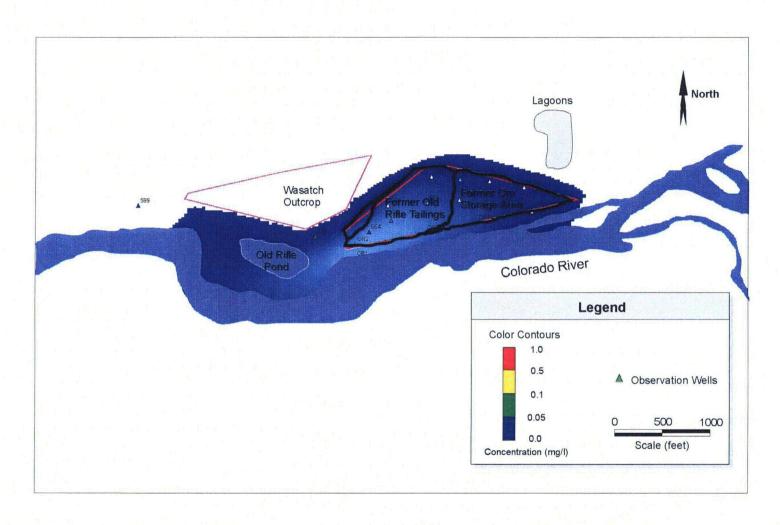
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Vanadium (0.33 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 100 years after Conditioning Time, 2098



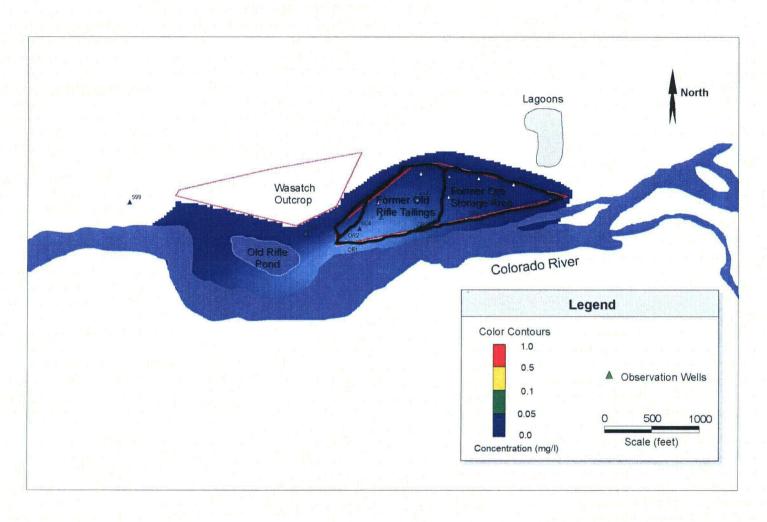
Average Selenium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - Conditioning Time, 1998



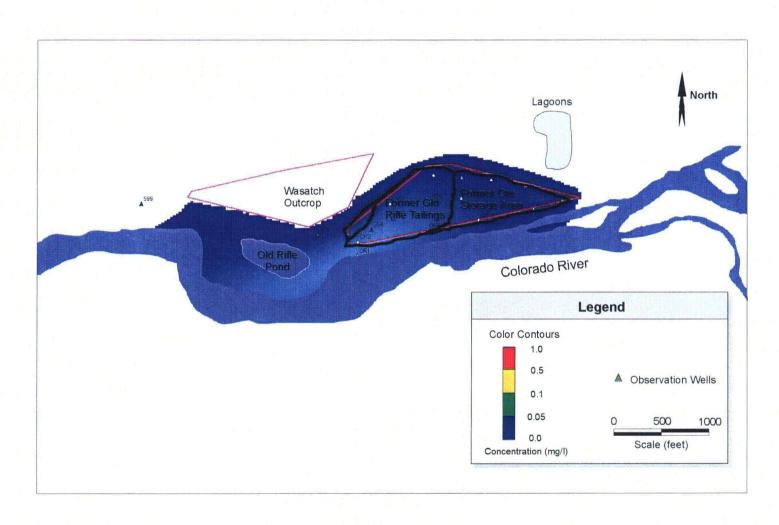
Average Selenium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 10 years after Conditioning Time, 2008



