

Appendix B, Appendix D
Mann-Kendall Test Description

16.3.3 Intervention Analysis and Box-Jenkins Models

If a long time sequence of equally spaced data is available, intervention analysis may be used to detect changes in average level resulting from a natural or man-induced intervention in the process. This approach, developed by Box and Tiao (1975), is a generalization of the autoregressive integrated moving-average (ARIMA) time series models described by Box and Jenkins (1976). Lettenmaier and Murray (1977) and Lettenmaier (1978) study the power of the method to detect trends. They emphasize the design of sampling plans to detect impacts from polluting facilities. Examples of its use are in Hipel et al. (1975) and Roy and Pellerin (1982).

Box-Jenkins modeling techniques are powerful tools for the analysis of time series data. McMichael and Hunter (1972) give a good introduction to Box-Jenkins modeling of environmental data, using both deterministic and stochastic components to forecast temperature flow in the Ohio River. Fuller and Tsokos (1971) develop models to forecast dissolved oxygen in a stream. Carlson, MacCormick, and Watts (1970) and McKerchar and Delleur (1974) fit Box-Jenkins models to monthly river flows. Hsu and Hunter (1976) analyze annual series of air pollution SO_2 concentrations. McCollister and Wilson (1975) forecast daily maximum and hourly average total oxidant and carbon monoxide concentrations in the Los Angeles Basin. Hipel, McLeod, and Lennox (1977a, 1977b) illustrate improved Box-Jenkins techniques to simplify model construction. Reinsel et al. (1981a, 1981b) use Box-Jenkins models to detect trends in stratospheric ozone data. Two introductory textbooks are McCleary and Hay (1980) and Chatfield (1984). Box and Jenkins (1976) is recommended reading for all users of the method.

Disadvantages of Box-Jenkins methods are discussed by Montgomery and Johnson (1976). At least 50 and preferably 100 or more data collected at equal (or approximately equal) time intervals are needed. When the purpose is forecasting, we must assume the developed model applies to the future. Missing data or data reported as trace or less-than values can prevent the use of Box-Jenkins methods. Finally, the modeling process is often nontrivial, with a considerable investment in time and resources required to build a satisfactory model. Fortunately, there are several packages of statistical programs that contain codes for developing time series models, including Minitab (Ryan, Joiner, and Ryan 1982), SPSS (1985), BMDP (1983), and SAS (1985). Codes for personal computers are also becoming available.

16.4 MANN-KENDALL TEST

In this section we discuss the nonparametric Mann-Kendall test for trend (Mann, 1945; Kendall, 1975). This procedure is particularly useful since missing values are allowed and the data need not conform to any particular distribution. Also, data reported as trace or less than the detection limit can be used (if it is acceptable in the context of the population being sampled) by assigning them a common value that is smaller than the smallest measured value in the data set. This approach can be used because the Mann-Kendall test (and the seasonal Kendall test in Chapter 17) use only the relative magnitudes of the data rather

From Eilbert, Richard O., 1987. Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold, NY, 320p.

than their measured values. We note that the Mann-Kendall test can be viewed as a nonparametric test for zero slope of the linear regression of time-ordered data versus time, as illustrated by Hollander and Wolfe (1973, p. 201).

16.4.1 Number of Data 40 or Less

If n is 40 or less, the procedure in this section may be used. When n exceeds 40, use the normal approximation test in Section 16.4.2. We begin by considering the case where only one datum per time period is taken, where a time period may be a day, week, month, and so on. The case of multiple data values per time period is discussed in Section 16.4.3.

The first step is to list the data in the order in which they were collected over time: x_1, x_2, \dots, x_n , where x_i is the datum at time i . Then determine the sign of all $n(n-1)/2$ possible differences $x_j - x_k$, where $j > k$. These differences are $x_2 - x_1, x_3 - x_1, \dots, x_n - x_1, x_3 - x_2, x_4 - x_2, \dots, x_n - x_{n-2}, x_n - x_{n-1}$. A convenient way of arranging the calculations is shown in Table 16.1.

Let $\text{sgn}(x_j - x_k)$ be an indicator function that takes on the values 1, 0, or -1 according to the sign of $x_j - x_k$:

$$\begin{aligned} \text{sgn}(x_j - x_k) &= 1 && \text{if } x_j - x_k > 0 \\ &= 0 && \text{if } x_j - x_k = 0 \\ &= -1 && \text{if } x_j - x_k < 0 \end{aligned} \quad 16.1$$

Then compute the Mann-Kendall statistic

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^n \text{sgn}(x_j - x_k) \quad 16.2$$

which is the number of positive differences minus the number of negative differences. These differences are easily obtained from the last two columns of Table 16.1. If S is a large positive number, measurements taken later in time tend to be larger than those taken earlier. Similarly, if S is a large negative number, measurements taken later in time tend to be smaller. If n is large, the computer code in Appendix B may be used to compute S . This code also computes the tests for trend discussed in Chapter 17.

Suppose we want to test the null hypothesis, H_0 , of no trend against the alternative hypothesis, H_A , of an upward trend. Then H_0 is rejected in favor of H_A if S is positive and if the probability value in Table A18 corresponding to the computed S is less than the a priori specified α significance level of the test. Similarly, to test H_0 against the alternative hypothesis H_A of a downward trend, reject H_0 and accept H_A if S is negative and if the probability value in the table corresponding to the absolute value of S is less than the a priori specified α value. If a two-tailed test is desired, that is, if we want to detect either an upward or downward trend, the tabled probability level corresponding to the absolute value of S is doubled and H_0 is rejected if that doubled value is less than the a priori α level.

EXAMPLE 16.1

We wish to test the null hypothesis H_0 , of no trend versus the alternative hypothesis, H_A , of an upward trend at the $\alpha = 0.10$

Table 16.1 Differences in Data Values Needed for Computing the Mann-Kendall Statistic S to Test for Trend

<i>Data Values Listed in the Order Collected Over Time</i>							<i>No. of + Signs</i>	<i>No. of - Signs</i>
x_1	x_2	x_3	x_4	...	x_{n-1}	x_n		
	$x_2 - x_1$	$x_3 - x_1$	$x_4 - x_1$...	$x_{n-1} - x_1$	$x_n - x_1$		
		$x_3 - x_2$	$x_4 - x_2$...	$x_{n-1} - x_2$	$x_n - x_2$		
			$x_4 - x_3$...	$x_{n-1} - x_3$	$x_n - x_3$		
				...	$x_{n-1} - x_{n-2}$	$x_n - x_{n-2}$		
						$x_n - x_{n-1}$		
							$S =$	$\left(\begin{array}{c} \text{sum of} \\ + \text{ signs} \end{array} \right) + \left(\begin{array}{c} \text{sum of} \\ - \text{ signs} \end{array} \right)$

Table 16.2 Computation of the Mann-Kendall Trend Statistic S for the Time Ordered Data Sequence 10, 15, 14, 20

Time Data	1 10	2 15	3 14	4 20	No. of + Signs	No. of - Signs
		15 - 10	14 - 10	20 - 10	3	0
			14 - 15	20 - 15	1	1
				20 - 14	1	0
				$S =$	$\bar{5}$	$\bar{1} = 4$

significance level. For ease of illustration suppose only 4 measurements are collected in the following order over time or along a line in space: 10, 15, 14, and 20. There are 6 differences to consider: 15 - 10, 14 - 10, 20 - 10, 14 - 15, 20 - 15, and 20 - 14. Using Eqs. 16.1 and 16.2, we obtain $S = +1 + 1 + 1 - 1 + 1 + 1 = +4$, as illustrated in Table 16.2. (Note that the sign, not the magnitude of the difference is used.) From Table A18 we find for $n = 4$ that the tabled probability for $S = +4$ is 0.167. This number is the probability of obtaining a value of S equal to +4 or larger when $n = 4$ and when no upward trend is present. Since this value is greater than 0.10, we cannot reject H_0 .

If the data sequence had been 18, 20, 23, 35, then $S = +6$, and the tabled probability is 0.042. Since this value is less than 0.10, we reject H_0 and accept the alternative hypothesis of an upward trend.

Table A18 gives probability values only for $n \leq 10$. An extension of this table up to $n = 40$ is given in Table A.21 in Hollander and Wolfe (1973).

16.4.2 Number of Data Greater Than 40

When n is greater than 40, the normal approximation test described in this section is used. Actually, Kendall (1975, p. 55) indicates that this method may be used for n as small as 10 unless there are many tied data values. The test procedure is to first compute S using Eq. 16.2 as described before. Then compute the variance of S by the following equation, which takes into account that ties may be present:

$$\text{VAR}(S) = \frac{1}{18} \left[n(n-1)(2n+5) - \sum_{p=1}^g t_p(t_p-1)(2t_p+5) \right] \quad 16.3$$

where g is the number of tied groups and t_p is the number of data in the p th group. For example, in the sequence {23, 24, trace, 6, trace, 24, 24, trace, 23} we have $g = 3$, $t_1 = 2$ for the tied value 23, $t_2 = 3$ for the tied value 24, and $t_3 = 3$ for the three trace values (considered to be of equal but unknown value less than 6).

Then S and $\text{VAR}(S)$ are used to compute the test statistic Z as follows:

$$\begin{aligned} Z &= \frac{S-1}{[\text{VAR}(S)]^{1/2}} && \text{if } S > 0 \\ &= 0 && \text{if } S = 0 \\ &= \frac{S+1}{[\text{VAR}(S)]^{1/2}} && \text{if } S < 0 \end{aligned} \quad 16.4$$

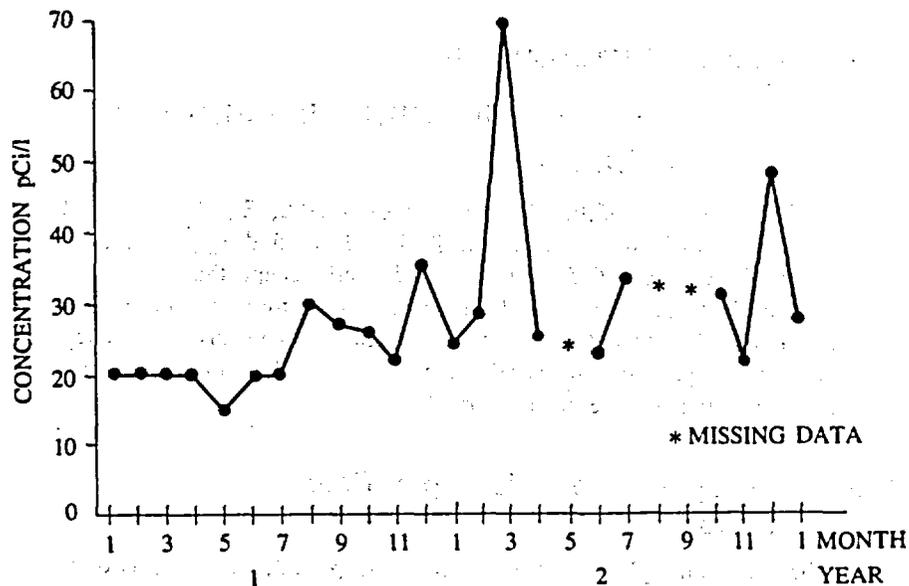


Figure 16.2 Concentrations of ^{238}U in ground water in well E at the former St. Louis Airport storage site for January 1981 through January 1983 (after Clark and Berven, 1984).

A positive (negative) value of Z indicates an upward (downward) trend. If the null hypothesis, H_0 , of no trend is true, the statistic Z has a standard normal distribution, and hence we use Table A1 to decide whether to reject H_0 . To test for either upward or downward trend (a two-tailed test) at the α level of significance, H_0 is rejected if the absolute value of Z is greater than $Z_{1-\alpha/2}$, where $Z_{1-\alpha/2}$ is obtained from Table A1. If the alternative hypothesis is for an upward trend (a one-tailed test), H_0 is rejected if Z (Eq. 16.4) is greater than $Z_{1-\alpha}$. We reject H_0 in favor of the alternative hypothesis of a downward trend if Z is negative and the absolute value of Z is greater than $Z_{1-\alpha/2}$. Kendall (1975) indicates that using the standard normal tables (Table A1) to judge the statistical significance of the Z test will probably introduce little error as long as $n \geq 10$ unless there are many groups of ties and many ties within groups.

EXAMPLE 16.2

Figure 16.2 is a plot of $n = 22$ monthly ^{238}U concentrations $x_1, x_2, x_3, \dots, x_{22}$ obtained from a groundwater monitoring well from January 1981 through January 1983 (reported in Clark and Berven, 1984). We use the Mann-Kendall procedure to test the null hypothesis at the $\alpha = 0.05$ level that there is no trend in ^{238}U groundwater concentrations at this well over this 2-year period. The alternative hypothesis is that an upward trend is present.

There are $n(n-1)/2 = 22(21)/2 = 231$ differences to examine for their sign. The computer code in Appendix B was used to obtain S and Z (Eqs. 16.2 and 16.4). We find that $S = +108$. Since there are 6 occurrences of the value 20 and 2 occurrences of both 23 and 30, we have $g = 3$, $t_1 = 6$, and $t_2 = t_3 = 2$. Hence, Eq. 16.3 gives

$$\begin{aligned}\text{VAR}(S) &= \frac{1}{18} [22(21)(44 + 5) \\ &\quad - 6(5)(12 + 5) - 2(1)(4 + 5) - 2(1)(4 + 5)] \\ &= 1227.33\end{aligned}$$

or $[\text{VAR}(S)]^{1/2} = 35.0$. Therefore, since $S > 0$, Eq. 16.4 gives $Z = (108 - 1)/35.0 = 3.1$. From Table A1 we find $Z_{0.95} = 1.645$. Since Z exceeds 1.645, we reject H_0 and accept the alternative hypothesis of an upward trend. We note that the three missing values in Figure 16.2 do not enter into the calculations in any way. They are simply ignored and constitute a regrettable loss of information for evaluating the presence of trend.

