

Optimization of Sampling at the Shiprock, New Mexico, Site

March 2013



U.S. DEPARTMENT OF
ENERGY

Legacy
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Shiprock, New Mexico, Site**

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Appendix

Appendix A	Semiannual Sampling Results 2003–2011
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Abbreviations

bgs	below ground surface
CM	conceptual model report
COC	contaminant of concern
DOE	U.S. Department of Energy
DQOs	Data Quality Objectives
EPA	U.S. Environmental Protection Agency
ft	feet
GCAP	Ground Water Compliance Action Plan
LMS	Legacy Management Support
LOWESS	locally weighted scatterplot smoothing
MCL	maximum concentration limit (established in 40 CFR 192)
MDW	Many Devils Wash
mg/L	milligrams per liter
NRC	U.S. Nuclear Regulatory Commission
SAP	<i>Sampling and Analysis Plan for U.S. Department of Energy Office of Legacy Management Sites</i>
SOWP	Site Observational Work Plan
UMTRCA	Uranium Mill Tailings Radiation Control Act
VSP	Visual Sample Plan

Executive Summary

The sampling regime at the U.S. Department of Energy (DOE) Office of Legacy Management Shiprock, New Mexico, Site is the most extensive and costly of the Uranium Mill Tailings Radiation Control Act sites currently managed by DOE. The number of monitoring locations has increased from that originally established in the Ground Water Compliance Action Plan (GCAP). The U.S. Nuclear Regulatory Commission concurred with the groundwater compliance strategy proposed in the GCAP, which is the approved remediation strategy for the site. Therefore, the approach to optimizing the sampling regime focuses on the locations added after the GCAP was issued. Stakeholder concerns regarding the compliance strategy in the GCAP have led to an expansion of the remediation system, resulting in a large number of additional monitoring locations. The current sampling regime has become complex, and the specific data objectives for monitoring some of the locations are not clear. This report uses both statistical and logical assessments to recommend changes to the sampling conducted at the Shiprock site while remaining in compliance with the GCAP and the site remediation goals, and ensuring protection of human health and the environment. The format of this report and assessment of current data objectives follow U.S. Environmental Protection Agency guidance on systematic planning using the data quality objectives process. Statistical approaches were used mainly to identify temporal redundancy in the data to support reducing the sampling frequency from semiannual to annual, as proposed in the GCAP. The number of locations and the analytes sampled at each location were compared to the sampling objectives to assess whether any locations or analytes could be eliminated. The report provides recommendations for reducing the magnitude of the sampling effort to be more consistent with the current approved strategy until a new strategy can be developed and the GCAP rewritten. This report makes recommendations as an initial evaluation of the site strategy and objectives that could lead to changes to the remediation strategy.

The changes recommended in this report include (1) reducing the sampling frequency at all locations from semiannual (March and September) to annual (September); (2) eliminating locations or reducing the sampling to water level only at locations where the objective is to delineate the plume for mapping purposes and where adjacent locations provide sufficient data for map preparation; and (3) eliminating locations that are dry and are still being checked and tracked by the sampling crew.

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1.0 Introduction

In 2003, the U.S. Department of Energy (DOE) established a pump-and-treat groundwater remediation system at the Shiprock, New Mexico, Disposal and Processing Site. Many sampling locations have since been added beyond the original 60 called for in the Groundwater Compliance Action Plan (GCAP; DOE 2002) approved by the U.S. Nuclear Regulatory Commission (NRC) to assess the performance of new remediation system components, to better delineate contaminant plumes, and to address stakeholder concerns. Currently, DOE conducts semiannual monitoring at 173 locations, consisting of monitoring wells, surface locations, and treatment system components. The purpose of this report is to evaluate whether the current sampling approach supports the site compliance goals, meets the Data Quality Objectives (DQOs), and complies with the requirements of Title 40 *Code of Federal Regulations* Part 192.20 (40 CFR 192.20), which establishes remedial action standards for the Shiprock site. Guidance in 40 CFR 192.20 (b) (4) states the following:

Monitoring for assessment and compliance purposes should be sufficient to establish the extent and magnitude of contamination, with reasonable assurance, through use of a carefully chosen minimal number of sampling locations. The location and number of monitoring wells, the frequency and duration of monitoring, and the selection of indicator analytes for long-term groundwater monitoring, and, more generally, the design and operation of the monitoring system, will depend on the potential for risk to receptors and upon other factors, including characteristics of the subsurface environment, such as velocity of groundwater flow, contaminant retardation, time of groundwater or contaminant transit to receptors, results of statistical evaluations of data trends, and modeling of the dynamics of the groundwater system. All of these factors should be incorporated into the design of a site-specific monitoring program that will achieve the purpose of the regulations in this subpart in the most cost-effective manner.

To ensure that an effective and efficient approach is used to monitor groundwater and surface water at the Shiprock site, this report incorporates requirements of the compliance strategy, sampling regime, and site DQOs¹ to design a monitoring approach that provides the data necessary to make decisions regarding groundwater cleanup. The objective is to identify an optimal number of monitoring locations and optimal sampling frequency that comply with the Uranium Mill Tailings Radiation Control Act (UMTRCA) requirements in 40 CFR 192.

2.0 Background

2.1 Site Description

The Shiprock site is located within the Navajo Nation in the northwest corner of New Mexico near the town of Shiprock, approximately 28 miles west of Farmington, New Mexico. The Shiprock site was used for milling of uranium and vanadium ores from 1954 until 1968 and processed about 1.5 million tons of ore. In 1983, DOE and the Navajo Nation entered into an agreement for site cleanup. By September 1986, all the tailings and associated contaminated materials were encapsulated in a disposal cell built on top of the existing tailings piles. The disposal cell and adjacent former mill site sit on a terrace that is trisected by two minor

¹ The EPA document *Guidance on Systematic Planning Using the Data Quality Objectives Process* (EPA 2006) will be used to better define site DQOs.

drainages, Bob Lee Wash and Many Devils Wash. At the northeast edge of the terrace, a steep escarpment 50 to 60 feet (ft) high forms the boundary between the San Juan River floodplain and the terrace areas (Figure 1).

The floodplain alluvial aquifer is north and east of the disposal cell in the floodplain area lying between the San Juan River and the base of the escarpment. Floodplain groundwater occurs in unconsolidated, medium- to coarse-grained sand, gravel, and cobbles underlain by Mancos Shale. This aquifer is hydraulically connected to the San Juan River.

The terrace alluvial groundwater system is bounded to the south of the former mill by a buried escarpment (Figure 1) that trends east-west about 1,500 ft south of the disposal cell. The terrace groundwater system also extends more than a mile to the west and northwest, on the west side of U.S. Highway 491. Terrace alluvium consists mainly of unconsolidated medium- to coarse-grained sand, gravel, and cobbles that are underlain by Mancos Shale. Silty, windblown sediments (loess) overlie many parts of the terrace groundwater system. Past milling operations have left contaminants in the terrace groundwater and in the floodplain alluvial aquifer. Contaminated groundwater from the terrace has infiltrated the upper few feet of the underlying weathered Mancos Shale bedrock and has migrated into the alluvial aquifer on the floodplain. The contaminants of concern (COCs) are ammonia, manganese, nitrate, selenium, strontium, sulfate, and uranium.

3.0 Current Sampling Regime

3.1 Sampling Locations

Sampling at the Shiprock site is conducted to assess the progress of groundwater remediation at the site and to ensure protection of human health and the environment. The remediation approach has been augmented over the years to meet remediation goals and to address stakeholder concerns. The original compliance strategy was established in the *Final Ground Water Compliance Action Plan for Remediation at the Shiprock, New Mexico, UMTRA Site* (DOE 2002). NRC has concurred with the plan. In 2005, DOE reviewed the strategy and updated the site conceptual model, as described in the *Refinement of Conceptual Model and Recommendations for Improving Remediation Efficiency at the Shiprock, New Mexico, Site* (DOE 2005). The strategy was recently reviewed again in the *2010 Review and Evaluation of the Shiprock Remediation Strategy* (DOE 2011). The GCAP and the site conceptual model established monitoring requirements for the site to match the remediation strategy.

Since 2005, a large number of wells and sampling locations have been added to the monitoring network (Figure 2 and Figure 3). Currently, 81 locations are on the sampling list for the floodplain, and 92 are on the sampling list for the terrace; each location is sampled semiannually. The GCAP required 20 floodplain and 40 terrace monitoring locations, whereas the refined conceptual model (DOE 2005) called for a total of 27 and 73 monitoring locations on the floodplain and terrace, respectively. Some of the additional monitoring locations were established in response to stakeholder requests, and others were added to monitor the performance of new treatment system components. Semiannual sampling is currently conducted at 173 locations. Sampling includes checking dry wells and taking water level measurements at

