5.0 Conceptual Site Model

This section describes the main physical and chemical characteristics and features of the Durango site—the site geology, hydrogeology, and geochemistry—including a discussion of selenium at the raffinate ponds area, and provides results of the ground water flow and transport modeling.

5.1 Geologic Setting

The mill tailings and raffinate ponds areas of the Durango site lie on the north rim of the San Juan Basin, a large basin that is situated mainly south of the site in northwestern New Mexico. Bedrock in the site area is of Late Cretaceous age and dips south to south-southeast at approximately 7 to 15 degrees toward the center of the basin along a basin-rim structure known as the Hogback monocline. Two northeast-striking normal faults displace the bedrock in the site areas. Both faults are high angle and have down-to-the-southeast displacements. The northern of the two faults, the Smelter Mountain Fault, occurs between the two site areas and does not affect the hydrogeology of either area. The southern fault, the Bodo Fault, passes through the center of the raffinate ponds area. This fault affects the hydrogeology and presents additional complications by hosting a diorite porphyry dike along most of its length.

The south-flowing Animas River is along the east side of both site areas. Quaternary alluvium occurs in a few places in the site areas along the west side of the river and along Lightner Creek. Quaternary terrace deposits laid down by the ancestral river occur in several places in the raffinate ponds area, and terrace deposits along Lightner Creek are present in the northwest part of the mill tailings area. Quaternary colluvial deposits cover bedrock exposures in both site areas in many places along the east- and northeast-facing slopes of Smelter Mountain. Details of the stratigraphy and structure of the two site areas are described in Section 4.2.

5.2 Hydrogeology

Because the Durango site consists of two areas, the tailings area and the raffinate ponds area, and because both sites are hydraulically isolated from one another, separate site conceptual models were developed for each area.

5.2.1 Mill Tailings Area

Ground water at the mill tailings area is within an unconfined alluvial aquifer, which is recharged by infiltration of precipitation and runoff, and by contact with the Animas River and Lightner Creek. The lateral boundaries of the aquifer are constant head along the Animas River and Lightner Creek, no-flux where the aquifer contacts the Mancos Shale, and head-dependent flux where ground water of the Lightner Creek alluvium enters the site. Ground water exits the alluvial aquifer via flow into the Animas River. The base of the alluvial aquifer is in contact with Mancos Shale bedrock. Lateral inflow to the alluvial aquifer from the Mancos Shale and vertical leakage out of the alluvial aquifer are both assumed to be negligible. The alluvial aquifer is composed of sand, silt, and gravel derived from the Animas River and Lightner Creek. Saturated colluvial debris shed from Smelter Mountain occurs along the edges of the alluvial aquifer at some locations. Ground water occurs in the alluvial and colluvial deposits. The porosity of these deposits is assumed to be about 30 percent (Freeze and Cherry 1979).

5.2.1.1 Hydraulic Properties

Hydraulic conductivities of the alluvial deposits near the mill tailings area were measured by Bendix in 1983 (DOE 1983), BOR in 1990, and MACTEC-ERS in 2001. Table 5–1 presents a summary of the measurements.

Table 5–1. Summary of Hydraulic Conductivity for Alluvial Deposits at the Mill Tailings Area

	Qal [a] Animas River	**Qal [a] Lightner Creek**
No. of cases	11	2
Minimum	1	66
Maximum	28.6	260
Range	27.6	194
Sum	190.5	326
Median	20.6	163
Mean	17.3	163
Std. Error	2.9	97
Standard Dev	9.6	137
Variance	92.4	18818
Coefficient of Variation	0.55	0.84

a Hydraulic conductivity is estimated in units of ft/day

Table 5–1 contains only two measured values for the Lightner Creek alluvium. The 260 ft/day result was obtained by Bendix (DOE 1983) using pneumatic pressure transducers that are insensitive to rapidly recovering water levels. The result of 66 ft/day obtained by MACTEC-ERS in 2001 is believed to be less biased and more precise because the equipment used — modern electronic pressure transducers and data loggers — are capable of capturing the rapidly changing water levels during a slug test. Therefore, the 66 ft/day value is used as the Lightner Creek alluvium hydraulic conductivity value.

For the Animas River alluvium, the median hydraulic conductivity value of 20.6 ft/day, rounded to 21 ft/day, is used to compute the water budget components.

5.2.1.2 Water Budget

The water budget for the mill tailings area is estimated from the hydraulic properties of the alluvial deposits, interpretations of alluvial thickness from borehole geologic logs, and projections of subcropping bedrock. Figure 5–1 presents a hydrogeologic map showing the water budget components for the mill tailings area. Components of the water budget are described in the following sections and summarized in Table 5–2.

Table 5–2. Water Budget for the Mill Tailings Area

Flow Component	**Inflow (ft^3/day)**	**Outflow (ft^3/day)**
Lightner Creek	990	840
Animas River	190	640
Areal Recharge	300	0
Total	1,480	1,480

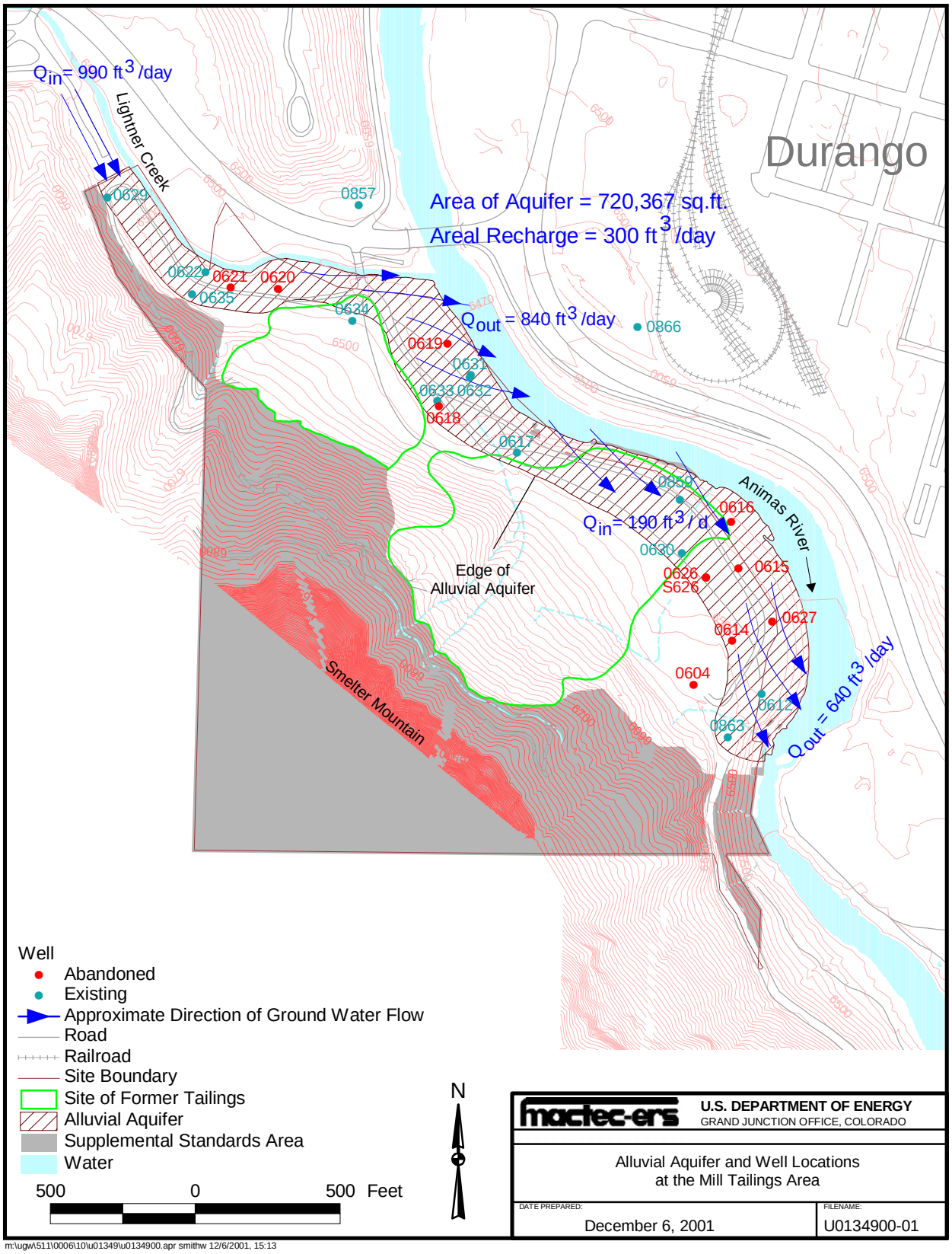

Figure 5–1. Alluvial Aquifer and Well Locations at the Mill Tailings Area

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5.2.1.3 Areal Recharge

No explicit data exist to quantify the amount of areal recharge at the mill tailings area. In a past modeling study of the raffinate ponds area, the recharge from precipitation was determined through calibration to be 0.4 inch per year, or about 2 percent of the average annual precipitation (BOR 1990). The average annual precipitation for Durango from January 1, 1900, through March 31, 1991, is 19.1 inches (Colorado Climate Center 2001). In the absence of direct data, a value of about 10 percent of the annual precipitation would seem more reasonable for the water budget. Thus, 1.91 inches per year is distributed uniformly across the area (720,367 square feet [ft^2]) of the aquifer. The annual recharge rate for the aquifer is 1.91 inches/year × (1 ft/12 inches) × (1 year/365 days) × (720,367 ft^2) = 300 cubic feet per day (ft^3/day) (rounded).

5.2.1.4 Ground Water Inflow from Lightner Creek Drainage

This component of flow crosses the western site boundary along Lightner Creek and contains the ground water that originates as flow in Lightner Creek alluvium upgradient of the mill tailings area. The flow component cannot be determined with a high degree of certainty because the cross-sectional area and geometry of the saturated zone can only be extrapolated from limited data. The cross-sectional area of the alluvial aquifer was estimated by assuming it attains a maximum thickness of 8 ft at the axis of Lightner Creek; and thins to the south where it pinches out against the bedrock of Smelter Mountain. The contact is assumed to be a straight line. Consequently, the cross-sectional shape circumscribed by the aquifer is a triangle whose length and width is 120 ft by 8 ft, or approximately 500 ft^2. Inflow (Q) to the tailings area through the Lightner Creek tributary is estimated as

$$Q = K\ (dh/dl)\ A$$

where

K = median hydraulic conductivity of the Lightner Creek alluvium (ft/day),
dh/dl = hydraulic gradient (dimensionless), and
A = cross-sectional area of the aquifer perpendicular to the flow direction.

$Q = 66\ ft/day\ (0.03)\ 500\ ft^2 = 990\ ft^3/day$

5.2.1.5 Outflow from Lightner Creek Alluvium

The Lightner Creek alluvial aquifer maintains a nearly constant width until it widens approximately 200 ft upstream of its confluence with the Animas River. The alluvial aquifer begins to widen just downstream of the bridge that provides access to the site. This region is where the alluvial characteristics of the aquifer change from those of predominantly Lightner Creek origin to those of Animas River origin, and the hydraulic conductivity in this region drops from 66 to 21 ft/day (Table 5-1). The reduction of hydraulic conductivity across this reach forces stream lines to diverge. Much of the flow from the Lightner Creek alluvium empties into the Animas River along a 750-ft reach extending from the Lightner Creek confluence to just east of well 0617. The outflow (Q) from this reach is estimated as

$$Q = K\ (dh/dl)\ A$$

where

K = 21 ft/day (Table 5-1, median value for Animas River alluvium),
dh/dl = 0.02 (dimensionless), and
A = 2,000 ft^2 (approximate cross-sectional area of the aquifer perpendicular to the flow direction).

Q = 21 ft/day (0.02) 2,000 ft^2 = 840 ft^3/day

5.2.1.6 Recharge from the Animas River

Downstream of the Lightner Creek discharge reach, the aquifer widens to more than twice its previous width. The reach over which the widening occurs is approximately 700 ft long. The aquifer gradually gains Animas River water along this stretch. The maximum width of the aquifer occurs near abandoned well 0616. The gain in the alluvial aquifer along this reach is estimated as

$$Q = K\ (dh/dl)\ A$$

where

K = 21 ft/day (Table 5-1, median value for Animas River alluvium),
dh/dl = 0.015 (dimensionless), and
A = 600 ft^2 (approximate cross-sectional area of the aquifer perpendicular to the flow direction).

Q = 21 ft/day (0.015) 600 ft^2 = 190 ft^3/day

5.2.1.7 Aquifer Discharge

The alluvial aquifer pinches out against a bedrock cliff of Mancos Shale near wells 0612 and 0863. All ground water in the alluvial aquifer empties into the Animas River at this point. Although discharge from this section could be estimated explicitly through flow-net construction, it is estimated here by the difference between the total inflows (1,480 ft^3/day from Table 5-2) and the Lightner Creek outflow component (840 ft^3/day). The estimated flow from the aquifer is approximately 640 ft^3/day in the discharge area.

5.2.1.8 Boundary Conditions

Lateral boundaries for the mill tailings area are as follows: (1) specified head along Lightner Creek and the Animas River, and (2) no-flux along the contact between the alluvium and the Mancos Shale bedrock.

5.2.1.9 Animas River/Aquifer Interaction

Wells 0863, 0859, and 0633 (completed in the colluvium, alluvium, and Mancos Shale, respectively) were equipped with dataloggers to monitor groundwater fluctuations between April and November, 2001. This data set is compared to the fluctuations of the Animas River stage in Figure 5–2. For comparison, the actual river elevation shown in Figure 5–2 is not as important as the fluctuation pattern shown, since the elevation is representative at only one point (stilling well 0876) along the Animas River.

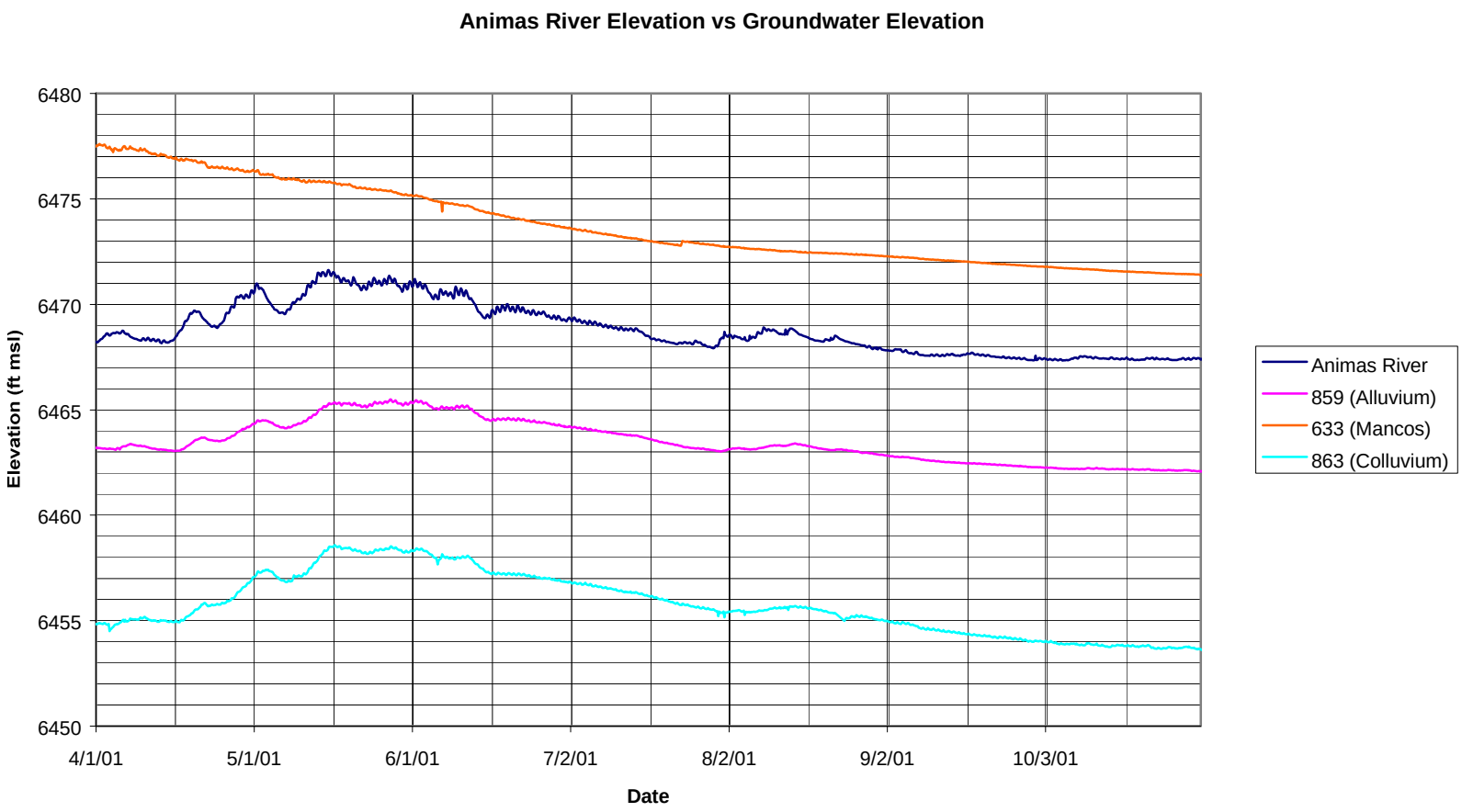

Figure 5–2. Animas River Elevation versus Ground Water Elevation

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Ground water in the colluvium and alluvium exhibit the same fluctuation pattern as displayed by the Animas River stage, confirming that water in these two units are hydraulically connected to the river. Ground water in the Mancos Shale onsite does not exhibit the same pattern. As shown in Figure 5–2, the Mancos Shale ground water surface does not show a definite peak in mid-May like the colluvium and alluvium units, suggesting the Mancos shale ground water flow system is impacted by a source other than the Animas River.

5.2.2 Raffinate Ponds Area

Ground water at the raffinate ponds site is assumed to be unconfined. It is recharged by infiltration of precipitation and runoff and by horizontal inflow from Smelter Mountain. Water enters the flow system at the intersection of the Bodo Fault with South Creek. This influx is intermittent because South Creek is an ephemeral stream. Lateral boundaries to the raffinate ponds area ground water flow system consist of influx from Smelter Mountain and constant (or nearly constant) head along the Animas River. The southern margin of the raffinate ponds area has no physical boundary, but ground water is assumed to flow parallel to it; consequently, the southern boundary to the flow system is an assumed no-flux boundary.

The sandstone units of the Menefee Formation and the massive sandstone unit of the Point Lookout Sandstone are assumed to have a porosity of 33 percent (Morris and Johnson 1967). The basal member of the Point Lookout Sandstone is assumed to have a maximum porosity of 5 percent (Freeze and Cherry 1979; Morris and Johnson 1967).

5.2.2.1 Hydraulic Conductivity

Hydraulic conductivity of the bedrock units was measured by Bendix (DOE 1983), BOR (1990), and MACTEC-ERS in 2001. Table 5–3 presents a statistical summary of the measurements. The hydraulic conductivity data for each hydrostratigraphic unit indicate that the Point Lookout Sandstone is the least conductive material. In addition, the lower member (predominantly shale and siltstone) of the Point Lookout Sandstone is apparently an aquitard. The lower member is present in the subsurface beneath the raffinate ponds area.

The Menefee Formation consists mostly of low-conductivity sandstone, but is relatively permeable where fractures or lenticular coal beds are present. The hydraulic conductivity of the fractured zones and the coal beds is comparable to the conductivity of the Bodo Fault. In Table 5–3, the maximum conductivity listed for the Menefee Formation of 5.3 ft/day was measured at well 0882 (Appendix F, MACTEC–ERS Calculation U0133300), which was completed in a coal bed. This measurement singularly skews the mean hydraulic conductivity considerably above the median value. The median value is more representative of the sandstone beds in the Menefee Formation.

Table 5–3. Basic Statistics of Hydraulic Conductivity by Geologic Formation at the Durango Site

	Point Lookout Sandstone	Menefee Formation	Bodo Fault
No. of cases	16	12	10
Minimum	0.006	0.003	0.120
Maximum	0.304	5.3	6.98
Range	0.298	5.297	6.86
Sum	1.089	12.73	23.394
Median	0.050	0.175	0.623
Mean	0.068	1.061	2.339
Std. Error	0.018	0.541	0.866
Standard Dev.	0.074	1.874	2.738
Variance	0.005	3.513	7.498
Coefficient of Variation	1.083	1.767	1.170

Hydraulic conductivity is in units of feet per day

5.2.2.2 Water Budget

The water budget for the raffinate ponds area is estimated from the hydraulic properties of the bedrock units and interpretations of geologic logs. Figure 5–3 presents a hydrogeologic map showing the water budget components for the raffinate ponds area. Components of the water budget are described in the following sections and summarized in Table 5–4.

Table 5–4. Water Budget for the Raffinate Ponds Area

Flow Component	Inflow (ft^3/day)	Outflow (ft^3/day)
Areal recharge	890	
Smelter Mountain	420	
South Creek	600	
Point Lookout Sandstone		260
Menefee Formation		1,780
Total[a]	1,910	2,070

[a] ± 10 percent

5.2.2.3 Lateral Inflow from Smelter Mountain

Lateral inflow from the Smelter Mountain area is inferred because the Point Lookout Sandstone is contiguous and underlies both the raffinate pond terrace and Smelter Mountain. Infiltration of snowmelt and runoff, together with vertical leakage, probably sustains a water table in the sandstone units beneath Smelter Mountain. Ground water is assumed to occur in the massive member of the Point Lookout Sandstone, and some component of flow is believed to migrate eastward to the raffinate pond terrace area. Discharge from Smelter Mountain is approximated as follows:

Hydraulic gradient (dh/dl) ≈ 0.01,
Hydraulic conductivity (K) ≈ 0.050 ft/day,
Width perpendicular to flow is 2,800 ft (the length), and
Saturated thickness of the bedrock is assumed to be 300 ft.

$$Q = K\,(dh/dl)\,A = (0.050\ ft/day) \times (0.01) \times (2{,}800\ ft) \times (300\ ft) = 420\ ft^3/day$$

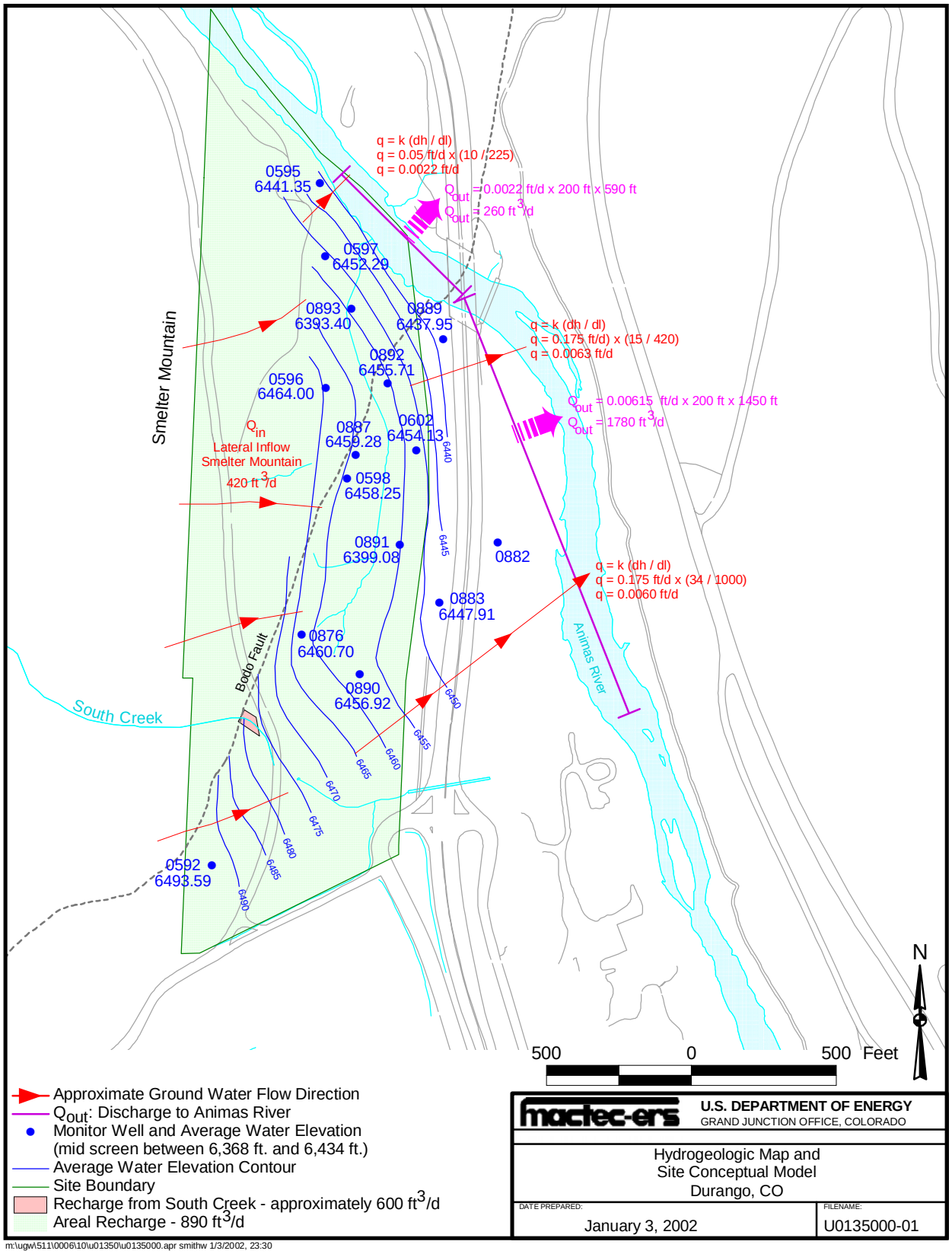

Figure 5–3. Hydrogeologic Map and Site Conceptual Model of the Raffinate Ponds Area

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5.2.2.4 Areal Recharge

Data were not collected to quantify the amount of areal recharge. In a past modeling study of the raffinate ponds area, the recharge from precipitation was estimated by model calibration to be 0.4 inch per year, or about 2 percent of the average annual precipitation (BOR 1990). The average annual precipitation at Durango from January 1, 1900, through March 31, 1991, is 19.1 inches (Colorado Climate Center 2001). In the absence of direct data, a value of about 10 percent of the annual precipitation would seem reasonable as a starting point for the water budget. The surface of the raffinate ponds area is approximately 2,040,000 ft^2 (46.8 acres). Based on 10 percent of average annual precipitation, the areal recharge would be 1.91 inches/year (1 ft/12 inches) (1 yr/365 days) (2,040,000 ft^2) = 890 ft^3/day.

