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February 4, 2008

By e-mail to: john.kieling@state.nm.us

John E. Kieling, Program Manager
Hazardous Waste Bureau
New Mexico Environment Department
2905 Rodeo Park Drive East, Building 1
Santa Fe, NM 87505-6303

Re: Comments about Selection of a Remedy for Corrective Action at
Material Disposal Area H, SWMU 54-004 at Technical Area 54
Facility: Los Alamos National Laboratory (LANL)
Facility Owner and Co-Operator: U.S. Department of Energy (DOE)
Facility Co-Operator: Los Alamos National Security, LLC (LANS)
EPA ID No.: NM0899910515

Dear Mr. Kieling:

Concerned Citizens for Nuclear Safety (CCNS) and Robert H. Gilkeson provide the following comments about the above-referenced remedy selection for Material Disposal Area H (MDA H) at Los Alamos National Laboratory (LANL).

CCNS is a non-governmental organization which formed in 1988 to voice citizen concerns about the transportation of nuclear waste from Los Alamos National Laboratory (LANL) to the then proposed Waste Isolation Pilot Plant (WIPP). For the past 20 years, CCNS has been devoted to its mission *to protect all living beings and the environment from the effects of radioactive and other hazardous materials now and in the future.*

CCNS participated in the MDA H Focus Group, which met from August 14, 2001 through October 8, 2003. CCNS provided one of two dissenting opinions for the recommended corrective measures alternative, which was an engineered evapotranspiration cover. AR 11822, "Final Report on MDA H Focus Group Process," January 1, 2004. Our dissent was based on the following:

1). The inadequate inventory of MDA H;

2). A lack of information about groundwater quality at MDA H. The nearest down-gradient Mesita del Buey characterization well is approximately two miles east of MDA H;

3). Predicted concentrations of RDX exceed Environmental Protection Agency (EPA) drinking water guidelines at MDA H;

4). A lack of analysis of fracture flow, lateral flow, convergent flow and matrix flow in the vicinity of MDA H. LANL concluded in its "Corrective Measures Study (CMS)," that fracture flow is not significant.

George Rice, groundwater hydrologist, provided an independent review of the CMS for the Focus Group. Rice, "Evaluation of Corrective Measures Study Report for MDA H, SWMU 54-004, August 7, 2003. CCNS requests that the Rice report be included in the Administrative Record and will deliver a copy to NMED this week.

Rice reported that LANL's conclusion "is not strongly supported by available information. Some of the information is ambiguous, and some appears to contradict this conclusion. Id., p. 16;

5). A lack of analysis of episodic fracture flow through the vadose zone at MDA H. See Rice report, p. 16;

6). A lack of information about the extent of the vapor-phase contaminant plumes; and

7). The failure of institutional controls at other Department of Energy sites, such as Weldon Springs in Missouri and Oak Ridge National Laboratory.

Robert H. Gilkeson is a registered geologist, former lead consultant to the groundwater protection program at LANL, and award-winning whistleblower. Gilkeson has written a number of reports and made presentations for the public, regulatory agencies as well as oversight boards about the problems with the drilling of the characterization wells at LANL with organic drilling fluids and bentonite clay muds which mask the detection of LANL contaminants. His work has been confirmed by the Department of Energy Inspector General,[1] National Academy of Sciences[2] and the Environmental Protection Agency (EPA) Kerr Research Laboratory in Ada, Oklahoma.[3] He has described how the

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[1] "Characterization Wells at Los Alamos National Laboratory," DOE/IG-0703, September 2005. Website: http://www.ig.energy.gov/documents/CalendarYear2005/ig-0703.pdf

[2] "Plans and Practices for Groundwater Protection at the Los Alamos National Laboratory," Final Report, National Research Council of the National Academies. Website: <http://www.nap.edu/catalog.php?record_id=11883>

[3] "EPA (U.S. Environmental Protection Agency), February 10, 2006. "Los Alamos National Laboratory, Los Alamos, New Mexico (05RC06-001), Impacts of Hydrogeologic Characterization Well Construction Practices," Environmental Protection Agency memorandum to R. Mayer (EPA/Region 6) from R. Ford (EPA/NRMRL), S.D. Acree (EPA/NRMRL), and R.R.

characterization wells do not comply with applicable regulations, including the New Mexico Hazardous Waste Act (HWA) and the federal Resource Conservation and Recovery Act (RCRA), including:

1). The wells are located too far from the boundaries of the waste sites. They are not located within 50 feet of the boundaries as required by RCRA guidance;

2). The sampling well screens are generally not located in the strata with the fast groundwater pathways for the early detection of contaminants;

3). All of the wells are invaded with drilling fluids with well-known properties to hide detection of many LANL contaminants;

4). All of the wells have stainless steel screens that will corrode and hide detection of many LANL contaminants;

5). The wells are not purged sufficiently before sampling is done as required by RCRA and the NMED/LANL Consent Order;

6). Sampling methods which allow the samples to be exposed to air, thereby causing the loss of contaminants prior to analysis;

7). The reporting of contaminants in groundwater, including problems with accessing the LANL Water Quality Database through the Internet.

CCNS and Gilkeson make three requests:

1). NMED retract its recommendation for Alternatives 3a and 3b – Shaft Encapsulation and Engineered ET Cover. NMED does not have the necessary information to made a remedy selection as explained in our comments; and

2). If NMED does not retract its recommendations, then we request a public hearing.

3). Prior to any public hearing, we request negotiations to resolve the many issues raised in these comments, as well as by the Permittees and other Interested Parties.

Ross (EPA/NRMRL), Office of Research and Development, Ada, Oklahoma. (EPA 2006, 094894). Attachment 1.

EPA (U.S. Environmental Protection Agency), February 16, 2006. "Los Alamos National Laboratory, Los Alamos, New Mexico (05RC06-001), Review of LANL Well Screen Analysis Report, (LA-UR-05-8615)," Environmental Protection Agency memorandum to R. Mayer (EPA/Region 6) from R. Ford (EPA/NRMRL) and S.D. Acree (EPA/NRMRL) Office of Research and Development, Ada, Oklahoma. Attachment 2.

Request for Public Hearing and Negotiations. For the reasons that follow, CCNS and Gilkeson request a public hearing about the proposed remedy selection for MDA H. Further, and prior to any notice of public hearing, pursuant to §20.4.1.901.A.4 NMAC, CCNS and Gilkeson request that NMED, Permittees, CCNS, Gilkeson and other Interested Parties conduct negotiations to attempt to resolve issues related to the MDA H remedy selection prior to a hearing. CCNS and Gilkeson believe that the other Interested Parties, Permittees and NMED would agree with some of the concerns and objections raised in the following comments and that a revised remedy could be developed prior to the public hearing.

CCNS participated in the 17-days of negotiations following the release of the draft RCRA permit for the WIPP in the spring of 2005. We found the negotiation process to be a productive way to reduce the number of issues through a consensus process among the NMED, Permittees and Interested Parties.

Alternative Dispute Resolution (ADR). CCNS and Gilkeson request that the negotiations are conducted under the purview of Governor Richardson's Alternative Dispute Resolution Executive Order. Executive Order 2005-047. We request that a representative from the NMED Office of Public Facilitation or ADR Council facilitate the negotiations.

CCNS and Gilkeson request that NMED fully consider the all the comments and issue a revised remedy before proceeding to a public hearing.

Foreword to Comments. This document is Revision 3, dated February 4, 2008 to the draft version that was presented at the Northern New Mexico Citizens' Advisory Board (CAB) meeting on December 19, 2007. The revision is to incorporate discussion at the CAB meeting and to include information from two LANL Reports -

1). the "Corrective Measures Study Report For Material Disposal Area H, Solid Waste Management Unit 54-004 at Technical Area 54-Revision 1" (CMS-1) that was submitted to NMED on June 30, 2005 and

2). the "Periodic Monitoring Report for Vapor-Sampling Activities at MDA H" that was submitted to NMED on 11-29-07.

The CMS-1 report was used by the New Mexico Environment Department (NMED) to select the remedy for MDA H in the NMED *Fact Sheet/Statement of Basis - Remedy Selection for MDA H* that was sent out for public comment on November 5, 2007 (i.e., the NMED remedy selection fact sheet or RSFS). However, new findings during the 28-months from the CMS-1 report to the selection of the NMED remedy demonstrate that there is insufficient data to select the remedy for MDA H. For example, the new LANL report on vapor sampling activities at MDA H was submitted to NMED *after* NMED selected the remedy for closure of MDA H.

The new findings that have developed over the 28-months and other issues raised by John Hopkins, the LANL Project Leader, at the CAB meeting on 12-19-07 require NMED

to retract the proposed remedy. The retraction is necessary because of the following factors:

- There is insufficient investigation of groundwater contamination from MDA H.
- There is insufficient investigation of vapor contamination in the unsaturated zone beneath MDA H.
- The NMED Consent Order has not required LANL to install the monitoring program required under RCRA Corrective Action for either the vadose zone or the regional aquifer for the RCRA regulated unit MDA H.
- The complete encapsulation remedy selected by NMED is not technologically feasible with the proposed circle of deep boreholes drilled around each of the 9 disposal shafts at MDA H.

There is insufficient investigation of groundwater contamination to select the remedy for MDA H. The reports by Gilkeson (2004), the Inspector General (IG) of the Department of Energy (2005), the U.S. Environmental Protection Agency (2006a, 2006b), and the National Academy of Sciences (2007) have described the failure of LANL to install a reliable network of monitoring wells at the Laboratory facility. In addition, the NMED RSFS report recognizes the failure of LANL to perform the required groundwater monitoring at MDA H and at MDAs G and L in the larger surrounding area of Technical Area 54 (TA-54):

> From page 5 of the NMED RSFS: "Reliable groundwater data has not been collected from the regional aquifer in the vicinity of MDA H. NMED has therefore directed the Permittees to evaluate the current monitoring well network at TA-54. The Permittees must replace or rehabilitate monitoring wells or selected well screens in existing wells, and evaluate the need for additional monitoring wells around TA-54."
>
> From page 12 of the NMED RSFS: "In addition, the groundwater monitoring wells installed by the Permittees in the vicinity of MDA H (including R-20, R-22, R-32, and R-16) cannot provide reliable data to evaluate whether or not VOCs released from TA-54 have reached the regional aquifer (LANL 2005b). The soil pore gas monitoring is the only means available at MDA H that can provide evidence to assure that vapor-phase VOCs are not a potential source of significant contamination for the regional aquifer. In particular, toluene was recently detected consecutively in two rounds of the regional groundwater samples collected from R-20, which is located between TA-54 and the municipal well PM-2 that supplies drinking water to the community. The source of the toluene has not been identified."