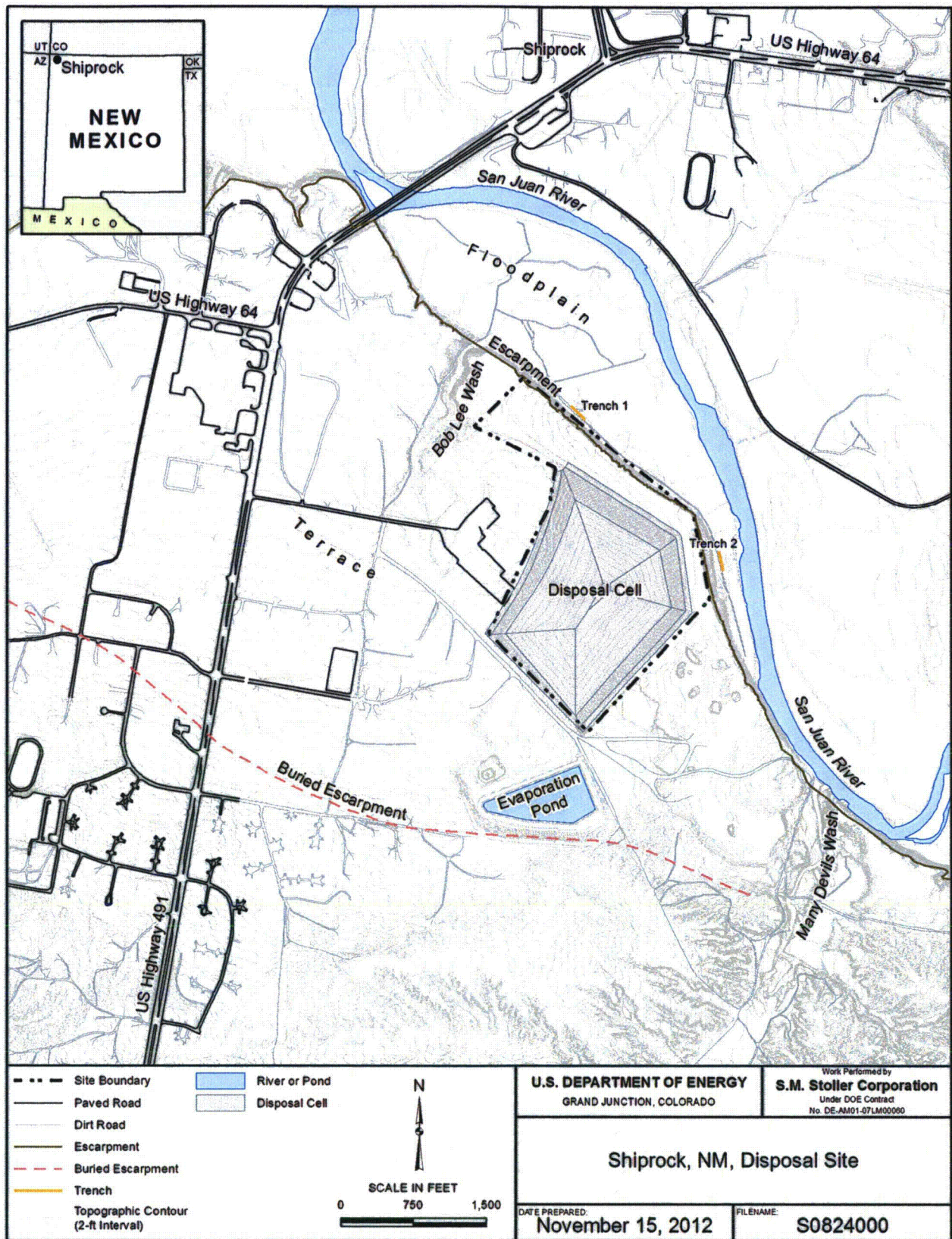
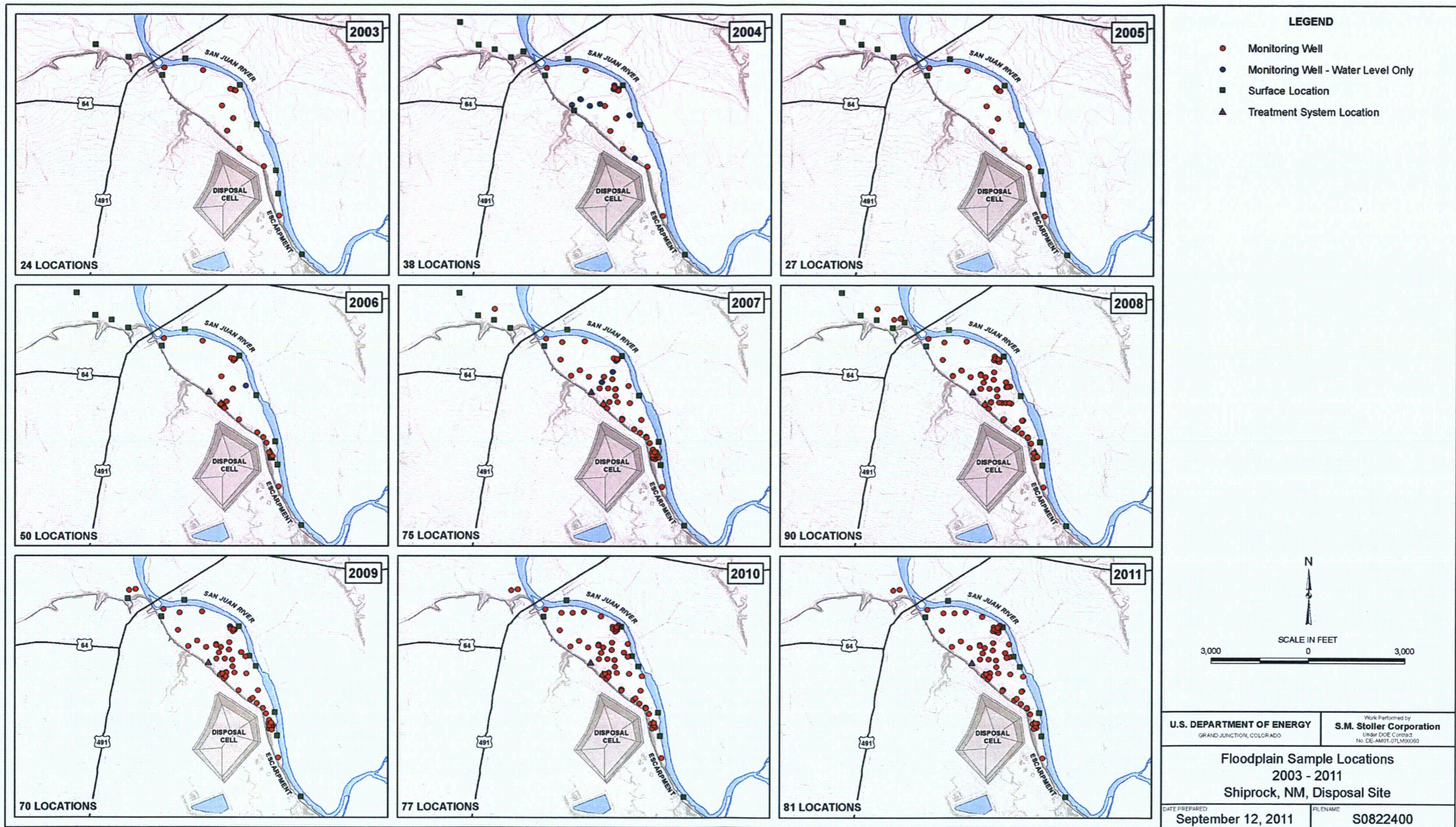


Figure 1. Shiprock Location and Site Features

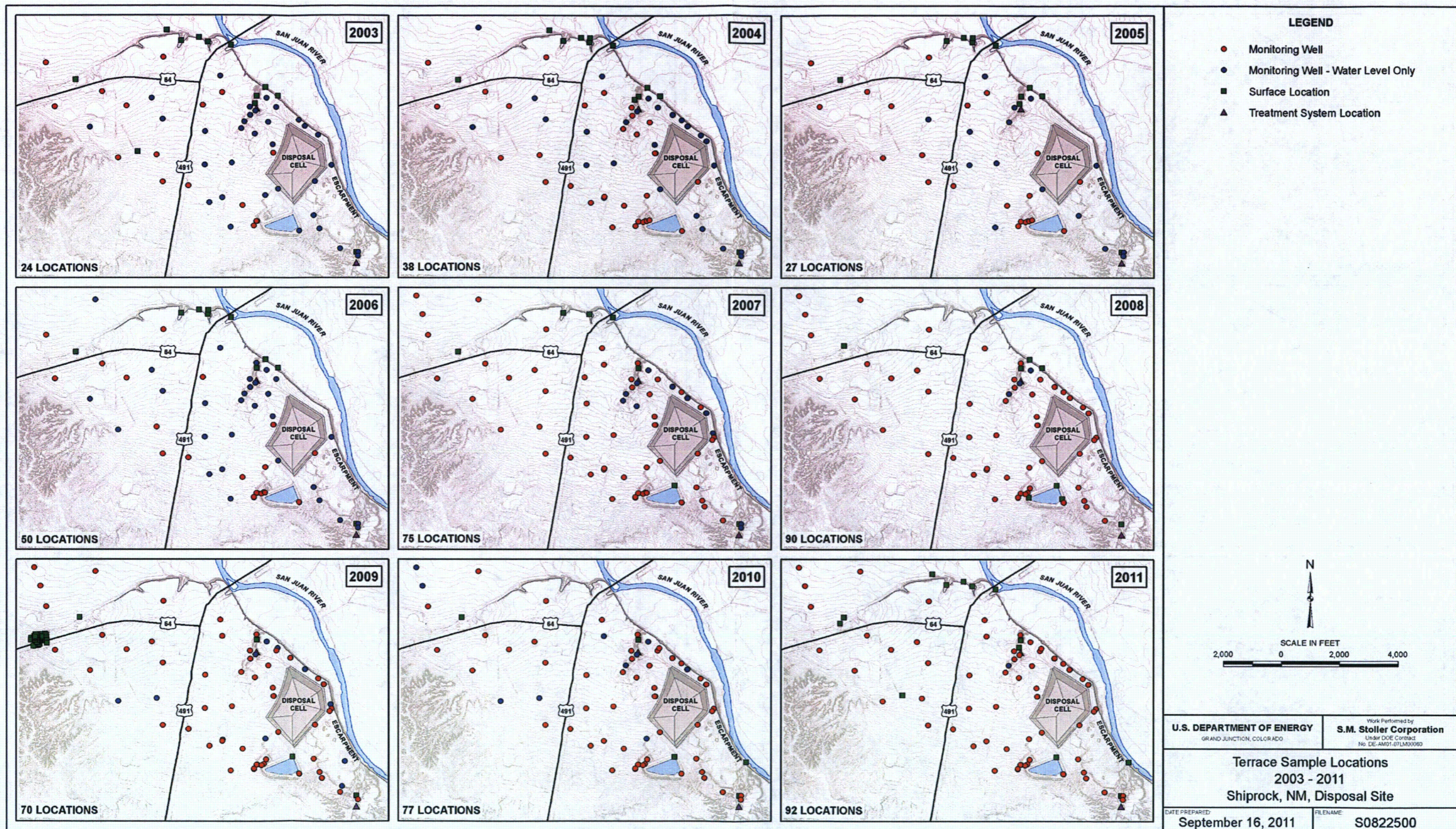
wells where water level is the only measurement; therefore, analytical results may not be obtained for all 173 locations. 14 locations that are not on the semiannual monitoring list are monitored remotely. In all, 187 locations are being monitored in some way at the site. Table 1 and Table 2 include all of the locations on the sampling list as well as locations that are listed in the GCAP and the refined conceptual model (DOE 2005) that are not on the current sampling list because they have been replaced by newer wells, replaced by a collection system, destroyed, or decommissioned (Table 1 and Table 2).



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Map represents all locations that had a result, including nondetects, dry wells, and special study/nonroutine locations. Dry surface locations are not shown.

Figure 2. Floodplain Monitoring Locations: 2003–2011



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Map represents all locations that had a result, including nondetects, dry wells, and special study/nonroutine locations. Dry surface locations are not shown.