Recharge from South Creek

South Creek is an ephemeral stream that enters the raffinate ponds area near the southwest corner of the property where it crosses the Bodo Fault. Table 5–3 shows the median hydraulic conductivity of the bedrock to be approximately 4 times higher along the fault. In addition, the maximum hydraulic conductivity in the fault zone is about 7 ft/day. The locally elevated hydraulic conductivity along the fault is believed to provide a conduit for recharge when South Creek contains water. The average recharge rate is estimated using Darcy's Law:

$$Q = K\ (dh/dz)\ A$$

where

Q is the total recharge in ft^3/day,
K is the median hydraulic conductivity (ft/day),
dh/dz is the vertical hydraulic gradient, assumed unity (dimensionless), and
A is the cross-sectional area where the recharge enters the aquifer (1,000 ft^2).

$Q = 0.6\ ft/day \times (1) \times (1{,}000\ ft^2) = 600\ ft^3/day$

Discharge to the Animas River

The thickness of the bedrock flow system is assumed to be approximately 200 ft. Wells screened in the middle elevations of the bedrock were used to estimate the ground water discharge to the Animas River. As shown on Figure 5–3, the hydraulic gradient through the Point Lookout Sandstone sections is approximately 0.044 (10/225). The width perpendicular to flow through the Point Lookout Sandstone is approximately 590 ft. Hydraulic conductivity of the Point Lookout Sandstone is 0.05 ft/day (Appendix F, MACTEC–ERS Calculation U0133300). Ground water discharge through the Point Lookout Sandstone from the site is estimated as

$Q = K\ (dh/dl)\ A = 0.05\ ft/day\ (0.044)\ (590\ ft)\ (200\ ft) = 260\ ft^3/day.$

The specific discharge is estimated at two locations in Figure 5–3 based on a hydraulic gradient through the Menefee Formation of between 0.034 and 0.036. The total discharge through the Menefee Formation is then estimated based on a width perpendicular-to-flow of approximately 1,450 ft. Median hydraulic conductivity of the Menefee Formation is 0.175 ft/day (Appendix F,

MACTEC–ERS Calculation U0133300). Ground water discharge through the Menefee Formation from the site is estimated as

$Q = K\ (dh/dl)\ A = 0.175$ ft/day (0.035) (1,450 ft) (200 ft) = 1,780 ft^3 /day.

Ground water exiting the site flows toward the Animas River. The course of the ground water flow eastward appears to approximately follow the strike direction of the bedrock.

5.2.2.5 Boundary Conditions

Lateral boundary conditions for the raffinate ponds area are assumed to be (1) specified head along the Animas River, (2) limited flux to account for ground water inflow from Smelter Mountain, and (3) no-flux along the southern boundary (assuming that the southern boundary of the model is parallel to a stream line).

5.2.2.6 Animas River/Aquifer Interaction

Figure 5–4 shows the comparison of the ground water fluctuations of the various aquifers at the raffinate ponds area to the Animas River. Dataloggers installed in wells 0889, 0882, and 0887 provided ground water surface elevations from wells completed in the Point Lookout Sandstone, Menefee Formation, and the Bodo Fault, respectively. The data presented for the Animas River were collected from stilling well 0906.

The data presented in Figure 5–4 suggests ground water flow in the Point Lookout Sandstone and Menefee Formation is hydraulically connected to the Animas River. The ground water fluctuation pattern provided by the well completed in the Bodo Fault zone does not match the pattern provided by the Animas River, suggesting the ground water flow system associated with the fault zone is impacted by a source other than the Animas River.

5.3 Geochemistry

DOE collected ground water data from the former processing site and vicinity from September 1982 through August 2001. The data from 1999 through August 2001 were used to assess surface water and ground water quality. The nature and extent of site-related constituents occurring above natural background concentrations are evaluated, and the fate and transport of the site-related constituents in the ground water are summarized in the following sections.

5.3.1 Natural Background

The water quality prior to milling operations is inferred by characterizing the water quality in areas upgradient of the site that are unaffected by process contamination. Surface waters, soils, and ground water from the alluvium, colluvium, Menefee Formation, Mancos Shale, and Point Lookout Sandstone were evaluated. Data used in this assessment are derived from background surface and ground water samples from both the mill tailings area and the raffinate ponds area. Mean analyte concentration data are reported in Table 5–5. The total number of samples analyzed and the number of samples that produced values greater than the detection limit are listed. The low, mean, and high concentrations of analytes with concentrations greater than the detection limit are also reported. The mean concentrations are derived only from the samples that have concentrations greater than the detection limit. The maximum concentration of an analyte is listed for those analytes that were not detected.

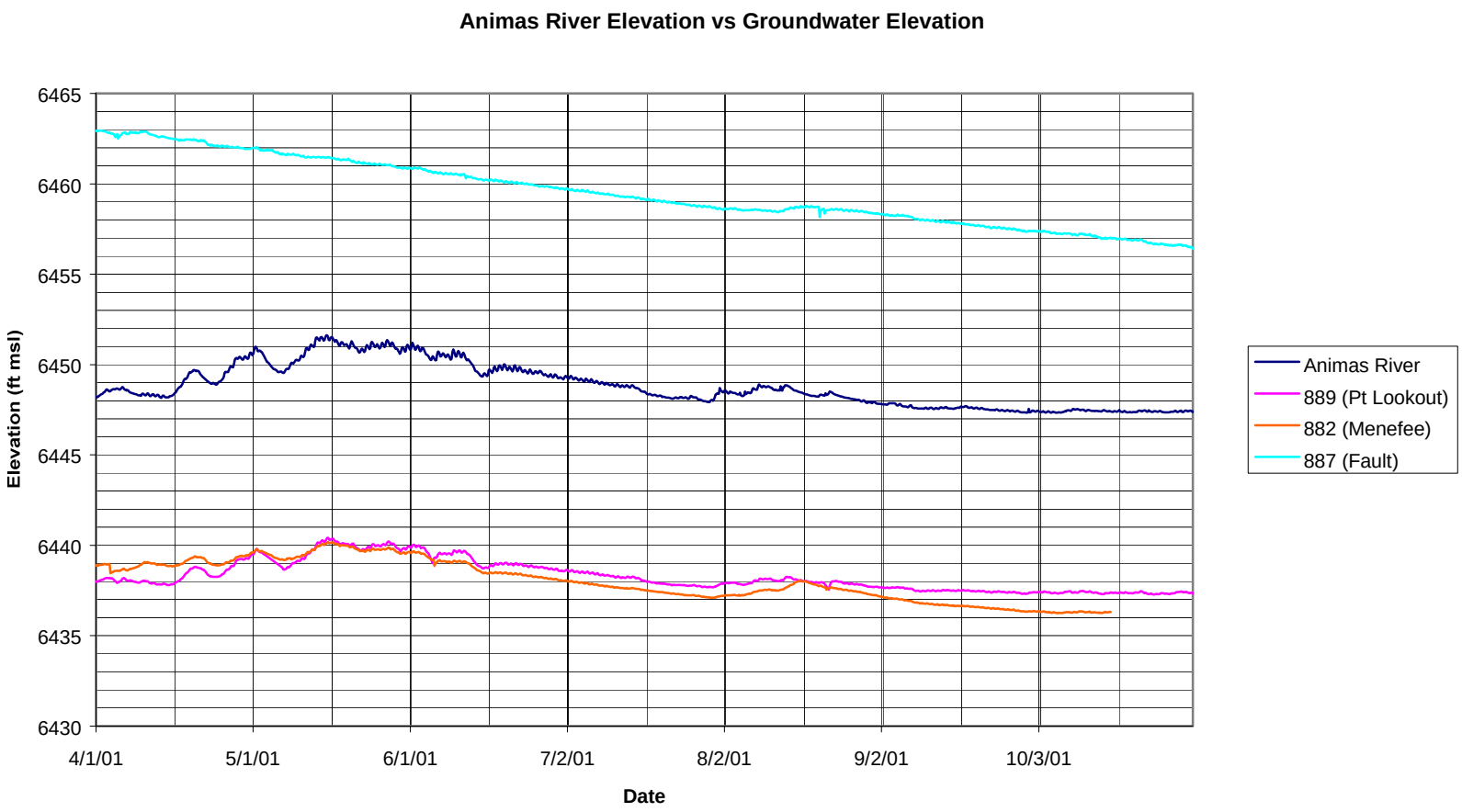

Figure 5–4. Animas River Elevation versus Ground Water Elevation

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Table 5–5. Background Mean Water Composition for Surface and Ground Waters from the Mill Tailings Area and the Raffinate Ponds Area
Samples were collected from June 1999 through August 2001. Samples were filtered unless otherwise noted.

Analyte	Unit	SURFACE WATER [a]			DURANGO MILL TAILINGS AREA [b]			DURANGO RAFFINATE PONDS AREA								
								Alluvial Aquifer [c]			Menefee Aquifer [d]			Point Lookout Aquifer [e]		
		FOD [f]	Mean	Range	FOD [f]	Mean	Range	FOD [f]	Mean	Range	FOD [f]	Mean	Range	FOD [f]	Mean	Range
Major Ions																
Ammonium	mg/L	0/27	U	*0.046*	11/18	1.20	0.135 - 2.28	3/4	0.36	0.116 - 0.767	12/13	0.935	0.036 - 1.41	6/11	1.01	0.468 - 1.39
Calcium	mg/L	31/31	57.5	21.0 - 89.8	20/20	267	126 - 583	4/4	141	78.2 - 170	15/15	148	95 - 242	11/11	158	7.34 - 371
Chloride	mg/L	31/31	8.50	1.44 - 20.9	20/20	64.2	9.90 - 265	4/4	59.0	22.1 - 82.4	15/15	50.8	42.8 - 83.6	11/11	42.7	15.9 - 73
Magnesium	mg/L	31/31	14.7	2.68 - 30.3	20/20	151	40.7 - 254	4/4	104	51.1 - 134	15/15	161	130 - 216	11/11	5.16	2.68 - 7.57
Nitrate	mg/L	12/31	1.36	0.503 - 3.15	9/20	8.32	0.257 - 11.2	4/4	9.36	0.926 - 18.9	5/15	2.27	0.508 - 4.99	11/11	62.0	2.32 - 140
Potassium	mg/L	31/31	1.83	0.677 - 3.40	20/20	4.36	2.38 - 8.17	4/4	5.43	5.24 - 5.65	15/15	6.56	5.65 - 8.85	5/11	8.17	7.87 - 8.41
Sodium	mg/L	31/31	12.6	2.53 - 20.6	20/20	246	35.3 - 488	4/4	208	99.1 - 367	15/15	242	186 - 270	11/11	481	299 - 722
Sulfate	mg/L	31/31	90.3	23.8 - 160	20/20	1255	114 - 2190	4/4	553	154 - 744	15/15	781	441 - 1330	10/11	826	4.13 - 1750
Metals																
Antimony	mg/L	0/31	U [g]	*0.0029* [h]	0/20	U [g]	*0.0012* [h]	0/4	U [g]	*0.0008* [h]	0/15	U [g]	*0.0012* [h]	0/11	U [g]	*0.0014* [h]
Arsenic	mg/L	0/31	U [g]	*0.0010*	0/20	U [g]	*0.0013*	0/4	U [g]	*0.0005*	0/15	U [g]	*0.001*	0/11	U	*0.0034*
Cadmium	mg/L	0/31	U [g]	*0.0009*	0/20	U [g]	*0.0007*	0/4	U [g]	*0.00069*	0/15	U [g]	*0.00071*	0/11	U	*0.0011*
Chromium	mg/L	1/31	0.011	0.011 - 0.011	0/20	U [g]	*0.0059*	0/4	U [g]	*0.0059*	0/15	U [g]	*0.0059*	0/11	U	*0.0063*
Copper	mg/L	0/27	U [g]	*0.0063*	0/18	U [g]	*0.0090*	0/4	U [g]	*0.0034*	0/13	U [g]	*0.0069*	0/11	U	*0.004*
Iron	mg/L	12/27	0.285	0.033 - 1.03	15/18	3.38	0.120 - 14.7	4/4	1.13	0.161 - 2.95	2/13	0.131	0.095 - 0.166	7/11	0.0346	0.035 - 1.71
Lead	mg/L	0/31	U [g]	*0.0048*	0/20	U [g]	*0.0023*	0/4	U [g]	*0.00028*	0/15	U [g]	*0.00051*	0/11	U	*0.0017*
Manganese	mg/L	21/31	0.068	0.010 - 0.205	20/20	0.601	0.073 - 1.05	4/4	0.274	0.09 - 0.605	15/15	0.141	0.052 - 0.58	6/11	0.382	0.289 - 0.49
Molybdenum	mg/L	0/31	U [g]	*0.0033*	0/20	U [g]	*0.0057*	0/4	U [g]	*0.0031*	0/15	U [g]	*0.0035*	2/11	0.013	0.011 - 0.0155
Selenium	mg/L	0/31	U [g]	*0.0015*	8/20	0.014	0.011 - 0.0148	2/4	0.0069	0.006 - 0.0078	1/15	0.008	0.008 - 0.0077	5/11	0.075	0.062 - 0.087
Thallium	mg/L	0/31	U [g]	*0.0004*	0/20	U [g]	*0.0004*	0/4	U [g]	*0.00033*	0/15	U [g]	*0.00037*	0/11	U	*0.00032*
Uranium	mg/L	8/31	0.001	0.001 - 0.0013	11/20	0.012	0.005 - 0.035	4/4	0.0048	0.0041 - 0.0056	6/15	0.004	0.001 - 0.0093	11/11	0.005	0.002 - 0.0321
Vanadium	mg/L	0/31	U [g]	*0.0042*	0/20	U [g]	*0.0020*	0/4	U [g]	*0.0015*	0/15	U [g]	*0.0023*	0/11	U	*0.0015*
Zinc	mg/L	9/27	0.062	0.052 - *0.079*	0/18	U [g]	*0.023*	0/4	U [g]	*0.0148*	2/13	0.178	0.126 - 0.23	0/11	U	*0.0416*
Other																
Alkalinity as $CaCO_3$ [i]	mg/L	40/40	133	37.0 - 214	34/34	413	334 - 499	8/8	534	356 - 876	26/26	638	387 - 794	20/20	778	325 - 1522
pH [j]	s.u.	25/25	7.95	6.82 - 8.53	19/19	6.98	6.41 - 8.24	4/4	7.30	7.08 - 7.75	14/14	7.10	6.61 - 7.64	11/11	7.44	7.03 - 7.86
Redox Potential [j]	mV	25/25	75.8	-107 - 198	19/19	-8.21	-126 - 230	4/4	-85.8	-147 - -20	12/12	-198	-380 - 83	10/10	-49	-187 - 173
Specific Conductance[j]	umhos/cm	25/25	697	169 - 2550	19/19	2641	1003 - 4080	4/4	2118	1439 - 2580	14/14	2554	2280 - 3020	11/11	2436	1147 - 3340
Temperature [j]	C	25/25	11.0	2.10 - 19.3	19/19	12.0	9.40 - 15.8	4/4	14.6	12.5 - 18.9	12/12	14.55	9.5 - 17.6	11/11	14.75	12 - 16.6
Total Dissolved Solids	mg/L	31/31	294	93.0 - 452	20/20	2528	623 - 3860	4/4	1545	1300 - 1920	15/15	1948	1620 - 2740	11/11	2175	1010 - 3140
Radiologic																
Lead-210	pCi/L	0/27	U [g]	*1.50*	0/18	U [g]	*1.47*	0/4	U [g]	*1.30*	0/13	U [g]	*1.46*	0/11	U	*1.32*
Polonium-210	pCi/L	5/27	0.078	0.060 - 0.110	2/18	0.075	0.060 - 0.090	0/4	U [g]	*0.350*	0/13	U [g]	*0.420*	2/11	0.105	0.09 - 0.12
Radium-226	pCi/L	9/27	0.144	0.100 - 0.230	9/17	0.160	0.120 - 0.220	4/4	0.328	0.16 - 0.65	10/13	0.258	0.16 - 0.61	8/11	0.46	0.1 - 0.7
Radium-228	pCi/L	0/27	U [g]	*1.53*	0/17	U [g]	*1.39*	1/4	0.73	0.73 - 0.73	0/13	U [g]	*1.31*	3/11	1.04	0.5 - 1.56
Thorium-230	pCi/L	0/27	U [g]	*12.0*	0/18	U [g]	*2.60*	0/4	U [g]	*1.70*	1/13	3.1	3.1 - 3.1	0/11	U	*3.2*

[a] Samples collected from locations 0506, 0515, 0650, and 0652. Data includes four unfiltered duplicate samples collected in August 2001, unless otherwise noted.
[b] Samples collected from wells 0629, 0857, and 0866.
[c] Samples collected from well 0886.
[d] Samples collected from wells 0592 and 0903.
[e] Samples collected from wells 0599 and 0875.
[f] Frequency of detection: number of samples above detection limit/number of samples analyzed.
[g] Values are less than the detection limit and are not reported.
[h] Maximum value (in *italics)* is less than the detection limit; reported to provide scale of the detection limit.
[i] Half of the samples were filtered and half were not filtered.
[j] All samples unfiltered.

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5.3.1.1 Background Surface Water

Surface water of the Durango site includes Lightner Creek, which flows along the northern edge of the mill tailings area, and the Animas River, which flows along the eastern and southern boundaries of the mill tailings area and along the eastern edge of the northern half of the raffinate ponds area. South Creek, which is along the southern edge of the raffinate ponds area, is dry except during heavy rainfall and when water is released from the toe drain collection pond at the disposal cell. South Creek joins the Animas River approximately 1,000 ft east of the raffinate ponds area.

The average major ion concentrations of Animas River water are plotted on the Piper diagram presented in Figure 5–5. Surface water samples were collected from locations 0506, 0515, 0652, and 0650. Surface water is a calcium-bicarbonate type with concentrations ranging from 93 to 440 mg/L. The mean pH is 7.96 and the water has a mean iron concentration of 0.0486 mg/L, which indicates the water is oxidizing. Concentrations of the following 13 analytes were less than or equal to the detection limit: ammonium, antimony, arsenic, cadmium, copper, lead, molybdenum, selenium, thallium, vanadium, lead-210, radium-228, and thorium-230 (Table 5–5).

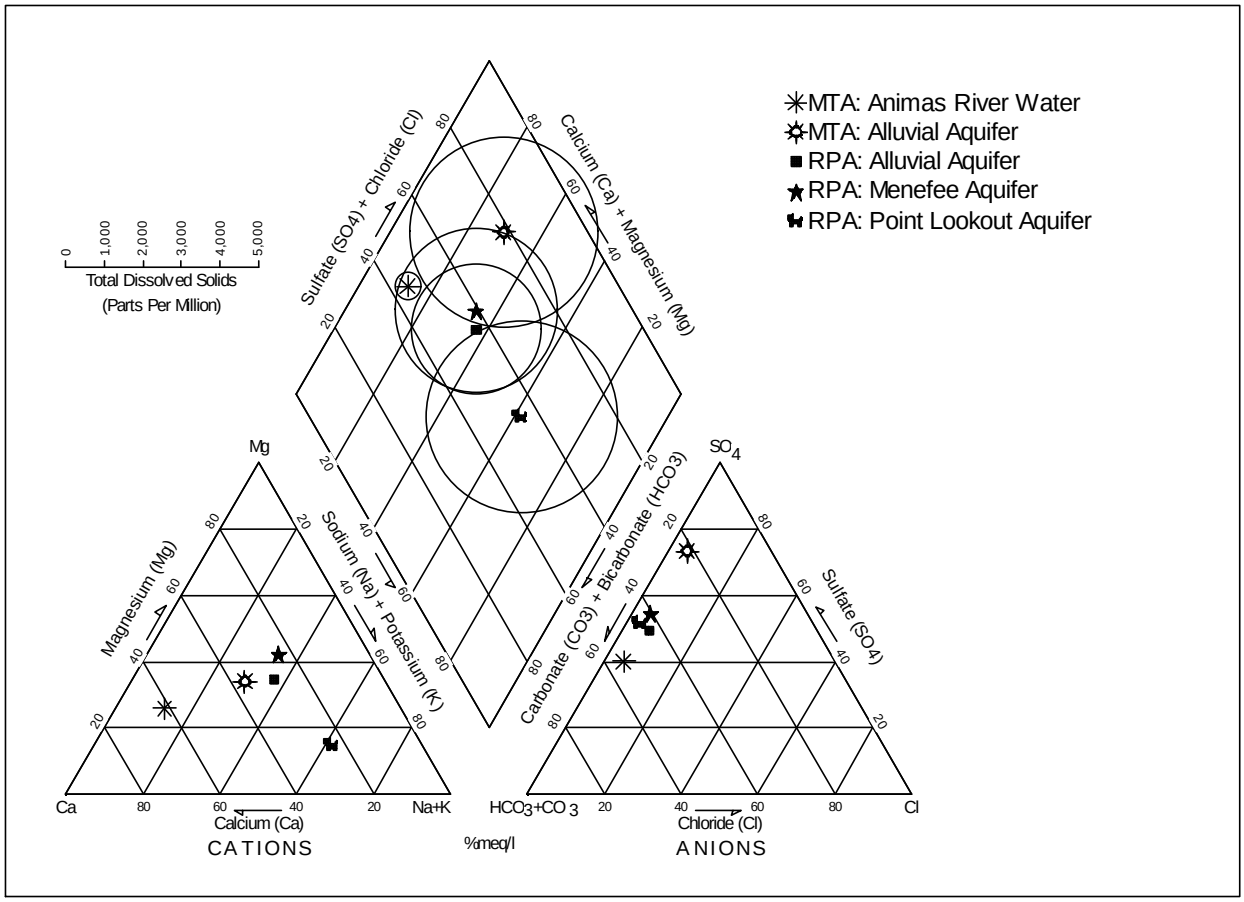

Figure 5–5. Piper Diagram for Mill Tailings Area (MTA) and Raffinate Ponds Area (RDA) Background Ground Water and Animas River Water using Mean Concentrations

5.3.1.2 Mill Tailings Area Background Ground Water

Background ground water data were obtained from monitor wells 0629, 0857, and 0866. Mean analyte concentrations are reported in Table 5–5. Concentrations of 13 analytes were below their detection limits: antimony, arsenic, cadmium, chromium, copper, lead, molybdenum, thallium, vanadium, zinc, lead-210, radium-228, and thorium-230.

The mean major ion concentrations are plotted on the Piper diagram presented in Figure 5–5. According to the Piper diagram, no cation dominates. The mean pH is 6.99, and the TDS concentrations range from 623 to 3,820 mg/L. Selenium concentrations range from 0.011 to 0.0148 mg/L; the MCL for selenium is 0.010 mg/L. Iron concentrations range from 0.120 to 14.7 mg/L, and the mean concentration is 3.38 mg/L.

5.3.1.3 Raffinate Ponds Area Background Alluvial Ground Water

Background ground water data for the alluvial aquifer of the raffinate ponds area were obtained from well 0886. Mean analyte concentrations are reported in Table 5–5. Concentrations of the following thirteen analytes were below their detection limits: antimony, arsenic, cadmium, chromium, copper, lead, molybdenum, thallium, vanadium, zinc, lead-210, polonium-210, and thorium-230.

Figure 5–5 shows the mean major ion concentrations. According to the Piper diagram, there is neither a dominant cation nor a dominant anion. No constituent exceeds its MCL. The mean pH is 7.30, and the measured TDS concentrations range from 1,300 to 1,920 mg/L. The iron concentration ranges from 0.161 to 2.95 mg/L; the mean iron concentration is 1.13 mg/L.

5.3.1.4 Raffinate Ponds Area Background Ground Water from the Menefee Formation

Background ground water data for the Menefee Formation of the raffinate ponds area were obtained from sampling wells 0592 and 0903. Analyte concentration data are reported in Table 5–5. Concentrations of the following twelve analytes were below their detection limits: antimony, arsenic, cadmium, chromium, copper, lead, molybdenum, thallium, vanadium, lead-210, polonium-210, and radium-228.

The mean major ion concentrations are interpreted using the Piper diagram presented in Figure 5–5. According to the Piper diagram, there is no dominant cation or anion. No constituent exceeds its MCL. The mean pH is 7.10, and measured TDS concentrations range from 1,620 to 2,740 mg/L. Iron concentrations range from 0.095 to 0.166 mg/L, and the mean iron concentration is 0.131 mg/L.