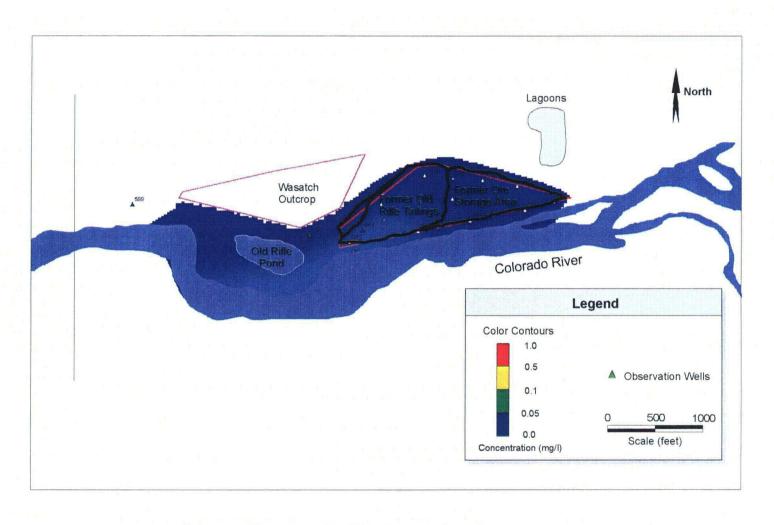
Average Selenium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 20 years after Conditioning Time, 2018



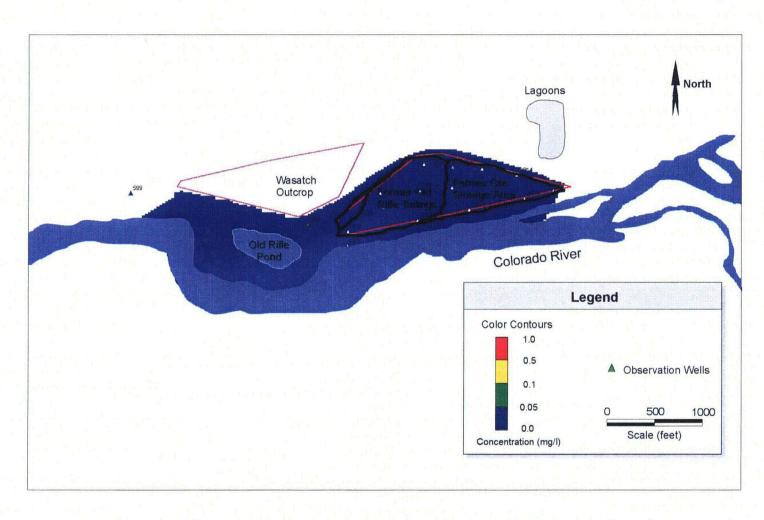
Average Selenium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 30 years after Conditioning Time, 2028



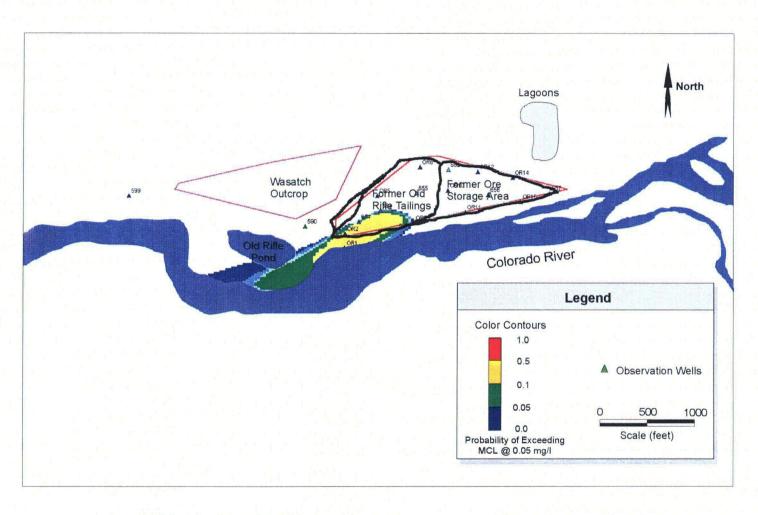
Average Selenium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 50 years after Conditioning Time, 2048