Figure 3. Terrace Monitoring Locations: 2003–2011

Table 1. Current Floodplain Monitoring Locations

Floodplain Wells										Floodplain Surface Locations				
Location	Date Location Established	Currently Sampled	GCAP 2002	Site Conceptual Model 2005	Location	Date Location Established	Currently Sampled	GCAP 2002	Site Conceptual Model 2005	Location	Date Location Established	Currently Sampled	GCAP 2002	Site Conceptual Model 2005
0608	8/29/1985	Semiannually	Semiannually	Semiannually	0856	10/12/1998	Semiannually			0501	5/19/1986	Semiannually		Semiannually
0610	8/30/1985	Semiannually			0857	10/11/1998	Semiannually			0655	5/19/1993	Semiannually	Semiannually	Semiannually
0611	9/3/1985	Semiannually			0862	9/21/1998	Water Level Only		Water Level Only	0887	12/10/1998	Not Sampled ^a	Semiannually	Semiannually
0612	9/4/1985	Semiannually			0863	11/22/1998	Water Level Only		Water Level Only	0897	12/10/1998	Semiannually	Semiannually	Semiannually
0614	9/4/1985	Semiannually	Semiannually	Semiannually	1000	4/8/2000	Water Level Only		Water Level Only	0898	8/5/1986	Semiannually	Semiannually	
0615	9/6/1985	Semiannually	Semiannually	Semiannually	1001	4/8/2000	Water Level Only		Water Level Only	0899	12/3/1998	Semiannually		
0617	9/5/1985	Datalogger Only			1008	4/13/2000	Semiannually		Semiannually	0937	4/8/1999	Not Sampled ^a		
0618	9/5/1985	Semiannually	Semiannually	Semiannually	1009	4/12/2000	Semiannually			0938	4/8/1999	Not Sampled ^a		
0619	9/6/1985	Semiannually	Semiannually	Semiannually	1062	4/7/2000	Water Level Only		Water Level Only	0939	4/8/1999	Not Sampled ^a		
0622	8/28/1985	Semiannually			1077	8/27/2002	Replaced by 1104		Semiannually	0940	6/6/1999	Semiannually	Semiannually	Semiannually
0623	9/7/1985	Semiannually			1089	6/25/2003	Semiannually		Semiannually	0956	6/16/2000 ^b	Semiannually	Semiannually	Semiannually
0625	9/7/1985	Semiannually			1104	4/1/2005	Semiannually			0957	6/19/2000 ^b	Replaced by 0965	Semiannually	
0626	9/8/1985	Semiannually			1105	3/3/2005	Semiannually			0959	9/21/2001 ^b	Not Sampled ^a	Semiannually	Semiannually
0628	9/9/1985	Semiannually			1109	4/1/2006	Semiannually			0965	3/4/2003	Semiannually		
0630	9/9/1985	Semiannually			1110	4/1/2006	Semiannually			1118	10/11/2006	Semiannually		
0734	3/25/1993	Semiannually	Semiannually	Semiannually	1111	6/7/2006	Semiannually			1203	3/14/2000	Semiannually		Semiannually
0735	3/26/1993	Semiannually	Semiannually	Semiannually	1112	6/7/2006	Semiannually			1205	3/14/2000	Semiannually	Semiannually	Semiannually
0736	3/24/1993	Semiannually	Semiannually	Semiannually	1113	6/7/2006	Semiannually							
0766	10/27/1999	Semiannually			1114	6/6/2006	Semiannually							
0768	10/27/1999	Semiannually			1115	6/6/2006	Semiannually							
0773	10/27/1999	Semiannually			1117	6/6/2006	Semiannually							
0775	10/27/1999	Semiannually			1128	2/6/2007	Semiannually							
0779	10/27/1999	Semiannually			1132	2/7/2007	Semiannually							
0782R	9/16/2008	Semiannually			1134	2/7/2007	Semiannually							
0783R	9/16/2008	Semiannually			1135	1/26/2010	Semiannually							
0792	3/1/2001	Semiannually			1136	1/27/2010	Semiannually							
0793	3/1/2001	Semiannually			1137	1/26/2010	Semiannually							
0797	3/2/2001	Semiannually	Semiannually	Semiannually	1138	1/26/2010	Semiannually							
0798	3/1/2001	Semiannually			1139	1/26/2010	Semiannually							
0850	10/23/1998	Semiannually	Semiannually	Semiannually	1140	5/15/2009	Semiannually							
0853	10/11/1998	Semiannually			1141	5/15/2009	Semiannually							
0854	10/25/1998	Semiannually	Semiannually	Omit	1142	1/27/2010	Semiannually							
0855	10/24/1998	Semiannually			1143	1/25/2010	Semiannually							

^a Channel destroyed

^b Date established not recorded; date listed is earliest sampling result

Table 2. Current Terrace Monitoring Locations

Terrace Wells										Terrace Surface Locations				
Location	Date Location Established	Currently Sampled	GCAP 2002	Site Conceptual Model 2005	Location	Date Location Established	Currently Sampled	GCAP 2002	Site Conceptual Model 2005	Location	Date Location Established	Currently Sampled	GCAP 2002	Site Conceptual Model 2005
0600	1/13/1982	Semiannually		WL	0841	11/7/1998	Semiannually	Semiannually	Semiannually	0425	1/7/1991	Replaced by FP 1118		Flow Rate
0602	12/12/1981	Semiannually		WL	0843	12/5/1998	Semiannually			0426	1/7/1991	Replaced by FP 1118		Flow Rate
0603	6/3/1983	Semiannually		WL	0844	11/11/1998	Semiannually		Water Level Only	0662	1/1/1901	Semiannually	Semiannually	
0604	5/27/1983	Semiannually		WL	0846	12/2/1998	Not Sampled ^a	Semiannually	Semiannually	0786	10/29/1999	Semiannually	Semiannually	Flow Rate
0648	10/29/1960	Biennially	Biennially	Biennially	0847	1/1/1995	Not Sampled	Semiannually	Omit	0884	12/10/1998	Not Sampled ^a	Semiannually	
0725	3/28/1993	Semiannually			0848	1/1/1995	Semiannually		Water Level Only	0885	12/3/1998	Semiannually	Semiannually	Water Level Only
0726	3/28/1993	Semiannually		Water Level Only	1002	3/28/2000	Not Sampled ^a		Water Level Only	0886	12/3/1998	Not Sampled	Semiannually	Omit
0727	3/27/1993	Semiannually			1003	3/29/2000	Not Sampled ^a		Water Level Only	0889	12/3/1998	Semiannually	Semiannually	
0728	3/25/1995	Semiannually	Water Level Only	Water Level Only	1004	3/30/2000	Not Sampled ^a		Water Level Only	0933	4/7/1999	Not Sampled ^a	Semiannually	
0730	3/26/1993	Semiannually		Semiannually	1007	4/16/2000	Semiannually	Water Level Only	Water Level Only	0934	4/7/1999	Not Sampled ^a	Semiannually	
0731	3/23/1993	Semiannually		Water Level Only	1011	4/15/2000	Semiannually			0936	4/8/1999	Not Sampled ^a	Semiannually	
0800	9/23/1998	Not Sampled ^a	WL—Annually	WL—Annually	1048	12/14/1999	Semiannually		Water Level Only	0942	6/8/1999	Not Sampled ^a	Semiannually	
0801	11/17/1998	Not Sampled ^a	WL—Annually	WL—Annually	1049	12/15/1999	Semiannually		Water Level Only	0949	9/9/2008 ^c	Not Sampled ^a		
0802	9/23/1998	Not Sampled ^a	WL—Annually	WL—Annually	1057	3/26/2000	Semiannually	Water Level Only	Water Level Only	0958	6/15/2000 ^c	Not Sampled ^a	Semiannually	Biennially
0803	11/18/1998	Not Sampled ^a	WL—Annually	WL—Annually	1058	3/27/2000	Semiannually			1215	3/8/2007	Semiannually		
0812	10/27/1998	Semiannually	Water Level Only	Water Level Only	1059	4/16/2000	Semiannually		Water Level Only	1218	3/25/2010 ^c	Semiannually		
0813	10/25/1998	Semiannually	Water Level Only	Water Level Only	1060	4/14/2000	Not Sampled ^a	Semiannually	Semiannually	1219	3/22/2011 ^c	Semiannually		
0814	11/4/1998	Semiannually	Water Level Only	Water Level Only	1065	6/27/2001	Decommissioned ^b	Water Level Only	Water Level Only	1220	3/25/2010 ^c	Semiannually		
0815	11/5/1998	Semiannually	Water Level Only	Water Level Only	1066	3/21/2002 ^c	Decommissioned ^b	Water Level Only	Water Level Only	1221	3/26/2010 ^c	Semiannually		
0816	11/5/1998	Semiannually		Water Level Only	1067	6/26/2001	Water Level Only	Water Level Only	Water Level Only					
0817	10/12/1998	Semiannually	Semiannually	Semiannually	1068	6/26/2001	Semiannually	Water Level Only	Water Level Only					
0818	10/8/1998	Semiannually	Water Level Only	Semiannually	1069	6/26/2001	Semiannually	Water Level Only	Water Level Only					
0819	10/14/1998	Semiannually		Water Level Only	1070	9/1/2002	Semiannually		Semiannually					
0820	9/16/1998	Semiannually		Water Level Only	1071	8/31/2002	Semiannually		Semiannually					
0821	9/17/1998	Not Sampled ^a		Water Level Only	1073	8/30/2002	Semiannually		Water Level Only					
0822	9/17/1998	Semiannually		Water Level Only	1074	8/30/2002	Semiannually							
0823	9/13/1998	Not Sampled ^a		Water Level Only	1078	8/28/2002	Semiannually		Semiannually					
0824	9/12/1998	Semiannually		Water Level Only	1079	8/31/2002	Semiannually	Semiannually	Semiannually					
0825	9/13/1998	Semiannually		Water Level Only	1087	3/3/2003	Semiannually		Semiannually					
0826	10/14/1998	Semiannually		Water Level Only	1088	3/3/2003	Semiannually		Semiannually					
0827	11/13/1998	Semiannually		Water Level Only	1091	7/11/2003	Semiannually		Semiannually					
0828	10/13/1998	Semiannually		Water Level Only	1092	7/19/2003	Semiannually		Semiannually					
0829	10/15/1998	Not Sampled ^a		Water Level Only	1093	7/14/2003	Replaced by 1093R		Semiannually					
0830	11/12/1998	Semiannually		Water Level Only	1093R	9/10/2007	Semiannually							
0832	11/10/1998	Not Sampled ^a	Semiannually	Semiannually	1094	7/24/2003	Replaced by 1093R		Semiannually					
0833	12/3/1998	Semiannually			1095	3/4/2005	Semiannually							
0835	12/6/1998	Semiannually	Semiannually	Semiannually	1096	3/7/2005	Semiannually							
0836	12/7/1998	Semiannually	Semiannually	Semiannually	1120	2/12/2007	Not Sampled ^a							
0837	12/5/1998	Semiannually			1122	2/12/2007	Not Sampled ^a							
0838	12/3/1998	Semiannually	Semiannually	Semiannually	MW1	2/4/1998 ^c	Semiannually		Water Level Only					
0839	11/6/1998	Not Sampled ^b	Semiannually	Semiannually	DM7	1/25/1982	Not Sampled ^a		Water Level Only					

^a Location dried up

^b Location destroyed

^c Date established not recorded; date listed is earliest sampling result

FP = Floodplain

3.2 Analytes Sampled

In addition to the site COCs, samples are analyzed for a variety of analytes that define the chemical characteristics of the site water. Table 3 shows the rationale and cost for the analytes monitored. Field measurements consist of data gathered during sampling and are also used as additional indicators of water quality.

