

5.0 Site Conceptual Model

The site conceptual model discusses the important processes that influence the distribution, present levels, and estimated future conditions of contamination at the Naturita site. Results of information gathered during the past year and a review of previous information were used to construct the model. The compliance strategies will be based on information in the site conceptual model.

5.1 Geology

5.1.1 Regional Geologic Setting

The Naturita site is in the Canyonlands physiographic region, along the northeastern side of the Colorado Plateau. This area is characterized by canyons deeply incised into red sandstones of Mesozoic age with isolated mesas. The plateau was uplifted about 10 million years ago, causing rivers to entrench as the uplift proceeded, and may still be experiencing some uplift (Cater 1970). The Uncompahgre Plateau is the dominant structure along the eastern side of the site that was reactivated during the Pliocene and possibly later (Cater 1970). It is a broad northwest-trending upwarp bounded on the west by the north-flowing San Miguel and Dolores Rivers. To the west is the Paradox Basin, a large Pennsylvanian basin that formed concurrently with the ancestral uplift along the Uncompahgre Plateau (Barrs and Stevenson 1981). The basin is characterized by numerous folds and faults produced by compressional forces during the Laramide orogeny. This event allowed lower salt beds to mobilize into elongate upward-piercing diapirs that produced anticlines. Later, the compressional forces were relaxed, allowing tension and the structural failure of the anticlines. Subsequent uplift of the entire region caused erosion and exposed the failed salt anticlines that weathered and produced further collapse and formation of the modern salt valleys. *The Remedial Action Plan for the Inactive Uranium Processing Site at Naturita, Colorado* (DOE 1998) presents a more detailed description of the geologic setting.

5.1.2 Local Geology and Stratigraphy

Locally, the San Miguel River valley follows part of the Nucla Syncline, a broad gentle downwarp off the eastern flank of the Salt Valley Anticline (a collapsed salt anticline) located to the west. Bedrock dips in the area of the site are subtle, 1 to 2 degrees to the northeast (DOE 1995).

The stratigraphy at the site is simple. Figure 5-1 shows a generalized geologic cross section trending from the south center of the site to the northwest and across Highway 141. The cross section was constructed from wells used during surface remediation; only well 0547 remains. Unconsolidated alluvium deposited by the San Miguel River fills the valley floor. This material consists of clayey gravel to sandy cobbles, interbedded with layers of silty to sandy clay that pinch off against the bedrock highs on the west and attain a thickness of 23 ft at well 0548. Toward the west side of the site, red to chocolate-colored clayey to sandy colluvium from weathering of Brushy Basin and stratigraphically higher sediments fill drainages entering from the west. Figure 5-2 shows the approximate bedrock surface below the site. Figure 5-3 (alluvium thickness) shows a thicker area of alluvium along the south side of the site where a gravel pit is currently operating. Another thick area of alluvium occurs farther north near the bend of the river. This contouring is based on one well log, well 0548, which recorded the top of the Brushy Basin at 23 ft, much deeper than in surrounding wells.

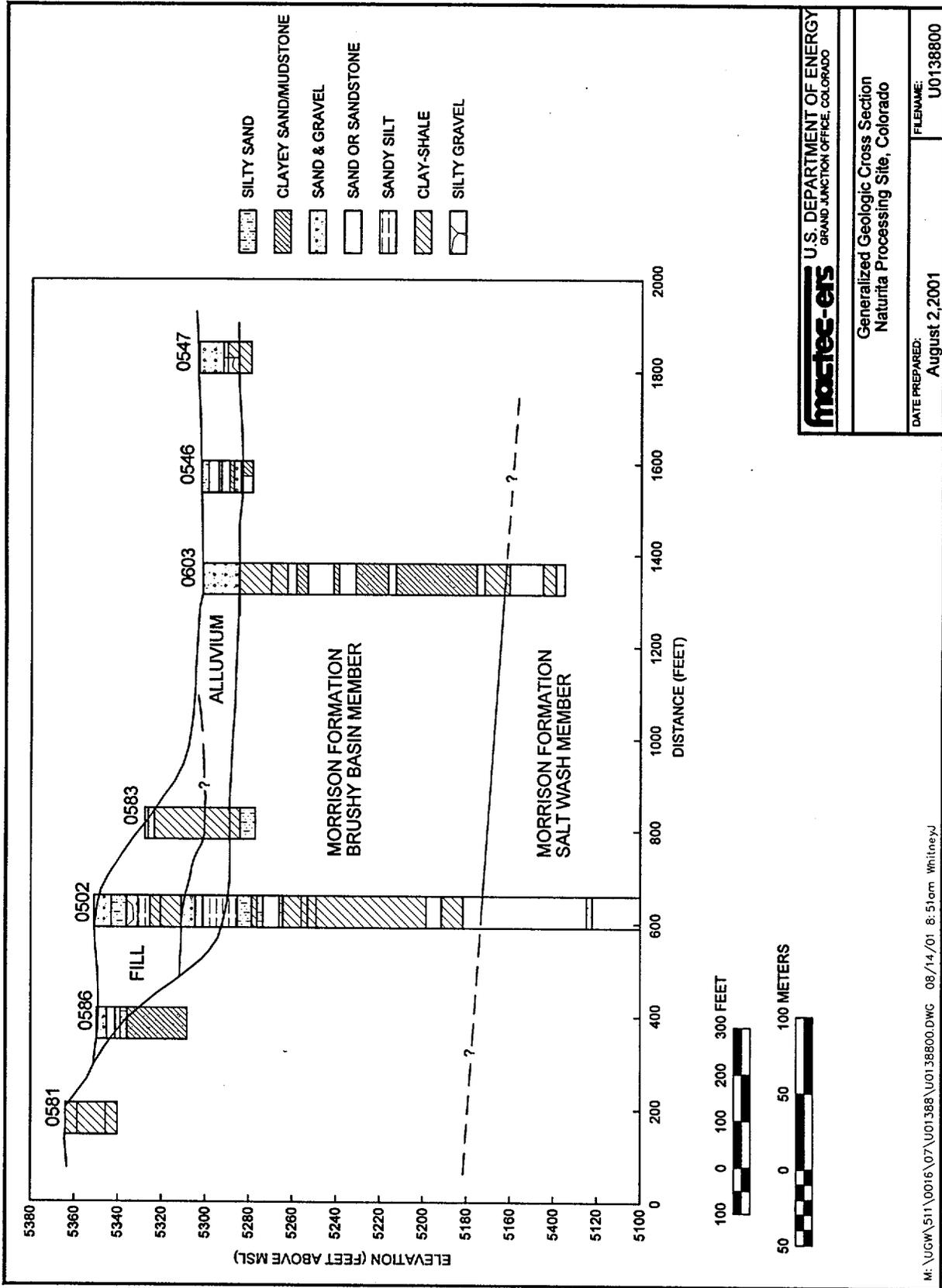


Figure 5-1. Generalized Geologic Cross Section of the Naturita Site

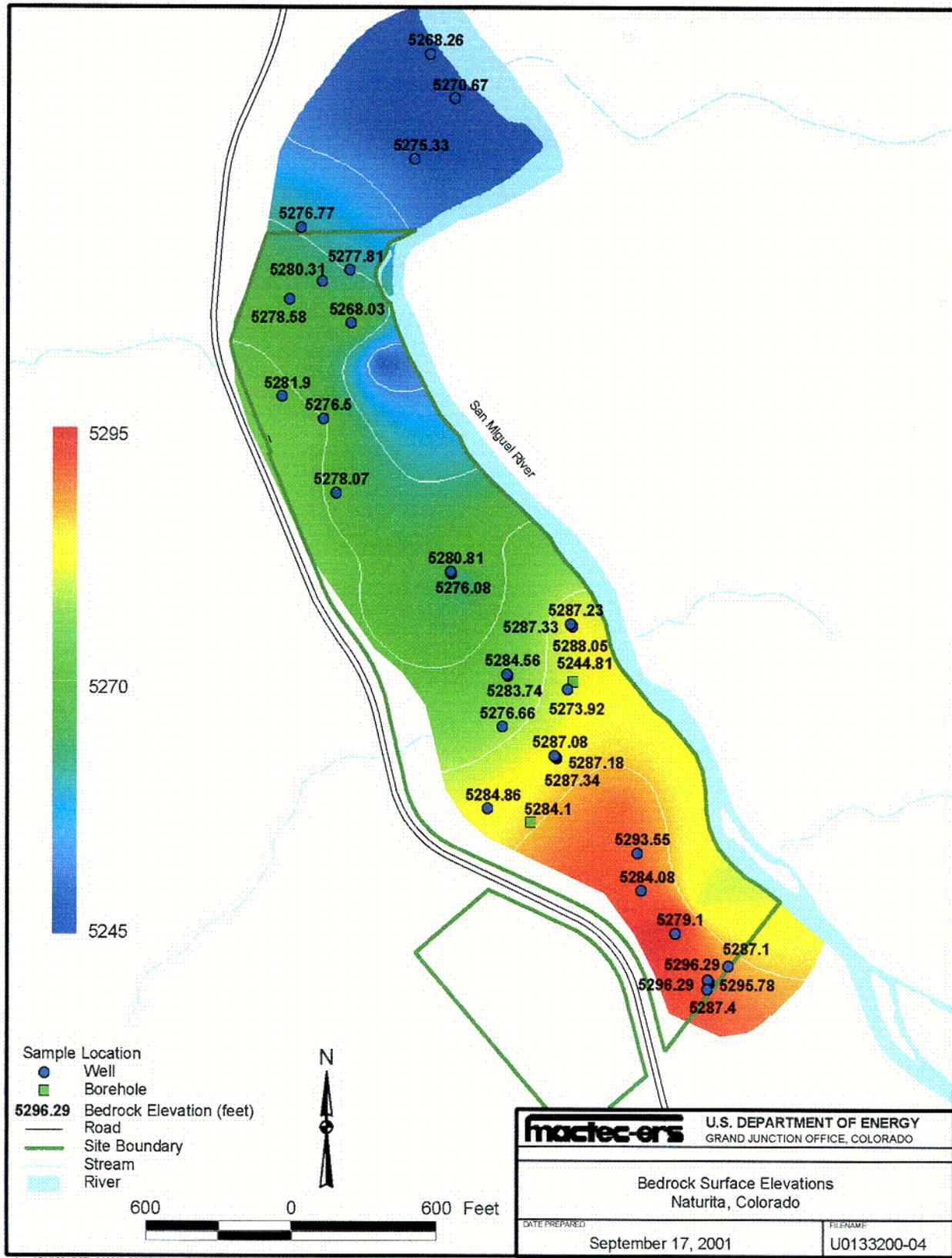


Figure 5-2. Bedrock Surface Elevations at the Naturita Site

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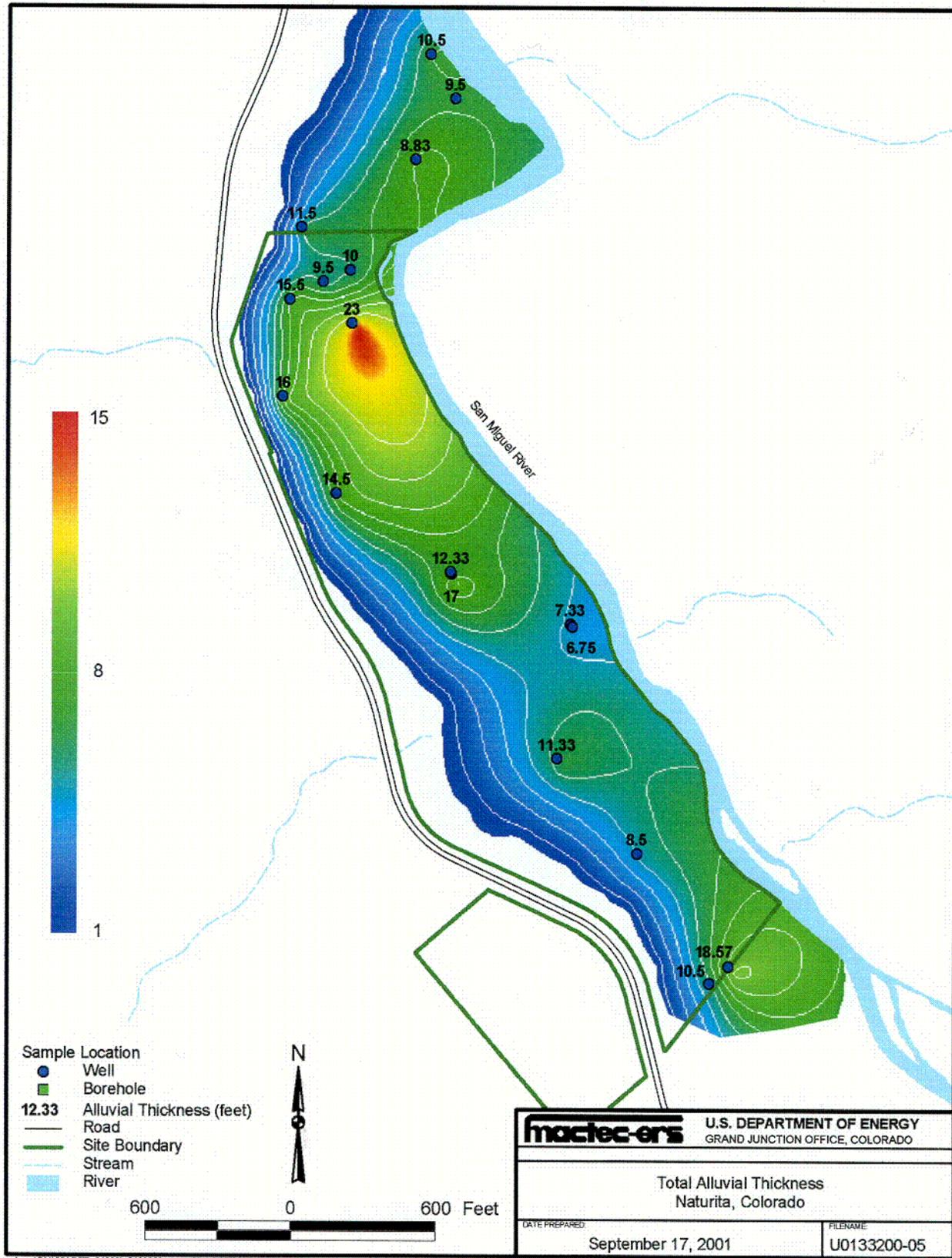


Figure 5-3. Thickness of the Alluvium at the Naturita Site

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Bedrock underlying the alluvium consists of the Brushy Basin and Salt Wash Members of the Jurassic Morrison Formation that range up to 820 ft in thickness in the Naturita area. This is the same formation that yielded most of the uranium and vanadium ore from the Uravan district and is unusually thick in this area. The upper Brushy Basin Member contains numerous sequences of variegated bentonitic fluvial to lacustrine mudstones, siltstones, claystones, and some sandstones that range in color from brown to red, green, and gray. It has been partly eroded away below the site but is still 120 to 150 ft thick and can be twice to three times this thickness (Williams 1964). Below the Brushy Basin is the Salt Wash Member, consisting of fluvial sandstones with some siltstone and conglomerate lenses. It sometimes contains carbonaceous plant fragments, which can act as a reducing agent that causes the precipitation and concentration of uranium and vanadium. This member contains several prominent sands and can be up to 300 ft thick (Williams 1964).

Above the Brushy Basin sediments are the sandstones and conglomerates of the Lower Cretaceous Burro Canyon Formation and above them the sandstones of the late Cretaceous Dakota Sandstone. The remnant of a coal mine high on the hillside on the east side of the San Miguel River near the site is in the Dakota Sandstone. These formations have little influence on the millsite.

5.2 Hydrologic System

5.2.1 Surface Water Hydrology

The San Miguel River is the dominant source of surface water at the site. It is a perennial stream that originates in the San Juan Mountains near Telluride and joins the Dolores River about 20 miles downstream from Naturita. A USGS gauging station at Naturita records an average maximum flow of 2,000 cubic feet per second and an average minimum of 60 cubic feet per second (DOE 1994). Maximum flows occur during the spring runoff usually in June and during summer storm events. The only current use of river water near the former millsite is for irrigation and livestock watering.

Several arroyos on the west side of Highway 141 drain Sawtooth Ridge and periodically contribute water and sediment to the site. A culvert near the middle of the site drains one of these valleys to the west. Water from summer storms in 2000 eroded the culvert, and it was repaired in 2001. Figure 3-1, an aerial photograph from 1954, shows a prominent delta deposit on the floodplain produced by another drainage located farther north.

Dry Creek enters the San Miguel River about 0.5 mile upgradient of the site and drains Mancos Shale and Dakota Sandstone in Dry Valley. It flows during the spring and intermittently during other parts of the year. Water from Dry Creek is usually turbid and increases the suspended sediment load in the San Miguel River near the site.

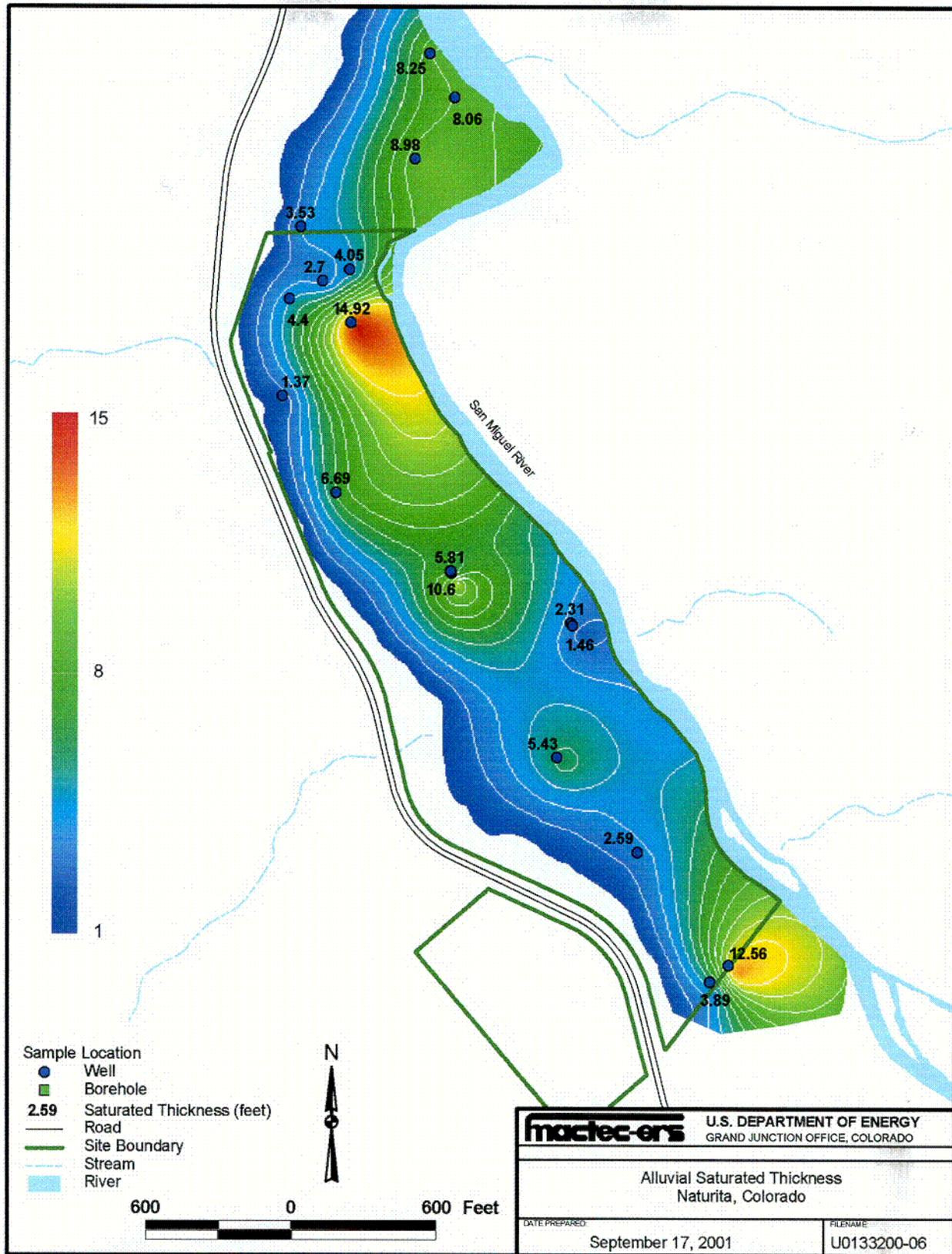
A distributary cutoff on the Maupin property is the source of several small ponds fed by springs. Surface location 0538 is recorded as a spring in the BLRA and is part this system. Figure 3-3 from 1974 shows the main course of the San Miguel River was located farther south and occupied the present seep/pond area of 0538. By 1986 (Figure 3-4) the current course of the river had shifted to the north, and by 1998 (Figure 3-7) the present course of the river had left the former channel as a low scarp along an expanding riparian willow-sapling zone.

5.2.2 Alluvial Aquifer

The alluvial aquifer is the uppermost aquifer at the Naturita site and consists of the saturated portion of the river-lain alluvium. It is the only aquifer of concern for ground water contamination because the underlying Brushy Basin Member of the Morrison Formation has an upward hydraulic gradient. The alluvial aquifer is a wedge of sediment that varies in thickness from zero as it pinches out along the western bedrock to about 23 ft along the San Miguel River near the northern portion of the site (Figure 5-3 and Figure 5-4). However it generally ranges from only about 5 to 10 ft in thickness over most of the site. The section of interest underlying the site is approximately 4,000 ft long and 700 ft wide. Recharge and discharge occur along the length of the San Miguel River depending on the river level. However, the primary recharge zone is thought to be a 600-ft strip from the San Miguel River about 2,400 ft south of the site near the confluence of Dry Creek, where the river makes a sharp bend. From there, water migrates slowly northwest through the aquifer until it finally exits back into the San Miguel River north of the site along a 500-ft zone where the river intersects bedrock on the Maupin property. The aquifer pinches off against the San Miguel River at that point. Another source of water entering the alluvial aquifer is from arroyos draining from the west. Their significance is probably greater locally where water from these drainages could contribute to flushing contaminants in the aquifer near the western edge of the site. The last source of recharge is infiltration of rainfall. The Hopkins-Montrose airport 2.5 miles east of the site receives approximately 11 inches of rain per year. The surficial aquifer below the site contains approximately 30,000,000 gallons (4 million cubic feet) of water at any one time.

Hydraulic characteristics of the alluvial aquifer were determined by water age determinations, stable isotope and chloride measurements, falling head slug tests, and bromide tracer tests. Ground water age determination studies using tritium-helium and chlorofluorocarbon methods generally indicate increases in the age of water near the western side of the site. Flow paths are generally parallel to the San Miguel River (Figure 5-41), and older ages suggest slower flow rates along the western side of the site. Discussion of the methods for determining ground water age and comparison of results of ground water ages are in Section 5.3.4. The results of the age determinations agree with modeling results that show the "dog-leg" portion of the aquifer in the northwestern part of the site has slower ground water flow rates than areas along the eastern side of the site. The open gravel pit at the southern end of the site intersects ground water. Chloride and stable isotope studies suggest that this dewatering of the upgradient head of the aquifer will have an important, although negative, effect on potential natural flushing or pumping of contaminated water at the site. Section 5.4.6 discusses this in greater detail.

Falling head slug tests were performed for 13 wells in November 1999 and May 2000. The hydraulic conductivity ranged from 19 ft/day (MAU07) to 333 ft/day (NAT09) and averaged 95 ft/day. Bromide tracer tests were performed on six wells. These results indicated hydraulic conductivities that ranged from 43 ft/day to 215 ft/day. No recongized pumping tests were performed for the site.



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5.2.3 Bedrock Aquifer

Two wells, 0502 and 0603, were drilled through the Brushy Basin Member and penetrated the Salt Wash Member of the Morrison Formation during the surface program. Falling head slug tests were conducted in the wells to estimate hydraulic conductivities in the Salt Wash and alluvial aquifers. Results indicated a low hydraulic conductivity in the Brushy Basin Member and a vertical hydraulic gradient from the Salt Wash Member into the Brushy Basin Member. This combination prevents any downward migration of contaminated water into the Salt Wash aquifer and demonstrates that the Brushy Basin acts as an effective aquitard. Appendix B of the Remedial Action Plan for the Naturita site (DOE 1998) provides details of the bedrock aquifer.

5.3 Geochemistry

5.3.1 Source Areas and Contaminants

The sources of contamination at the Naturita site were ores hauled from the surrounding area, mostly within a 50-mile radius, from 1939 to 1958 and processed at the mill. These ores typically contained, in addition to uranium and vanadium, elevated concentrations of arsenic, molybdenum, selenium, and sulfate. During the period from 1947 to 1963, 704,000 tons of ore were processed at the site. Sulfuric acid, bases, and other chemicals were used to process the ores. Estimated volumes of production water and wastewater were not found in a search of the literature, but millions of gallons of contaminated water may have seeped into the ground.

Tailings at the Naturita site were hauled away for further processing in the late 1970s, and the site underwent surface remedial action to remove approximately 771,000 cubic yards of RRM from 1993 to 1998. A number of areas containing contaminated soils were left in place under the application of supplemental standards. The most contaminated ground water on the site is below the former tailings pile area. There, vanadium concentrations still reflect the footprint of the former surface contamination.

5.3.2 Surface Water Quality

The only permanent surface water features at the Naturita site are the San Miguel River and a ground water seep that discharges near location 0559 and flows to the San Miguel River near location 0538. Contaminated alluvial ground water from the site has the potential to discharge to these two areas, both of which are downgradient of the former tailings area. Impacts to these surface water locations are evaluated by comparison to water quality measurements at locations that are unaffected by site-related contamination.

5.3.2.1 Background Surface Water Quality

Background surface water quality samples were collected from the San Miguel River at location 0531 during November 2000 and March 2001. Location 0531 is upstream and upgradient from the site (Figure 5-5). Table 5-1 summarizes the analytical results of these background samples.

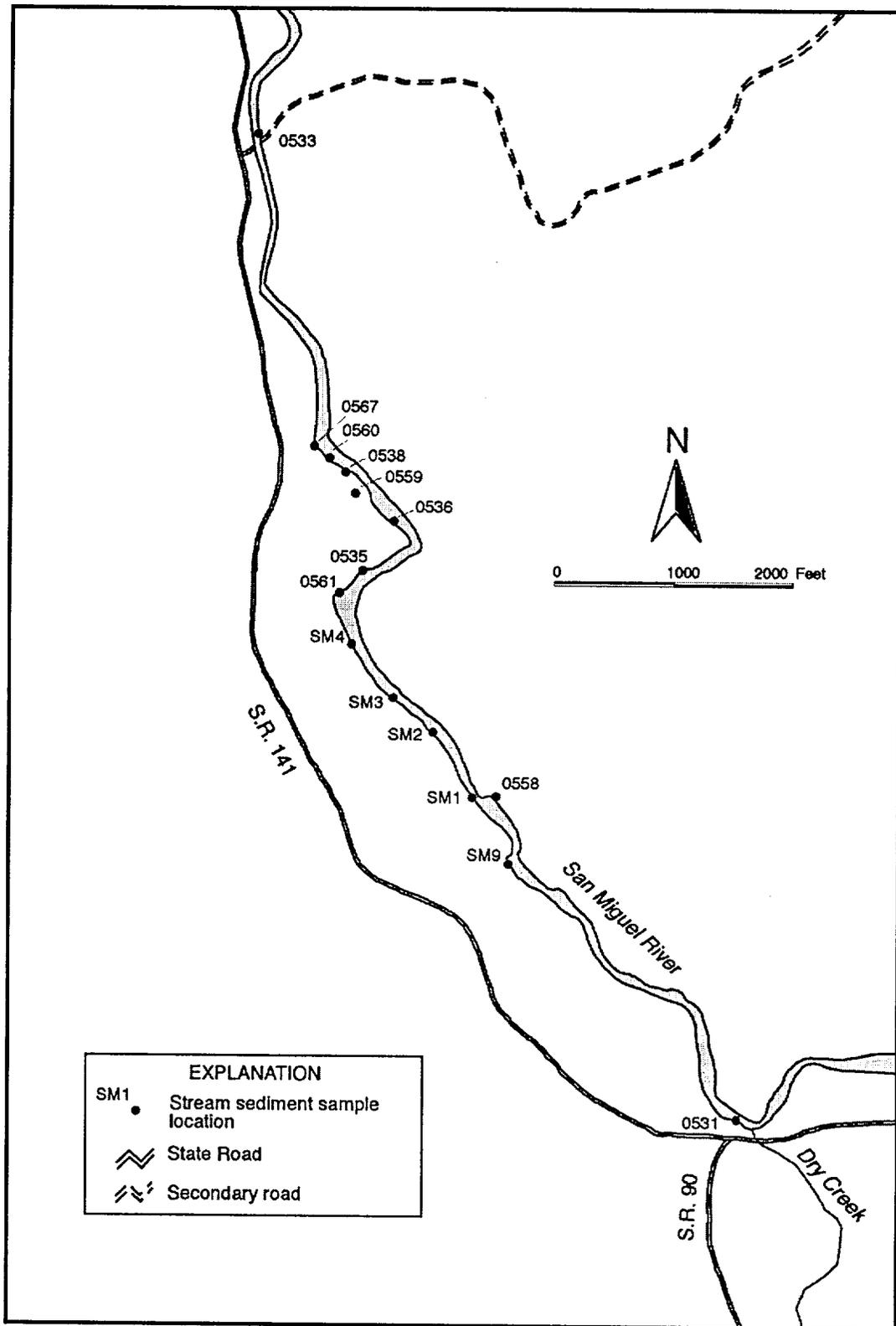


Figure 5-5. Locations of Surface Water and Sediment Samples at the Naturita Site

Table 5-1. Background Surface Water Quality at Location 0531

Analyte	Units	Concentration		
		December 2000	March 2001	Average
Major Ions				
Calcium	mg/L	54	82	68
Chloride	mg/L	0.40	8.4	4.40
Magnesium	mg/L	29	27	28.2
Nitrate	mg/L	0.05	<0.02	
Potassium	mg/L	1.7	1.8	1.74
Sodium	mg/L	23	28	25.4
Sulfate	mg/L	236	239	238
Metals				
Aluminum	mg/L	<0.28	<0.28	
Arsenic	mg/L	0.0007	0.0007	0.0007
Cadmium	mg/L	<0.04	<0.04	
Chromium	mg/L	<0.04	<0.04	
Cobalt	mg/L	<0.04	<0.04	
Copper	mg/L	<0.04	<0.04	
Iron	mg/L	<0.03	<0.03	
Lead	mg/L	<0.20	<0.20	
Manganese	mg/L	<0.04	<0.04	
Molybdenum	mg/L	<0.04	<0.04	
Nickel	mg/L	<0.04	<0.04	
Selenium	mg/L	0.0008	0.001	0.0009
Uranium	mg/L	0.0029	0.0023	0.0026
Vanadium	mg/L	<0.04	<0.04	
Zinc	mg/L	<0.04	<0.04	
Other				
Barium	mg/L	0.08	0.05	0.06
Boron	mg/L	<0.04	0.09	
Bromide	mg/L	6.6	0.05	3.33
Lithium	mg/L	<0.03	<0.03	
Phosphorus	mg/L	<0.04	<0.04	
Silicon	mg/L	3.4	2.4	2.90
Strontium	mg/L	1.2	1.1	1.15
Field Measurements				
Alkalinity as CaCO ₃	mg/L	134	108	121
Dissolved oxygen	mg/L	10.8	13.6	12.2
Oxidation-Reduction Potential	mV	290	361	325
pH	standard units	8.43	8.48	8.46
Specific Conductance	µS/cm	730	816	773
Temperature	°C	1.57	3.82	2.70

Notes:

The mean was not calculated if at least one result was below detection limit. Specific conductance, oxidation-reduction potential, and pH were measured on unfiltered samples; samples for all other measurements were filtered through a 0.45 µm filter.

µS/cm = microsiemens per centimeter
mV = millivolts

5.3.2.2 Site Impacts on Surface Water

Samples were collected adjacent to the millsite at locations SM9, SM1, 0558, SM2, SM3, SM4, 0561, 0535, 0536, 0560 and downgradient of the site at location 0533 to evaluate the effects of ground water contaminants on the San Miguel River. Samples were also collected from a ground water seep at locations 0559 and 0538. Ponded water at location 0567 was collected in March 2001.

A comparison of San Miguel River sampling results from on-site, upgradient, and downgradient locations generally indicates that water quality is unaffected by discharge from the contaminated alluvial aquifer.

Figure 5-6 through Figure 5-10 show concentrations of arsenic, chloride, selenium, sulfate, and uranium, respectively, at surface water locations along the San Miguel River. Vanadium, molybdenum, and nitrate concentrations were at or below detection limits at all locations and are not shown. Most arsenic (Figure 5-6), selenium (Figure 5-8), and uranium (Figure 5-10) concentrations at locations adjacent to and downstream of the former tailings area are all near the background concentration measured at location 0531. However, samples collected during March 2001 at locations 0567 and 0561 have elevated concentrations of most constituents, including uranium, which exceeded the maximum concentration limit established for the UMTRA Project. These samples were collected during low-flow conditions in pools close to the bank of the river. These values most likely represent concentrations of discharging ground water before it is diluted with river water. Some further concentration of contaminants may have occurred through evaporation. At low river stage, flow from these pools to the river is minimal. When the river rises in the spring and summer, this contaminated water should be diluted and flushed out of the stagnant pool areas.