5.3.1.5 Raffinate Ponds Area Background Ground Water from the Point Lookout Sandstone

Background ground water data for the Point Lookout Sandstone of the raffinate ponds area were obtained from sampling wells 0599 and 0875. Analyte concentration data are reported in Table 5–5. Concentrations of the following eleven analytes were below their detection limits; antimony, arsenic, cadmium, chromium, copper, lead, thallium, vanadium, zinc, lead-210, and thorium-230.

The mean major ion concentrations are interpreted using the Piper diagram presented in Figure 5–5. Ground water is a sodium-sulfate type with TDS concentrations ranging from 1,010 to 3,140 mg/L. The mean pH is 7.44. Sodium concentrations range from 299 to 722 mg/L, and sulfate concentrations range from 4.13 to 1,750 mg/L. Iron concentrations range from 0.035 to 1.71 mg/L.

5.3.1.6 Raffinate Ponds Area Background Ground Water and Sulfide

A rotten-egg odor is strongly present at several locations in the raffinate ponds area, which indicates the presence of reduced sulfur. Sulfur occurs in oxidation states ranging from S^{2-} to S^{6+}; consequently, the chemical behavior of sulfur is related strongly to redox properties of aqueous systems. The geochemical cycle of sulfur is characterized by a rather rapid recycling of solute forms in water and of gases and aerosols in the atmosphere. Sulfide species are the final reduction product, and if the pH is above 7, $HS^-_{(aq)}$ will form rather than $H_2S_{(aq)}$.

Reduced sulfur, such as H_2S and $HS^-_{(aq)}$, are highly toxic to most organisms, so biota are strongly affected. Most people can detect the rotten-egg odor of hydrogen sulfide in waters that have only a few tenths of a milligram per liter of this material in solution. The risk-based value for $H_2S_{(aq)}$ as a contaminant in drinking water is 0.11 mg/L, assuming the contaminated water is the primary source of drinking water over a period of 30 years for adults. Natural waters subjected to unusual conditions may attain high concentrations of hydrogen sulfide.

Ground water samples were collected from nine wells to measure the sulfide concentration in order to fully assess the health risks. The sample collected from well 0592 has a hydrogen sulfide, $H_2S_{(aq)}$, concentration of 45.9 mg/L. The remaining eight wells had concentrations less than the GJO Analytical Laboratory detection limit of 1 mg/L. The GJO Analytical Laboratory method, G-3 R05, is based upon EPA method 376.1. A field method with a lower detection limit was used to better determine sulfide concentrations. Hach method 8131 is a colorimetric method that measures sulfide, S^{2-}, concentrations in the field (Hach 1998). The range of reliable detection is from 0.08 to 0.70 mg/L. Concentrations of $H_2S_{(aq)}$ in ground water samples from wells 0598 and 0875 were 0.15 and 0.11 mg/L, respectively; the risk-based value is 0.11 mg/L. The presence of sulfide was indicated by the slightly blue color of the samples from wells 0599, 0884, and 0886 after the addition of the reagents. However, the concentrations were less than 0.08 mg/L and could not be estimated reliably.

If any reactive iron compounds are present, the sulfide species will react to form solid sulfides. The reduced sulfur ion, S^{2-}, forms sulfides of low solubility with most metals. Sulfur that occurs in reduced form in the sulfide minerals is relatively immobile. Species, such as heavy metals, adsorbed onto ferric oxyhydroxides will be released to solution. Many of the heavy metals, such as copper, zinc, molybdenum, lead, and mercury, that are relatively soluble in oxidizing waters (provided that the pH is not too high), are highly insoluble in the presence of dissolved sulfide species. Because iron is common and widely distributed, the iron sulfides have a substantial influence on sulfur geochemistry. There are many consequences of ferric iron and sulfate reduction. When sulfide minerals undergo weathering in contact with aerated water, the sulfur is oxidized to yield sulfate ions that go into solution in the water. Hydrogen ions are produced in considerable quantity in this oxidation process and can decrease the pH. Pyrite crystals occur in many sedimentary rocks and constitute a source of both ferrous iron and sulfate in ground water. Pyrite, particularly, is commonly associated with biogenic deposits such as coal, which form under strongly reducing conditions.

5.3.1.7 Stiff Diagrams and Background Waters

Mean major ion concentrations are also plotted on a Stiff diagram (Figure 5–6). Stiff diagrams are a way of plotting the major ion composition of a water to produce a symbol whose shape indicates the relative proportions of the different ions, and whose size indicates total concentrations (Drever 1997). Similarities and differences can be quickly identified. The three major anions plot on the right side of the center axis, and the major cations plot on the left side.

As shown in Figure 5–6, Animas River water contains the lowest concentrations of major ions. The shape of the Animas River water Stiff diagram is hexagonal and is a calcium-bicarbonate-type water, as indicated by the Piper diagram (Figure 5–5). The major ion concentrations of the background ground waters of the mill tailings area vary. The diagram is not symmetric. The background ground water has higher concentrations of all major ions and a higher mean concentration of sulfate than of any other anion.

In the raffinate ponds area, the Stiff diagrams are similar for the alluvial aquifer and for the Menefee aquifer and indicate that concentrations of the major cations and anions are similar. The Point Lookout aquifer has higher concentrations of sodium and potassium and lower concentrations of magnesium.

5.3.1.8 Mill Tailings Area Background Soil Chemistry

Data for the background soils are presented in Table 5–6. Section 4 presents a full description of the subpile soil sampling methods and results. Background surface soil samples were collected from subpile soil sample locations 0930, 0931, and 0932 (Figure 5–7).

Cadmium concentrations in the background soils were greater than the crustal mean concentration of 0.2 mg/kg. Two soil samples had lead concentrations greater than the crustal mean concentration of 13 mg/kg. Molybdenum concentrations were greater than the detection limit and were less than the crustal mean concentration of 1.5 mg/kg. Selenium concentrations of all three samples were greater than the detection limit of 0.35 mg/kg and the crustal mean of 0.05 mg/kg. Uranium concentrations were greater than the detection limit and less than the crustal mean.

Table 5–6. Constituent Concentrations in Durango Background Soil Samples

Sample	Cadmium	Lead	Molybdenum	Selenium	Uranium
Mill Tailings Area (mg/kg)					
930-AL	**1.27** [a]	**141**	*0.5* [b]	**0.60**	0.77
931-COL	**0.85**	**13.6**	*0.66*	**0.88**	1.22
932-COL	**0.57**	6.95	*0.13*	**0.72**	0.54
Raffinate Ponds Area (mg/kg)					
903-04	*0.041*	4.40	*0.12*	*0.35*	0.18
903-14	*0.057*	4.81	*0.11*	*0.35*	0.18
903-23	**2.17**	4.50	*0.13*	*0.35*	0.29
903-28	0.11	10.0	*0.12*	*0.35*	0.21
Crustal mean [c]	0.2	13	1.5	0.05	1.8

[a] **Bold:** Value is greater than the crustal mean.
[b] *Italic:* Value is less than the detection limit.
[c] Mason and Moore (1982).

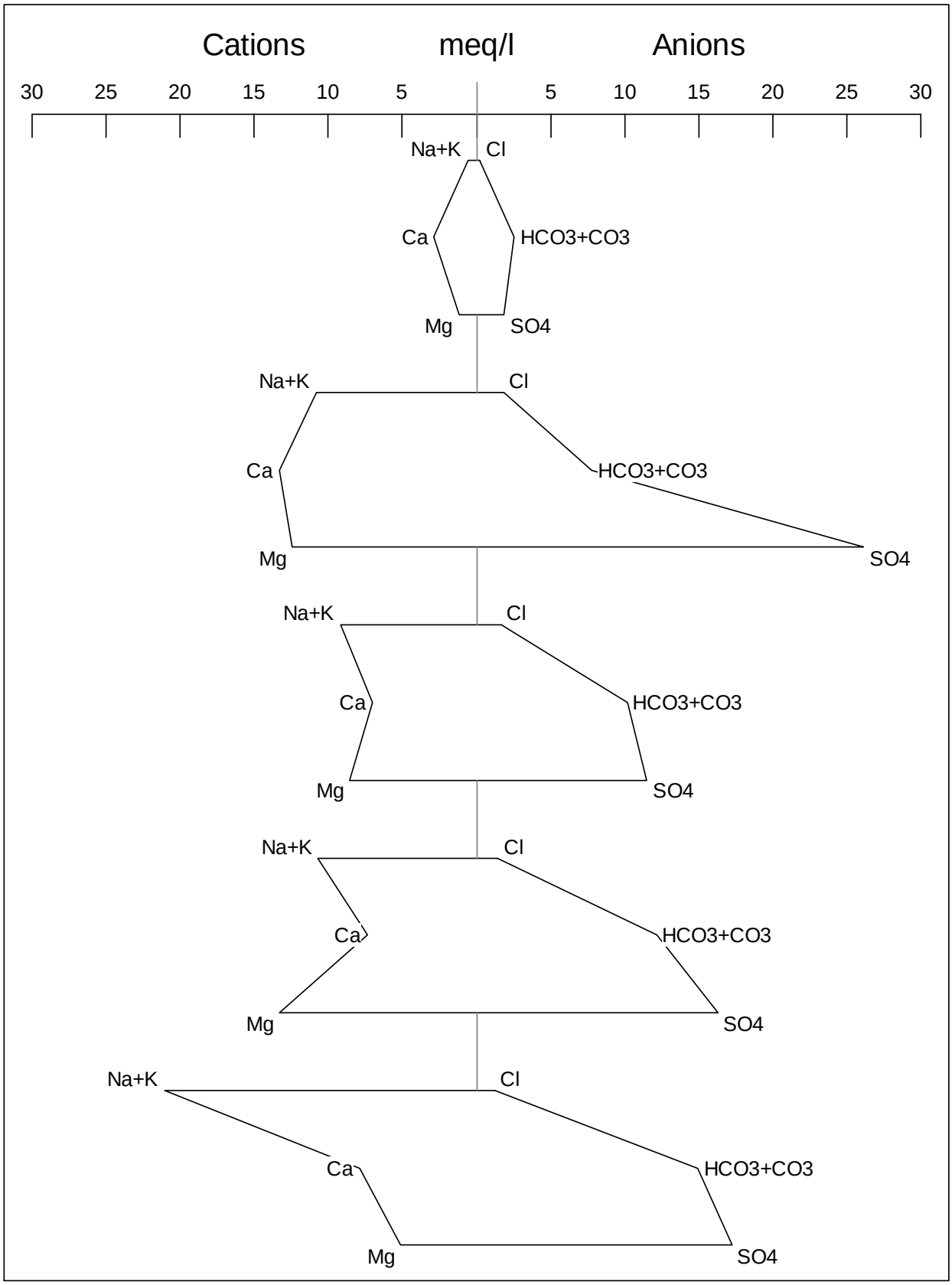

Figure 5–6. Stiff Diagram for Mill Tailings Area (MTA) and Raffinate Ponds Area (RPA) Background Ground Waters and Animas River Water using Mean Concentrations

5.3.1.9 Raffinate Ponds Area Background Sediment and Soil Chemistry

Data for the raffinate ponds area background soils are presented in Table 5–6. Section 4 presents a full description of the subpile soil sampling methods. Background samples were collected at depths of 4 ft, 14 ft, 23 ft, and 28 ft at location 0903 (Figure 5–8).

The cadmium concentrations in one sample exceeded the crustal mean of 0.2 mg/kg. None of the other mean crustal concentrations were exceeded. Lead and uranium concentrations were greater than the detection limits but less than the crustal mean. Molybdenum and selenium concentrations were less than the detection limits.

5.3.2 Mill Tailings Area: Areal Extent of Ground Water Contamination

Maximum constituent concentrations in background ground waters are listed in Table 5–7. The highest background concentration of manganese was less than the human health risk-basked level for manganese. The highest background concentration of selenium is greater than the MCL. The highest background concentration of uranium was less than the MCL. The areal extent of ground water contamination is discussed in terms of those samples and well locations that have constituent concentrations greater than the MCL.

Table 5–7. Maximum Constituent Concentrations in Background Ground Waters

Water	Constituent Concentration (mg/L)					
	Cadmium	Lead	Manganese	Molybdenum	Selenium	Uranium
UMTRA MCL [a]	0.01	0.05	1.7	0.1	0.01	0.044
Mill Tailings Area						
Alluvial Aquifer	0.00034	0.007	1.050	0.0057	0.0148	0.0354
Raffinate Ponds Area						
Alluvial Aquifer	U	U	0.605	0.0031	0.0078	0.0056
Menefee Aquifer	U	U	0.58	0.0035	0.0077	0.0093
Point Lookout Aquifer	0.0003	0.005	0.49	0.0155	0.087	0.0321

[a]The human health risk-based value is listed for manganese.
U = less than detection.

Cadmium concentrations in well 0612 exceeded the 0.01 mg/L MCL; the highest value was in the November 2000 sample (Figure 5–9). From 1999 through August 2000 concentrations ranged from 0.0258 to 0.0435 mg/L. The only other location where cadmium concentration has exceeded the MCL is at well 0630, where the concentration of 0.0167 mg/L, was detected in a sample from the November 2000 sampling. The lead concentrations in all samples from June 1999 through August 2001 were below the 0.05 mg/L MCL and were below the detection limit (Figure 5–10). Concentrations of manganese have exceeded the human health risk-based level of 1.7 mg/L seven times at 0612 and two times at location 0630 from June 1999 through August 2001 (Figure 5–11). The 0.1 mg/L MCL for molybdenum was exceeded five times at well location 0612 (Figure 5–12). Molybdenum concentrations ranged from 0.116 to 0.150 mg/L. Selenium concentrations exceeded the MCL at well locations 0612, 0617, 0622, 0630, 0633, 0635, 0857, and 0866, which is the background well (Figure 5–13). Uranium concentrations exceed the MCL of 0.044 mg/L at seven locations: 0612, 0617, 0630, 0631, 0633, 0634, and 0859 (Figure 5–14).

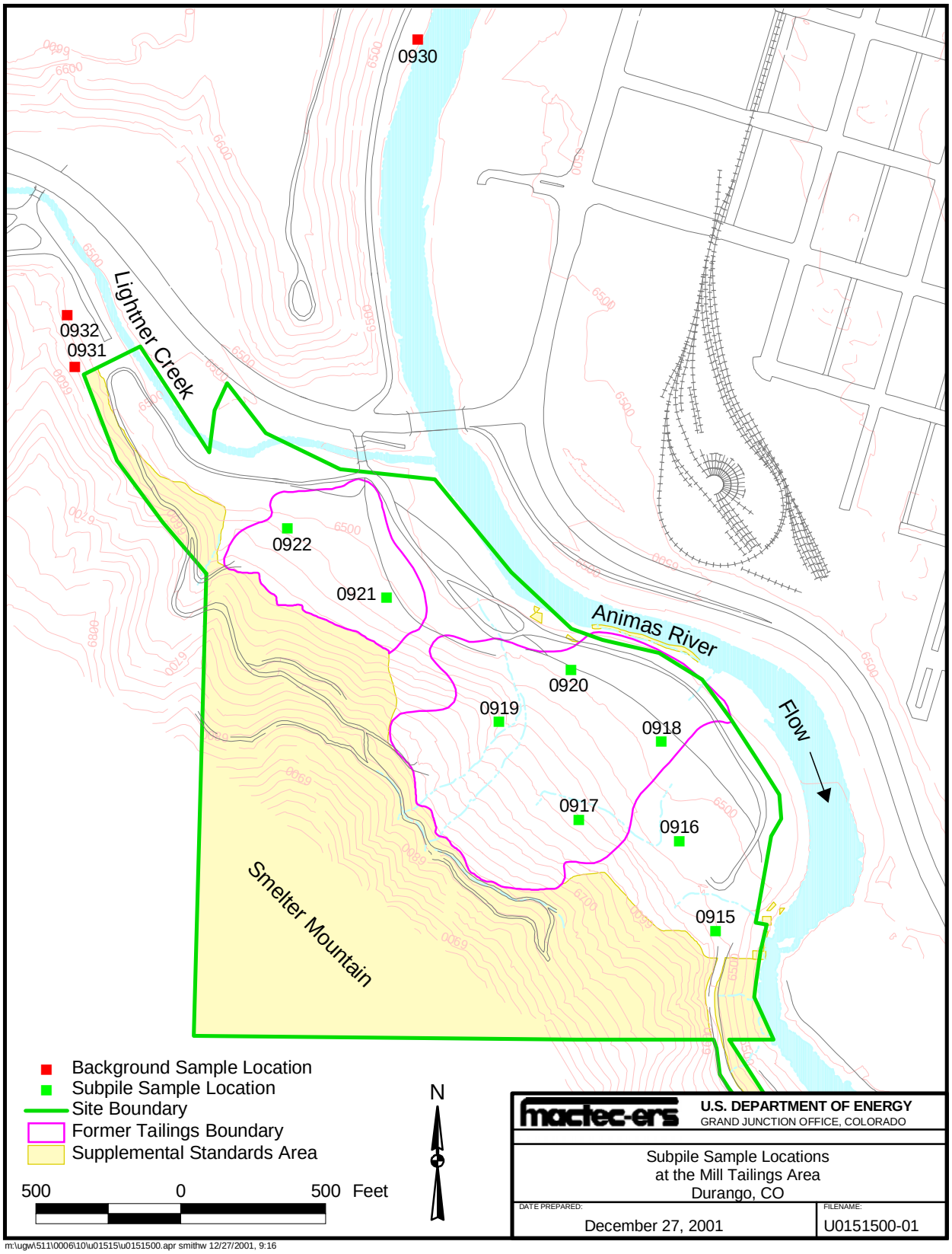

Figure 5–7. Subpile Soil Sample Locations at the Mill Tailings Area

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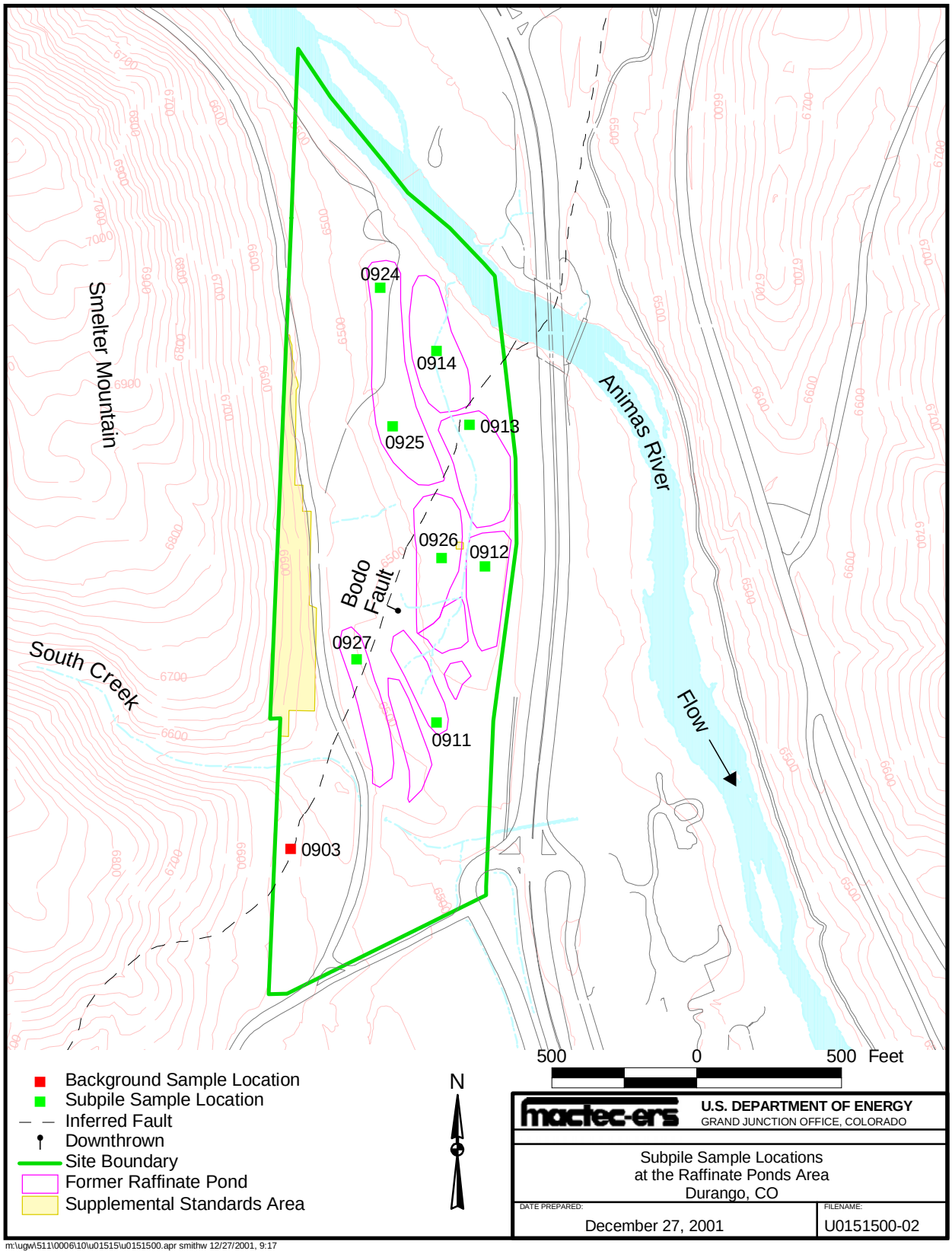

Figure 5–8. Subpile Soil Sample Locations at the Raffinate Ponds Area

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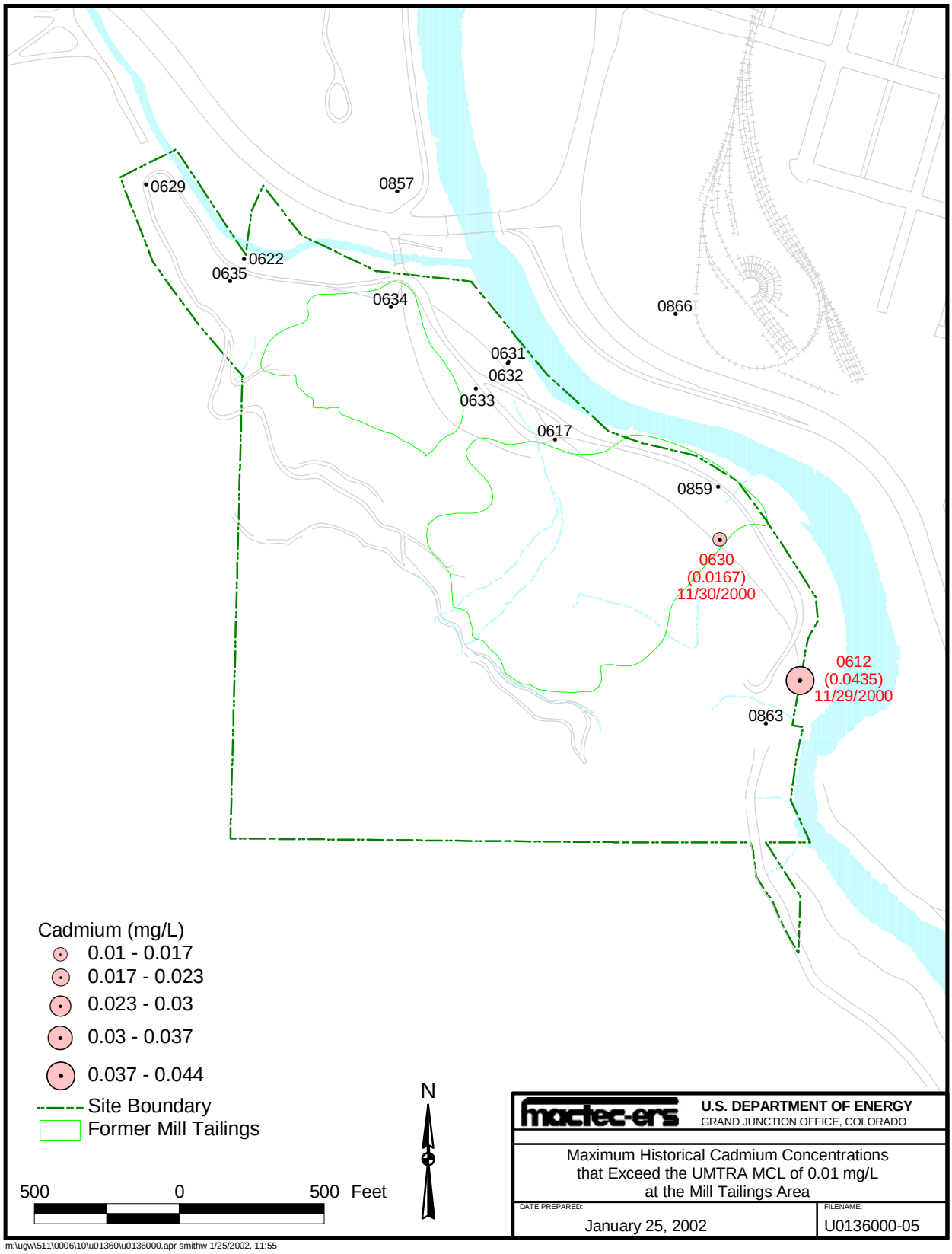

Figure 5–9. Maximum Historical Concentrations of Cadmium at the Mill Tailings Area