Table 3. Rationale and Costs for Analytes Monitored at the Shiprock Site

Analyte	Analysis Type	Reason for Monitoring	Cost per Sample
Alkalinity	Field	Assess Water Chemistry	Negligible
Ammonia as N	Laboratory	GCAP COC	\$13
Calcium	Laboratory	Assess Water Chemistry	\$16.50
Chloride	Laboratory	Assess Water Chemistry	\$13
Magnesium	Laboratory	Assess Water Chemistry	\$16.50
Manganese	Laboratory	GCAP COC	\$16.50
Nitrate + Nitrite as N	Laboratory	GCAP COC	\$22
pH	Field	Assess Water Chemistry	Negligible
Potassium	Laboratory	Assess Water Chemistry	\$16.50
Oxidation-Reduction Potential	Field	Assess Water Chemistry	Negligible
Selenium	Laboratory	GCAP COC	\$22
Sodium	Laboratory	Assess Water Chemistry	\$16.50
Specific Conductance	Field	Assess Water Chemistry	Negligible
Strontium	Laboratory	Ecological Concerns	\$16.50
Sulfate	Laboratory	GCAP COC	\$13
Temperature	Field	Assess Water Chemistry	Negligible
Turbidity	Field	Assess Water Chemistry	Negligible
Uranium	Laboratory	GCAP COC	\$22

3.3 Sampling Quality

Sampling at the Shiprock site is conducted according to the *Sampling and Analysis Plan for U.S. Department of Energy Office of Legacy Management Sites (SAP) (LMS/PLN/S04351)*. Data of known, documented quality are produced through the following aspects of the SAP:

- Defensible and comprehensive sampling procedures
- Calibration of field instrumentation
- Collection of field quality-control samples
- Documentation of sampling activities
- Training of sampling personnel
- Records management

- Use of accredited commercial laboratories that:
 - Conform to Quality Systems for Analytical Services requirements
 - Are DOE Consolidated Audit Program (DOECAP)-audited annually
 - Use approved analytical procedures
- Data validation and qualification

The SAP sets the DQOs for data quality; however, DQOs also identify what information is needed for decision-making. In particular, the SAP specifies the analytes and parameters that need to be monitored, monitoring frequency, and monitoring locations. The GCAP established the DQOs for monitoring at the site.

4.0 Compliance Strategy

4.1 Floodplain

The compliance strategy for the floodplain outlined in the GCAP is natural flushing with monitoring supplemented by limited active remediation consisting of groundwater extraction from two extraction wells. The monitoring strategy was designed to determine the progress of natural flushing in meeting compliance standards for the site COCs and to determine the effectiveness of contaminant mass removal from the two extraction wells, which are located in one of the most contaminated parts of the plume. The purpose of the wells was to interdict contaminated groundwater migrating toward the river, thus preventing its discharge to the river. Information in Table 4 is reproduced from Table B-3 of the GCAP and outlines the monitoring requirements for the floodplain.

Table 4. Floodplain Monitoring Requirements Documented in the GCAP

Location	Purpose	Analyses/Measurement	Frequency
Wells 608, 614, 615, 618, 619, 734, 735, 736, 854	Compliance action levels (40 CFR 192)	COCs: manganese, nitrate, selenium, sulfate, uranium (and ammonia and strontium based on ecological concerns) Water chemistry: calcium, chloride, magnesium, potassium, sodium Onsite field analyses: alkalinity, conductivity, oxidation-reduction potential, pH, water level (in wells)	Semiannually through the first 7-year period, then annually through year 12, and every 5 years thereafter
Wells 797,850	Floodplain, background		
Surface 898	San Juan River, background		
Surface 897, 940, 1205	Intake on north side of San Juan River, risk		
Surface 956	San Juan River, downgradient, risk		
Surface 957	Floodplain drainage channel, risk		
Surface 655	Floodplain drainage channel, risk		
Surface 887	Distributary channel, risk		
Surface 959	Distributary channel, risk		

The GCAP requires semiannual monitoring for the initial 7 years of remediation (i.e., after initiation of pumping in 2003), followed by annual monitoring for the next 5 years, then monitoring every 5 years thereafter. The seventh year of semiannual monitoring was in 2009, and monitoring frequency would have been reduced to annually starting in 2010. However, because stakeholders had expressed concerns about the compliance strategy, and recently installed enhancements to the remediation system required additional data, DOE elected to continue sampling semiannually on the floodplain. Sampling locations included the locations required by the GCAP plus numerous additional locations.

4.2 Terrace

The compliance strategy for the terrace as outlined in the GCAP is organized into two parts referred to in the Site Observational Work Plan (SOWP; DOE 2000) as terrace east and terrace west. The strategy for terrace east is active remediation until potential risks to human health and the environment are eliminated. The strategy for terrace west is application of supplemental standards with monitoring. The monitoring strategy for terrace east calls for determining the effectiveness of active remediation in cutting off recharge to terrace west and in drying up the seeps on the escarpment and in the washes. The terrace west monitoring strategy calls for determining whether recharge from terrace east is being cut off (resulting in drying up of seeps in washes), and that milling-related constituents do not affect the current beneficial, limited use of the groundwater. Table 5 is reproduced from Table B-2 of the GCAP and outlines the monitoring requirements for the terrace.

Table 5. Terrace Monitoring Requirements Documented in the GCAP

Location	Purpose	Analyses/Measurement	Frequency
Flowing artesian well 648	Cleanup standards for floodplain	COCs: ammonium, manganese, nitrate, selenium, sulfate, uranium; strontium for ecological risk concerns	Semiannual flow measurements; sample for chemical analyses every 2 years
Terrace east well: 817 Terrace west wells: 832, 835, 836, 838, 839, 841, 846, 847/1079, 1060	Water level and groundwater chemistry	Water chemistry: calcium, chloride, magnesium, potassium, sodium Onsite field analyses: alkalinity, conductivity, oxidation-reduction potential, pH, water level	Semiannually through the 7 year extraction period, then annually through year 12, and every 5 years thereafter
Terrace east wells: 728, 812, 813, 818, 1007, 1057, 1065, 1066, 1067, 1068, 1069 Terrace west wells: 814, 815	Monitor lowering of water levels	Water level	

Table 5 (continued). Terrace Monitoring Requirements Documented in the GCAP

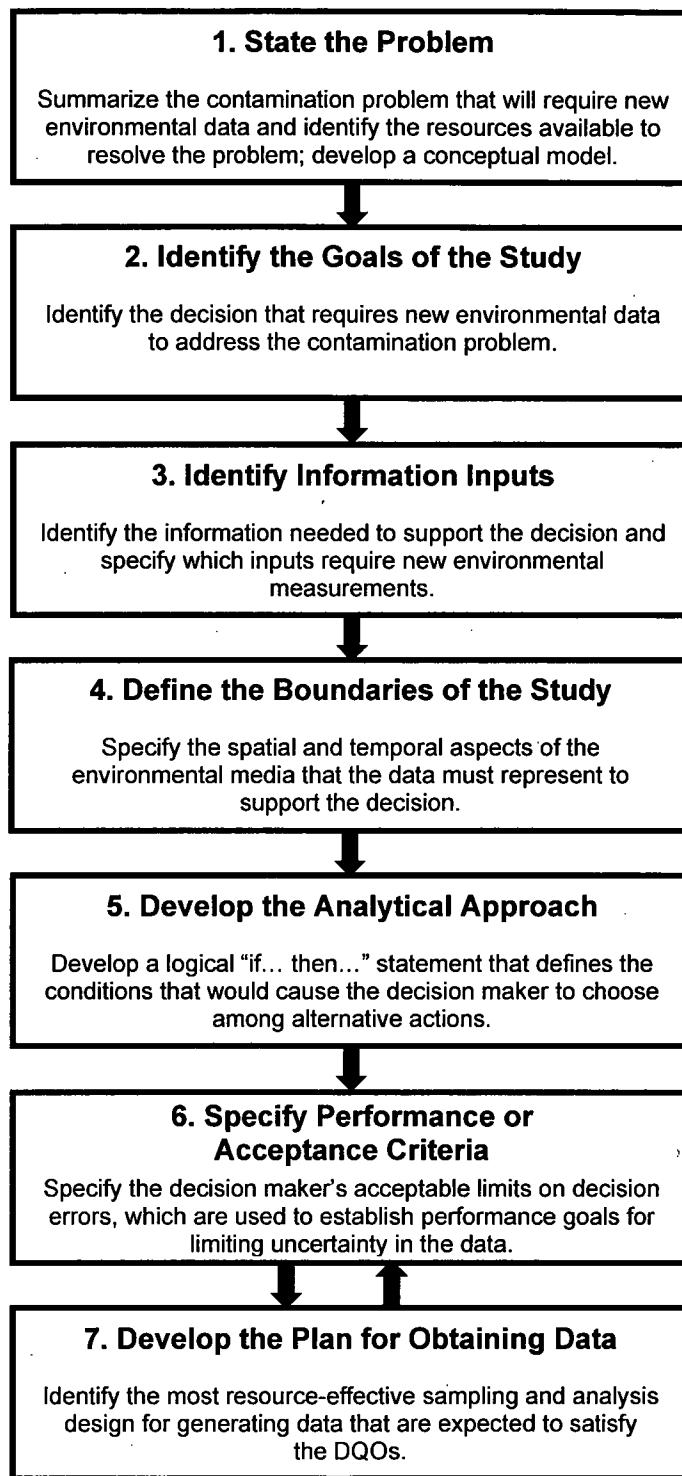
Location	Purpose	Analyses/Measurement	Frequency
Terrace east surface water: 425, 426, 662, 786, 885, 886, 889 Terrace west surface water: 884, 933, 934, 936, 942, 958	Monitor for ecological risks and lowering of water levels	COCs: ammonium, manganese, nitrate, selenium, sulfate, uranium; strontium for ecological risk concerns Water chemistry: calcium, chloride, magnesium, potassium, sodium Onsite field analyses: alkalinity, conductivity, oxidation-reduction potential, and pH Water level for 885, 886, and 889 Flow rate for 425, 426, and 786	Sample location 958 for chemical analysis once every 2 years
Terrace background wells: 800, 801, 802, 803	Presence of groundwater in terrace background	Water level	Annually for the first 5 years

Monitoring is required semiannually for the initial 7 years and then annually for the next 5 years followed by sampling every 5 years. The seventh year of semiannual sampling was in 2009, and annual sampling would have begun in 2010 according to the GCAP. However, as with the sampling frequency for the floodplain, because stakeholders had expressed concerns about the compliance strategy, and recently installed enhancements to the remediation system required additional data, DOE elected to continue sampling semiannually on the terrace. Sampling locations included those required by the GCAP plus numerous additional locations.

5.0 Data Quality Objectives

DQOs identify and document information needed for decision-making, as well as requirements for data quality; specifically, DQOs direct how complete, accurate, timely, and consistent the data need to be to support the decision-making process. Sampling at the Shiprock site is being conducted to monitor the progress of remediation at the site. Indicators of progress are the levels of COCs in the groundwater system and water levels in areas where dewatering is a goal. The approved compliance strategy in the GCAP allows for a reduction in sampling frequency from semiannual to annual. Based on stakeholder comments received on the update to the site conceptual model (DOE 2005) and the 2010 review and evaluation of the remediation system (DOE 2011), the compliance strategy may need to be evaluated. Additionally, an updated GCAP may need to be issued. As a preliminary evaluation, the remediation goals are discussed and matched to an optimal sampling regime to support decisions on the remediation system.