Figure 5-11 through Figure 5-16 compare arsenic, chloride, selenium, and sulfate concentrations, sulfate/chloride ratio, and uranium concentrations, respectively, in samples from the ground water seep locations. Because the chemistry of water discharging from the seep more closely resembles that of ground water than surface water, the concentrations shown in Figure 5-11 through Figure 5-15 are compared to background ground water concentrations measured at well DM1. The water is similar in chemistry to that of nearby wells MAU03, MAU04, and MAU07, which are also shown for comparison. Water quality results from the ground water seep at locations 0559 and 0538 show that concentrations of most constituents exceed the background concentrations measured at location 0531 and well DM1. Vanadium, molybdenum, and nitrate concentrations were at or below detection limits at all locations and are not shown.

Concentrations of arsenic, chloride, and selenium in the ground water seeps shown in Figure 5-11 through Figure 5-13, respectively, are at or near background concentrations measured at location 0531 and well DM1. These values are also well below the UMTRA Project maximum concentration limits.

Figure 5-14 shows sulfate concentrations in samples from the ground water seep locations. Almost all concentrations exceed background values measured at location 0531 and DM1 and exceed the Colorado secondary drinking water standard. An exception is the sample collected in November 2000, which has less sulfate than that measured in 0538 and in the background samples. During March 2001, sulfate concentrations were above background levels and were similar to those measured at location 0538. A similar pattern can also be seen in chloride concentrations shown in Figure 5-12. Figure 5-15 shows the sulfate/chloride ratio in the ground

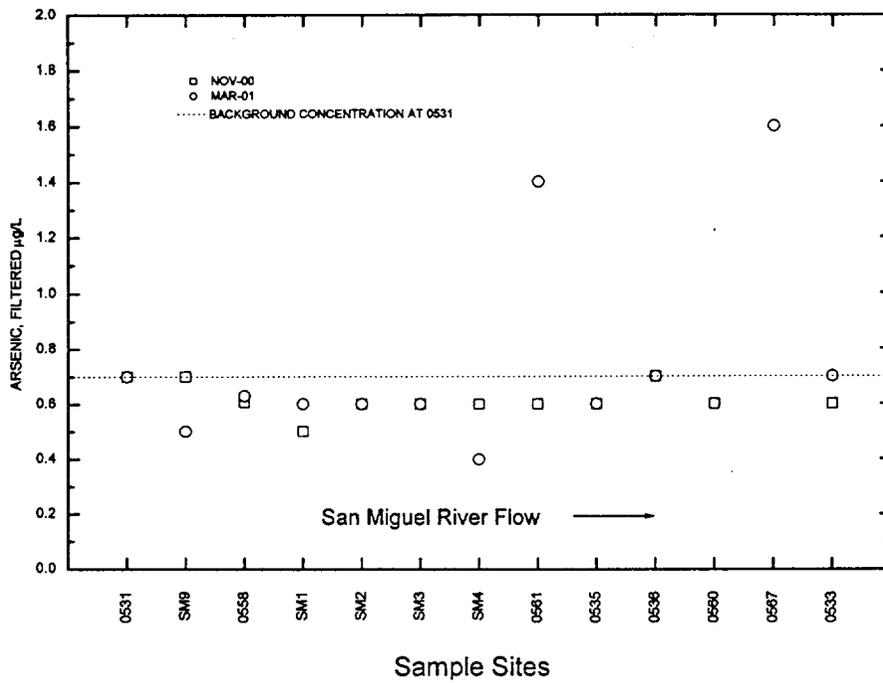


Figure 5-6. Arsenic Concentrations at Surface Water Sampling Locations Along the San Miguel River

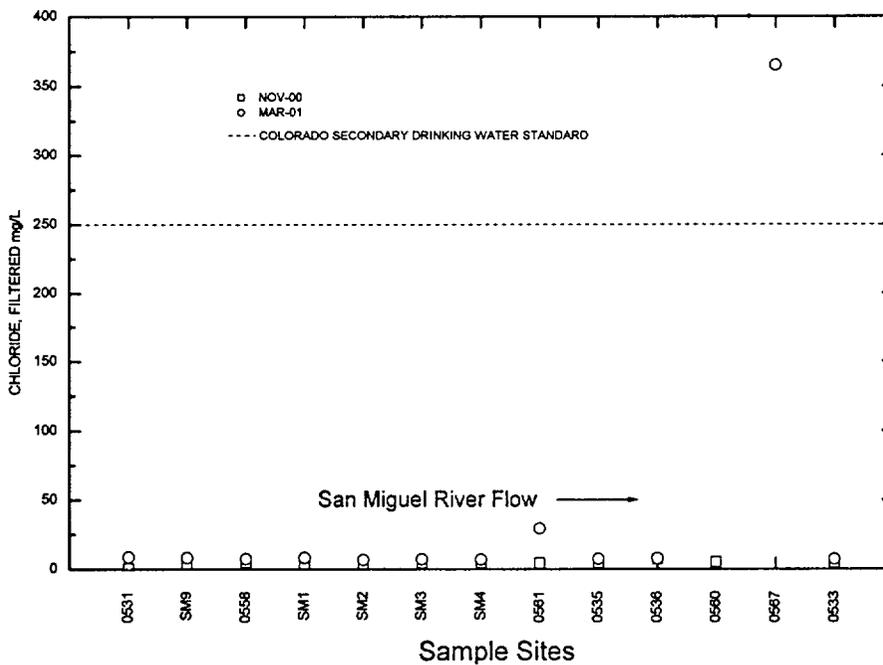


Figure 5-7. Chloride Concentrations at Surface Water Sampling Locations Along the San Miguel River

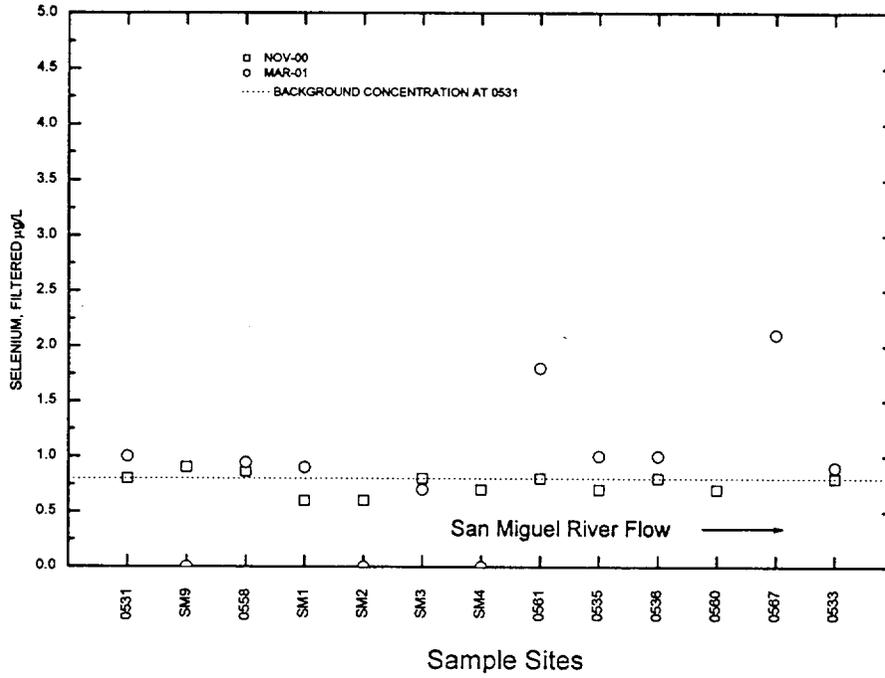


Figure 5-8. Selenium Concentrations at Surface Water Sampling Locations Along the San Miguel River

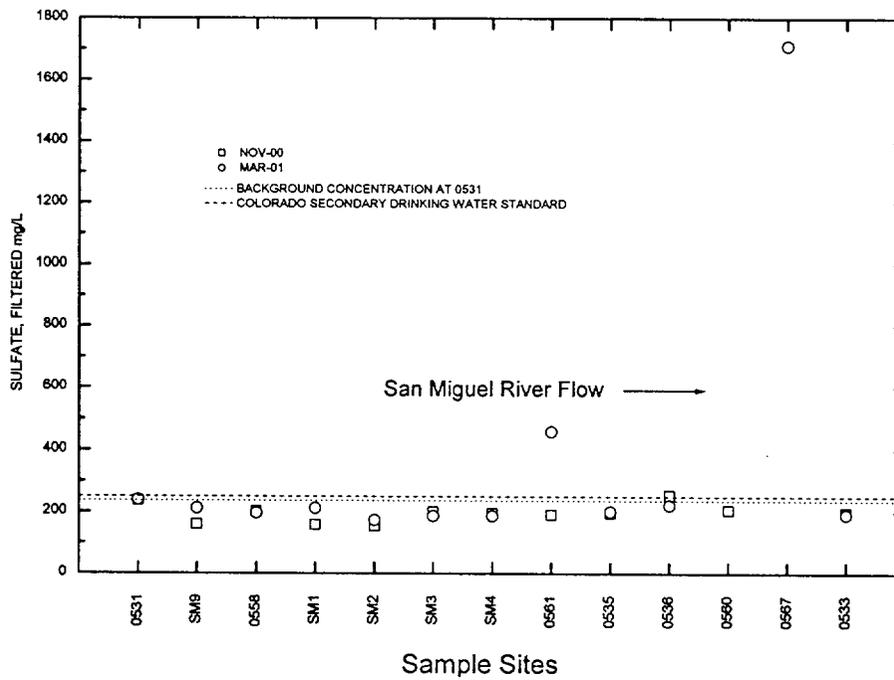


Figure 5-9. Sulfate Concentrations at Surface Water Sampling Locations Along the San Miguel River

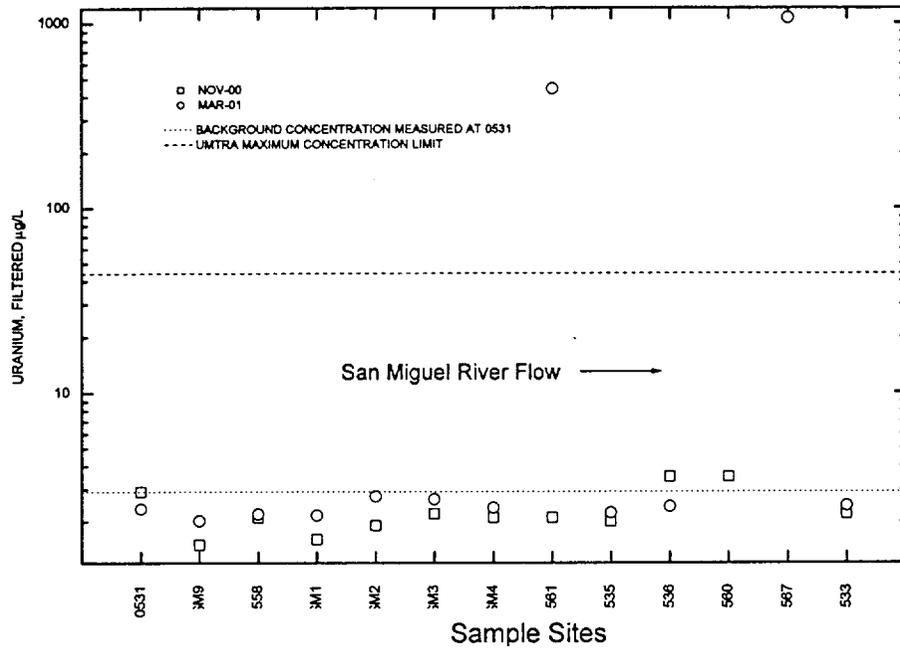


Figure 5-10. Uranium Concentrations at Surface Water Sampling Locations Along the San Miguel River

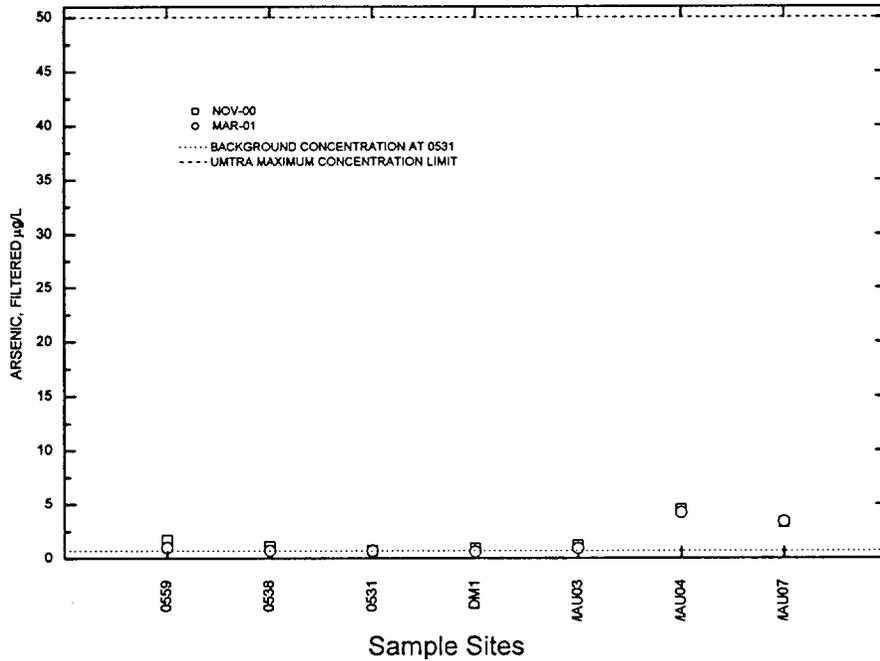


Figure 5-11. Arsenic Concentrations at the Ground Water Seep Locations

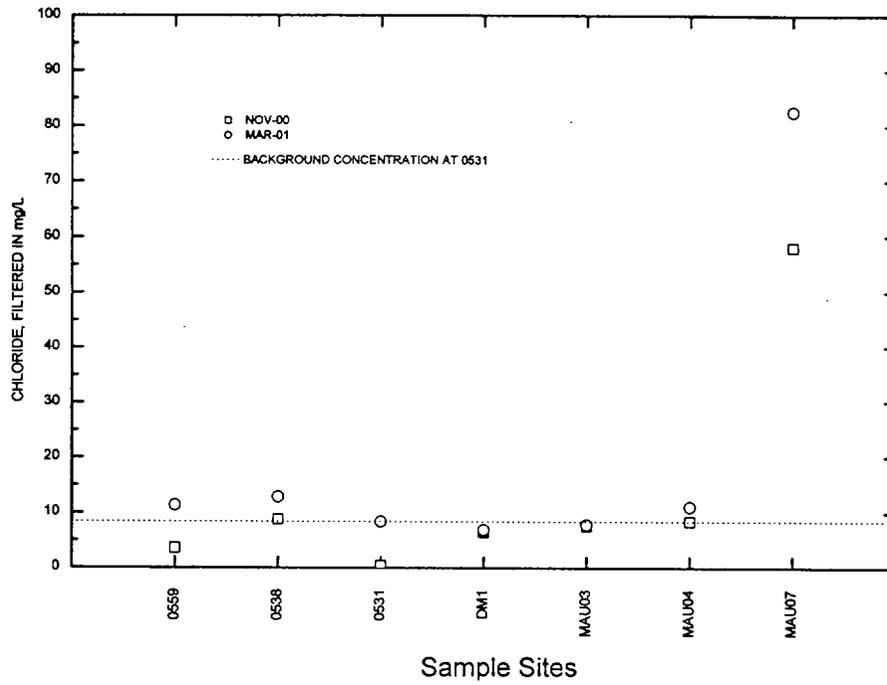


Figure 5-12. Chloride Concentrations at the Ground Water Seep Locations

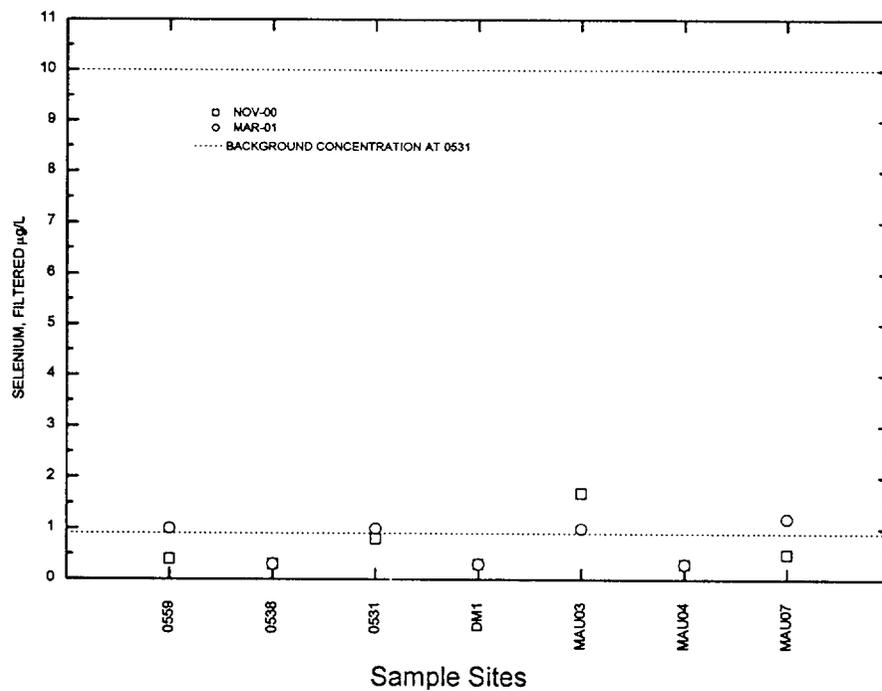


Figure 5-13. Selenium Concentrations at the Ground Water Seep Locations

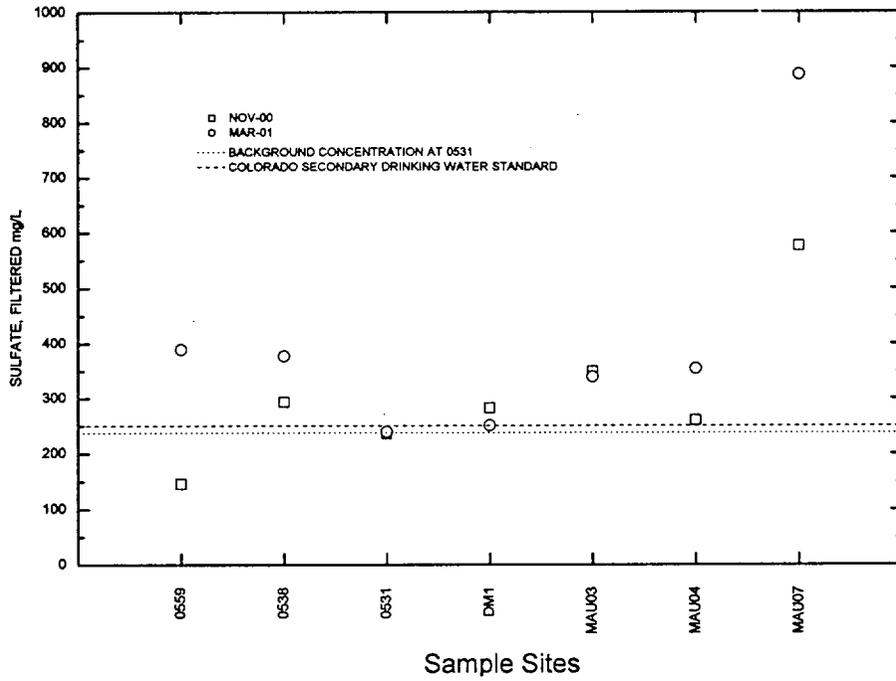


Figure 5-14. Sulfate Concentrations at the Ground Water Seep Locations

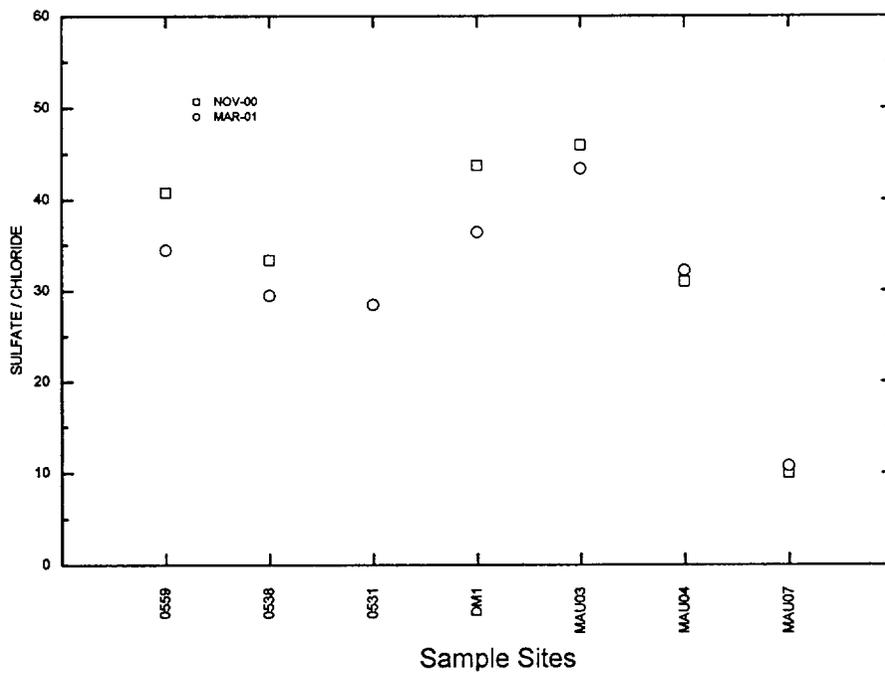


Figure 5-15. Sulfate/Chloride Ratio at the Ground Water Seep Locations

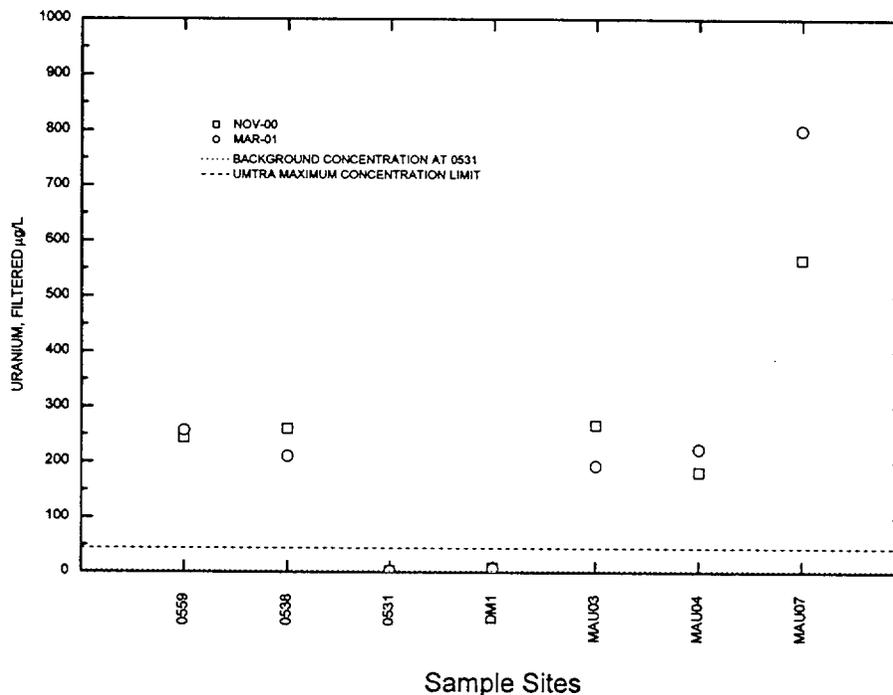


Figure 5-16. Uranium Concentrations at the Ground Water Seep Locations

water seeps. The ratio for the two sites is similar to that calculated for the San Miguel River and nearby wells MAU03 and MAU04. Well MAU07 has a lower sulfate/chloride ratio than the ground water seeps and is more typical of the ratio found in the contaminated area of the alluvial aquifer away from the San Miguel River (see Section 5.3.3.2). This suggests that ground water in the area of the seeps, MAU03, and MAU04 has a greater influence from surface water than that located at MAU07.

As seen in Figure 5-16, uranium concentrations exceed background concentrations and exceed the UMTRA Project maximum concentration limit. Concentrations in the seeps are similar to those in nearby wells MAU03 and MAU04. Uranium concentration in well MAU07 is much higher than in the ground water seeps. The sulfate/chloride ratio indicates that ground water in the area of MAU03, MAU04, and the ground water seeps has a significant component of surface water from the San Miguel River that has been contaminated by buried uranium tailings near surface water location 0535 (Figure 5-5). Because samples were collected from the ground water seep locations only in November 2000 and March 2001, no historical trend in uranium concentration can be inferred. However, USGS has collected data at nearby wells MAU03 and MAU04 since November 1998 and at MAU07 since September 1999. As shown in Figure 5-17, Figure 5-18, and Figure 5-19, respectively, uranium concentrations in wells MAU03, MAU04, and MAU07 have not decreased with time, but rather appear to be controlled by the water table, which is controlled by river stage. Uranium concentrations at location 0559 show a trend similar to that observed in the wells, that is, concentration was greater in March 2001 than in November 2000; location 0538 shows the opposite trend in comparison to the wells (uranium concentration was greater in November 2000 than in March 2001). Additional data are needed to determine if the uranium concentration in the ground water seeps varies directly with river stage and with uranium concentrations in nearby wells.

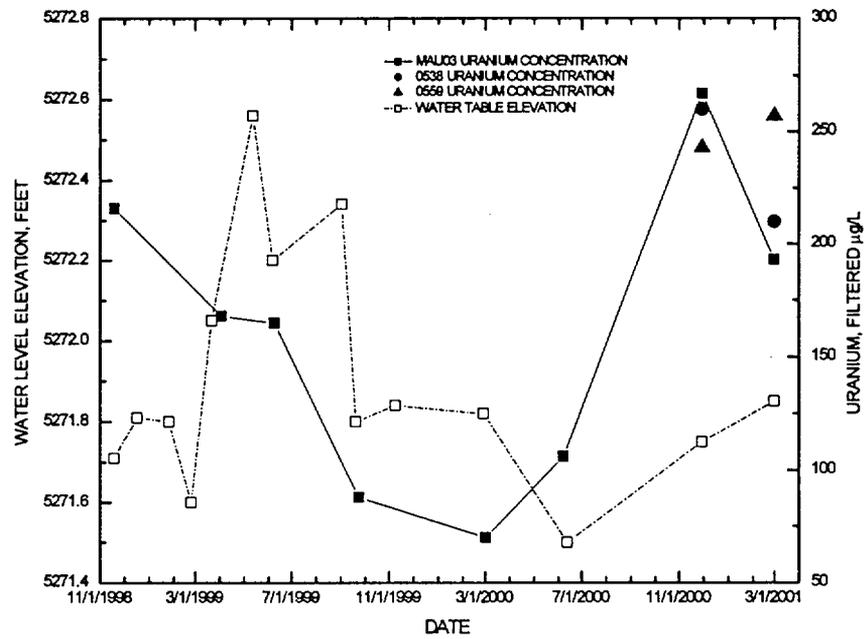


Figure 5-17. Uranium Concentrations and Water Table Elevation in Well MAU03

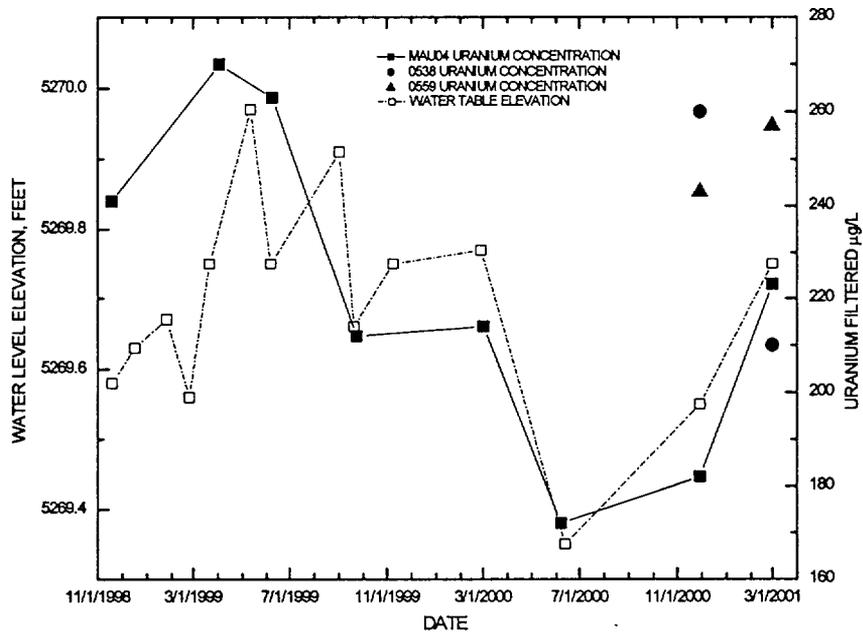


Figure 5-18. Uranium Concentrations and Water Table Elevation in Well MAU04

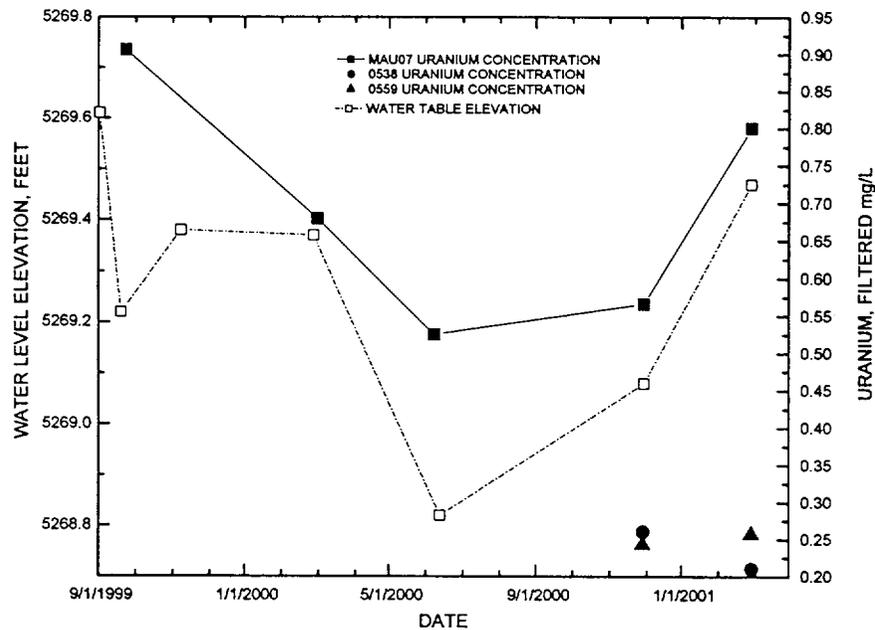


Figure 5-19. Uranium Concentrations and Water Table Elevation in Well MAU07

5.3.3 Alluvial Aquifer Water Quality

USGS has collected ground water quality data at the Naturita site since November 1998 as part of a uranium transport study. The most recent samples were collected in November and December 2000 and in February and March 2001 to support DOE's monitoring of ground water quality.

5.3.3.1 Background Alluvial Ground Water Quality

Background ground water quality is characterized by samples from a site located in the same aquifer upgradient from the former millsite (Figure 5-20). Data from these samples are summarized in Table 5-2; Appendix B is a complete list of ground water monitoring results.

Background ground water quality at the Naturita site is generally good, with slightly high levels of sulfate and manganese. Sulfate concentration at background location DM1 exceeded the Colorado secondary drinking water standard of 250 mg/L during November 2000 and March 2001. Mean background concentrations are lower than the UMTRA Project maximum concentration limits for arsenic (0.05 mg/L), cadmium (0.01 mg/L), molybdenum (0.1 mg/L), nitrate (44 mg/L as NO₃), selenium (0.01 mg/L), and uranium (0.044 mg/L). Vanadium concentrations were below detection. Concentrations of all the trace elements and nitrate were at or near detection limits. Chloride and iron concentrations are also below the limits set by the Colorado secondary drinking water standard of 250 mg/L and 0.3 mg/L, respectively.

