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Date: May 8, 2009
Refer To: EP2009-0223

James P. Bearzi, Bureau Chief
Hazardous Waste Bureau
New Mexico Environment Department
2905 Rodeo Park Drive East, Building 1
Santa Fe, NM 87505-6303

Subject: Submittal of the Response to the Notice of Disapproval Periodic Monitoring Report for Pajarito Watershed; September 8-September 19, 2008

Reference: Letter, Bearzi to Messrs. Gregory and McInroy, dated 04/07/09

Dear Mr. Bearzi:

Enclosed please find two hard copies with electronic files of the response to the Notice of Disapproval Periodic Monitoring Report for Pajarito Watershed; September 8-September 19, 2008, and replacement pages. Los Alamos National Laboratory has received U.S. Department of Energy concurrence on the contents of this response and is transmitting it today to meet the New Mexico Environment Department's due date.

If you have any questions, please contact Ardyth Simmons at (505) 665-3935 (asimmons@lanl.gov) or Hai Shen at (505) 665-5046 (hshen@doeal@doeal.gov).

Sincerely,

Michael J. Graham, Associate Director
Environmental Programs
Los Alamos National Laboratory

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MG/DG/PH/AS:sm

Enclosures: 1) Two hard copies with electronic files - Response to the Notice of Disapproval Periodic Monitoring Report for Pajarito Watershed; September 8–September 19, 2008, and Replacement Pages (LA-UR-09-2595)

Cy: (w/enc.)
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Response to the Notice of Disapproval of the
Periodic Monitoring Report for Pajarito Watershed, September 8–September 19, 2008,
Los Alamos National Laboratory, EPA ID No: NM0890010515, HWB-LANL-09-004
Dated April 7, 2009

INTRODUCTION

To facilitate review of this response, the New Mexico Environment Department's (NMED's) comments are included verbatim. Los Alamos National Laboratory's (LANL's) responses follow each NMED comment.

SPECIFIC COMMENTS

NMED Comment

1. *Table 3.4-1 (Observations and Deviations) contains inaccurate information and also some incomplete information. The following table lists information from the PMR and summarizes the requirements of the 2008 Interim Facility-Wide Groundwater Monitoring Plan (2008 IFGMP) for affected monitoring locations:*

Monitoring Point	PMR Listed Deviation	2008 IFGMP Requirement
03-B-9	The location could not be sampled on 09/18/08: only water level was measured per 2008 IFGMP.	2008 IFGMP only specifies quarterly water level measurements.
PCO-3	The location could not be sampled on 09/12/08; only water level was measured per 2008 IFGMP.	2008 IFGMP specifies quarterly sampling for TAL metals, VOCs+TICs. SVOCs-TICs, HEXP, GI, perchlorate and FD, continuous water level measurements and annual sampling for RAD. low- level tritium and stable isotopes.
R- 19. Screen 5; R-19. Screen 7	The locations were sampled on 9/I5/08 for only T'KN and ammonia (per 2008 IFGMP).	2008 IFGMP specifies quarterly sampling for sulfide, ammonia, total Kjeldah1 nitrogen (TKN), FD, and continuous water level measurements.
R-22, Screen 1; R-22, Screen 4	The locations were sampled on 09/17-18/2008 for only TKN and ammonia (per 2008 IFGMP).	2008 IFGMP specifies quarterly sampling for sulfide, ammonia, TKN, VOCs+TICs, FD, low-level tritium and continuous water level measurements.
R-22, Screen 5	The location was sampled on 09/16/08 for only TKN and ammonia (per 2008 IFGMP).	2008 IFGMP specifies quarterly sampling for sulfide, ammonia, TKN and FD and continuous water level measurements.