Developing DQOs is a seven-step process (EPA 2006): (1) state the problem, (2) identify the goals of the study, (3) identify information inputs, (4) define the boundaries of the study, (5) develop the analytical approach, (6) specify performance or acceptance criteria, and (7) develop the plan for obtaining data (Figure 4). Sections 6 through 12 of this report describe how these steps in the DQO process are applied to the Shiprock site.



Source: EPA 2006

Figure 4. Data Quality Objectives Process Flow Chart

6.0 State the Problem

In this step, a concise description of the problem is developed, the planning team is established, the site conceptual model is investigated, and resources and constraints are identified.

6.1 Problem Description

The scope and extent of sampling at the Shiprock site has greatly expanded over the years without clear objectives on how the data will be used. An optimized sampling regime is needed that will obtain the necessary data required to make decisions on the progress of remediation at the site while still being protective of human health and the environment.

6.2 Planning Team

Planning team members include:

DOE Office of Legacy Management Site Manager
Legacy Management Support (LMS) Site Lead
LMS technical staff
LMS Task Order Manager

6.3 Site Conceptual Model

The site conceptual model was first developed in the SOWP (DOE 2000) and was updated in the refinement of the site conceptual model report (DOE 2005). Since those documents were prepared, experience with the site conditions and results of remediation have led to further refinements to the site conceptual model. The current understanding of the site conceptual model is summarized below.

6.3.1 Terrace

Terrace groundwater occurs primarily in the alluvium overlying Mancos Shale and in the weathered, upper few feet of the shale. Lesser amounts of groundwater migrate through fractures in the underlying, competent portions of the Mancos Shale. Many sources of water have contributed to the terrace groundwater system. Findings derived from well installation and well development activities at the site, along with observed low extraction rates from terrace wells, indicate that the spatial continuity of saturated alluvium in the terrace groundwater system is limited. Weathered shale may provide a medium for transferring groundwater between isolated locales of saturated alluvium. The largest hydraulic conductivities are observed in the alluvium, whereas competent Mancos Shale is the least-permeable medium in the system. Hydraulic conductivities in the weathered Mancos Shale are intermediate in value between those of the alluvium and competent shale.

In past years, much of the recharge to the groundwater system was provided by infiltrating water used at the former mill and from saturated tailings at the Shiprock site. From the late 1950s to the early 2000s, irrigation water applied to agricultural areas west of Highway 491 also contributed recharge to the groundwater system. Currently, limited amounts of recharge may be attributed to operations conducted at the Navajo Engineering and Construction Authority gravel pit located

immediately south of the disposal cell. In addition, it is possible that some remnant moisture in tailings within the disposal cell is gradually seeping downward into underlying, saturated alluvium. The hydrogeologic conceptual model adopted in the SOWP (DOE 2000) and the GCAP (DOE 2002) assumed that the terrace groundwater system was anthropogenic in origin, and that any natural recharge to the system was insufficient to maintain a saturated domain.

The terrace groundwater system is contaminated as a result of former mill operations and historical leaching of moist to saturated tailings that were emplaced on the terrace during milling years. A recent study of historical field investigations and records associated with milling and the construction of the disposal cell estimated that between 50 million and 390 million gallons of mill-related fluids percolated into the subsurface during the operational life of the mill (DOE 2012). Previous site characterization work and additional recent investigations have shown that some of the high constituent concentrations detected in terrace groundwater could be caused by leaching of constituents that occur naturally in the Mancos Shale. It is also possible that transient leakage from the disposal cell, if it continues to this day, is adding some contaminants to the groundwater system.

Some of the groundwater contaminated by former mill-related activities migrated through competent Mancos Shale adjacent to the escarpment and subsequently migrated toward the floodplain. A portion of this contaminated water historically discharged to seeps located on the escarpment wall, but the vast majority of the contaminated terrace water discharges directly to the alluvial floodplain groundwater system. Although flow in the escarpment-wall seeps has diminished over the past 10 years, available data indicate that contaminated groundwater continues to discharge directly to the floodplain alluvial aquifer. The source of the water causing this discharge is unclear.

6.3.2 Floodplain

The floodplain groundwater system occurs primarily within a surficial alluvial aquifer consisting mostly of coarse-grained sand and gravel. The upper few feet of Mancos Shale underlying the alluvium is typically soft and weathered. Much of the groundwater within the floodplain alluvial aquifer stems from recharge of surface water at the mouth of Bob Lee Wash, which originates as flowing water from artesian well 0648 at the head of a tributary to the wash. Seepage losses from the San Juan River, particularly along the southern third of the river's reach adjacent to the site floodplain area, are another major source of groundwater in the alluvial aquifer. A third, distinctive source of the alluvial aquifer is the terrace groundwater discharge to the floodplain, much of which is contaminated. The floodplain groundwater system is dynamic and is subject to seasonal changes in flow direction due to seasonally variable flows on the river, losses of water to evapotranspiration during summer months, and pumping within the floodplain remediation system.

6.3.3 Contaminants of Concern

The COCs for the site were based on the original risk assessment from the *Baseline Risk Assessment of Ground Water Contamination at the Uranium Mill Tailings Site near Shiprock, New Mexico* (DOE 1994) and an updated risk assessment developed for the SOWP.

Remediation efforts to date have removed contaminant mass from some areas of the terrace groundwater and the floodplain aquifer. The highest concentrations of different COCs occur in different areas of the site.

Figure 5 through Figure 11 show plume configurations based on 2011 sampling results at wells and treatment system locations. The color denotations on these maps are different from those of plume maps shown in previous reports, and the current maps cannot be compared visually to previous maps. The compliance standard or cleanup goal established in the GCAP was added to the color scale on the current plume maps for manganese, nitrate, selenium, sulfate, and uranium. The color scale was set to break from blue/green to yellow/red at the concentration corresponding to the standard or goal; therefore, locations with results above the standard or goal will appear as yellow or red. Strontium and ammonia do not have compliance standards or cleanup goals established in the GCAP. The Secondary Acute Value (discussed in Section 12.2.4) was used as a threshold for the strontium map, since strontium is being monitored based on ecological risk. No standard was applied to the ammonia map because the aquatic water quality standard for ammonia varies depending on temperature and pH. Although the plume maps in Figure 5 through Figure 11 depict groundwater conditions for the entire site, the standards and compliance goals do not apply to terrace groundwater. The maps represent all site data; plumes are generated from data for wells screened in both the alluvium [floodplain well depths of 7–25 ft below ground surface (bgs), terrace well depths of 8–72 ft bgs] and Mancos Shale (floodplain well depths of 10–135 ft bgs, terrace well depths of 19–205 ft bgs) and include data from artesian (Jurassic) well 648 (screened in the Morrison Formation; well depth 1,850 ft bgs). These maps should be viewed as a representation of the site data rather than an actual picture of the extent of the groundwater plume. Data from all the well locations were used to interpolate contaminant concentrations between the wells. The floodplain and terrace data were processed separately and placed on the same map; therefore, the floodplain results do not affect the interpolated areas between data points in the terrace, and the terrace data do not affect the floodplain. Three of the floodplain wells (0784, 0783R, and 0782R) were processed as part of the terrace data because their locations are separated from the rest of the floodplain by the river. The background locations on the floodplain southeast of the site were not included in the interpolation process; the results are shown in a box in the lower-right corner of the figures. San Juan River sampling results were also not included on these maps, as the low levels (equivalent to river background levels) typically detected in the river would affect the interpolation of the areas along the river. Excluding the river locations gives a more conservative view of site contamination levels.

6.3.3.1 Manganese

Manganese is monitored as a site COC because it could negatively impact human health if the groundwater were used as a source of drinking water, and the potential for ecological risk was considered high in the floodplain (DOE 2000). Manganese concentrations in groundwater are highest on the terrace at the south corner of the disposal cell in the area of the radon cover borrow pit, and concentrations are also elevated in well 0837 (Figure 5). Floodplain areas with elevated concentrations are along the escarpment from wells 1114 to 0735; between wells 0792, 0857, and 0854; between wells 0628 and 0623; and at well 0782R. Manganese concentrations in background location 0797 also exceed the cleanup goal, which was set at the maximum background concentration detected at the time the GCAP was issued. This indicates that the manganese contamination onsite may be from natural sources. It is likely that the elevated levels

in terrace well 0837 and floodplain well 0782R are from natural sources, given the distance from the former mill site and the disposal cell and the fact that the area between the wells and the mill site/disposal cell has lower concentrations of manganese.

6.3.3.2 Nitrate

Nitrate is monitored as a site COC because concentrations exceeded the maximum concentration limit (MCL) established in 40 CFR 192. Nitrate concentrations in groundwater are highest on the terrace from east of the disposal cell out to wells 1079 and 0835 and in Many Devils Wash. A small area of elevated concentrations is present in the floodplain along the base of the escarpment from well 0735 to seep 0118 (Figure 6).

6.3.3.3 Selenium

Selenium is monitored as a site COC because concentrations exceeded the MCL, and potential ecological risks were considered high in some areas of the site (DOE 2000). Selenium concentrations are elevated in Many Devils Wash, along the buried escarpment on the terrace, and north to well 0843. On the floodplain, elevated concentrations are present along the base of the escarpment and extend northeastward toward well 0618 (Figure 7).

6.3.3.4 Sulfate

Sulfate is monitored as a site COC because concentrations were high enough to be of probable concern (DOE 2000). No standard for sulfate is established in 40 CFR 192, and the GCAP proposed a cleanup goal of 2,000 milligrams per liter (mg/L), which was the maximum background concentration detected at the time. Sulfate concentrations in groundwater are above the compliance goal across most of the site; only a few wells on the terrace and in an area along the river have concentrations below 2,000 mg/L (Figure 8). The concentration in background well 0797 is 3,800 mg/L, which exceeds the current cleanup goal.

6.3.3.5 Uranium

Uranium is monitored as a site COC because concentrations in groundwater at multiple locations exceeded the MCL of 0.044 mg/L (DOE 2000). The highest levels on the terrace occur in the Mancos wells just west of the disposal cell. On the floodplain, the levels are highest along the base of the escarpment and around wells 0618, 0779, and 1104. The background wells have concentrations that are only 0.015 mg/L lower than the MCL, indicating that there is likely a natural component to the uranium levels onsite (Figure 9).

6.3.3.6 Ammonia

Ammonia was retained as a COC because inhalation could present a potential health risk under a residential groundwater-use scenario and could present an ecological risk (DOE 2000).

Ammonia concentrations in groundwater are highest on the terrace in the Mancos wells just west of the disposal cell and in a few alluvial wells southeast of the cell. On the floodplain, levels are highest in a small area at the base of the escarpment (Figure 10).