16.4.3 Multiple Observations per Time Period

When there are multiple observations per time period, there are two ways to proceed. First, we could compute a summary statistic, such as the median, for each time period and apply the Mann-Kendall test to the medians. An alternative approach is to consider the $n_i \geq 1$ multiple observations at time i (or time period i) as ties in the time index. For this latter case the statistic S is still computed by Eq. 16.2, where n is now the sum of the n_i , that is, the total number of observations rather than the number of time periods. The differences between data obtained at the same time are given the score 0 no matter what the data values may be, since they are tied in the time index.

When there are multiple observations per time period, the variance of S is computed by the following equation, which accounts for ties in the time index:

$$\begin{aligned}\text{VAR}(S) &= \frac{1}{18} \left[n(n-1)(2n+5) - \sum_{p=1}^g t_p(t_p-1)(2t_p+5) \right. \\ &\quad \left. - \sum_{q=1}^h u_q(u_q-1)(2u_q+5) \right] \\ &\quad + \frac{\sum_{p=1}^g t_p(t_p-1)(t_p-2) \sum_{q=1}^h u_q(u_q-1)(u_q-2)}{9n(n-1)(n-2)} \\ &\quad + \frac{\sum_{p=1}^g t_p(t_p-1) \sum_{q=1}^h u_q(u_q-1)}{2n(n-1)}\end{aligned}\tag{16.5}$$

where g and t_p are as defined following Eq. 16.3, h is the number of time periods that contain multiple data, and u_q is the number of multiple data in the q th time period. Equation 16.5 reduces to Eq. 16.3 when there is one observation per time period.

Equations 16.3 and 16.5 assume all data are independent and, hence, uncorrelated. If observations taken during the same time period are highly correlated, it may be preferable to apply the Mann-Kendall test to the medians of the data in each time period rather than use Eq. 16.5 in Eq. 16.4.

Table A18 Probabilities for the Mann-Kendall Nonparametric Test for Trend

S	Values of n				S	Values of n		
	4	5	8	9		6	7	10
0	0.625	0.592	0.548	0.540	1	0.500	0.500	0.500
2	0.375	0.408	0.452	0.460	3	0.360	0.386	0.431
4	0.167	0.242	0.360	0.381	5	0.235	0.281	0.364
6	0.042	0.117	0.274	0.306	7	0.136	0.191	0.300
8		0.042	0.199	0.238	9	0.068	0.119	0.242
10		0.0 ² 83	0.138	0.179	11	0.028	0.068	0.190
12			0.089	0.130	13	0.0 ² 83	0.035	0.146
14			0.054	0.090	15	0.0 ² 14	0.015	0.108
16			0.031	0.060	17		0.0 ² 54	0.078
18			0.016	0.038	19		0.0 ² 14	0.054
20			0.0 ² 71	0.022	21		0.0 ³ 20	0.036
22			0.0 ² 28	0.012	23			0.023
24			0.0 ³ 87	0.0 ² 63	25			0.014
26			0.0 ³ 19	0.0 ² 29	27			0.0 ² 83
28			0.0 ⁴ 25	0.0 ² 12	29			0.0 ² 46
30				0.0 ³ 43	31			0.0 ² 23
32				0.0 ³ 12	33			0.0 ² 11
34				0.0 ⁴ 25	35			0.0 ³ 47
36				0.0 ⁵ 28	37			0.0 ³ 18
					39			0.0 ⁴ 58
					41			0.0 ⁴ 15
					43			0.0 ⁵ 28
					45			0.0 ⁶ 28

Source: From Kendall, 1975. Used by permission.

Repeated zeros are indicated by powers; for example, 0.0³47 stands for 0.00047.

Each table entry is the probability that the Mann-Kendall statistic S equals or exceeds the specified value of S when no trend is present.

This table is used in Section 16.4.1.

Appendix C

Alternate Concentration Limits Application

**Application for Alternate Concentration Limits
for the New Rifle, Colorado, UMTRA Project Site**

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1.0 Introduction

1.1 Purpose

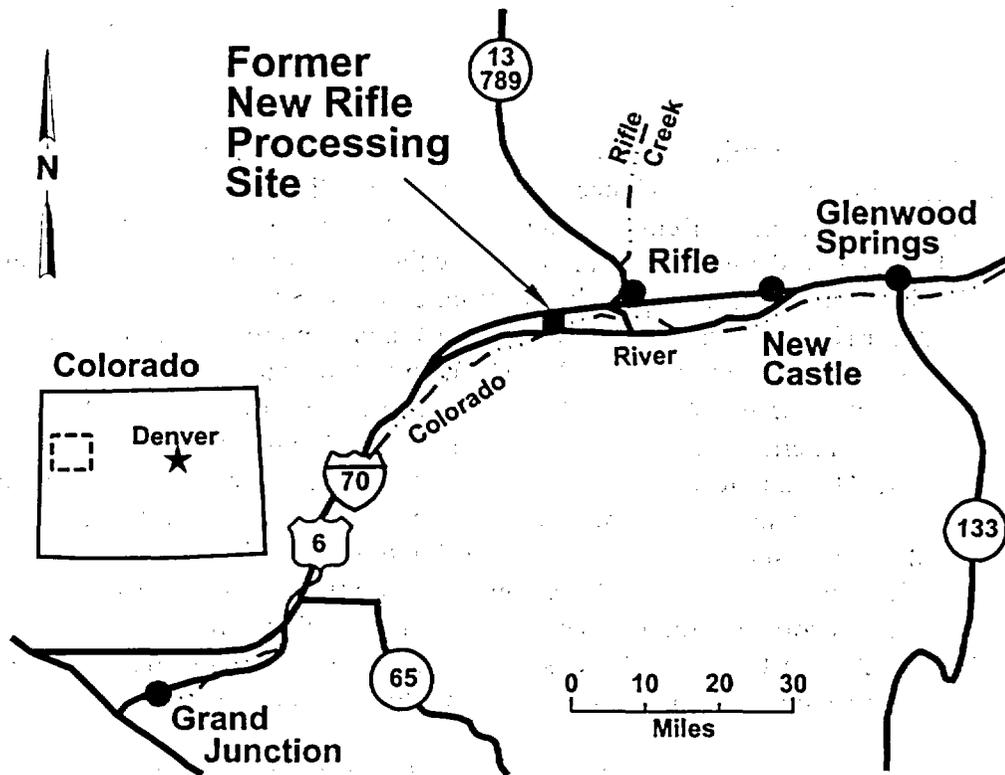
The purpose of this document is to fulfill the Nuclear Regulatory Commission (NRC) requirements for an application for Alternate Concentration Limits (ACLs) for three constituents at the Uranium Mill Tailings Remedial Action (UMTRA) Project New Rifle Site ("New Rifle"), Colorado. Much of the information required by the NRC for an ACL application (10 CFR Part 40, Appendix A and NRC 1996) has been compiled in the Site Observational Work Plan (SOWP; DOE 1999) for New Rifle as well as the Ground Water Compliance Action Plan (GCAP). This document is an attachment to the GCAP. The intent of this attachment is not to duplicate information found elsewhere, but to provide a link between NRC evaluation criteria and relevant detailed discussion pertaining to those criteria in previously prepared documents. NRC guidance for preparing ACL applications for Title II sites (NRC 1996) was used as a model for this application. This document summarizes pertinent information from the SOWP regarding "Factors Considered in Making Present and Potential Hazard Findings" (Table 1 in NRC 1996; also specified in 40 CFR Part 192 with slight modifications). It also identifies sections of the SOWP that contain information corresponding to sections listed in the "Standard ACL Application Format" (Table 2 in NRC 1996). This ensures that all factors and information related to the proposed ACLs have been considered, while minimizing duplication of effort.

NRC's ACL guidance was prepared for Title II UMTRA sites. It is also noted that the guidance can be applied to Title I sites, with modifications made to accommodate the differences between Title II and Title I sites. One of the major differences between these sites is that the regulations for Title I sites (40 CFR Part 192) permit natural flushing as the selected ground water compliance strategy, providing that ground water will reach acceptable levels (UMTRA standards, background, or ACLs) within a period of 100 years. Therefore Title I sites have an extended timeframe for achieving compliance, which is factored into the alternatives evaluation.

Section 2.0 of this document briefly discusses the constituents for which ACLs are proposed and the rationale for the numerical values. Section 3.0 summarizes the factors considered in making hazard findings. Section 4.0 presents the "roadmap" to the SOWP following the standard ACL application format. References are included in Section 5.0.

1.2 Brief Site Background

Historically, vanadium and uranium ores were processed at two different mill sites located near the city of Rifle, Colorado. U.S. Vanadium Company constructed the first mill in 1924 for the production of vanadium (Merritt 1971). This plant was located approximately 0.3 miles east of the city and is referred to as the Old Rifle site. Union Carbide and Carbon Corporation (Union Carbide) purchased the assets of the U.S. Vanadium Company in 1926 and established the U.S. Vanadium Corporation as a subsidiary (Chenoweth 1982). The subsidiary operated the former Old Rifle plant intermittently until 1946 when it was modified to include the recovery of uranium as well as vanadium. Production continued until 1958 when the old plant was replaced with a new mill located approximately 2.3 miles west of the Old Rifle site. The former location of the new mill is referred to as the New Rifle site (Figure 1).



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Figure 1. Location of the New Rifle Site

Uranium and vanadium production at the New Rifle mill lasted from 1958 to 1984. Concentrated ore was shipped to the New Rifle mill from 1958 to the early 1960s from a variety of locations in the region. From 1964 to 1967, the New Rifle mill also processed lignite ash. From 1973 to 1984, part of the mill was used to produce vanadium; this operation, which did not produce tailings, involved processing vanadium-bearing solutions.

The Atomic Energy Commission (AEC) records document that 2,259,000 cubic yards of Old Rifle tailings and 1,802,019 tons of ore were processed. The west central portion of the New Rifle mill site contained 33 acres of tailings in two distinct piles. The combined piles measured approximately 1,600 ft in the north-south direction and approximately 1,150 ft in the east-west direction. Former holding ponds that held processing wastes (including vanadium and gypsum) were located east of the piles. The location of tailing piles, evaporation ponds, ore storage area, and mill buildings as they existed in 1974 are shown in Figure 2).

The tailing piles were partially stabilized by Union Carbide with the application of mulch and fertilizer. An irrigation system was installed to promote growth of native grasses that were planted. However, much of the pile did not revegetate, and wind and water eroded some of the tailings. The tailings pile at the beginning phase of surface remediation in 1989 is shown in Figure 3. All tailings, radiological contaminated materials, and associated process buildings and structures were removed from the site during the surface remedial action completed in 1996.

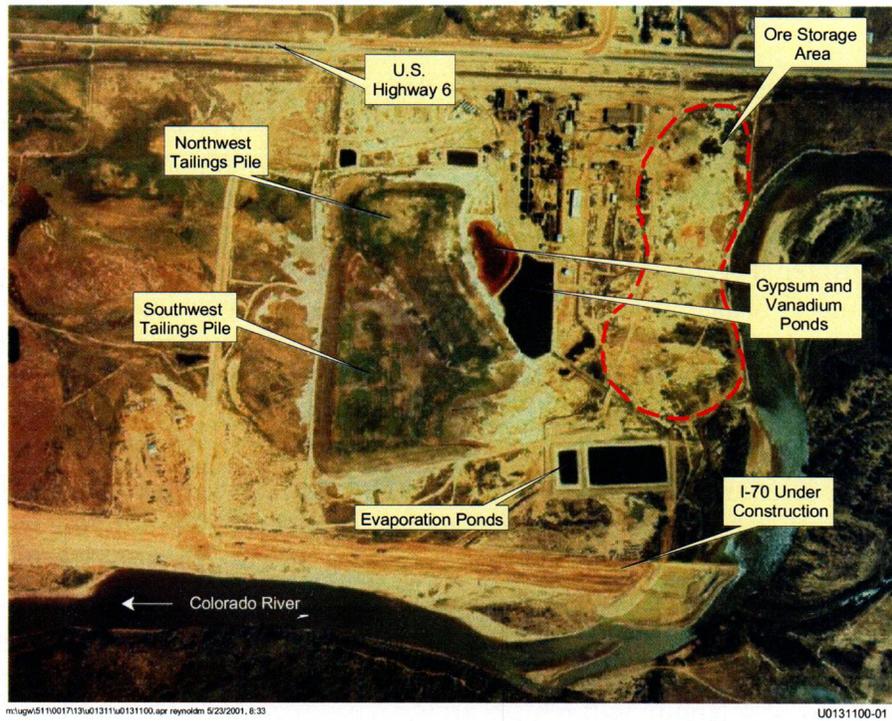


Figure 2. New Rifle Mill Site Showing the Location of the Northwest and Southwest Tailings Piles, Holding Ponds, Mill Buildings, and the Ore Storage Area—August 1974



Figure 3. View of the New Rifle Site Looking West During the Early Stages of Surface Remedial Action—August 1989

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2.0 Proposed ACLs

ACLs are proposed for three constituents at the New Rifle site—ammonia (as NH_4), selenium, and vanadium. An ACL for selenium is required because background concentrations in the surficial aquifer system exceed the UMTRA standard of 0.01 milligrams per liter (mg/L). An ACL is required for ammonia and vanadium because these constituents are elevated at the site above background concentrations and no standards have been established for ammonia and vanadium in ground water. The ACLs for ammonia and selenium are proposed cleanup goals (200 mg/L and 0.05 mg/L, respectively). The ACL for vanadium is considered to be an action level. Institutional controls will be put in place to ensure that no inappropriate uses of ground water take place during natural flushing or the extended period of time during which vanadium exceeds 0.33 mg/L.

The proposed ACL for selenium to be achieved by natural flushing is the Safe Drinking Water Act standard of 0.05 mg/L. This value corresponds to the national primary drinking water standard as well as the Colorado state drinking water standard. It is also well below the risk-based concentration of 0.18 mg/L, which corresponds to a maximum acceptable risk when used as drinking water on a regular basis (EPA 2001; EPA Region III risk-based concentration table). As long as the ACL is maintained at points of compliance (POC; any well in the monitoring network), concentrations of selenium will remain protective at the points of exposure (POE) in the Colorado River and in the ground water to the west (downgradient) of the UMETCO site, which is located adjacent to the mill site. Contaminants discharging to the river are diluted by a factor of 30,000 because of the high volume of river water; the selenium plume is not predicted to migrate beyond the UMETCO property boundary.