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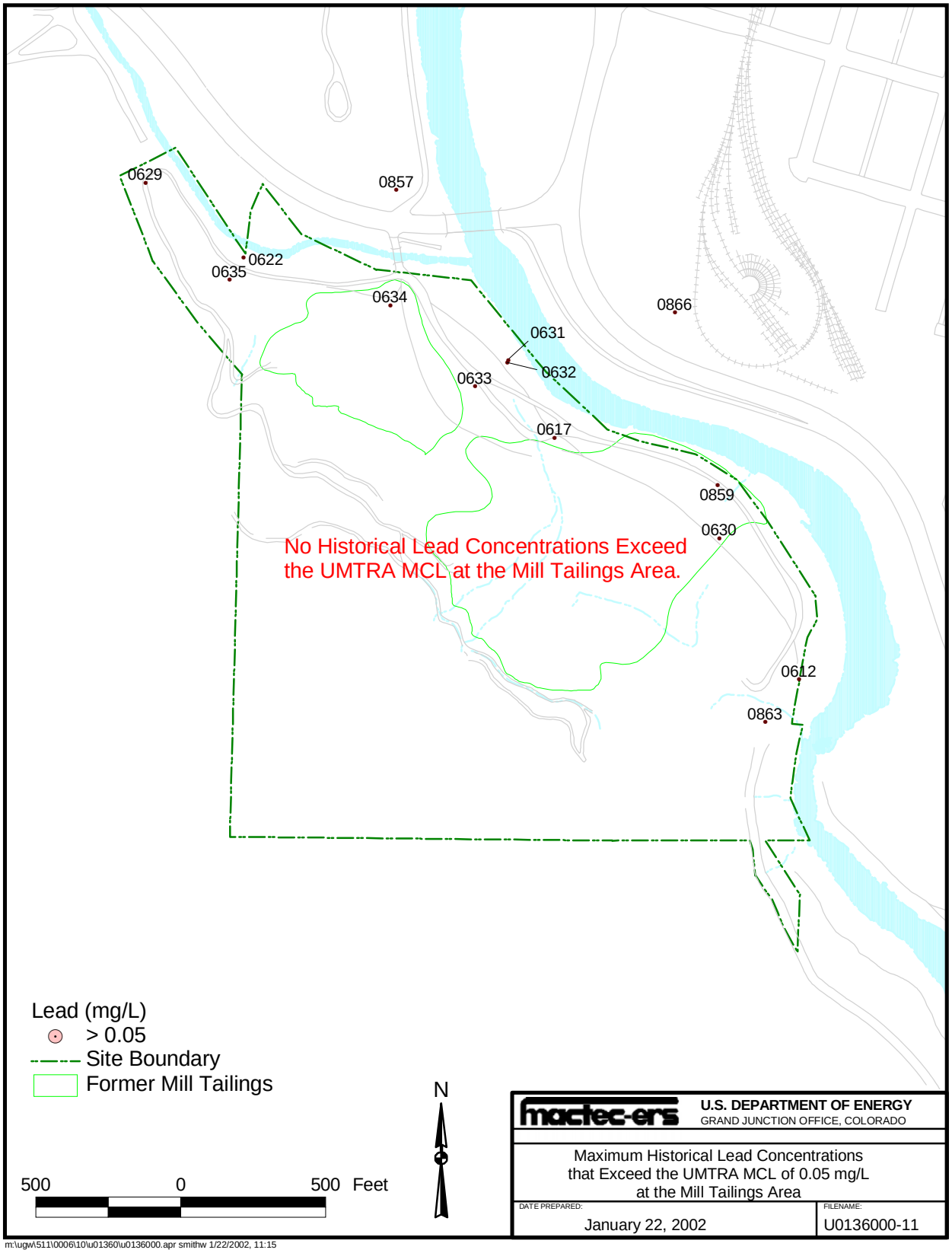

Figure 5–10. Maximum Historical Concentrations of Lead at the Mill Tailings Area

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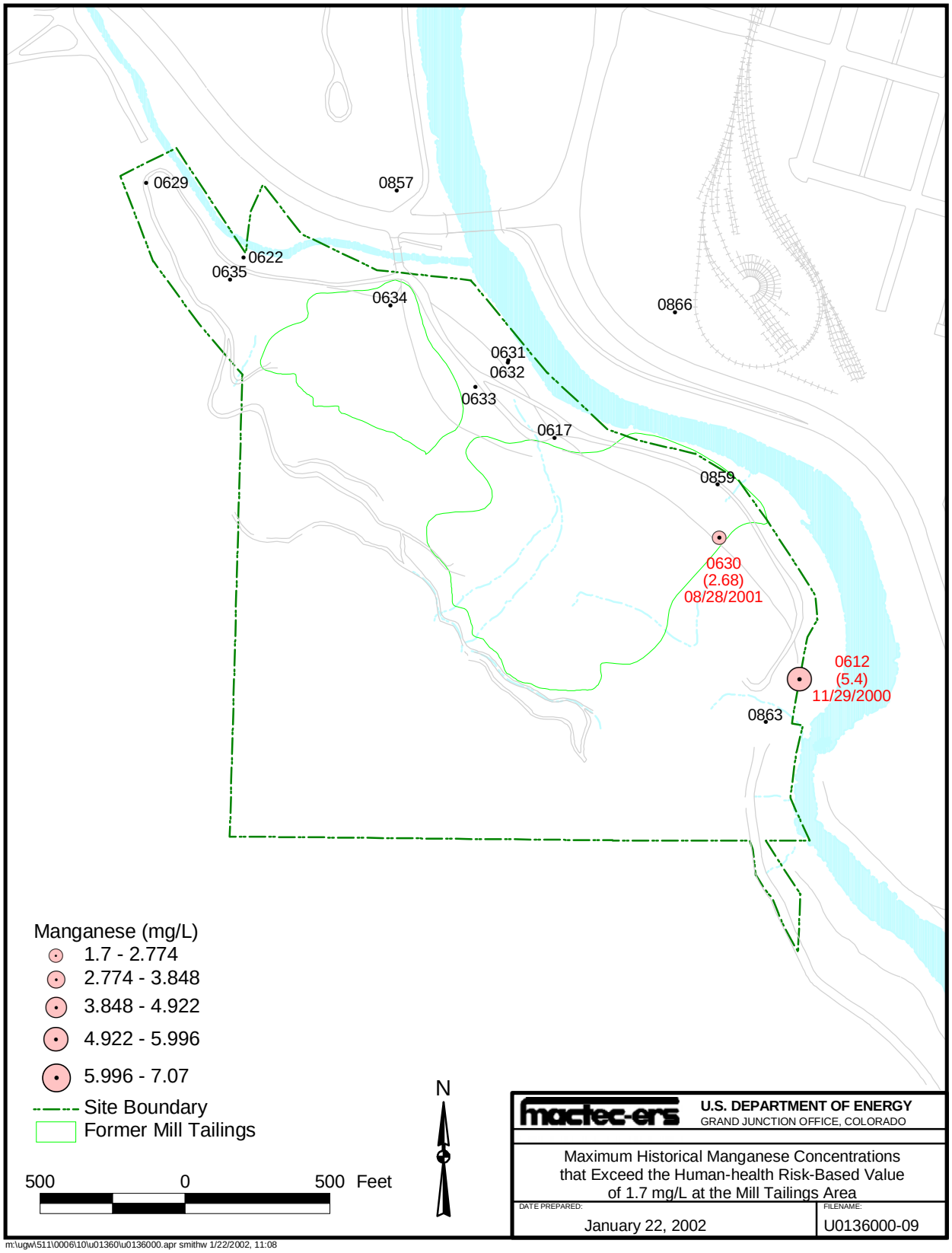

Figure 5–11. Maximum Historical Concentrations of Manganese at the Mill Tailings Area

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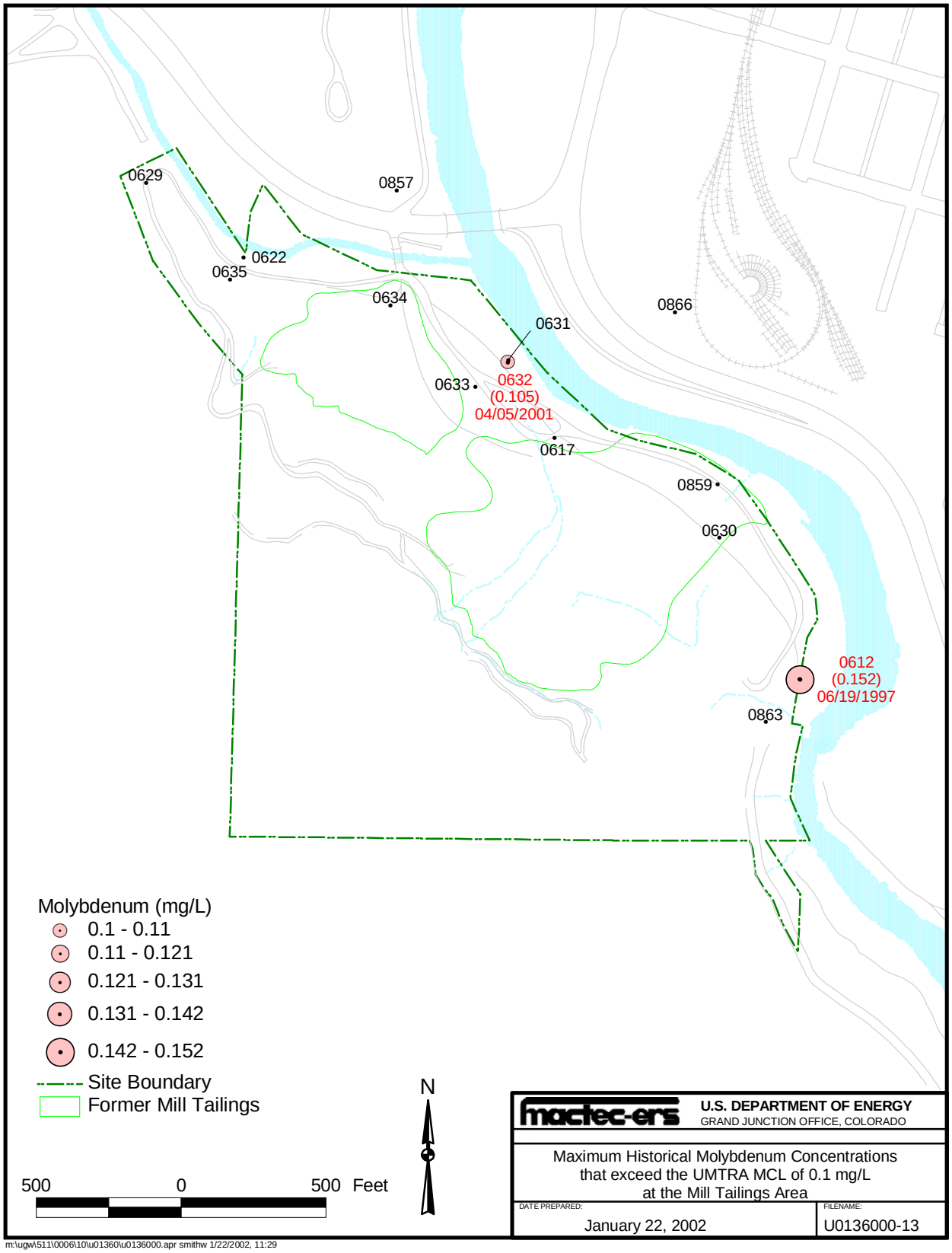

Figure 5–12. Maximum Historical Concentrations of Molybdenum at the Mill Tailings Area

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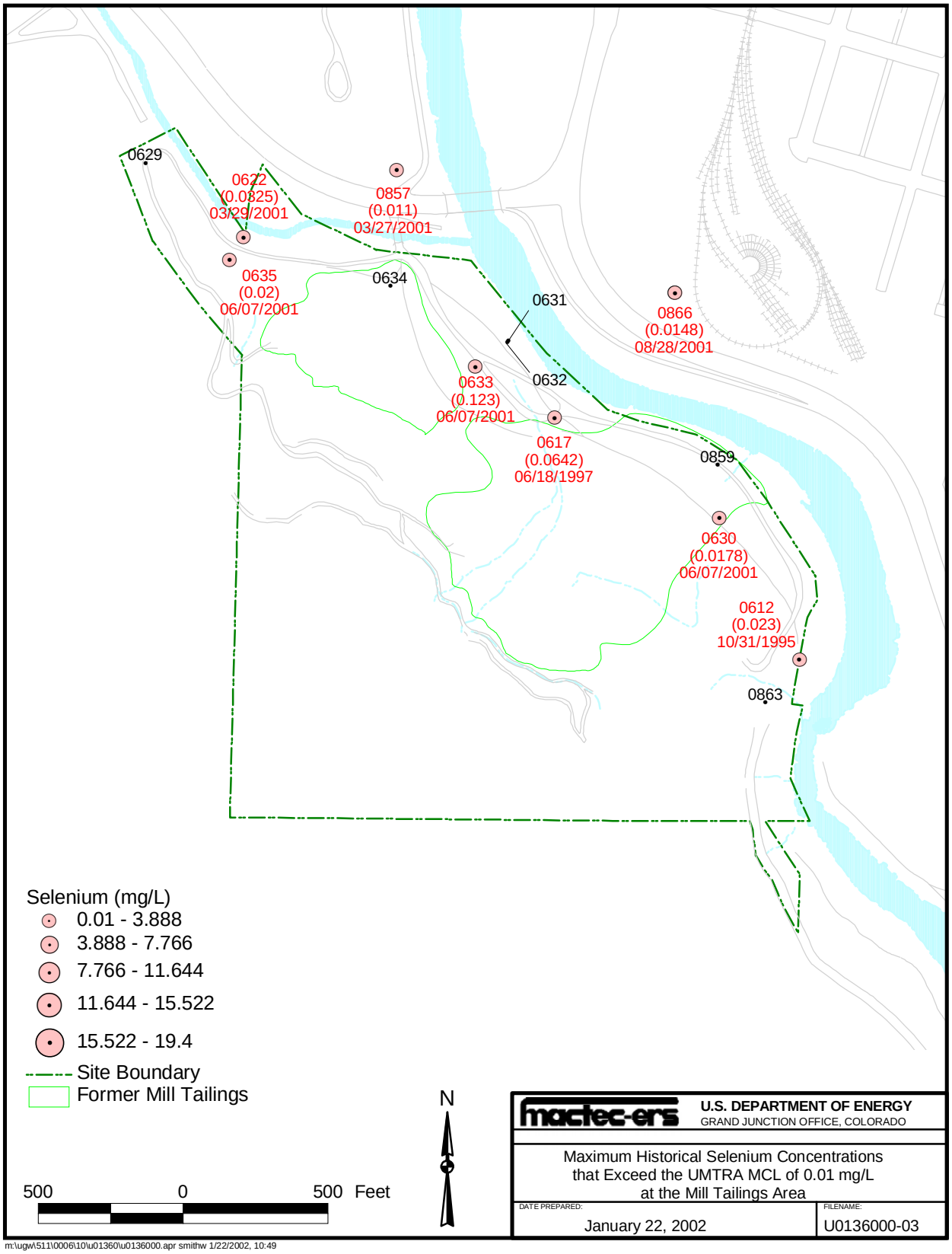

Figure 5–13. Maximum Historical Concentrations of Selenium at the Mill Tailings Area

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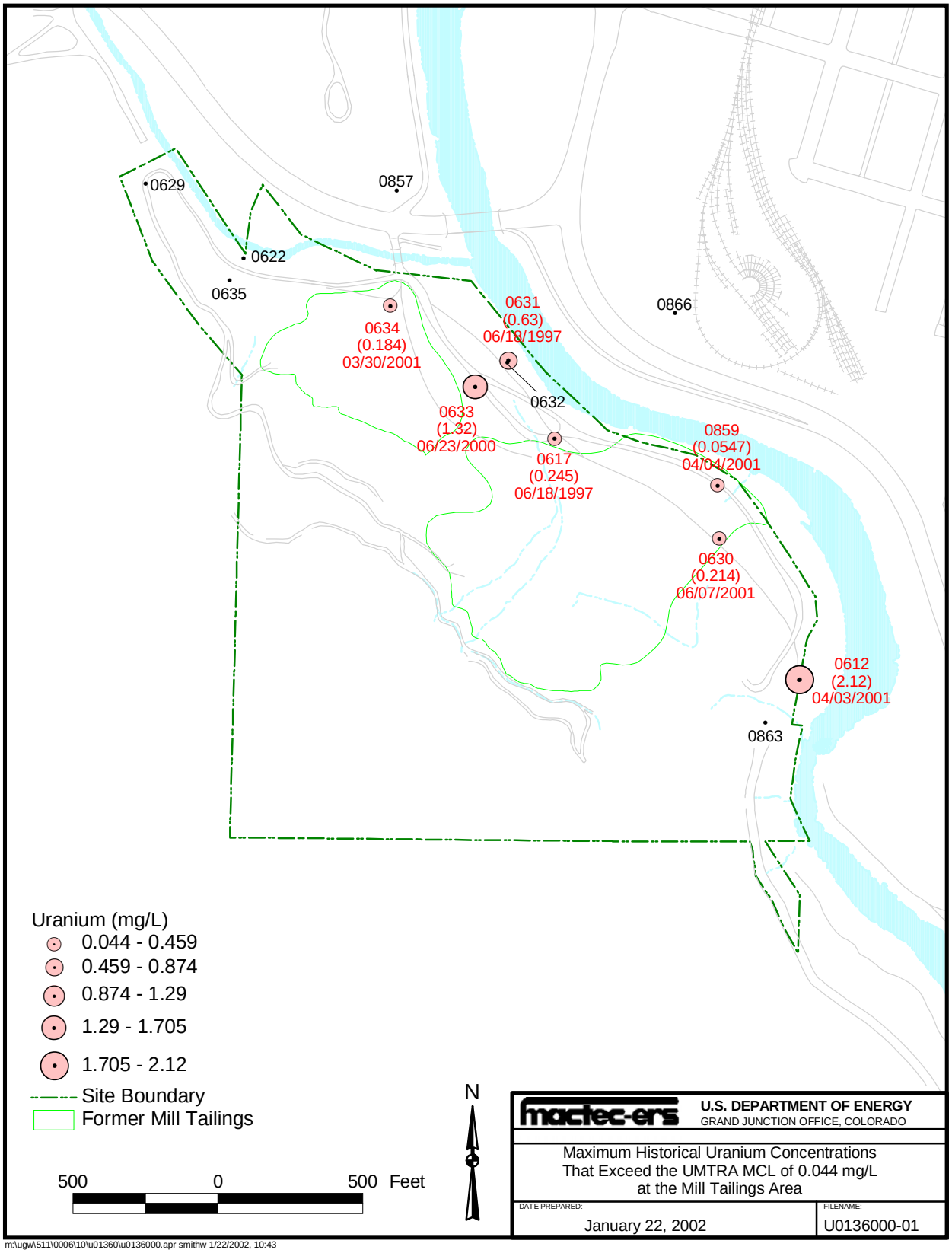

Figure 5–14. Maximum Historical Concentrations of Uranium at the Mill Tailings Area

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5.3.3 Raffinate Ponds Area: Areal Extent of Ground Water Contamination

Constituents that exceeded their MCL or human health risk-based standard (manganese), at the raffinate ponds area are displayed in Figure 5–15 through Figure 5–20**.** The concentrations shown are the maximum historical values for each well location from June 1999 through August 2001; where no historical value has exceeded an MCL or the human health risk-based standard, the constituent concentrations are not listed.

No sample from any well has exceeded the MCL for cadmium (Figure 5–15) or lead (Figure 5–16). Manganese concentrations have exceeded the human health risk-based levels at six wells: 0593, 0598, 0628, 0879, 0880, and 0882 (Figure 5–17). The molybdenum MCL was exceeded in December 2000 at well 0905 (Figure 5–18). Selenium concentrations exceeded the MCL at 10 wells in 2001: 0594, 0596, 0598, 0599, 0600, 0607, 0628, 0879, 0880, and 0884 (Figure 5–19). Uranium concentrations have exceeded the MCL at six wells: 0594, 0598, 0628, 0879, 0880, and 0884 (Figure 5–20).

5.3.3.1 Alluvial Aquifer

Well 0886 is the only background location where alluvium is present. Maximum constituent concentrations in alluvial background ground water from this well are listed in Table 5–7. Concentrations of cadmium, lead, and molybdenum were at or below their detection limits in background alluvial ground water. Concentrations of manganese were less than the human health risk-based level, and concentrations of selenium and uranium were less than their respective MCLs in background alluvial ground water.

Alluvial ground water occurs on site in only one isolated location, at well 0607. *Table 5–8* lists the constituents in alluvial ground water at the raffinate ponds area with concentrations that exceed an MCL or the human health risk-based level for manganese. Selenium is the only constituent in alluvial ground water (i.e., in well 0607) with concentrations that exceed its MCL. Concentrations of cadmium, lead, manganese, molybdenum, and uranium were all below both background and their MCLs.

5.3.3.2 Menefee Aquifer

Maximum constituent concentrations in background water in the Menefee Formation are listed in Table 5–7. Cadmium, lead, and molybdenum were not detected in Menefee Formation background waters. The highest background concentration of manganese was less than the human health risk-basked level and the highest background concentrations of selenium and uranium were less than their MCLs.

Table 5–8 shows the constituents with concentrations in Menefee Formation ground water that exceeded an MCL or the human health risk-based level. In samples from on-site Menefee Formation wells, concentrations of cadmium, lead, and molybdenum were less than their MCLs. Cadmium concentrations exceeded the background concentration and the detection limit at wells 0594, 0598, 0628, 0879, 0884, and 0891. Lead concentrations exceeded the background concentration and the detection limit at wells 0603, 0879, and 0880. Molybdenum concentrations exceeded the background concentration and the detection limit at wells 0603, 0876, and 0891.

Manganese concentrations were greater than the human health risk-based value at wells 0593, 0598, 0879, 0880 and 0882. Manganese concentrations were greater than the maximum

background concentration and greater than the detection limit at wells 0593, 0598, 0602, 0628, 0879, 0880, 0888, and 0892.

Table 5–8. Raffinate Ponds Area Sample Concentrations Greater Than an UMTRA MCL or the Human Health Risk-Based Value for Manganese

	1999		2000			2001				
Well	**June**	**November**	**June**	**November**	**December**	**March**	**April**	**May**	**June**	**August**
Alluvial Aquifer										
0607	Se	Se	Se		Se		Se		Se	Se
0886[a]										
Menefee Aquifer										
0592[a]										
0593			Mn			Mn			Mn	Mn
0594						Se, U			Se, U	
0598	U	U	U		U		Mn, Se, U		Mn, Se, U	Se, U
0602										
0603										
0628	Se, U	Se, U	Se, U		Se, U		Se, U		Se, U	Se, U
0876										
0878										
0879					U	Mn, Se, U			Mn, Se, U	Mn, Se, U
0880					Mn	Se, U			Se, U	Se, U
0882					Mn		Mn		Mn	Mn
0883										
0884					Se, U		Se, U		Se, U	Se, U
0888										
0890										
0891										
0892										
0902										
0903[a]										
Point Lookout Aquifer										
0595										
0596									Se	Se
0597										
0599[a]			Se		Se		Se		Se	Se
0600							Se			
0875[a]										
0881										
0887										
0889										
0893										

NOTE: Listed is the ground water sampling schedule from June 1999 through August 2001. The listed constituent exceeded its UMTRA MCL or the human health risk-based value for manganese.

[a] Background well

Well was sampled.

Well not sampled.