Notes:
TAL – Target analyte list metals, see also footnote C, Table 8.4-1, 2008 IFGWP
VOCs + TICs – Volatile organic compounds including tentatively identified compounds
SVOCs – TICs-Semi-volatile organic compounds including tentatively identified compounds
RAD – See footnote D, Table 8.4-1, 2008 IFGWP
HEXP – See footnote F, Table 8.4-1, 2008 IFGWP
G1 – General Inorganics: see footnote E, Table 8.4-1, 2008 IFGWP
FD – Field data, see footnote B, Table 8.4-1. 2008 IFGWP

The Table 3.4-1 entry for wells PCAO-8 and PCAO-9 indicates the wells were sampled for an abbreviated analytical suite due to slow or limited well recharge conditions. However, no explanation is provided for the limited sampling performed at PCO-3, R-19-Screen 5, R-19-Screen 7, R-22-Screen 1, R-22-Screen 4 or R-22-Screen 5. The Permittees must comply with the sampling requirements outlined in the NMED-approved 2008 IFGMP or provide informative and justifiable explanation(s) for why a given requirement was not followed.

LANL Response

1. The entire Table 3.4-1 for the Pajarito watershed September 8–September 19, 2008, monitoring event is attached with revisions and clarifications.

NMED Comment

2. *Two of the concentration versus time graphs presented in Figure 4.2-1 (1,4-dioxane at wells 03-B-10 and 03-B-13) apparently were not updated to include data from the September 2008 sampling event.*

LANL Response

2. The concentration versus time graphs presented in Figure 4.2-1 display the most recently available 1,4-dioxane values acquired via the semivolatile method for wells 03-B-10 and 03-B-13. 1,4-dioxane results are obtained by both volatile organic analysis (VOA) and semivolatile organic analysis (SVOA) methods, and both methods are reported in the periodic monitoring reports (PMRs). For the September 2008 PMR, samples were not collected in wells 03-B-10 and 03-B-13 for analysis by the SVOA method; this was an error. Thus, no data were added to the plots. For future PMRs, the analytical method for 1,4-dioxane results in the graph will be noted in the document text and on associated graphs.

NMED Comment

3. *The field parameter results for well 03-B-10 presented in Appendix B of the PMR indicate sample specific conductance values ranging from 2.14 to 1,623 microSiemens per centimeter (μS/cm) during five sampling events conducted between September 18, 2007 and September 18, 2008. Turbidity measurements from the same well during the period from September 18, 2007 to September 18, 2008 are reported to have ranged from 8.03 to 78 nephelometric turbidity units (NTU). Oxidation reduction potential (ORP) values ranged from 14 to 390 millivolts (mV) at this well over the same timeframe. These wide ranges of field measurement values do not seem to be indicative of stabilized well sampling conditions. However, well purge volumes (ranging from one to five gallons) are only reported for three sampling events at this well, making it impossible to determine the relationship(s) between purge volumes and the associated field measurements. Wide ranges for conductivity (2.18 – 1,850 μS/cm), turbidity (19.1 – 100 NTU) and ORP (-11 – 348 mV) measurements are also reported for well 03-B-13 during the period covered by the PMR. Purge volumes at this location ranged from one to 11 gallons during the last four monitoring events.*

   NMED noted other Pajarito Watershed sampling locations are also showing what may be significant variability in field measurement data. Examples include Homestead Spring (conductivity 26.9 – 324 μS/cm) PCAO-5 (ORP -227 – 96 mV), PCAO-8 (turbidity 62.1 – 264 NTU). Pajarito below confluences of South and North Anchor East Basin (turbidity 7.69 – 72 NTU) and R-22, Port 722, depth1273.5 (turbidity 0.19 – 8.59).

Generally, the purpose of purging wells prior to collecting samples is to document that stabilized. representative samples are obtained from a given well. The Permittees must review the sample collection procedures outlined in Appendix C of the 2008 IFGMP and verify that field sampling personnel are following appropriate well purging and field data collection procedures. If the Permittees determine that current well purging and field data collection procedures do not reliably produce representative groundwater samples. the Permittees must revise applicable portions of Appendix C of the 2009 IFGMP.