Figure 1 shows that NMED is incorrect to describe LANL characterization wells R-20, R-22, R-32, and R-16 as *"in the vicinity of MDA H."* Well R-16 is located east of the eastern side of Figure 1. In fact there are no monitoring wells installed close to MDA H as required by the Resource Conservation and Recovery Act (RCRA) and by DOE Orders. The LANL report *TA-54 Well Evaluation and Network Recommendations, Revision 1* (LA-UR-07-6436, October 2007) identifies the need for a monitoring program at MDA H that is in compliance with 40 CFR S 264 Subpart F:

> "The following requirements from 40 CFR 264.90-.99, Subpart F apply to permitted units or regulated units that received waste after July 26, 1982. The regulations apply throughout the active life of the units and the closure and post-closure period if the units are not

> "clean-closed" under RCRA. The groundwater-monitoring network and facility process must be able to detect, evaluate, and respond to releases of hazardous waste or hazardous waste constituents into the uppermost aquifer. Detection monitoring is required to establish that a release has occurred. It is assumed that because of the significant depth to groundwater beneath TA-54, vadose-zone monitoring will be a key component of the overall monitoring program in support of both CMEs and the RCRA Part B permit.
>
> An integrated groundwater-monitoring system must consist of a sufficient number of near-field wells and downgradient monitoring wells installed at appropriate locations and depths to obtain representative groundwater samples from the uppermost aquifer. These samples must represent both the quality of background water not affected by the regulated unit and the quality of groundwater passing beneath the regulated unit to allow for detection of contamination in the uppermost aquifer" (p. 6).

NMED will not have the knowledge necessary to select a remedy until reliable groundwater data is collected from a network of monitoring wells installed into the regional aquifer immediately at the location of MDA H. The requirements of RCRA for detection monitoring wells located immediately downgradient of MDA H (i.e., point of compliance monitoring under 40 CFR § 264.95) and a background water quality well located at a close distance upgradient of MDA H under 40 CFR § 264.97 are displayed on Figure 2.

The LANL CMS-1 report also makes the mistake to represent that reliable groundwater data has been collected in the vicinity of MDA H. LANL has not met the requirements of RCRA 264 Subpart F or DOE Order 450.1 for monitoring wells at the immediate location of MDA H. LANL must install:

1). a minimum of three hydraulically downgradient monitoring wells within 50-feet of MDA H at appropriate locations for detection of groundwater contamination released from MDA H to any perched zones of saturation and to the regional aquifer, and

2). a minimum of one hydraulically upgradient monitoring well at an appropriate location not greater than 500 feet of MDA H to measure background water quality. This background well will provide important information for characterizing groundwater contamination from MDA H, MDA L and MDA G.

The new wells must be drilled with the air-rotary reverse circulation casing advance drilling methods that were used in 2006 for the successful installation of wells R-35a and R-35b into the regional aquifer without invading the screened intervals with any organic drilling additives or bentonite clay drilling muds. Only air may be used as a drilling fluid.

<u>There is insufficient investigation of vapor-phase contamination to select the remedy for MDA H</u>.

> <u>From page 11 of the NMED RSFS</u>: "Recent monitoring data show that trichloroethylene (TCE), a carcinogen, has been detected in the subsurface pore gas [below MDA H] at a concentration of 2,600 micrograms (ug) per cubic meter, which is a high enough concentration to partition into groundwater and theoretically result in an aqueous concentration greater than the drinking water maximum contaminant level (MCL) of 5 ug per liter (LANL, 2006b)."

> From page 12 of the NMED RSFS: "Due to continuous releases of VOCs from the shafts to the subsurface, however, the Permittees cannot ensure that the vapor-phase contaminant concentrations will remain below the criteria established using Henry's law. More specifically, the Permittees have not sampled soil gas at depths greater than approximately 250 feet below the ground surface. The vapor-phase transport of VOCs beneath MDA H is complex and has not been fully evaluated by the Permittees (LANL 2005a). In addition, the groundwater monitoring wells installed by the Permittees in the vicinity of MDA H (including R-20, R-22, R-32, and R-16) cannot provide reliable data to evaluate whether or not VOCs released from TA-54 have reached the regional aquifer (LANL 2005b). The soil pore gas monitoring is the only means available at MDA H that can provide evidence to assure that vapor-phase VOCs are not a potential source of significant contamination for the regional aquifer. In particular, toluene was recently detected consecutively in two rounds of the regional groundwater samples collected from R-20, which is located between TA-54 and the municipal well PM-2 that supplies drinking water to the community. The source of the toluene has not been identified. NMED therefore has determined that it is appropriate to implement Alternative 3b (complete encapsulation of the shafts), along with a soil-vapor extraction system, at MDA H to prevent biointrusion and eliminate the VOC contaminant source detected in soil pore gas so that the drinking water resource can be conservatively protected" [emphasis added].

In fact, the NMED has made a mistake in the position that soil gas monitoring is the only means available to assure that significant contamination of the regional aquifer has not occurred or will occur in the future. For groundwater protection, both RCRA and DOE Orders require installation of reliable monitoring wells immediately at MDA H but NMED has not enforced RCRA.

At the CAB meeting on 12-19-07, John Hopkins stated that improved sampling methodologies show that high levels of TCE and other volatile organic contaminants are not present below MDA H. The improvements in sampling methodology are the installation of flexible inflated membranes with multiple sampling ports in each of the three boreholes at MDA H that are displayed on Figure 2. LANL published a report dated 11-29-07 on the low levels of TCE measured at MDA H *after* NMED released the selected remedy for MDA H on 11-05-07.

Figure 3 shows that two of the vapor wells in the LANL report are each located at distances of 90 feet from the nearest disposal shaft at MDA H and only one vapor well is at an appropriate location immediately near the disposal shafts. In addition, the LANL report shows a routine operation of removing the flexible membranes from the boreholes repeatedly for performance of borehole geophysics to measure moisture profiles. The schedule for removal of the sampling membranes and the period of time that the boreholes are open for introduction of atmospheric air before samples are collected to measure contamination is not presented in the report. The flow of atmospheric air into the open boreholes will greatly dilute the levels of vapor-phase contaminants in the soil gas samples that are collected after reinstallation of the flexible sampling membranes.

There is a need to install two additional multiple-port vapor wells immediately near the disposal shafts to a depth of approximately 400 feet and to permanently install a multiple-port vapor sampling system in each borehole. Similarly, the existing borehole 54-1023 should be deepened to the 400-foot depth with installation of permanent sampling equipment. Eight quarters of samples should be collected from each vapor

well to provide data for selection of the remedy at MDA H. An appropriate location for one of the new vapor wells is close to the disposal shafts and between shafts 6 and 2. The appropriate location for the second new vapor well is close to the disposal shafts and between shafts 5 and 9.

Complete encapsulation of the disposal shafts at MDA H is not feasible with the parallel intersecting boreholes. Technology does not exist for drilling intersecting parallel boreholes in circles surrounding each of the nine shafts. The boreholes will wander apart during drilling and create gaps in the "complete encapsulation." In addition, the data does not exist at this time to support the need for complete encapsulation of the disposal shafts at MDA H.

Groundwater Monitoring Requirements Under the LANL Consent Order

The New Mexico Environment Department (NMED) and the Department of Energy (DOE) have agreed to a Compliance Order on Consent (Consent Order) dated March 1, 2005, which requires the Los Alamos National Laboratory (LANL) to conduct RCRA Corrective Action at all MDAs, solid waste management units (SWMUs) and Areas of Concern (AOCs), at the Facility to fulfill the requirements of 40 CFR § 264.101.

NMED describes the Consent Order as an enforceable document pursuant to 40 CFR §§ 264.90(f) and 270.1(c)(7). However, the "fence to fence cleanup activities" conducted at LANL under the Consent Order have not met the requirements in RCRA for installing monitoring wells to investigate contamination in the regional aquifer. Specifically, RCRA Corrective Action requires installation of contaminant detection wells and a background water quality well immediately at the location of MDA H. The requirements in 40 CFR §§ 264.101, 264.90(f) and 270.1(c)(7) are as follows:

Requirements of RCRA 40 CFR § 264.101. Corrective Action for Solid Waste Management Units.

(a) The owner or operator of a facility seeking a permit for the treatment, storage or disposal of hazardous waste must institute corrective action as necessary to protect human health and the environment for all releases of hazardous waste or constituents from any solid waste management unit at the facility, regardless of the time at which waste was placed in such unit.

(b) Corrective action will be specified in the permit in accordance with this section and subpart S of this part. The permit will contain schedules of compliance for such corrective action (where such corrective action cannot be completed prior to issuance of the permit) and assurances of financial responsibility for completing such corrective action.

(c) The owner or operator must implement corrective actions beyond the facility property boundary, where necessary to protect human health and the environment, unless the owner or operator demonstrates to the satisfaction of the Regional Administrator that, despite the owner's or operator's best efforts, the owner or operator was unable to obtain the necessary permission to undertake such actions. The owner/operator is not relieved of all responsibility to clean up a release that has migrated beyond the facility boundary where off-site access is denied. On-site measures to address such releases will be

determined on a case-by-case basis. Assurances of financial responsibility for such corrective action must be provided.

(d) This section does not apply to remediation waste management sites unless they are part of a facility subject to a permit for treating, storing or disposing of hazardous wastes that are not remediation wastes.