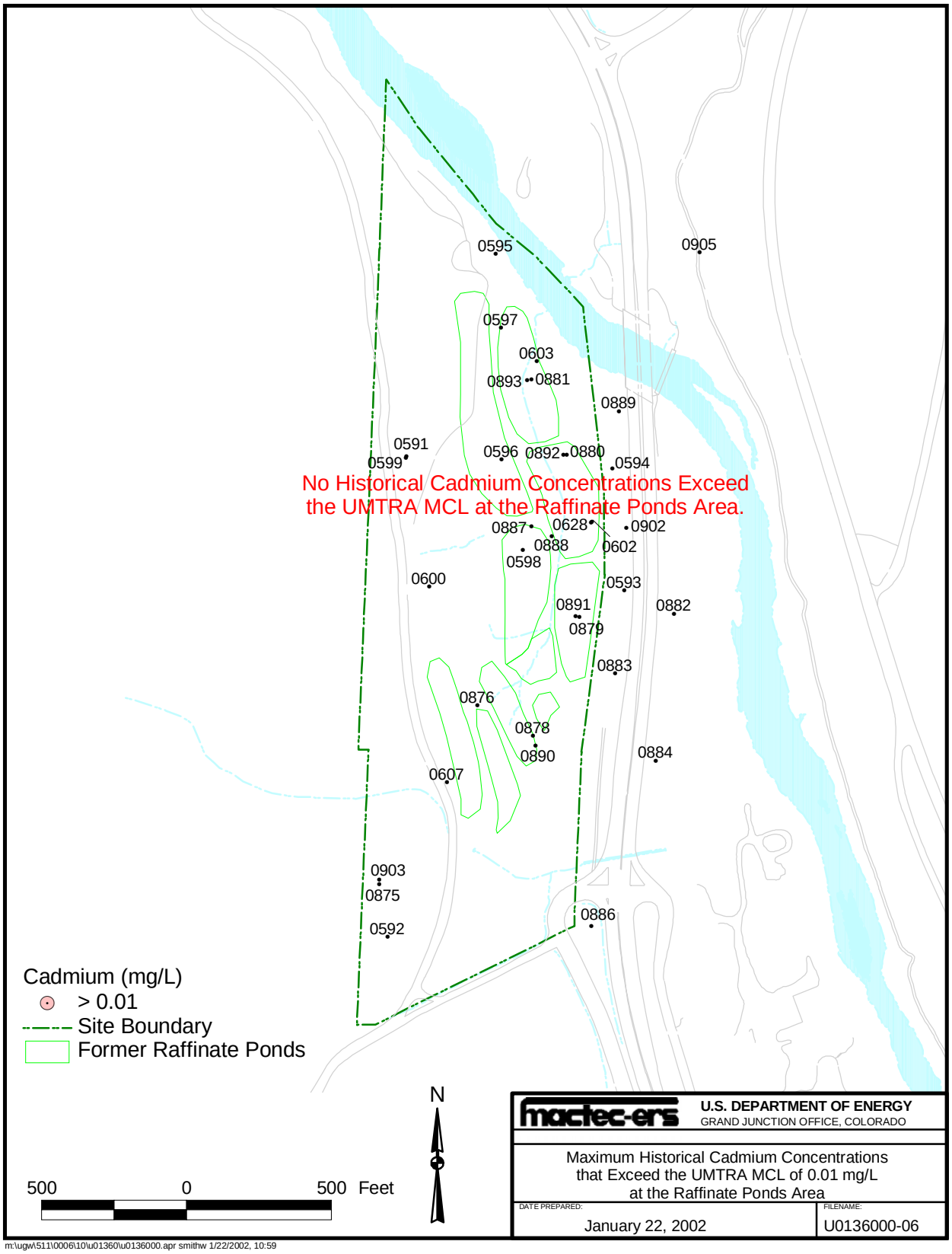

Figure 5–15. Maximum Historical Concentrations of Cadmium at the Raffinate Ponds Area

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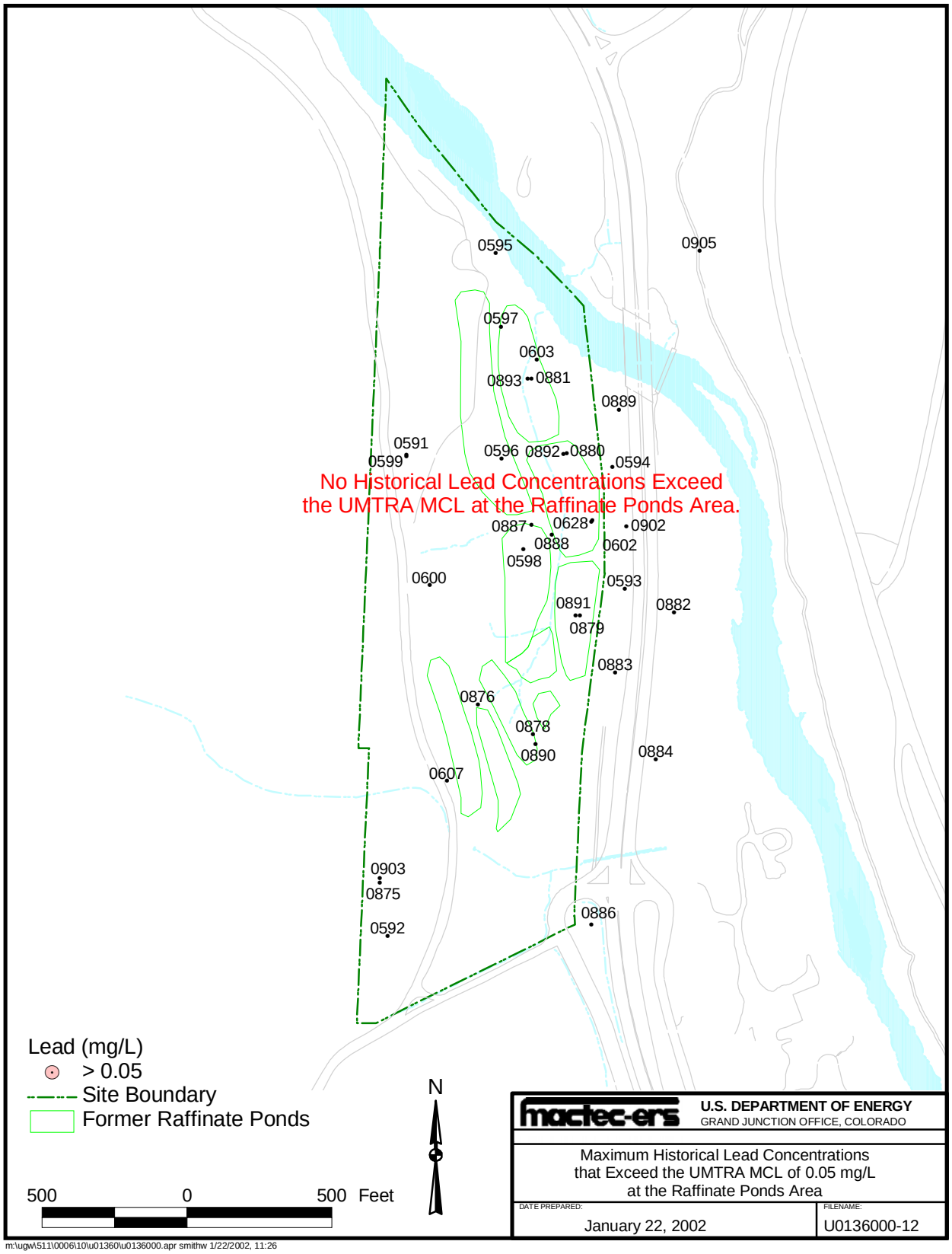

Figure 5–16. Maximum Historical Concentrations of Lead at the Raffinate Ponds Area

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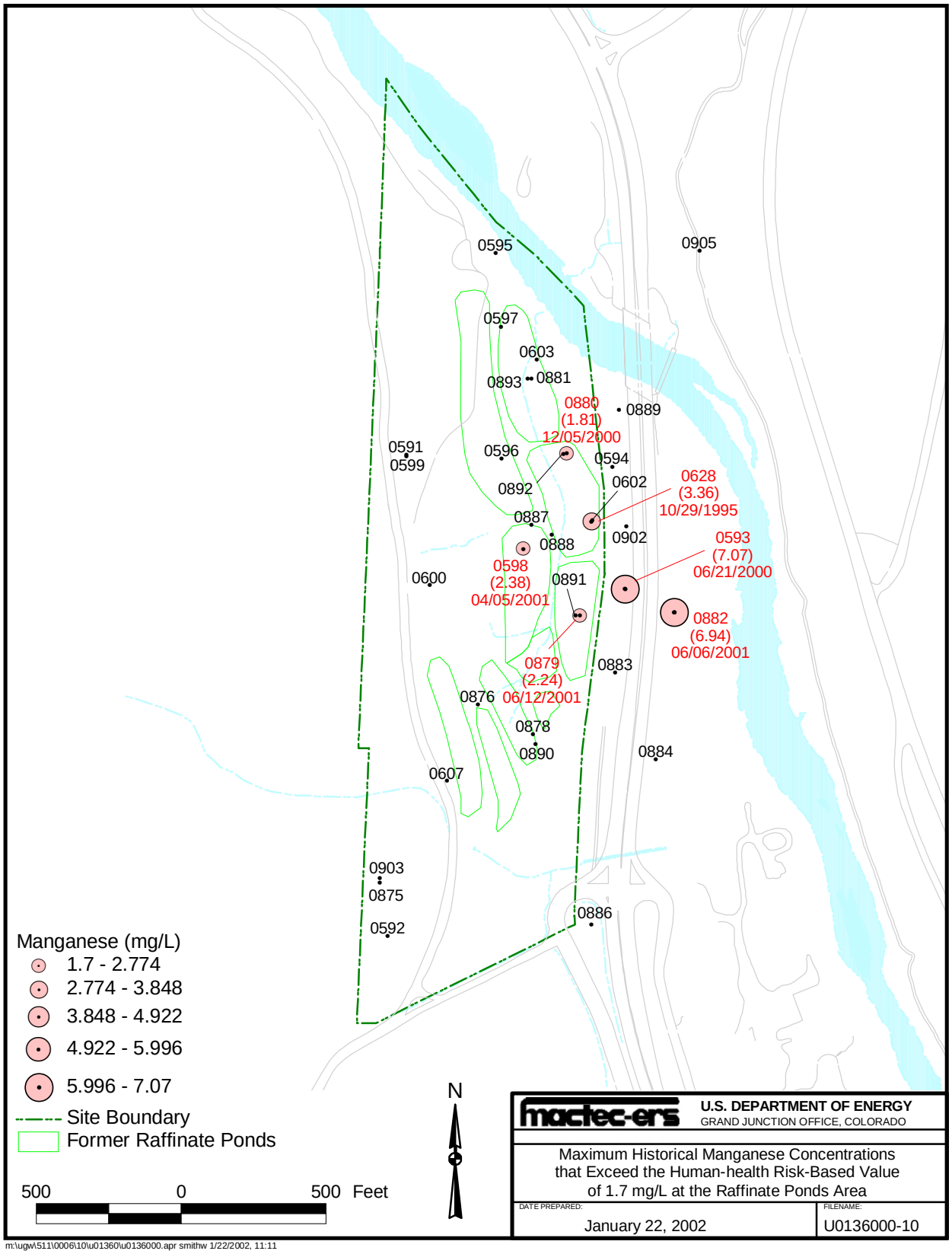

Figure 5–17. Maximum Historical Concentrations of Manganese at the Raffinate Ponds Area

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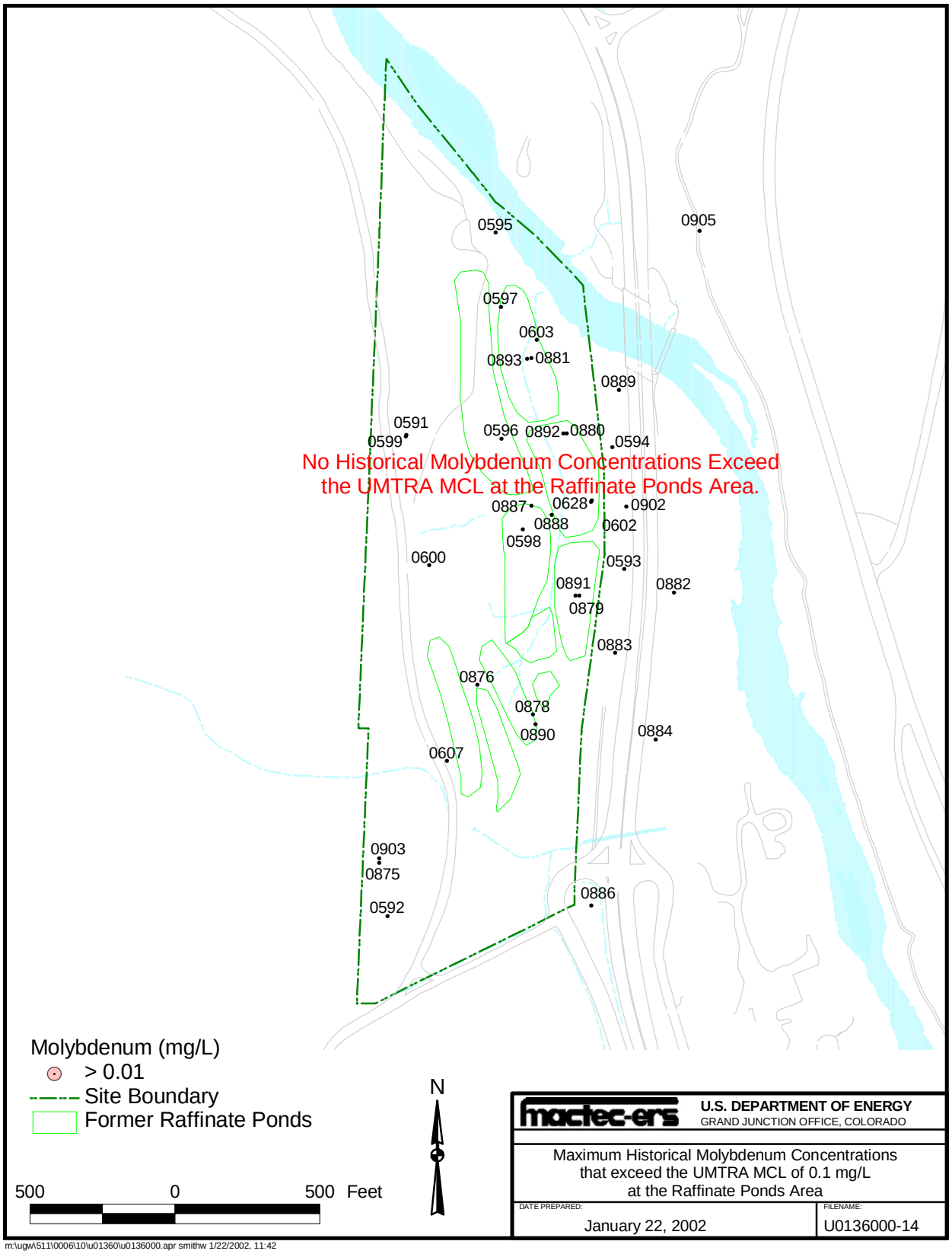

Figure 5–18. Maximum Historical Concentrations of Molybdenum at the Raffinate Ponds Area

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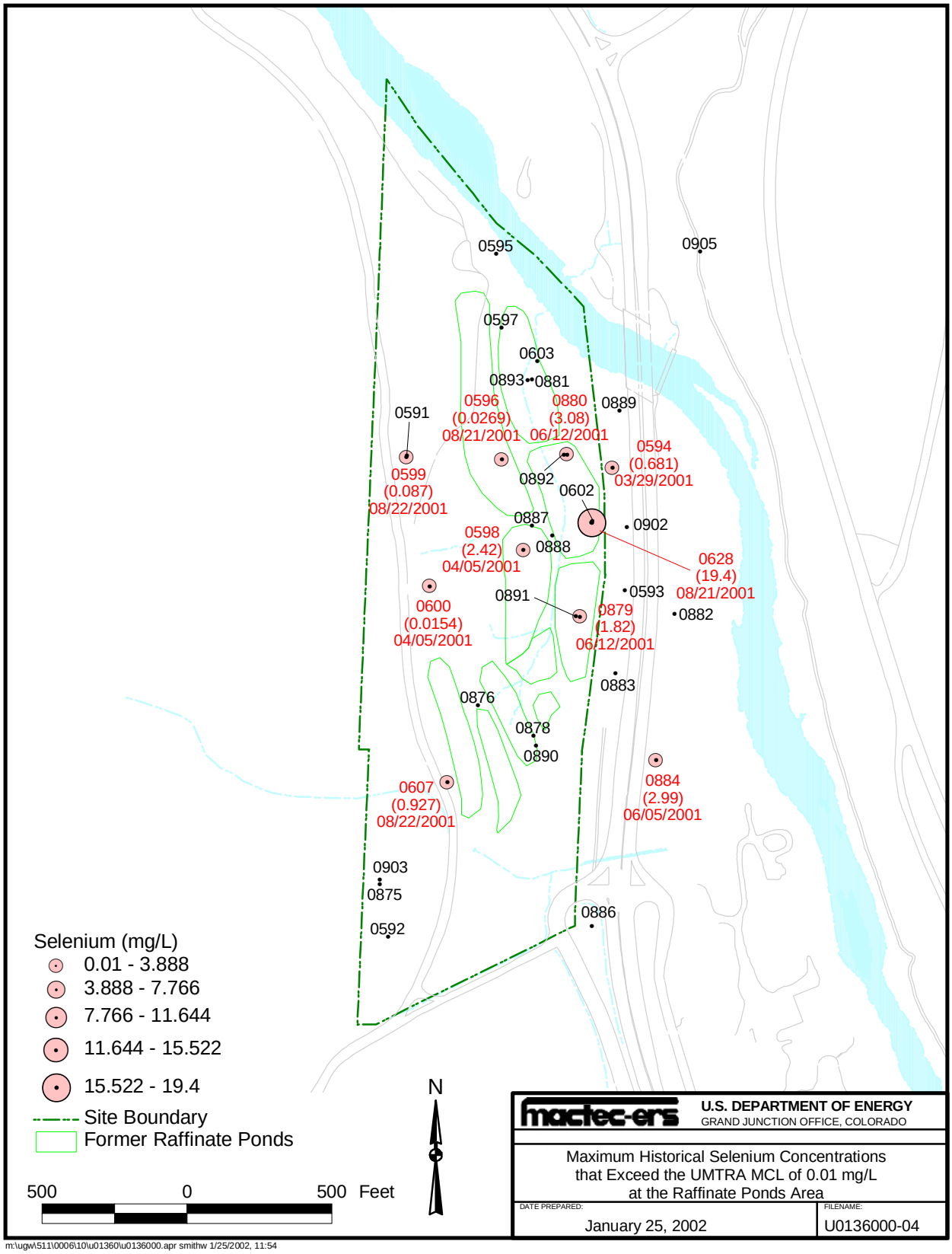

Figure 5–19. Maximum Historical Concentrations of Selenium at the Raffinate Ponds Area

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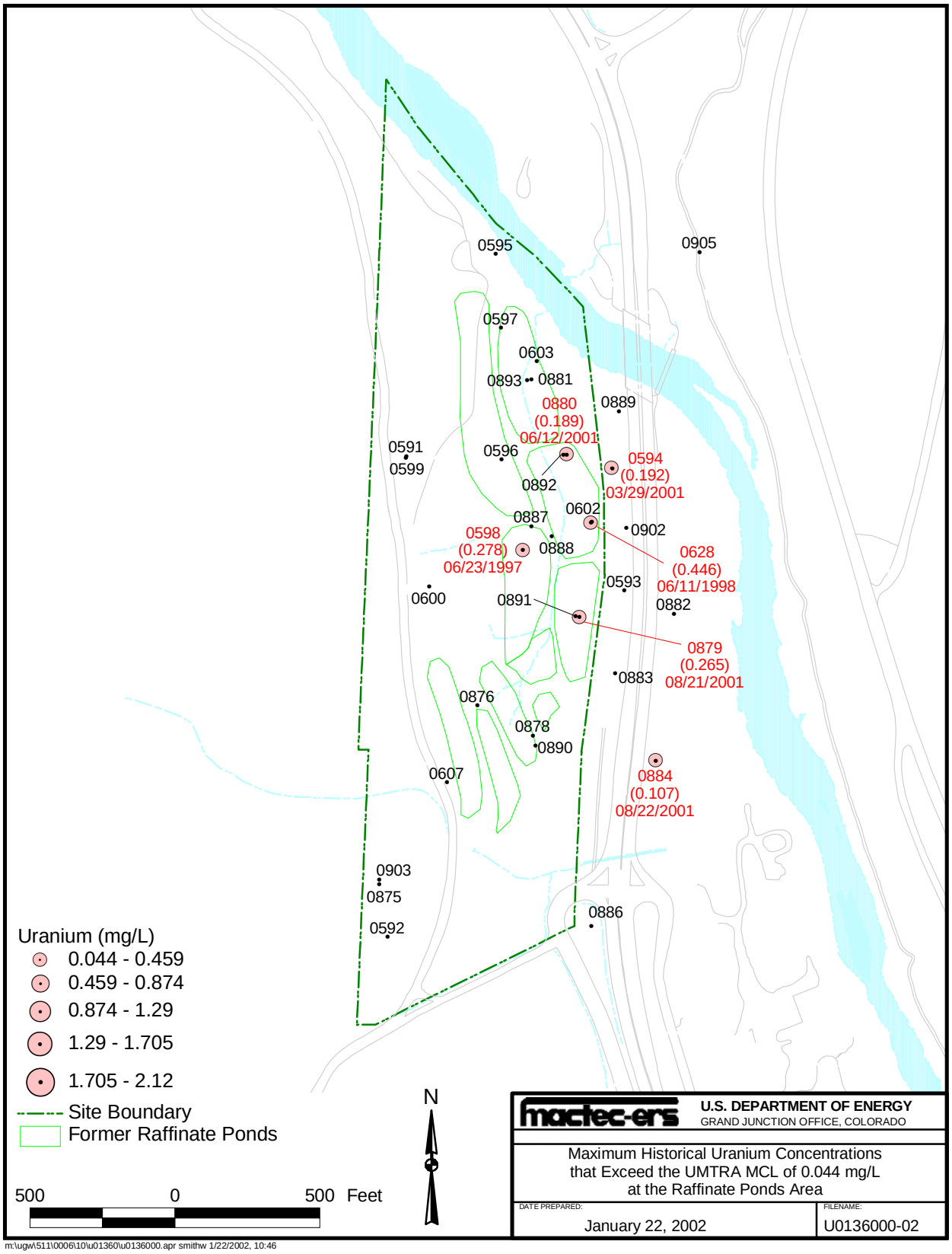

Figure 5–20. Maximum Historical Concentrations of Uranium at the Raffinate Ponds Area

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Selenium and uranium concentrations were greater than their MCLs at wells 0594, 0598, 0628, 0879, 0880, and 0884. At well 0593, the selenium concentration in the sample from August 2001 was greater than the background concentration and the detection limit. Uranium concentrations were greater than the highest background concentration and the detection limit at wells 0602, 0891, and 0892.

5.3.3.3 Point Lookout Aquifer

Table 5–7 lists the maximum background concentrations in Point Lookout Sandstone ground water. Cadmium and lead were not detected. The highest background concentration of manganese was less than the human health risk-basked level and the highest concentrations of molybdenum, selenium, and uranium were less than their MCLs.

Table 5–8 lists the Point Lookout Sandstone wells where selenium concentrations exceeded the MCL. In on-site Point Lookout Sandstone wells, concentrations of cadmium, lead, molybdenum, and uranium were less than their MCLs. Cadmium concentration exceeded both the background and the detection limit at one location in December 2000. The lead concentration exceeded background and the detection limit at well 0893 in December 2000. Manganese concentrations were less than the human health risk-basked level. Molybdenum concentrations exceeded background and the detection limit at well 0887 in November 2000 and at well 0893 in December 2000 and March 2001. All uranium concentrations were above the detection limit but were less than the highest background concentration. Selenium concentrations exceeded the MCL at wells 0596 and 0600, and background well 0599. Selenium concentrations in the remaining samples were below the detection limit.

5.3.4 Fate and Transport of COPCs

In the mill tailings area, antimony, cadmium, iron, lead, lead-210, manganese, molybdenum, polonium-210, radium-226+228, selenium, sodium, sulfate, thorium-230, uranium, and vanadium were identified as COPCs in the Baseline Risk Assessment (BLRA) (DOE 1995a). In the raffinate ponds area, antimony, arsenic, cadmium, chloride, iron, lead, lead-210, manganese, molybdenum, polonium-210, radium-226+228, selenium, sodium, sulfate, thallium, thorium-230, and uranium were identified as COPCs in the BLRA. Analysis of ground water data resulted in the reduction of the number of COPCs to five: cadmium, lead, molybdenum, selenium, and uranium. These five analytes were the only constituents with concentrations that regularly exceeded the MCLs. Although manganese does not have an MCL, it was retained as a COPC because its concentrations were above the human health risk-based level of 1.7 mg/L. Mobility of the COPCs in the subsurface environment is a function of the types of solution complexes formed, the affinity and capacity of the solid-phase adsorption sites for the contaminant, and the solubilities of the reactive minerals containing the contaminant. The dominant solution species are summarized for all aquifers in Table 5–9.

Table 5–9. Dominant Aqueous Species in the Background Ground Waters

Ion	Mill Tailings Area	Raffinate Ponds Area		
	Alluvium	Alluvium	Menefee Formation	Point Lookout Sandstone
Cadmium	Cd^{2+} $CdSO_4$	$CdCO_3$ Cd^{2+}	Cd^{2+} $CdCO_3$	$CdCO_3$ Cd^{2+}
Manganese(II)	Mn^{2+} $MnSO_4$	Mn^{2+} $MnSO_4$	Mn^{2+} $MnSO_4$	Mn^{2+} $MnSO_4$
Molybdenum	$CaMoO_4$ MoO_4^{2-}	MoO_4^{2-} $CaMoO_4$	MoO_4^{2-} $CaMoO_4$	MoO_4^{2-} $CaMoO_4$
Lead	$PbCO_3$ $PbHCO_3^{+}$	$PbCO_3$ $PbHCO_3^{+}$	$PbCO_3$ $PbHCO_3^{+}$	$PbCO_3$ $Pb(CO_3)_2^{2-}$
Selenium(IV)	$HSeO_3^{-}$ SeO_3^{2-}	$HSeO_3^{-}$ SeO_3^{2-}	$HSeO_3^{-}$ SeO_3^{2-}	$HSeO_3^{-}$ SeO_3^{2-}
Uranium(VI)	$UO_2(CO_3)_3^{4-}$ $UO_2(CO_3)_2^{2-}$	$UO_2(CO_3)_3^{4-}$ $UO_2(CO_3)_2^{2-}$	$UO_2(CO_3)_3^{4-}$ $UO_2(CO_3)_2^{2-}$	$UO_2(CO_3)_3^{4-}$ $UO_2(CO_3)_2^{2-}$

Note: Species were predicted using the geochemical computer code PHREEQC2.2 (Parkhurst and Appelo 1999). These species do not take into account changes in redox potential because an average redox potential was used.

5.3.4.1 Cadmium

Cadmium contamination at the mill tailings area is limited to wells 0612 and 0630 (Figure 5–9). Cadmium concentrations at well 0612 range from 0.0258 to 0.0435 mg/L and have exceeded the MCL in seven samples collected from June 1999 through August 2001. With the exception of a single sample in which cadmium concentration exceeded the MCL at well 0630, the zone of contamination is limited to well 0612.

According to geochemical models generated using the computer code PHREEQC2.2 (Parkhurst and Appelo 1999), the dominant aqueous cadmium species in the alluvial ground water are Cd^{2+} and $CdSO_4$ (Table 5–9). The ground water has a mean pH of 6.99, and the conditions are oxidizing. Under these conditions cadmium is soluble and mobile; however, the data do not indicate that cadmium concentrations are increasing in neighboring wells. This may be due to ground water flow direction or to the adsorption of cadmium onto iron and manganese oxyhydroxides. According to the geochemical modeling, ground water is supersaturated in iron hydroxides and iron oxyhydroxides (Table 5–10). Supersaturation indicates sufficient concentrations of ions are present for precipitation of a solid, such as iron hydroxides. Modeling cannot predict when or at what rate precipitation will occur.