LANL Response

3. LANL's well-purging and field data collection procedures meet the requirements of the NMED Compliance Order on Consent and are consistent with U.S. Environmental Protection Agency and U.S. Geological Survey guidelines for well purging and sampling.

   LANL's groundwater sampling procedure for non-Westbay wells is presented in Standard Operating Procedure 5232, available at http://www.lanl.gov/environment/all/qa/adep.shtml. The procedure requires a minimum purge volume of 1 casing volume (plus the volume of the drop pipe) for alluvial wells and a minimum purge volume of 3 casing volumes (plus drop pipe) for intermediate and regional wells (where possible).

   To ensure groundwater samples are representative, the stability of field parameters is also required. The procedure requires that samples be collected only after the minimum volume has been purged, and stability has been reached. During purging, field parameters are measured at regular intervals, and stability is defined when field parameters have stabilized within their allowable ranges for at least three consecutive measurements a minimum of 5 min apart.

   The stabilization criteria used to ensure representativeness of groundwater samples are presented in the following table.

Field Parameter	Stabilization Criteria
Turbidity	<5 Nephelometric turbidity units (NTUs), if possible; if turbidity remains >5 NTUs, ± 10% of the reading
Dissolved Oxygen	± 10% of the reading, or ± 0.2 mg/L, whichever is greater
pH	± 0.2 pH units
Specific Conductance	± 10% of the reading
Temperature	± 0.2°C

   Oxidation reduction potential (ORP) is also measured but is not used to define stability.

   In late 2008, a review of field parameter data collected during groundwater sampling activities showed some problems with consistency, including some values being recorded outside of their reasonable ranges.

   Corrective action was taken to improve the quality of the field parameter data. A meeting was held with the groundwater sampling teams to discuss the importance of the field parameter data and to review the inconsistency with field parameter data collected in the past. Reasonable ranges for field parameter data were discussed. The sampling teams reported that the older meters used to measure field parameters were problematic.

It was determined that the older meters were no longer reliable. In December 2008, the field instruments used were replaced with new YSI 556 multiprobe meters. In addition, the groundwater sampling teams were trained regarding the importance of these field parameter data and the reasonable ranges for these parameters.

For the above reasons, the Permittees are confident that current well purging and field data collection procedures are yielding representative groundwater samples.

Several chemical and field parameters measured at these wells (03-B-10 and 03-B-13) at SM-30 indicate that the water quality shows seasonal variability. The values of several of these parameters are not likely to be affected by purging time. Similar values appear at the same time in both wells, also indicating that purging has not affected the results.

Figure 1 shows the histories for specific conductance (measured in both the field and the analytical laboratory) and total dissolved solids (TDS). In each well, values for these parameters track quite well, and similar values are observed in both wells. High TDS in early winter corresponds to high chloride and sodium concentrations and is the result of road salting in the parking lots. Infiltration of summer runoff lowers these concentrations by the end of autumn.