RCRA 40 CFR § 264.90 Applicability.
* * * * *
(f) The Regional Administrator may replace all or part of the requirements of §§ 264.91 through 264.100 applying to a regulated unit with alternative requirements for groundwater monitoring and corrective action for releases to groundwater set out in the permit (or in an enforceable document) (as defined in 40 CFR 270.1(c)(7)) where the Regional Administrator determines that:

(1) The regulated unit is situated among solid waste management units (or areas of concern), a release has occurred, and both the regulated unit and one or more solid waste management unit(s) (or areas of concern) are likely to have contributed to the release; and
(2) It is not necessary to apply the groundwater monitoring and corrective action requirements of §§ 264.91 through 264.100 because alternative requirements will protect human health and the environment.

RCRA 40 CFR § 270.1 Purpose and scope of these regulations.
* * * * *
(c) *Scope of the RCRA permit requirement.* RCRA requires a permit for the ''treatment,'' ''storage,'' and ''disposal'' of any ''hazardous waste'' as identified or listed in 40 CFR part 261.

The terms ''treatment,'' ''storage,'' ''disposal,'' and ''hazardous waste'' are defined in § 270.2. Owners and operators of hazardous waste management units must have permits during the active life (including the closure period) of the unit.

Owners and operators of surface impoundments, landfills, land treatment units, and waste pile units that <u>received waste after July 26, 1982, or that certified closure (according to § 265.115 of this chapter) after January 26, 1983,</u> *[emphasis added]* must have post-closure permits, unless they demonstrate closure by removal or decontamination as provided under § 270.1(c)(5) and (6), or obtain an enforceable document in lieu of a postclosure permit, as provided under paragraph (c)(7) of this section.

> ***(Note by the authors:*** *The waste disposal sites at TA-54 (MDAs G, H, and L received waste after July 26, 1982, and have not certified closure to the present time. Therefore, operations at MDAs G, H, and L require post-closure permits, or an enforceable document in lieu of a post-closure permit. However, as described in the following parts of* **§ 270.1,** *the Consent Order has failed to meet the requirements of RCRA for installing monitoring wells at MDA H and the many other LANL SWMUs where hazardous wastes are buried.****)***

Continued from **RCRA 40 CFR § 270.1(c):** If a postclosure permit is required, the permit [or enforceable document, i.e., the Consent Order] must address applicable 40 CFR part 264 groundwater monitoring, unsaturated zone monitoring, corrective action, and post-closure care requirements of this chapter. The denial of a permit for the active life of a hazardous waste management facility or unit does not affect the requirement to obtain a post-closure permit under this section.
* * * * *
(c)(7) *Enforceable documents for postclosure care.* At the discretion of the Regional Administrator, an owner or operator may obtain, in lieu of a postclosure permit, *an enforceable document imposing the requirements of 40 CFR 265.121 [emphasis added - the groundwater monitoring requirements of 40 CFR 265.121 are listed below].*
''Enforceable document'' means an order, a plan, or other document issued by EPA or by an authorized State under an authority that meets the requirements of 40 CFR 271.16(e) including, but not limited to, a corrective action order issued by EPA under section 3008(h), a CERCLA remedial action, or a closure or postclosure plan.

40 CFR § 265.121 Post-closure requirements for facilities that obtain enforceable documents in lieu of post-closure permits.
(a) Owners and operators who are subject to the requirement to obtain a post-closure permit under 40 CFR 270.1(c), but who obtain enforceable documents in lieu of post-closure permits, as provided under 40 CFR 270.1(c)(7), must comply with the following requirements:

(1) The requirements to submit information about the facility in 40 CFR 270.28;
(2) The requirements for facility-wide corrective action in § 264.101 of this chapter;
(3) The requirements of 40 CFR 264.91 through 264.100 [emphasis added].

The NMED and DOE have failed to meet the groundwater monitoring requirements in 40 CFR 264.90 through 264.101 for MDA H and also for MDAs G and L. The overarching problems are:

1). the great distance of the six LANL characterization wells from the three MDAs (the locations of five of the six existing wells are displayed on Figure 1),

2). the invasion of the screened intervals in all of the wells with organic drilling additives that have well known properties to mask the detection of many of contaminants of concern for MDAs G, H, and L,

3). the invasion of the screened intervals in four of the wells (wells R-16, R-20, R-23 and R-32 with bentonite clay drilling muds that have well known properties to mask the detection of many contaminants of concern,

4). all six wells are constructed with stainless steel screens that form corrosion products with properties to mask the detection of many contaminants of concern for MDAs G,H and L. LANL claims that corrosion is now occurring in the stainless steel screens in the first characterization well installed in 1999 under the LANL Hydrogeologic Workplan. In 2007, NMED ordered Sandia National Laboratories to replace monitoring wells with corroded stainless steel screens with new monitoring wells that have PVC screens. The Sandia wells were

installed in 1988 to 1990 approximately 10 years before the first LANL characterization wells.

5). four of the wells (R-16, R-20, R-22, and R-32) are a multiple-screen design where no-purge water samples are collected from the stagnant zone formed by the organic additives and bentonite clay muds,

6). some of the screens in the six wells have a length of 60 feet and mask the detection of contamination by dilution. RCRA and the standard industry practice is to limit the length of screens to a preferred length of 10 feet and not greater than 20 feet. and

7). the wells are not installed in the aquifer strata near the water table where contamination is most likely present. Instead, most of the screens are installed in inappropriate geologic formations too deep below the water table and with low permeability.

Figure 2 displays the requirements of RCRA §264 Subpart F for locating monitoring wells directly along the hydraulically downgradient limit of disposal sites and also installation of monitoring wells hydraulically upgradient of the disposal sites to measure background water quality. Comparison of Figures 1 and 2 shows the failure of DOE and NMED to install the necessary network of monitoring wells at MDAs G, H, and L that are required by RCRA.

<u>The Inconsistent Record of NMED for Installation of Monitoring Wells at LANL and at Sandia National Laboratories Albuquerque Facility (Sandia).</u>

NMED has required the installation of many monitoring wells immediately at the legacy waste disposal sites at Sandia. Two examples are the monitoring well network at the Sandia Mixed Waste Landfill (MWL dump) and the network of monitoring wells installed at the Sandia Chemical Waste Landfill. The network of wells installed at the Sandia MWL dump are displayed on Figure 4. Both the MWL dump and MDA H operated over a similar period of time and both legacy waste disposal sites received hazardous wastes and mixed wastes after the date in 1982 when RCRA requires a network of monitoring wells for "RCRA regulated units. The required network of monitoring wells is described in RCRA 40 CFR § 264.91 through 264.100.

In 2007, DOE/SNL released the proposed *Long-Term Monitoring and Maintenance Plan for the Sandia Mixed Waste Landfill.* The proposed network of six monitoring wells are displayed on Figure 5. The proposal includes installation of three new monitoring wells close to the western or hydraulically downgradient side of the MWL dump and a new background water quality well at an upgradient location close to the dump. However, NMED issued a letter that required installation of two of the new monitoring wells at the Sandia MWL dump at locations immediately along the hydraulically downgradient boundary of the buried wastes (i.e., at locations even closer than the proposed locations on Figure 5. Below is an excerpt from the NMED letter dated 10-30-07 to DOE/Sandia:

> "The new wells need to be placed as close to the old landfill boundary as possible to ensure the detection of any contaminants in the groundwater. Thus, NMED approves the work plan with the following conditions.

- Both new wells shall be positioned as close as possible to the former west fence that originally surrounded the Mixed Waste Landfill."

Comparison of Figure 1 to Figures 4 and 5 show the inconsistent practice of DOE and NMED between groundwater monitoring at SNL and LANL. Note the close distance of monitoring wells at the Sandia MWL dump compared to the distant locations of the few wells proposed for the long-term monitoring program for the three MDAs at TA-54. The NMED Consent Order has not required any monitoring wells or background water quality wells close to MDA H, MDA G or MDA L either for characterization or for long-term monitoring. The groundwater monitoring at the three MDAs at TA-54 is not in compliance with RCRA.

NMED must require DOE/LANL to install a network of monitoring wells immediately at each of the legacy waste disposal sites at LANL including the buried waste sites at TA-21, TA-49, TA-50 and TA-54. In addition DOE has not installed the network of monitoring wells across the LANL facility that are required by DOE Order 450.1.

Conclusion. NMED does not have the necessary information in order to select a remedy at this time. Therefore, NMED must retract its remedy selection of Alternatives 3a and 3b – Shaft Encapsulation and Engineered ET Cover.

Please contact us should you have any questions or comments.

Sincerely,

Joni Arends Robert H. Gilkeson

Reports referenced in these comments. If these documents are not in the administrative record, then we request that they be placed in the administrative record.

U.S. Department of Energy Office of Inspector General Office of Inspections and Special Inquiries. "Inspection Report: Characterization Wells at Los Alamos National Laboratory." September 2005.

EPA (U.S. Environmental Protection Agency), February 10, 2006. "Los Alamos National Laboratory, Los Alamos, New Mexico (05RC06-001), Impacts of Hydrogeologic Characterization Well Construction Practices," Environmental Protection Agency memorandum to R. Mayer (EPA/Region 6) from R. Ford (EPA/NRMRL), S.D. Acree (EPA/NRMRL), and R.R. Ross (EPA/NRMRL), Office of Research and Development, Ada, Oklahoma. (EPA 2006, 094894)

EPA (U.S. Environmental Protection Agency), February 16, 2006. "Los Alamos National Laboratory, Los Alamos, New Mexico (05RC06-001), Review of LANL Well Screen Analysis Report, (LA-UR-05-8615)," Environmental Protection Agency memorandum to R. Mayer (EPA/Region 6) from R. Ford (EPA/NRMRL) and S.D. Acree (EPA/NRMRL) Office of Research and Development, Ada, Oklahoma.

Gilkeson, Robert. "Groundwater Contamination in the Regional Aquifer beneath the Los Alamos National Laboratory." July 13, 2004.