The ACL proposed for ammonia (as NH_4) is 200 mg/L, which will be met by natural flushing. The ACL is protective at the POE, and the remediation level would be protective of both human health and aquatic life. For human health in a residential exposure scenario 200 mg/L would be protective for the pathway posing the greatest risk—exposure to ammonia through inhalation in a residential setting. For ecological risk, if ground water with a concentration of 200 mg/L ammonia were to discharge to the Colorado River, levels of ammonia in the river would still be below applicable water quality criteria. Well RFN-635 is located directly adjacent to the Colorado River and surface water sampling location RFN-322. During the last few rounds of sampling of both the river and ground water, concentrations of ammonia in ground water ranged from 200 to 400 mg/L. Concentrations in river water ranged from 0.009 to 0.54 mg/L. Ambient water quality criteria for ammonia in surface water for pH and temperature conditions that existed during sampling are in the 2 to 3 mg/L range. Institutional controls would prevent unrestricted access to ground water for as long as the ACL is required. Therefore, the proposed ACL is protective of human health and aquatic life.

Vanadium concentrations in the ground water increased during surface remedial action and have been dropping ever since. Original modeling suggested that 300 years would be required for vanadium concentrations to be reduced to a risk-based value of 0.33 mg/L. Sampling data collected for the past 4 years does not agree with this prediction. The model was re-evaluated (see Appendix B) and found not to be reliable for predicting concentrations of vanadium. Instead another analytical technique was applied to vanadium data that indicated vanadium concentrations should decrease to levels below the 0.33 mg/L value in less than 100 years. Therefore, vanadium was added to the list of other COCs that will flush to acceptable

concentrations within 100 years. The risk-based concentration of 0.33 mg/L is the ACL for vanadium.

3.0 Factors Considered In Making Present and Potential Hazard Findings

The list of factors below is from the Title I regulations [40 CFR 192.02(c)(3)(ii)(B)(1) and (2), which differ slightly from those in the NRC Title II guidance, and add another factor to the ground water quality list.

3.1 Potential Adverse Effects on Ground Water Quality

- 3.1.1 The physical and chemical characteristics of constituents in the residual radioactive material at the site, including their potential for migration.** No disposal cell is present at the site. Surface remediation was completed in 1996. Subpile soil analysis for most constituents indicates that no significant contamination remains in place that would contribute to ground water contamination (see SOWP, Section 5.3.1.3). Recent characterization data for vanadium indicate some vanadium contamination in subsurface soils. The low mobility of vanadium will result in slow migration.
- 3.1.2 The hydrogeological characteristics of the site and surrounding land.** The hydrogeology of the site was characterized for input to the flow and transport model (see SOWP, Sections 5.1 "Geology," and 5.2 "Hydrologic System"). Ground water flows in a west to southwesterly manner. Contamination has migrated downgradient of the site, though the worst contamination is confined to the site. Modeling predicts that contaminated ground water will eventually discharge to the Colorado River, where it will be diluted. There is a mitigation wetland on the site that was artificially constructed. Ground water discharges to this wetland. Ground water is pumped on the property directly west and adjacent to the site as part of a dewatering operation. The extracted water is discharged to a holding pond on the site. The pumping operation does have an influence on ground water flow.
- 3.1.3 The quantity of contaminated ground water and the direction of ground water flow.** Ground water flow is generally west-southwest at an average rate of 0.8 to 1.7 ft/day. The total volume of contaminated ground water is estimated at approximately 600 million gallons (DOE 1996).

- 3.1.4 **The proximity and withdrawal rates of ground water users.** One well (RFN-442) is located approximately 1.5 miles downgradient of the site within the plume. It is equipped with a reverse osmosis unit that can treat enough water to serve five properties. Two of the properties are currently occupied—one by a business and one by a church. It is likely the three other properties served by the one well will be light industrial. Exact withdrawal rates are not available, but because of the nature of the development it is probably less than a few hundred gallons per day. A second well (RFN-617) is located 0.75-mile farther downgradient at a cement company. It is also equipped with a reverse osmosis unit. Withdrawal rates are also expected to be low as the well is for potable use and not for process-related purposes. DOE regularly samples and analyzes water from these wells to ensure water is suitable for drinking.
- 3.1.5 **The current and future uses of ground water in the region surrounding the site.** There are some private ground water wells in the site vicinity. Wells used for drinking water have some sort of treatment system, as the quality of ground water in the area is generally poor. Other uses for well water at residences include bathing, showering, and watering plants and livestock. There are some wells that obtain ground water for industrial purposes. The zoning for the land encompassing the site is agricultural/industrial. Potential future uses could be open space/agricultural, wildlife habitat enhancement, environmental education, passive recreation, and mine reclamation. Institutional controls prevent the use of ground water for any purpose at the site itself; water use at nearby properties is most likely to be agricultural or industrial.
- 3.1.6 **The existing quality of ground water, including other sources of contamination and their cumulative impact on ground water quality.** Ground water quality at the site is generally poor, as is most of the ground water in the Rifle vicinity. Historically, background concentrations of molybdenum, selenium, and uranium have exceeded EPA standards. Fluoride, iron, manganese, and sulfate in background water all exceed EPA's secondary drinking water standards. Water at the site also has elevated concentrations of arsenic, ammonium, selenium, uranium, and vanadium as a result of milling activities.
- 3.1.7 **The potential for health risks caused by human exposure to constituents.** The only potentially unacceptable risks to humans would occur through regular use of untreated ground water as drinking water in a residential scenario, which currently does not exist. Incidental use would not result in any unacceptable risks. Institutional controls imposed by Garfield County require residents to prove a source of potable water to develop property in county jurisdiction. Any property located within the Rifle city limits is required to tap into the city's municipal water system. Therefore, institutional controls and the designation of the site as agricultural/industrial will ensure that ground water will not be used in any manner resulting in unacceptable human health risks.

- 3.1.8 The potential damage to wildlife, crops, vegetation, and physical structures caused by exposure to constituents.** The ecological risk assessment showed that wildlife exposure to ground water would result in little risk (see SOWP section 6.2). Vegetation is exposed to ground water in the mitigation wetland. This is an artificial wetland, therefore no previously existing vegetation has been damaged. A wetland management plan is in place to establish wetland vegetation. Water from the site discharges into the Colorado River and is rapidly diluted to undetectable levels, leaving aquatic life unaffected. No physical structures exist on the site.
- 3.1.9 The persistence and permanence of the potential adverse effects.** It is possible that ground water contamination could remain at levels determined to be unacceptable for drinking water for an extended period of time. However, during that period of time institutional controls will ensure that no improper use of water occurs that could produce adverse effects (see 3.1.7).
- 3.1.10 The presence of underground sources of drinking water and exempted aquifers identified under §144.7 of this chapter.** There are down gradient drinking water wells installed into the contaminant plume. However, DOE has committed to ensuring that users of those wells have treatment units and that water is of suitable quality for drinking. DOE will continue to ensure that any property owners within the plume boundary have a potable source of drinking water.

3.2 Potential Adverse Effects on Hydraulically Connected Surface Water Quality

- 3.2.1 The volume and physical and chemical characteristics of the residual radioactive material at the site.** No disposal cell is present at the site. Surface remediation was completed in 1996. Subpile soil analysis indicates that no significant contamination remains in place that would contribute to ground water contamination with the possible exception of vanadium. However, any subsurface soil contamination should not affect surface water quality (see SOWP, Section 5.3.1.3).
- 3.2.2 The hydrogeological characteristics of the site and surrounding land.** Only the surficial aquifer at the site is contaminated. It is composed of unconsolidated alluvial material deposited by the Colorado River; the material ranges in size from clay to cobbles. The alluvial material is approximately 20 to 30 feet thick over most of the site. The saturated thickness of the aquifer ranges from 5 to 10 feet. Ground water movement is generally west-southwest. Ground water from the site moves through the mitigation wetland and the Roaring Fork pond, and discharges to the Colorado River (Sections 5.1 and 5.2 of the SOWP describe the geology and hydrology of the site, respectively.)
- 3.2.3 The quantity and quality of ground water and the direction and of ground water flow.** Ground water flow is generally west-southwest at an average rate of 0.8 to 1.70 ft/day. Water quality is poor, with several constituents exceeding ground water standards. For a detailed discussion of ground water quality, see Section 5.3.3 of the SOWP. The quantity of contaminated ground water is estimated at approximately 600 million gallons (DOE 1996).

- 3.2.4 **The patterns of rainfall in the region.** The site receives on average approximately 11.0 inches of total precipitation per year. Rainfall occurs during the summer in high-intensity, short-duration, late afternoon thunderstorms that are conducive to runoff. Precipitation occurs in the winter as snowfall. Precipitation events have no measurable effect on quality of water in the Colorado River as a result of site contamination.
- 3.2.5 **The proximity of the site to surface waters.** The Colorado River forms the eastern and southern boundaries of the site. The mitigation wetland is on and downgradient of the site. The Roaring Fork gravel pond is located on the property adjacent to and downgradient from the site; it is within the plume boundary.
- 3.2.6 **The current and future uses of surface waters in the region surrounding the site and any water-quality standards established for those surface waters.** The Colorado River in the site vicinity is classified for use as recreation, water supply (i.e., source of drinking water for a community), and agriculture. Water quality standards for the river are established in Regulation No. 37 of the Colorado Department of Public Health and the Environment's Water Quality Control Commission. The river water in the site vicinity does not exceed any of these standards or any of the Colorado state standards established for agricultural water use. No water quality criteria have been established for the mitigation wetland. State surface water standards generally do not apply to constructed wetlands. For details about surface water quality, see Section 5.3.2 of the SOWP.
- 3.2.7 **The existing quality of surface water, including other sources of contamination and the cumulative impact on surface water quality.** Water in the Colorado River is the vicinity of the site is designated high quality by the State of Colorado. The site has no measurable impact on the river water quality. Water in the vicinity of the site is indistinguishable from background Colorado River water samples. Water quality in the mitigation wetland and the Roaring Fork gravel pond is currently of poor quality, but will improve as site remediation occurs.
- 3.2.8 **The potential damage to wildlife, crops, vegetation, and physical structures caused by exposure to constituents.** The ecological risk assessment (section 6.2 of the SOWP) has indicated that risks to wildlife are low due to exposure to contaminated water at the wetland area and the Roaring Fork gravel pond. There is no potential damage associated with the Colorado River as site contamination has little to no impact on the Colorado River quality. Vegetation in the mitigation wetland is currently of limited diversity, but will become more diverse as water quality improves through natural flushing and active remediation. No physical structures or crops are exposed to contaminated surface water.
- 3.2.9 **The persistence and permanence of potential adverse effects.** No adverse affects are currently present and none are expected in the future.

4.0 "Roadmap" to the New Rifle SOWP

4.1 General Information

4.1.1 Introduction—Section 1.0 of SOWP

- 4.1.2 Facility Description—Sections 3.2 and 5.3.1 of SOWP
- 4.1.3 Extent of Ground Water Contamination—Section 5.3.3.2 of SOWP
- 4.1.4 Current Ground Water Protection Standards—Table 2-1 of SOWP
- 4.1.5 Proposed Alternate Concentration Limits—Section 2.2 of GCAP

4.2 Hazard Assessment

Generally corresponds to Section 6 of SOWP, which contains human health and ecological risk assessments

- 4.2.1 Source and Contamination Characterization—Sections 5.3.1 and Table 6-1 of SOWP
- 4.2.2 Transport Assessment—Section 5.3.5 and Appendix D of SOWP
- 4.2.3 Exposure Assessment—Sections 6.1.2.2 and 6.1.2.3 of SOWP for human health; Section 6.2.2 of SOWP for ecological risk

4.3 Corrective Action Assessment—Section 8 of the SOWP

- 4.3.1 Corrective Action Costs—Section 8.4.3 of the SOWP
- 4.3.2 ALARA Demonstration

The As Low As Reasonable Achievable (ALARA) concept does not directly apply to the proposed ACLs because its intent is to limit exposure to radioactivity. However, the general goal of achieving a cleanup goal that is as low as can reasonably be met is satisfied by application of the proposed ACLs. The ACL for selenium is proposed because of elevated background concentrations. The ACL proposed for ammonia will be protective of human health and the environment; it is highly likely that even lower concentrations than proposed can be met within the 100-year natural flushing period based on historical trends.

4.4 Proposed Alternate Concentration Limits

- 4.4.1 Proposed Alternate Concentration Limits—Section 2.2 of GCAP
- 4.4.2 Proposed Implementation Measures—Section 7.2 and 7.3 of SOWP; Sections 2.6 and 3.0 of the GCAP)

4.5 References—Section 9 of SOWP

4.6 Appendices and Supporting Information—Appendices A through E of SOWP

5.0 References

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40 CFR Part 192. "Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings," *U.S. Code of Federal Regulations*, July 1, 1996.

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Appendix D

Data Analysis of Vanadium at the New Rifle UMTRA Project Site, Rifle Colorado

Data Analysis of
Vanadium at the New Rifle UMTRA Project Site,
Rifle, Colorado

April 2003

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Appendix

Appendix A—Evaluation of Modeling in View of Recent Time/Concentration Data

Plates

Plate 1a—Vanadium Plume at New Rifle Site for 1998

Plate 1b—Vanadium Plume at New Rifle Site for 2002

Executive Summary

The U.S. Department of Energy (DOE) conducted studies from 1997 to 1999 at the New Rifle Uranium Mill Tailings Remedial Action (UMTRA) Project site to understand the types, distributions, interactions, and movement of contaminants in ground water and to evaluate the risks posed to human health and the environment from these contaminants. A site conceptual model incorporating this information was used to propose a future course of action (i.e., compliance strategy) for the site. Based on results of these studies, a compliance strategy for all of the contaminants of concern (COC), except vanadium, was proposed in the Site Observational Work Plan (SOWP) (DOE 1999). This strategy was natural flushing of ground water to meet maximum concentration limits, alternate concentration limits, or background concentrations. Institutional controls and monitoring were to be implemented to ensure protectiveness of the compliance strategy until cleanup goals were met. Additional studies regarding vanadium, including distribution, behavior, and removal from the ground water were recommended and have been ongoing until recently (DOE 2000 and DOE 2002).