Cadmium concentrations in all samples from the raffinate ponds area are below the MCL (Figure 5–15), although concentrations are increasing at wells 0879 and 0884. Alluvial ground water has a mean pH of 7.30; water in the Menefee Formation has a mean pH of 7.10, and Point Lookout Sandstone ground water has a mean pH of 7.44. Redox conditions of the ground waters range from strongly reducing, where the $H_2S_{(aq)}$ concentration is 45.9 mg/L, to oxidizing. Cadmium itself does not respond readily to changes in redox conditions. However, it does respond to redox changes in sulfur species and iron and manganese. If sulfur is present, cadmium will precipitate as a sulfide. Under oxidizing conditions cadmium may precipitate with manganese oxide and adsorb onto iron and manganese oxyhydroxides, which are important substrates for adsorption. According to the geochemical model, ground water from the alluvium and the Point Lookout Sandstone is supersaturated in iron hydroxides and iron oxyhydroxides (Table 5–10).

Table 5–10. Calculated Saturation Indices in the Background Ground Waters

Phase	Mill Tailings Area	Raffinate Ponds Area			
	Alluvium	Alluvium	Menefee Formation	Point Lookout Sandstone	Chemical Formula
Aragonite	**0.14**	**0.40**	**0.25**	**0.68**	$CaCO_3$
Calcite	**0.29**	**0.55**	**0.4**	**0.83**	$CaCO_3$
Dolomite	**0.66**	**1.30**	**1.17**	**1.58**	$CaMg(CO_3)_2$
$Fe(OH)_{2.7}Cl_{0.3}$	**7.02**	**6.02**	**2.59**	**6.52**	$Fe(OH)_{2.7}Cl_{0.3}$
$Fe(OH)_{3\ (a)}$	**2.04**	**1.14**	-2.33	**1.72**	$Fe(OH)_3$
Goethite	**7.93**	**7.03**	**3.56**	**7.61**	FeOOH
Hematite	**17.9**	**16.1**	**9.13**	**17.2**	Fe_2O_3
Jarosite-K	**0.26**	-3.86	-13.38	-2.21	$KFe_3(SO_4)_2(OH)_6$
Magnetite	**19.3**	**17.7**	**9.37**	**18.6**	Fe_3O_4
$Fe_3(OH)_8$	**2.78**	**1.19**	-7.11	**2.13**	$Fe_3(OH)_8$
Rhodochrosite	**0.06**	**0.16**	-0.28	**0.47**	$MnCO_3$
Se(metal)	-5.7	-1.89	**6.76**	-4.26	Se
Siderite	**0.54**	**0.56**	-0.54	**0.35**	$FeCO_3$
Aragonite	**0.14**	**0.40**	**0.25**	**0.68**	$CaCO_3$
Calcite	**0.29**	**0.55**	**0.4**	**0.83**	$CaCO_3$
Dolomite	**0.66**	**1.30**	**1.17**	**1.58**	$CaMg(CO_3)_2$
$Fe(OH)_{2.7}Cl_{0.3}$	**7.02**	**6.02**	**2.59**	**6.52**	$Fe(OH)_{2.7}Cl_{0.3}$

Note: Saturation indices were calculated using the geochemical code PHREEQC2.2 (Parkhurst and Appelo 1999). Phases that are super saturated (positive value) are listed in the table.

5.3.4.2 Lead

Lead concentrations in ground water samples from the mill tailings area are all below the MCL (Figure 5–10**)**. Mobility of lead is naturally low because of its low solubility under both oxidizing and reducing conditions. Lead concentrations may be low because of solubility constraints, adsorption, or precipitation. Under oxidizing conditions, lead may coprecipitate with manganese oxide and adsorb onto organic matter and inorganic surfaces, such as manganese and iron oxides. Iron or manganese solids present in sufficient amounts may scavenge lead from solution. According to the geochemical model, ground water is supersaturated in iron hydroxides and iron oxyhydroxides (Table 5-10). Supersaturation indicates sufficient concentrations of ions are present for precipitation of a solid, such as iron hydroxides. Modeling cannot predict when or at what rate precipitation will occur.

In ground water samples from the raffinate ponds area, lead concentrations are all below the MCL (Figure 5–16). Lead concentrations exceeded background in samples from wells 0603, 0879, 0880, and 0893. Lead levels are not increasing within the raffinate ponds area. Concentrations may be low because of solubility constraints, adsorption, or precipitation. According to the geochemical model, ground water from the alluvium and the Point Lookout Sandstone is supersaturated in iron hydroxides and iron oxyhydroxides (Table 5–10).

5.3.4.3 Manganese

At the mill tailings area, manganese concentrations in ground water have exceeded the risk-based value seven times at well 0612 and two times at well 0630 from June 1999 through August 2001 (Figure 5–11). Manganese mobility is related to redox conditions of the subsurface, and its chemistry is similar to that of iron. Manganese forms oxide minerals under oxidizing conditions and is soluble under reducing conditions. Manganese can substitute for calcium in calcite. According to the geochemical model, the dominant manganese species are Mn^{2+} and $MnSO_4$ (Table 5–9). The geochemical model shows that background ground waters are supersaturated with respect to calcite and various iron minerals (Table 5–10). Supersaturation indicates sufficient concentrations of ions are present for precipitation of a solid, such as iron hydroxides. Modeling cannot predict when or at what rate precipitation will occur.

In the raffinate ponds area, manganese concentrations exceeded the detection limit, background, and the human health risk-basked value in samples from wells 0598 and 0880, and the well cluster 0593, 0879, and 0882 (Table 5–8). Concentrations do not appear to be increasing in those wells but are increasing in well 0892, which is near well 0880. Redox conditions of the ground waters range from strongly reducing, where the $H_2S_{(aq)}$ concentration is 45.9 mg/L, to oxidizing. Under reducing conditions, manganese is dissolved and present in aqueous form. Under oxidized conditions, manganese may be in both aqueous form and precipitated as manganese oxide. Speciation is dependent upon redox conditions. Manganese behavior is similar to that of iron and generally takes longer to precipitate from solution than iron. The geochemical models for water from the alluvium and the Point Lookout Sandstone indicate that background ground waters are supersaturated with respect to calcite and various iron minerals (Table 5–10). Ground water from the Menefee Formation is supersaturated with respect to calcite and is undersaturated for some iron minerals. Undersaturation indicates precipitation of a solid is unlikely.

5.3.4.4 Molybdenum

At the mill tailings area, molybdenum contamination is limited to wells 0612 and 0630 (Figure 5–12). Concentrations do not appear to be increasing at any location, and the data do not indicate molybdenum is migrating. Dominant species include $CaMoO_{4(aq)}$ and MoO_4^{2-} (Table 5–9). Molybdenum has a relatively high geochemical mobility that allows it to enter into solution in water under oxidizing conditions. Molybdenum will precipitate in reduced waters. Solubility controls include precipitation with common metals as metal molybdates. The effectiveness of this control depends on the solubility of the metal. Molybdenum can be adsorbed by amorphous ferric oxyhydroxides. Geochemical modeling indicates that iron minerals are supersaturated in the background ground water (Table 5–10). Supersaturation indicates sufficient concentrations of ions are present for precipitation of a solid, such as iron hydroxides. Modeling cannot predict when or at what rate precipitation will occur.

In ground water samples from the raffinate ponds area, molybdenum concentrations are all below the MCL (Figure 5–18). Two samples from well 0891 indicate concentrations at this location are increasing slightly; levels have increased to values above the detection limit from concentrations that were less than the detection limit. In all other locations, concentrations are not increasing. Dominant species include MoO_4^{2-} and $CaMoO_{4(aq)}$ (Table 5–9). Ground water from the alluvium and from the Point Lookout Sandstone is supersaturated with respect to iron minerals. Ground water from the Menefee Formation is undersaturated with respect to these minerals (Table 5–10).

Table 5–11. Mill Tailings Area Sample Concentrations Greater Than an UMTRA MCL or the Human Health Risk-Based Value for Manganese.

	1999		2000			2001				
Well	**June**	**November**	**June**	**November**	**December**	**March**	**April**	**May**	**June**	**August**
0612	Cd, Mn, U	Cd, Mn, Mo, U	Cd, Mn, Mo, U	Cd, Mn, Mo, U			Cd, Mn, Mo, U		Cd, Mn, U	Cd, Mn, Mo, U
0617	Se, U	Se, U	Se, U	Se, U			Se, U		Se, U	Se, U
0622						Se				
0629										
0630	Se, U	U	Se	U			Mn, U		U	Mn, U
0631	U	U	U	U			U		U	U
0632							Mo			
0633	Se, U	Se, U	Se, U	Se, U			Se, U		Se, U	Se, U
0634						U			U	U
0635						Se			Se	Se
0658										
0857[a]						Se				
0859				U			U			
0863										
0866[a]				Se		Se		Se	Se	Se

NOTE: Listed is the Ground Water Sampling Schedule from June 1999 Through August 2001. The Listed Constituent Exceeded its UMTRA MCL or the Human Health Risk-Based Value for Manganese.

[a] Background well locations

Well was sampled.

Well not sampled.

5.3.4.5 Uranium

Uranium concentrations exceed the MCL and are greater than background concentrations in samples from seven locations (Figure 5–14). Concentrations are increasing in wells 0630 and 0633. In the remaining five wells, concentrations are fluctuating but do not give a steady indication of increasing or decreasing. Uranium concentrations at well 0612 are greater than 1 mg/L. Because there are no wells between well 0612 and the Animas River, the extent and direction of uranium migration is difficult to determine. However, well 0612 is in an area where a lens of uranium was left in place beneath the lead slag following remediation; concentrations may continue to remain elevated (see Section 4.6.2.2). Uranium concentrations at well 0633 have been greater than 1 mg/L in five sampling events. Uranium concentrations have not increased at wells 0617, 0631, and 0632 and may indicate the uranium migration has not extended to these locations or that concentrations have attenuated. According to the geochemical model, the dominant aqueous uranium species are $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ (Table 5–9). The background ground water is supersaturated with respect to calcite, $Fe(OH)_{2.7}Cl_{0.3}$, goethite, hematite, and magnetite (Table 5–10). Under oxidizing conditions, uranium is soluble in ground water and mobile due to the presence of aqueous carbonate, a strong complexing agent. Uranium is often sequestered by adsorption to iron oxyhydroxides in soil or through the precipitation of calcite.

In the raffinate ponds area, uranium concentration in ground water samples from the one alluvial well (0607) and the Point Lookout Sandstone are below the MCL (Figure 5–20). Concentration in samples from the Menefee Formation exceeded the MCL at six wells (0594, 0598, 0628, 0879, 0880, and 0884). Of these locations, well 0598 is along the Bodo Fault. At well 0592, the uranium concentrations are less than the MCL; the screen depth of well 0592 is 42.5 ft, below that of well 0880, where concentrations exceed the MCL. Similarly, uranium concentrations at well 0891 are less than the MCL, and the screen depth of well 0891 is 37.5 ft below that of well 0879, where concentrations are greater than the MCL. In both cases, the well pairs are close to each other. These data suggest uranium concentrations are not increasing with depth. Wells that neighbor the six contaminated wells do not show the influence of contamination and may indicate the uranium migration has not extended to these locations or that uranium concentrations have attenuated. Redox conditions range from reducing to oxidizing. According to the geochemical model, the dominant aqueous uranium species under oxidizing conditions are $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ (Table 5–9). Under reducing conditions, it is likely that uranium is present in solid form, as U(IV). Saturation indices for iron phases depend upon the redox conditions. Under reducing conditions, iron is present in aqueous form; oxidizing conditions produce solid iron phases. Regardless of the redox conditions, all waters are supersaturated with respect to calcite (Table 5–10). Under oxidizing conditions, uranium is soluble in ground water and mobile due to the presence of aqueous carbonate, a strong complexing agent. This mobility is limited under reducing conditions. Uranium mobility can be limited by adsorption to iron oxyhydroxides in soil under oxidizing conditions or through the precipitation of calcite.

5.3.4.6 Selenium

At the mill tailings area, selenium concentrations have exceeded the MCL at eight locations in samples of both background ground water and site ground water (Figure 5–13). Concentrations have increased at wells 0617, 0630, 0633, 0635, and 0866. The mobility of selenium is low. In the presence of iron, selenium may form the mineral $FeSe_2$ and may coprecipitate with pyrite under reducing conditions. Under oxidizing conditions, selenium may be adsorbed on or interact with ferric oxyhydroxides. The geochemical model indicates selenium is present as Se(VI), and the dominant species are $HSeO_3^-$ and SeO_3^2 (Table 5–9). Iron hydroxides and oxyhydroxides are supersaturated in the water (Table 5–10). Supersaturation indicates sufficient concentrations of ions are present for precipitation of a solid, such as iron hydroxides. Modeling cannot predict when or at what rate precipitation will occur.

In the raffinate ponds area, selenium concentrations exceed the MCL in samples from 10 wells (Figure 5–19). Selenium levels in each of these wells have exceeded the MCL at least twice, and the concentration in well 0607 has exceeded the MCL seven times from June 1999 through August 2001. According to the data, selenium concentrations are not increasing in wells downgradient from well 0607. The mean background concentrations range from 0.0069 mg/L in alluvial ground water to 0.075 mg/L in ground water of the Point Lookout Sandstone. Selenium concentrations have been greater than 1 mg/L in five wells (0598, 0628, 0879, 0880, and 0884), all of which are completed in the Menefee Formation. These higher concentrations appear to be limited in location and not part of a continuous plume. Concentration is increasing at well 0628 but is below the detection limit in well 0602, approximately 5 ft downgradient. Selenium concentration in well 0598 is decreasing from its highest value of 2.42 mg/L in April 2001. Yet, adjacent wells 0888 and 0892 have concentrations below the detection limit. Selenium concentrations above the MCL in well 0884 occur in an isolated location downgradient and off

site. Selenium migration may be limited by adsorption and precipitation and is discussed in the following section.

5.4 Selenium at the Raffinate Ponds Area

Selenium is the constituent present at relatively high concentrations in the greatest number of wells at the raffinate ponds area. Selenium concentration has exceeded the MCL on at least one occasion at wells 0593, 0594, 0596, 0598, 0600, 0602, 0603, 0607, 0628, 0879, 0880, and 0884. In wells 0593 and 0600, selenium levels have exceeded the MCL on only one occasion. Concentrations in well 0607 have been increasing since the completion of surface remediation. In the remainder of the wells, historical concentrations of selenium have fluctuated from below detection limits to orders of magnitude above the MCL, often over short periods of time. With the exception of well 0598 screened in the Bodo Fault, the locations where selenium levels are above the MCL are shallow wells (screened 50 ft or less below ground surface). With the exception of wells 0596 and 0600, all wells with elevated selenium concentrations are screened within or below coal or carbonaceous shale units (no concentrations are above the MCL in any of the wells screened solely within the massive sandstone units). Results of the field investigation (along with historical data) indicate that selenium in the ground water is derived from naturally occurring sources (coal, carbonaceous shale, and pyrite), and is not related to raffinate from the ore processing.

Selenium concentrations in all samples from background well 0599 have exceeded the 0.01 mg/L MCL; concentrations have ranged from 0.62 to 0.87 mg/L. Although elevated selenium concentrations are not detected in other background wells at the raffinate ponds area, the ground water in all other background wells is reducing and under reducing conditions selenium is not mobilized into the ground water (in background wells at the mill tailings area where the conditions are oxidizing selenium concentrations exceed the MCL).

As an indication of the abundance of naturally occurring selenium in the area, a hazard rating method was developed to determine whether surface waters would have sufficient selenium to be toxic to aquatic life. This method has been applied to the proposed Animas-La Plata water project. That review indicated the proposed reservoir will cause selenium toxicity in sensitive aquatic life (Lemly 1997). Selenium concentrations in background surface waters, collected by the BOR for the Animas-La Plata project have exceeded the UMTRA MCL (BOR 1996).

5.4.1 Literature Review

It is well known that selenium occurs naturally in high concentrations in the western United States. Most occurrences are related to Cretaceous sedimentary deposits (Seiler 1998), although elevated concentrations are found in rocks from Pennsylvanian to Quaternary age (Stephens and others 1992). Selenium occurrences are usually associated with sulfur because the two elements are closely related in ionic size, permitting selenium to commonly substitute for sulfur in sulfide minerals.

Evaporite deposits from the Mancos Shale are often implicated for degrading water quality in irrigated regions in the Intermountain West (Stephens and others 1992). However, coals can also be sources of selenium. For example, Naftz and Rice (1989) reported total selenium values of 0.5 to 2 mg/kg for early Tertiary sandstones associated with coal seams from the Powder River Basin. Selenium may be the most enriched trace element in coal (Valkovic 1983). The

occurrence of selenium in conjunction with coal has relevance to the Durango site because the Menefee Formation is coal bearing and thus may be a source for the naturally occurring selenium.

Coleman and Delevaux (1957) performed an extensive review of selenium occurrences on the Colorado Plateau. These investigators found the following sulfides contained selenium in decreasing amounts: galena, chalcopyrite, arsenopyrite, sphalerite, pyrite, and pyrrhotite. Selenium was also found to be associated with pyrite and coalified wood in Emery County, Utah. Samples of pyrite and marcasite collected from the Mancos Shale near Slick Rock, Colorado, had an average of 140 mg/kg of selenium. The highest selenium level in Colorado Plateau pyrites or marcasites reported in their study was 300 mg/kg. Chalcocite (Cu_2S) in the Slick Rock district contained as much as 1.2 percent (12,000 mg/kg) selenium. However, of particular importance to the circumstances at Durango is the selenium content of pyrite, which is abundant in the bedrock units underlying the site (Section 4.2).

5.4.2 Durango Site Historical Data

Historical data indicate selenium was not unusually abundant in the Durango processing operations and was not detected at all in the effluent (raffinate) that flowed to the raffinate ponds area (Tsivoglou and others 1960). This suggests that highly variable and increasing selenium concentrations at the raffinate ponds area are not a result of contamination associated with uranium processing operations.

In 1958 and 1959, the U.S. Department of Health, Education, and Welfare conducted an intensive field study of interstate pollution of the Animas River, with special emphasis on the contributions from the Durango processing site while the mill was in operation. The studies were a cooperative effort of the Public Health Service, the New Mexico and Colorado State Departments of Health, the San Juan County Health Department, and the AEC (Tsivoglou and others 1960). The studies included extensive sampling (over a period of several months in 1958) of the main plant discharges, the tailings pond discharges, and the organic raffinate effluents (acid liquor from solvent extraction) (Tsivoglou and others 1960). Additional samples were collected through the first half of 1959 by State of Colorado and local health agencies.

The studies concluded seepage from both the tailings piles and the raffinate ponds contained a similar suite of contaminants derived from the processing reagents. The analyses indicated the tailings seepage was more diluted, with a pH of 4.1 and total dissolved solids (TDS) of 8,450 mg/L. By contrast, seepage from the raffinate ponds had a pH of 0.8 and a TDS of 116,000 mg/L. (Tsivoglou and others 1960). However, dissolved selenium was not detected in either contaminant source (it was present in the main plant effluent). Chemical analyses of the raffinate ponds liquor as reported by Tsivoglou and others (1960) is shown in Table 5–12.

Table 5–12. Chemical Analyses of Mill Discharge to the Raffinate Ponds

Chemical	Concentration (mg/L)
Arsenic	16
Selenium	<0.01
Beryllium	30
Vanadium	250
Copper	23
Manganese	200
Iron	370
Sodium	16,000
Fluoride	12
Sulfate	66,000
Chloride	6,500
Total Hardness	20,000
Total Dissolved Solids	116,000
PH	0.8

Historical data and the occurrence of selenium in background well 0599 (Section 4.6.3.1) indicate variable and increasing selenium concentrations in ground water at the raffinate ponds are related to naturally occurring sources of selenium, and not the former mill operations.

5.4.3 Data Review of Selenium in Well 0628

Because of the screen length and current condition of well 0628, analytical results from this well are not considered to be a valid and reliable assessment of ground water conditions at this location. However, results from this well are included in the discussion because of anomalously high selenium concentrations detected from 1993 to the present (Table 5–13). Selenium concentrations in well 0628 have historically demonstrated a large degree of fluctuation, with values ranging from 0.14 mg/L to a most recent value of 19.4 mg/L. Well 0628 is screened continuously from its total depth of 32 ft to 2 ft below the surface, and the protective concrete surface pad is no longer intact. Analytical results from this well may reflect the transport of surface or near-surface materials into the well by precipitation, runoff from storm events, or snowmelt.

As shown in Plate 3, the screened interval nearly to the surface in well 0628 is near a subcropping zone of coal beds in the Menefee Formation. The screened interval is not shown at the ground surface in the cross section because it was projected to identify lithology. These nearby subcropping coal beds are a likely source for selenium to be mobilized by increasing contact with oxidizing water. This interpretation is supported by the correlation between water levels and selenium concentrations in this well. As shown in Figure 5–21, with the exception of the most recent value, there is a direct correlation between water levels and selenium concentrations.

Well 0602 is downgradient within 5 ft of well 0628, but with a screened interval from 32 to 57 ft. Selenium concentrations in well 0602, although variable (the well is screened in a coal bed), have been below the detection limit since 1990, indicating that elevated selenium concentrations are not derived from ground water flow below the water table. Sampling events for well 0602 since 1993 are listed in Table 5–13.

Table 5–13. Selenium Concentration in Well 0628 at the Durango Raffinate Ponds Area

Date Sampled	Concentration (mg/L)
11/21/1993	1.11
06/03/1994	0.14
11/03/1994	1.70
10/29/1995	0.33
06/19/1997	6.54
06/11/1998	1.85
06/29/1999	0.70
11/11/1999	2.66
06/21/2000	4.01
12/06/2000	1.77
04/04/2001	12.3
06/12/2001	10.9
08/21/2001	19.4

The values for iron in well 0628 have also decreased dramatically since 1995 (Figure 5–22), indicating the ORP has likely increased, which enhances the mobilization of naturally occurring selenium.

Well 0628 was installed in 1993, and since that time concentrations of uranium, sulfate, and TDS have all shown a clear downward trend. The decrease in levels of millsite-related constituents in well 0628, the absence of selenium in deeper adjacent well 0602, and the increasing oxidation (decreasing iron concentrations) indicate geochemical conditions are mobilizing naturally occurring selenium in the nearby subcropping coal beds.

5.4.4 Data Review of Selenium in Well 0607

At the raffinate ponds area, only well 0607 has data before and after surface remediation (from 1982 to present). Other wells in place before remediation were lost because of the on-site activities associated with remediation (except well 0602, see Section 4.1.2). Post-remediation (1991) well 0607 has had an increase in selenium from near the detection limit to nearly 1 mg/L. The increase in concentration is not correlated with increases in other uranium-ore related contaminants.