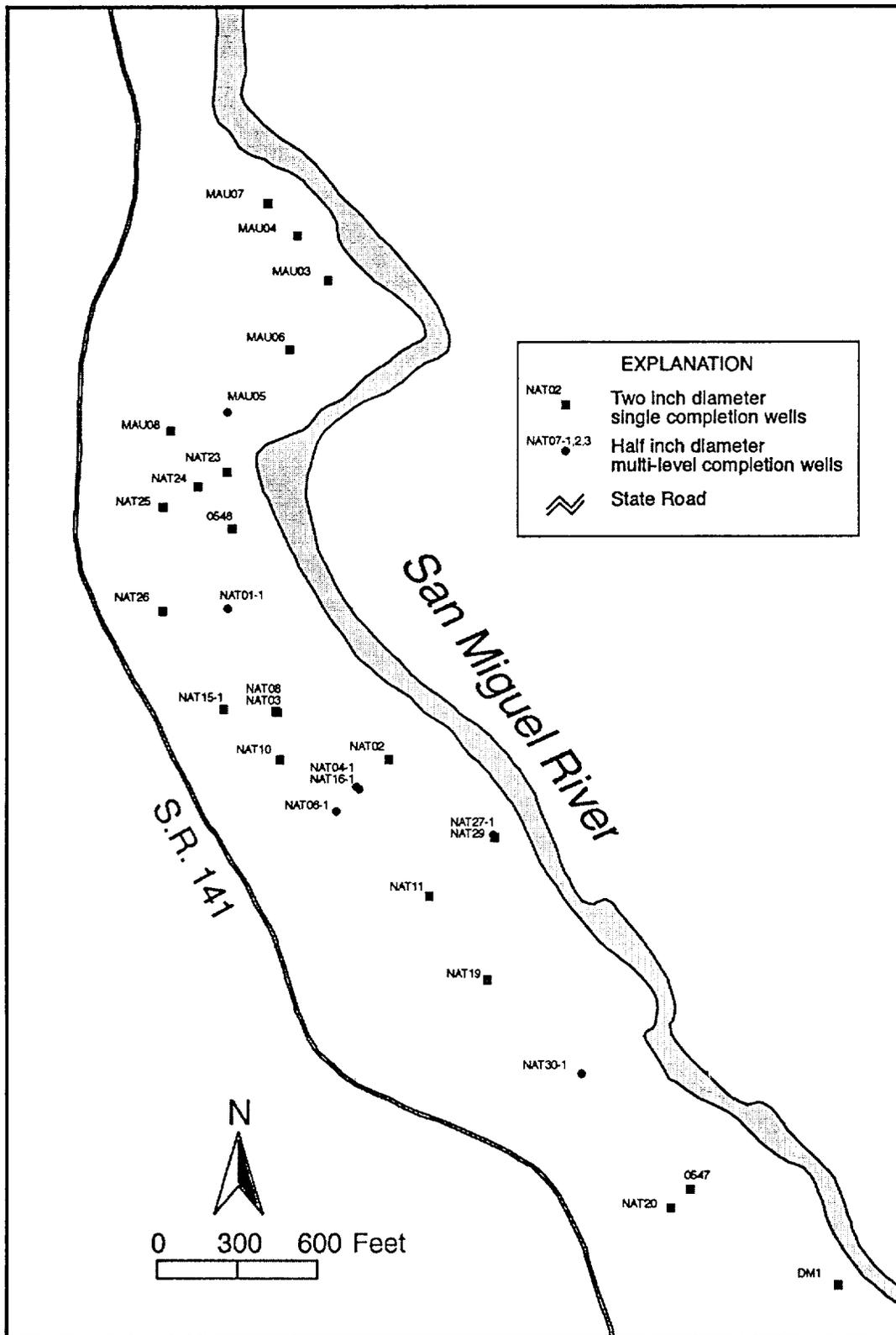


Figure 5-20. Locations of Naturita Wells Sampled in November 2000 and March 2001 During the DOE UMTRA Phase

Table 5-2. Background Concentrations in Well DM1

Analyte ^a	Units	June 2000	November 2000	March 2001	DM1 Mean ^b
Major					
Calcium	mg/L	54.1	111	109	91.4
Chloride	mg/L	4.70	6.45	6.90	6.02
Magnesium	mg/L	20.3	28.9	27.2	25.5
Nitrate	mg/L	NA ^c	0.05	0.05	0.05
Potassium	mg/L	1.85	1.76	1.44	1.68
Sodium	mg/L	18.2	25.1	25.1	22.8
Sulfate	mg/L	131	282	251	221
Metals					
Aluminum	mg/L	<0.29	0.18	0.34	0.22
Arsenic	mg/L	ND ^d	0.0009	0.0006	0.00075
Cadmium	mg/L	<0.04	<0.02	<0.04	
Iron	mg/L	0.29	0.08	0.09	0.15
Lead	mg/L	<0.21	<0.10	<0.20	
Manganese	mg/L	0.32	0.29	0.19	0.27
Molybdenum	mg/L	<0.04	<0.02	<0.04	
Selenium	mg/L	ND ^d	<0.0003	<0.0003	
Uranium	mg/L	0.00432	0.0087	0.00707	0.0067
Vanadium	mg/L	<0.04	<0.02	<0.04	
Other					
Silicon	mg/L	4.64	4.05	4.07	4.25
Strontium	mg/L	0.83	1.28	1.10	1.07
Field Measurements					
Alkalinity	mg/L CaCO ₃	227	156	159	180
Dissolved oxygen	mg/L	0.35	0.16	0.25	0.25
Oxidation-Reduction Potential	mV	138	210	214	187
pH	standard units	7.12	7.13	7.33	7.19
Specific Conductance	µS/cm	589	851	852	764

Detection limits may vary due to sample dilution during analysis

^aSpecific conductance, pH, and oxidation-reduction potential were measured on unfiltered samples; all other analysis were performed on samples that were filtered through a 0.45µm filter.

^bFor results less than the detection limit, one-half the detection limit was used to calculate the mean of the three sampling rounds. If at least two of the three values were below the detection limit, the mean was not calculated.

^cNA = not analyzed.

^dND = Not detected. Method detection limit was too high to be used. Subsequent samples were analyzed using a different method to achieve a lower detection limit (see Table 4-5).

In general, background anions are dominated by sulfate, and the cations are composed of a calcium-sodium-magnesium mixture in which calcium is the most abundant. Background alkalinity as calcium carbonate ranges from 156 to 227 mg/L. Sulfate concentrations range from 131 to 282 mg/L. Calcium concentrations range from 54 to 111 mg/L. Sodium concentrations range from 18 to 25 mg/L. Magnesium concentrations range from 20 to 29 mg/L. The pH ranges from 7.1 to 7.3 with a mean value of 7.2. Oxidation-reduction potential referenced to the standard hydrogen electrode ranges from 138 to 214 mV and averages 187 mV, which is slightly oxidizing.

5.3.3.2 Nature and Extent of Alluvial Ground Water Contamination

From August 1998 through June 2000, USGS sampled ground water at the Naturita site to provide data for the surface complexation modeling being performed for the NRC. During November 2000 and March 2001, sampling was done to monitor the nature and extent of ground water contamination at the site to support this Site Observational Work Plan. Results from all the sampling activities are listed in Appendix B and are summarized in Table 5-3. Locations of the monitoring wells are shown in Figure 5-20.

All the constituents listed in Table 5-3 except nitrate, aluminum, cadmium, lead, and molybdenum are fairly prevalent in the aquifer, as shown by the high frequency (greater than 50 percent) of constituents with concentrations that exceeded the upper limit of the background concentration range. Constituents that exceeded background concentration in less than 50 percent of the wells (nitrate, aluminum, cadmium, lead, and molybdenum) were most often present in quantities below detection limit.

Uranium, chloride, and vanadium exceed background concentrations by the greatest amount. The maximum uranium concentration of 2.51 mg/L detected in well NAT26 is 289 times greater than the background concentration measured in well DM1. The maximum vanadium concentration of 7.55 mg/L detected in well NAT08 is 189 times greater than background. The maximum chloride concentration of 632 mg/L was also detected in well NAT26 and is 92 times greater than background. The remaining constituents show less contrast; arsenic exceeds the background concentration by a factor of 71, sodium exceeds by a factor of 47, selenium exceeds by a factor of 46, potassium exceeds by a factor of 22, manganese exceeds by a factor of 20, and iron exceeds by a factor of 19.

Concentrations of arsenic, molybdenum, selenium, and uranium all exceed their UMTRA maximum concentration limits (Table 2-1). Chloride and sulfate concentrations both exceed the Colorado secondary drinking water standard of 250 mg/L, although the background range of sulfate also slightly exceeds this value. Vanadium concentrations are elevated above risk-based levels for drinking water (see Section 6.1). These constituents have been selected for the remainder of this discussion.

Arsenic

Figure 5-21 shows the concentrations of arsenic measured during the November 2000 and March 2001 sampling. Arsenic concentrations at most wells were near the detection limit of 0.00018 mg/L, and concentrations in the March 2001 samples exceeded the UMTRA maximum concentration limit of 0.05 mg/L in only three wells (NAT03, NAT08, and NAT11). The maximum concentration was detected in well NAT08, which is near the center of the former tailings area. These three samples all show an increase in arsenic concentration from the November 2000 sampling. This pattern is also seen in well NAT16-1. However, concentrations in samples from wells NAT04-1, NAT06-1, NAT10, and NAT08 all decreased slightly. As shown in Figure 5-22, the highest concentrations of arsenic have not migrated beyond the area of the former tailings pile. This is most likely due to the low mobility of arsenic under the reducing conditions found in this area. Under these conditions, arsenic is readily adsorbed onto iron hydroxides that may coat sediments.

Table 5-3. Ground Water Quality at the Naturita Site, August 1998 to March 2001

Analyte ^a	Units	Mean ^b	Range	Max Well	Number of Samples	Percent of Samples Over Background	Background Range
Major Ions							
Calcium	mg/L	202	60.2-492	NAT01-2	315	94	54.1-111
Chloride	mg/L	74	0.05-632	NAT26	315	98	4.70-6.90
Magnesium	mg/L	59.1	16.2-145	NAT01-2	315	96	20.3-28.9
Nitrate	mg/L		<0.02-3.56	NAT26	54	9	0.05
Potassium	mg/L	10.5	1.41-40.2	MAU08	315	99	1.44-1.85
Sodium	mg/L	211	20.8-1,170	NAT26	315	99	18.2-25.1
Sulfate	mg/L	735	120-1,930	NAT01-2	315	95	131-282
Metals							
Aluminum	mg/L		0.15-0.74	MAU08	315	30	0.18-0.29
Arsenic	mg/L	0.0136	0.0005-0.064	NAT08	54	74	0.0006-0.0009
Cadmium	mg/L		<0.04		315		<0.04
Iron	mg/L	0.41	<0.02-5.54	NAT01-2	315	76	0.08-0.29
Lead	mg/L		<0.1-0.65		315		<0.04
Manganese	mg/L	1.30	<0.04-6.46	MAU05	315	87	0.19-0.32
Molybdenum	mg/L		<0.02-0.18	NAT26	121	30	<0.04
Selenium	mg/L	0.00182	<0.0003-0.014	NAT26	54	94	<0.0003
Uranium	mg/L	0.727	0.003-2.510	NAT26	315	98	0.00432-0.0087
Vanadium	mg/L	1.48	<0.02-7.55	NAT08	315	56	<0.04
Other							
Silicon	mg/L	7.98	3.43-12.4	MAU01	315	99	4.05-4.64
Strontium	mg/L	2.44	0.64-6.35	NAT01-2	315	88	0.83-1.28
Field Measurements							
Alkalinity	mg/L CaCO ₃	343	124-596	MAU01	306	93	156-227
Dissolved oxygen	mg/L	0.31	<0.1-1.73	NAT09	296	27	0.16-0.35
Oxidation-Reduction Potential	mV	198	-12-426	MAU01	282	43	138-214
pH	standard units	7.10	6.54-7.53	MAU06	307	8	7.12-7.33
Specific Conductance	µS/cm	2,060	615-5,730	NAT26	307	92	589-852

Detection limits may vary due to sample dilution during analysis

^aAll measurements were performed on filtered samples except specific conductance, pH, and oxidation-reduction potential.

^bOne-half the detection limit was used to calculate the mean; mean was not calculated if concentrations in more than half the samples were below detection limit.

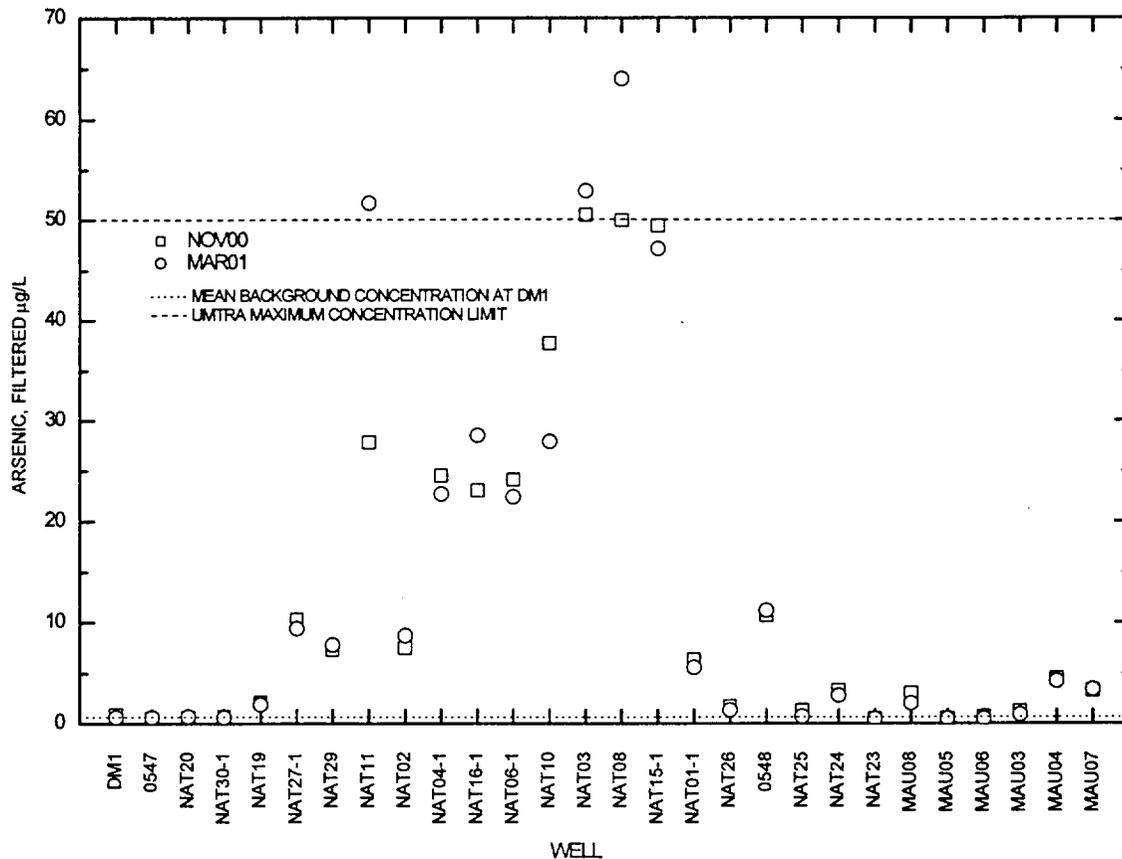


Figure 5-21. Arsenic Concentrations in Selected Wells at the Naturita Site Measured During November 2000 and March 2001

Molybdenum

Most measurements of molybdenum were at or near the detection limit (Figure 5-23). Concentrations in samples from wells NAT15-1, NAT01-1, NAT26, and in one sample from well MAU05 were over the UMTRA maximum concentration limit of 0.1 mg/L. The maximum concentration of 0.18 mg/L was detected in well NAT26. All these wells except MAU05 are located in the area of the former tailings pile. Figure 5-24 shows the distribution of molybdenum concentrations.

Selenium

As Figure 5-25 shows only well NAT26 had selenium concentrations that were greater than the UMTRA maximum concentration limit of 0.01 mg/L. Most wells located near the former tailings area had concentrations of selenium that were in the range found in upgradient wells 0547 and NAT20 (Figure 5-26). As with arsenic, selenium is also less mobile under reducing conditions, and any selenium contamination that came from the former tailings area should still be present at the site.

Uranium

Figure 5–27 shows uranium concentrations in selected wells at the Naturita site. There is a large range in concentration, from 0.003 mg/L in well 0547, which is upgradient from the former tailings area, to 2.510 mg/L in well NAT26. As shown in Figure 5–28, concentrations in all wells located downgradient from well NAT30 exceed the UMTRA maximum concentration limit for uranium (0.044 mg/L). This is the approximate extent of the former mill yard area. Uranium concentration continues to increase as ground water moves downgradient into the former tailings area. Concentrations decrease slightly near the bend in the San Miguel River at the northern end of the site. Chloride and sulfate concentrations along with ground water age and flow modeling suggest that ground water in wells MAU06, MAU03, and MAU04 comes mainly from recent recharge by the San Miguel River, and well MAU07 is a mixture of fresh river water and contaminated water from the alluvial aquifer. However, wells MAU06, MAU03, and MAU04 have uranium concentrations that are orders of magnitude greater than that of the San Miguel River. This contamination is most likely due to buried tailings located near well 0700.

As discussed in Section 5.3.2.2, uranium concentrations in wells MAU03, MAU04, and MAU07 have not been observed to decrease with time, but rather appear to be influenced by the water table and river stage. Wells in the alluvial aquifer can be divided into four groups based on the response of uranium concentration to water level. Figure 5–29 shows the locations of these zones. Zone A wells are located away from the San Miguel River in the central portion of the aquifer and include wells NAT01–1, NAT15–1, NAT25, NAT26, and MAU08. Figure 5–30 shows well NAT25 from this group. These wells typically have the highest concentrations of uranium. Zone B wells are also located in the central region of the study area but closer to the river than wells in Zone A. These wells show a fluctuation in uranium that lags behind fluctuations in water level. In this case, water level peaks are followed by high uranium concentrations a few months later. This trend is apparent in well 0548, shown in Figure 5–31. Zone C wells are located closest to the San Miguel River in the central portion of the study area. Small spikes in uranium concentration can be seen following water level peaks similar to the wells in Zone B; however, these spikes are much less pronounced than those in Zone B wells. Zone C wells also show a general decrease in uranium over time. Figure 5–32 illustrates this trend, which is observed in well NAT02. Zone D wells are located near the bend in the river at the northern end of the site. Uranium concentrations appear to fluctuate more quickly in this region in response to changes in water level. This is best seen in well MAU04 (Figure 5–18).

From these trends it appears that wells in Zone C receive the greatest inflow of fresh water from the San Miguel River and should be the first to be decontaminated by natural flushing. Wells in Groups B and D are also undergoing natural flushing; however, they are still receiving an intermittent inflow of ground water uranium that is coupled with water level. On the timescale of the measurements made, wells in Zone A show no signs of natural flushing. There is no evidence in this area that changes in water level will affect uranium concentrations.

Two mechanisms have been proposed to explain the changes in uranium concentration with water level. The first involves desorption of uranium from sediments as the water table rises. This desorbed uranium is then transported to downgradient wells where it is measured a few months later. If this is the dominant process, then attempts to induce a greater degree of natural flushing may result in short-term increases in the mass of uranium being desorbed from sediments in the vadose zone. This effect should be much more pronounced in Zones B and D than in Zone C. Zone A wells should not show a significant change.

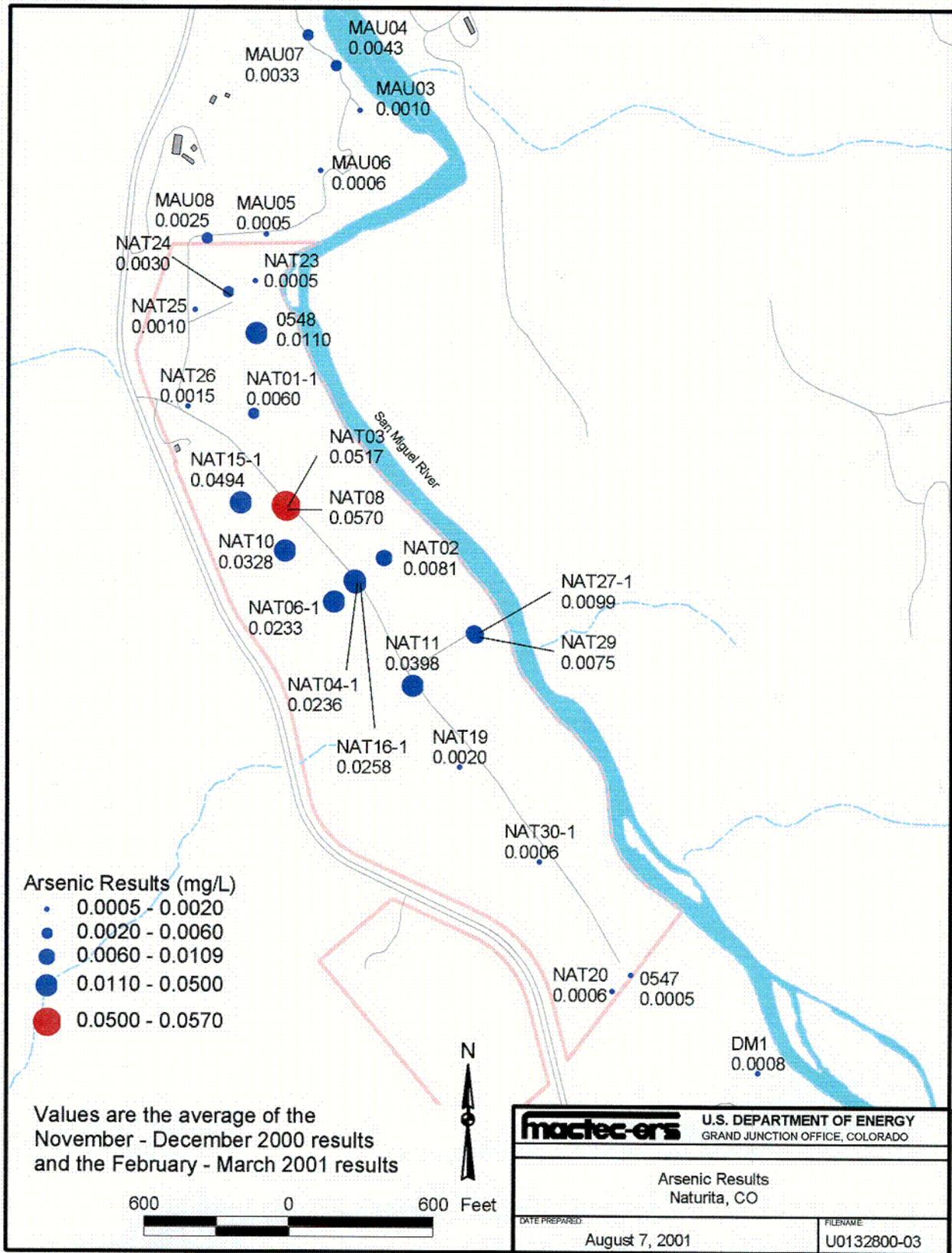


Figure 5-22. Average Arsenic Concentrations Measured in November and December 2000 and February and March 2001

COY

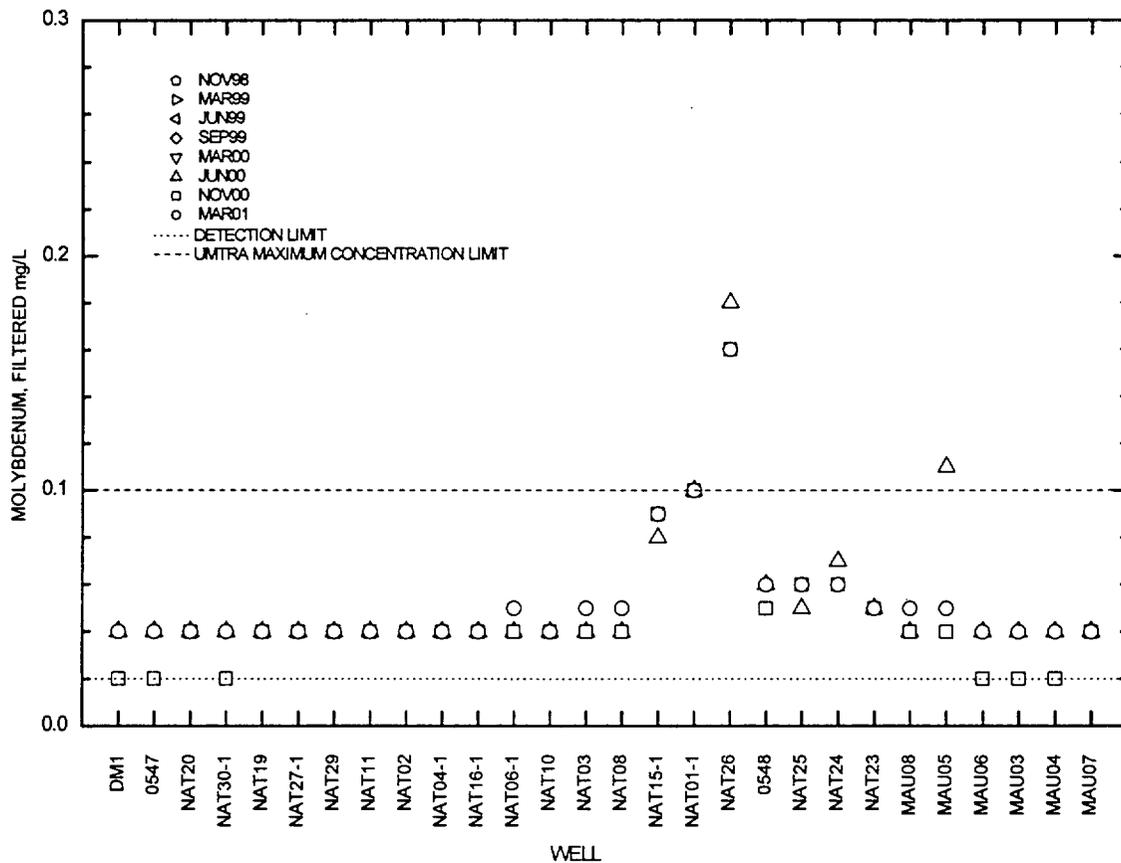


Figure 5-23. Molybdenum Concentrations in Selected Wells at the Naturita Site Measured from November 1998 to March 2001

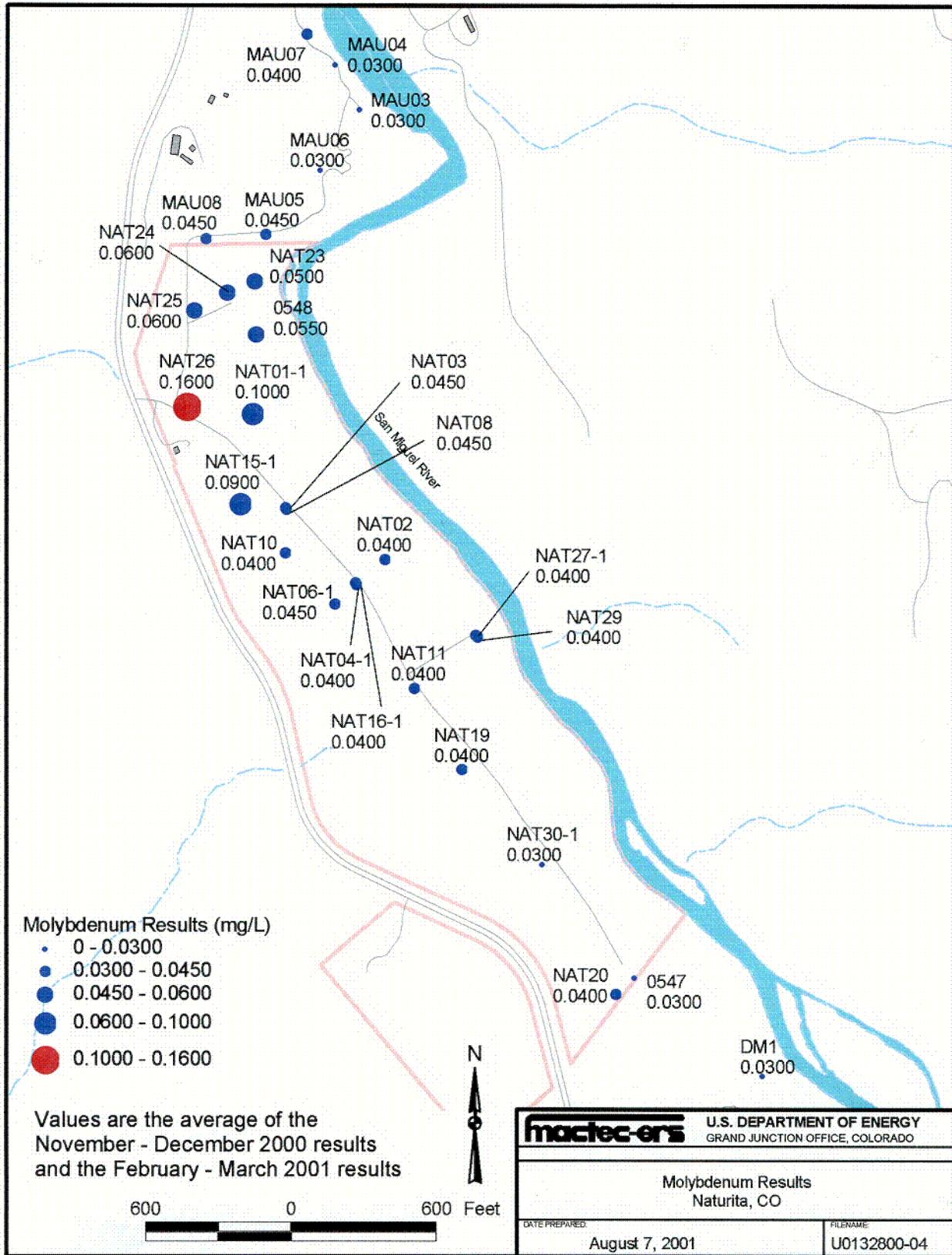


Figure 5-24. Average Molybdenum Concentrations Measured in November and December 2000 and February and March 2001

05

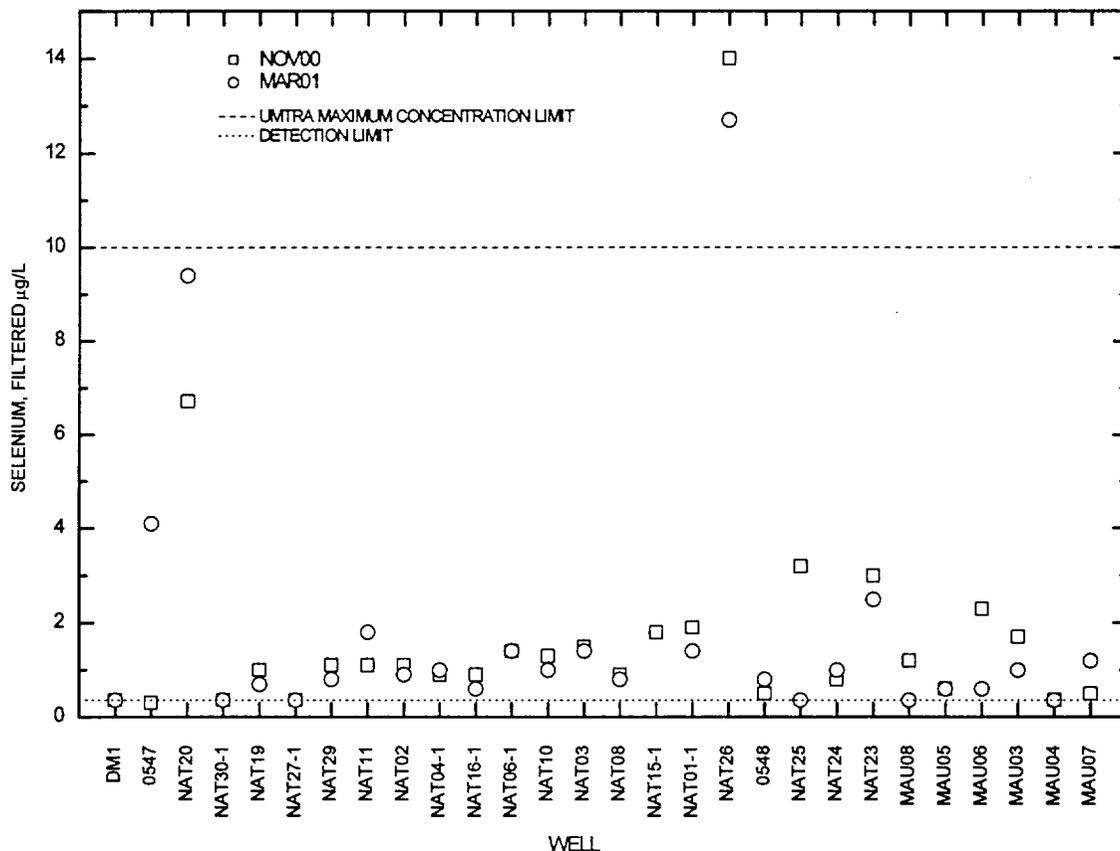


Figure 5-25. Selenium Concentrations in Selected Wells at the Naturita Site Measured During November 2000 and March 2001