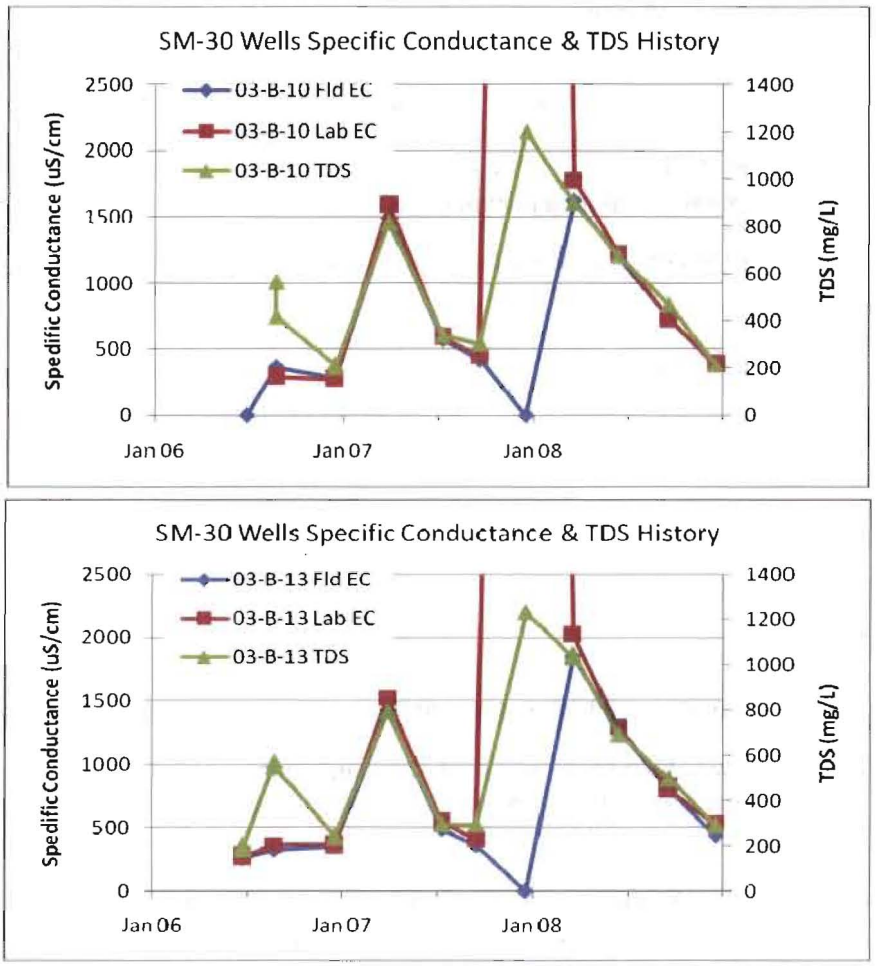

Figure 1 Histories for specific conductance (measured in the field and the analytical laboratory) and TDS at 03-B-10 (top) and 03-B-13 (bottom)

For the measurements made on 12/17/08 and 12/18/08 both the field-measured and analytical laboratory specific conductance values are in error. The field values were reported as near 2.2 µS/cm and should have been reported as near 2.2 mS/cm. The analytical laboratory results of about 20,500 µS/cm also appear to be unit errors.

Figure 2 shows histories for turbidity and unfiltered iron in these wells. These parameters show a similar seasonal variation. The variation in filtered iron and both filtered and unfiltered manganese, for example, is similar to that for iron and turbidity. The high turbidity in late summer may be the result of a change in reducing conditions in the groundwater; under more reducing conditions, iron and manganese are more soluble.