Initial modeling of ground water flow and vanadium transport, conducted in 1998 and using established methods for measuring vanadium mobility, showed that about 300 years would be required to decrease dissolved vanadium levels to a risk-based screening level of 0.33 milligrams per liter (mg/L) (EPA 2003). Actual data obtained from monitor wells during the 4 years since that modeling was completed indicate that the concentration of vanadium in ground water is decreasing faster than the modeling predicted. Recent evaluation of the initial model indicates that geochemical processes controlling vanadium in ground water at the site are more complex than originally assumed and could vary significantly over small distances, making it difficult to produce an accurate sitewide model for vanadium fate and transport. Consequently, an analytical solution describing localized vanadium transport has been applied to individual sets of time-concentration data to better match the more rapid decrease in observed vanadium concentrations and to develop a more realistic predictive tool. This analysis indicates that vanadium concentrations in ground water are likely to decrease to levels below the risk-based screening level of 0.33 mg/L in less than 100 years.

The apparent reason for the discrepancy between the earlier model and observed vanadium concentrations stems from the behavior of vanadium in this ground water setting. Vanadium attaches itself or sorbs to various materials in the subsurface, more so than most ground-water contaminants. These materials that act as sorbents include iron and manganese hydroxides, clays, and organic materials; all are commonly found in alluvial sediments at the New Rifle site. Therefore, vanadium tends to be easily sorbed but slowly released from these locations into the ground water. Changes in ground water chemistry, such as the addition or loss of oxygen, may accelerate the vanadium uptake to or release from the alluvial materials. The resulting sorption and desorption processes are controlling the natural flushing of vanadium observed today. The ground water system at New Rifle, in the area of the vanadium plume, is apparently more variable than characterization data suggested; therefore, it is more difficult to predict how these sorption-desorption processes will influence vanadium movement. Evidence strongly suggests that disturbing the subsurface tends to release vanadium from sorbed sites and increases concentrations in the ground water; consequently, further disturbance should be minimized. Studies indicate that the risk to human health and environmental for allowing vanadium to slowly flush from the New Rifle site is low, especially with institutional controls to prevent access to the contamination.

This information, when considered with other vanadium studies at the site, was used to select a compliance strategy for vanadium of natural flushing that is the same for all contaminants at New Rifle. Institutional controls and monitoring will continue for all contaminants at the New Rifle site until cleanup objectives are met. This strategy will be discussed in the Ground Water Compliance Action Plan and the Environmental Assessment for the New Rifle UMTRA Project site.

1.0 Background Information

Contaminated soil and sediment were removed from the New Rifle site during the UMTRA Project from 1992 to 1996 (DOE 1999). After the surface program concluded, contamination remaining in the ground water was characterized and evaluated. The purpose of this characterization was to select a compliance strategy for ground water contamination based on selection processes shown in the Programmatic Environmental Impact Statement (PEIS) (DOE 1996). This process was followed for all contaminants except vanadium, which required additional study. This data analysis discusses these results.

After information was collected from the site, the first attempt at quantifying the migration of vanadium and other contaminants in ground water was made in the Site Observational Work Plan (SOWP) that was prepared for on the basis of conditions observed in the late 1990s (DOE 2000). Studies of vanadium chemistry during that time revealed that numerous geochemical processes, including sorption on aquifer solids and chemical precipitation, might influence levels of dissolved vanadium in ground water. Although these processes can vary greatly in both space and time at a given site, the conceptual model developed for the New Rifle site assumed that the result of all of these processes could be described through the use of contaminant sorption theory based on a linear soil-water distribution coefficient, which is often denoted by the term K_d . In 1998, in accordance with the conceptual model for vanadium, a numerical model of ground water flow and an associated transport model, using both deterministic and probabilistic methods, was developed for the site using this distribution coefficient theory.

One of the purposes of modeling ground water flow and transport at the site was to assess the potential for vanadium to naturally flush. Chemical transport principles dictate that, as the K_d for a ground water constituent increases, the mobility of that constituent is reduced, and its potential to flush naturally decreases. In such a case, the constituent shows a preference to attach to solid particles that the aquifer comprises, and its transport in ground water is said to be "retarded." The corresponding decrease in transport rate compared to a constituent that does not attach to aquifer solids is described using a dimensionless retardation factor R , which is calculated using the K_d for the chemical, the dry bulk density of aquifer materials, and porosity of the aquifer. The larger the K_d value, the greater the retardation and the value of R .

With an emphasis on soil-water distribution coefficients, attempts were made during preparation of the SOWP to derive reasonable estimates of K_d for vanadium in the alluvial aquifer at the New Rifle site. Laboratory estimates of vanadium K_d based on samples of alluvial aquifer material ranged from 3.1 to 58.8 milliliters per gram (mL/g). A standard correction factor was applied to the fraction of smaller size (< 2 millimeter) particles in the samples of aquifer material that act as locations for sorption of ground water contaminants more than the coarse fraction. The resulting K_d values were lower and ranged from 1.2 to 10.5 mL/g. However, even these revised estimates of the soil-water distribution coefficient suggested that vanadium transport in ground water would be heavily retarded. Assuming an aquifer porosity of 25% and an aquifer material density of 1.5 g/ml, the range of revised K_d s resulted in computed retardation factors of about 8 to 64. This in turn meant that vanadium could be migrating downgradient and toward the Colorado River anywhere from 8 to 64 times slower than a non-retarded constituent, thereby diminishing the potential for natural flushing of vanadium within a reasonable time frame.

With the concerns over the apparent low potential for vanadium flushing from the site, DOE recommended that additional study be conducted to better understand the lateral and vertical extent of vanadium in ground water and soil before a remediation strategy could be selected for vanadium. In October 1999, a series of backhoe trenches were dug and soil samples were collected every 2 feet to a depth of 10 feet. (DOE 2000). Analytical results showed that vanadium was most concentrated in the deepest intervals. In the spring of 2000, 20 boreholes were drilled and sampled. Soil and ground water grab samples were collected from the top of the water table, from just above bedrock, and from a point halfway in between. Soil samples were also collected above the water table. In addition, four sets of three nested wells were constructed near the edges of the vanadium plume, and samples were collected from the same depths as the borehole samples. Results suggested that vanadium in the soil was most concentrated near well cluster 855, 856, and 867 and that the maximum vanadium concentration in ground water was in the middle part of the saturated zone located about 400 feet downgradient of the area of maximum soil contamination.

DOE then decided to evaluate the effectiveness of removing vanadium from the ground water and established a pilot plant for this purpose in the center of the plume. A pump and treat system using zero valent iron to remove vanadium and other metals operated from January until November of 2001 and treated nearly 3,000,000 gallons of water. This resulted in removal of approximately 99 kilograms (kg) of vanadium from the ground water in the plume area (DOE 2002).

In the past 3 years since modeling was completed, and in the past year since the pilot study was conducted, vanadium concentrations in most wells at the site were decreasing faster than the model predicted. In 2002, the model was reevaluated using several probabilistic modeling techniques. Probabilistic simulations were conducted with the ground water transport model for the site to determine if conditioning of model results on observed vanadium concentrations collected during the past few years would produce parameter ranges leading to a decrease in the time needed for natural flushing of vanadium. Most of this evaluation was accomplished using the model previously developed for the site as part of the SOWP (DOE 1999). This model was constructed using the ground water flow simulator MODFLOW (McDonald and Harbaugh 1988; Harbaugh and McDonald 1996) and the transport code MT3DMS (Zheng 1999) with the Ground Water Vistas (ESI 1998) graphical user interface.

A probabilistic model is distinguished from a deterministic model in the sense that the latter consists of a single set of parameter inputs, rather than numerous combinations of parameters in the probabilistic realm. The parameter set in the deterministic model is developed through the process of model calibration, wherein the model user manually adjusts input parameter values until a single, reasonable combination of provides model results that compare favorably with observed conditions within a specified criterion. The calibrated deterministic model is then used to provide a best estimate of future vanadium concentrations. In contrast, the probabilistic approach does not produce a best estimate, but rather a suite of simulation results that are expected to span the expected future behavior of vanadium.

The probabilistic modeling consisted of making multiple runs with the original SOWP model, with each run based on input parameters that were randomly sampled from prescribed probability density functions (PDF) for each parameter. This approach, which is generally referred to as Monte Carlo simulation, made it possible to examine hundreds of different parameter sets to better match observed trends in vanadium concentration.

The most significant finding from the recent probabilistic modeling (discussed in Attachment A) was that no better fits to observed natural flushing data could be derived than had been predicted previously using the same SOWP model. The model is not capable of predicting what actual data are showing. This conclusion was drawn despite the fact that additional probabilistic runs took into account distribution coefficients that would cause less sorption than was simulated in the SOWP model. Therefore, it was unlikely that reasonable distribution coefficients could be used to fully explain the decrease in dissolved vanadium levels observed at site monitor wells during the past several years. Attachment A provides a more detailed discussion of the steps taken with the probabilistic modeling and the applied logic that led to these findings.

Given the uncertainties regarding vanadium fate at the site, DOE concluded that tools other than the existing model should be used to evaluate the observed decreases in vanadium with time. A simpler analytical solution was employed to evaluate current time-concentration curves and to predict future vanadium concentrations (see Section 1.3, Alternative Deterministic Simulations," this report).

1.1 General Behavior of Vanadium

The behavior of vanadium in sediments and ground water is not well understood. Vanadium may be removed from water by sorption onto clays, amorphous iron, manganese hydroxides, or organic matter in the soil or sediment. EPA (1999) defines sorption as any variety of processes by which an aqueous phase partitions to a solid, such as by precipitation of a three-dimensional solid molecular coating on the surface of a solid, adsorption onto the surface of a solid, adsorption into the structure of a solid, or partitioning into organic matter. This general usage is helpful because it is usually not known how the contaminant is associated with the solid. This varied chemical behavior is true of vanadium, which has oxidation states of +3, +4, and +5 for most environments of normal, near-surface pH ranges and oxidation potentials (Rai and Zachara 1986). These oxidation states affect the mobilization or sorption of vanadium. A decrease in pH could lead to the dissolution of carbonates and iron or manganese hydroxides along with any metals sorbed onto them because of competition with the more strongly adsorbed hydrogen ion (Hounslow 1995). Mobilization of vanadium might also be caused by changes in dissolved oxygen, which can be produced by the addition of organic matter (Bloomfield and Kelso 1973). These or other processes could be acting on vanadium-hosted soils and sediments at the New Rifle site. Drilling and excavation may have introduced oxygen from the atmosphere to the ground water, thus increasing desorption of vanadium from the sediments and concomitantly increasing concentrations of vanadium in ground water.

Vanadium contamination in ground water was identified in the eastern portion of the New Rifle site during the 1980s. Most of this contamination appeared to be associated with the gypsum and vanadium ponds located immediately east of the former tailings pile at the site (DOE 1999). The observed vanadium concentrations in the 1980s steadily and gradually decreased over time. Increased vanadium concentrations at the New Rifle site first appeared in 1992 when surface cleanup began; concentrations declined following completion of these activities in 1996. Plots of vanadium concentration over time at several monitor wells (ones that have a long monitoring history) show high concentration spikes during the early to mid 1990s, indicating a distinct correlation with the cleanup activities. The best example of this is shown in Figure 1 for well 0590, which has a long monitoring history. Well 0590 is located farthest from the center of the of the vanadium plume; the graph shows an increase in the concentration of vanadium during

surface remedial action from about 1994 to 1996. Well 0658 (Figure 2) is near the center of the vanadium plume and shows vanadium mobilization during remedial action around 1996 and again in 2001 when new wells were being installed in this area. At most monitor wells that have existed since the 1980s, post cleanup vanadium concentrations have returned to, or are below, levels that were observed prior to the cleanup period.