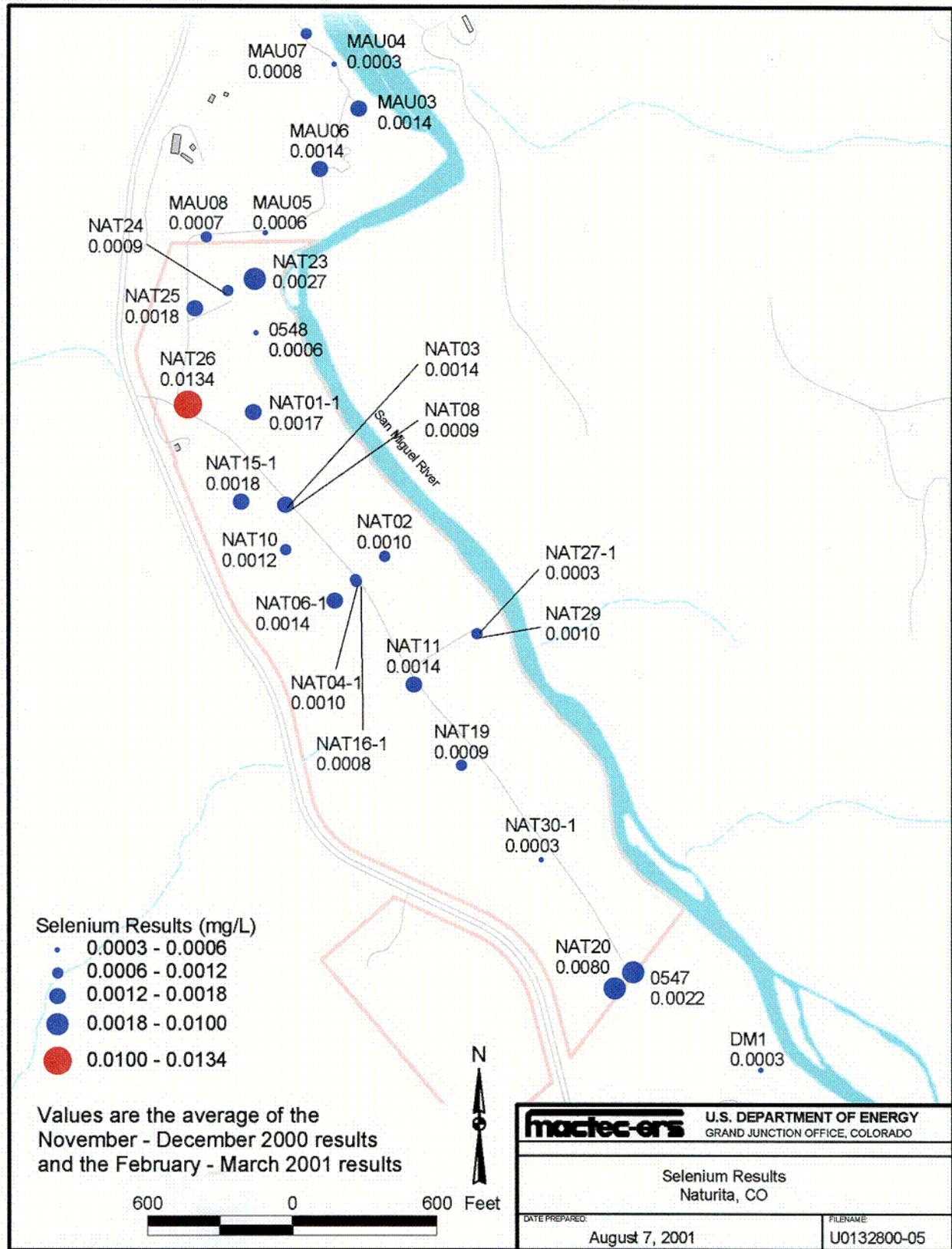


Figure 5-26. Average Selenium Concentrations Measured in November and December 2000 and February and March 2001

COG

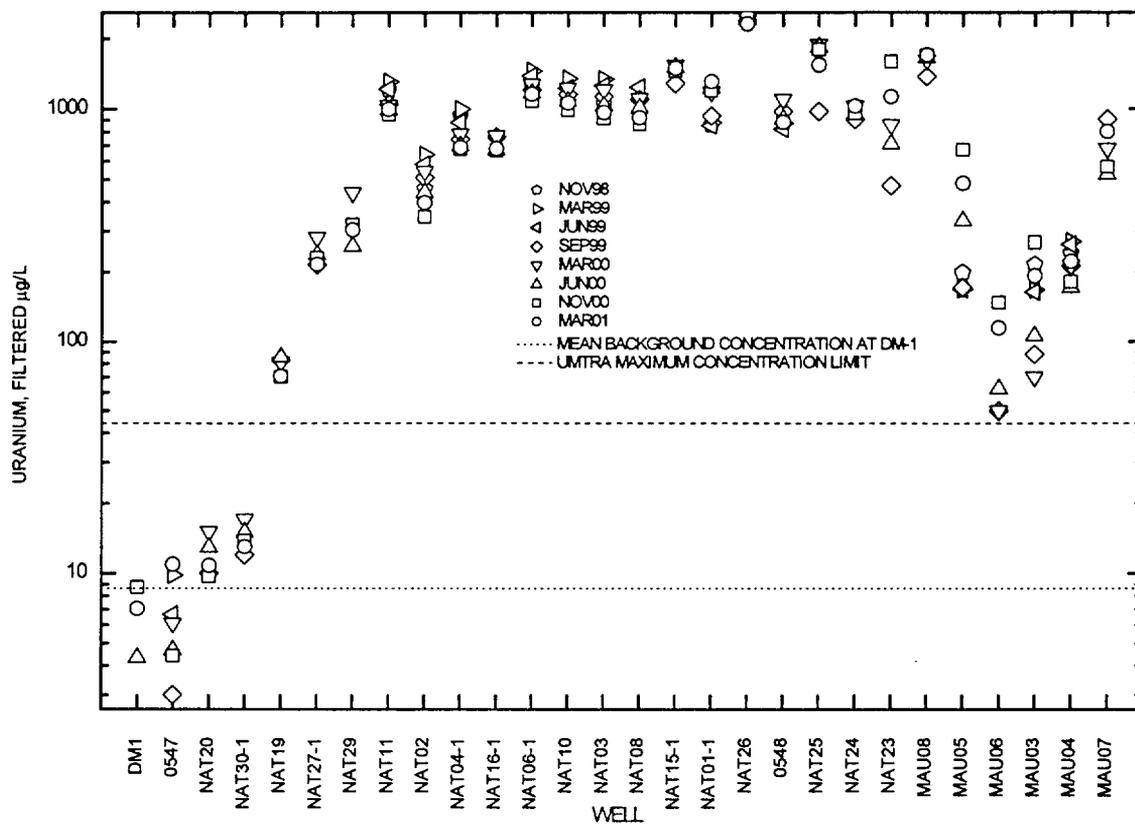


Figure 5-27. Uranium Concentrations in Selected Wells at the Naturita Site Measured from November 1998 to March 2001

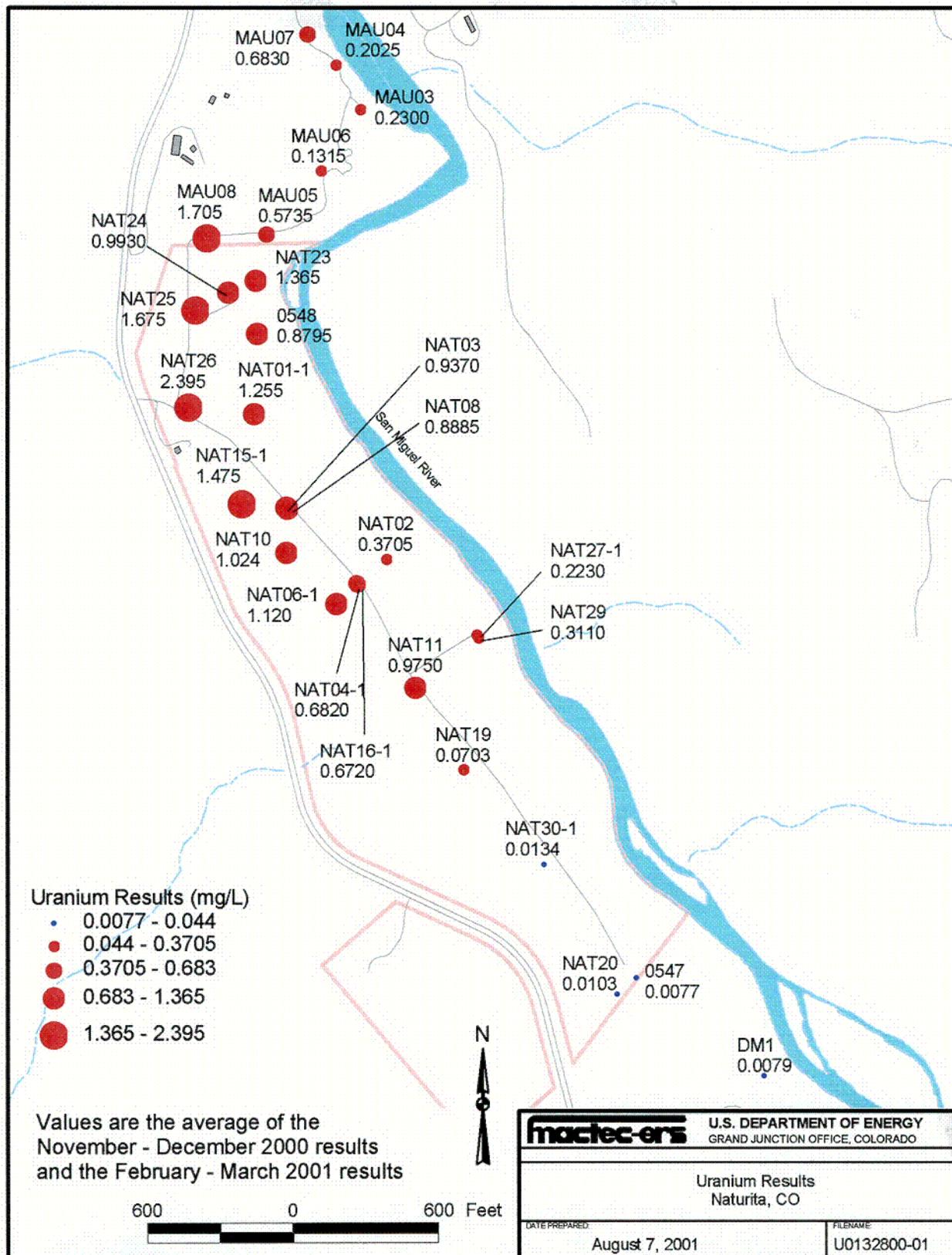


Figure 5-28. Average Uranium Concentrations Measured in November and December 2000 and February and March 2001

007

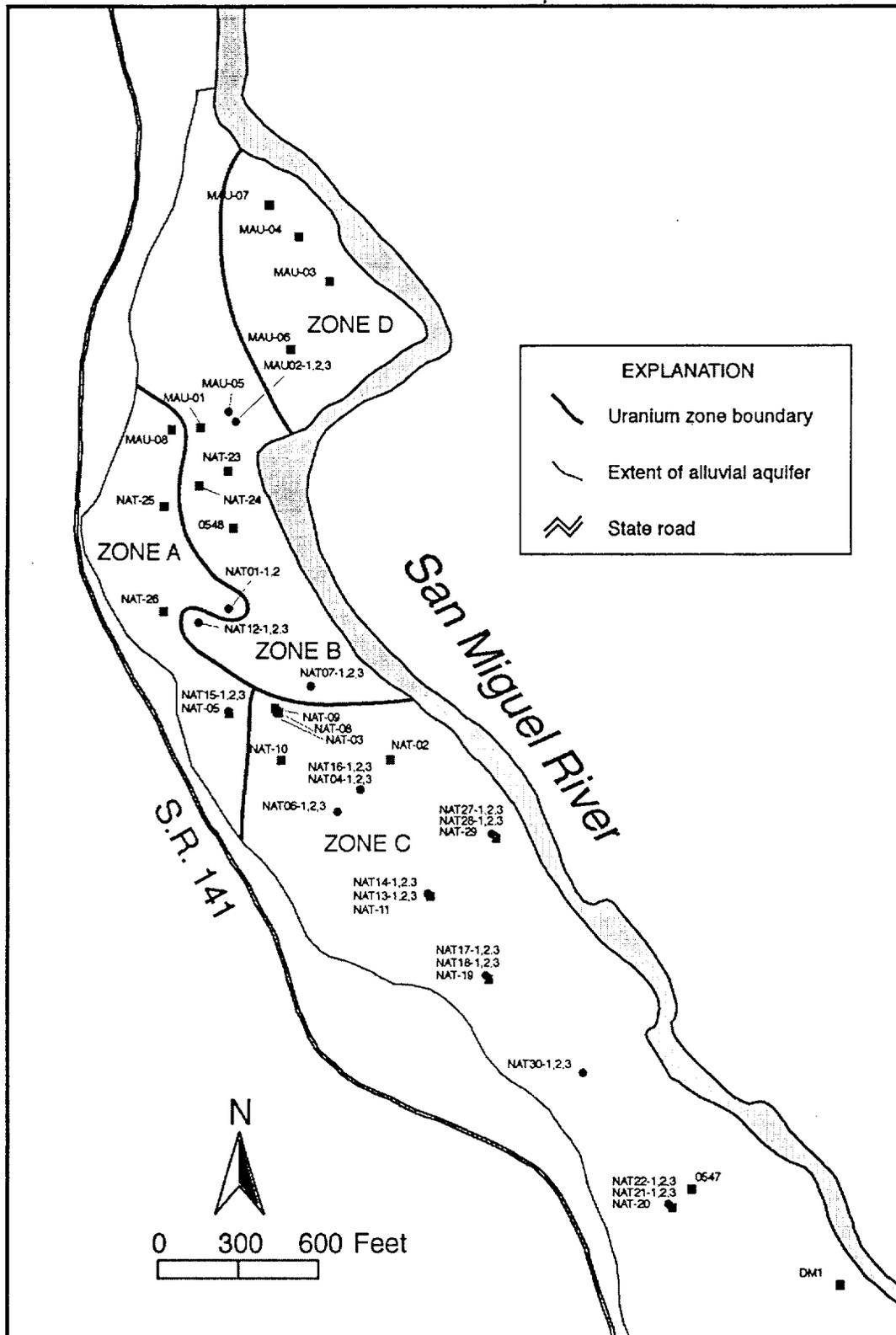


Figure 5-29. Alluvial Aquifer Zones Based on the Response of Uranium Concentration to Changes in Water Level

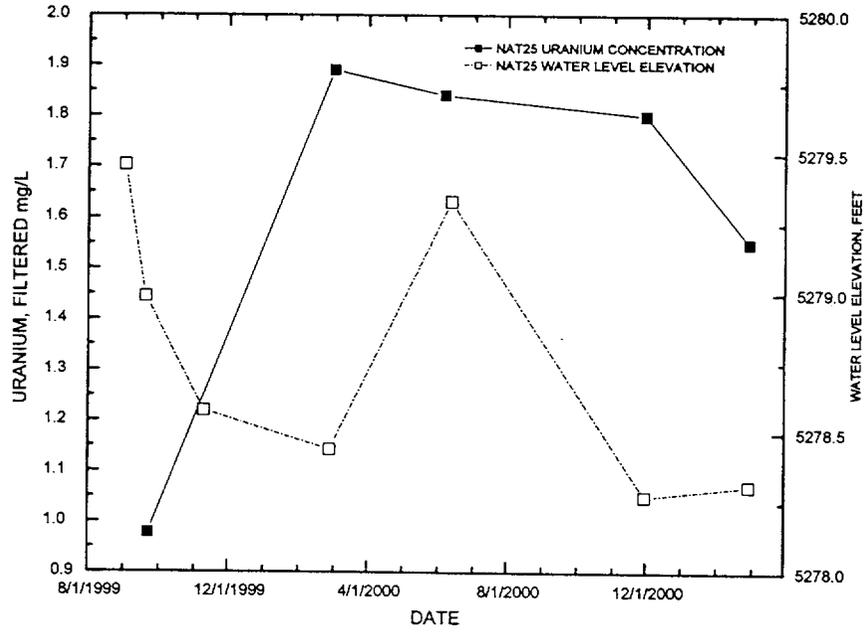


Figure 5-30. Time-Concentration Plot for Uranium and Water Level at Well NAT25

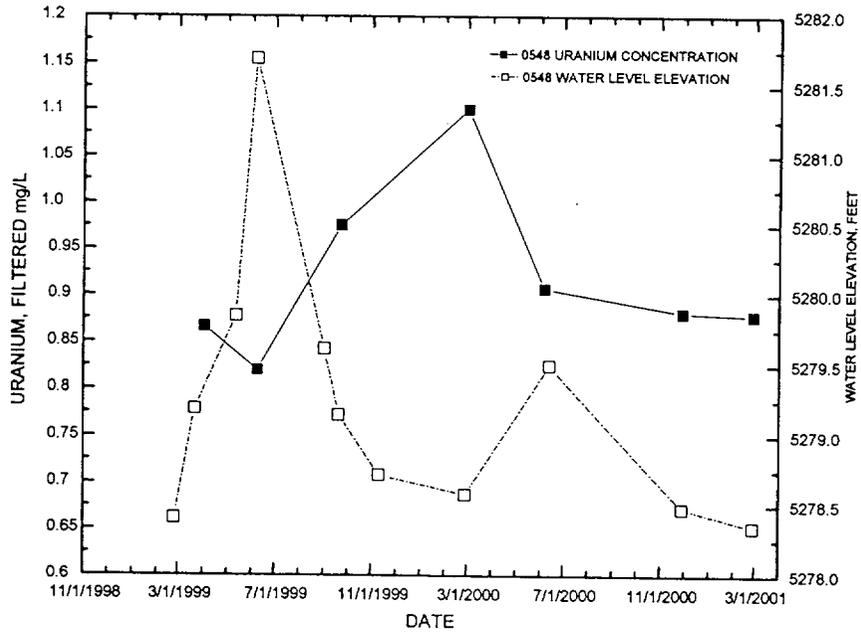


Figure 5-31. Time-Concentration Plot for Uranium and Water Level at Well 0548

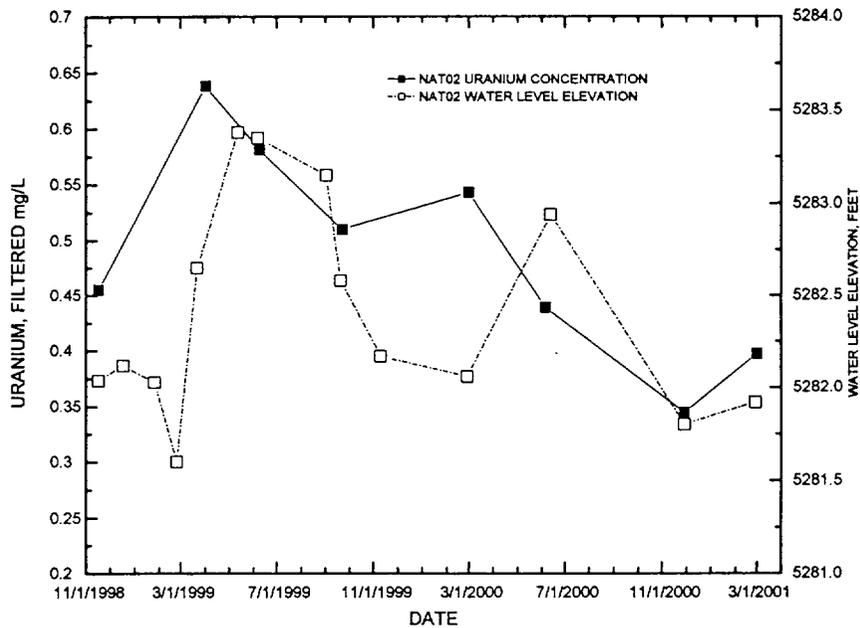


Figure 5-32. Time-Concentration Plot for Uranium and Water Level at Well NAT02

The second proposed mechanism involves lateral fluctuations of the uranium-contaminated zone due to increased inflow from the San Miguel River. When the water level is high, more fresh water flows to the Zone B wells, effectively diluting uranium concentration. This fresh water does not reach the Zone A wells, and they are therefore unaffected. When the water level is low, there is a greater degree of flow from the highly contaminated area to the Zone B wells, increasing the uranium concentration. A small amount of this ground water with high uranium levels may reach the Zone C wells. This is shown by small increases in uranium concentrations as water level decreases. If natural flushing were to be augmented in this case by increasing irrigation and raising the water table, changes in uranium concentration may depend strongly on where the irrigation is applied. For instance, if the water table is raised in Zone A, this may increase uranium concentrations in wells in Zones B and C. If water is applied to Zone C, however, wells in Zone B should continue to show decreasing uranium concentrations. It is unclear whether water applied in this area would clean up wells in Zone A.

If the first mechanism is the dominant process, uranium and other sorbed ions should be the only species to increase in concentration following an increase in water level. Conservative ions like chloride should have been removed from the sediments at an early stage. However, Figure 5-33 shows an increase in chloride concentration with uranium, which suggests that changes in uranium concentration in Zone B wells is most likely due to a greater influx of contaminated water from Zone A. In addition to the close correlation of uranium and chloride, there is also a good correlation between uranium and specific conductance (Figure 5-34). Because of this strong correlation, specific conductance can be used as a proxy to monitor uranium concentrations at the site. This could be done continuously over extended periods using a data recorder with a specific conductance meter.

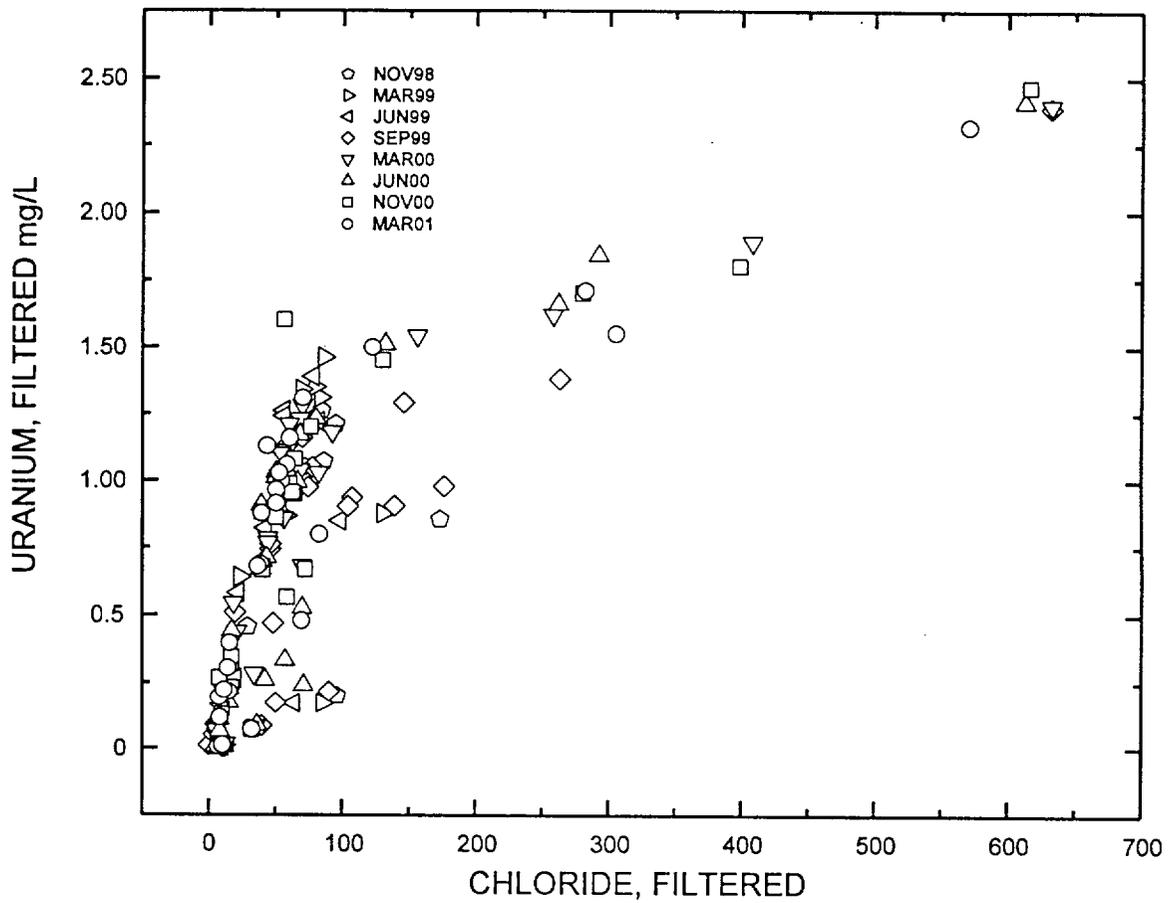


Figure 5-33. Uranium Versus Chloride Concentration in Ground Water

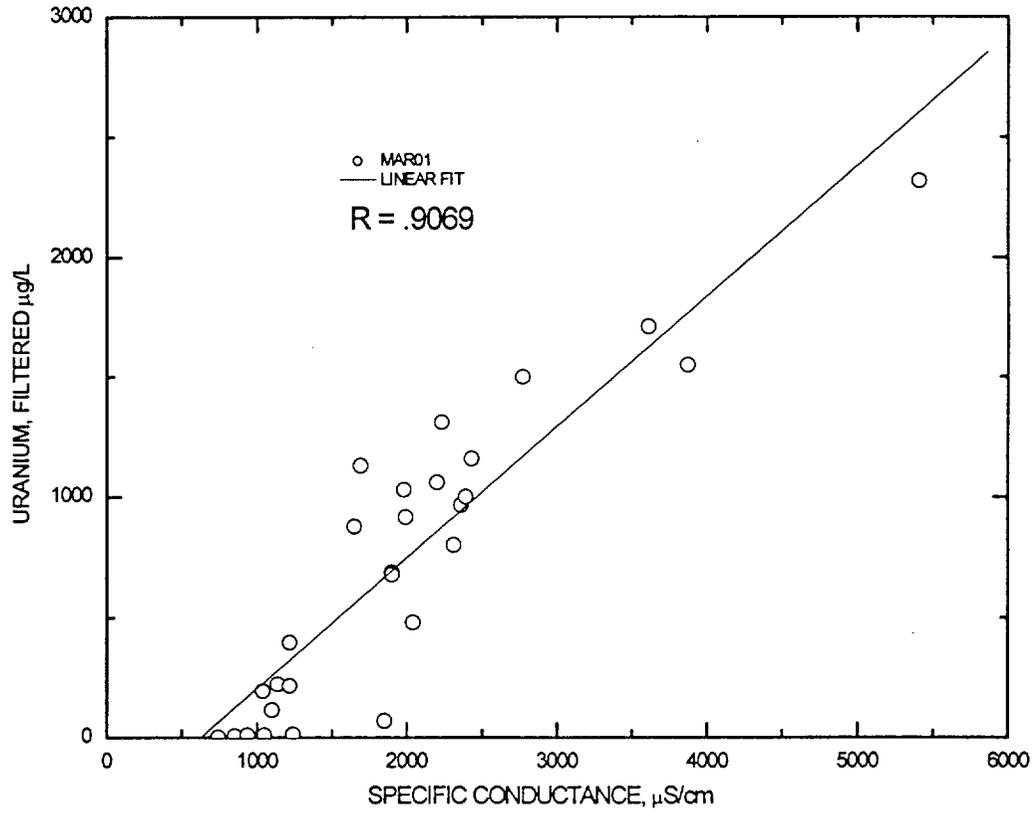


Figure 5-34. Uranium Concentration Versus Specific Conductance in Ground Water.
R = Correlation Coefficient

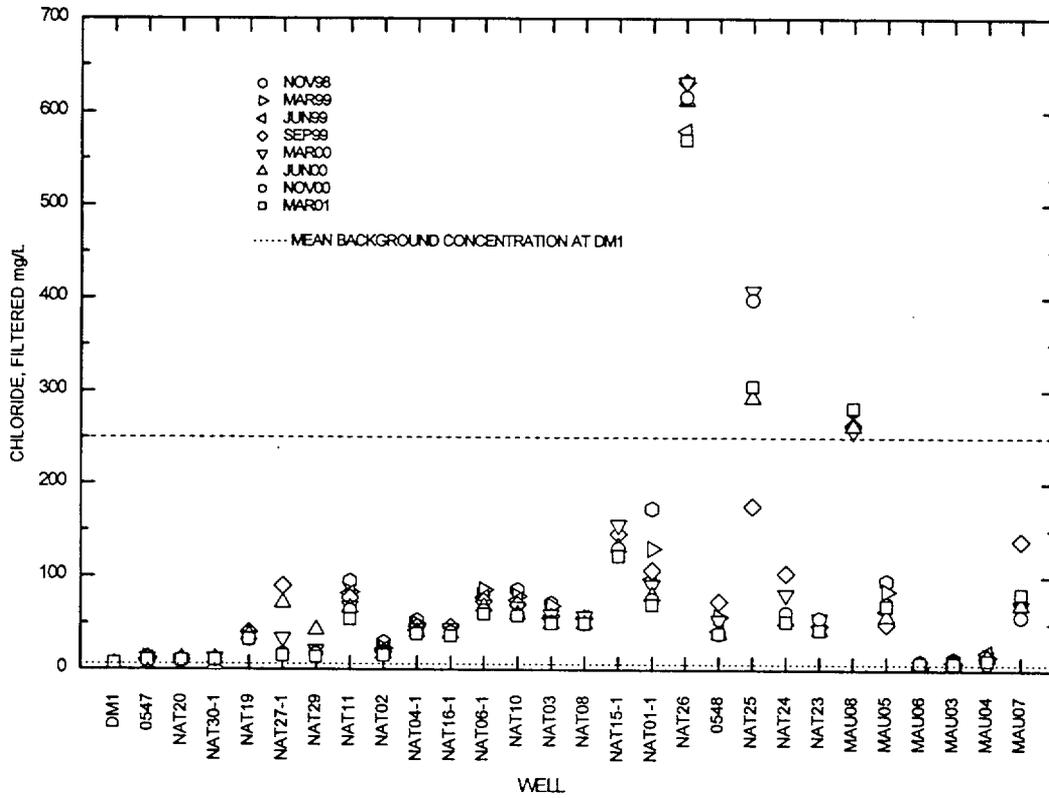


Figure 5-35. Chloride Concentrations in Selected Wells at the Naturita Site Measured from November 1998 to March 2001

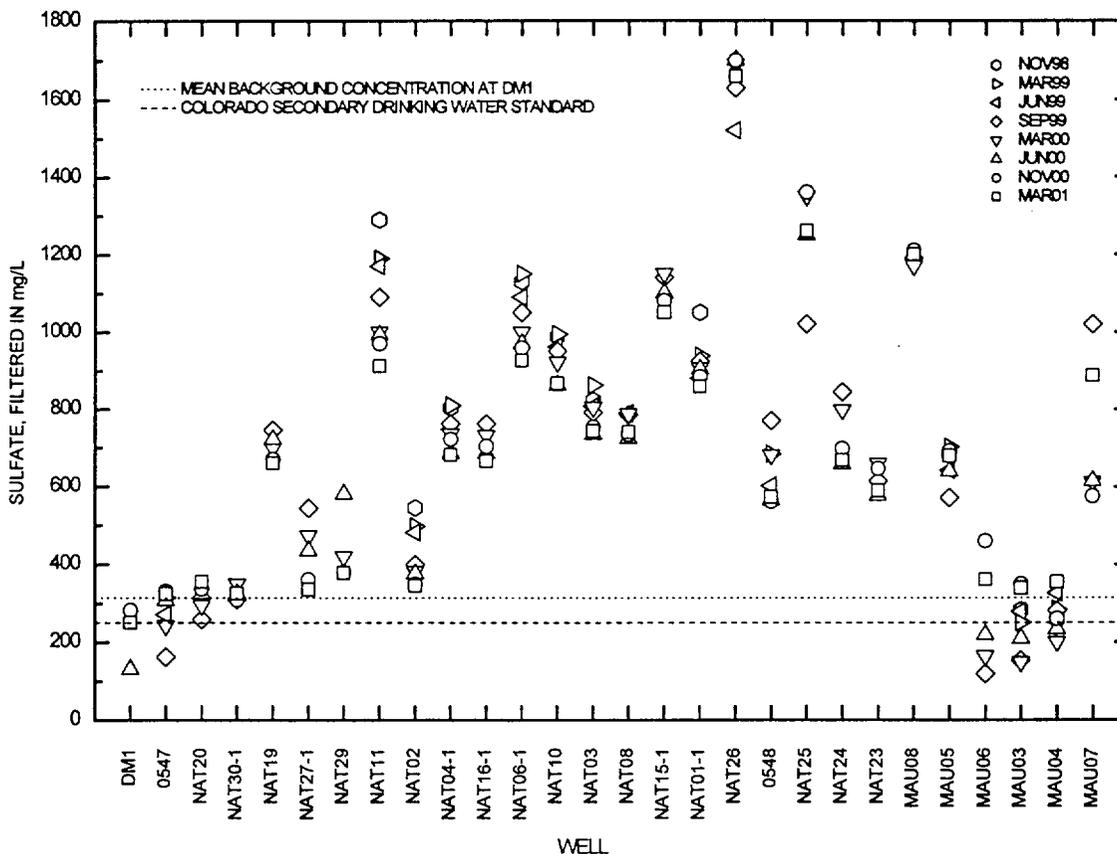


Figure 5-36. Sulfate Concentrations in Selected Wells at the Naturita Site Measured from November 1998 to March 2001

Chloride

When sampled in March 2001, wells NAT25, NAT26, and MAU08 were the only wells with chloride concentrations that exceeded the Colorado secondary drinking water standard of 250 mg/L. However, almost all the wells downgradient of well NAT30-1 had significantly more chloride than the concentration measured in background well DM1 (Figure 5-35). The increase in chloride concentration from inflow of San Miguel River water ranges from 1.72 to 11.3 mg/L; therefore, concentrations greater than this range indicate another source of chloride. The main source of additional chloride comes from the sodium chloride used during processing of the uranium ore (DOE 1995). Because chloride is considered a conservative species and is largely unaffected by adsorption, it is a good indicator of the degree of natural flushing taking place in the aquifer. The wells with the highest chloride concentrations are located in the western portion of the alluvial aquifer. This area corresponds to Zone A (Figure 5-29). Wells closer to the San Miguel River on the eastern portion of the site have lower concentrations of chloride (less than 100 mg/L). This distribution is the result of two factors. The first that more alkaline tailings were deposited on the western half of the site, and acidic tailings were deposited on the eastern portion closest to the river (DOE 1995). The second factor is that the eastern zone receives a greater degree of fresh water inflow from the San Miguel River and undergoes a greater degree of natural flushing. Wells MAU03, MAU04, and MAU06 have chloride concentrations ranging

from 3.8 to 19.8 mg/L, indicating they receive most of their inflow directly from the nearby river. Concentrations in well MAU07, which is just downgradient from well MAU04, range from 58 to 139 mg/L. The higher chloride concentration in MAU07 suggests that this well receives some component of ground water from the contaminated alluvial aquifer. A simple mixing calculation using chloride concentrations can be made by assuming a binary mixture of water from the contaminated alluvial aquifer near well MAU08 and from the San Miguel River. During June 2000 the concentration of chloride in well MAU08 was 262 mg/L, and the concentration in the river was 1.72 mg/L. The concentration in well MAU07 was 70 mg/L. This indicates that 26 percent of the water in well MAU07 came from the contaminated alluvial aquifer, and 74 percent came from the river. This ratio should be considered a maximum inflow from the river, because these values were recorded during high river stage. The values measured during March 2001, which corresponds to a period of low flow, indicate that 27 percent of the flow came from ground water and 73 percent came from surface water. This is a small percentage change over a large difference in flow.