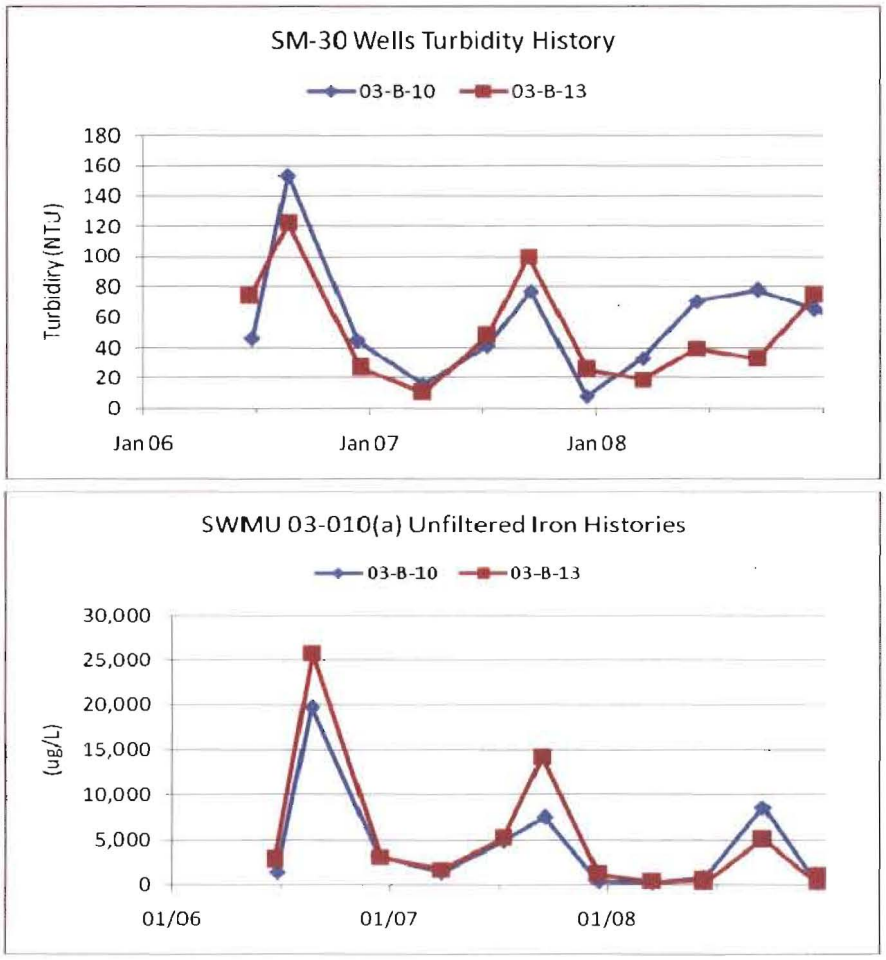

Figure 2 Histories for turbidity (top) and unfiltered iron concentrations (bottom) at 03-B-10 and 03-B-13

Figure 3 shows histories for ORP and total organic carbon (TOC). Higher ORP values of indicate more oxidizing conditions, and lower ORP values indicate more reducing conditions. The ORP values peak in late autumn, just after the observed high iron values. TOC shows the opposite behavior: high TOC suggests higher concentration of microorganisms and/or organic matter in the groundwater. The resulting anaerobic conditions lower the ORP values.