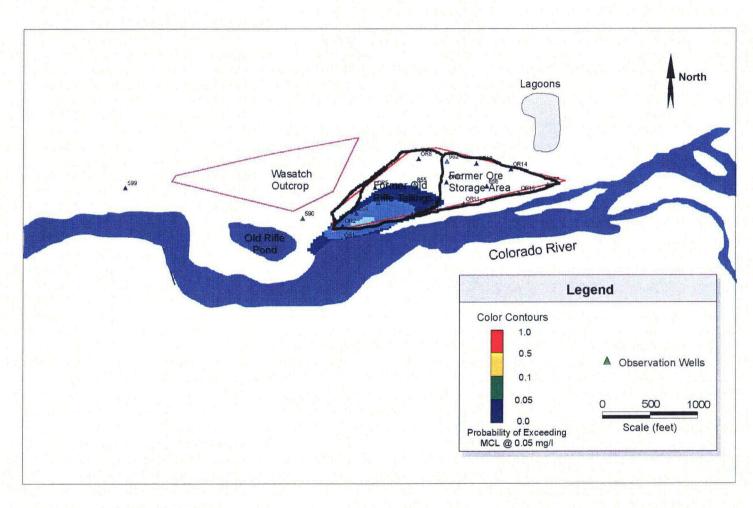
Average Selenium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 75 years after Conditioning Time, 2073



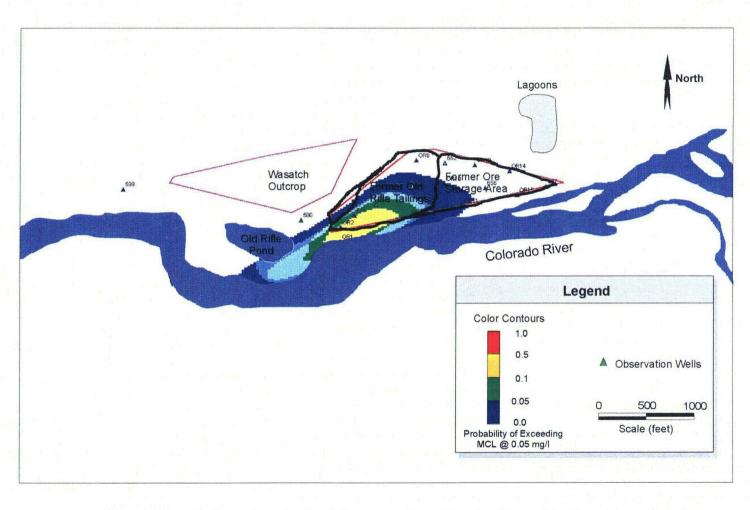
Average Selenium Concentration Distribution From Uncertainty Analysis at the UMTRA Old Rifle Site - 100 years after Conditioning Time, 2098



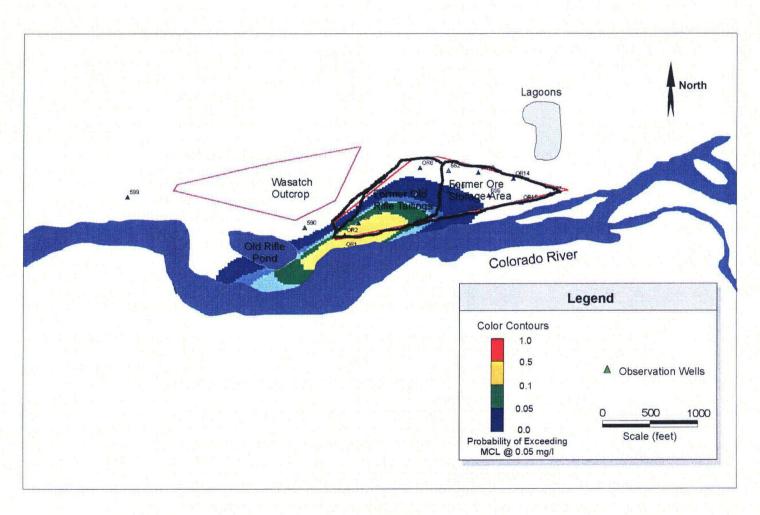
Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Selenium (0.05 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - At the Conditioning Time, 1998



Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Selenium (0.05 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 10 years after Conditioning Time, 2008



Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Selenium (0.05 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 20 years after Conditioning Time, 2018



Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Selenium (0.05 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 30 years after Conditioning Time, 2028