LANL (Los Alamos National Laboratory, 2007. *TA-54 Well Evaluation and Network Recommendations, Revision 1* (LA-UR-07-6436, October 2007)

NAS (National Academies of Science), 2007. – "Plans and Practices for Groundwater Protection at the Los Alamos National Laboratory." Report by the NAS Committee for Technical Assessment of Environmental Programs at the Los Alamos National Laboratory. THE NATIONAL ACADEMIES PRESS – Washington, D.C.

NMED (New Mexico Environment Department) October 30, 2007. Letter from James Bearzi, Chief, NMED Hazardous Waste Bureau, instructing DOE/Sandia to install two new monitoring wells at the Sandia Mixed Waste Landfill.

Rice, George. "Evaluation of Corrective Measures Study Report for MDA H, SWMU 54-004, at TA-54." August 7, 2003.

Southwest Planning and Marketing. "Final Report on MDA H Focus Group Process." January 2004.

Figure 1. Existing and proposed monitoring wells installed in the regional aquifer (R-wells) at the RCRA "regulated unit" waste disposal sites MDA G, H, and L. Existing R-wells are displayed as black dots. Proposed R-wells are displayed as red dots. (From LANL Report LA-UR-07- 6436, October 2007)

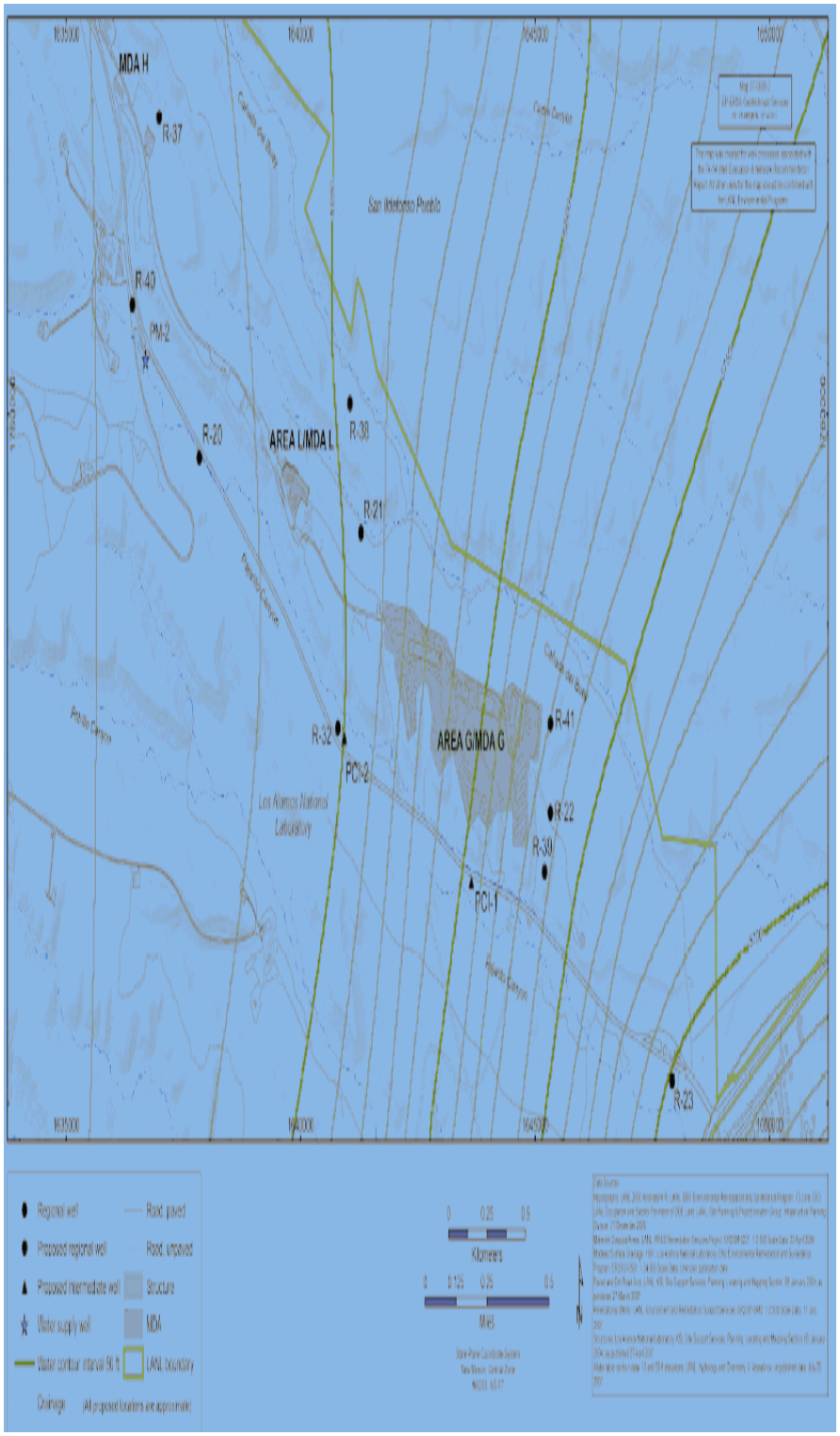
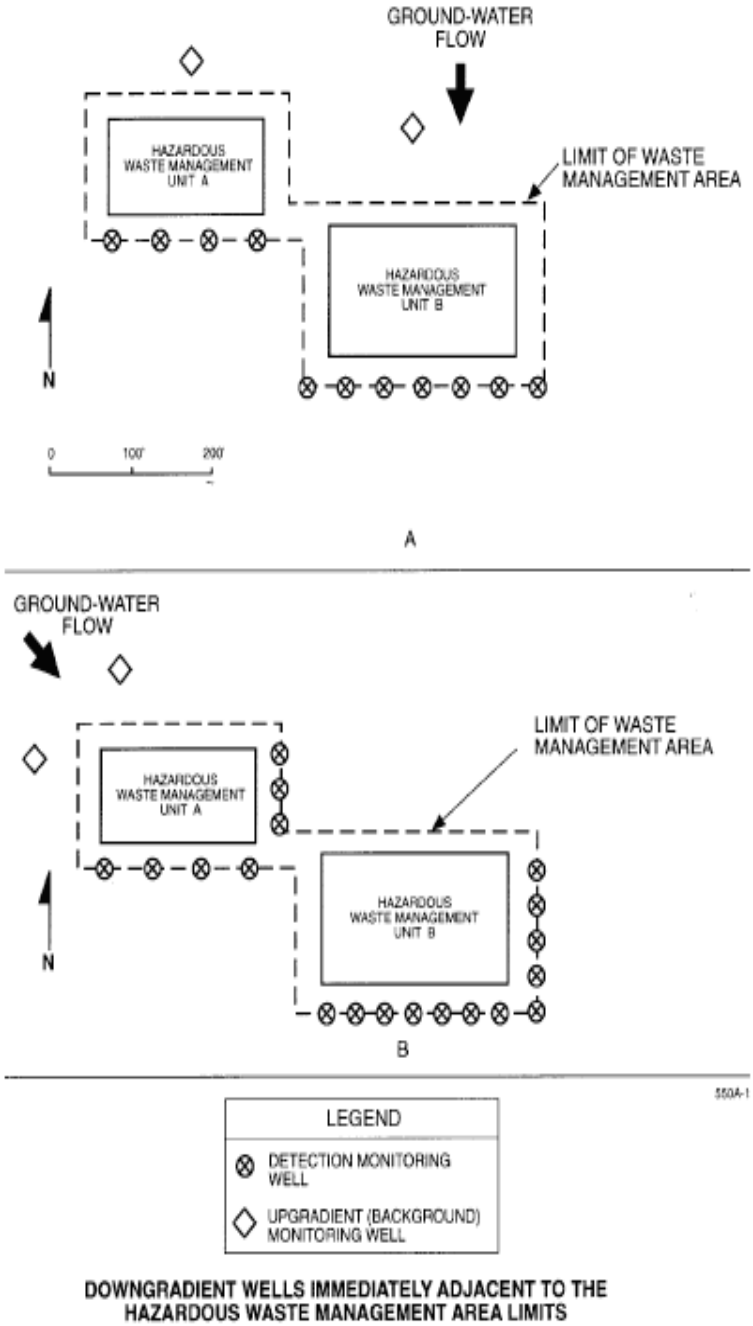
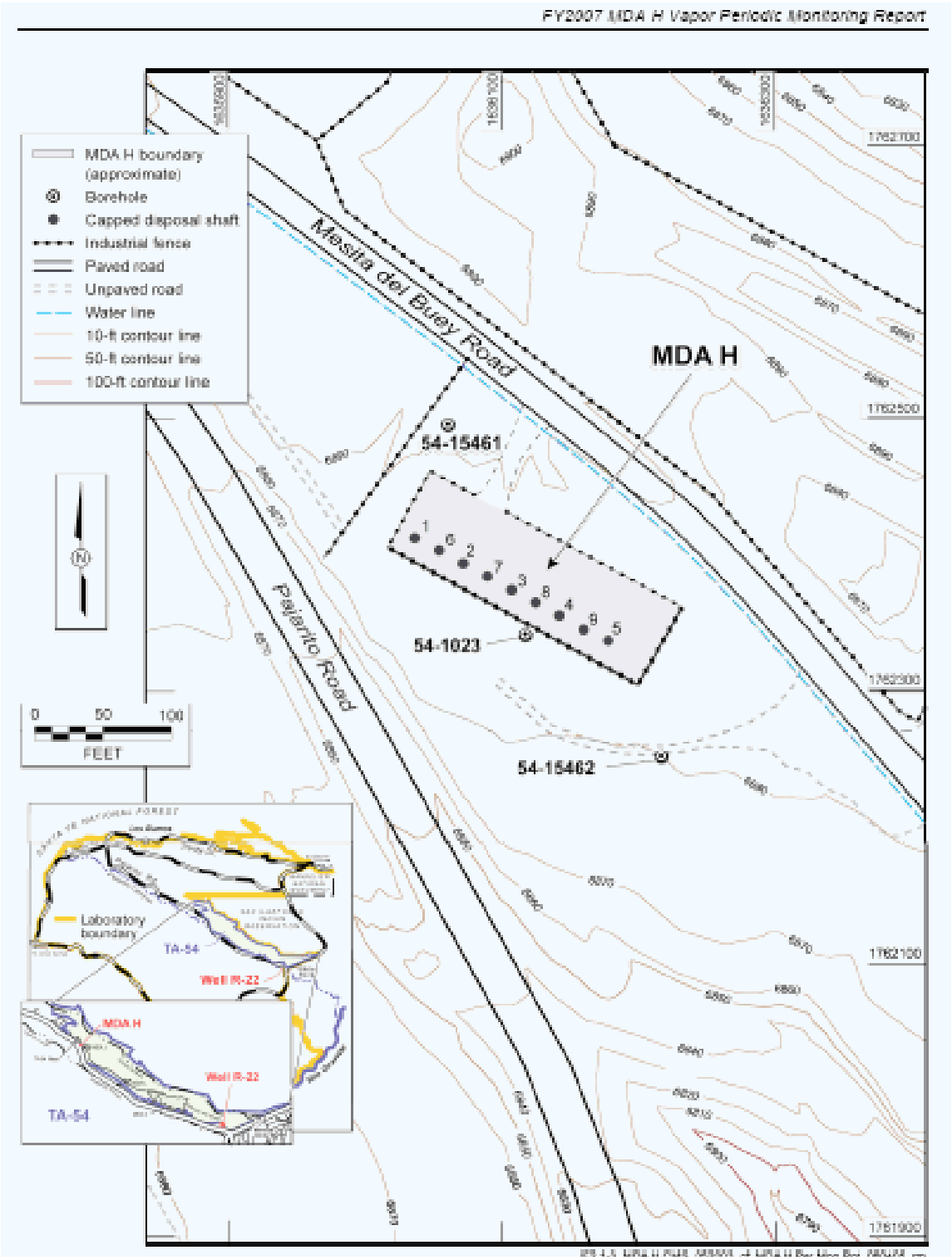