6.3.3.7 *Strontium*

Strontium was not retained as a health based COC in the SOWP; however, it is listed in the GCAP to be monitored for ecological risk concerns, even though the SOWP stated that strontium was a minor contributor to ecological risk (DOE 2000). Strontium concentrations in groundwater exceed the ecological risk secondary acute value in only a few locations on the terrace. On the floodplain, concentrations are elevated at wells 0735 and 0630. Background concentrations are below the secondary acute value but are high enough to indicate that strontium may occur naturally at the site, and its presence is not milling-related (Figure 11).

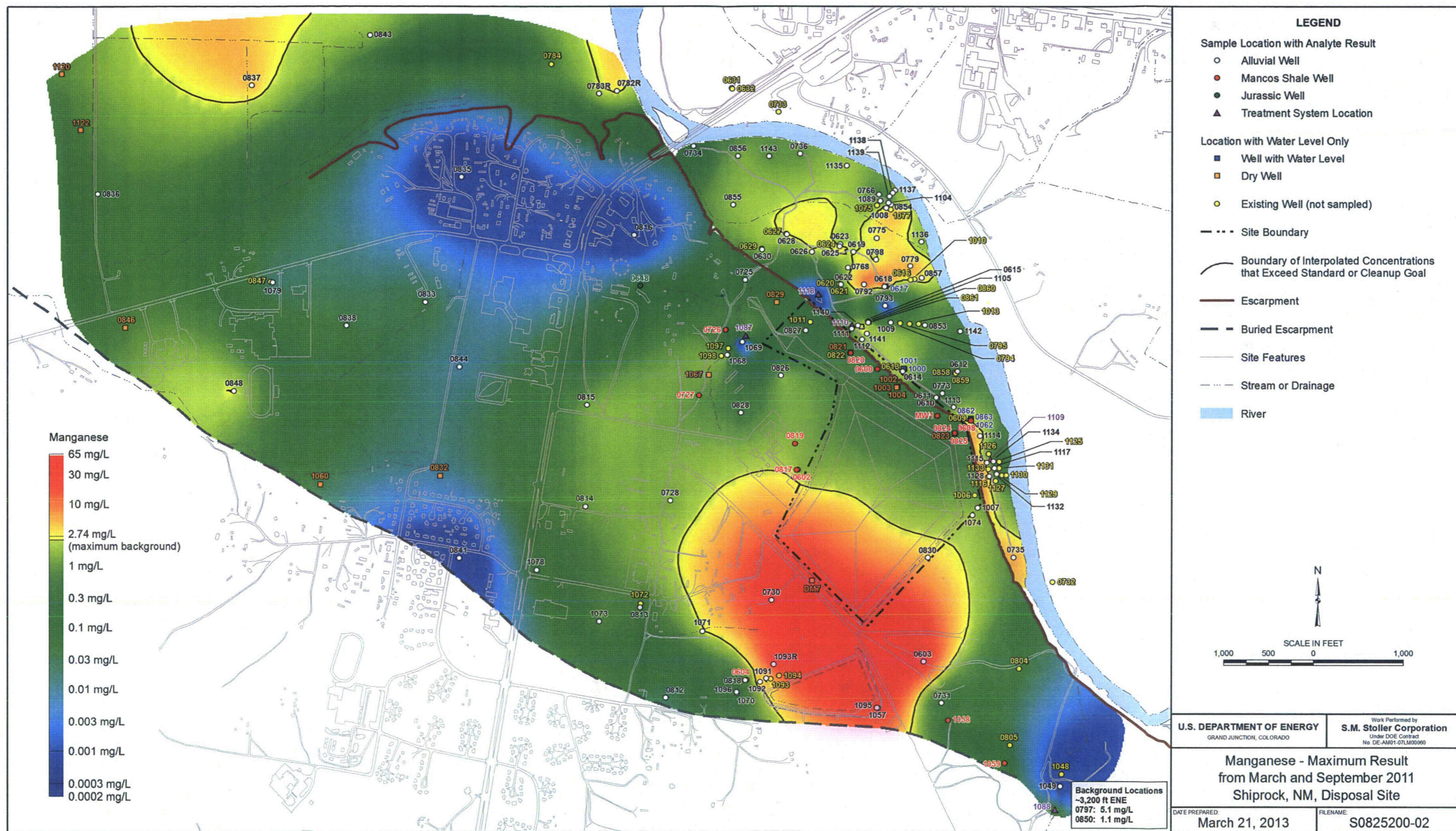


Figure 5. Manganese Maximum Result March and September 2011

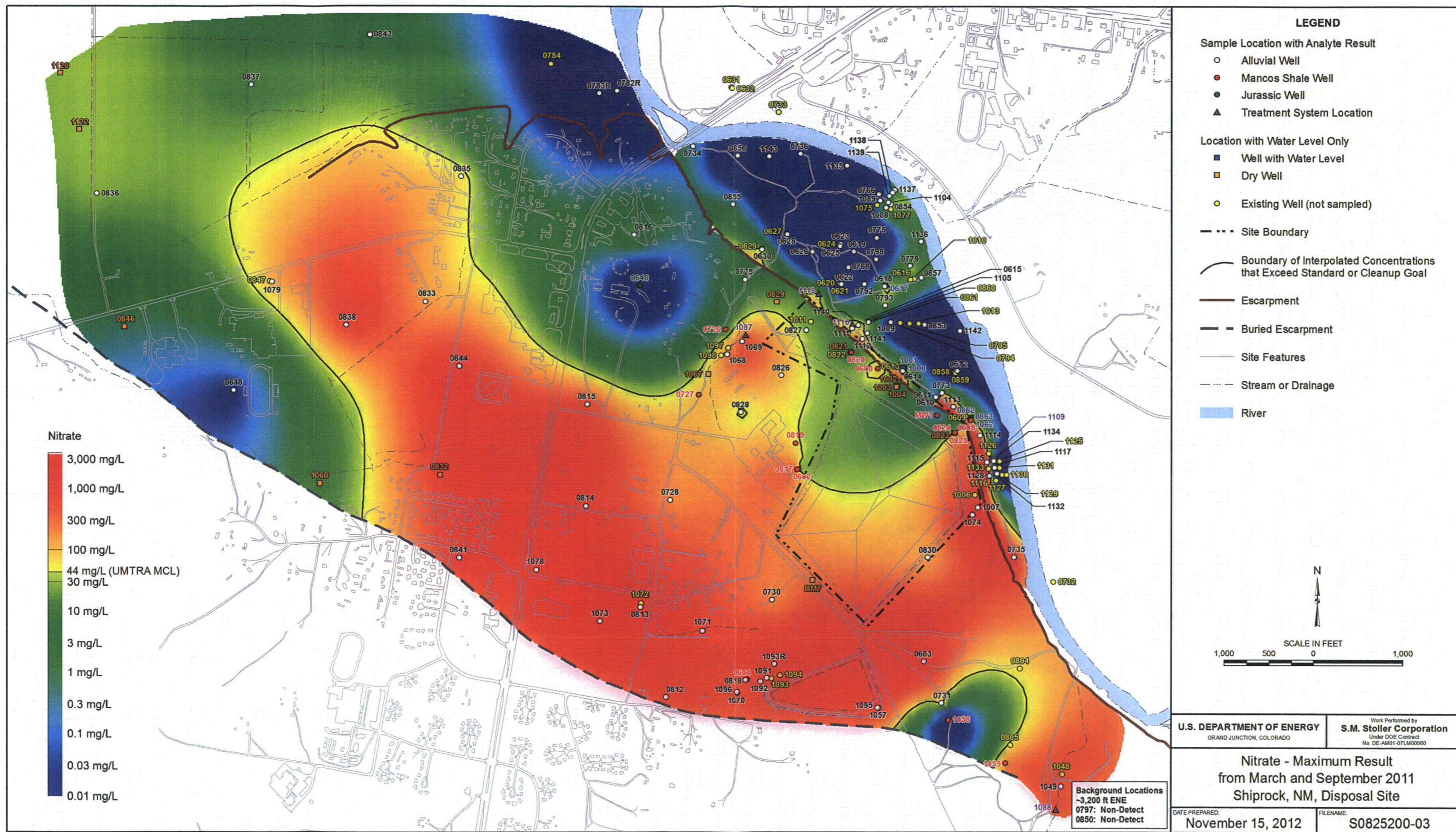


Figure 6. Nitrate Maximum Result March and September 2011

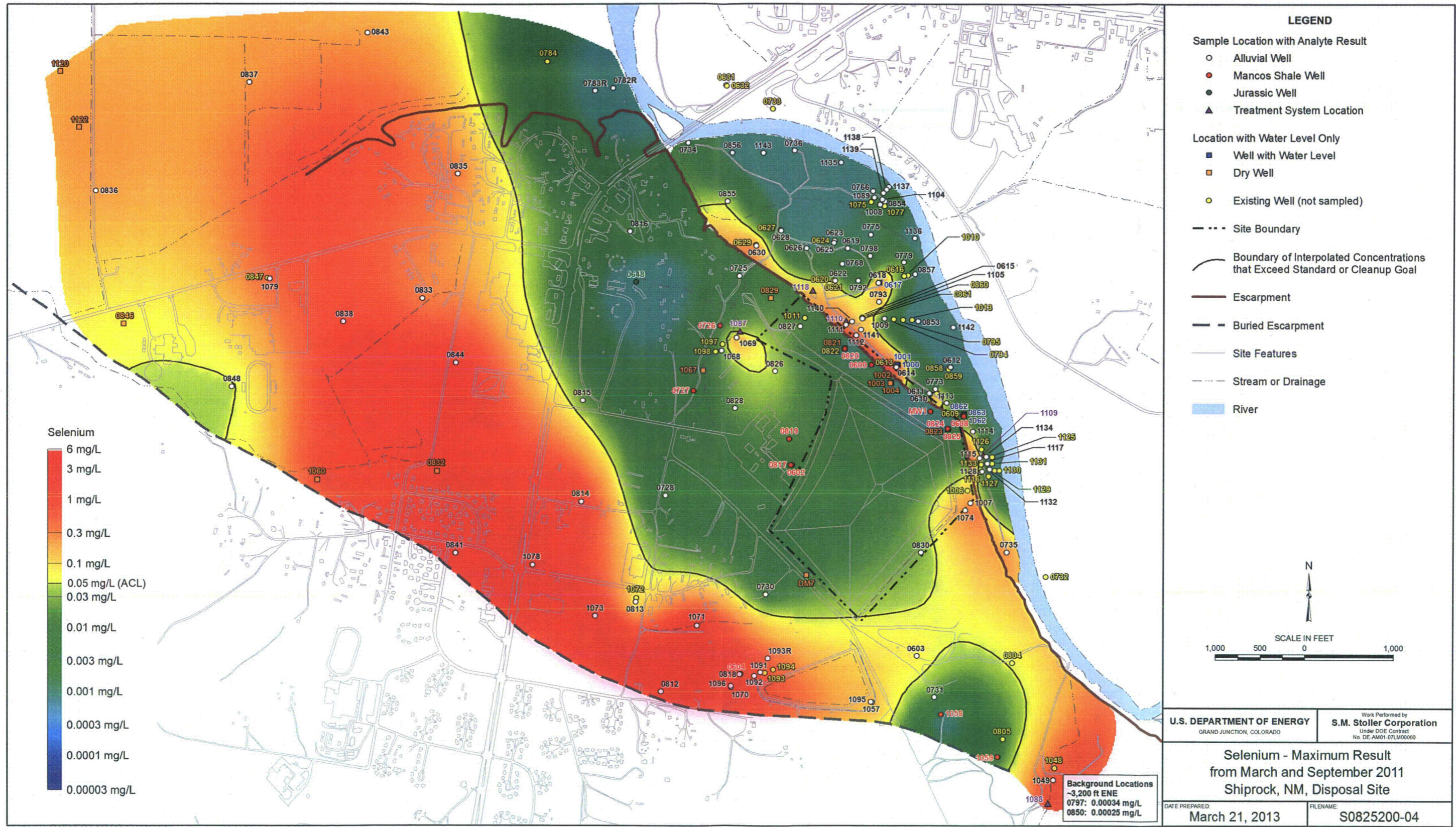


Figure 7. Selenium Maximum Result March and September 2011

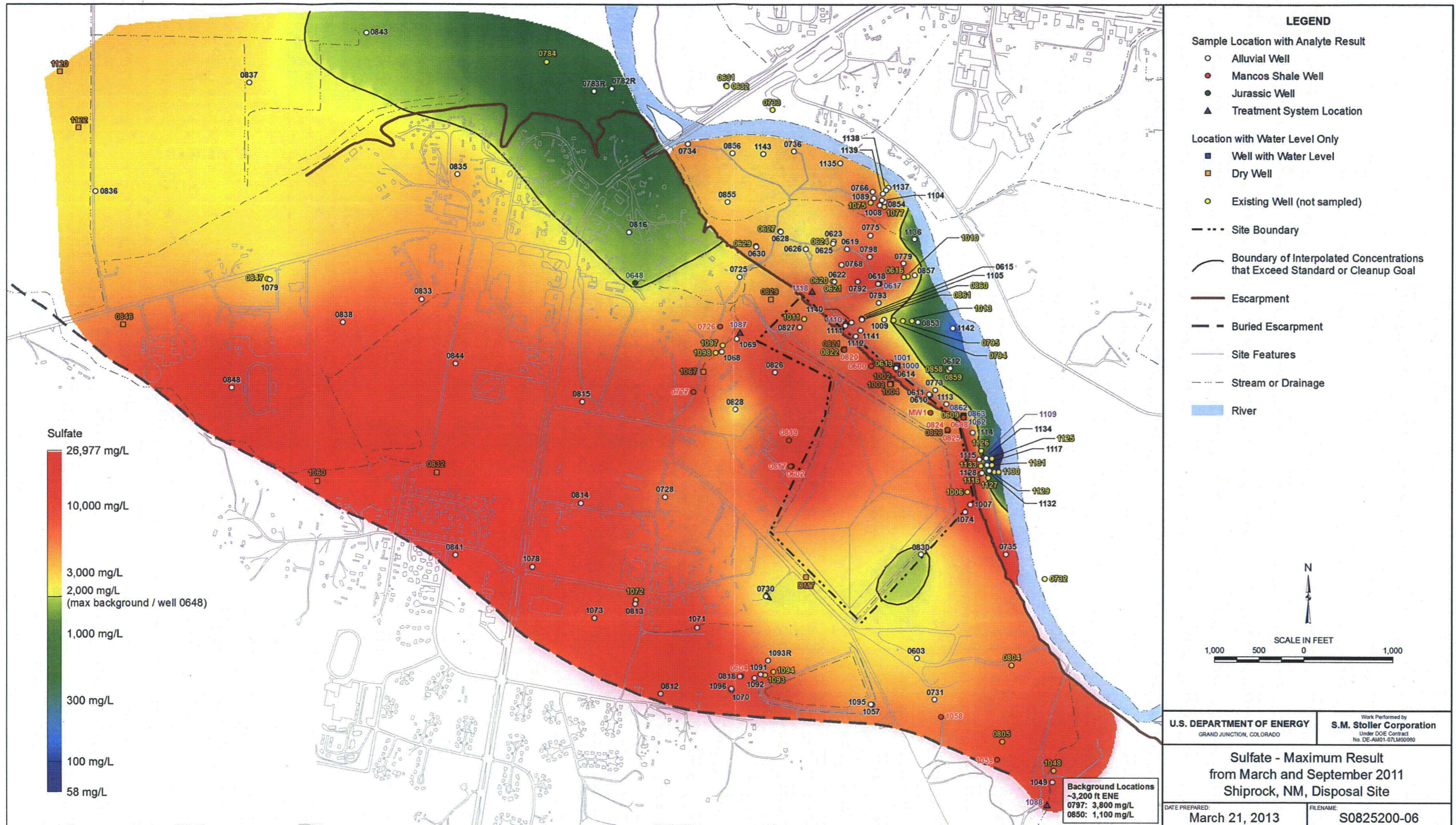


Figure 8. Sulfate Maximum Result March and September 2011

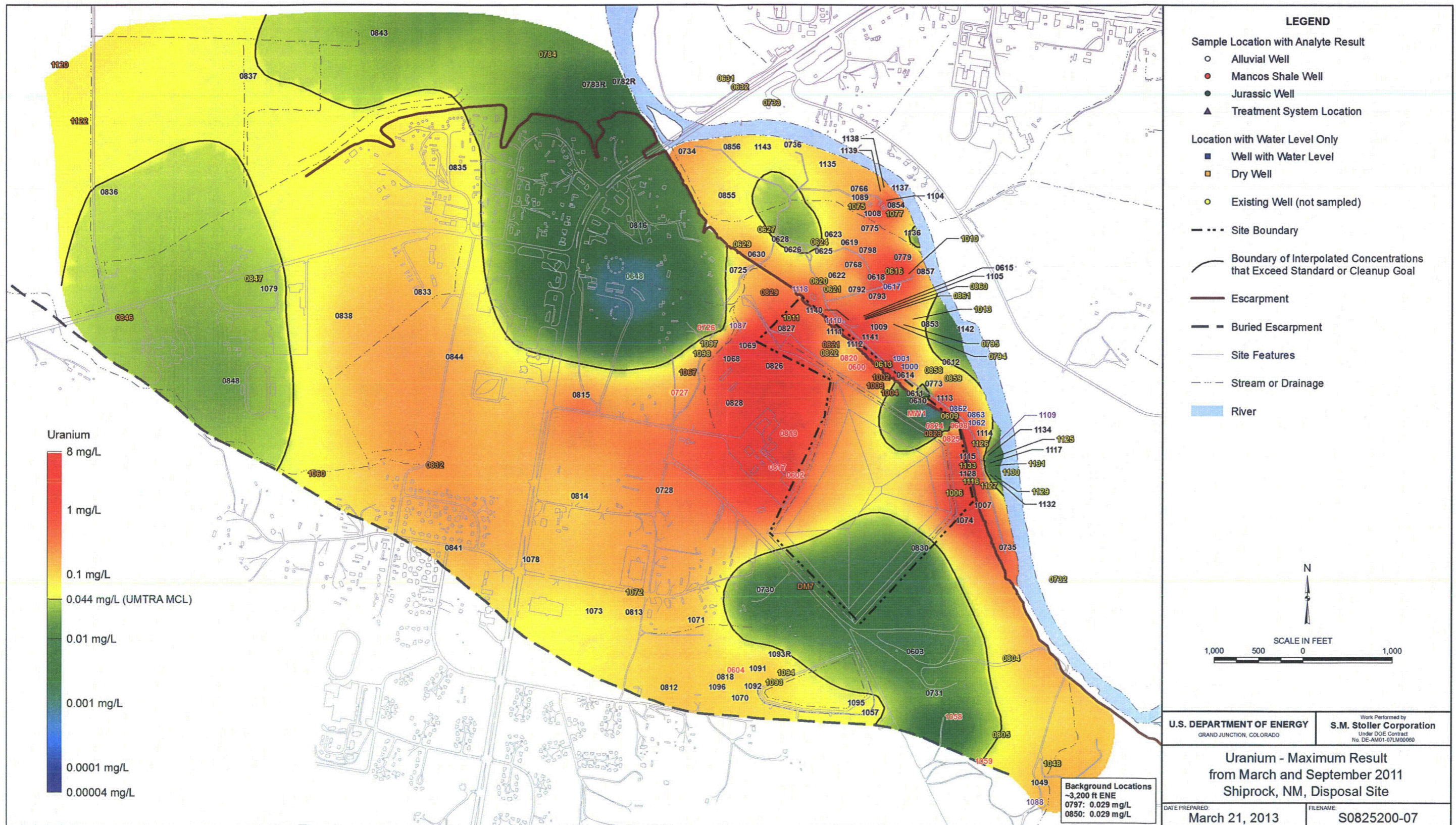


Figure 9. Uranium Maximum Result March and September 2011

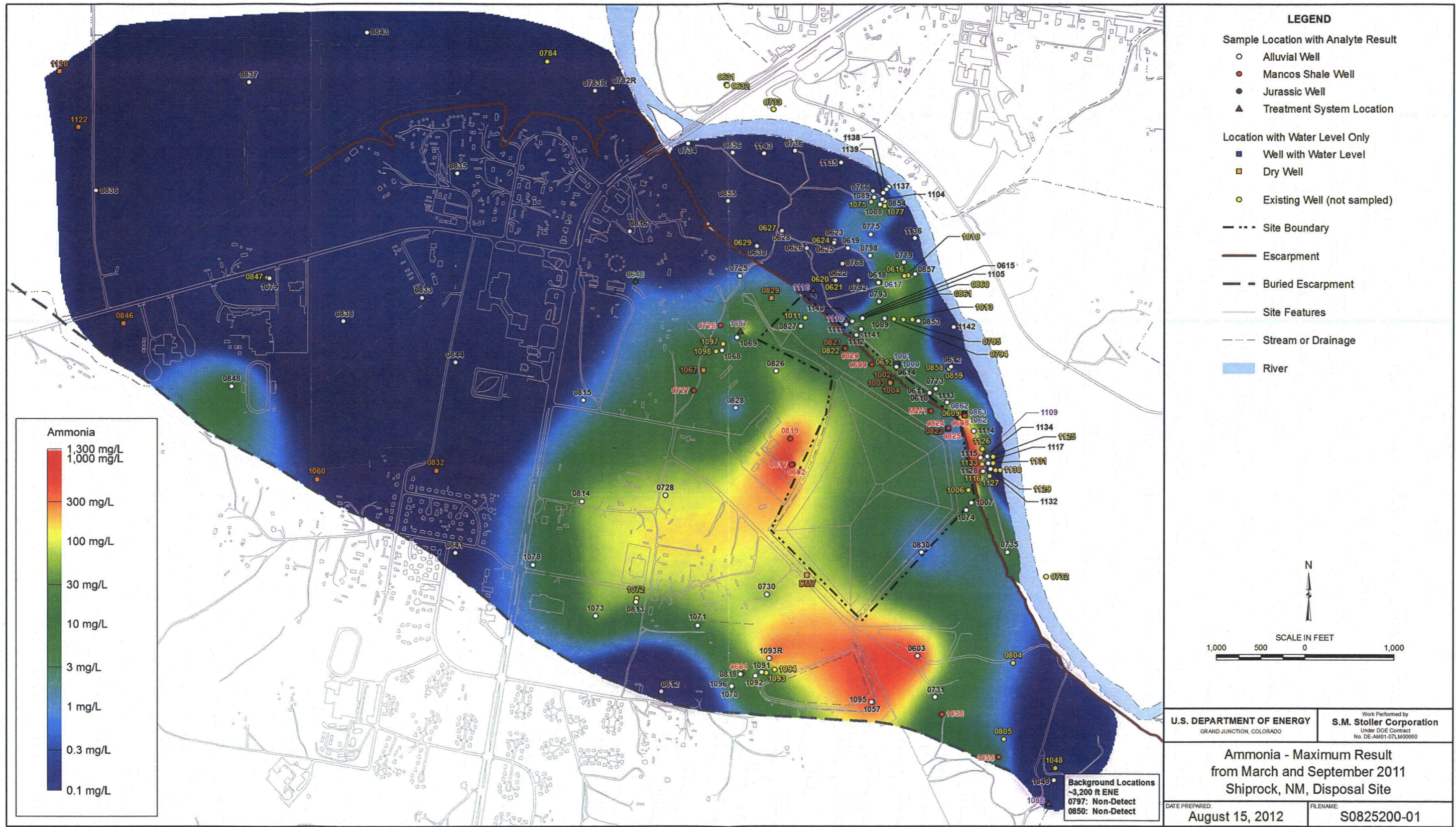


Figure 10. Ammonia Maximum Result March September 2011



Figure 11. Strontium Maximum Result March and September 2011

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6.3.4 Define Exposure Scenarios

The site conceptual model includes an evaluation of scenarios for potential exposure to site-related contamination. The exposure scenarios were originally assessed in the Baseline Risk Assessment (DOE 1994), which assumed residential use of contaminated groundwater. Contaminated groundwater is not being used as a drinking water source, and because no complete exposure pathway exists, groundwater contaminants currently present no risk to human health. In addition, fence enclosures have been constructed around areas of seeps where humans or livestock could come into contact with groundwater contaminants.

6.4 Resources and Constraints

Of the UMTRCA sites currently managed by DOE, Shiprock has the most extensive monitoring and the highest annual sampling costs (Table 6). The sampling costs exceeded the budget in 2011, and the optimization of the sampling regime would address these budget constraints.

Table 6. 2011 Direct Monitoring Costs at UMTRCA Sites

Site Name	Location	2011 Monitoring Costs
Shiprock	Navajo Nation	\$269,969
Tuba City	Navajo Nation	\$204,770
Bluewater	New Mexico	\$135,888
Monument Valley	Navajo Nation	\$102,962
Rifle	Colorado	\$90,379
Riverton	Wyoming	\$41,077
Shirley Basin South	Wyoming	\$40,617
Durango	Colorado	\$38,529
Gunnison	Colorado	\$33,241
Grand Junction	Colorado	\$30,493
Lakeview	Oregon	\$30,267
Slick Rock	Colorado	\$26,373
L-Bar	New Mexico	\$25,952
Sherwood	Washington	\$21,886
Falls City	Texas	\$19,123
Ambrosia Lake	New Mexico	\$16,555
Green River	Utah	\$13,415
Naturita	Colorado	\$10,814
Canonsburg	Pennsylvania	\$9,616

7.0 Identify the Goal of the Study

This step comprises four activities: (1) identify the principal study questions, (2) consider alternative outcomes or actions that can occur upon answering the questions, (3) develop decision statements, organize multiple decisions, and (4) for estimation problems, state what needs to be estimated and key assumptions (not addressed as part of this evaluation).

7.1 Principal Study Question

Are the current temporal, spatial, and analyte requirements in the sampling regime justified and supportive of the site DQOs and regulatory requirements?

7.2 Alternative Outcomes or Actions

Study Question	Potential Outcome or Action
Are there temporal redundancies?	Recommend that the sampling frequency be reduced. Recommend that sampling frequency remain unchanged.
Is there sufficient coverage of hot-spot locations?	Recommend that the number of sampling locations be decreased in well-defined hot-spot areas. Recommend that the number of sampling locations be increased in hot-spot areas that are not well-defined. Recommend that sampling locations remain unchanged.