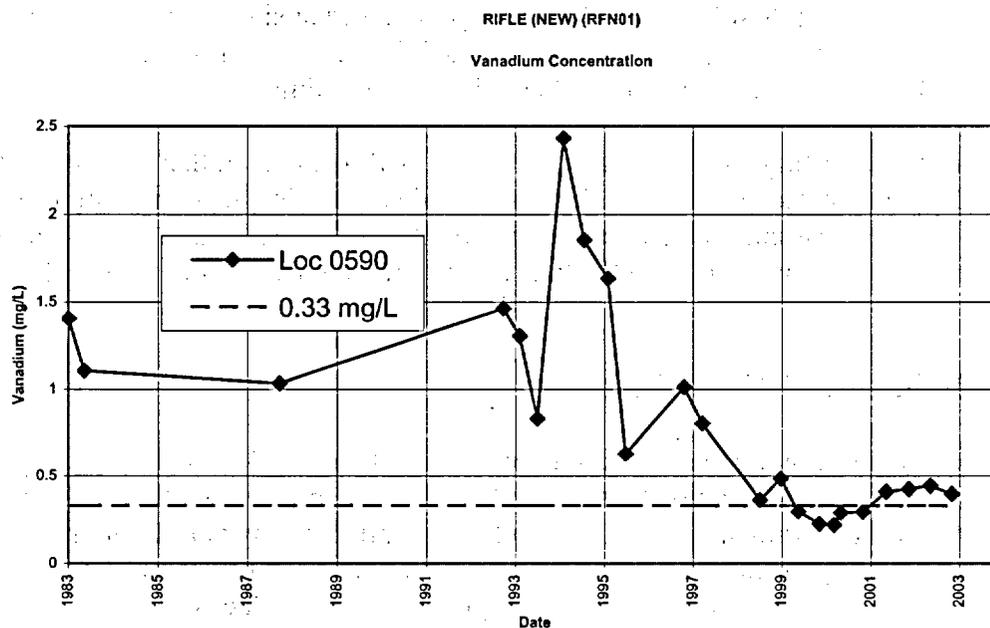


Figure 1. Vanadium Concentration Through Time for Monitor Well 0590

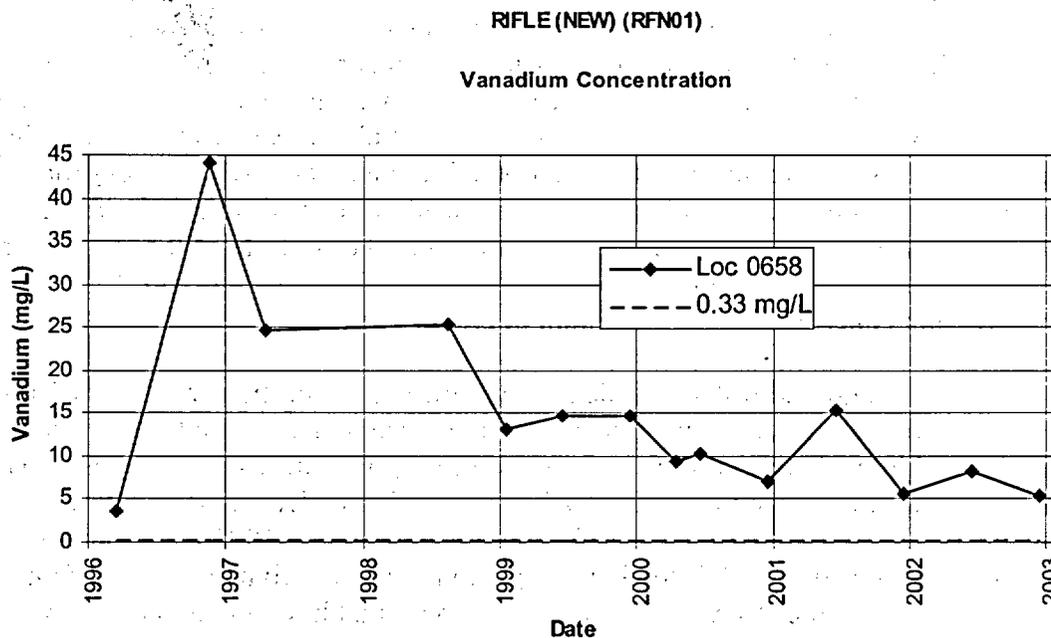


Figure 2. Vanadium Concentration Through Time for Monitor Well 0658

Regardless of the relationship between pre-cleanup and post cleanup vanadium levels at monitor wells, declines in dissolved vanadium concentration have been observed in recent years at nearly all wells now used to monitor site contamination in the vanadium plume area (see Plates 1a and 1b). This observation indicates a general trend toward natural flushing of vanadium. Such flushing is occurring now, during the period following the surface remediation program, and was probably occurring prior to surface remediation.

1.2 Vanadium as a Risk

The current site-related contamination does not pose any unacceptable risk to human health or the environment. The only exposure pathway that presents a potential risk is ingestion of ground water. The vanadium ground water plume is mainly confined to the site and the wetland area, and there are no uses of ground water in those areas. Institutional controls will prevent ground water use for at least 100 years while contaminants flush. Although concentrations of some constituents, including vanadium, are somewhat elevated in the wetland area surface water, these levels do not present unacceptable risk to ecological receptors, or livestock. As contaminated ground water slowly discharges to the Colorado River, it is rapidly mixed with river water and diluted by a factor of about 30,000 times. It has no detectable effect on surface water quality. Thus, no unacceptable risks to human health and the environment are expected as contaminants flush. For additional information, see Section 6 in the SOWP (DOE 1999), *Summary of Human Health and Ecological Risk*.

1.3 Alternative Deterministic Simulations

Despite the fact that the probabilistic modeling was inconclusive as to whether vanadium is naturally flushing at a faster rate than previously indicated, the fact that most monitor wells show a gradual decrease in dissolved vanadium suggested that further analysis of vanadium fate and transport was warranted. To carry out additional analyses, several deterministic modeling runs were made with the site model using various model conditions and parameters that led to improved simulation of vanadium flushing at selected wells during the past 5 to 6 years. The approach allowed model conditioning (i.e., model calibration) to be based on individual wells rather than several wells together and also allowed the use of initial conditions and flow and transport parameters different from those used in either the SOWP model or the probabilistic analyses in this study.

Part of the rationale behind conducting alternative deterministic simulations was that the SOWP modeling did not account for the spatial variability in geochemical conditions at the site that control observed levels of dissolved vanadium. Additional rationale was based on the assumption that the initial vanadium concentrations adopted in the SOWP model were representative of observed concentrations at monitor wells where they were measured but not necessarily representative of actual concentrations between monitor points. This latter reasoning was tantamount to saying that the interpolation techniques employed to develop initial concentrations in the SOWP model provided smoothed estimates of concentration between observed concentrations, when in fact the actual concentrations in these locales, though not known, were different from the smoothed estimated values. The combination of these rationales suggested that the behavior of dissolved vanadium at one well is independent of vanadium fate at all other monitor wells. Such a conclusion was warranted by the fact that the probabilistic modeling performed earlier revealed no combinations of parameters for the entire model that provided better fits to observed concentrations at all wells.

Ultimately, it was found that the observed gradual decline in vanadium concentration at each monitor well was best matched by allowing the initial vanadium distribution to be focused on the area surrounding the well and not distributed in space in the manner that previous models had adopted. In addition, various combinations of initial spatial distribution of vanadium and vanadium K_d could be applied to specific areas while still providing accurate simulations of observed concentrations. Application of these techniques to numerous wells using the existing site flow model led to three major conclusions:

- Geochemical conditions that control vanadium dissolution and transport in the alluvial aquifer are very heterogeneous, and vary strongly over distances of a few hundred feet or less. Such spatial heterogeneity appears to be partly the result of surface remediation conducted during the early to mid-1990s, during which time natural background geochemistry was disturbed.
- The spatially variable geochemical conditions make it extremely difficult to accurately model how dissolved vanadium throughout the New Rifle site will behave in coming years, particularly since the numerous factors governing the distribution of vanadium between dissolved and solid phases can only be modeled using relatively simple soil-water distribution coefficients. This conclusion is likely to be true even if concerted efforts were made to further characterize the site over spatial scales of tens of feet.
- Because the numerical model did not work, simple models applied in the area of specific wells were tried.

In accordance with the third bullet, simple models were developed for several of the monitor wells onsite for which dissolved vanadium concentrations had been declining during the past several years. These simple models were developed using an analytical solution (as opposed to a numerical model) included in a package of solutions referred to as 3DADE (Leij and Bradford 1994), as provided and supported by the U.S. Salinity Laboratory of the U.S. Department of Agriculture. The specific solution used at each well allows for an initial vanadium concentration uniformly distributed over a block of finite dimensions, advective and dispersive transport along a uniform ground water flow path, and control of vanadium partitioning between the dissolved and solid phases in accordance with a soil-water distribution coefficient (K_d).

All of the simple model evaluations were made by adjusting the K_d value and the size of the block containing the uniform initial concentration of vanadium. In each case, the monitor well being analyzed was assumed to lie at the center of the initial concentration block. By running multiple simulations with varying initial concentration blocks and K_d s, it was possible to identify a range of natural flushing estimates that all correlated well with observed vanadium concentrations at the monitor well. If the range of these estimates all fell within a 100-year time frame, it was reasonable to conclude that decreases of dissolved vanadium to levels below the 0.33 mg/L risk-based screening level over the entire site was possible within 100 years, and that natural flushing was a viable alternative. As shown in Table 1, the projected cleanup dates all fall within the 100-year time frame.

Table 1. 3DADE Simulations and Estimated Year of Vanadium Cleanup

Well	Initial Concentration Block Dimensions – Width x Length x Height (feet)	Initial Concentration C_0 (mg/L)	Soil-Water Distribution Coefficient K_d (mL/g)	Retardation Factor R (dimensionless)	Projected Year of Cleanup ^a
0216	100 x 100 x 30	0.55	11.5	70.0	2002
0216	100 x 100 x 30	0.50	13.2	80.0	2001
0216	100 x 100 x 30	0.47	14.8	90.0	2001
0216	100 x 300 x 30	0.55	2.7	17.0	2002
0216	100 x 300 x 30	0.50	3.2	20.0	2002
0216	100 x 300 x 30	0.47	3.5	22.0	2002
0218	100 x 100 x 30	3.5	4.8	30.0	2009
0218	100 x 100 x 30	3.2	6.5	40.0	2012
0218	100 x 300 x 30	3.5	1.5	10.0	2006
0219	100 x 100 x 30	0.268	4.8	30.0	1998
0219	100 x 100 x 30	0.24	7.3	45.0	1998
0219	100 x 300 x 30	0.24	1.5	10.0	1998
0590	100 x 100 x 30	0.90	8.2	50.0	2002
0590	100 x 300 x 30	0.80	2.3	15.0	2001
0657	100 x 100 x 30	1.31	19.8	120.0	2015
0657	100 x 300 x 30	1.31	4.8	30.0	2010
0658	100 x 100 x 30	35.0	5.7	35.0	2035
0658	100 x 100 x 30	35.0	4.8	30.0	2029
0658	100 x 300 x 30	35.0	1.8	12.0	2018
0659	100 x 100 x 30	10.0	6.5	40.0	2023
0659	100 x 300 x 30	10.0	2.5	16.0	2016
0669	100 x 100 x 30	14.5	7.3	45.0	2032
0669	100 x 300 x 30	14.5	1.8	12.0	2014
0670	100 x 100 x 30	5.2	14.8	90.0	2040
0670	100 x 300 x 30	5.2	3.2	20.0	2017

^aYear at which simulated vanadium concentration decreases to risk-based screening level of 0.33 mg/L.

Figures 3 through 6 graphically show the decreasing trends of vanadium for several representative wells from Table 1, both in the form of observed information and plots for two predicted curves using the simple analytical model. The vanadium concentrations predicted by the flow and transport model used in the SOWP are also included for comparison. In each of these illustrated cases, the time needed for dissolved vanadium concentration to drop below the risk-based concentration as predicted by the simple analytical model is much shorter than the corresponding time predicted by the SOWP model. Well 0659 shows three spikes for vanadium concentrations that correspond to three June sampling events, when the river stage was high. This might suggest that vanadium is mobilized when water levels are high at this location.

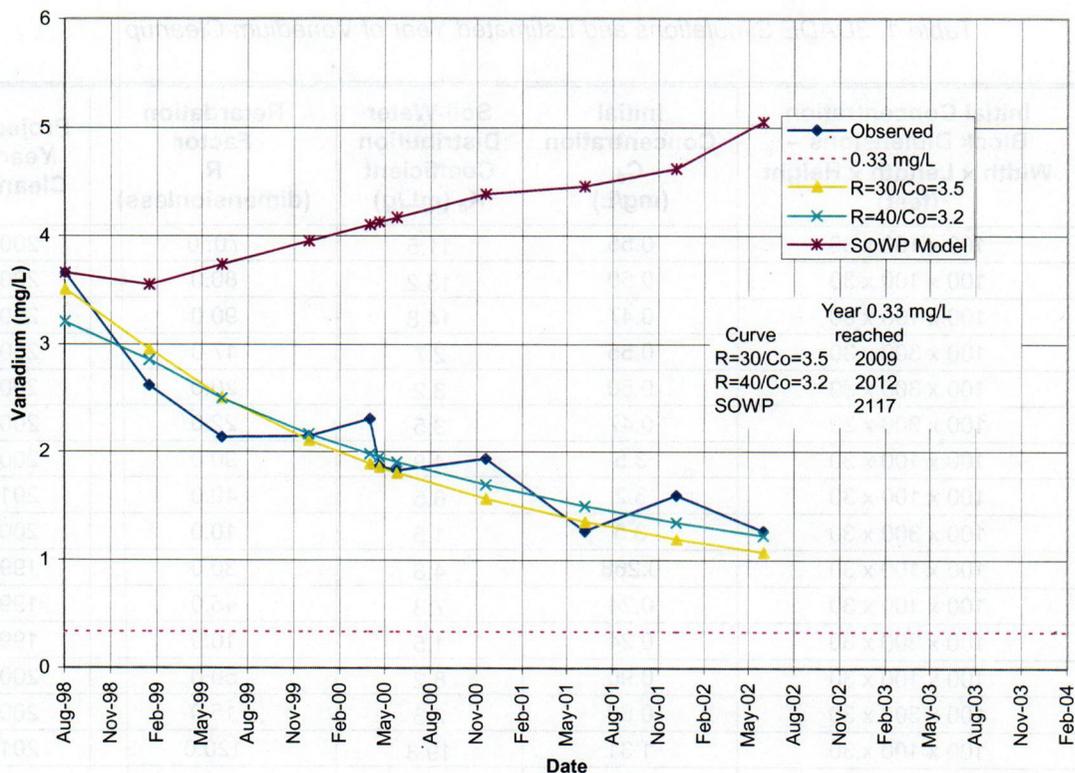


Figure 3. Vanadium Concentrations, 3DADE Evaluations, and Original Modeling Curve for Well 0218

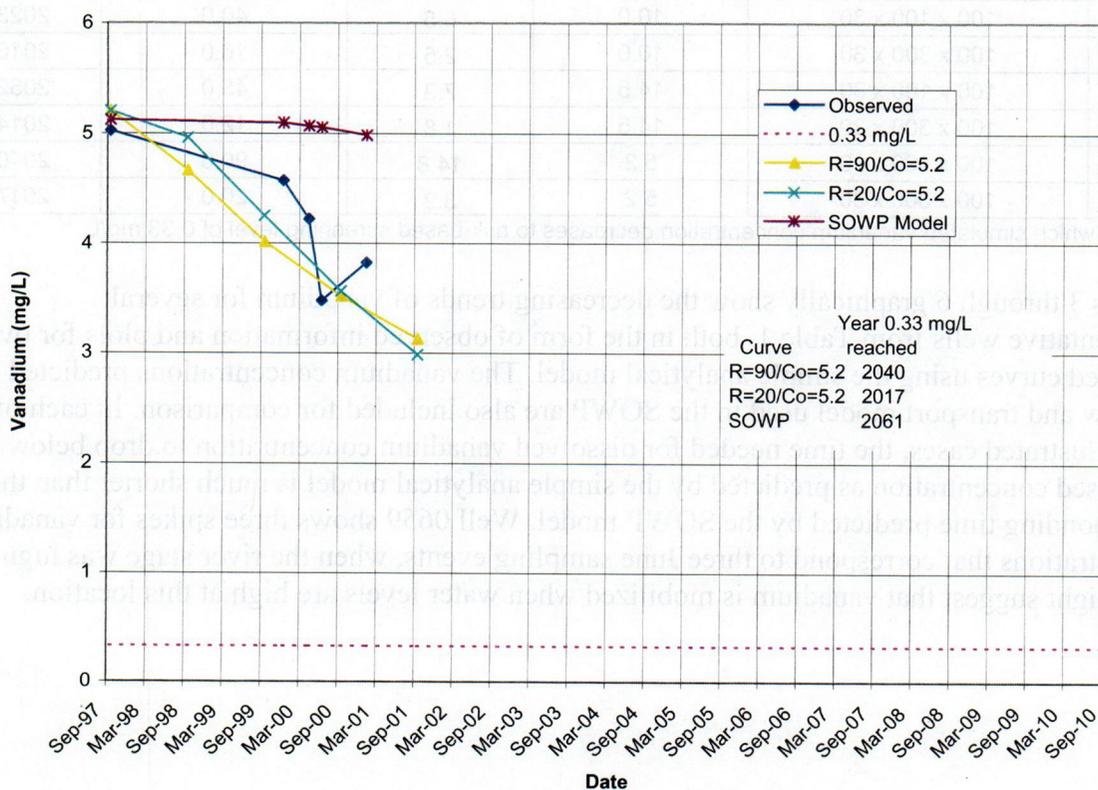


Figure 4. Vanadium Concentrations, 3DADE Evaluations, and Original Modeling Curve for Well 0670