Figure 2. Figure illustrating the requirements in RCRA regulations (40CFR Subpart F) for monitoring wells at disposal sites that contain hazardous wastes-
1. detection wells located immediately along the hydraulically downgradient boundary of the buried wastes (40CFR § 264.95 - wells at point of compliance), and
2. background wells at appropriate locations hydraulically upgradient of the buried wastes (40CFR § 264.97 - general groundwater monitoring requirements).



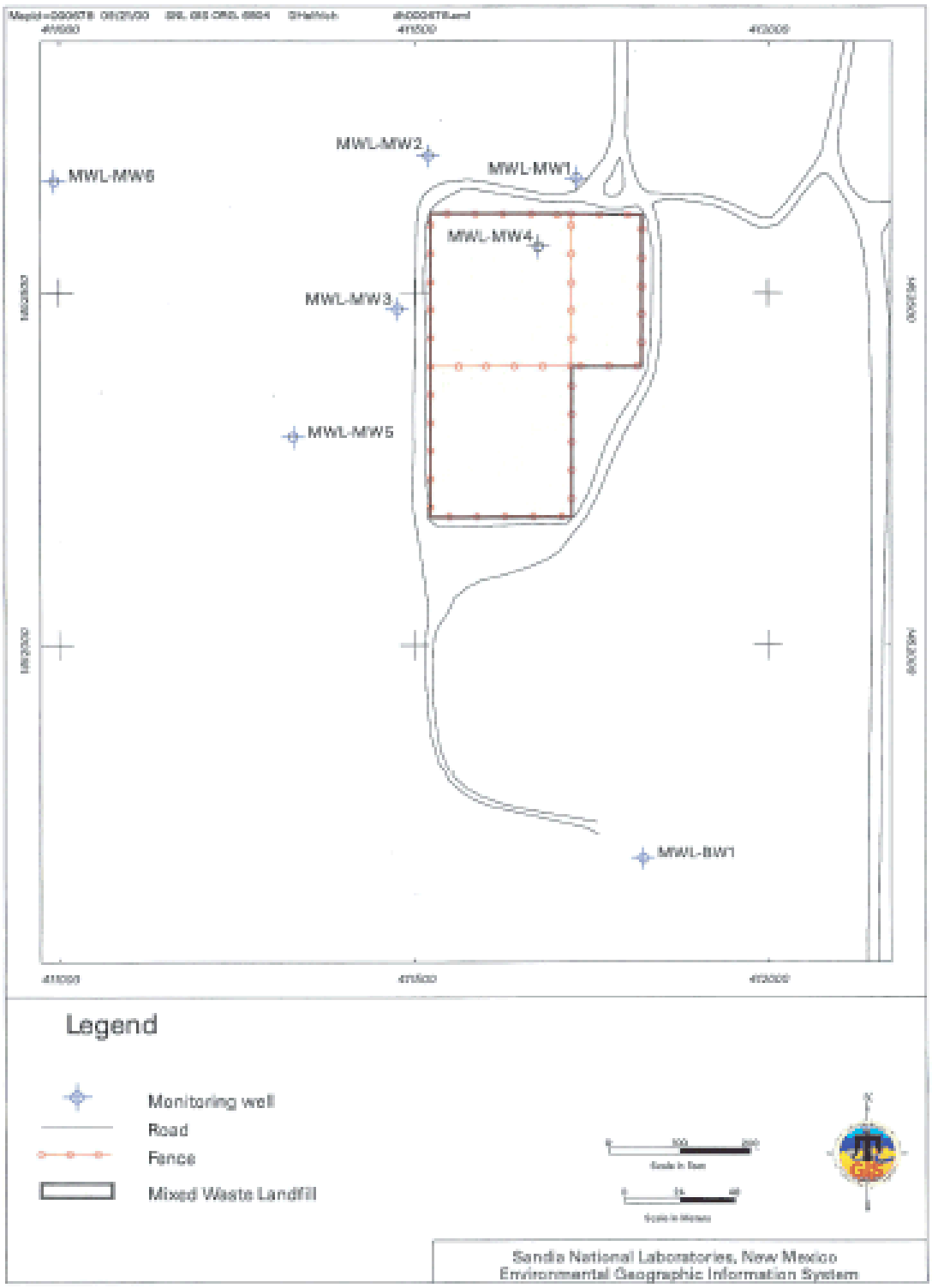
Source: RCRA GROUND-WATER MONITORING: DRAFT TECHNICAL GUIDANCE (U.S. EPA, Washington, D.C. November 1992)

Figure 3. The locations of the three vapor sampling wells 54-15461, 54-1023 and 54-1-23 at MDA H.



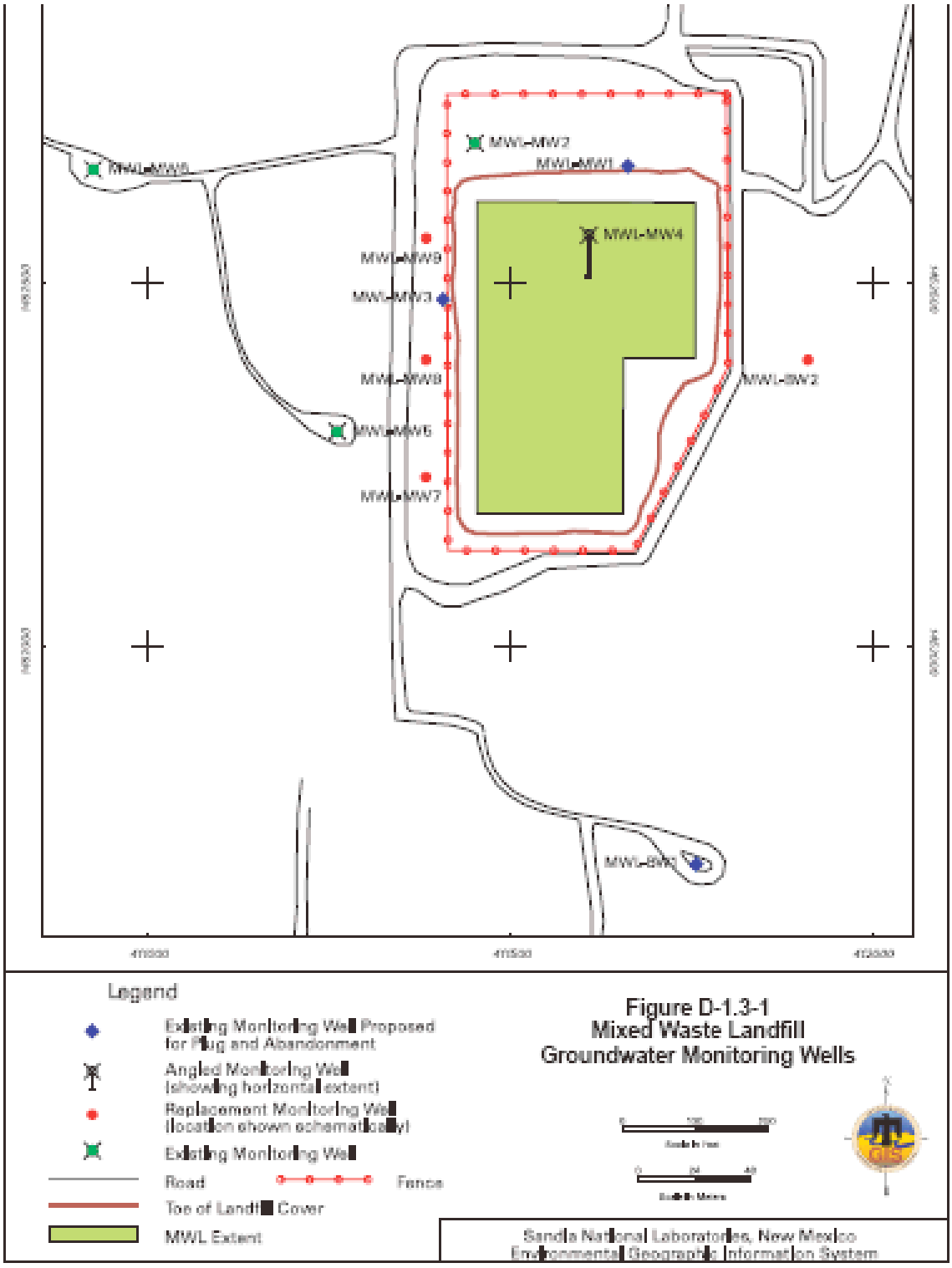
From LANL report LA-UR-07-7803, November 2007

Figure 4. Map of the Sandia Mixed Waste Landfill showing the locations of the six monitoring wells MW1 to MW6 and the background water quality well BW1.