Are the appropriate analytes being sampled?	Recommend that the number of analytes be reduced. Recommend that the number of analytes remain unchanged. Recommend sampling for different or additional analytes.

7.3 Decision Statement

Determine if (1) the wells sampled are covering the areas of the site where information is needed, (2) sampling frequency is appropriate, (3) the right analytes are being monitored, and (4) the current reasons for sampling can be adequately supported.

8.0 Identify Information Inputs

The Shiprock site has a large historical data set that can be analyzed to resolve the decision statement. This section provides an overview of the tools that can be used to evaluate the sampling data at Shiprock. The data were analyzed using the following tools: (1) Visual Sample Plan Temporal Redundancy module; (2) percent difference between paired averages of spring and fall results; (3) assessment of the reason for sampling an analyte based on compliance goals and DQOs; (4) visual assessment of the spatial distribution of sampled wells in relation to hot-spot areas of the site; and (5) assessment of the reason for sampling a location based on regulatory requirements and site DQOs. Sections 8.1 through 8.5 present an overview of these tools; the results of these analyses and optimization of the sampling design using site-specific information are presented in Sections 12 and 13.

8.1 Visual Sample Plan

Visual Sample Plan (VSP; PNNL 2012) software was used to assess the sampling regime at the Shiprock site. VSP is a tool that supports the development of a defensible sampling plan based on statistical sampling theory and the statistical analysis of sample results. VSP was developed by Pacific Northwest National Laboratory with support from DOE, the U.S. Environmental Protection Agency (EPA), the U.S. Department of Defense, the Department of Homeland Security, the Centers for Disease Control and Prevention, and the United Kingdom. VSP is being recommended by many regulators for defensible sampling design and statistical analysis. The

underlying methodology employs statistically defensible approaches and has strong DQO process underpinnings. The objective is to ensure that the right type, quality, and quantity of data are gathered to support confident decisions. Many statistical sampling designs are available, including random, systematic, sequential, adaptive cluster, collaborative, stratified, transect, multi-increment, combined judgment/probabilistic, and rank set sampling. The Temporal Redundancy module of VSP was used to analyze sampling at the Shiprock site.

8.1.1 Temporal Redundancy Analysis Using VSP

The Temporal Redundancy module of VSP provides methods for examining the temporal spacing of observations. Temporal redundancy is used to analyze data to determine whether sampling can be performed less frequently without losing important trend information or if more frequent sampling is needed. The objective of the module is to identify a technically defensible temporal spacing. Two different sampling goals are addressed here. One is determining if fewer observations could be used to characterize the contaminant concentrations at a sample location over time. A second is to identify the minimum temporal spacing between observations so that they are independent from one another.

Two options—variogram analysis and iterative thinning—are available in the Temporal Redundancy module.

Variogram Analysis

Variogram analysis requires the use of geostatistical techniques to determine a distance relationship between data points in a two-dimensional spatial field. The geostatistical techniques in this module have been adapted where the distance relationship is replaced by a time relationship. Variogram analysis determines how far apart in time samples can be taken before temporal correlation is eliminated. To detect temporal patterns or trends, the sampling interval should be smaller than the estimated maximum interval. Variogram analysis requires a significant amount of data; typically 30 or more observations for each location are needed for this analysis. This method is more complex and requires more data than the iterative thinning method. Insufficient data were available to use variogram analysis for the Shiprock site, and that approach is not used in this report.