O-RFL-13) LOOKING EAST DURING REMEDIAL ACTION RIFLE, CO - JULY 13, 1994

NEG# 94-RFL-JUL-22



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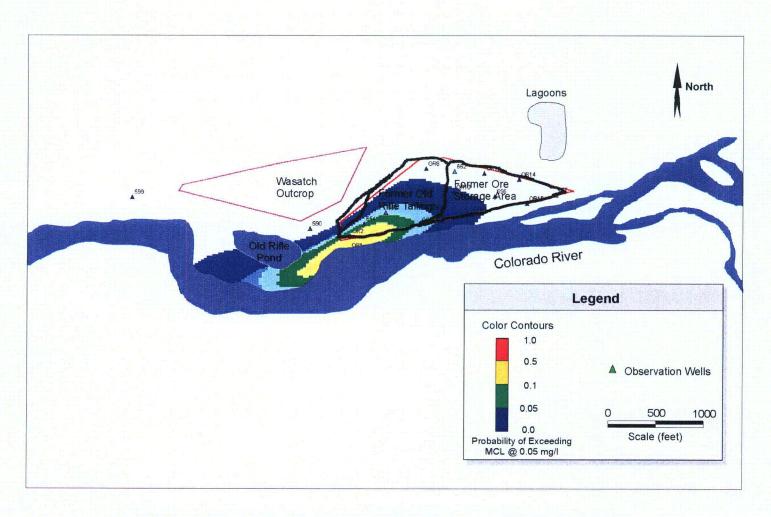
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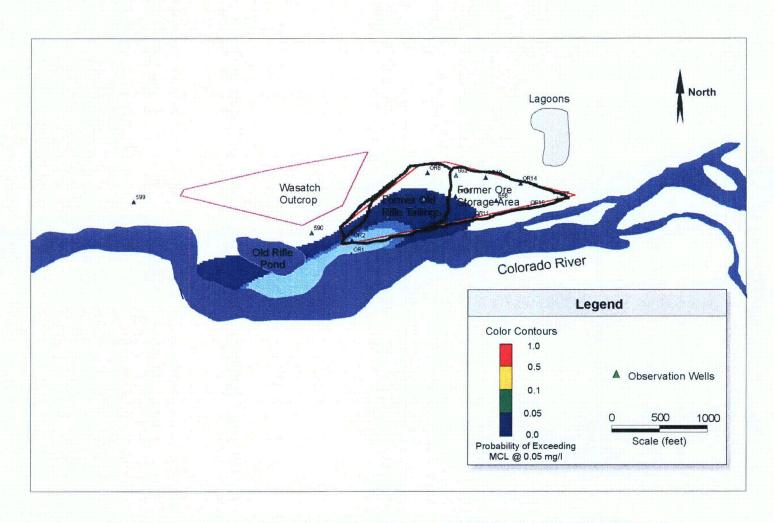


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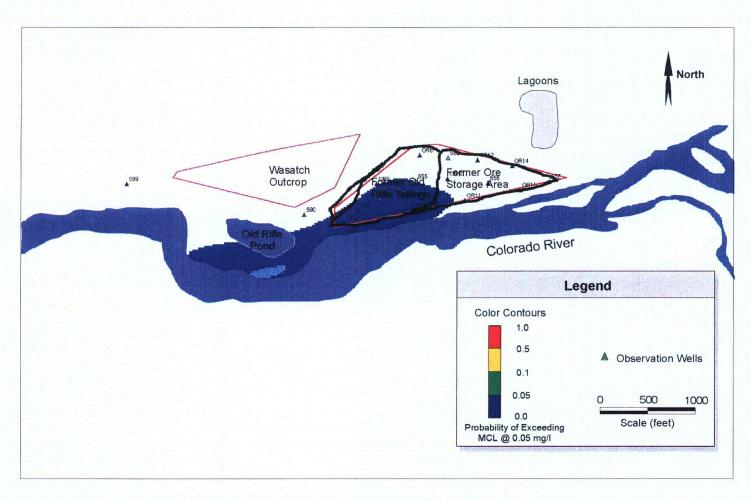
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Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Selenium (0.05 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 50 years after Conditioning Time, 2048



Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Selenium (0.05 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 75 years after Conditioning Time, 2073



Spatial Distribution of the Probability That Groundwater Concentrations Exceed the MCL for Selenium (0.05 mg/l) From Uncertainty Analysis at the UMTRA Old Rifle Site - 100 years after Conditioning Time, 2098