From Sandia Report SAND 2002-4098

Figure 5. Proposed Locations by DOE/SNL for Long-Term Monitoring Wells at the Sandia MWL Dump.



Source: DOE/SNL Long-Term Monitoring and Maintenance Plan for the Mixed Waste Landfill, September 2007

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NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
GROUND WATER AND ECOSYSTEMS RESTORATION DIVISION
P.O. Box 1198 Ada,OK 74820

OFFICE OF
RESEARCH AND DEVELOPMENT

February 10, 2006

MEMORANDUM

SUBJECT: Los Alamos National Laboratory, Los Alamos, New Mexico (05RC06-001)
Impacts of Hydrogeologic Characterization Well Construction Practices

FROM: Robert Ford, Ph.D., Environmental Scientist
Subsurface Remediation Branch

Steven D. Acree, Hydrologist
Randall R. Ross, Ph.D., Hydrologist
Applied Research & Technical Support Branch

TO: Richard Mayer
U.S. EPA, Region 6

As requested, various documents concerning well construction practices and water quality evaluations at the Los Alamos National Laboratory (LANL) have been reviewed by Greg Davis, a hydrogeological consultant to Dynamac Corporation, and the above named staff of the National Risk Management Research Laboratory (NRMRL) – Ground Water and Ecosystems Restoration Division. Dynamac is an off-site contractor providing technical support services to this laboratory. The review and recommendations contained in this memorandum represent a technical evaluation of site-specific conditions based on the current state of the science and are neither policy nor prescriptive guidance. This memorandum is provided to clarify issues discussed in our memorandum to you dated September 30, 2005, and contains the material provided in the previous memorandum with modifications intended to better convey the requested information. The current review does not include the recent document entitled, "Well Screen Analysis Report" (LANL, 2005c), which will be reviewed under separate cover.

The focus of this review has been on the questions posed by the Northern New Mexico Citizens' Advisory Board (NNMCAB) in a memorandum from DeLong to Mayer dated 1/4/05. The questions which were posed center on the capability of the existing hydrogeologic characterization wells to provide representative ground-water samples for all site-related constituents of concern. The specific questions are summarized below:

Issue 1: If LANL decides to convert characterization wells to monitoring wells, can wells drilled with bentonite clay or commercial fluids, such as EZ-MUD, Quik-FOAM, TORKEASE, and LIQUI-TROL, ever be developed and cleaned up adequately to

provide analytical data representative of the ground water in the aquifer unit being sampled?

Issue 2: Will the use of commercial drilling fluids and bentonite clay preclude any contaminants from being accurately sampled even after well cleanup? If so, which ones?

Issue 3: In public reports, LANL indicates that contamination from LANL operations has not reached certain ground-water regions. LANL bases these statements on analytical results which show that certain fast-moving contaminants, such as tritium, that are not affected by drilling fluids or clays have not been detected in concentrations above background in samples from the wells. Are tritium and other mobile constituents suitable indicators of possible impacts for the entire suite of site-specific constituents at LANL?

Issue 4: (a) Can LANL derive an independent estimate of background concentrations of potential contaminants from accumulated ground-water data without using analytical results from the wells associated with the Hydrogeologic Work Plan? (b) Would such data constitute reliable criteria for judging when wells are suitable as monitoring wells?

The issues which have been raised by the NNMCAB are valid and, in many cases, difficult to reliably answer. The NNMCAB and LANL are correct in identifying intrusion of bentonite and organic drilling fluids as a potential problem for reactive contaminants of concern. The following review attempts to answer the questions, where possible, to provide insight into the scientific aspects of the individual issues, and to recommend additional types of studies that may be useful in filling existing data gaps. It should be noted that this review does not provide a detailed list of contaminants that are affected by the residual drilling additives at each impacted well screen. Examples of constituents that are most likely to be affected are given at appropriate points in the discussion. However, preparation of a comprehensive list for each well screen is beyond the scope of this review and would require better knowledge of the degree of impact at each screen and would be expected to change with time, particularly for the screens impacted by organic additives, as the geochemical environment in the impacted zone changes.

In general, it is often difficult to obtain fully representative samples of subsurface materials, particularly in a highly complex setting such as at LANL. This does not imply that available data are always appropriate regardless of objectives and intended data uses. This review highlights potential data quality problems and uncertainties. Since data quality objectives (DQOs) were not explicitly stated in the limited set of documents available for review, it is recommended that the DQOs addressing the specific requirements for the samples and the intended use of the data from the wells impacted by residual drilling fluids at LANL be reviewed to determine the applicability of the suggestions provided below.

For convenience, the review is divided into an executive summary describing findings related to the core issues of the effects of residual drilling additives on ground-water samples, a discussion of background information describing the effects of the drilling additives used at

LANL in more technical terms, and sections corresponding to the individual issues raised by the NNMCAB followed by a brief summary. Recommendations for additional studies or changes in practices are included under each section, where appropriate.

Executive Summary

One of the central issues to be addressed as part of this review is whether representative ground-water samples can be obtained from wells installed as part of the Hydrogeologic Work Plan, considering the methods and techniques used by LANL to drill the boreholes, install, develop and sample the wells. There are two questions that must be answered in order to provide a complete answer to this question:

1) Has the introduction of drilling fluids, including bentonite and biodegradable organic polymers, resulted in changes in ground-water chemistry from pre-drilling conditions?

2) Will alterations of the aquifer material around a well, either through the introduction of bentonite or changes brought about by the break-down of organic drilling fluids, alter how contaminants move toward the well screen, relative to pre-drilling conditions?

The ability to answer the central question of whether 'ground-water samples are representative' depends on how much we know about existing geochemical conditions next to the well screen and in areas that have not been affected by drilling fluids, further into the formation. Analytical results of ground-water samples indicate that drilling additives have changed the geochemical conditions around numerous wells. As acknowledged by LANL, these well screens should not be considered to currently provide samples representative of reactive contaminants of concern.

The second question cannot be addressed through direct measurements without acquiring samples of aquifer solids in the affected zone adjacent to the well screens. For wells drilled using bentonite additives, the inability to sample and directly measure the level of residual bentonite in sediments adjacent to screened intervals makes the representativeness of water samples for strongly sorbing contaminants uncertain. These contaminants include isotopes of americium, cerium, plutonium and radium. For wells drilled using organic polymer additives, the alteration of aquifer sediments is of particular concern for well screens impacted by biodegradation, since these reactions are known to result in alterations of iron- and manganese-bearing minerals. This is a critical issue, since these minerals often exert a dominant influence on the movement of inorganic contaminants in the subsurface. Changes to the aquifer minerals can result in the removal of many of the more reactive inorganic contaminants of importance to LANL and make water samples from the impacted well screens non-representative of aquifer conditions. The extent and time period of this impact will depend on the types of new minerals that are formed and the persistence of these new minerals after the complete break-down of the organic polymer.

Since determining how much the geochemistry of an aquifer has changed due to drilling, well installation, and sampling activities depends on a *best estimation* based on a range of direct measurements and inferences, the answer to this question is complex and uncertain. The

question concerning whether changes in water chemistry have occurred may be answered directly by analyzing water samples and comparing the results with those obtained from suitable background samples. However, using changes in water chemistry to determine changes in aquifer mineralogy and the resulting changes in sorptive properties of the aquifer materials is not as straight forward.

The problem with using water quality data to determine changes in the sorptive properties of aquifer materials is illustrated by the following analogy. Suppose one wanted to determine the temperature of water in a glass sitting on a table. Two approaches to this problem, each with different levels of confidence, are: 1) use a calibrated instrument (*e.g.*, thermometer) to directly measure the temperature of the water with a level of confidence dependant on the accuracy of the thermometer, and 2) use an indirect method to estimate a temperature range. For example, if the water is not solid (*i.e.*, ice) or bubbling (*i.e.*, boiling), then it could be assumed that the water temperature is between 32°F/0°C and 212°F/100°C. However, it would be difficult to accurately determine the water temperature without using a thermometer. Similarly, trying to determine changes in aquifer properties resulting from reducing conditions using only water chemistry data would result in a wide range of possible values. The use of more direct methods would be necessary to determine the extent of mineralogical changes to aquifer materials following the return of oxidizing conditions near the well screen.

Relative to addressing the question of whether ground-water samples are representative of the undisturbed aquifer chemistry, water quality data alone provide an unreliable indication of whether there is sustained impact to sediment sorption characteristics. The margin of error of determining, through measurements of water chemistry, what sediment minerals exist at any given point in time at a well screen is comparable to the level of uncertainty in estimating the temperature of a glass of water solely through visual observations. This is a limitation of the approach proposed for determining the condition of screened intervals at wells for which alterations have been identified by LANL. In many cases, the reducing environment established by the degradation of organic drilling additives has exposed the aquifer minerals to conditions far different from the conditions that have been established by many years of undisturbed ground-water flow. This is a significant limitation for the purpose of using these wells for assessing potential contaminant transport, in light of independent research that documents the extent that iron- and sulfate-reducing conditions may alter sediment mineralogy.

None of the documents available for review provide definitive evidence of the types of new minerals that have been formed or the degree of alteration of the aquifer materials. Consequently, a detailed evaluation of the changes in the degree to which reactive contaminants would be removed from water passing through the screened zone cannot be reliably performed. Further, the altered minerals will remain for some period of time following the return of oxidizing conditions. The time frame for this continuing impact to the representativeness of ground-water samples may be years to decades, depending on the types and degree of alterations. Documents provided for review by LANL do not explicitly acknowledge this potentially long-term data quality limitation.