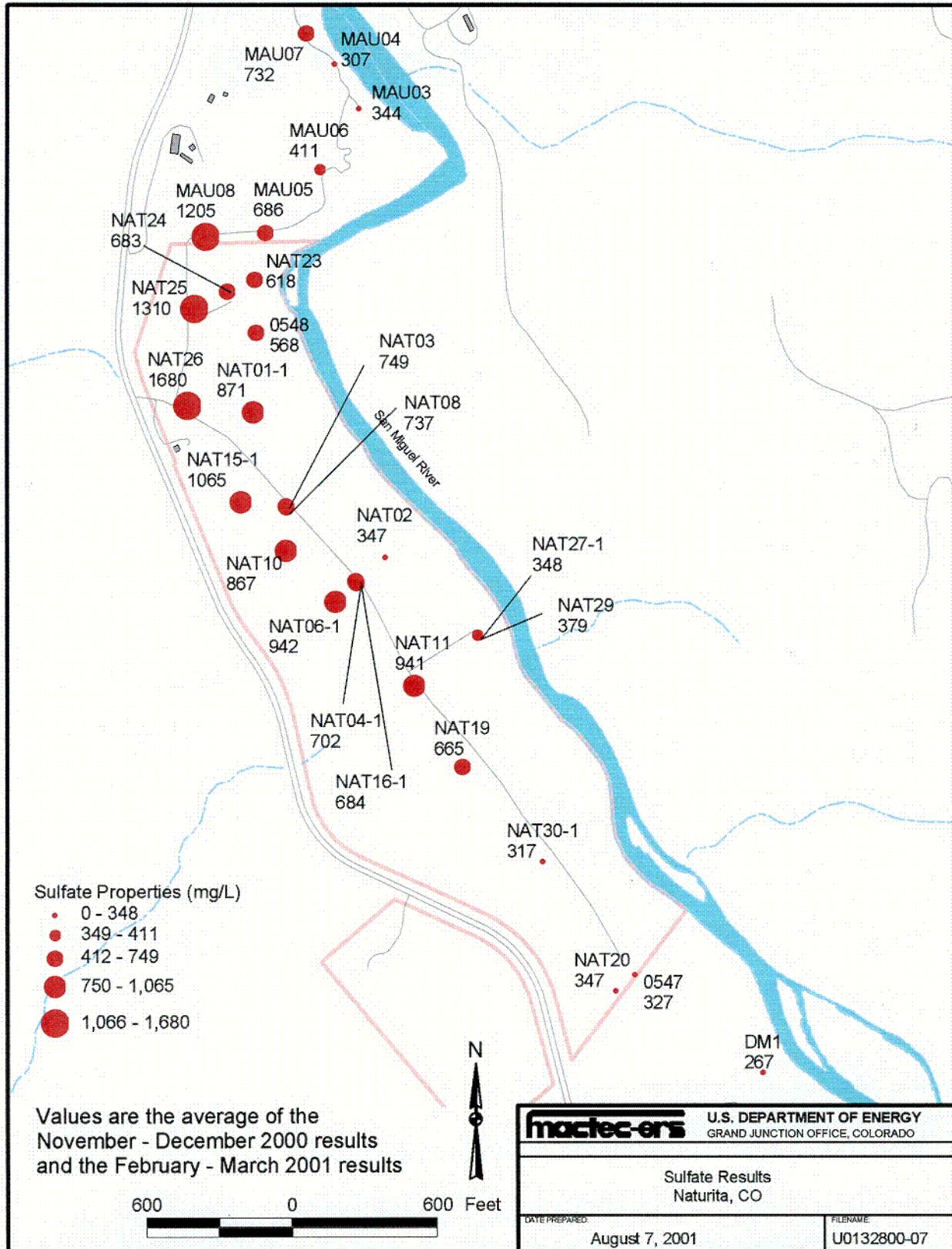
Sulfate

Between August 1998 and March 2001, sulfate concentrations exceeded background levels in 95 percent of the samples collected at the site (Table 5-3) and exceeded the Colorado secondary drinking water standard of 250 mg/L in 97 percent of the samples. As shown in Figure 5-36, concentrations range from 120 mg/L to 1,930 mg/L. Figure 5-37 shows that the distribution of sulfate concentrations is similar to that of chloride and uranium; the highest levels are in the west-central portion of the alluvial aquifer. Wells in the northern section near the bend in the river show a mixing trend similar to that of the chloride concentrations.

As Figure 5-38 shows the sulfate/chloride ratio is also a good indicator of the influence of surface water from the river. Wells near the river or upgradient from the contaminated zone have larger sulfate/chloride ratios and show a broader range of ratios. With the exception of well MAU07, this group corresponds to Zones C and D (Figure 5-29). Wells located in the contaminated area (Zones A and B) have a much narrower range of sulfate/chloride ratios, and the ratios are generally lower than those in Zones C and D. Although located near the San Miguel River, water in well MAU07 has a sulfate/chloride ratio that is more typical of the ratio in ground water from the contaminated area of the alluvial aquifer. As discussed in the chloride section, it is believed that this well receives a significant inflow of water from the contaminated portion of the alluvial aquifer, which gives it a different sulfate/chloride ratio than that of other wells in the area.

Vanadium

Vanadium concentrations range from below the detection limit (0.02 mg/L) to 7.55 mg/L and are shown in Figure 5-39. The highest value was measured in September 1999 in well NAT08, the same well in which the maximum level of arsenic was detected. Figure 5-40 shows the distribution of vanadium concentrations. Due to its lower mobility, the vanadium has not been transported as far downgradient as other constituents such as uranium (Figure 5-28), and the higher concentrations are generally confined to the area of the former tailings pile. This distribution is similar to that of arsenic (Figure 5-22).



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Figure 5-37. Average Sulfate Concentrations Measured November and December 2000 and February and March 2001

008

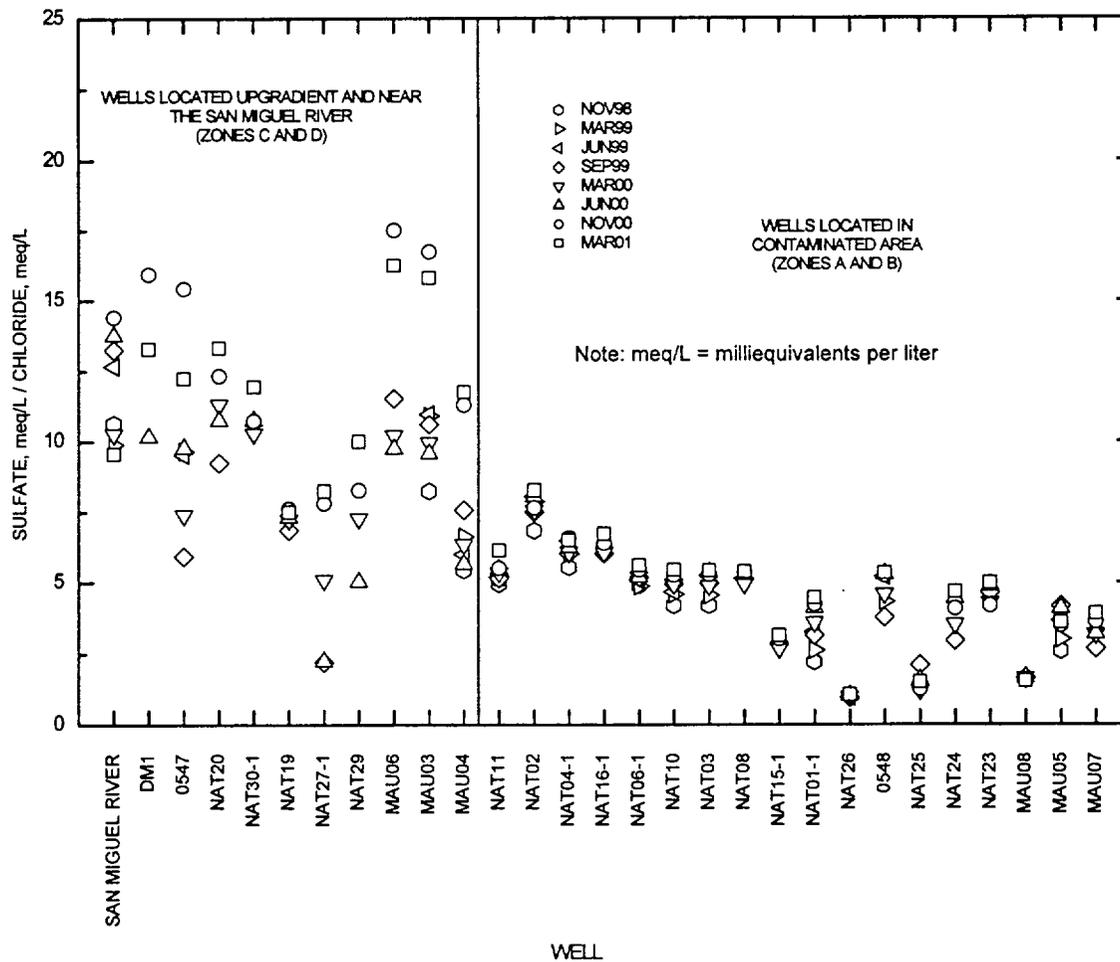


Figure 5-38. Sulfate/Chloride Concentration Ratio in Selected Wells at the Naturita Site Measured from November 1998 to March 2001

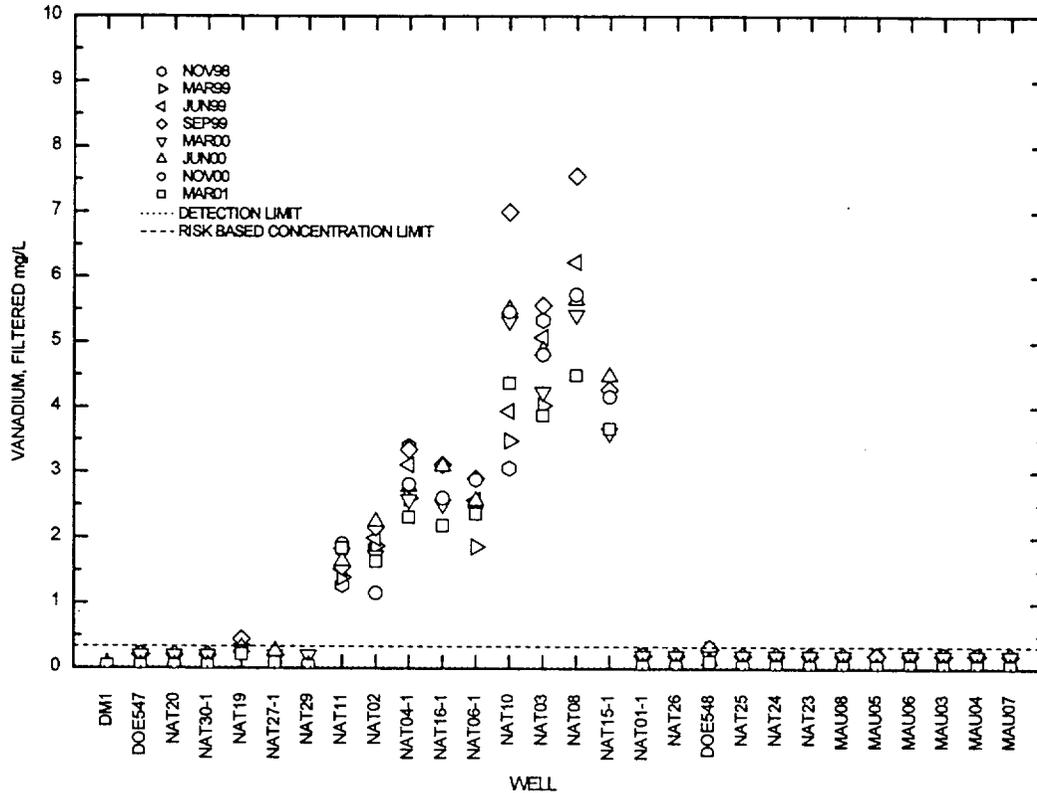


Figure 5-39. Vanadium Concentrations in Selected Wells at the Naturita Site Measured from November 1998 to March 2001

5.3.4 Age Dating Alluvial Ground Water

To better understand flow paths and travel times of alluvial ground water at the Naturita site, samples were collected in June 2000 to age date ground water. The age of ground water is defined as the time since water was isolated from the atmosphere (Freeze and Cheery 1979). Two techniques were used to determine the age of ground water at Naturita. The first involves measuring the ground water concentration of chlorofluorocarbons (CFCs). Because the solubility of CFCs is known, and the air concentration of CFCs for the past 50 years is also known (or reconstructed), ground water age can be measured based on the concentration of dissolved CFCs. The second method measures the ratio of hydrogen-bomb-produced tritium (³H) to its decay product helium-3 (³He) in ground water. Both methods have been used successfully at a number of sites to date relatively young ground water (less than 60 years old) (Plummer and Busenberg 2000, Solomon and Cook 2000).

All the wells at Naturita with 2-inch-diameter casings and one site along the San Miguel River were sampled for CFCs; samples were analyzed by the USGS at the Reston Chlorofluorocarbon Laboratory. Twelve of these wells were also sampled for ³H/³He analysis. These samples were analyzed at the Lamont-Doherty Earth Observatory at Columbia University. In addition to the 2-inch-diameter wells, 6 CFC samples were collected from 0.5-inch-diameter wells and were analyzed at the University of Utah Department of Geology and Geophysics. Table 5-4 presents a complete list of the samples collected at each well.

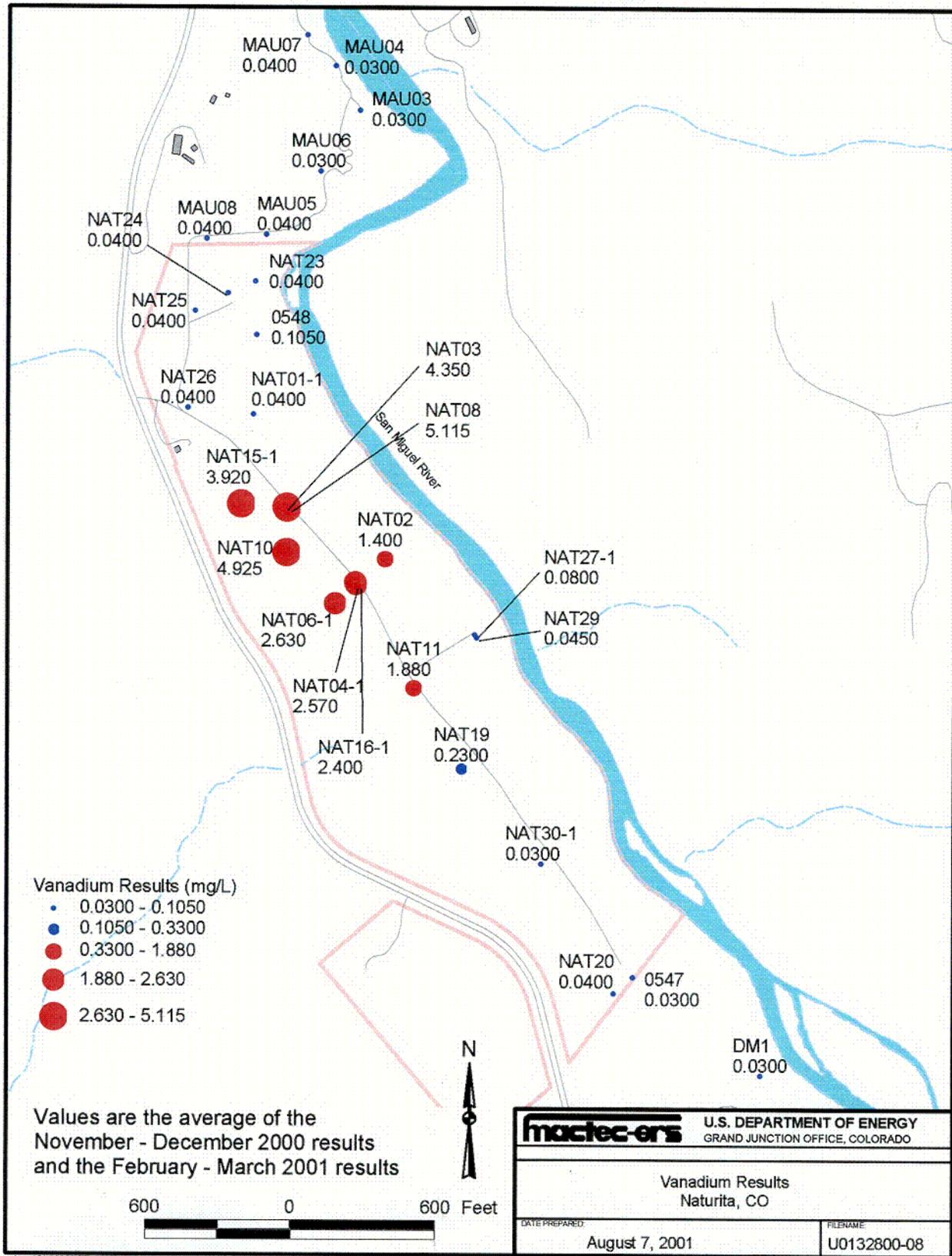


Figure 5-40. Average Vanadium Concentrations Measured in November and December 2000 and February and March 2001

CD9

Table 5-4. Samples Collected During June 2000 for Age Dating of Ground Water at the Naturita Site

Location	Sample Date	USGS Analyzed Samples	University of Utah Analyzed Samples	Tritium-Helium-3 Samples
DM1	6-7-2000	x		x
0547	6-7-2000	x		
0548	6-7-2000	x		
MAU01	6-8-2000	x		
MAU02-2	6-12-2000		x	
MAU03	6-8-2000	x		
MAU04	6-8-2000	x		x
MAU06	6-8-2000	x		
MAU07	6-8-2000	x		x
MAU08	6-8-2000	x		x
NAT02	6-6-2000	x		x
NAT03	6-7-2000	x		
NAT05	6-6-2000	x		x
NAT06-1	6-11-2000		x	
NAT08	6-7-2000	x		
NAT09	6-7-2000	x		
NAT10	6-7-2000	x		
NAT11	6-7-2000	x		
NAT15-1	6-12-2000		x	
NAT15-2	6-12-2000		x	
NAT15-3	6-12-2000		x	
NAT19	6-6-2000	x		x
NAT20	6-10-2000	x		
NAT23	6-8-2000	x		x
NAT24	6-8-2000	x		x
NAT25	6-7-2000	x		x
NAT26	6-6-2000	x		x
NAT29	6-6-2000	x		x
NAT30-1	6-9-2000		x	
San Miguel River	6-8-2000	x		

5.3.4.1 Tritium-Helium Data

Tritium-Helium Sampling

Twelve ground water samples were collected for $^3\text{H}/^3\text{He}$ age dating from the alluvial aquifer at Naturita (Table 5-4). The samples were collected from 2-inch-diameter wells using a Bennett gas-piston pump driven by compressed nitrogen. Three well casings were purged before samples were collected. Collecting water samples for $^3\text{H}/^3\text{He}$ determination requires filling a special copper sample tube that is sealed with pinch-off clamps. The copper tube sample is used for dissolved helium and neon analysis, determination of the $^3\text{H}/^3\text{He}$ isotope ratio, and tritium concentration. If the tritium concentration is low, a more accurate determination can be made using the helium-ingrowth method. In case this analysis was needed, a duplicate sample was collected in a 500-mL bottle with a polyseal lid. The samples were analyzed at the Lamont-Doherty Earth Observatory at Columbia University.

Tritium-Helium Results

Table 5–5 shows the calculated age and recharge year for nine samples collected for $^3\text{H}/^3\text{He}$ analysis, analytical results were not yet available for samples MAU08, NAT05, and NAT26. Ages range from 0.2 years to 33.9 years. As Figure 5–41 shows ground water generally increases in age as it moves downgradient. This is consistent with ground water flow modeling results that indicate water recharges the aquifer from the San Miguel River and flows downgradient parallel to the river. Ground water age decreases downgradient from well NAT24 and in wells NAT23, MAU04, and MAU07. These younger ages are most likely the result of influx of young water from the San Miguel River in that area. Figure 5–41 also shows inferred flow paths based on ground water ages and chloride concentrations. These flow paths indicate that water is entering the alluvial aquifer all along the San Miguel River. This figure is really a snapshot of the ground water ages and concentrations during June 2000. Beyerle et al. (1999) have shown that the amount and area of infiltration of river water to a shallow aquifer, and thus the ground water ages, can fluctuate seasonally. This fluctuation is seen mainly in the area nearest to the river. Parts of the aquifer that are deeper and farther removed from the river typically show less of an influence from young recharge (Beyerle et al. 1999)

Helium-4 is produced in the aquifer by radioactive decay of uranium and thorium. As minerals and dissolved uranium release ^4He to ground water, the ^4He concentration in the water increases. If the ^4He release rate to the aquifer can be quantified, and other sources of ^4He are accounted for, the ^4He concentration should be proportional to the ground water travel time (Solomon 2000). As seen in Figure 5–42, a strong correlation can be made between ^4He - and $^3\text{H}/^3\text{He}$ -based ground water ages at the Naturita site. Because high concentrations of uranium are dissolved in the ground water or sorbed onto the surfaces of mineral grains, this curve represents the release rate of ^4He directly to the ground water. Therefore, ground water at the Naturita site can be dated directly by measuring the ^4He concentration. Sampling and measuring ^4He is cheaper and easier than other common age-dating methods such as CFCs and $^3\text{H}/^3\text{He}$, so this may be an important tool to further quantify ground water travel times at Naturita.

As suggested by the chloride and sulfate concentrations, well MAU07 is most likely a mixture of older ground water from the contaminated portion of the aquifer and fresh, younger water from the San Miguel River (Section 5.3.3.2). If it is assumed that the water at MAU07 is a binary mixture of older water from the alluvial aquifer and younger water (age 0 to 5 years) from the river, the mixing ratios can be calculated using ^4He as a tracer. Assuming the input concentration of ^4He from the aquifer is equal to that in well NAT25 ($70.27 \times 10^{-8} \text{ cm}^3 \text{ (STP) g}^{-1}$), and the younger concentration is similar to that measured in well MAU04 ($14.14 \times 10^{-8} \text{ cm}^3 \text{ (STP) g}^{-1}$), well MAU07 receives approximately 22 percent of its water from the alluvial aquifer. This roughly agrees with the mixing ratio calculated using chloride (26 percent alluvial, 74 percent river).

Table 5-5. Tritium-Helium Age-Dating Results

Location	Tritium/Helium Age (years)	Tritium/Helium Recharge Year	Tritium in Tritium Units	$^4\text{He } 10^{-8} \text{ cm}^3 \text{ (STP) /g}$
DM1	0.2	2000	10.58	5.42
NAT02	15.1	1985	10.9	30.97
NAT05	nd	nd	10.18	nd
NAT19	9.2	1991	10.33	17.12
NAT23	13.5	1987	10.54	25.8
NAT24	33.9	1966	10.68	79.42
NAT25	28.2	1972	10.36	70.27
NAT26	nd	nd	11.01	nd
NAT29	5.8	1994	10.61	5.2
MAU04	5.6	1994	10.61	14.14
MAU07	12.4	1988	10.39	26.4
MAU08	nd	nd	10.27	nd

All samples were collected June 6 through 8, 2000.

nd = No data.

As shown in Figure 5-43, a strong correlation can also be made with ground water age and uranium concentration ($R = .83$). This is not surprising, because uranium concentration generally increases along the ground water flow path. However, this would suggest that uranium concentration could be used as an estimation of ground water age (higher uranium concentration equals greater age). Comparing ground water ages with uranium concentration can give an idea of the extent of natural attenuation at the site. If natural flushing of uranium is occurring, there should be relatively old ground water present with low uranium concentrations. Figure 5-43 shows increasing uranium with age, suggesting natural flushing at these wells has not yet begun. More detailed age dating of the aquifer could possibly show areas where natural flushing is occurring.

5.3.4.2 Chlorofluorocarbon Data

CFC Sampling

CFC samples were collected from each of the 2-inch-diameter wells using a Bennett gas-piston pump driven by compressed nitrogen. Three well casings were purged before five replicate samples were collected. To isolate samples from the modern atmosphere, the samplers collected them in sealed borosilicate glass ampoules that were flushed with ultra-high-purity nitrogen. The samples were analyzed at the USGS Reston Chlorofluorocarbon Laboratory by purge-and-trap gas chromatography using an electron capture detector. Busenberg and Plummer (1992) provide a more detailed description of the sampling procedure. CFC samples from the 0.5-inch-diameter wells were collected in copper tubes sealed with pinch-off clamps. During sampling, a peristaltic pump was attached to a 3/8-inch-diameter copper pipe that was inserted into the well. The well was purged of at least 3 gallons before sampling. A 3/8-inch copper sample tube similar to those used in tritium-helium sampling (see Section 5.3.4.1) was connected to the sample pipe and to the intake side of the pump head. Once flushed with ground water to remove any trapped air, the copper sample tube was sealed with pinch off-clamps. Three replicate samples were collected at each well. These samples were analyzed at the University of Utah Department of Geology and Geophysics by purge-and-trap gas chromatography using an electron capture detector. Wilkowske (1998) presents a more detailed description of the copper tube sampling technique.

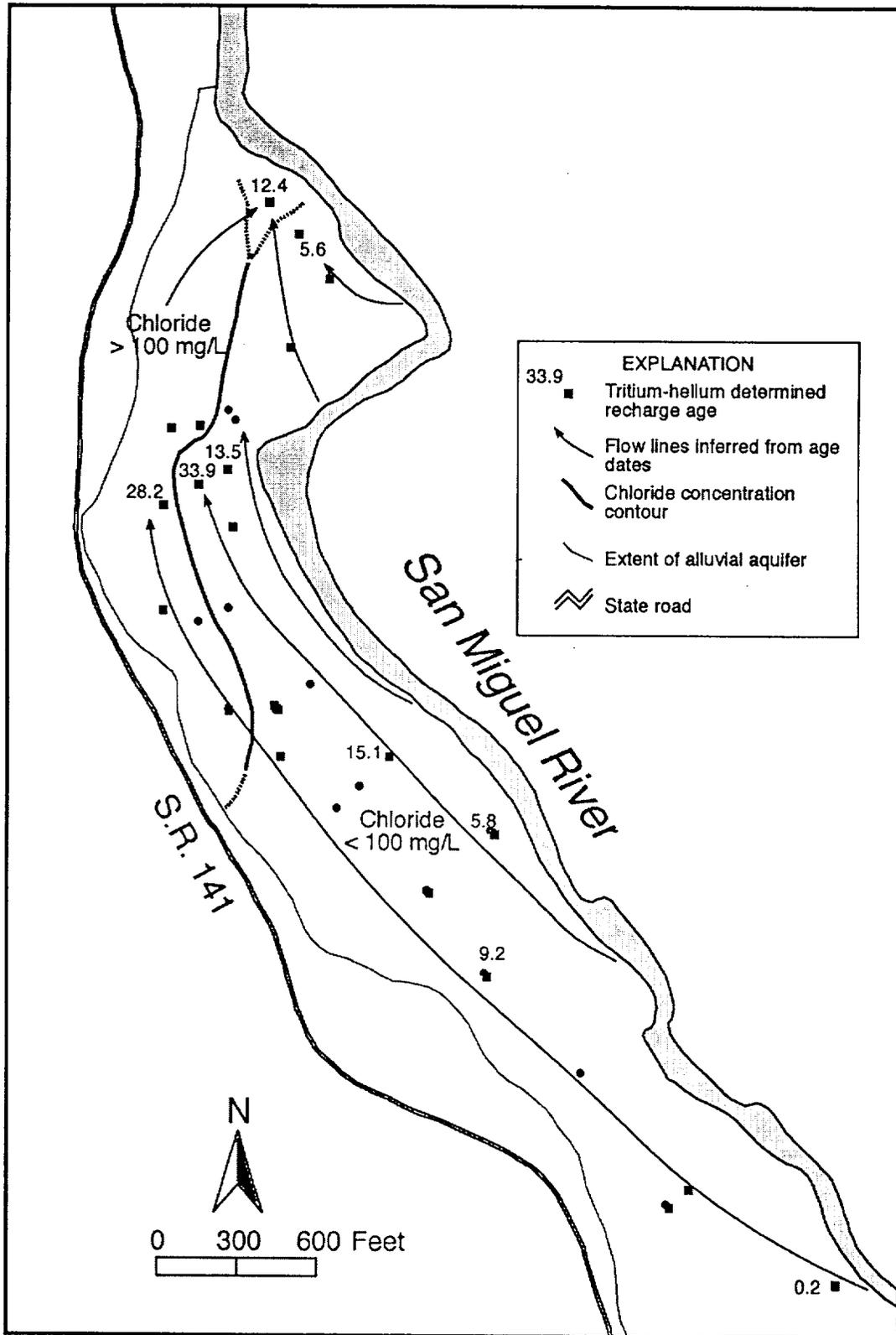


Figure 5-41. Tritium-Hellum-Determined Recharge Ages and Inferred Flow Paths at the Naturita Site

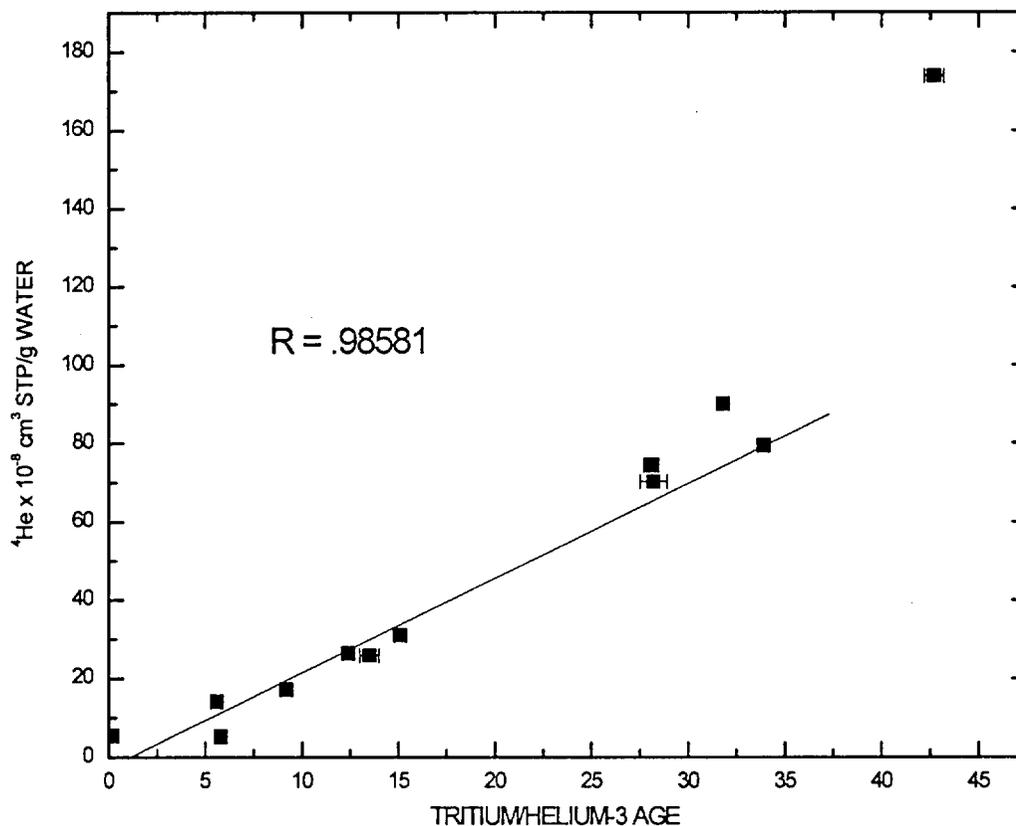


Figure 5-42. ^4He Concentration versus Ground Water Age as Determined by $^3\text{H}/^3\text{He}$ Dating

Calculation of Recharge Temperature

The calculated equivalent air concentration of CFCs is based on the solubility of CFCs in water and is therefore temperature dependent. It is important to get a good estimate of the temperature of the water at the time it recharged the aquifer. To measure the recharge temperature, samples were collected from well MAU06 for dissolved gas analysis at the USGS Reston Chlorofluorocarbon Laboratory. The analyses included dissolved nitrogen, argon, methane, carbon dioxide, and oxygen. The concentration, as well as the ratios of concentrations of these gases, can be used to calculate the recharge temperature of a ground water sample. Based on the N_2/Ar ratio, the calculated recharge temperature for the Naturita aquifer is 16°C . This is similar to the value of 13°C , which was the average temperature of the San Miguel River during peak flow in May and June 2000.