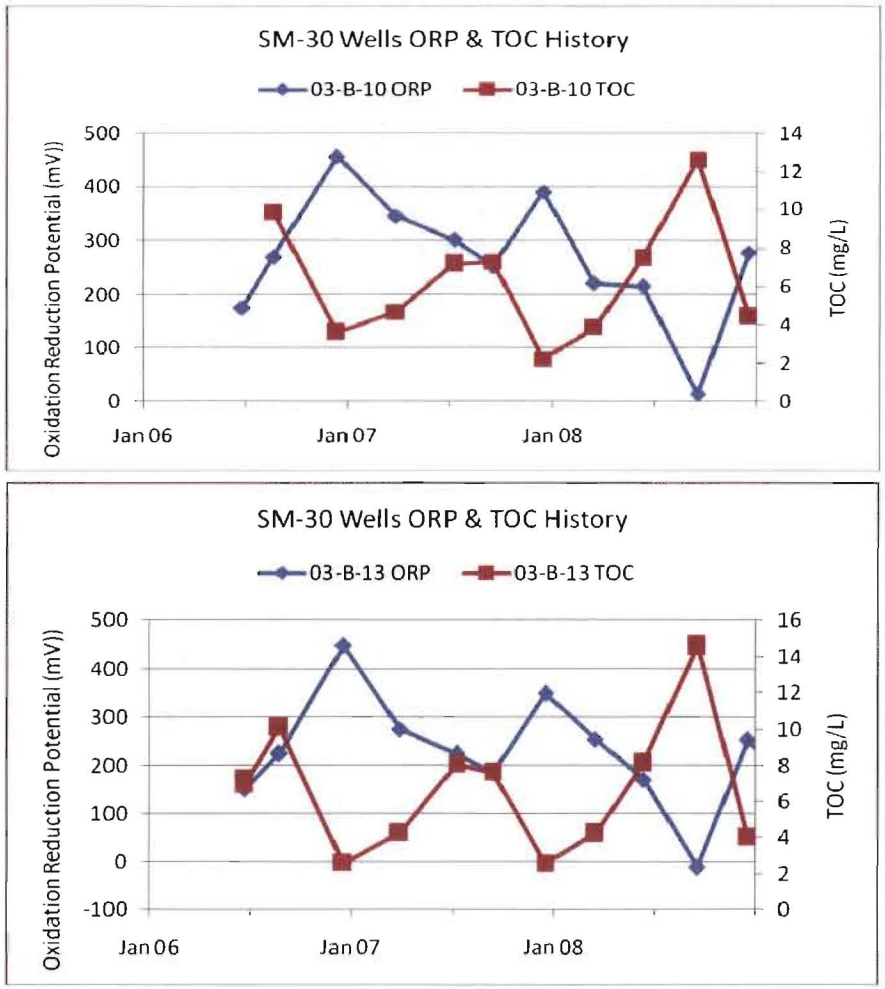

Figure 3 Histories for ORP and TOC at 03-B-10 (top) and 03-B-13 (bottom)

In conclusion, the variation in the field parameters electrical conductance, turbidity, and ORP at these wells show seasonal variability in water quality. The water quality is affected by infiltration of road salt or summer runoff, which changes the chloride and sodium content. This infiltration apparently also changes the oxidation state of the groundwater, affecting bacterial activity, metal solubility, and turbidity.

NMED Comment

4. *NMED noted elevated 1,1-dichloroethylene, 1,1,1-trichloroethane and 1,4-dioxane concentrations at well 03-B-10 and elevated 1,1,1-trichloroethane, 1,1-dichloroethylene and 1,4-dioxan concentrations at well 03-B-13. The reported concentrations of these constituents greatly exceed applicable water quality. standards. In the case of 1,4-dioxane at both wells, NMED noted that the constituent concentrations dropped significantly (i.e., to below or only slightly above applicable standards) during the subsequent December 18, 2008 sampling period as reported in the current RACER database. It is not clear what is causing concentration differences to vary. by orders of magnitude between sampling events for these wells. The Permittees must carefully review. well purging field records in relation to constituent concentration data at these wells when preparing future PMRs for the watershed.*

LANL Response

4. For some solvents, their retention on solid surfaces is lower in higher ionic strength solutions. One possible cause for changes in concentration of 1,1-dichloroethylene and 1,1,1-trichloroethane is that variation in concentration of sodium and chloride releases these compounds from the aquifer matrix. One possibility is that the high TDS observed in the groundwater in December 2007 (Figure 1) resulted in release of these compounds at high concentrations during the following months (Figure 4).