Background

In order to respond to the issues raised by the NNMCAB, the nature of the impacts due to the presence of residual drilling additives must be understood. The following background information and assessment is provided to facilitate this understanding. The drilling fluids used at LANL can introduce new reactive minerals into the screened interval that may retard contaminant transport relative to un-impacted zones within the aquifer. Alteration of aquifer sediment reactivity results from one of two processes: 1) introduction of a reactive clay mineral, bentonite, that has significant sorption capacity for many of the site contaminants of concern, and 2) alteration of in-situ aquifer mineralogy during degradation of residual organic additives that results in the production of new reactive mineral phases such as Mn/Fe carbonates, Mn/Fe sulfides, and/or reduced Mn/Fe oxides and hydroxides (Figure 1). Based on a review of information presented in Bitner *et al.* (2004), intrusion of organic drilling fluids may have occurred in one or more screened intervals at all of the well locations whereas the intrusion of bentonite-based drilling fluids is likely to have occurred in fewer wells due to the more limited use that was reported (Table 1).

In an attempt to explain the possible impacts of these two classes of drilling fluids, two diagrammatic conceptual models were introduced in Figures 6 and 7 of Bitner *et al.* (2004) to depict the evolution of aqueous and solid phase chemistry within the impacted zone of a well screen. According to Figure 6 and accompanying discussion, degradation of organic drilling fluids leads to reducing conditions that result in dissolution of Mn and Fe (hydr)oxides (with stated concomitant increases in dissolved Mn and Fe) and the reduction of sulfate, nitrate, and some site-specific contaminants of concern (Bitner *et al.*, 2004). These processes will also result in the production of dissolved carbonate from organic carbon biodegradation and dissolved sulfide from microbial sulfate reduction. It is implied that dissolved Mn and Fe derived from reductive dissolution of the original Mn- and Fe-bearing aquifer 'mineral coatings' will be conservatively transported from the zone of influence adjacent to the impacted well screen. However, a more probable scenario is the re-precipitation of Mn and Fe as new mineral phases in the presence of elevated concentrations of carbonate and sulfide produced during biodegradation of organic polymer drilling additives. The amount of these new mineral phases and the time frame over which they may be produced will depend on 1) the amount of organic polymer drilling additive introduced into the aquifer, 2) the amount of sulfate transported in ground water at a particular well screen, and 3) the concentrations of Mn and Fe within the original aquifer sediments. It is not possible to project amounts or time frames at a given well screen with any certainty without knowledge of the amount of organic polymer additives that may have been introduced into the aquifer. Upon recovery of more oxidizing conditions, these newly-formed reactive mineral phases can subsequently be re-oxidized to their oxide forms with no net loss of Fe and Mn from the formation. This overall scenario is presented schematically in Figure 2 with changes in the relative abundance of specific aqueous and solid phase components documented as a function of the evolution of the aquifer adjacent to an impacted well screen.

The types of mineral transformations alluded to in the previous discussion have been identified in a number of experimental systems. Examples of the reported observations of transformations in Fe-bearing oxide minerals are documented in Table 2. These experimental systems replicate the type of conditions (*i.e.*, iron- and sulfate-reducing) observed in some of the

well screens as documented in Bitner *et al.* (2004). A visual depiction of the impact of iron-reducing conditions on changes in the mineralogy of iron oxide coated sands is shown in Figure 3 (Benner *et al.*, 2002). Thus, the current state of technical knowledge supports the contention that stimulation of microbial processes that lead to iron- and sulfate-reducing conditions within an aquifer can significantly alter the characteristics of redox-sensitive minerals. However, the extent of knowledge relative to the persistence of mineral alteration products following the return to oxidizing (pre-drilling) conditions is limited. No studies have been documented in the scientific literature or within written materials provided for this review to properly assess

1) how long the reduced mineral phases will survive, or
2) to what type of mineral phase(s) they will transform back to following the return of more oxidizing conditions.

The body of research that has examined redox processes active in soils and sediments indicates that significant time periods (years to decades) may be necessary for aquifer sediments to return to a condition that resembles the initial condition that existed prior to a significant change in redox chemistry. For well screens impacted by reducing conditions established during degradation of organic polymer drilling additives, any projections relative to the time to recovery or the characteristics of the 'recovered' aquifer sediments would need to be verified by direct observations in order to reduce the uncertainty associated with establishing whether ground-water samples are representative of pre-drilling conditions within the aquifer. In this respect, any information that could be obtained relative to the amounts and types of minerals produced at impacted well screens due to biodegradation of organic polymer additives would be very useful in the screening analysis of the utility of existing well installations for the collection of representative ground-water samples.

For screened intervals at which aquifer sediments may have been collected and retained during the drilling program, implementing microcosm studies similar to those illustrated in Table 2 could be beneficial. These microcosm studies could incorporate representative amounts of organic polymer drilling additives and, thus, provide an indirect assessment of in-situ aquifer sediment conditions that may exist for those well screens impacted by biodegradation of organic polymer additives introduced during drilling. In addition, the sediments obtained from these microcosm studies would provide a representative material that could be used to evaluate the extent that site contaminants of concern may be sorbed (and thus not detected) at well screens impacted by biodegradation reactions. This would provide a useful constraint to evaluating the extent to which this may be a concern for the various ground-water flow paths being sampled by the existing well network.

The mineralogical alterations depicted in Figures 2 and 3 will result in changes to the chemical reactivity of aquifer solids within the impacted zone adjacent to the well screen. A likely outcome resulting from a change in aquifer solids reactivity is that contaminants of concern will interact with altered aquifer solids to various degrees and some will be retarded or removed from solution (Figure 4). Since the contaminants of concern relevant to LANL's ground-water characterization effort represent a wide range of chemical affinity for sorption onto aquifer solids, the potential exists for inaccurate assessment of the concentrations of contaminants under the given conditions at an impacted well screen.

There is currently no definitive identification of the specific new mineral phases that are being formed and the amounts of mineral alteration products within the impacted zones adjacent to affected well screens. This lack of information increases the uncertainty as to whether a non-detect concentration (or a value below "background") of a strongly-sorbing contaminant of concern is indicative of 1) the absence of the contaminant in that portion of the aquifer being sampled or 2) sorption of the contaminant within the impacted zone surrounding wells where residual drilling additives resulted in significant alteration of the geochemical environment.

Issue 1: If LANL decides to convert characterization wells to monitoring wells, can wells drilled with bentonite clay or commercial fluids, such as EZ-MUD, Quik-FOAM, TORKEASE, and LIQUI-TROL, ever be developed and cleaned up adequately to provide analytical data representative of the ground water in the aquifer unit being sampled?

With respect to screens where bentonite-based additives were used, it is possible that even trace amounts of residual bentonite that remain following development may render ground-water samples non-representative for highly sorbing constituents. This situation would be difficult to accurately characterize. Therefore, the quality of samples for constituents such as isotopes of americium, cerium, plutonium, and radium obtained from these screens will likely remain uncertain even after re-development.

With respect to screened intervals where organic additives were used, it is possible that development procedures used in some wells following installation may have been sufficient to remove enough of the additives to prevent significant alteration of the geochemical environment surrounding the well screen. Vigorous redevelopment may be useful in removing additional quantities of the residual organic materials from some impacted screens and shorten the time frame for the return to oxidizing conditions, particularly if large quantities of additives did not infiltrate the screened zone. However, it is unlikely that the new mineral phases formed during biodegradation of the organic materials would be fully removed during re-development using conventional physical techniques. It is possible that some or all of these impacted wells may be capable of providing representative samples following degradation of the residual organic additives, the return of oxidizing conditions, and transformation of the altered minerals. Sampling methodologies that may aid in ultimately obtaining representative samples from such wells and better assessing the representativeness of those samples include: 1) use of methods that include purging of water prior to sampling to minimize retention time in the impacted zone and 2) sample collection, preservation and analysis procedures that minimize changes in chemical speciation of redox-sensitive parameters. It is recommended that current sampling procedures be critically evaluated and the potential benefits of any possible modifications in these areas be considered.

Resolution of Issue 1 first requires identification of the wells that may be sufficiently impacted by drilling fluids as to affect the chemistry in the aquifer surrounding the well screen. In this regard, LANL proposed draft criteria, dated September 6, 2005, for determining impacts (LANL, 2005b), which have been included in this review. The reviewed criteria are attached to this document and labeled as Appendix A. An evaluation and recommendations concerning the

September 6, 2005, version of these criteria are provided below. It is noted that a recent report (LANL, 2005c) may contain updated criteria and will be reviewed under separate cover.

1. The proposed criteria are based on analysis of water chemistry. It should be noted that while analysis of changes in aqueous chemistry at a given well screen presents one potential tool for characterizing well recovery, there is a high degree of uncertainty associated with this avenue of analysis. Specifically, aqueous chemistry data cannot be used to infer the distribution of contaminant mass (between water and solids) within the impacted zone adjacent to a well screen without knowledge of the initial concentration of the contaminant entering the impacted zone (*i.e.*, background constituent concentrations). In addition, comparison of measured concentrations of indicator parameters (or contaminants of concern) to background ground-water concentrations are useful only when the chosen background condition is representative of the un-impacted aquifer adjacent to the well screen being sampled. Reliance on an uncertain background condition to assess apparent well recovery limits the reliability of this approach (see additional discussion under Issue 4).

In this regard, the data used to characterize background conditions (LANL, 2005a) appear to be too sparse, derived from sources representing mixtures of water that are significantly different from the samples obtained from the hydrogeologic characterization wells, and representative of significantly different flow paths within the aquifer. It is recommended either that additional background data be obtained from monitoring wells screened solely within the specific units of interest and installed without the use of additives within the screened interval or that much less dependence be placed on the use of currently available background data in this evaluation.