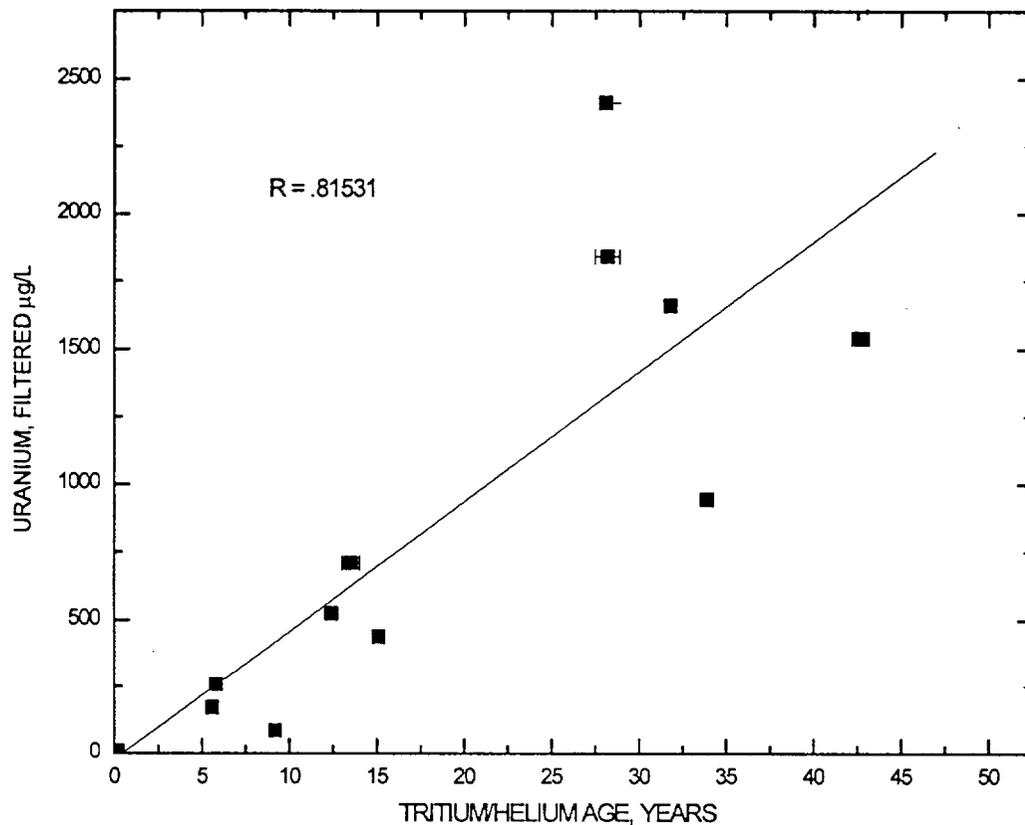


Figure 5-43. Uranium Concentration versus Age as Determined by $^3\text{H}/^3\text{He}$ Dating

CFC Age Dating Results

CFC samples were analyzed for three compounds: CFC-11 (trichlorofluoromethane, CFCl_3), CFC-12 (dichlorodifluoromethane, CF_2Cl_2), and CFC-113 (trichlorotrifluoroethane, $\text{C}_2\text{F}_3\text{Cl}_3$). Table 5-4 shows the average CFC concentration for each of the three species and their modeled recharge age. Because tritium-helium age dating is unaffected by factors such as biodegradation, sorption, and urban contamination, these dates are considered to more accurately model the recharge age of ground water. Figure 5-44 shows that recharge ages modeled from CFC-11 and CFC-12 values are too young in comparison to $^3\text{H}/^3\text{He}$ ages. This suggests either biodegradation of both CFC species or mixing of old CFC-free water that is presumably upwelling through the underlying consolidated rock. This mixing would effectively dilute the CFC concentration and give an apparent older recharge age. Degradation of CFC-11 and CFC-12 under anaerobic conditions is well documented (Plummer and Busenberg 2000). Degradation of CFC-11 is typically more pronounced than that of CFC-12, which is the case with the samples from the aquifer at Naturita (Figure 5-44). In a water sample with no biodegradation that is a mixture of old CFC-free water and young water containing CFCs, the CFC-11 and CFC-12 ages should match. Therefore, it is apparent that CFC-11 has been significantly degraded and cannot be used for age determination.

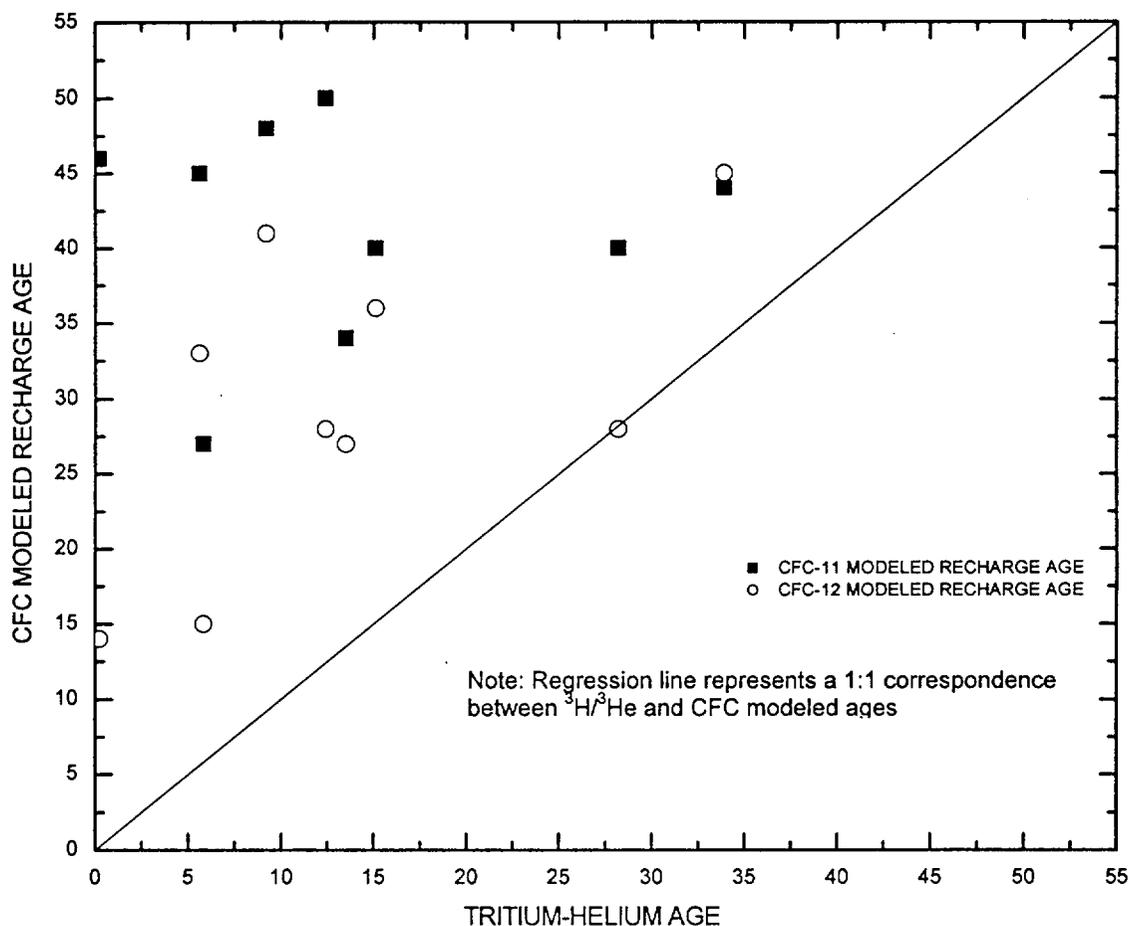


Figure 5-44. Recharge Age Modeled from CFC-11 and CFC-12 Data Compared to $^3\text{H}/^3\text{He}$ Age

The deep ground water from the Morrison Formation has high chloride concentrations, and the head gradient between the deep and alluvial aquifer is upward. Simple mixing calculations can be made to evaluate the percentage of water in the alluvial aquifer that could have originated from the deep, and presumably old, ground water. These calculations assume that (1) chloride is conservative, (2) the end member waters are the San Miguel River and the deep ground water, and (3) there are no other chloride sources. Table 5-6 summarizes these mixing calculations. These calculations suggest that upgradient of the former mill yard, less than 2 percent of the water is from the deep aquifer. In the contaminated area, the calculations are approximate because of contamination from sodium chloride used in processing the ore (Section 5.3.3.2). This is evident from the high chloride concentrations observed in historical data from abandoned well 0656. Well NAT03 is located close to the former location of well 0656. If the assumption is made that the 6 years from 1992 to 1998 and the surface soil remediation were sufficient to flush the mill-related chloride from the NAT03 area, then the deep ground water could have accounted for 7.6 percent of the total water. Because much of the chloride in this area could very likely be left from contamination, this value should be considered as a maximum amount of mixing. The results at NAT04, which is several hundred meters upgradient of NAT03, are similar to the results at NAT03.

Table 5-6. Chloride Concentrations and Mixing Ratios in Different Waters at the Naturita Site

Location	Measurement Period	Concentration mg/L	Percentage of Water from the Deep Aquifer
River			
SM1	1998-2001	5.2	0
Deep Aquifer			
0502	1986-1995	699	100
Upgradient Wells			
0547	1986-1997	9.0	0.5
0547	1998-2001	11	0.8
NAT20-22	1999-2001	10	0.7
Contaminated Wells			
0656	1990-1992	155	21.6
NAT03	1998-2001	58	7.6
NAT04	1998-2001	44	5.6

The $^3\text{H}/^3\text{He}$ age-dating technique only dates the young, tritium-containing fraction of ground water, because the isotope ratio is nearly independent of dilution with old tritium-free water (Plummer et al. 1998b). Therefore, these ages should be comparable to the CFC dates of the young water fraction. This fraction can be calculated using the mixing ratios from the chloride concentrations. Assuming that the water at well NAT02 is mixed with 7.6 percent old CFC-free water, the remaining young fraction should have a CFC-12 apparent age of 1986. The tritium-helium recharge age at this well is 1994. At well NAT29, assuming a mixing ratio of 7.6 percent old water, the young fraction should have an apparent CFC-12 recharge age of 1965. The $^3\text{H}/^3\text{He}$ recharge age at well NAT29 is 1985. In order to match the $^3\text{H}/^3\text{He}$ recharge ages at well NAT02 to the CFC-modeled ages, San Miguel River water would have to be mixed with about 85 percent old CFC-free water. Well NAT29 would need to be mixed with about 25 percent old water. Because the maximum amount of older water based on chloride concentrations is about 7.6 percent, it would appear that the CFC-12 ages are affected by some other process, such as biodegradation, and also cannot be used for age determination.

CFC-113 also proved unacceptable for ground water age dating. All samples except those from NAT09, NAT11, NAT24, and the San Miguel River were contaminated with CFC-113. CFC-113 contamination is defined by a sample concentration that is greater than would be present if the sample were equilibrated with modern air.

5.3.5 Contaminant Fate and Transport

5.3.5.1 Ground Water Flow and Transport Modeling

A ground water flow and transport model was developed to evaluate if natural processes will reduce concentrations of site-related COPCs to regulatory levels in the alluvial aquifer within 100 years. Two versions of the model were developed and employed to address conditions at the site. A steady state deterministic flow and transport model was used as the basis for the steady state stochastic flow and transport model. The steady state stochastic flow and transport model was used to quantify the uncertainty in flow and transport parameters. Modeling results indicate that natural flushing is not an acceptable compliance strategy to reduce ground water concentrations of uranium and vanadium to acceptable levels within 100 years.

The USGS was contracted to develop a steady state deterministic flow model for the Naturita site. The existing ground water flow pattern at the site was modeled using the MODFLOW software (McDonald and Harbaugh 1988), a multilayered, three-dimensional hydrologic flow model published by USGS. USGS uses the Argus Open Numerical Environments (Argus ONE) family of product for the pre- and post-processing for MODFLOW. The calibrated MODFLOW files created by the Argus ONE products were then converted to a format compatible with the version of MODFLOW in GWVistas.

The gravel mining operation upgradient of the former site has recently expanded and it is likely that there will be future expansions. This operation was not considered in the USGS flow model and subsequently not considered in the transport modeling. The recent and future expansion of this operation could significantly impact the ground water flow and the transport of contaminants. Without modeling the impacts from the gravel mining operation, the predicted concentrations of the COPC in this report are most likely underestimated.

The calibrated steady state deterministic flow model of the USGS was used as a basis for a steady state stochastic flow model developed using GWVistas. The steady state deterministic and stochastic transport models were developed using GWVistas.

Output from the flow model was used as input to MT3DMS (Zheng 1999), a version of a modular three-dimensional transport model to simulate advection, dispersion, and chemical reactions of contaminants in the ground water system. A steady state deterministic transport model was developed to predict future concentrations of COPCs. Sensitivity analysis of the flow and transport parameters, within the deterministic models, determined that hydraulic conductivity and recharge are sensitive and affect the transport simulation results. These two flow parameters and the transport parameters of porosity, longitudinal dispersivity, and the K_d were treated as uncertain for stochastic simulation.

Section 4.5.1.4 briefly discusses the determination of K_d values from R_d values. The K_d values of 0.6078 and 12.46 mL/g for uranium and vanadium, respectively, that are used for the deterministic modeling are 25 percent of the average R_d value. For the stochastic modeling the estimated range of values is 25 percent of the minimum and maximum R_d values. For uranium the estimated range of values is from 0.3975 to 1.1225 milliliters per gram (mL/g). For vanadium the estimated range of values is from 4.445 to 20.6575 mL/g.

Details of the model construction, steady state calibration, and steady state stochastic parameters are presented in Appendix F. The codes used are fully described in the references cited and have been verified, benchmarked, and approved for use by most government and regulatory agencies. The following sections present a summary of the modeling results.

Steady State Deterministic Model

Predicted uranium concentrations in ground water after 100 years are presented in Figure 5–45. The simulation predicts that the maximum concentration will decrease to 0.23654 mg/L, which is above the UMTRA Project MCL of 0.044 mg/L. Vanadium simulations show similar results. Vanadium concentrations in ground water after 100 years are presented in Figure 5–46. The simulation predicts the maximum concentration will decrease to 4.3286 mg/L, which is well above the risk-based concentration of 0.33 mg/L. Simulation results show that at 10 years the maximum remaining arsenic concentration is 0.045 mg/L, which is below the UMTRA Project MCL of 0.05 mg/L.

Steady State Stochastic Model

The steady state stochastic modeling predicts similar results. Only uranium was modeled using the stochastic models. Figure 5–47 presents the results for uranium after 100 years. Maximum average concentrations are above the standard at 0.12087 mg/L. The stochastic simulations predict that after 100 years there is a 49 percent probability that the maximum concentration will be greater than the proposed standard over a significant area of the alluvial aquifer, as shown in Figure 5–48.

5.4 Pattern Recognition Modeling of Natural Attenuation Processes

The first step in documenting the natural removal of contaminants in ground water systems is to identify the “footprint” of the natural attenuation process (National Research Council 2000). The mechanisms that destroy or sequester the constituents cannot be observed directly; however, the removal process can leave a number of footprints that are directly related to the loss of the contaminant (National Research Council 2000). Multiple chemical and physical footprints of a specific natural attenuation process are usually required to provide a defensible link between cause and effect. Some footprints can be obscured by reactions that produce or use the footprint materials. For example, dissolution of calcareous materials along a ground water flowpath could mask the footprints of biodegradation reactions that change the total inorganic carbon concentration in the ground water (National Research Council 2000). These same principles are applicable to documenting the geochemical and hydrologic footprints of the natural attenuation of selected contaminants at the Naturita site.

Statistical techniques collectively referred to as pattern recognition modeling are useful in extracting chemical information from large, multivariate databases that may otherwise be difficult or impossible to interpret (Meglen 1988). Pattern recognition modeling uses statistical and graphical techniques to chemically fingerprint groups of multivariate data that have undergone similar geochemical and hydrologic processes. These techniques can be used to efficiently identify the footprints related to natural attenuation processes at the Naturita site.

The objectives of this section are to (1) describe how pattern recognition modeling techniques were used to model multivariate data from the Naturita site, and (2) interpret the results of pattern recognition modeling with respect to the geochemical and hydrologic footprints controlling uranium removal at the site.

5.4.1 Methodology

Pattern recognition modeling techniques were applied to the multivariate data matrix collected from the Naturita site during June 2000 (Table 5–7 and Appendix G). The data set consists of 66 locations (Figure 5–49) and 23 chemical, physical, and isotopic constituents. The constituents in the data set are Al, alkalinity as CaCO₃, B, Br, Ca, Cl, dissolved oxygen (DO), Fe, K, Mg, Mn, Na, oxidation-reduction potential, pH, Si, SO₄, specific conductance, Sr, temperature, U, V, delta oxygen-18 ($\delta^{18}\text{O}$), and delta deuterium (δD). The pattern recognition modeling of the database consisted of (1) hierarchical cluster analysis (HCA) and (2) principal component analysis (PCA) combined with data visualization techniques using the software package PIROUETTE 3.01 (Infometrix 2000).

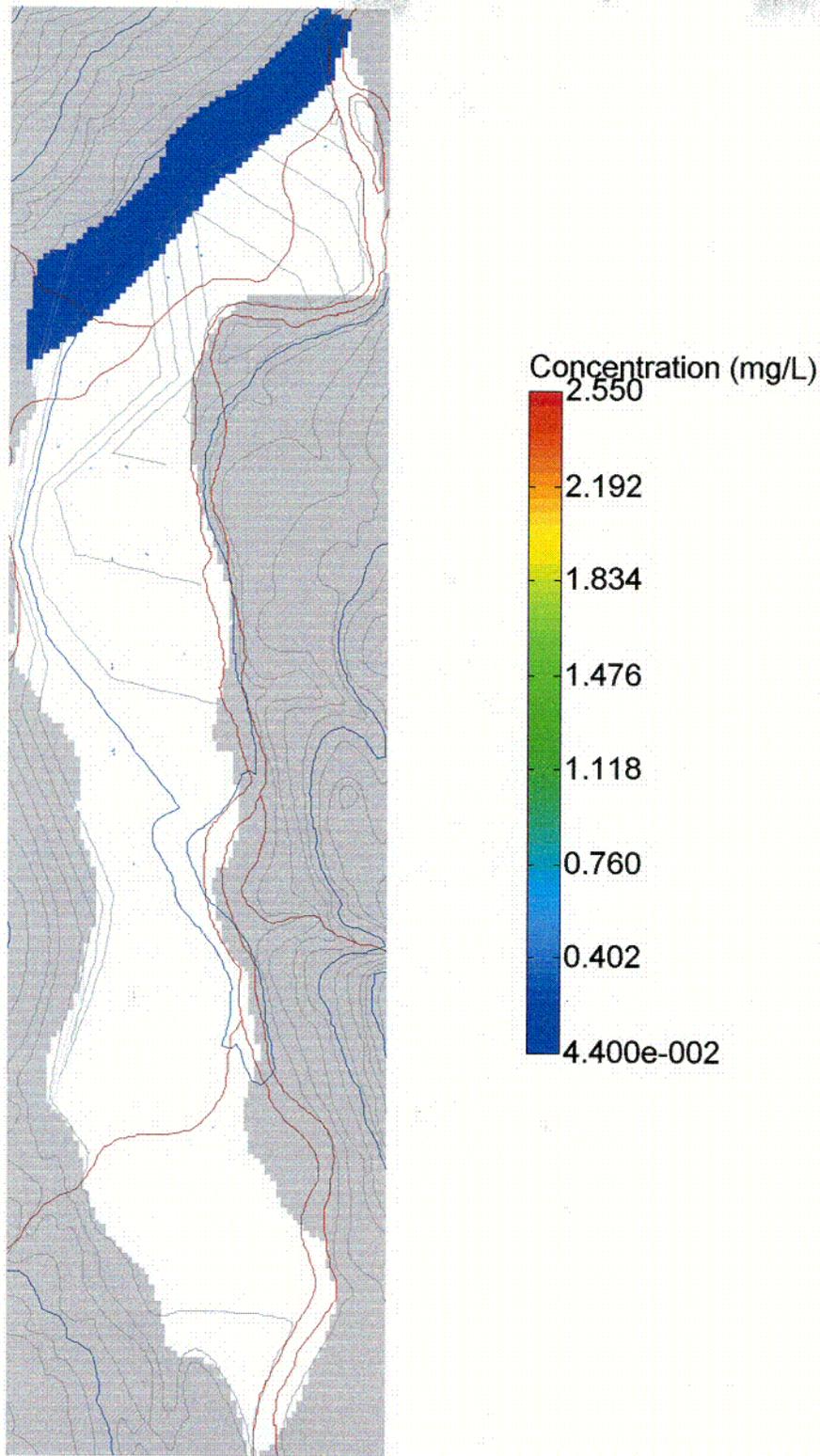


Figure 5-45. Predicted Uranium Concentration in Ground Water After 100 Years
(steady state deterministic model)

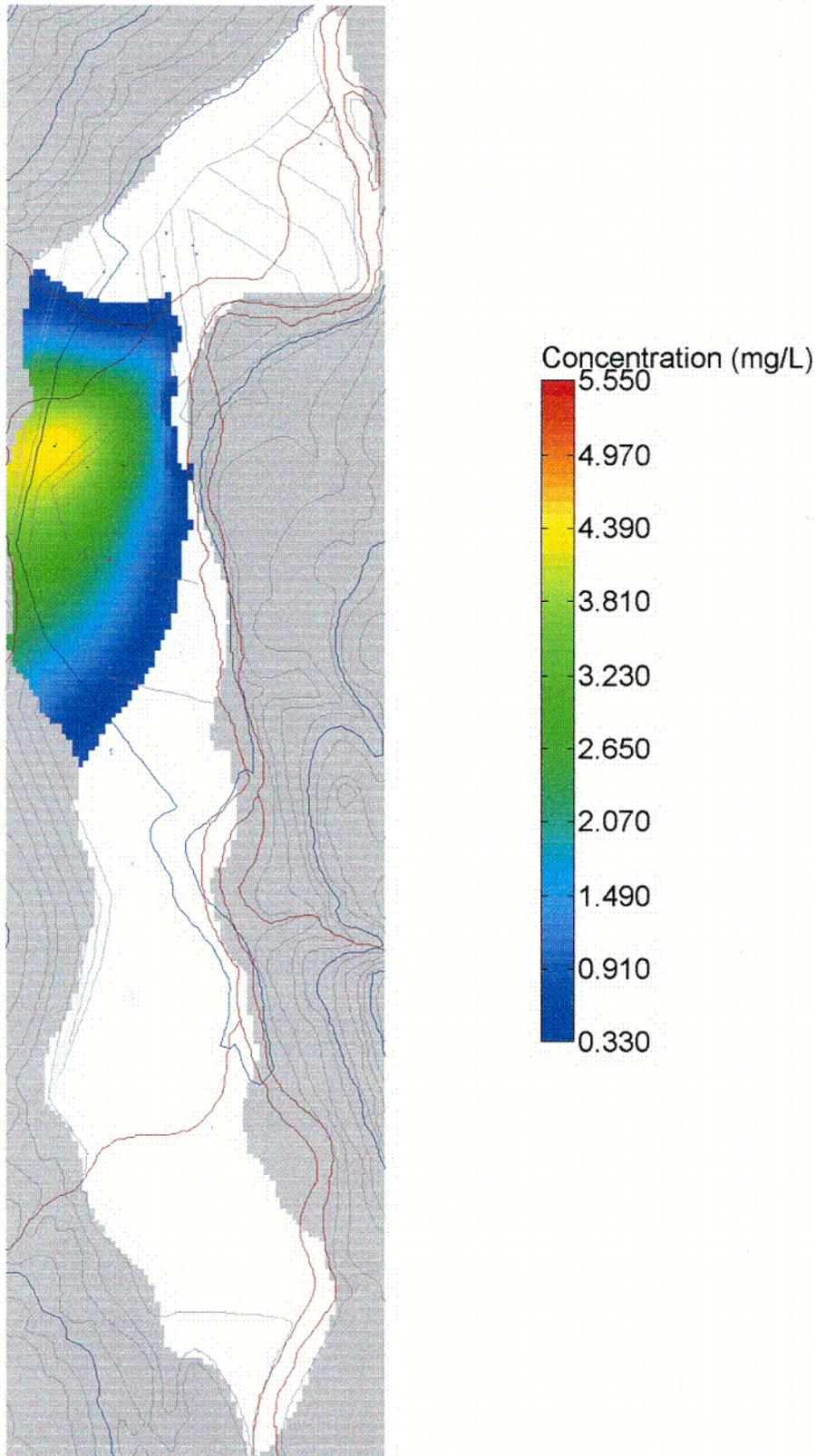


Figure 5-46. Predicted Vanadium Concentrations in Ground Water After 100 Years
(steady state deterministic model)

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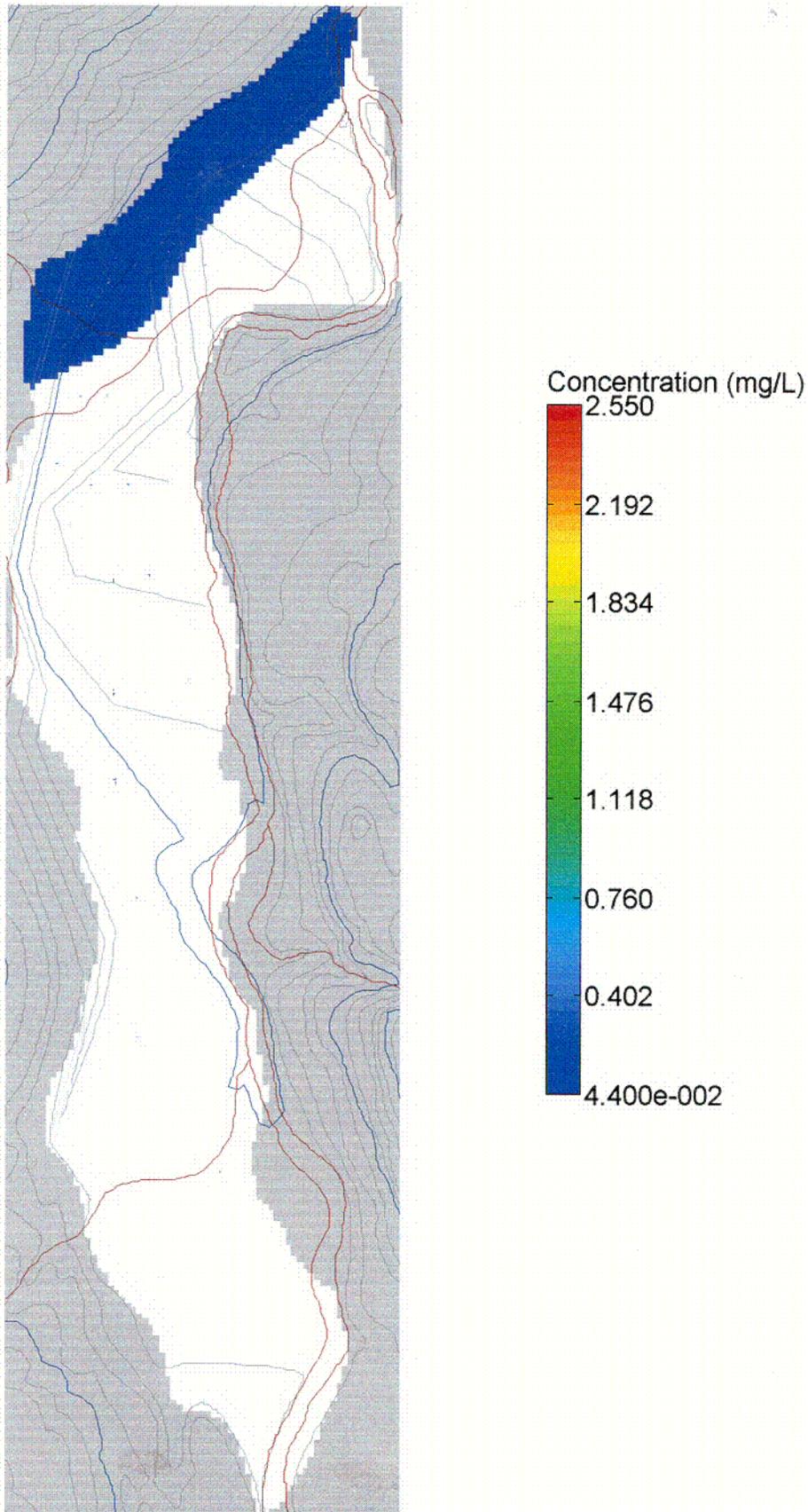


Figure 5-47. Predicted Uranium Concentrations in Ground Water After 100 Years
(steady state stochastic model)

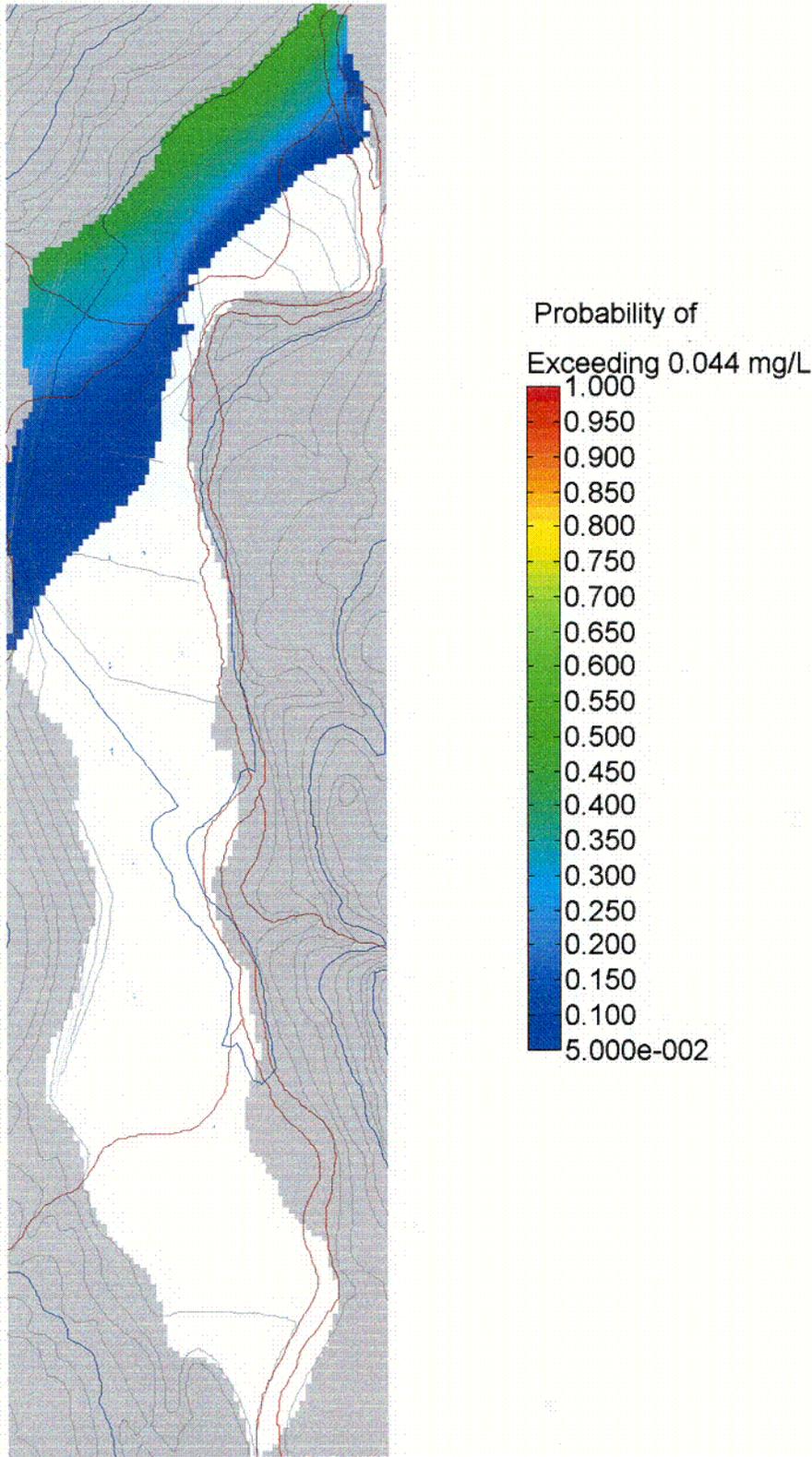


Figure 5-48. Probability of Exceeding 0.044 mg/L After 100 Years

Table 5-7. Principal Component Loadings of Each Chemical Constituent Used in Pattern-Recognition Modeling of Geochemical Data at the Naturita Site

Chemical Constituent	Principal Component 1 Loadings, Unitless	Principal Component 2 Loadings, Unitless	Principal Component 3 Loadings, Unitless
Aluminum	0.170188	-0.017381	0.003615
Alkalinity as CaCO ₃	0.274251	-0.113037	-0.031143
Boron	0.244010	0.147747	0.175510
Bromide	0.141018	0.302378	0.280969
Calcium	0.270638	-0.006266	-0.048917
Chloride	0.249546	-0.001928	0.146143
Dissolved oxygen	-0.086892	0.310780	0.291254
Iron	0.036257	-0.255583	-0.316834
Potassium	0.243880	0.198122	0.064084
Magnesium	0.281352	-0.063129	0.091898
Manganese	0.199061	0.097277	-0.252004
Sodium	0.281358	-0.073263	0.046984
Oxidation-reduction potential	-0.048781	0.175063	0.195769
pH	-0.134528	0.391981	0.102914
Silicon	0.247714	0.025142	-0.100777
Sulfate	0.280173	-0.103272	0.067179
Specific conductance	0.283692	-0.069284	0.090751
Strontium	0.268836	0.014925	0.180447
Water temperature	-0.100691	0.155468	0.376458
Uranium	0.267012	0.141107	-0.084516
Vanadium	0.132422	0.131755	-0.201817
Delta deuterium	-0.007406	-0.458933	0.377873
Delta oxygen-18	-0.049736	-0.425400	0.406542

Note: Loadings highlighted in yellow are greater than 0.20 or less than -0.20. This cutoff value best explains the most probable geochemical processes controlling the elemental distribution in each principal component.