CO2

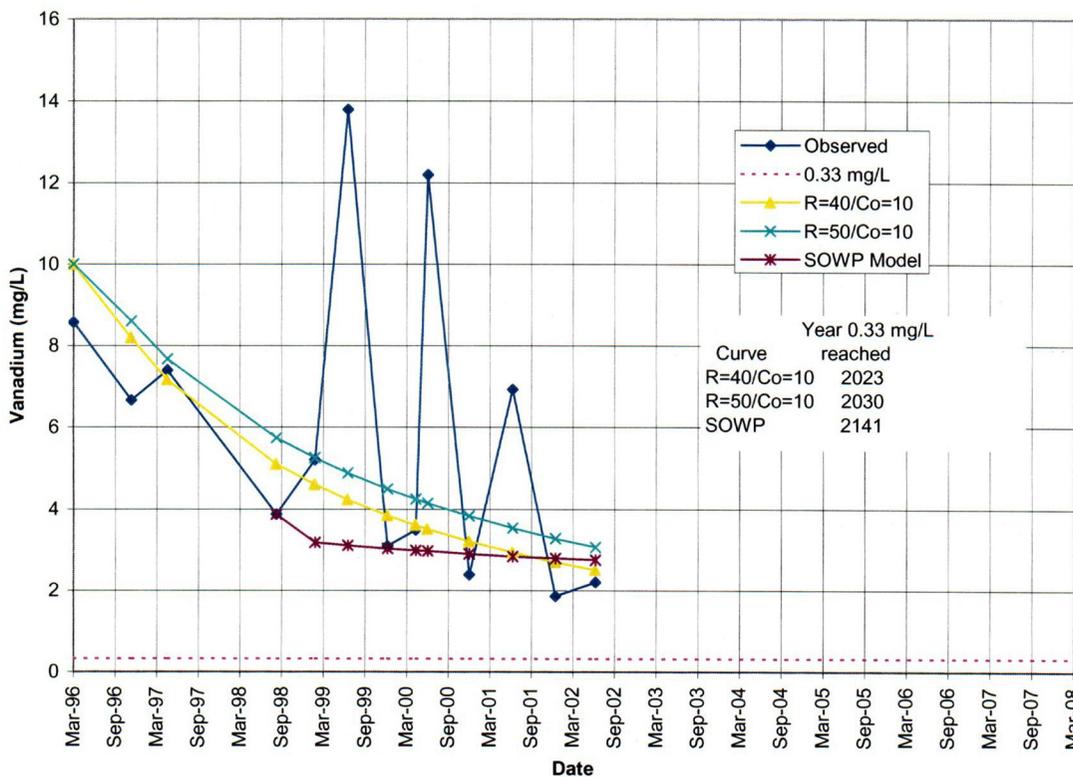


Figure 5. Vanadium Concentrations, 3DADE Evaluations, and Original Modeling Curve for Well 0659

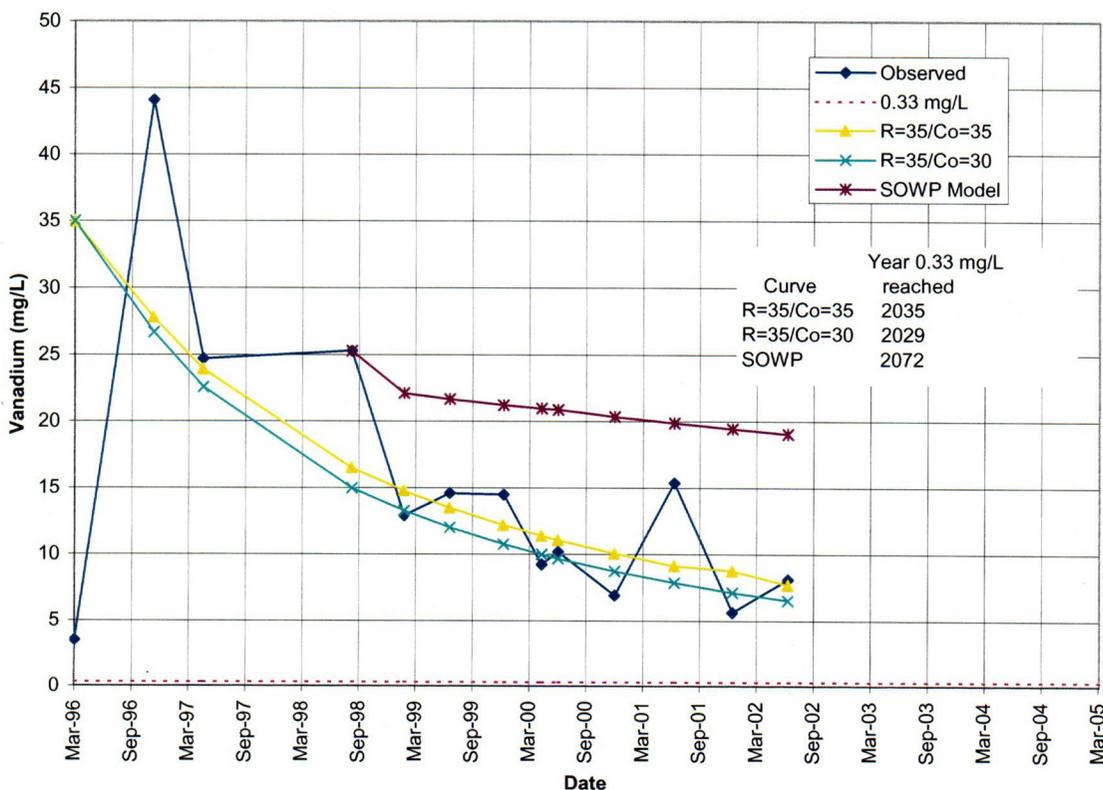


Figure 6. Vanadium Concentrations, 3DADE Evaluations, and Original Modeling Curve for Well 0658

C03

1.4 Uncertainty

The observations made regarding spatial variability of geochemical conditions at the New Rifle site along with the difficulties encountered in providing an accurate vanadium transport model for the entire site highlight the large degree of uncertainty associated with the assessment of vanadium fate. The SOWP model made the best available use of site data at the time it was prepared in 2000. And though this model properly emphasized the generally retarded movement of vanadium in comparison to more mobile constituents like uranium and selenium, it was apparently unable to account for the uncertain geochemical conditions that have existed for the past several years in the vicinity of and downgradient of the gypsum and vanadium ponds.

In addition to the uncertainty associated with the SOWP model, the simple models used in this study to represent vanadium flushing at selected wells are also uncertain. Though these simple models match recent vanadium data relatively well and project quicker cleanup times than predicted by the SOWP model, the fact remains that the exact year at which complete flushing to the risk-based screening level will be achieved cannot be predicted with complete confidence. Actual cleanup time could be somewhat longer than the 35 to 40 years that is indicated by the simple models, or possibly less. Continued monitoring of dissolved vanadium, and maintaining undisturbed conditions at the site are the key components to refining the estimated time of cleanup.

1.5 Moving Vanadium Contaminated Soils

The alternative to remove the most contaminated portion of the vanadium-contaminated soil area is not considered prudent for the following four reasons.

1. Recent time-concentration data strongly suggest that vanadium levels will diminish to acceptable risk-based concentrations in less than 100 years. This is a change from previous estimates.
2. Time-concentration plots (Figures 1 and 2) show that vanadium can be mobilized or desorbed into ground water by any of several poorly understood means. The graphs for well 0590, which is removed from the center of the vanadium plume, well 0658, which is near the apparent center of the vanadium plume, demonstrate the increase in vanadium concentration when either remedial action has occurred or other disturbances, such as drilling of wells, has occurred. Active excavation of the vanadium plume would likely remobilize vanadium in the area of the plume. For this reason, it is suggested that, since vanadium is flushing at a faster rate than was originally estimated, the ground water system should not be disturbed and should be allowed to continue this steady decrease in concentration naturally. The area containing the highest vanadium concentrations was excavated in most places to the water table and clean fill was replaced in the excavation. It is unlikely that future construction activities in the vanadium plume area would require excavation below the water table; accordingly, disturbance of the aquifer materials is unlikely. The water table in the main area of the vanadium plume varies spatially and seasonally from about 7 to 18 feet below the ground surface. Ground water is shallower near the Colorado River.

3. Vanadium is residual radioactive material (RRM) according to the first part of the definition in the Uranium Mill Tailings Radiation Control Act of 1978. Title 1, Section 101, states that RRM is "(A) waste in the form of tailings resulting from the processing of ores from the extraction of uranium and *other valuable constituents of the ores.*" The materials removed during surface cleanup at the New Rifle site were disposed of in a U.S. Nuclear Regulatory Commission (NRC)-approved disposal cell. Removal of any additional material from the New Rifle site would require written permission from NRC and would similarly require disposal in an NRC-approved facility.
4. Extensive soil characterization was conducted as part of the vanadium pilot study for the New Rifle site. Soil samples were collected on an approximately 400- ft by 400- ft grid. Four samples were collected from each location—one each from the unsaturated zone, upper saturated zone, middle saturated zone, and the saturated zone just above bedrock. The less-than-2 mm fraction of the samples was leached with a 5 percent nitric acid solution. Results of these analyses showed a range of vanadium concentrations from approximately 3 milligrams per kilogram (mg/kg) to 6,200 mg/kg. All but three concentrations were less than 1,000 mg/kg. Only 38 percent of the aquifer material is represented by the less-than-2 mm fraction (DOE 1999); the rest of the alluvial materials are generally much larger than this and probably contain little if any leachable vanadium. Available vanadium in the bulk aquifer is therefore on the order of 1 to 2,400 mg/kg (with all numbers adjusted to the 38 percent value), and samples from all but three locations at less than 380 mg/kg (EPA 2001). EPA's vanadium soil screening levels for protection of ground water range from 300 mg/kg (no attenuation in ground water) to 6,000 mg/kg (a 20-fold attenuation factor). The upper end of this range is reportedly more realistic (EPA 2001). Concentrations of vanadium in New Rifle alluvial material are well below the upper end of EPA's screening range; most areas are below the lower end of the range. Because EPA's default soil screening levels represent conservative estimates, it is unlikely that the soils remaining at the New Rifle site represent a significant source of long-term ground water contamination.

The fact that vanadium concentrations in ground water are currently higher than should be expected from this analysis would suggest the Rifle geochemical system is not in equilibrium, a criterion assumed for the EPA study. From historical information, original milling-related concentrations of vanadium in solution may have been much higher than the current concentrations and contributed more vanadium to the substrate. Merritt (1971) discusses standard practices for vanadium beneficiation. Unused portions of the solute from the milling process could still contain 2 to 3 grams of vanadium per liter. Concentrations of vanadium at this level may have been sent to the former vanadium pond at Rifle for disposal. It is unknown how long and at what concentrations vanadium was sent to the evaporation pond, but sorbed concentrations in sediments beneath this former pond were probably higher in the past than current sampling suggests. The remedial action disturbance during the mid-1990s may have mobilized sorbed vanadium, leaving dissolved concentrations potentially out of equilibrium with corresponding soil concentrations. This equilibrium state, if not already present, should be obtained everywhere at New Rifle in the future if no further intrusions into the system occur.

According to the Performance Report for the Pilot Study (DOE 2002), 99 kg of vanadium was removed from ground water during pumping of the nearly 3,000,000 gallons of water. This report also concludes that about 31,766 kg of vanadium is sorbed onto soil

matrices and about 271 kg is dissolved in the ground water. However, the mean concentration sorbed in the upper third of the saturated subpile soil (where it is most concentrated) is 553 mg/kg. If the upper end of EPA's soil screening levels for vanadium applied at the New Rifle site, it suggests that vanadium concentrations in soils are acceptable and should not result in ground water concentrations of greater than 0.33 mg/L; therefore, removal of only the dissolved vanadium would be needed to remediate the ground water to this level. This would indicate that the pilot study removed in excess of 30 percent of dissolved vanadium from ground water. This is probably an overestimate of the percentage of vanadium removed, and in all likelihood there is continued desorption of vanadium from soils in some areas. However, the mass of vanadium removed probably does represent a significant amount of the mass that was in solution at the time and most likely will have a positive impact on the ability of the system to naturally flush.

2.0 Compliance Strategy

The proposed compliance strategy for vanadium and all other contaminants at New Rifle is natural flushing in conjunction with institutional controls and monitoring. The natural flushing strategy is discussed in the Programmatic Environment Impact Statement (DOE 1996). Natural flushing allows the natural ground water movement and geochemical processes to decrease contaminant concentrations. These chemical processes include:

- Dissolution – the process of dissolving minerals from the aquifer matrix
- Precipitation – the separation of chemical constituents from ground water to form new minerals on the aquifer matrix
- Adsorption – the adhesion of chemical constituents from the aquifer matrix
- Desorption – the removal of a chemical constituent from the aquifer matrix by the reverse of adsorption
- Ion Exchange – the replacement of adsorbed chemical constituents by constituents in the ground water, and
- Biological – the process of transforming chemical compounds into different chemical compounds by bacteria or other biological agents

Of these processes, adsorption and desorption are most likely the controlling factors for vanadium movement at the New Rifle site. If this assumption is true for vanadium, the best course of action is to not disturb the ground water system and continue to observe the decrease in vanadium concentration.