Iterative Thinning

The iterative thinning approach is based on an algorithm published by Cameron (2004). The goal of the algorithm is simple: identify the sampling frequency required to reproduce the temporal trend of the full data set (the full data set is assumed to adequately capture the variation in the site data). The trend may include simple upward or downward trends, but the algorithm also allows reproduction of more complex patterns (e.g., cyclical patterns related to seasonal variations in concentration).

The median temporal sample spacing between historical observations is first calculated and used as the baseline sample spacing. The iterative thinning algorithm uses the locally weighted scatterplot smoothing (LOWESS) algorithm to fit a smooth trend and confidence bands (Cleveland 1979) around the full temporal data set. LOWESS is a regression method for applications that fit the general framework of least-squares regression. A percentage of the data

points are removed from the data set, and LOWESS is used with the same bandwidth to fit a smooth trend to the reduced data set.

The ability of the reduced data set to reproduce the temporal trends in the full data set is evaluated by calculating the percentage of the data points on the trend for the reduced data set that fall within the 90 percent confidence interval established using the full data set. Increasing numbers of data points are removed from the data set, and each reduced data set is evaluated for its ability to reproduce the trend observed in the full data set. A default level of 75 percent of the points on the trend for the reduced data falling within the confidence limits around the original trend is deemed acceptable (Cameron 2004). In order to guard against artifacts that might arise from the selection of a single set of data points to remove, the iterative removal process is repeated a large number of times (default number of iterations is 500). The data that can be removed while still reproducing the temporal trend of the full data set is used to estimate an optimal sampling frequency presented as days between sampling events.

8.2 Percent Difference Temporal Analysis

The averages of the spring and fall analytical results from the same calendar year were paired for all of the sampling locations and the five main COCs (uranium, nitrate, manganese, sulfate, and selenium). The percent difference was calculated by subtracting the spring average concentration from the fall average concentration and then dividing by the spring average concentration. Locations with at least two pairs were included. This analysis was used to explore the temporal variation in the data and to supplement and expand on the VSP results. More locations could be assessed using percent difference, since the statistical methods in VSP required 10 or more sampling events. The location analyte pairs in which the percent difference was 100 percent or more and concentrations also exceed a compliance standard or cleanup goal for the spring or fall average, or both, were further assessed graphically.

8.3 Assessment of Analytes

The rationale for retaining a COC based on the risk assessment in the SOWP was reviewed and compared to the current site conditions to see if the rationale was still relevant and if the risk is still present. Non-COC analytes were assessed based on site DQOs and GCAP requirements.

8.4 Spatial Assessment of Hot Spots

A comparison of all the site wells available for sampling and visual representation of site data for the five main COCs was used to determine whether the sampling locations sufficiently cover the different areas of the site with elevated concentrations (hot spots).

8.5 Assessment of Sampling Objectives

This assessment evaluates whether the sampling locations are still appropriate based on the sampling objectives and regulatory requirements. The rationale for adding the location to the sampling regime is compared to the DQOs to determine if the location can be removed from the sampling regime.