5.4.2 Hierarchical Cluster Analysis Results

The purpose of HCA is to group multivariate data so that underlying links between the groups can be discerned (Davis 1973, Meglan 1991). This grouping is accomplished by calculating a similarity distance of all variables in the data set between all possible pairs of samples. After sample distances have been computed, the two most similar samples are linked, and this linkage continues until all the samples and clusters have been linked. Identical samples would have a similarity value (SV) of 1.0, and the most dissimilar sample/cluster in the data set would have a SV of 0.0. Prior to HCA, the data were autoscaled and the complete linkage method was used to calculate the SVs between sample pairs (Infometrix 2000). Results of the HCA are displayed in the form of a dendrogram constructed with the SV scale on top decreasing from 1.0 (most similar) to 0.0 (least similar) (Figure 5-50).

Six distinct data clusters (designated groups 1, 2, 3, 4, 5, and 6+7) were distinguished using a SV = 0.66 and defined by the vertical line on the dendrogram (Figure 5-50). Sample locations in each of the groups plot in distinct geographic regions of the site (Figure 5-49) that are related to similar geochemical and hydrologic processes. Group 1 is surface water in the San Miguel River. Group 2 is associated with water samples from wells at the southern edge of the site, immediately downgradient of the gravel pits and upgradient of the historical tailings and

associated facilities. Group 3 consists of water samples from well DM1 upgradient of the gravel pits and south of the study area boundary plus wells MAU03, 04, and 06 at the north end of the study area. Group 4 consists of water samples from wells in the center of the site and adjacent to the river. Group 5 consists of water samples from wells in the central part of the site; however, they are farther away from the San Miguel River than wells belonging to Group 4. Water samples from wells MAU01, MAU08, NAT25, and NAT26 are members of group 6+7 and are located in the northern half of the study and are, in general, farther removed from the San Miguel River than Group 5 wells.

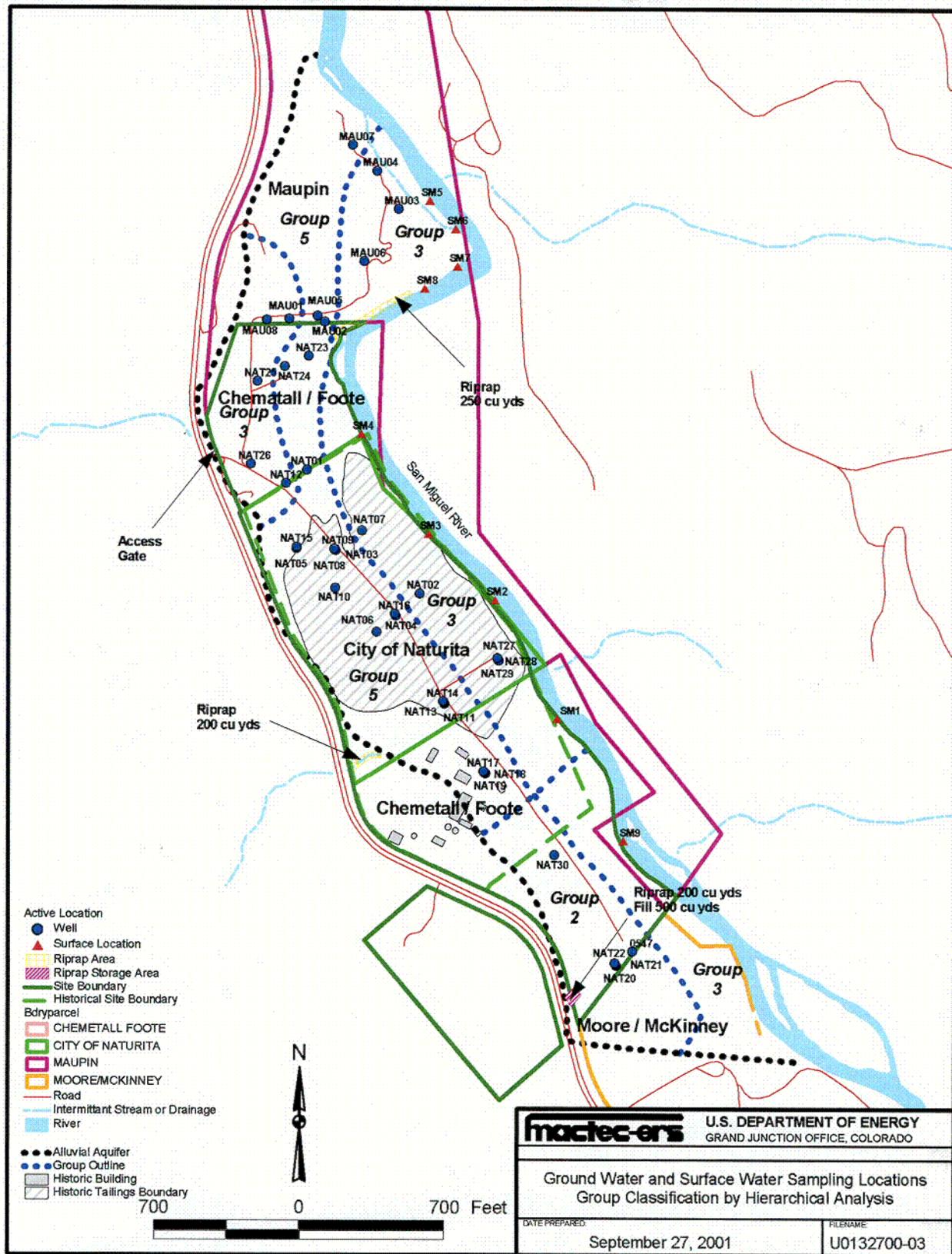
The uranium concentrations for each group are distinctly different (Figure 5–51). The median uranium concentrations are lowest (median concentration < 14 µg/L) for locations in groups 1 and 2. Geographically, these locations represent the San Miguel River or areas upgradient of the former uranium processing facilities. Higher median uranium concentrations are present in locations classified in Group 3 (median concentration = 172 µg/L) and Group 4 (median concentration = 466 µg/L). Both Group 3 and 4 locations are downgradient from the former uranium processing facilities, but close to the San Miguel River where elevated river stage during seasonal snowmelt tends to create some localized flushing zones that could dilute the uranium concentration in the ground water. The uranium concentrations are highest at locations in groups 5 and 6+7 (median concentrations = 908 and 1,660 µg/L). Geographically, these locations are both downgradient of the former millsite and farther removed from the mixing influence of the San Miguel River than locations in groups 1–4 (Figure 5–49).

Age dating of water in each of the groups supports the interpretation of interaction with the San Miguel River and the observed uranium concentrations (Figure 5–51). Because water samples belonging to Group 1 represent surface water in the San Miguel River, they are assumed to have an age date of 2000. Unfortunately, no age dating was done on water samples from wells belonging to Group 2. Wells from Groups 3 and 4 are close to the San Miguel River and have relatively young recharge ages (1985 to 2000) and low median uranium concentrations, indicating significant mixing with recently recharged water from the San Miguel River. In contrast, Group 5 and 6+7 wells that are farther away from the San Miguel River have older recharge ages (1966 to 1991) and higher median uranium concentrations, indicating less mixing with recently recharged water from the San Miguel River. The youngest recharge age measured in Group 5 wells was 1991 and was measured in water from well NAT17, which is the farthest upgradient well in Group 5.

5.4.3 Principal Component Analysis Results

Results from the HCA of the multivariate data set (Table 1, Appendix G) indicate a significant clustering of the data that is directly related to the geographic distribution of the wells in terms of distance from the San Miguel River and relation to the tailings material. PCA was applied to the same data set and data groupings identified in the HCA to determine the underlying geochemical and hydrologic processes that may be controlling the observed variations in the individual chemical, isotopic, and physical constituents that were analyzed.

The goal of PCA is to find a new set of coordinate axes that are mutually orthogonal, onto which the multivariate data can be projected. Each new axis is referred to as a principal component (PC) and is independent of the other PCs. The number of PCs used to represent the multivariate data set is not exact; however, the first two or three PCs generally explain most of the variance from the original data matrix.



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Figure 5-49. Location of Ground and Surface Water Sampling in Relation to Group Classification by Hierarchical Cluster Analysis

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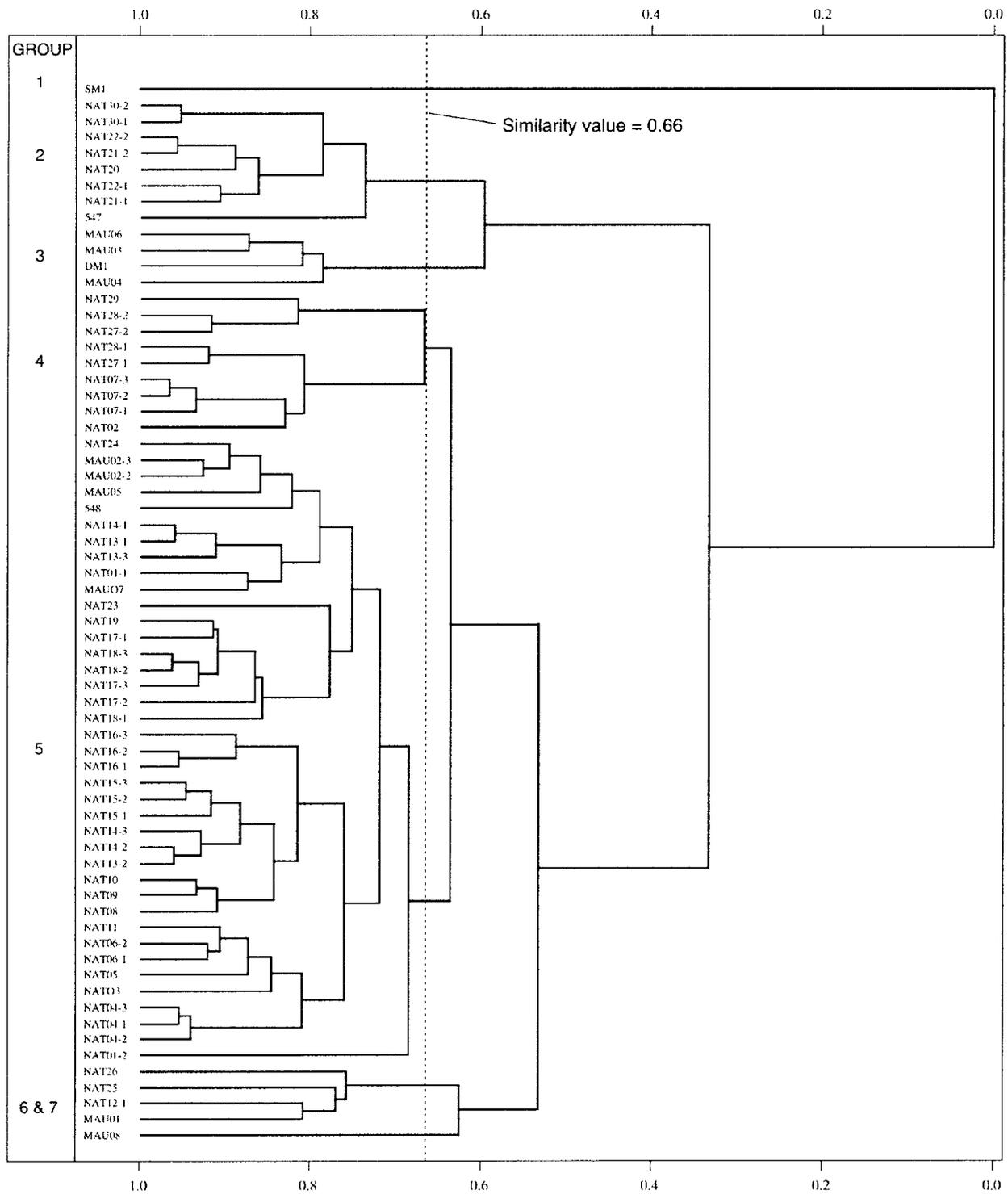
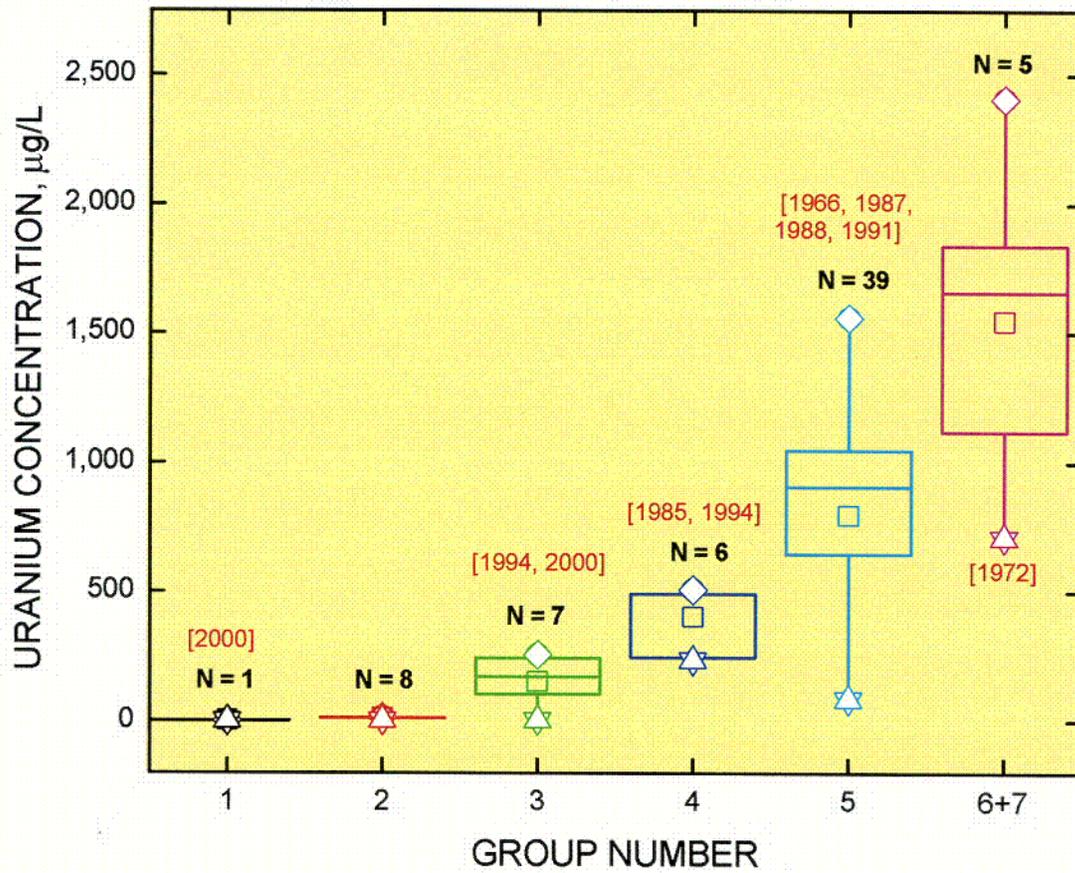


Figure 5-50. Dendrogram Showing the Results of the Hierarchical Cluster Analysis Performed on the Multivariate Data Set Collected During June 2000, Naturita, Colorado. Each Group Consists of One or More Sample Sites Within the Study Area.



EXPLANATION

- — Maximum
- ◇ — 99th percentile
- — 95th percentile
- — 75th percentile
- — Mean
- — Median
- — 25th percentile
- ▽ — 5th percentile
- — 1st percentile
- △ — Minimum

N = 6 – Number of samples

[1994, 2000] – Date(s) of ground water recharge

Figure 5-51. Box Plots Comparing the Uranium Concentrations and Dates of Ground Water Recharge for Each Group Identified by the Hierarchical Cluster Analysis of Ground and Surface Water Data Collected at the Naturita Site

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During PCA, the multivariate data set is decomposed into two matrices consisting of loadings and scores for each of the PCs that were selected. The product of the scores and loadings matrices will reproduce the original data set. For example, if three PCs were selected to represent the original data matrix, each PC would have a loading value between ± 1.0 for each of the original variables. The PC loadings near -1.0 and $+1.0$ are considered significant and are used to identify the chemical, physical, and isotopic constituents that compose each PC. The PC scores are simply the coefficients of the loadings used to transform the original responses from each data point onto the PC axis. Prior to PCA, the original data matrix was transformed into the base 10 logarithm of the original value and autoscaled. The first three PCs were found to best explain the original data set and accounted for 73 percent of the total variance.

Figure 5-52 shows the PC 1 and PC 2 scores. The two axes are linear combinations of the original multivariate data set consisting of 23 variables and 66 samples and can be thought of as a new set of plotting axes. Instead of each axis representing the concentration of a particular trace metal or other inorganic constituent, each axis represents combinations of the different chemical, physical, and isotopic constituents in the water samples, thereby representing geochemical or hydrologic footprints that could provide insight into natural attenuation processes at the site.

The suite of chemical constituents contained in each plotting axis can be used to determine what geochemical and hydrologic process is represented, such as the effect of uranium mill tailings or natural flushing from the San Miguel River. The x-axis in Figure 5-52 is referred to as PC 1 and best represents the ground water contamination from tailings material. Chemical constituents making a substantial positive contribution to PC 1 include alkalinity, B, Ca, Cl, K, Mg, Mn, Na, Si, SO_4 , specific conductance, Sr, and U (Table 5-7). Uranium is derived from the leaching of tailings material. The positive sulfate loading is probably related to the use of sulfuric acid in the ore processing and the dissolution of sulfate mineral phases in the soil below the mill tailings. Dissolution of carbonate mineral phases in the soil zone beneath the tailings pond could result in the elevated loadings for calcium, alkalinity, and strontium. The substantial positive loadings for sodium and chloride may be related to the use of NaCl during salt roasting of the ore material at the site. Positive loadings for boron, chloride, magnesium, sodium, and specific conductance could also be related to the evaporation of tailings process water at the surface before infiltration into the alluvial aquifer.

The y-axis in Figure 5-52 is referred to as PC 2 and represents river flushing with limited evaporation. Chemical, physical, and isotopic constituents making a substantial positive and negative contribution to PC 2 include Br, dissolved oxygen, Fe (negative loading), K, pH, δD (negative loading), and $\delta^{18}\text{O}$ (negative loading) (Table 5-7). The geochemical association in PC 2 is consistent with what would be expected from significant amounts of river water flushing into the alluvial aquifer at the site. Water from the San Miguel River has pH values that are greater than 8.0 units and dissolved oxygen concentrations that exceed 8.0 mg/L (Table 1, Appendix G). The substantial negative loading for iron in PC 2 is consistent with the low solubility of iron under the oxidizing conditions characteristic of the San Miguel River. The substantial negative loadings for δD and $\delta^{18}\text{O}$ are reflective of the isotopically light values of water from the San Miguel River derived from high elevation snowmelt, prior to evaporative enrichment. The positive loading for bromide may be the result of domestic sewage effluent containing elevated concentrations of bromide entering the San Miguel River upstream of the site (Vengosh and Pankratov 1998, Davis and others 1998). It is also possible that part of the bromide and

potassium sources could be residual tracer that was injected into selected wells during May 2000; however, the concentration of the injected tracer compared to natural concentrations is not known.

The individual points in Figure 5–52 represent where individual water samples plot on the newly defined axes (PC 1 and PC 2). Samples from the six groups identified in the HCA show distinct clusters with respect to their PC 1 (tailings contamination) and PC 2 (river flushing) scores (Figure 5–52). Water samples belonging to Group 1 represent water from the San Miguel River and have the largest PC 2 scores (river flushing) and lowest PC 1 scores (tailings contamination) of all 66 samples. Water samples belonging to Groups 3 and 4 contain the largest overall river flushing scores (Figure 5–52), which are confirmed by their proximity to the San Miguel River (Figure 5–52). Water samples belonging to Group 2 have low PC 1 and 2 scores, indicating limited flushing from the San Miguel River and limited influence from uranium mill tailings. This classification is consistent with the location of Group 2 samples, which is upgradient of the historical tailings area and offset at least 250 ft from the San Miguel River and downgradient from a gravel pit (Figure 5–49).

Group 5 and 6+7 samples have the overall largest PC 1 scores (tailings contamination) (Figure 5–52). With the exception of wells NAT23, MAU02, MAU05, and MAU07, all the wells in these groups are relatively distant from the flushing influence of the San Miguel River and downgradient from the historical tailings area (Figure 5–49). Group 6+7 water samples have the largest PC 1 (tailings contamination) scores relative to all six-sample groups.

The PC 3 scores for the 66 water samples are plotted on the y-axis in Figure 5–53 and compared to PC 1 scores (tailings contamination) plotted on the x-axis. Water samples having large PC 3 scores appear to be influenced by strong evaporative effects. Chemical, physical, and isotopic constituents making a substantial positive or negative contribution to PC 3 include bromide, iron (negative loading), manganese (negative loading), dissolved oxygen, oxidation-reduction potential, water temperature, vanadium (negative loading), δD , and $\delta^{18}O$ (Table 5–7). The geochemical association in PC 3 is consistent with what would be expected from evaporation of surface water from the San Miguel River. The positive loadings for dissolved oxygen and oxidation-reduction potential, in combination with negative loadings for iron and manganese, indicate an oxidizing surface water source. The negative loadings for δD and $\delta^{18}O$ and positive loading for water temperature are consistent with isotopic enrichment of surface water by evaporation. As with PC 2, the positive loading for bromide may be an indicator of a domestic sewage component in water from the San Miguel River or could be related to the bromide that was used in a series of tracer tests at selected wells with low hydraulic conductivity during May 2000. Because of the conservative nature of bromide, evaporative processes could substantially increase its concentration in water. The negative loading for vanadium in PC 3 is not apparent.

The individual points in Figure 5–53 represent where individual water samples plot on the newly defined axes (PC 1 and 3). Water samples in Groups 2, 4, and 6+7 have the largest PC 3 scores. Group 2 water samples were collected from wells immediately downgradient from a series of gravel pits at the southern part of the site (Figure 5–49). The gravel pits intercept the water table in the alluvial aquifer and expose recently recharged water from the San Miguel River to potentially large amounts of evaporation (Figure 5–54). In general, PC 3 scores in Group 2 wells decrease in a downgradient direction from the gravel pits (Figure 5–53), which could be the result of mixing of evaporated water from the gravel pit with nonevaporated water resident in the alluvial aquifer.

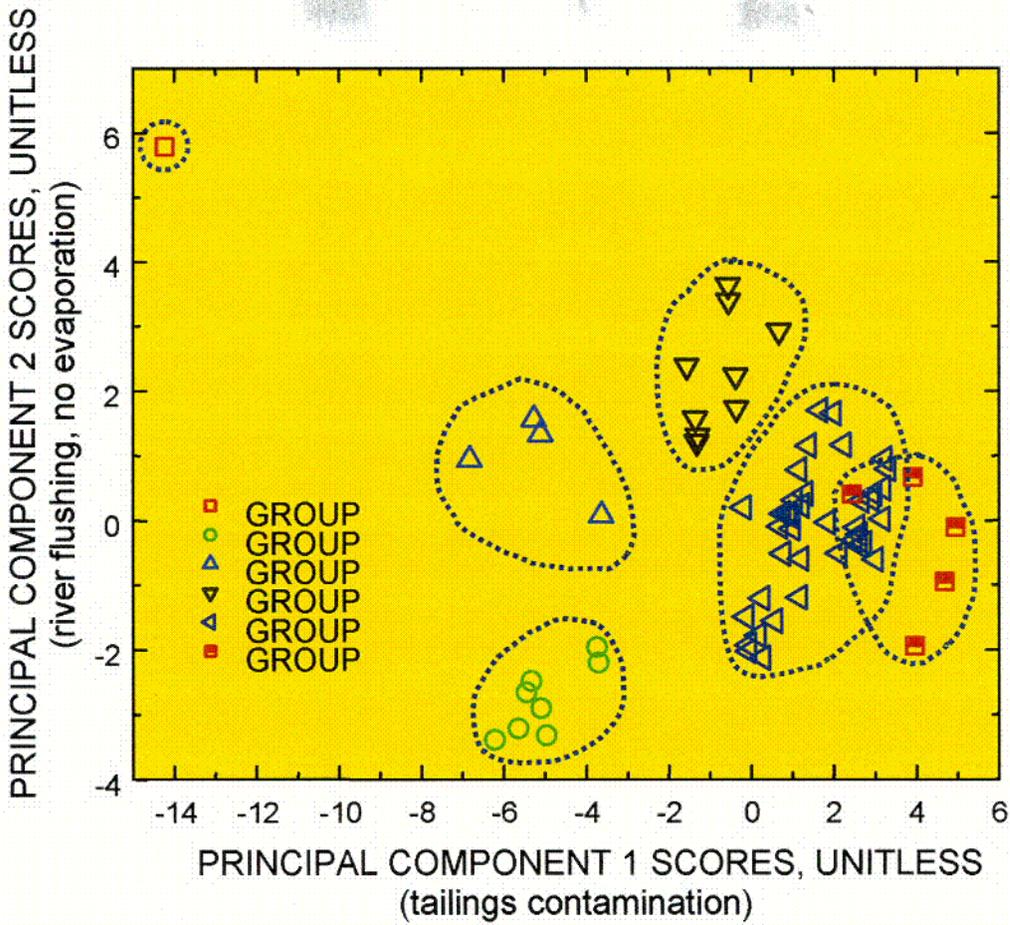


Figure 5-52. Principal Component 1 and 2 Scores for Ground and Surface Water Samples Collected at the Naturita Site

C16

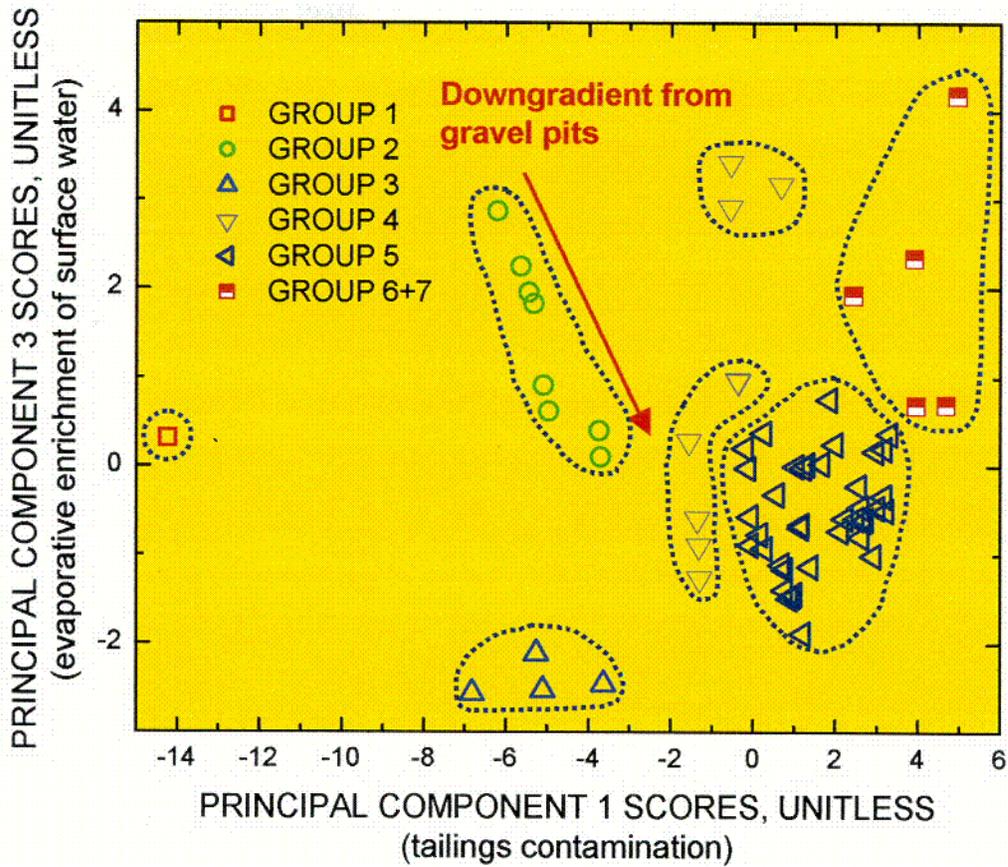


Figure 5-53. Principal Component 1 and 3 Scores for Ground and Surface Water Samples at the Naturita Site

C17

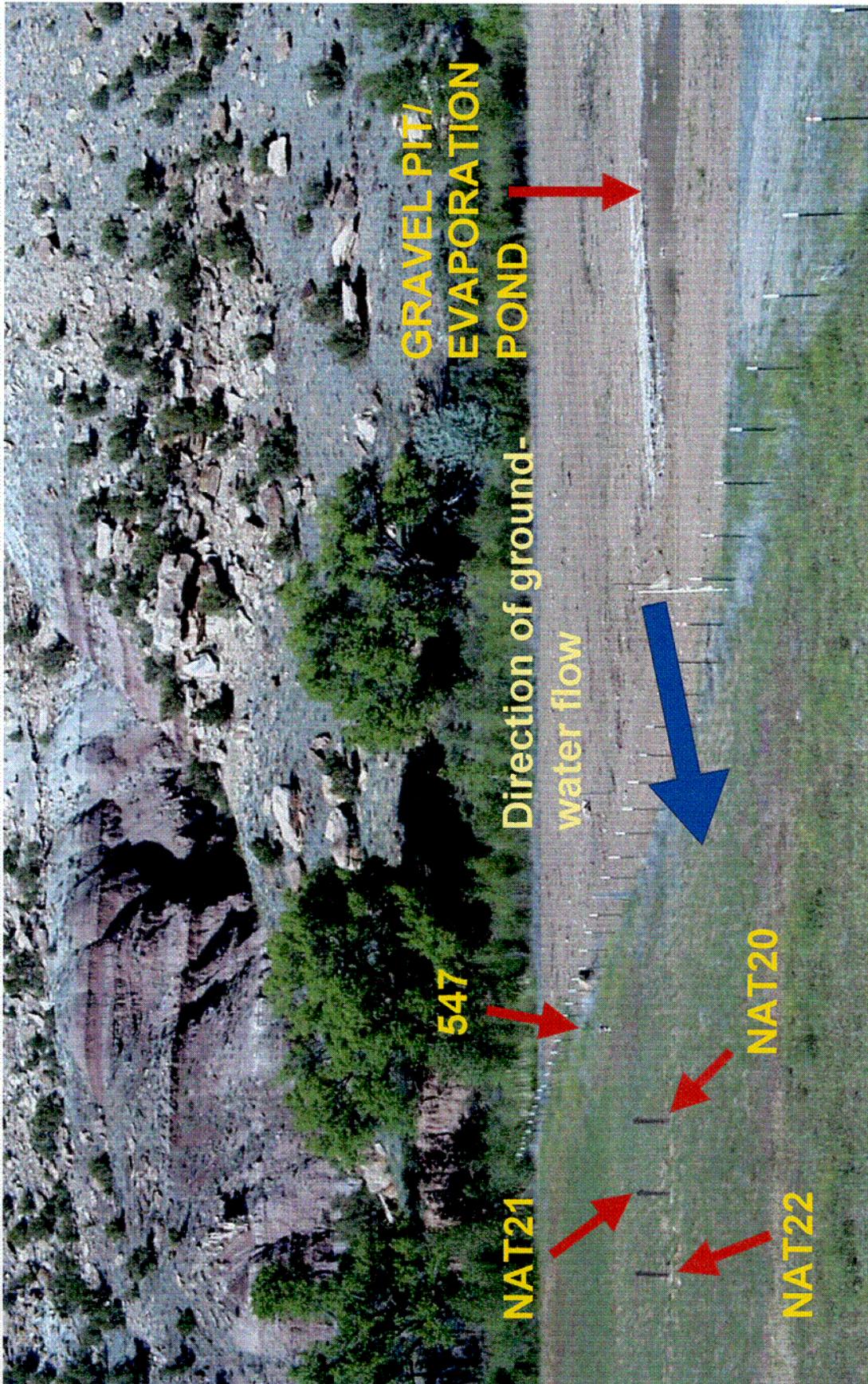


Figure 5-54. Photograph Showing the Location of the Gravel Pit Relative to the Direction of Ground Water Flow in the Alluvial Aquifer and Selected Monitoring Wells During May 2001, Naturita, Colorado

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A subset of samples in Group 4 has a large PC 3 score (Figure 5–53). This subset is composed of water samples collected from wells NAT 27, 28, and 29, which are adjacent to the San Miguel River (Figure 5–49) and should not have a strong evaporative signal. It is unclear why a strong evaporative signal would exist this close to the San Miguel River. Part of this signal may be related to potassium bromide tracer tests conducted at these wells during May 2000; it is likely that the elevated bromide concentrations in wells NAT 27, 28, and 29 (ranging from 0.08 to 0.15 mg/L) are from these tests. It is also possible that a smaller contributor to the evaporation signal in wells NAT 27, 28 and 29 is from direct infiltration of ponded and evaporated water close to the wells. The wells are located in a surface depression adjacent to a berm along the San Miguel River (Figure 5–49). Significant ponding of water was observed in this area during summer 1999.