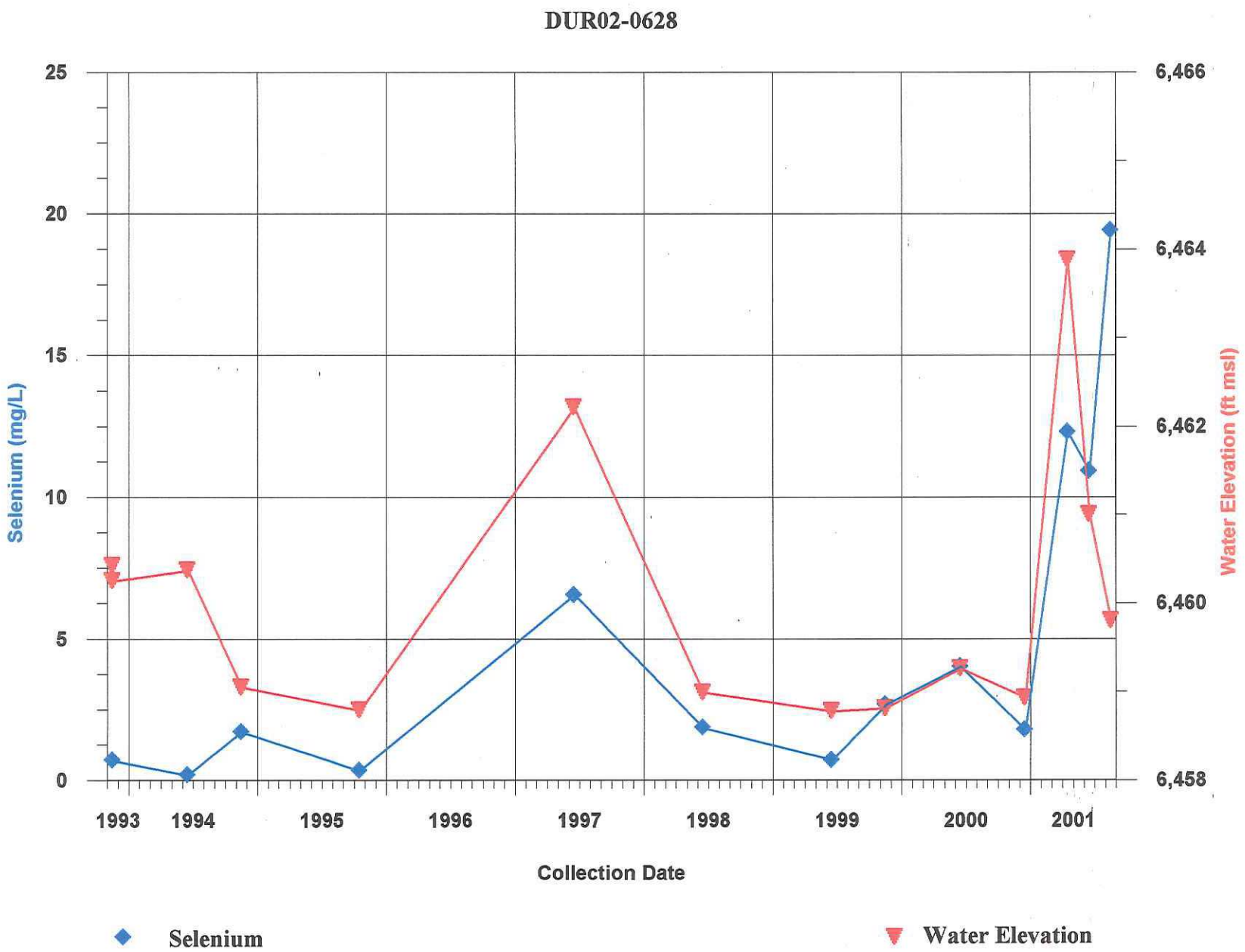

Figure 5–21. Selenium Concentrations and Ground Water Elevations at Well 0628

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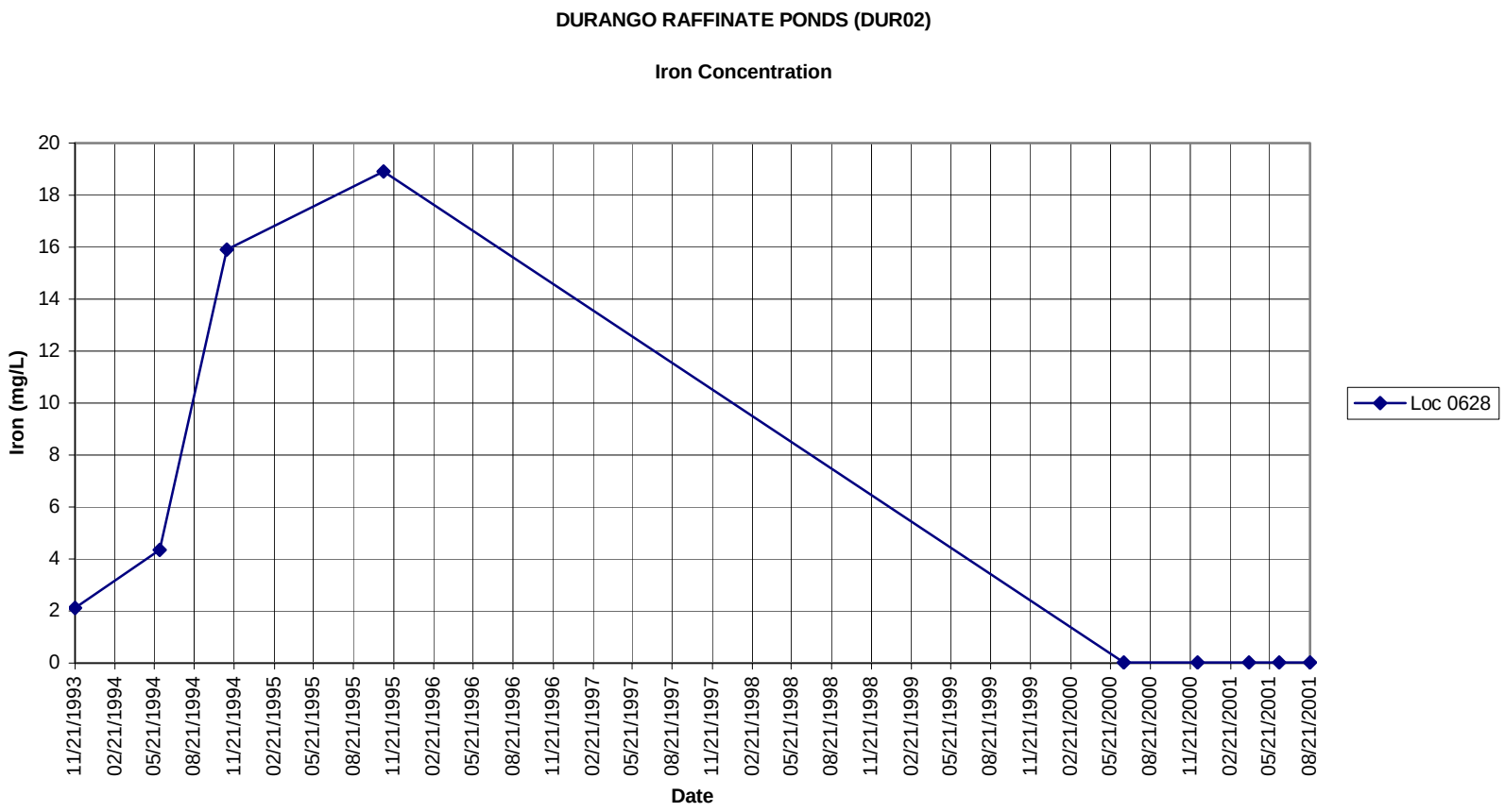

Figure 5–22. Time-Concentration Plot of Iron in Well 0628

A review of the data for well 0607 indicates that increased selenium is not due to the former processing operations. The reasons are as follows

- Well 0607 is hydraulically upgradient from the former raffinate ponds. Ground water in the area of well 0607 is receives surface recharge from South Creek (Section 5.2.2). Because ground water flows past the well toward the former ponds, the former ponds are not a source for the increasing selenium concentrations in well 0607.
- All available data regarding contamination at the site, historical evidence regarding selenium occurrence, and geochemical principles that explain selenium mobility indicate that if selenium were from the uranium operations, concentrations of other contaminants (e.g., uranium, molybdenum) would increase in the same manner. The fact that only selenium levels are increasing indicates its source is not the former uranium operations.
- Geochemical changes in ground water from pre-to post-remediation explain the dissolution of selenium from the Menefee Formation. As noted by Masscheleyn and others (1990), "Redox potential and pH are key factors in the biogeochemistry of selenium." Little change in pH has been observed; thus, an increase in naturally occurring selenium would require an increase in the redox potential. Plots of iron and ORP versus time (Figure 5–23 through Figure 5–25) demonstrate redox potential has increased. Iron precipitates when the pH is near neutral and conditions are oxidizing. The plot of iron versus time shows a significant decrease from pre- to post-remediation, indicating an increase in redox potential. Similarly, although there is not a large ORP database, the data available indicate an increase in ORP. Collecting valid ORP measurements is difficult and the results are often unreliable, or at best usable to compare general redox conditions and very general trends. Processes associated with the precipitation of iron under oxidizing conditions are well understood and are probably the more reliable indicators of redox conditions.
- Except for the levels of selenium (Figure 5–26), ground water quality has improved. For the selenium increase to be caused by site-related activities, the overall water quality of the aquifer should be degraded further as well. At other millsites, water contaminated by past uranium-ore processing activities has high a concentration of dissolved solids, a high alkalinity, and a high conductance. The ions chiefly responsible for TDS, alkalinity, and conductance (e.g., sodium, calcium, sulfate, carbonate) are highly mobile in ground water. There is no explanation for how these could decrease while an associated contaminant could increase. As shown in Figure 5–27 through Figure 5–29, TDS, alkalinity, and conductance have all decreased since remediation. In other words, with respect to general water quality, the water in well 0607 has been diluted with cleaner water since remediation. Hence, the only explanation for the increase in selenium is that an influx of water with greater oxidation potential is causing the release of naturally occurring selenium from the aquifer solids.

Figure 5–23 shows all historical iron concentrations for well 0607, and Figure 5–24 shows more recent concentrations in detail. The results are notable because of the time frame when redox conditions began to change. As shown in the figures, the increase of ORP and the resulting decrease in iron concentrations began in 1983, approximately 4 years before surface remediation began. This indicates surface remediation activities were not a factor in changing the oxidizing conditions at this location.

5.4.5 Selenium Concentrations Before Surface Remediation

Before surface remediation, ground water in the raffinate ponds area occurred in both the surficial deposits and the bedrock (DOE 1995a). At present, ground water occurs primarily in the

bedrock units. Prior to the start of surface remediation in 1987, selenium concentrations exceeded the MCL in seven raffinate ponds area wells, all of which were subsequently abandoned during remediation. Figure 5–30 shows the maximum selenium concentrations in wells sampled from 1982 to 1986 (prior to remediation) where the MCL was exceeded. Tables 5–14 through 5–16 show pre-remediation selenium and uranium concentrations at these locations.

Table 5–14. Selenium and Uranium Concentrations in Alluvial Wells from 1982 to 1985 at the Raffinate Ponds Area

Well	Date Sampled	Selenium (mg/L)	Uranium (mg/L)
0606	09/01/1982	6.80	1.10
0606	07/01/1983	2.40	0.76
0606	08/15/1983	3.00	1.00
0606	11/10/1983	3.70	2.00
0606	03/14/1985	2.64	-
0623	09/01/1982	0.929	0.80
0623	07/01/1983	1.60	0.71
0623	08/15/1983	1.80	0.50
0623	11/01/1983	2.20	0.60
0625	09/01/1982	0.34	1.20
0625	07/01/1983	2.00	2.90
0625	08/15/1983	0.96	2.00
0625	11/01/1983	0.43	2.40

Table 5–15. Selenium and Uranium Concentrations in Bedrock Wells from 1982 to 1985 at the Raffinate Ponds Area

Well	Date Sampled	Selenium (mg/L)	Uranium (mg/L)
0602	09/01/1982	ND	0.01
0602	07/01/1983	ND	0.02
0602	08/15/1983	ND	0.03
0602	11/01/1983	0.02	0.50
0602	03/14/1985	0.06	-
0602	11/10/1985	ND	1.31
0603	09/01/1982	ND	0.002
0603	07/01/1983	ND	0.004
0603	08/15/1983	ND	0.002
0603	11/01/1983	ND	0.003
0603	03/15/1985	0.01	-
0603	11/10/1985	ND	0.004

ND = Not Detected

Table 5–16. Selenium and Uranium Concentrations in Bodo Fault Wells from 1982 to 1985 at the Raffinate Ponds Area

Well	Date Sampled	Selenium (mg/L)	Uranium (mg/L)
0610	09/01/1982	0.014	0.026
0610	07/01/1983	0.03	0.083
0624	09/01/1982	0.042	0.70
0624	07/01/1983	0.03	0.58
0624	08/15/1983	0.02	1.00
0624	11/01/1983	0.03	0.40
0624	03/15/1985	2.56	-