3.0 Institutional Controls, Monitoring Plan, Performance Measures

Currently, zone overlays have been adopted by the City of Rifle and Garfield County for the site that will prevent anyone from accessing contaminated water. Interpretation of the most recent time-concentration information suggests that vanadium from most locations will flush to levels below 0.33 mg/L in less than 100 years. Deed restrictions will be imposed when the property is transferred from the State of Colorado to the future landowner (possibly the City of Rifle) to prevent access to ground water. DOE has also provided funding for a water line in the area to furnish future users with municipal water.

Monitoring of the vanadium plume area has been expanded to include two sample rounds per year and the inclusion of the five additional wells: 0217, 0219, 0664, 0669, and 0670. Wells 0215, 0216, 0218, 0590, 0657, 0658, 0659, 0855, and 0856 are already being monitored in this area, resulting in 14 wells in the plume area that will be monitored two times per year. Monitoring will be conducted when water levels are at approximately the same levels to allow better correlation of data for the two annual events. This monitoring program will continue for 5 years and results will be reevaluated at this time.

As vanadium is monitored semiannually during the next 5 years, it will be important to establish measures to evaluate the performance of the natural flushing alternative. These performance measures are currently being developed and will probably consist of time-concentration graphs of a contaminant that were predicted by some modeling technique with actual sampling data superimposed on the graph.

4.0 Summary

- Most of the vanadium-contaminated soils were removed during surface remedial action; therefore, the principal mass of vanadium is gone.
- Vanadium concentrations in soils at the site do not pose a threat to human health and the environment. Vanadium in the ground water could be harmful to humans only if they used it as their only source of drinking water.
- Vanadium entering the Colorado River is diluted by a factor of about 30,000 times and does not present a threat to ecological receptors such as aquatic life and livestock.
- Vanadium is apparently mobilized when the ground water system is disturbed. This was observed during and immediately after surface remedial action and during subsequent well installations in the vanadium plume area. Natural flushing will work best if the ground water system is not disturbed in the future. Vanadium should not be removed as disturbing the saturated zone would probably result in increased concentrations in the ground water.
- Previous modeling indicated that vanadium would require about 300 years to naturally flush from the alluvial aquifer.

- Data collected in the 4 years since modeling was completed indicate that dissolved vanadium is flushing more quickly than suggested by the model.
- Analysis of modeling and investigations of vanadium geochemistry indicates that the system is complex and that transport-modeling parameters do not adequately portray the sorption/desorption qualities for vanadium.
- Extrapolation of time-concentration curves for vanadium at 12 wells in the plume area, where data have been collected most consistently, suggests that vanadium concentrations at most sampling locations will decrease to a risk-based level of 0.33 mg/L within 50 to 60 years and all will flush in less than 100 years.
- The proposed compliance strategy for vanadium is natural flushing with institutional controls and continued monitoring.
- Institutional controls in the form of a zone overlay and deed restriction will prevent access to ground water.

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End of current text

Attachment A

Evaluation of Modeling in View of Recent Time/Concentration Data

Probabilistic Simulations

Uncertain Parameters

Stochastic simulations with the New Rifle ground water flow and transport model were accomplished using a conventional Monte Carlo simulation module built into GW Vistas. Initially, several different model parameters were treated as uncertain in the analysis. However, the simulations ultimately used to assess the potential for natural flushing were limited to three: aquifer hydraulic conductivity, aquifer dispersivity, and the vanadium soil-water distribution coefficient, which is denoted by K_d . These parameters were observed to have the most significant effect on dissolved vanadium concentrations over time.

Initial Concentrations

The stochastic simulations made use of an initial vanadium distribution drawn from observed vanadium concentrations during a sampling event that occurred between October 26 and November 4 of 1987. At the time, vanadium concentrations were monitored at 17 alluvial monitoring wells, which appeared to provide a realistic representation of the vanadium distribution. The well numbers, coordinates, and vanadium concentrations (mg/L) from this sampling event are shown in Table 1. The data in Table 1 were imported into the program Surfer, and were subsequently used in a kriging module to determine a starting concentration value for each active cell in the New Rifle transport model.

Use of the 1987 vanadium concentrations as initial conditions in the model differed from the approach taken with the modeling performed for the SOWP (DOE 2000), wherein vanadium concentrations measured in the summer of 1998 were applied as initial conditions. The rationale for employing initial conditions from an earlier year stemmed from the effects that surface remediation apparently continued to have on dissolved vanadium concentrations in the mid- to late- 1990s, but had since declined in the 2000s. This observation suggested that vanadium concentrations during the last few years had largely returned to pre-remediation levels, and that the fate of vanadium today was now governed solely by the processes that previously affected the site in the late 1980s. Accordingly, it was believed that forward predictions with the model using 1987 concentrations as starting conditions would provide reasonable fits to observed vanadium levels during the last few years.

Conditioning Times and Locations

Conditioning of stochastic model results was accomplished using vanadium concentrations that have been measured in recent years. The conditioning exercise made use of differences between observed and simulated vanadium concentrations, which are referred to as model residuals. The criterion used to assess the overall fit of a model run to observed concentrations was the root mean squared error (RMSE) (Anderson and Woessner 1992), which is defined as the square root of the sum of all squared residuals. In effect, the conditioning exercise comprised a method for attempting to calibrate the model, as only the simulations that resulted in the lowest residuals (i.e., the lowest RMSE values) were examined to discern representative values for flow and transport model parameters.

Table 1: Initial Vanadium Concentrations

Well Location	X coordinate	Y coordinate	Concentration (mg/L)
0581	1346316.	623212.6	0.35
0585	1348610.8	625132.8	0.03
0588	1347475.3	623701.7	0.7
0589	1344251.04	623257.37	0.05
0590	1345383.69	623244.7	1.03
0591	1348693.	624928.1	0.03
0592	1348684.1	624921.8	0.03
0594	1347389.9	624261.4	1.78
0595	1346365.5	623163.7	0.22
0599	1344572.79	624314.81	0.05
0600	1345807.2	622993.3	0.29
0603	1341394.73	623420.95	0.03
0609	1343083.9	624827.2	0.04
0610	1346191.5	625242.5	0.84
0615	1346756.2	625071.4	9.86
0616	1346603.1	622918.3	0.19
0618	1343239.48	623073.25	0.06

The selection of a threshold RMSE value as a conditioning criterion was subjective. Following guidance provided in Knowlton and Peterson (1998), initial values for the threshold RMSE were set at values that were of the same general magnitude as the model calibration targets (i.e., measured concentrations during recent years). As discussed later, difficulties were encountered in producing simulations that meet threshold criteria of these magnitudes.

Three sampling events, each with five monitoring locations within the area of vanadium contamination, were used for the model conditioning. Table 2 shows the well locations, conditioning times, and measured vanadium concentrations that were applied. During some of the stochastic simulations, all sampling times and wells were used in the conditioning, whereas other stochastic analyses were conditioned on just one or two sampling events and fewer wells.

Table 2: Locations, Times, and Measured Vanadium Concentrations (mg/L) Used for Model Conditioning

Well Location	June 2000	November/ December 2000	June 2002
0218			1.26
0590	0.289	0.294	0.443
0657	0.896	0.945	0.666
0658	10.2	6.94	8.09
0659	12.2	2.4	2.22

Uncertain Parameter Distributions

Characteristics of the probability density function (PDF) used for each of the three parameters treated as uncertain in the probabilistic simulations (aquifer hydraulic conductivity, aquifer

dispersivity, vanadium soil-water distribution coefficient [K_d]) are presented in Table 3. As this table shows, uniform distributions were assigned to each parameter. The choice of the PDF type was somewhat arbitrary; that is, no statistical tests were performed to determine if the assumed distribution conformed with measured or literature estimates of distributions for each parameter. Nevertheless, the use of a uniform distribution was believed to be sufficient for identifying parameter combinations, if any, that would improve the fit between modeled and observed vanadium concentrations.

During each Monte Carlo analysis with the site model, constant values were assigned to all flow and transport parameters that were not considered uncertain. The constant values were identical to those employed in the SOWP model.

Table 3: Distribution Characteristics of Uncertain Parameters in the Probabilistic Simulations

Parameter	Minimum Value	Maximum Value	Distribution Type
Hydraulic Conductivity (ft/day)	94.0	174.0	Uniform
Dispersivity (ft)	50.0	150.0	Uniform
Distribution Coefficient (mL/g)	2.0	7.8	Uniform

Probabilistic Results

Several probabilistic analyses were performed, each varying with respect to the sampling times and monitor wells used for conditioning of the predicted vanadium concentrations. During each analysis, three hundred (300) realizations of parameter combinations were generated, which in turn resulted in 300 sets of modeling results. This number of simulations was believed to be sufficient for analyzing the effects of all possible parameter combinations on computed vanadium concentrations. Though no statistical tests were performed to demonstrate that this was accomplished, visual inspection of the parameter values generated in each model realization did appear to support this goal. To help demonstrate this point, Figures 1 and 2 show plots of realization number versus hydraulic conductivity and soil-water distribution coefficient, respectively. These plots provide a subjective indication of how well the simulated parameter values represent their respective theoretical distributions.

Four probabilistic analyses that were conducted are listed in Table 4 along with the assumed RMSE criterion and resulting minimum and maximum RMSE values for each analysis. An obvious conclusion drawn from the table is that none of the Monte Carlo analyses was capable of producing a simulation with an RMSE value less than the respective RMSE criterion. This result strongly suggested that the behavior of dissolved vanadium in ground water at the site varies considerably in time and space, and, as a consequence, it is very difficult to produce a flow and transport model that can perform reasonably in matching observed vanadium concentrations at monitor wells.