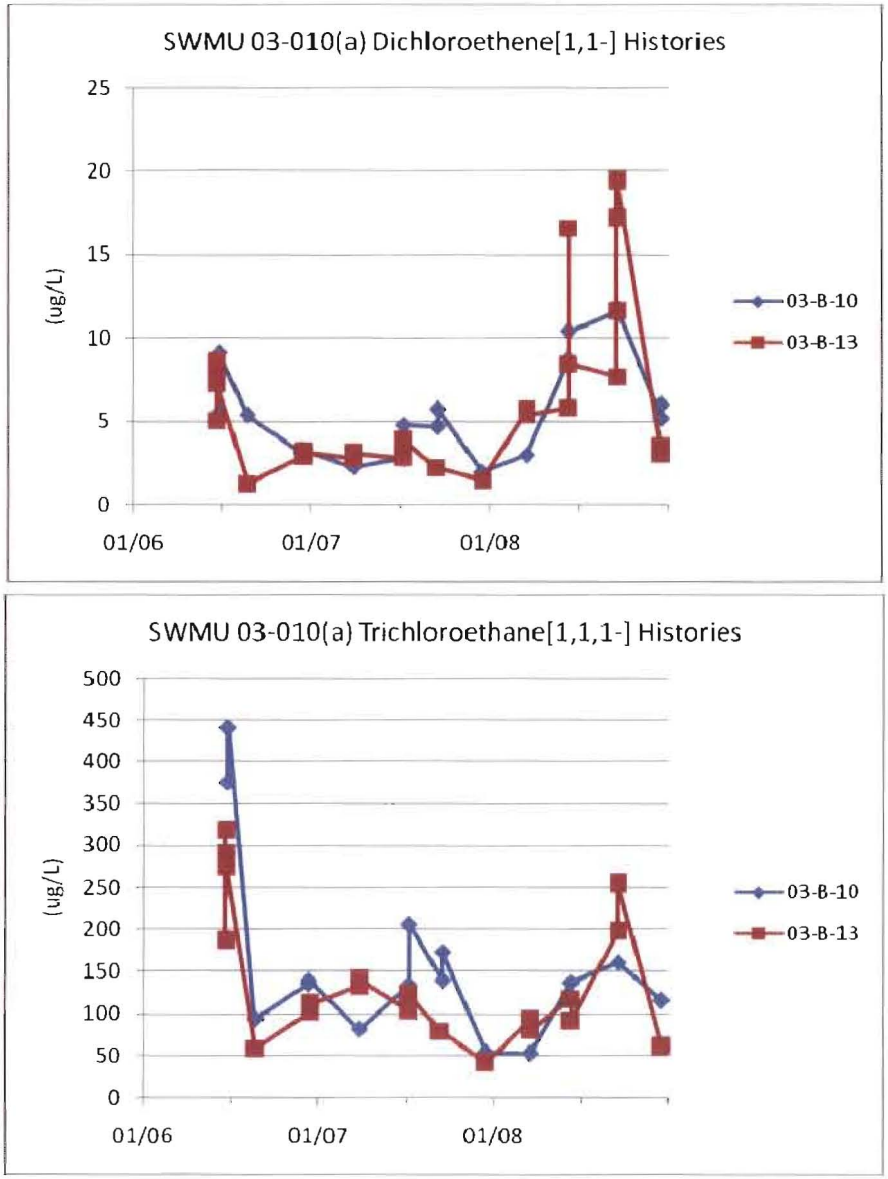

Figure 4 Histories for 1,1-dichloroethylene (top) and 1,1,1-trichloroethane (bottom) at 03-B-10 and 03-B-13;

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Appendixes

Appendix A	Conceptual Model
Appendix B	Field Parameter Results
Appendix C	Groundwater-Level Measurements
Appendix D	Analytical Results
Appendix E	Screening Results
Appendix F	Investigation-Derived Waste Management
Appendix G	Analytical Reports (on DVD included with this document)

Acronyms and Abbreviations

AK	acceptable knowledge
amsl	above mean sea level
AOC	area of concern
BCG	Biota Concentration Guide (DOE)
bgs	below ground surface
C	cancer
Consent Order	Compliance Order on Consent
DCG	Derived Concentration Guideline (DOE)
DOE	Department of Energy (U.S.)
DOT	Department of Transportation (U.S.)
EPA	Environmental Protection Agency (U.S.)
F	filtered
gpm	gallons per minute
IDW	investigation-derived waste
IFGMP	Interim Facility-Wide Groundwater Monitoring Plan
LANL	Los Alamos National Laboratory
MCL	maximum contaminant level (EPA)
MDA	material disposal area
MDL	method detection limit
N	noncancer
NMED	New Mexico Environment Department
NMWQCC	New Mexico Water Quality Control Commission
NOI	notice of intent

Table 3.4-1
Pajarito Canyon Sampling Event September 8–September 19, 2008, Observations and Deviations