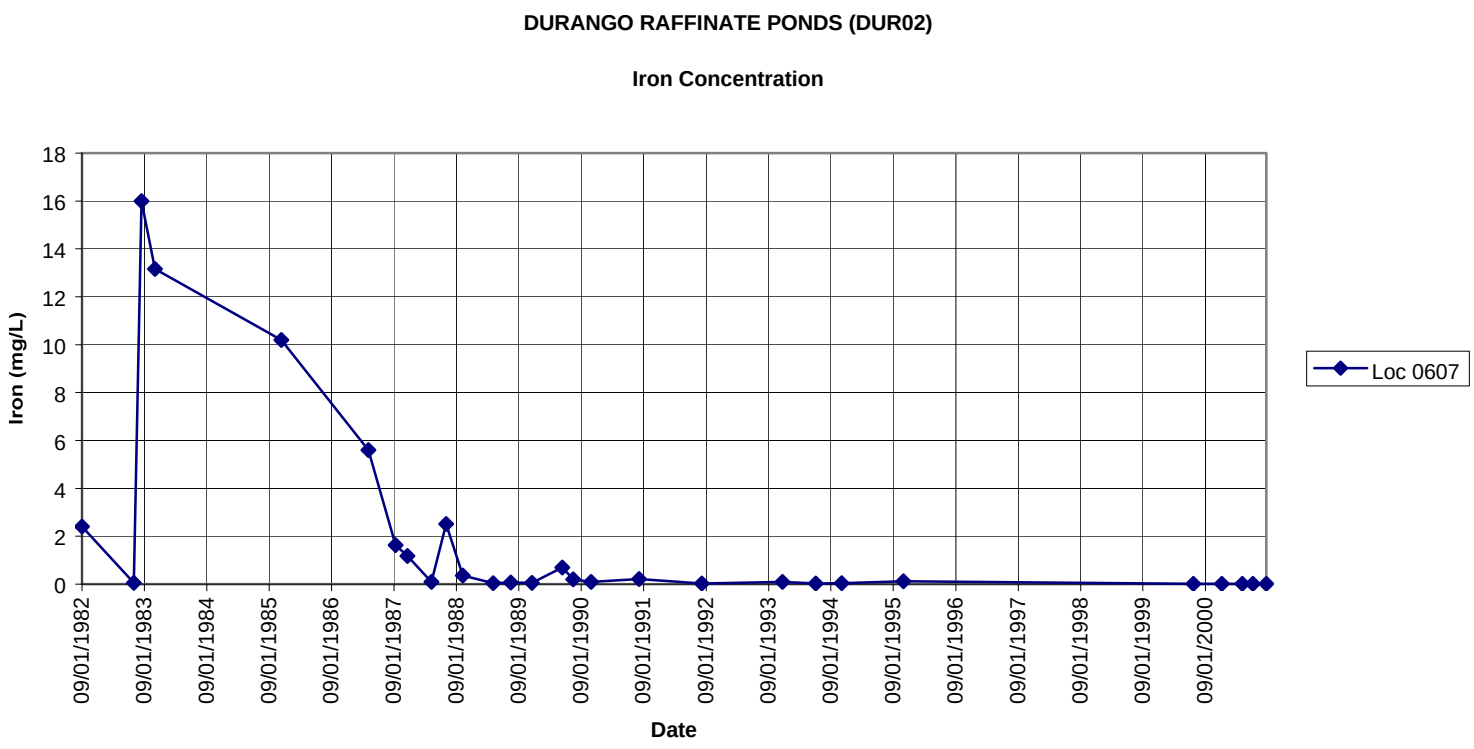

Figure 5–23. Time-Concentration Plot of Iron in Well 0607

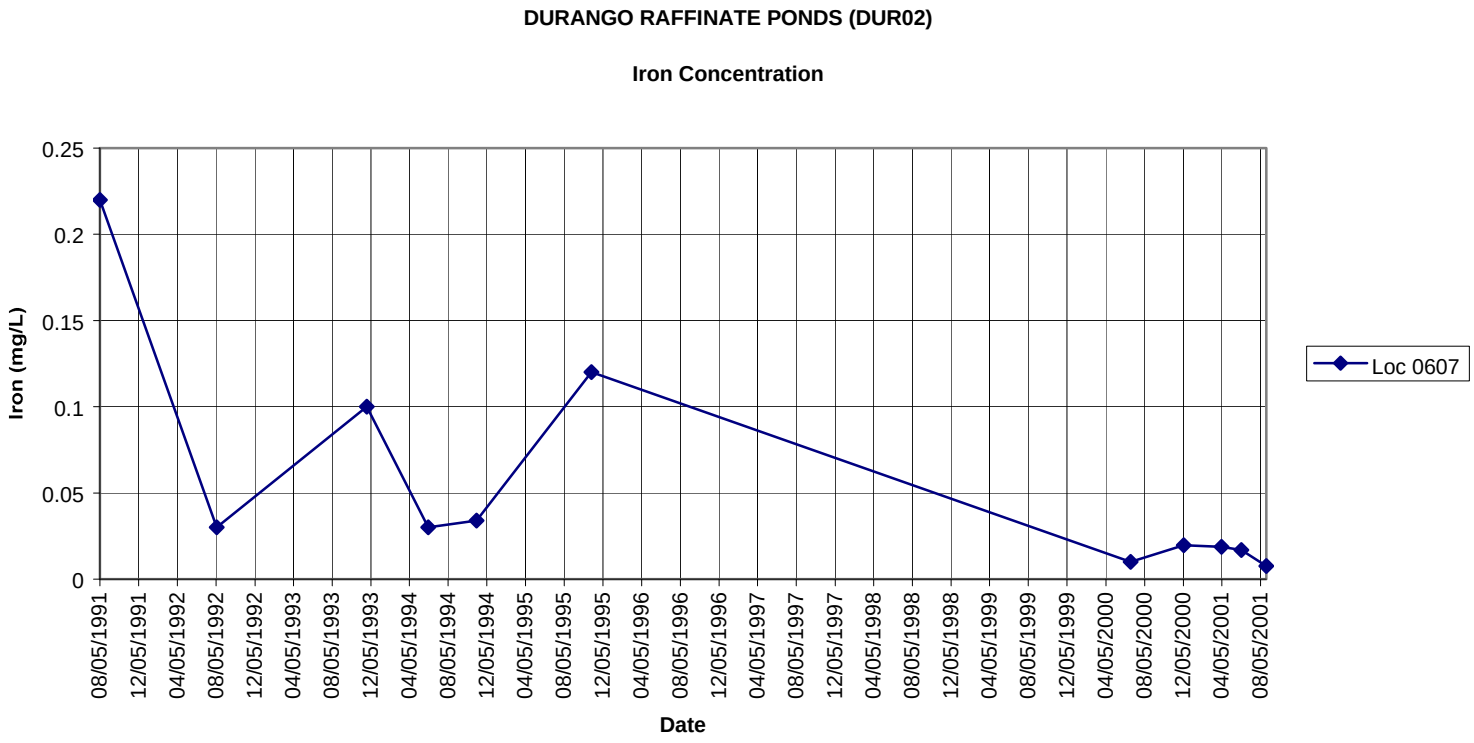

Figure 5–24. Time-Concentration Plot Detail of Iron in Well 0607

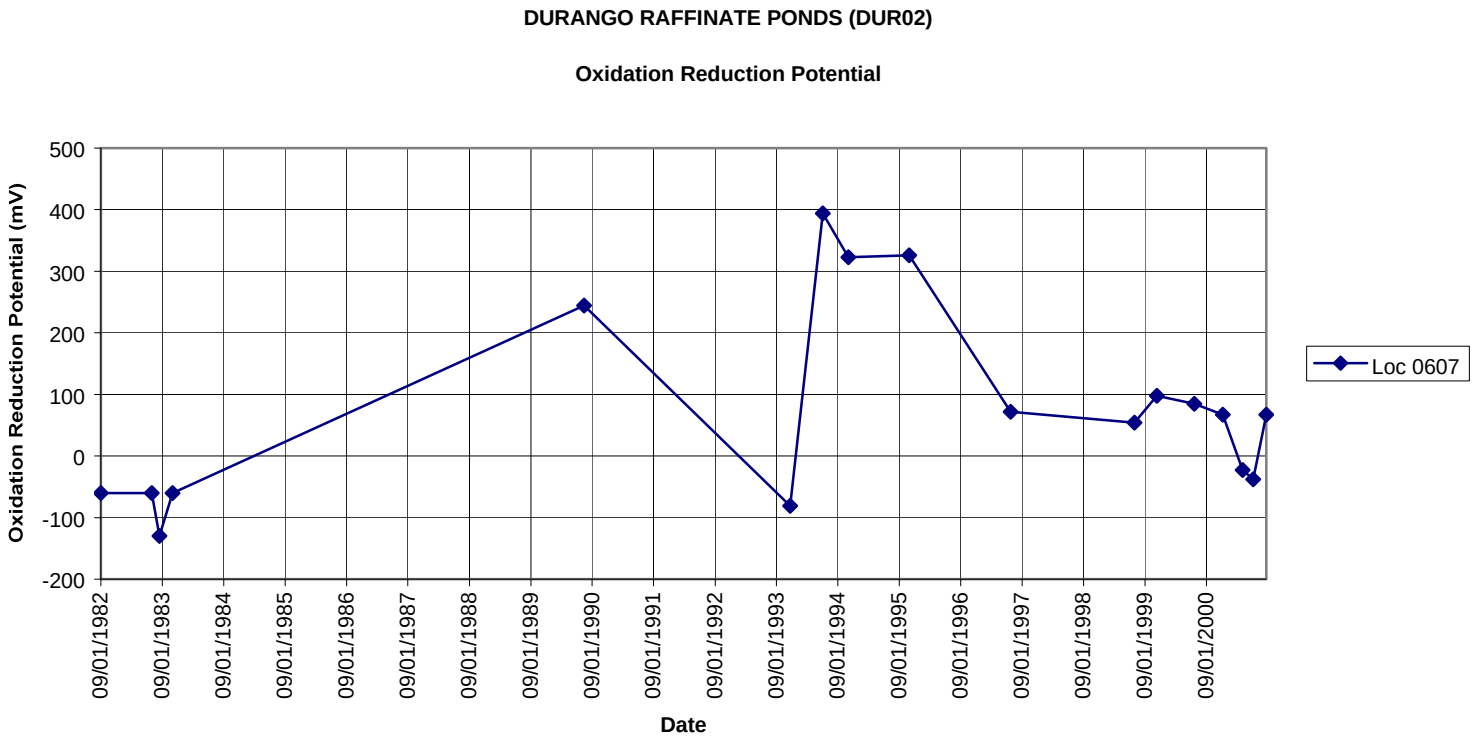

Figure 5–25. Oxidation Reduction Potential Measurements in Well 0607

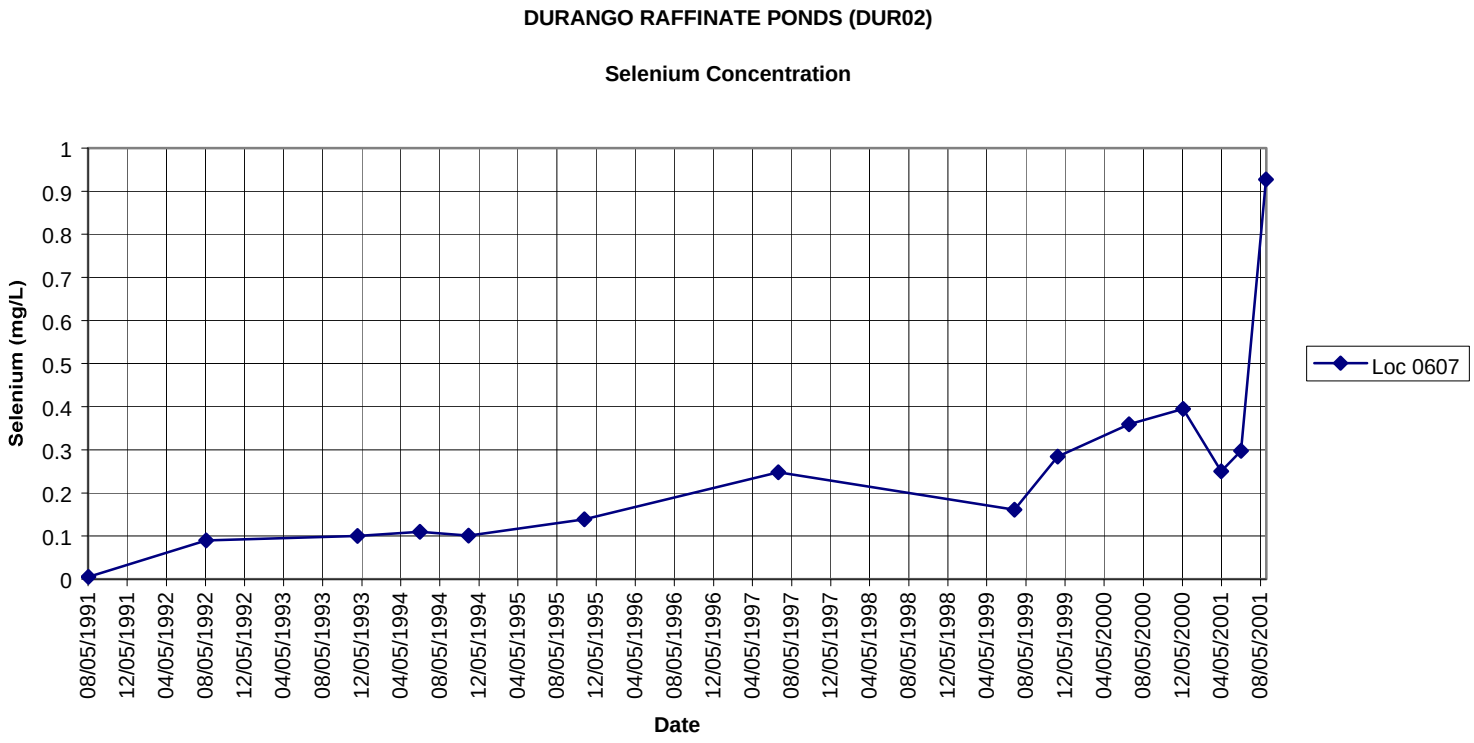

Figure 5–26. Time-Concentration Plot of Selenium in Well 0607

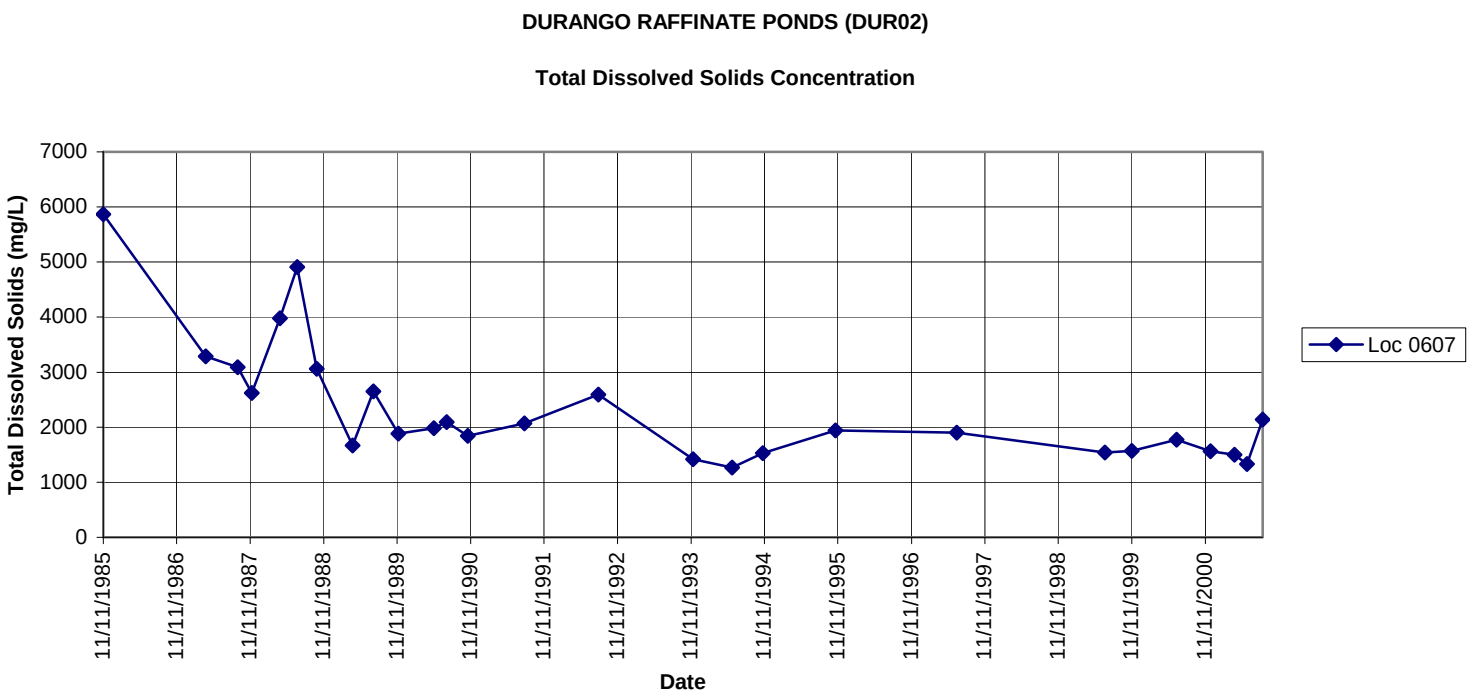

Figure 5–27. Time-Concentration Plot of TDS in Well 0607

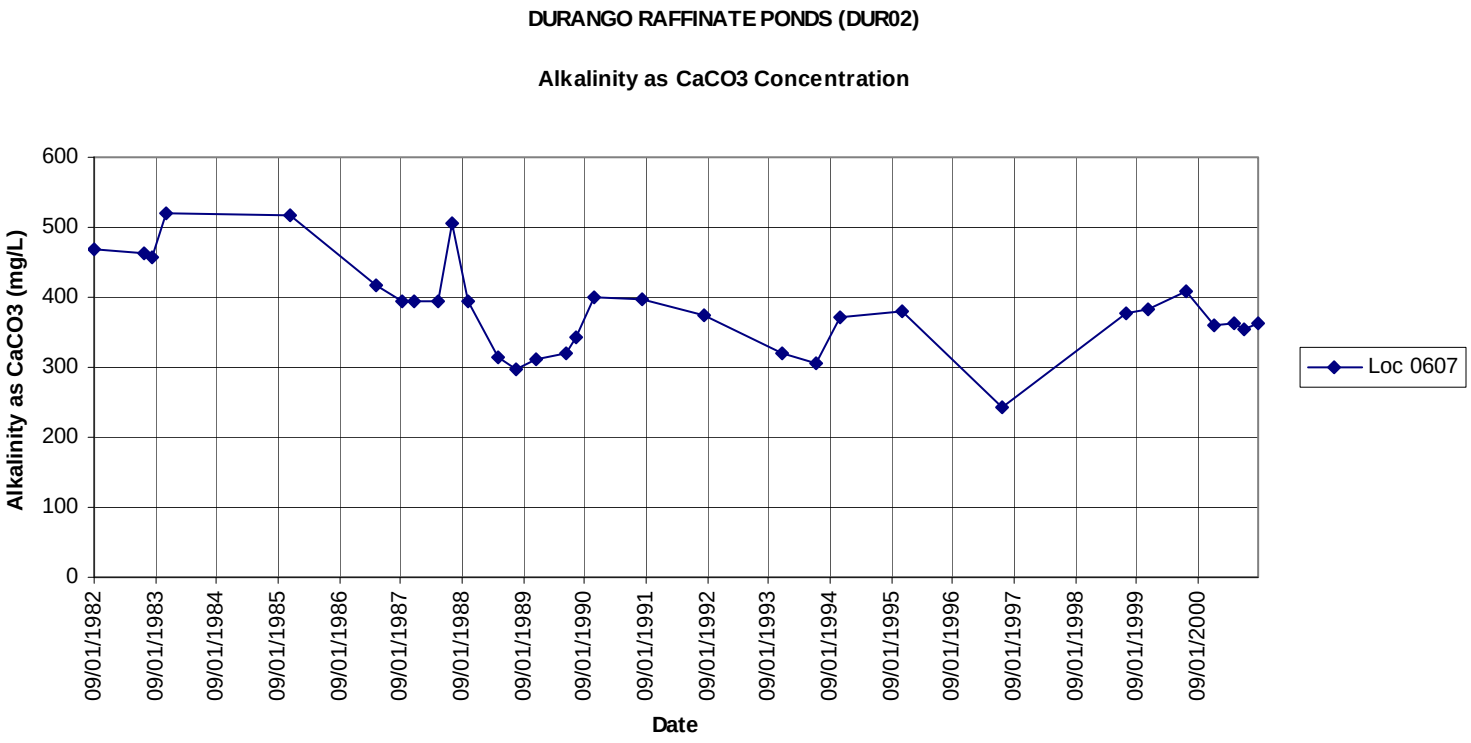

Figure 5–28. Time-Concentration Plot of Alkalinity as $CaCO_3$ in Well 0607

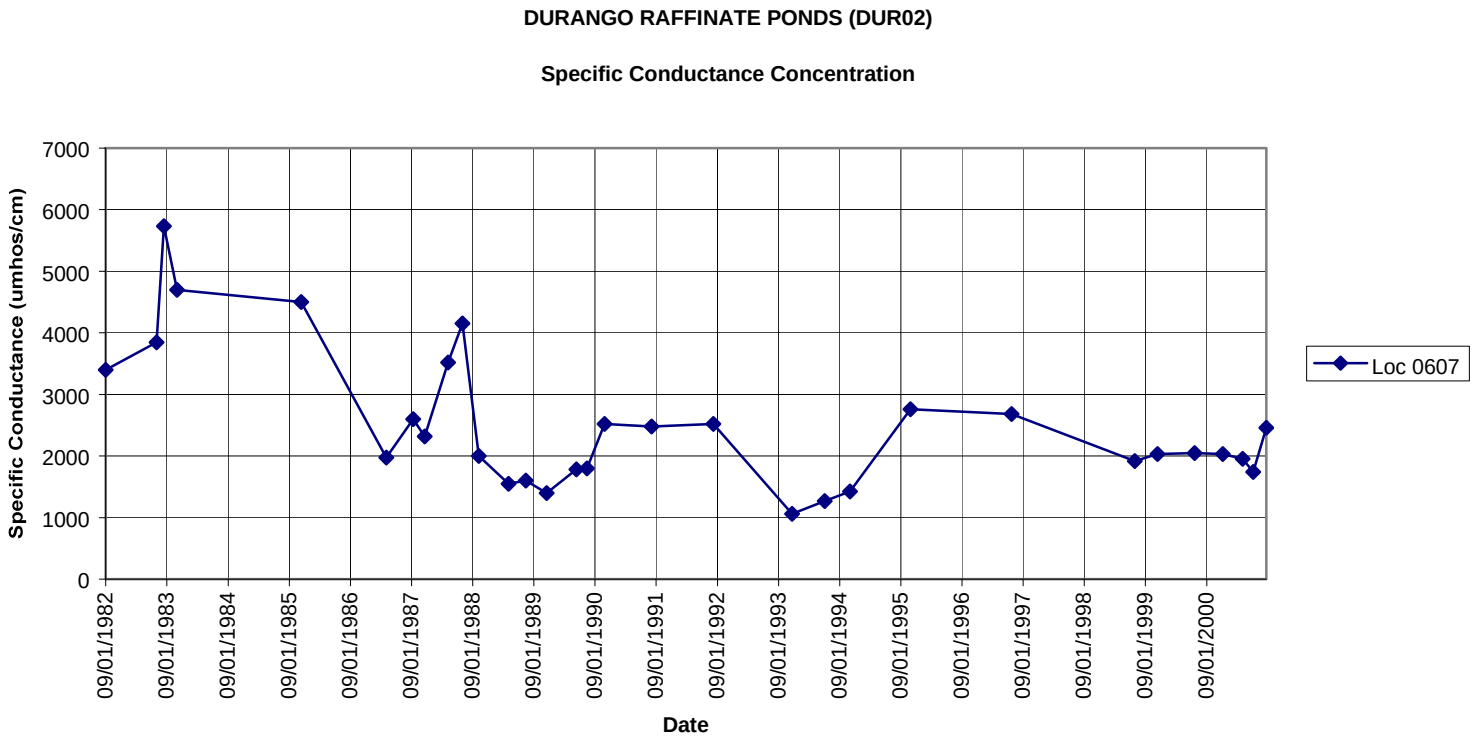

Figure 5–29. Specific Conductance in Well 0607

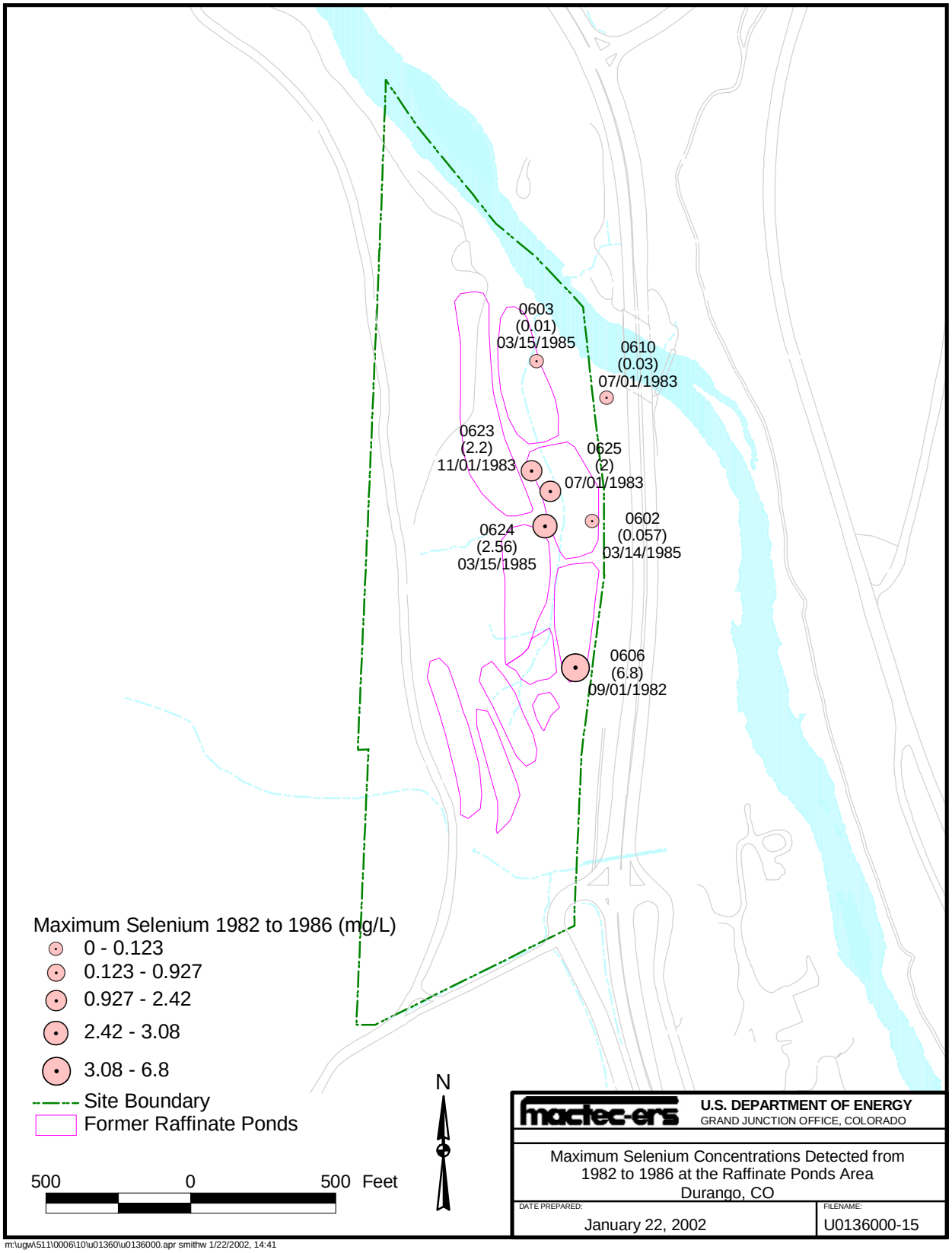

Figure 5–30. Maximum Selenium Concentrations Detected from 1982 to 1986 at the Raffinate Ponds Area

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Selenium concentrations from historical alluvial wells are presented in Table 5–14. In alluvial well 0606, concentrations of selenium decreased from 1982 to 1985 (6.80 to 2.64 mg/L); uranium concentrations ranged from 76 to 1.10 mg/L, with one slightly higher occurrence of 2.0 mg/L. Concentrations of both constituents were above their respective MCLs. Well 0606 was identified as an alluvial well, but the well completion log shows it was screened in the upper shales of the Menefee Formation (Appendix A).

Alluvial well 0607 is not shown in Table 5–14 because all selenium and uranium values were below the detection limit during the 1982 to 1985 time period. This is the only historical well that still exists and is screened across gravels above the Menefee Formation and its contained coal and carbonaceous shales. This is the only present day occurrence of alluvial ground water at the raffinate ponds area.

In alluvial well 0623, concentrations of selenium increased from 0.929 to 2.20 mg/L; uranium concentrations remained relatively unchanged (between 0.50 and 080 mg/L). Concentrations of both constituents were above their respective MCLs. This well was screened in gravels directly above the upper shales of the Menefee Formation.

In alluvial well 0625, concentrations of selenium and uranium showed no specific trend; selenium results show one anomalously high value, and uranium results show one anomalously low value. Concentrations of both constituents were above their respective MCLs. This well was screened in gravels directly above the upper shales of the Menefee Formation.

If alluvial soils at the raffinate ponds area were a continuing source for selenium contamination in ground water prior to their removal, then selenium concentrations in alluvial wells would have been expected to remain at elevated concentrations as long as the source was present.

Selenium concentrations in bedrock wells from 1982 to 1985 are shown in Table 5–15. In bedrock well 0602, concentrations of selenium show no trend; some are below the detection limit and others above the MCL. Uranium levels trend upward during this period from 0.012 to 1.31 mg/L. This well was screened in two locations in the Menefee Formation; the upper screen was in sandstone and the lower screen was in coal.

Selenium concentrations in bedrock well 0603 show no trend; all concentrations are below the detection limit except for one value at the MCL. Uranium concentrations remained relatively unchanged (0.002 to 0.004 mg/L). A description of the lithology for this location is not available.

Table 5–16 shows selenium and uranium concentrations in wells completed in the Bodo Fault zone. In bedrock well 0610, only two values each were available for selenium and uranium.

In Bodo Fault well 0624, selenium values show no trend, although one value is significantly above the MCL at 2.56 mg/L. Uranium values show no real trend; concentrations range from 0.40 to 1.0 mg/L.

Data from wells that existed before surface remediation, monitor wells installed by the BOR, and the most recent monitor wells installed as part of this field investigation, indicate selenium concentrations across the site, historically and at present, are variable and in some cases increasing, and concentrations of other mill-related contaminants are decreasing. The variability (over short periods in some cases) suggests that levels of selenium are not a result of residual contamination but rather geochemical conditions. Under oxidizing conditions selenium exists

dominantly as selenate, and the selenite forms dominate under more reducing conditions. Under conditions at the raffinate ponds area, it is probable selenide in the coal or pyrites is oxidized (a rapidly occurring process) to selenite, which converts to hydrogen selenite because of the pH. Hydrogen selenite is then oxidized to selenate, which is a slow process (Korte 2000). Also, historical selenium concentrations above the MCL in wells that existed prior to surface remediation indicate that remediation activities did not contribute to increasing the selenium concentrations.

5.4.6 Selenium Summary

Several lines of evidence argue against the possibility that contamination associated with uranium-ore processing could be responsible for the recent increases and historical variability in selenium concentrations from certain wells. The most important is that selenium levels have increased without corresponding increases from the other site-related contaminants. Ground water investigations at numerous other UMTRA Project sites indicate selenium is not the dominant water-related contaminant from a uranium-ore processing operation. This experience is supported by examples shown by DeVoto (1978). When uranium ore is formed due to redox processes (the probable source for all the ore processed at Durango), selenium is the first oxyanion to precipitate when the dissolved constituents enter a reducing zone (DeVoto 1978). In the geochemical circumstances under review, uranium, arsenic, selenium, vanadium, and molybdenum are all oxyanions as dissolved species. Selenium levels can still be significantly elevated in the uranium ore, but typically molybdenum and vanadium will be present in higher concentrations. Thus, wherever selenium contamination related to uranium-ore processing is found, there are higher concentrations of other contaminants, particularly uranium and molybdenum. Vanadium and arsenic are also usually present in ground water contaminated by uranium processing. The fact that selenium is the sole element of this group to increase in concentration at the raffinate ponds area indicates the increase is not related to uranium-ore processing. Moreover, existing evidence demonstrates that selenium was not unusually abundant in the Durango processing operations, as shown by the following facts:

- Samples of raffinate from the original process water did not show selenium levels were elevated relative to other ore-related contaminants (Tsivoglou and others 1960).

- Present-day pore water associated with tailings from the site contained the oxyanion contaminants in the following proportions: uranium (2.6 mg/L), molybdenum (0.89 mg/L), selenium (0.17 mg/L), and arsenic (0.16 mg/L) (MSE 1999).

These data indicate selenium was not the dominant contaminant associated with either the raffinate or the tailings. This fact is further demonstrated by the zero-valent iron treatment cell used to remove contaminants in leachate from the tailings repository. A black-orange sludge formed on top of the iron on the inlet side of the tank. This sludge was 0.7 percent selenium, which was the highest of the oxyanions except for vanadium, showing that selenium was preferentially removed under somewhat less reducing conditions than other contaminants that precipitated to a greater degree farther inside the treatment cell. The mass balance for oxyanions removed from the treatment cell clearly demonstrated selenium was not the dominant oxyanion.

A similar situation was evident during surface and ground water remediation of the former uranium-ore processing mill in Monticello, Utah, under CERCLA. At Monticello, selenium levels began to increase dramatically in downgradient wells following remediation where

contaminated soil was removed above the Mancos Shale and Dakota Sandstone formations (DOE 2001c). Like the Point Lookout Sandstone and Menefee Formation, the Dakota Sandstone has an abundance of coal, carbonaceous shale, and pyrite.

5.5 Ground Water Flow and Transport Modeling

The BOR has developed a ground water flow model for the raffinate ponds area for purposes related to the proposed Animas-La Plata pumping plant. It would not be prudent for two federal agencies to expend effort in modeling the same site. Therefore, the DOE did not develop a ground water flow and transport model for the raffinate ponds area. Instead, the BOR model was reviewed and results were incorporated in the developing the hydrogeology portion of the conceptual site model (Section 5.2).

A ground water flow and transport model was developed for the mill tailings area to evaluate whether natural processes will reduce site-related contaminant concentrations below applicable standards within 100 years. The contaminants modeled were cadmium, manganese, molybdenum, selenium, sulfate, and uranium. Appendix G contains the details of this modeling.

The first step of the modeling process included development of a steady-state stochastic flow model, which was then used as the basis for a steady-state stochastic transport model. Both stochastic models are able to quantify uncertainty in both the flow and transport parameters. Contaminant transport was simulated for each of the six contaminants using the stochastic transport model.

Based on the modeling results, natural flushing appears to be an acceptable compliance strategy that allows natural processes to reduce ground water contaminant concentrations to levels below applicable UMTRA Project standards for molybdenum and uranium. Modeling results also indicate manganese and sulfate concentrations will be reduced below the risk-based and background concentrations, respectively. Because of the relatively high K_d values determined for selenium, modeled concentrations of this contaminant will not decrease below the UMTRA Project Standard of 0.01 mg/L. However, selenium will naturally flush below the value of 0.05 mg/L from the EPA's Safe Drinking Water Act (EPA 1996). The expected concentration after 100 years is 0.0246 mg/L. Cadmium concentrations will not drop below the UMTRA Project standard of 0.01 mg/L after 100 years because of the very high K_d value measured for this contaminant.

The existing ground water flow pattern at the mill tailings area was modeled using the MODFLOW software (McDonald and Harbaugh 1988), a finite-difference three-dimensional hydrologic flow model published by the USGS. Output from the flow model was used as input to MT3DMS (Zheng and Wang 1999), a version of a modular three-dimensional transport model that simulates advection, dispersion, and chemical reactions in the ground water system. 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. A summary of the modeling results is provided in the following section.

Steady State Stochastic Modeling Results

Input flow parameters with the most impact on results include horizontal hydraulic conductivity (for three different zones) and recharge; the most sensitive transport parameters include K_d and

longitudinal dispersivity. Table 5–17 presents the maximum average contaminant concentrations (the maximum concentration calculated for each realization, averaged over 100 realizations) for selected time intervals and the associated probability of exceeding the applicable standard for each contaminant.

Table 5–17. Predicted Maximum Average Contaminant Concentrations for Selected Time Intervals

	Contaminant											
	Cadmium		**Manganese**		**Molybdenum**		**Selenium**		**Sulfate**		**Uranium**	
Concentration Goal	0.01 mg/L		1.7 mg/L		0.1 mg/L		0.05 mg/L		1,276 mg/L		0.044 mg/L	
Source	MCL		Risk-based		MCL		EPA–SDWS[c]		Background		MCL	
Time (yrs)	**Conc[a] (mg/L)**	**Prob[b] (%)**	**Conc[a] (mg/L)**	**Prob[b] (%)**	**Conc[a] (mg/L)**	**Prob[b] (%)**	**Conc[a] (mg/L)**	**Prob[b] (%)**	**Conc[a] (mg/L)**	**Prob[b] (%)**	**Conc[a] (mg/L)**	**Prob[b] (%)**
5	0.0365	100	3.848	100	0.0812	0	0.0686	100	2,792	100	1.3650	100
10	0.0363	100	3.505	100	0.0652	0	0.0625	100	2,537	100	1.0820	100
15	0.0362	100	3.234	100	0.0519	0	0.0576	86	2,310	100	0.8628	100
25	0.0357	100	2.794	100	0.0318	0	0.0500	54	1,919	100	0.5311	100
50	0.0347	100	1.916	99	0.0094	0	0.0379	2	1,571	100	0.1301	100
60	0.0343	100	1.630	17	0.0061	0	0.0345	0	1,471	100	0.0726	100
70	0.0340	100	1.388	0	0.0038	0	0.0315	0	1,374	99	0.0442	51
80	0.0336	100	1.167	0	0.003	0	0.0289	0	1,280	54	0.0287	1
90	0.0333	100	0.973	0	0.003	0	0.0266	0	1,190	2	0.0185	0
100	0.033	100	0.815	0	0.003	0	0.0246	0	1,105	0	0.0118	0

[a]Value represents the predicted maximum average contaminant concentration (mg/L).
[b]Value represents the probability (%) that the applicable standard will be exceeded.
[c]EPA Safe Drinking Water Standard.

As shown in Table 5–17, results of the steady state stochastic MT3DMS predictive simulations indicate:

- The maximum average cadmium concentrations only reduce slightly (0.033 mg/L) after 100 years of flushing. This very slight reduction in concentration is mainly a function of the high K_d (range of 17 to 418 mL/g, average of 60.4 mL/g) associated with this contaminant. The predicted maximum average concentration does not drop below the 0.01 mg/L UMTRA standard after 100 years.

- Manganese predicted maximum average concentrations drop below the 1.7 mg/L risk-based standard between 50 and 60 years. At 60 years there is a 17 percent probability that the concentration will exceed the standard, and at 70 years there is a 0 percent probability.

- The maximum average molybdenum concentration drops below the 0.1 mg/L MCL prior to 5 years, with a 0 percent probability of the standard being exceeded at 5 years. An initial concentration just above the standard in conjunction with a very low K_d results in rapid flushing of this contaminant below the standard.

- Predicted selenium concentrations drop below the 0.05 mg/L EPA Safe Drinking Water standard after 25 years, at which time there is a 54 percent probability of the standard being exceeded. At 50 years, there is only a 2 percent probability of exceeding 0.05 mg/L, and 0 percent probability at 60 years.

- Predicted sulfate maximum average concentrations drop below the 1,276 mg/L background concentration between 80 and 90 years. At 80 years there is a 54 percent probability that the background concentration will be exceeded, and by 90 years the probability drops to 2 percent. The probability drops to 0 percent at 100 years.

- Maximum average uranium concentrations reach the 0.044 mg/L standard at 70 years, with a 51 percent probability of exceeding the standard. At 80 years the maximum average concentration is predicted to be 0.0287 mg/L, with a 1 percent probability of exceeding the standard. The probability drops to 0 percent at 90 years.

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