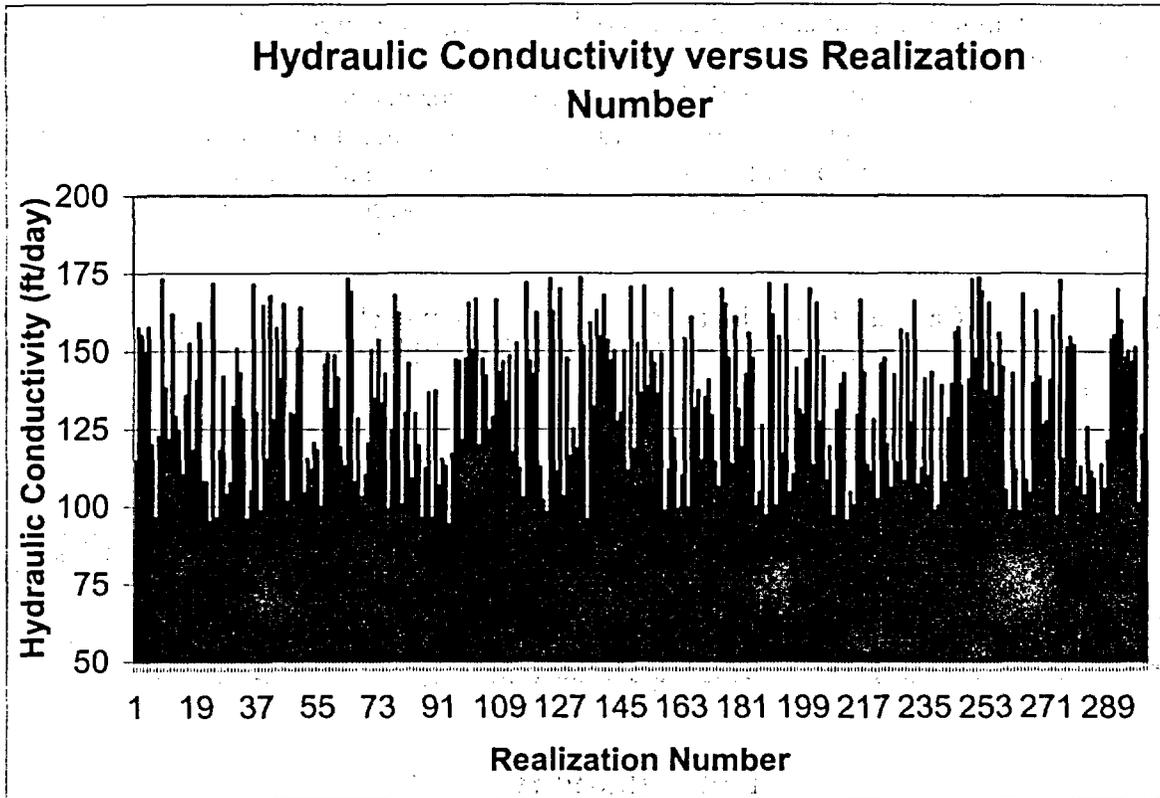


Figure 1. Generated Hydraulic Conductivity versus Realization Number

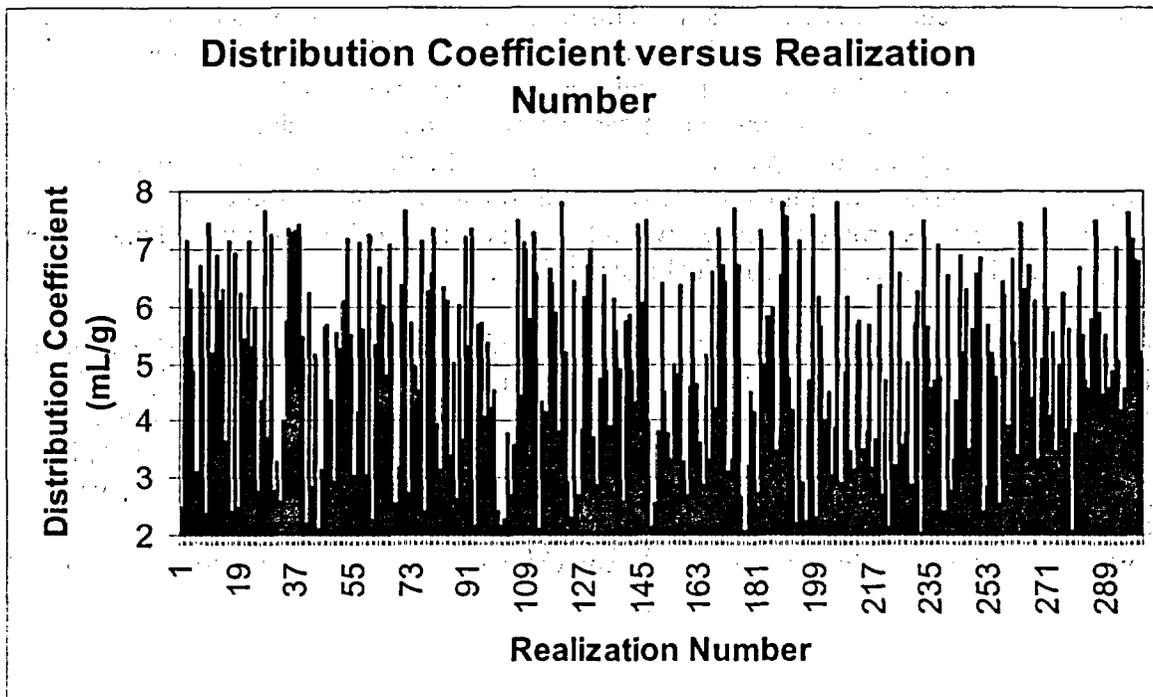


Figure 2. Generated Distribution Coefficient versus Realization Number

Table 4. Conditioning Results from Monte Carlo Analyses

Monte Carlo Analysis	Conditioning Times	Conditioning Locations	RMSE Criterion (mg/L)	RMSE Minimum (mg/L)	RMSE Maximum (mg/L)
1	June 2000 N/D 2000 June 2002	All Wells	3.60	4.42	4.73
2	June 2000 June 2002	All Wells	4.03	5.02	5.32
3	June 2002	All Wells	1.15	2.82	3.24
4	June 2000 N/D 2000 June 2002	Well 0590	0.342	0.531	0.851

Inspection of Table 4 also reveals that the range of RMSE values resulting from each Monte Carlo analysis is very narrow. This observation suggests that, despite the relatively wide range in possible values of uncertain parameters that can be utilized in the model (See Table 3), no particular parameter value or combination of values exists that allows the model to perform significantly better than other realizations in matching observed vanadium concentrations. To examine this latter issue further, analyses were performed on the probabilistic modeling results with the intent of identifying explicit trends in parameter values that are most representative of site conditions. These additional analyses are discussed in the following section.

It should be noted that several simulation scenarios other than those listed in Table 4 were performed during this study. Though the results of those additional analyses are similar to those mentioned above, they are excluded from this report in the interest of brevity.

Potential Relationships Between RMSE and Uncertain Parameter Values

Regression analyses were conducted to determine if any correlation existed between the values of uncertain parameters used in each Monte Carlo simulation and the corresponding RMSE for that simulation. Results from one of the regression analyses is shown in Figure 3, which contains a scatter plot of RMSE (mg/L vanadium) and associated hydraulic conductivity for Monte Carlo Analysis 1 in Table 4. Also listed are the coefficient of determination (R^2) and the equation describing the least squares fit between RMSE (y) and hydraulic conductivity (x). An obvious conclusion taken from Figure 3 is that there is no apparent relationship between RMSE and hydraulic conductivity. The scatter plot does indicate that RMSEs tend to be slightly smaller when lower hydraulic conductivities are used, but the low R^2 value associated with the regression do not suggest that such a relationship is strong.

The results of a similar regression analysis are illustrated in Figure 4, which comprises a scatter plot of RMSE and the vanadium distribution coefficient (K_d) for Monte Carlo Analysis 1. Again, there appears to be no distinct correlation between RMSE and the model parameter being investigated, in this case vanadium K_d . However, unlike the potential relationship between RMSE and aquifer hydraulic conductivity, RMSE values show no distinct trends toward increasing or decreasing with increases in K_d . Thus, it is impossible to discern whether model performance improves with lower K_d values, an observation that would be expected if natural flushing were to be more rapid than has been previously observed or predicted.

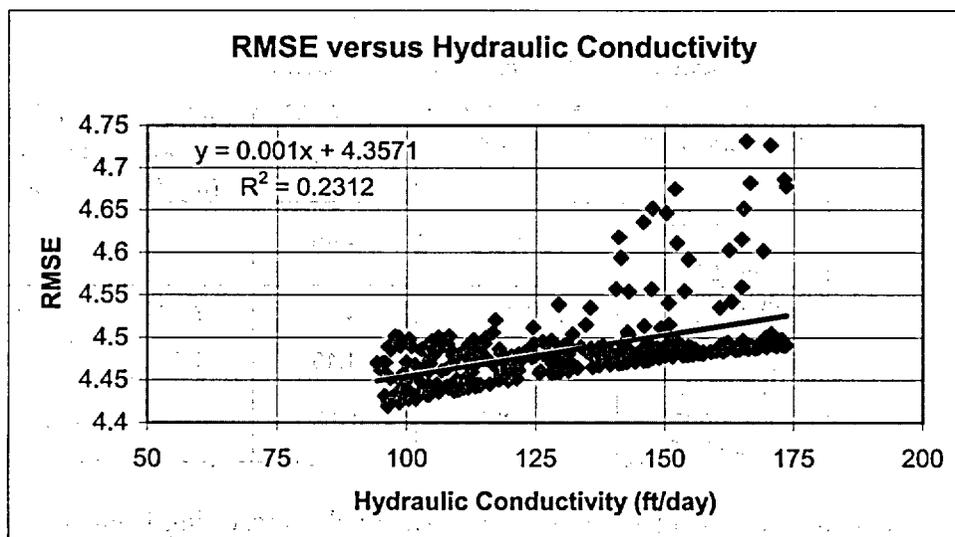


Figure 3. RMSE (mg/L) Versus Hydraulic Conductivity in Monte Carlo Analysis 1

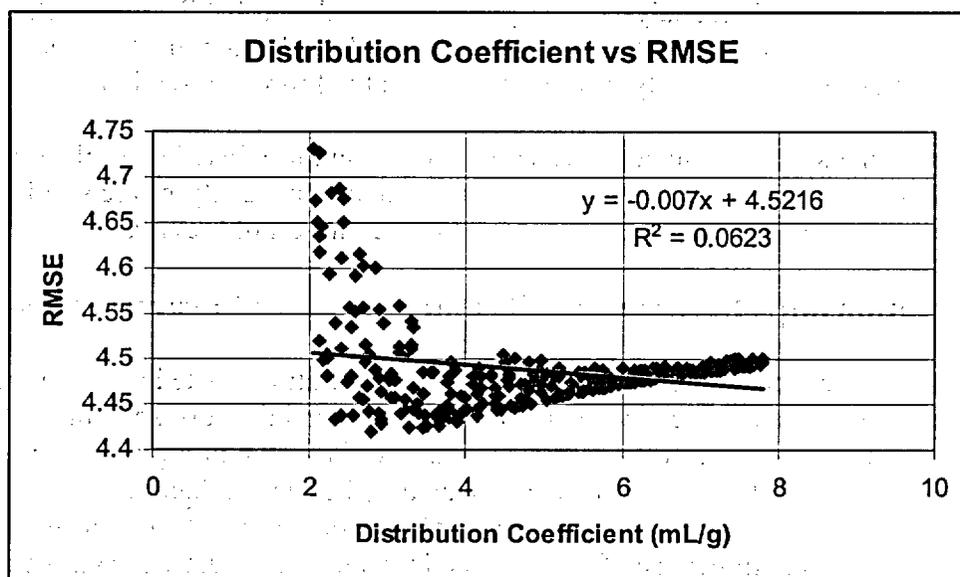


Figure 4. RMSE (mg/L) Versus Vanadium Distribution Coefficient for Monte Carlo Analysis 1

Because the limited RMSE ranges produced the model makes it difficult to pick a meaningful RMSE criterion for assessing model uncertainty, additional analyses were arbitrarily conducted on the 50 model runs from Monte Carlo Analysis 1 with the smallest RMSE values. The intent of these additional assessments was to ascertain whether distinct correlations exist between RMSE and uncertain parameter values with the simulations that perform best in matching observed vanadium concentrations that could not be discerned from analyzing all simulations simultaneously.

Figure 5 shows the results of a regression analysis between RMSE of the 50 best performing simulations and associated aquifer hydraulic conductivities from Monte Carlo Analysis 1. An

analogous evaluation of the vanadium distribution coefficient is provided in Figure 6. Though the scatter plot in each of these figures shows a tendency for RMSE values (i.e., better model fit)

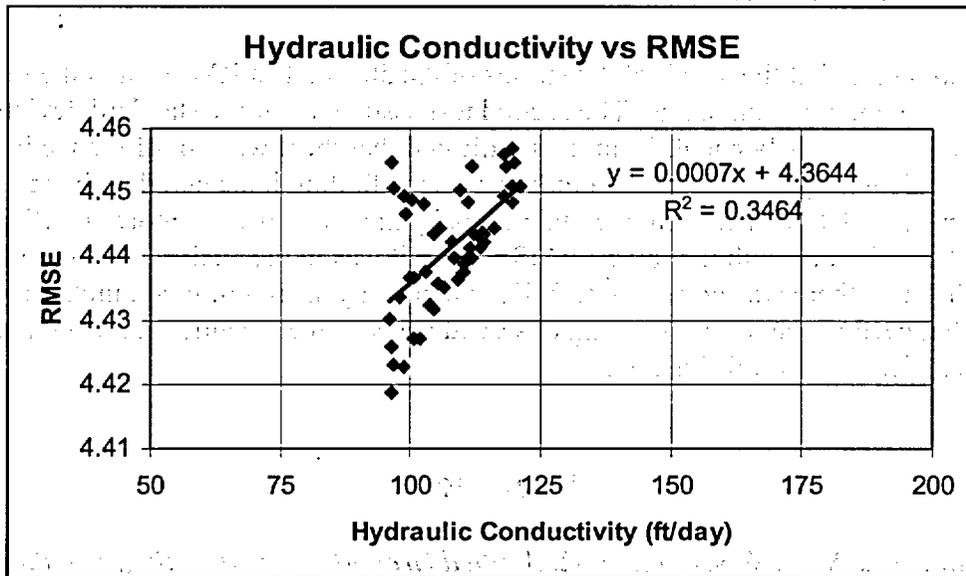


Figure 5. RMSE(mg/L) Versus Hydraulic Conductivity for the 50 Model Runs with the Lowest RMSE values, Monte Carlo Analysis 1

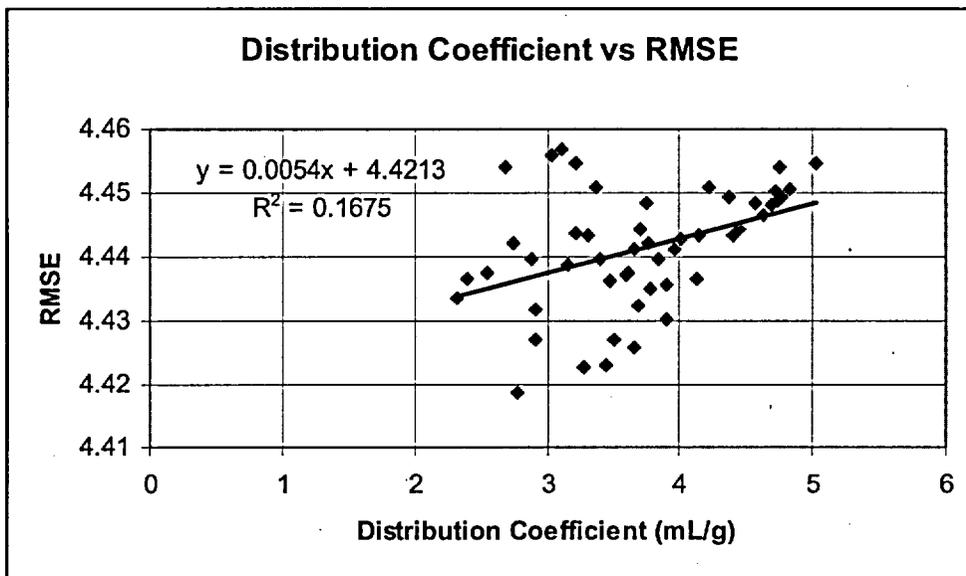


Figure 6. RMSE(mg/L) Versus Vanadium Distribution Coefficient for the 50 Model Runs with the Lowest RMSE values, Monte Carlo Analysis 1

to occur with decreasing values of hydraulic conductivity and K_d , neither analysis indicates that such tendencies translate into strong correlations. This observation again suggests there is little evidence to indicate that, in general, dissolved vanadium is flushing from the New Rifle Site than had previously been predicted in the SOWP (DOE 2000).

To provide some quantitative evidence as to whether the distribution of the 50 smallest RMSEs in Monte Carlo Analysis 1 was significantly different from the distribution of the remaining 250 realizations, two statistical tests were performed. Both tests made use of the t-statistic with a level of significance of 1% for each test.

The first test assumed that the standard deviations of the 50 smallest RMSEs and the remaining 250 RMSEs were unknown but equal. The second test assumed that the standard deviations were unknown and not necessarily equal. Both tests indicated that there was no difference in the mean RMSE values calculated for each set of simulations. This finding indicated that the results of attempts to find correlations between uncertain model parameters was no more significant in the case of the 50 simulations with the lowest RMSEs than it was in the analysis based on all simulations. That is, there was no reason to believe that analysis of a limited number of simulations that perform better in matching observed vanadium concentrations would provide evidence of accelerated natural flushing.

References

Anderson, M.P., and W.W. Woessner, 1992. *Applied Ground water Modeling, Simulation of Flow and Advective Transport*, 381 p.

Knowlton, R.G., and D.M. Peterson, 1998. *Analysis of Natural Attenuation as a Possible Ground water Remedial Alternative at the DOE UMTRA New Rifle Site at Rifle, CO*, September.

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