Location	Deviation	Cause	Comment
03-B-9	No deviation; water level is all that is required.		
03-B-10, 03-B-13	Samples not collected for SVOA method analysis	Human error	Samples will be collected for appropriate method during next sampling round.
Pajarito below TA-18 (PBF-5)	No data are included in this report for this location.	The location could not be sampled on 9/19/08 because it was dry.	Location will be checked again during next scheduled sampling round.
PCAO-6	No data are included in this report for this location.	The location could not be sampled on 9/10/08 because it was dry.	Location will be checked again during next scheduled sampling round.
PCAO-7b1	No data are included in this report for this location.	The location could not be sampled on 9/10/08 because it was dry.	Location will be checked again during next scheduled sampling round.
PCAO-7b2	No data are included in this report for this location.	An abbreviated suite was collected on 9/13/2008 due to low water level and slow recharge (Radium-226, radium-228, and filtered radionuclides were not collected.)	Location will be checked again during next scheduled sampling round.
PCAO-8	Limited data are included in this report for this location.	The location was sampled for an abbreviated analytical suite on 9/17/2008 because the well purged dry. (Total metals were not collected.)	Location will be checked again during next scheduled sampling round.
PCAO-9	Limited data are included in this report for this location.	The location was sampled for an abbreviated analytical suite on 9/17/2008 because the well purged dry. (Radium-226, radium-228, and radionuclides were not collected.)	Location will be checked again during next scheduled sampling round.
PCO-2	No data are included in this report for this location.	The location could not be sampled on 9/12/08 because it was dry.	Location will be checked again during next scheduled sampling round.
PCO-3	No data are included in this report for this location.	The location could not be sampled on 9/12/08 because it was dry.	Location will be checked again during next scheduled sampling round.
R-19, screen 1	No data are included in this report for this location.	The location could not be sampled on 9/10/08 because it was dry.	Location will be checked again during next scheduled sampling round.
R-19, screen 5	No deviation from IFGMP; the only sample collected was for well-quality-monitoring purposes and was sent to an internal laboratory.		
R-19, screen 6	No deviation from IFGMP; the only sample collected was for well-quality-monitoring purposes and was sent to an internal laboratory.		
R-19, screen 7	No deviation from IFGMP; the only sample collected was for well-quality-monitoring purposes and was sent to an internal laboratory.		

Table 3.4-1 (continued)

Location	Deviation	Cause	Comment
R-22, screen 1	No deviation from IFGMP; the only sample collected was for well-quality-monitoring purposes and was sent to an internal laboratory.		
R-22, screen 4	No deviation from IFGMP; the only sample collected was for well-quality-monitoring purposes and was sent to an internal laboratory.		
R-22, screen 5	No deviation from IFGMP; the only sample collected was for well-quality-monitoring purposes and was sent to an internal laboratory.		
TA-18 Spring	No data are included in this report for this location.	The location could not be sampled on 9/10/08 because it was dry.	Location will be checked again during next scheduled sampling round.
Threemile Spring	No data are included in this report for this location.	The location could not be sampled on 9/09/2008 because the spring was covered by baseflow.	Location will be checked again during next scheduled sampling round.
TW-1.72 Spring	No data are included in this report for this location.	The location could not be sampled on 9/19/2008 because the spring was under water.	Location will be checked again during next scheduled sampling round.

Table 4.2-1
Screening Levels for Groundwater and Surface Water at Los Alamos National Laboratory

Standard Type	Groundwater	Surface Water
BCG	n/a[a]	X[b]
DOE 100-mrem Public Dose DCG	X	n/a
DOE 4-mrem Drinking Water DCG	X	n/a
EPA MCL	X	n/a
EPA Region 6 Tap Water Screening Level	X	n/a
New Mexico Environmental Improvement Board Radiation Protection Standards	X	X
NMWQCC Fisheries Standards Chronic	n/a	X
NMWQCC Fisheries Standards Chronic, Hardness = 100 mg/L	n/a	X
NMWQCC Groundwater Standard	X	n/a
NMWQCC Livestock Watering Standard	n/a	X
NMWQCC Wildlife Habitat Standard	n/a	X
NMWQCC Human Health Standard Ephemeral	n/a	X
NMWQCC Human Health Standard Perennial	n/a	X

[a] n/a = Not applicable.

[b] X = Standard applied to data screen for this report.