Group 6+7 wells are the third group that has elevated PC 3 scores (Figure 5–53). The five wells in this group are clustered in the extreme western part of the site. This is a discharge area for an ephemeral channel that brings surface water into this part of the site. Ponding and the potential for evaporation of surface water was noted in this part of the area during summer 1999. Direct recharge of surface water in this area on an intermittent basis could result in the observed evaporative signal.

5.4.4 Variations in Stable Isotope Values

The stable isotope values for δD and $\delta^{18}O$ determined from water samples collected during June 2000 were compared to the sample groupings determined from the pattern recognition modeling (Figure 5–55). Samples belonging to Groups 1 and 3 (San Miguel River and the alluvial aquifer adjacent to the river) have the lightest isotopic signature and plot close to the Global Meteoric Water Line (GMWL) (Craig 1961). The isotopically light values in Groups 1 and 3 samples indicate a high-elevation source water (snowmelt) to the San Miguel River. Groups 1 and 3 isotopic data plot almost directly on the GMWL, indicating no evaporation (Figure 5–55).

In contrast to Groups 1 and 3 members, the isotopic signature in Group 2 samples plots to the right of the GMWL and shows significant isotopic enrichment (Figure 5–55) of recharge water from the San Miguel River. Wells belonging to Group 2 plot along the evaporation trend line with a slope significantly less than the GMWL, which is characteristic of evaporative processes (Ingraham 1998). As indicated in the pattern recognition modeling results, it appears that the gravel pits immediately upgradient from the Group 2 wells are causing a significant isotopic enrichment by evaporation of ground water originally recharged from the San Miguel River. The highest amount of evaporative enrichment is in wells 0547 and NAT20, which are closest to the gravel pits (Figure 5–54). An intermediate amount of evaporative enrichment is indicated in the wells farther downgradient from the gravel pits (wells NAT21 and NAT22). Wells NAT30–1 and 30–2 have the least amount of evaporative enrichment and are farthest downgradient from the gravel pits (about 800 ft).

The isotopic data indicate that evaporative loss of ground water from the gravel pits at the upgradient part of the site is occurring and could affect the natural flushing rates of uranium from the alluvial aquifer. The mass of ground water lost via evaporation from the gravel pits was estimated. A free-water surface evaporation rate of 53 inches per year, calculated for the Dolores–Ute Mountain area in western Colorado (Seiler 1998), was used and assumed to represent similar climatic conditions as the Naturita site. A gravel pit size of 78,400 ft² was estimated from the aerial photo taken of the site during April 15, 2001 (Figure 5–49). Because of

seasonal variations in the water table elevation, only part of the gravel pit will have standing water that can be evaporated, and this surface area will change as a function of changes in hydrologic conditions. Unfortunately, an aerial view of the extent of standing water on a daily or weekly resolution is not currently available. Assuming that, on average, 25 percent of the gravel pit area is subject to evaporative processes each year, approximately 650,000 gallons of water could be lost by surface evaporation of ground water exposed in the gravel pits. Currently it is unknown how the alluvial aquifer is responding to the evaporative water loss. For example, it is possible that increased inflow from the San Miguel River may be partly or fully compensating for the evaporative loss of the ground water from the gravel pits; however, this seems unlikely.

Based on the 2001 ground water flow model of the alluvial aquifer, annual ground water flux upgradient of the gravel pit is approximately 1.4 million gallons (G. Curtis, USGS, written communication, June 2001). The estimated annual evaporative loss (assuming 25 percent of the gravel pit area is subject to evaporation) is approximately 46 percent of the annual ground water flux moving through the alluvial aquifer immediately upgradient of the gravel pit. Future expansion of the gravel pit could potentially increase these estimated water losses, further affecting the natural flushing rates of uranium in the downgradient parts of the alluvial aquifer. Detailed pan evaporation measurements, monitoring of free-water areas, and ground water modeling of present and future gravel pit scenarios are needed before the impacts to uranium flushing rates can be fully assessed.

The observed isotopic enrichment between the average $\delta^{18}\text{O}$ value of recharge water and the $\delta^{18}\text{O}$ value observed in wells 0547 and NAT20 downgradient of the gravel pits can be used to estimate the amount of ground water loss. The following assumptions were used: (1) open system; (2) water vapor is instantaneously removed; and (3) a constant fractionation factor of 1.010 (newly formed vapor is always 10 permil (per thousand, i.e., percent \times 0.1) lighter than the residual water). The observed isotopic enrichment of $\delta^{18}\text{O}$ was equal to approximately +5 permil for well 0547 and +4 permil for well NAT20 (Figure 5-56). With this observed isotopic enrichment, an evaporative ground water loss of approximately 44 percent is calculated for well 0547, and a ground water loss of 31 percent is calculated for well NAT20 (Figure 5-56).

The isotopic values of water samples belonging to Groups 4, 5, and 6+7 show some evaporative enrichment of water from the San Miguel River but are not as isotopically enriched as those of the Group 2 water samples (Figure 5-55). This is consistent with the hydrology of the northern part of the site, especially with respect to water samples belonging to Group 4. As discussed in the pattern recognition modeling results, Group 4 wells are close to the San Miguel River, and the geochemical footprints indicate the presence of flushing zones. The isotopic signature of samples belonging to Group 4 is very similar to the isotopic signature of water from the San Miguel River with limited evaporation (Figure 5-55).

Temporal variations in $\delta^{18}\text{O}$ and δD at selected wells within each group were compared to better understand the different seasonal hydrologic processes occurring at the Naturita site. Large seasonal variations in the isotopic values are observed in water from the San Miguel River (Figure 5-57); however, all the samples plot close to the GMWL, indicative of limited amounts of evaporation. For a given geographic region, there is an elevation effect in the isotopic composition of precipitation (Ingraham 1998). In general, the result of the elevation effect is that precipitation at higher elevations has a lighter isotopic composition than precipitation at lower

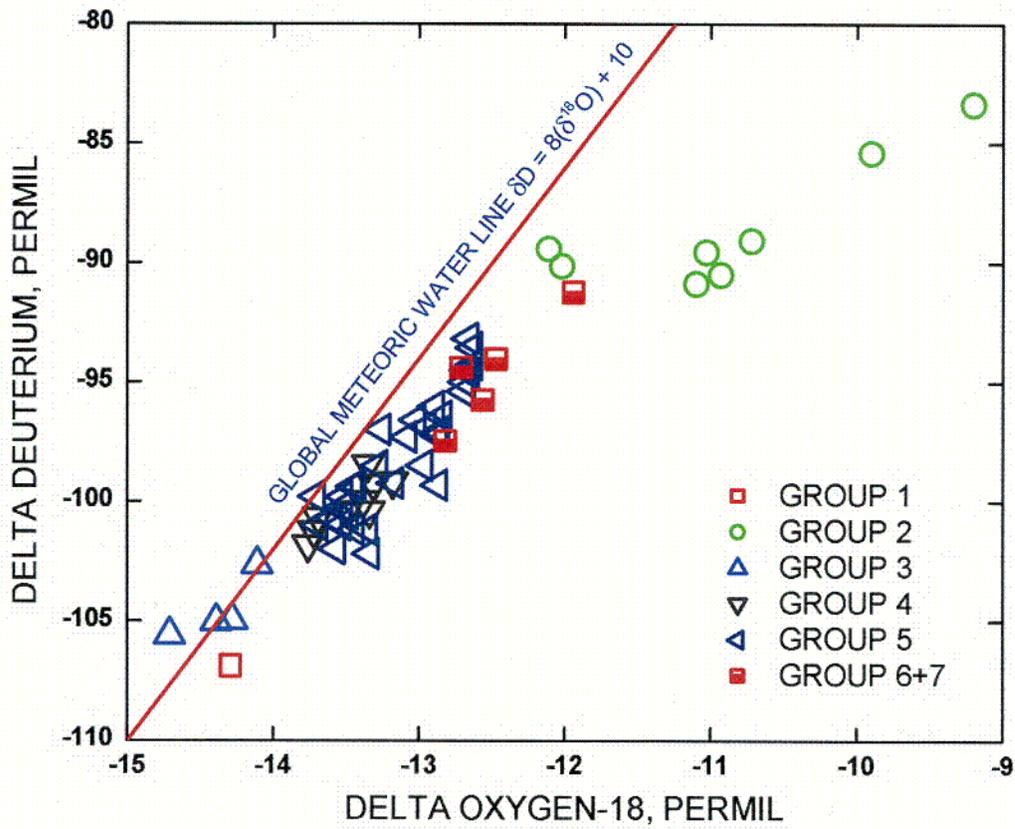


Figure 5-55. The $\delta^{18}O$ and δD Values In Ground and Surface Water Data Compared to Geochemical Groupings Identified by Pattern Recognition Modeling of Data Collected During June 2000, at the Naturita Site

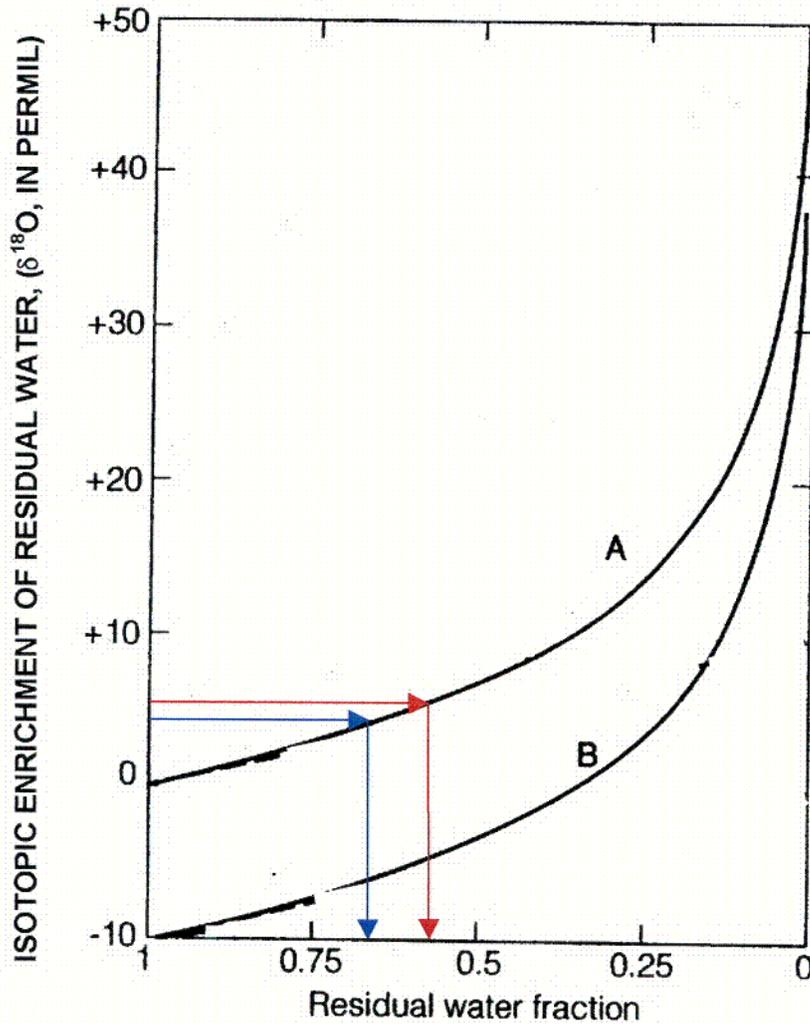


Figure 5-56. Isotopic Change Under Open-System Rayleigh Conditions for Evaporation with a Fractionation Factor = 1.01 for an Initial Liquid Composition of $\delta^{18}\text{O} = 0$. The $\delta^{18}\text{O}$ of the Remaining Water (Line A) and the $\delta^{18}\text{O}$ of the Instantaneous Water Vapor Being Removed (Line B). Modified From Kendall and Caldwell (1998). Red Arrows Indicate Observed Isotopic Enrichment In Water From Well 0547 and Residual Water Fraction Remaining. Blue Arrows Indicate Observed Isotopic Enrichment in Water from Well NAT20 and Residual Water Fraction

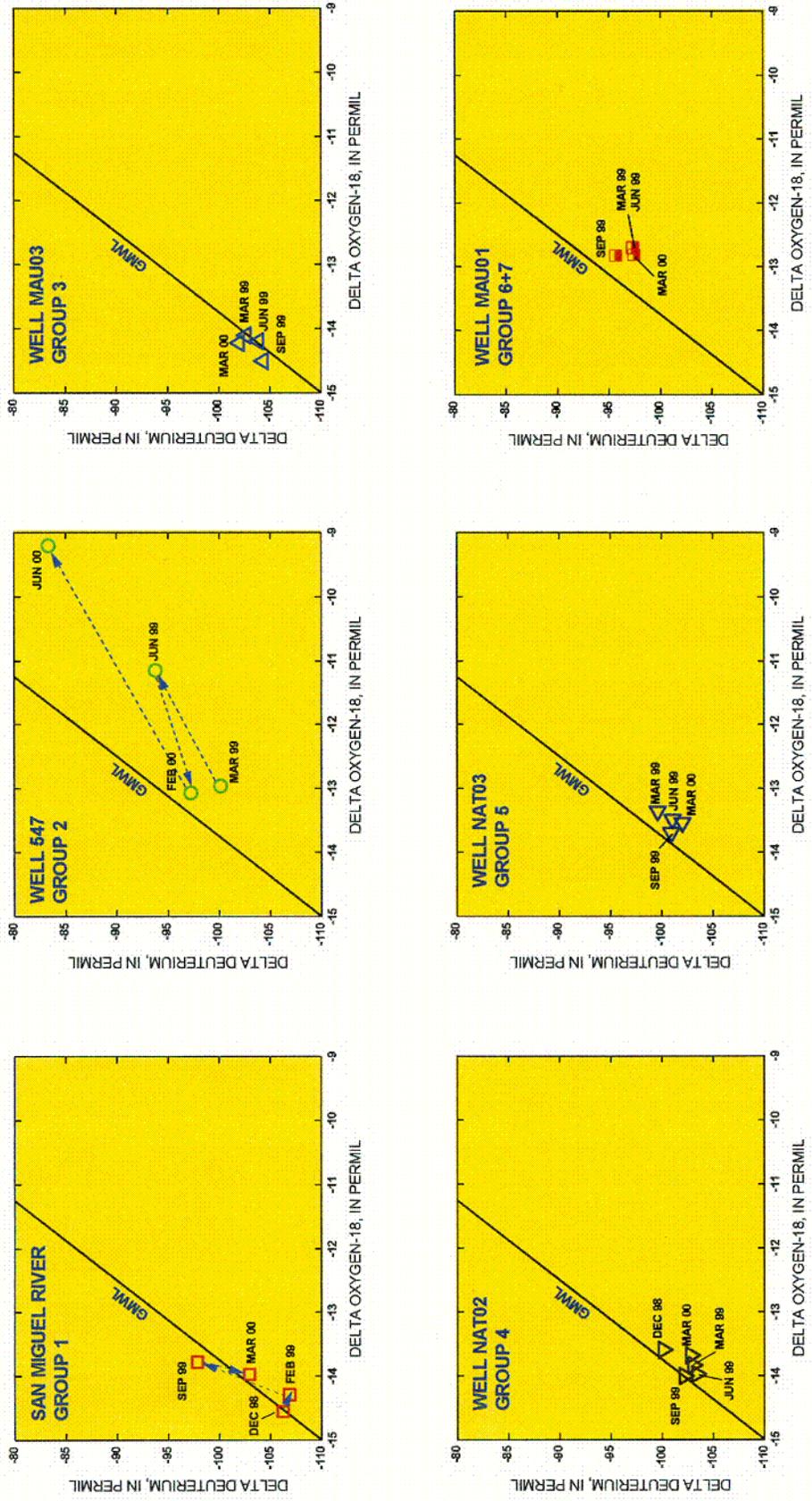


Figure 5-57. Variations in $\delta^{18}\text{O}$ and δD Values Over Time in Ground- and Surface-Water Data from Selected Sampling Sites Representative of Geochemical Groupings Identified by Pattern Recognition Modeling of the Data Collected During June 2000, at the Naturita Site [GMWL = global meteoric water line]

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elevations. The isotopically enriched values in water from the San Miguel River during September 1999 probably reflect isotopically enriched, lower-elevation precipitation events typical of the monsoonal storms that occur in southwestern Colorado from late July through September each year. Water from the San Miguel River collected at Telluride, Colorado (upstream from the Naturita site), during June 1999 had very light isotopic values ($\delta^{18}\text{O} = -16.44$ and $\delta\text{D} = -117.98$), reflective of snowmelt runoff from high-elevations areas of the watershed.

Large isotopic variations were also observed in well 0547 (Group 2) during the monitoring period from March 1999 through June 2000 (Figure 5-57). During times of potentially large evaporation rates in the gravel pits (June 1999 and June 2000), the isotopic signature was enriched and also deviated significantly from the GMWL, indicative of strong evaporative effects. In contrast, water samples collected during periods of low evaporations rates (March 1999 and February 2000) contained an isotopic signature that was much lighter and close to the GMWL (Figure 5-57). The temporal variations in the isotopic values in well 0547 indicate a strong hydrologic connection with ground water flowing through the gravel pit and also show the strong seasonal influence of evaporation.

The isotopic values for water from well MAU03 (Group 3) showed little variation over time and plotted close to the GMWL with an isotopic composition similar to that of water from the San Miguel River (Figure 5-57). As indicated during the pattern recognition modeling, water samples belonging to Group 3 contain element associations typical of river flushing zones. The elevated uranium concentrations in Group 3 samples (Figure 5-51) from wells MAU03, MAU04, and MAU06 on the Maupin property are inconsistent with the strong river influence indicated by the stable isotope data. This inconsistency may indicate a more localized uranium source to the ground water, perhaps from the river-deposited tailings in the supplemental standards area on the Maupin property. The young ground water age date (1994) determined in water collected from well MAU04 indicates that significant quantities of water from the San Miguel River may be entering the alluvial aquifer at the river bend on the Maupin property, possibly leaching uranium from the supplemental standards area as it flows in a northerly direction.

The seasonal isotopic variation in well NAT02 (Group 4) appears to indicate some river flushing during different river stages. The lightest isotopic composition was measured during June 1999 when the river stage is at the annual high. This could cause pressure-induced movement of ground water closer to the San Miguel River, presumably with a lighter isotopic signature, to areas of the aquifer farther removed from the river. In contrast, during low-flow conditions (December 1998) the lower river stage would cause a reverse trend, and the more isotopically enriched water in areas farther from the river would tend to have a flow component toward the river.

The seasonal isotopic variation in wells belonging to Groups 5 (well NAT03) and 6+7 (well MAU01) is small (Figure 5-57). As indicated during the pattern recognition modeling, water samples belonging to Groups 5 and 6+7 do not contain element associations typical of the river flushing zones, exemplified by Groups 3 and 4. The small seasonal variations in $\delta^{18}\text{O}$ and δD values support this conclusion.

5.4.5 Chloride Enrichment

The pattern recognition modeling and stable isotope results indicate that Group 2 wells are strongly influenced by evaporative processes. Variations in chloride concentration in wells belonging to Group 2 can be used to provide additional evidence to support the previous results. Ideally, chloride is not removed or supplied in significant quantities to ground water from interaction with rocks and is not precipitated until very high salinity is attained (Drever 1988). Under these assumptions, the chloride concentration in water is indicative of the amount of evaporation that has occurred since the water started out as rainfall. This is not always the case in arid and semiarid regions where salts containing chloride are periodically dissolved and precipitated during wet/dry cycles; however, chloride can still provide important information with respect to evaporative processes.

The changes in chloride concentrations in wells 0547 and NAT20 were compared to chloride concentrations in the San Miguel River (location SM1) from December 1998 through March 2001 (Figure 5–58). A strong seasonal variation in chloride concentration is observed in the San Miguel River. The chloride concentrations are lowest during snowmelt in May through June and highest during lower river stages in November through February. The elevated chloride concentrations during this time period are probably the result of shallow ground water inflow (slightly enriched in chloride from evaporation or water-rock interaction) and localized surface water contributions to the San Miguel River from intermittent channels that could contain chloride-bearing salt crusts.

Three peaks in chloride concentrations in well 0547 were observed during the monitoring period and occurred in the late winter/early spring (Figure 5–59) for three consecutive years (1999, 2000, and 2001). The concentrations were lowest in the fall. In general, the oscillations in chloride concentration were out of phase with respect to the $\delta^{18}\text{O}$ values (Figure 5–59). For example, the two most enriched $\delta^{18}\text{O}$ values, which occurred during June 1999 and June 2000, were out of phase with the lowest chloride concentration. The lack of correlation between the chloride and $\delta^{18}\text{O}$ data could indicate some nonconservative behavior with respect to chloride, for example higher baseline chloride concentrations from the deeper completion depth in well 0547 (20.3 ft below land surface). The chloride and $\delta^{18}\text{O}$ data become positively correlated (in phase) beginning in June 2000 (Figure 5–59).

Although the period of record is shorter, the $\delta^{18}\text{O}$ and chloride data from well NAT20 were positively correlated and in phase from March 2000 through November 2000 (Figure 5–59). The chloride concentration was highest in June 2000 and had a positive correlation with the highest evaporation enrichment shown by the stable isotope data during the same time period (Figure 5–59). Chloride concentrations were lowest during March 1999, November 2000, and February 2001 and support the lighter isotopic values that were observed during lower evaporation periods.

Changes in chloride concentration in well NAT20 can be used to estimate water lost by evaporation from the gravel pits. The difference in chloride concentration between the March and June 2000 sampling periods was used to estimate the approximate mass of ground water lost from evaporation. Between March and June 2000, the chloride concentration increased from 9.5 to 11 mg/L in well NAT20, equating to a 14 percent loss of ground water from evaporation.

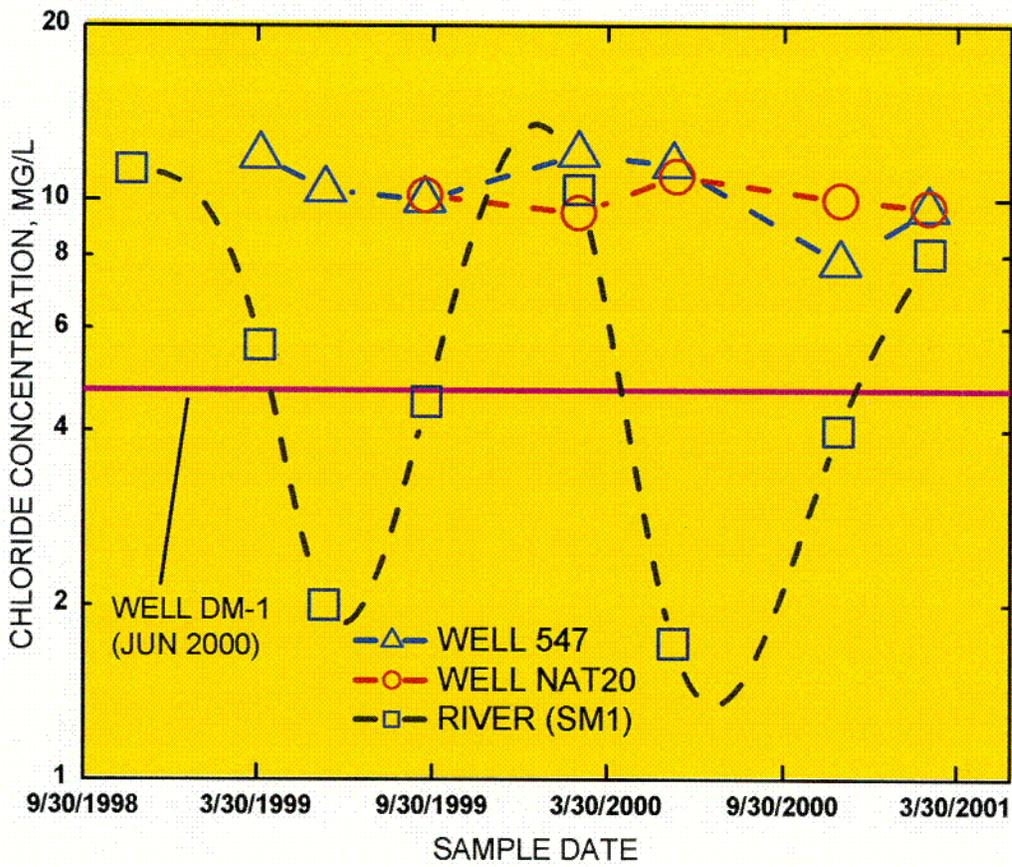


Figure 5-58. Variations in Chloride Concentration with Time in Wells 0547, NAT20, and DM1 Compared to Chloride Concentrations in the San Miguel River (location SM1), Naturita Site, Colorado. A Spline Function was Used to Display the Chloride Data from the San Miguel River

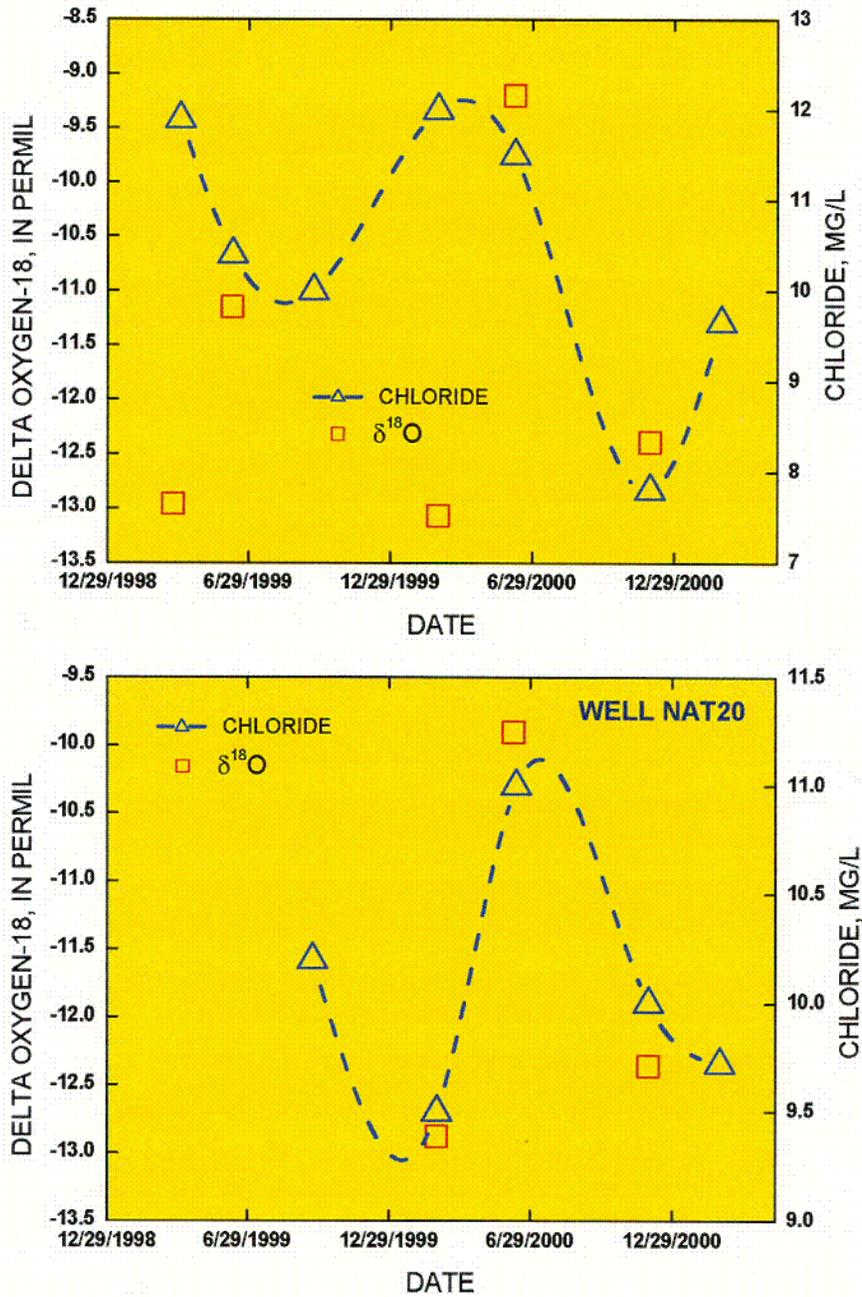


Figure 5-59. Variation in Chloride Concentration and $\delta^{18}O$ Values with Time in Water Samples from Wells 0547 and NAT20, Naturita Site, Colorado. A Spline Function was Used to Display the Chloride Data. The δD Data are not yet Available from the November 2000 Sampling Period

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The evaporative water loss calculated from the differences in chloride concentration is different from the evaporative loss calculated from the observed isotopic enrichment. For well NAT20 the evaporative water loss calculated from the $\delta^{18}\text{O}$ data is 31 percent, compared to a water loss of 14 percent calculated with the chloride data. Both methods indicate measurable loss of ground water from the gravel pits immediately upgradient. The calculated water loss from the isotopic data is probably more accurate because of potential contributions of small amounts of chloride to the ground water and surface water during wet/dry cycles in this semiarid environment.

5.4.6 Implications of Pattern Recognition Modeling, Stable Isotope, and Chloride Results to Natural Attenuation

DOE can use the insight gained from the pattern recognition modeling, stable isotope, and chloride data to evaluate specific ground water remediation and monitoring options at the Naturita site. The grouping of the data by HCA and PCA have identified specific geographic areas within the site that have similar geochemical and hydrologic processes. These areas should be considered individually when assessing particular remediation scenarios. Listed below are potential areas of concern that should be considered during the design of the final ground water remediation and monitoring plan.

All the data analysis (pattern recognition modeling, stable isotopes, and chloride) indicates that potentially significant amounts of ground water are being lost from gravel pits through free-water evaporation in the upgradient parts of the alluvial aquifer. As the gravel pits continue to expand in the future, the potential exists to increase the loss of ground water through evaporation. Loss of ground water in the upgradient parts of the alluvial aquifer could significantly decrease the rate that uranium flushes naturally from the aquifer. Additional, site-specific monitoring data to better quantify the evaporative loss in ground water coupled with ground water model simulations that include the gravel pit are needed to determine long-term effects on natural flushing processes.

Seasonal changes in evaporative loss of ground water from the site are indicated from the stable isotope and chloride data. One possible mitigation option would be to replace the evaporative losses of ground water. For example, during the peak evaporation times (determined from site-specific monitoring), water from the San Miguel River could be pumped into the open pits to compensate for evaporative water loss. This alternative could be much more cost effective than acquisition and restoration of the gravel pit.

The integration of stable isotope data ($\delta^{18}\text{O}$ and δD) during long-term site monitoring will be useful in assessing the progress of natural flushing at the site. For example, monitoring the location and movement of the evaporation-enriched ground water in the alluvial aquifer could be used to assess the success of any gravel pit remediation scenarios that may be instituted. Because of the nonconservative behavior of chloride observed in upgradient wells at the site, it is likely that stable isotopes will be the most reliable measurement of water evaporation effects in the alluvial aquifer.

Results of the pattern recognition modeling in combination with the ground water age dating indicate that the supplemental standard area on the Maupin property may be acting as a localized uranium source to the alluvial ground water.

Future pattern recognition modeling in combination with the determination of stable isotope values and age dating of the ground water should be considered to monitor the effects of the final land use on long-term natural flushing. For example, if a golf course is placed on the property, the surface irrigation could increase the natural flushing of the alluvial aquifer. This enhancement of natural flushing could be efficiently monitored using pattern recognition modeling in combination with the determination of selected chemical and isotopic constituents.