2. Due to the relatively large variability observed in the background data set (LANL, 2005a), the trigger values proposed by LANL may not be conservative enough to identify some impacted wells due to uncertainty associated with appropriate background values. For example, LANL criteria 2.1-2a and 2.1-2b (Appendix A) use the minimum background concentrations for strontium and uranium as triggers to flag data as possibly non-representative. Actual background values at the locations of the characterization wells may be significantly different from the proposed values for reasons stated in the discussion under Issue 4 below. In similar fashion, it is not clear that detections of a parameter at concentrations above a maximum background value are a firm indication that bentonite is the source for the elevated constituent, as stated in LANL criterion 2.1-1a.

3. Where applicable, comparison of chemistry data for suspected well screens impacted by bentonite and/or organic polymers to background concentrations should include constituents that represent the full range of reactivity for potential site contaminants of concern. Examples of inorganic constituents that may be anticipated in background ground-water samples that represent a useful range of sorption reactivity (and mechanism) with respect to potential site contaminants of concern include zinc (Zn), strontium (Sr), molybdenum (Mo), cesium (Cs), barium (Ba), europium (Eu), thorium (Th), and uranium (U). The current criteria are structured to make use of comparisons between background values and data obtained from characterization wells for some but not all of these constituents. If present in background water from the monitoring zones of interest, these may be useful indicators in an assessment of the range of

impacts of the drilling additives. It is recommended that the utility of the constituents not currently used in the well assessment criteria be considered.

4. Development of a tiered process to assess the evolution of water chemistry at impacted well screens does provide one of several tools that should be implemented to judge the appropriate disposition of ground-water wells. The decision process should be based on comparison of measured ground-water chemistry to the anticipated chemical conditions derived from the presumed conceptual model of the geochemical evolution of impacted well screens. Based on analysis of the current conceptual model proposed by LANL, it is recommended that the tiered review process be re-evaluated and revised to more appropriately represent the conceptual model depicted in Figures 1 and 2 of this review. It is also recommended that the tiered review process be preceded by a screen-by-screen determination of where organic, bentonite, or both drilling fluids were used and the approximate quantities that were used. Our examination of the data provided by LANL on a borehole-by-borehole basis regarding this issue indicates that all boreholes were drilled using organic drilling fluids, and some boreholes were also drilled using bentonite. If it is determined that all screened intervals were drilled using organic drilling fluids, some re-structuring of the flow of the tiered process may be appropriate.

The following three issues should be considered with respect to the choice of analytes that are used in criteria to assess apparent well recovery:

A. A subset of the analytes chosen for assessing impact of drilling fluid at a given well screen should be a component of the drilling fluid and have concentrations that are much higher than typical for site ground-water background conditions,
B. Analytes chosen to assess geochemical conditions or possible contaminant sequestration should not be susceptible to changes in chemical speciation during sample collection and preservation, and
C. Analytes chosen to assess the possible sequestration of contaminants of concern on aquifer solids surrounding impacted screens should possess a higher affinity for partitioning to the unaltered/altered aquifer solids.

With regard to issue (A), it appears that the currently recommended list of analytes used to assess drilling fluid impact may not be complete. A summary of deionized water extraction data made available for review by LANL is shown in Table 3. Analytes highlighted in yellow for a subset of drilling fluids may serve as appropriate indicators of the continued presence of several of the drilling fluids. It should be noted that no data were available for review for a number of the drilling fluids that were frequently employed during drilling operations (including EZ-MUD, Quik-FOAM, TORKEASE, and LIQUI-TROL). These data should also be obtained and evaluated as part of revisions to the analyte list.

With regard to issue (B), there is concern that sulfate may not be a reliable indicator under reducing conditions. Specifically, it is possible to obtain a false positive for the presence of sulfate due to inappropriate collection and preservation that will result in the oxidation of dissolved sulfide. This problem is magnified by a water collection method using a no-purge technology. Based on our on-site observation of ground-water sampling activities at well R-22 on June 28, 2005, it appeared that there were few controls implemented to limit oxygen intrusion

into water samples retrieved from the well screen. First, sampling vessels that are lowered to the well screen are potential sources of oxygen exposure to sampled water, even though the sampling vessels are deployed under vacuum. Quality control data were not available for this review to assess the reliability of this sampling configuration to prevent oxidation of dissolved sulfide [and Fe(II) or Mn(II)] during the timeframe of a typical sampling event. Secondly, oxygen exposure again may occur during transfer of collected water to individual containers prior to submission for laboratory analysis, since sample transfer was not conducted without air exposure. Based on our observations in the field, it did not appear that dissolved sulfide was measured in the field, so there was no analytical mechanism in place to evaluate whether sulfate measured in the laboratory represents the true concentration at the well screen, the concentration following oxidation of dissolved sulfide after sample collection, or some combination thereof. This is of particular concern since sulfate is used as one of the initial criteria (LANL criterion 2.2-2) for screening the impact of residual organic drilling fluids.

It should also be noted that the existence of sulfate-reducing conditions does not preclude the presence of sulfate in water. The concentration of sulfate and dissolved sulfide in ground water within a sulfate-reducing zone will depend on two factors: 1) the kinetics of sulfate reduction relative to the concentration of sulfate (*i.e.*, supply of sulfate may exceed capacity for its reduction leading to continued persistence of sulfate in ground water), and 2) the relative concentrations of dissolved ferrous iron and sulfide produced by sulfate reduction. If ferrous iron is present in molar excess of sulfide (*i.e.*, moles Fe(II) > moles dissolved sulfide), then precipitation of iron sulfides could effectively sequester biologically-produced sulfide and prevent its detection in the dissolved phase (*i.e.*, ground water).

No methods are available to directly measure ferrous iron, sulfate, or dissolved sulfide within the well screen; these parameters require measurement by various analytical techniques following collection of a water sample. Reliable field methods exist for the determination of ferrous iron and dissolved sulfide in ground water. For analytes like ferrous iron or dissolved sulfide that are susceptible to transformations following sample collection (*e.g.*, exposure to air), the most reliable method of sampling usually involves continuous pumping of water from the well screen followed by immediate analysis using these field methods. Continuous pumping (or purging) of the well screen during sample collection helps ensure that the field technician can collect water samples for measurement of these parameters exactly at the time at which the analysis can be made. This also allows the field technician to collect additional fresh samples in the event that some level of dilution is required prior to analysis. Delays in sample processing for field measurements generally result in unreliable water chemistry data. Current uncertainties associated with the no-purge method of water sampling from the impacted well screens and the observed practices used to preserve sample integrity prior to analytical measurements limit the reliability of these parameters for screening the condition of wells impacted by organic drilling fluids.

For issue (C), it is important to identify analytes that are transported less conservatively than the contaminants of concern. Dissolved zinc is proposed for screening the condition of wells impacted by bentonite relative to the possible loss of cesium-137, cobalt-60, europium isotopes, and neodymium-147 onto residual bentonite solids adjacent to the impacted well screen (LANL criterion 2.1-2). One significant limitation to this approach is that zinc has not been

universally detected in site ground water. LANL (2005a) reports non-detectable zinc in about 56% of the samples evaluated. Thus, non-detectable zinc at a given well screen could indicate either sorption onto residual bentonite or the lack of this constituent at measurable concentration in the native ground water at the interval sampled by the well screen. In addition, there are some published ion exchange selectivity series that indicate cobalt partitions more strongly than zinc to clay minerals (including bentonite). Thus, detection of zinc would not preclude loss of cobalt-60 on residual bentonite. LANL criterion 2.1-2 should be re-evaluated in an effort to identify a more reliable replacement or supplemental candidate to zinc. Barium presents a potential alternative/additional candidate (99% detect in area ground water), although it is unclear how prevalent this metal may be as a site contaminant of concern.

5. The LANL Tier 2.2 criteria are designed under the assumption that once oxidizing conditions have been re-established the sorption characteristics of the aquifer material immediately adjacent to the well screen have returned to pre-drilling conditions. This is not necessarily the case. As described above, the reducing conditions established by biodegradation of organic drilling fluids are likely to alter the mineralogical composition of the aquifer solids adjacent to impacted well screens. These processes generally increase the mass of reactive minerals resulting in an increase in the sorption capacity of aquifer materials impacted by biodegradation of organic drilling fluids. Thus, contaminant concentration data collected from impacted well screens where oxidizing conditions have returned may still be biased low relative to the actual concentration of contaminants in un-impacted aquifer materials in the same flow path. Without collection and characterization of altered aquifer materials, it is difficult to determine the extent of this problem on a screen-by-screen basis. In this regard, it may be beneficial to attempt removal and analysis of mineral alteration products via physical or even chemical processes that mobilize or dissolve these phases. However, it should be noted that the use of chemical extraction may affect future analyses and may only be appropriate if a well is determined to be too impacted for use in the current monitoring program or is replaced by another well to meet appropriate data quality objectives for that particular monitoring location.

6. There is also concern regarding the use of only the three most recent measurements in these assessments without examination of trends. Although the concentrations of the parameters used as indicators in the LANL criteria may change with time and eventually meet the proposed triggers, this does not imply that the data are now representative of the aquifer for each of the listed parameters for the reasons stated above.

7. It is noted that technetium is not mentioned under these criteria and should be included.

8. Due to uncertainties in the utility of aqueous chemistry assessments for the determination of whether samples are fully representative of aquifer conditions, it is recommended that field studies be designed to validate these or similar criteria. It is possible that push-pull tests using a conservative tracer and surrogates for the contaminants of concern may provide a qualitative evaluation of differences in sorptive capacity, if performed in impacted wells and, possibly, adjacent wells of similar design that were installed without additives in the screened zone or if performed in well screens with different degrees of impact. Although detailed quantitative interpretations of such tests would likely be uncertain in this setting and the test would require injection of surrogates for contaminants of concern, the data may still provide one of the few

available insights into the current well conditions. It is unlikely that this type of invasive test would provide sufficient information to fully understand or characterize the impacts to the representativeness of samples and may negatively impact future analyses of some samples from the tested well screen. However, limited use of this type of test may serve as one line of evidence within a more comprehensive investigation. Push-pull tests designed to characterize various aquifer parameters, including sorption, are discussed in more detail in a variety of references, including Istok *et al.* (1999).

Another line of evidence may be direct comparisons between water samples obtained from impacted screens and new wells installed without additives at locations determined to be critical to the monitoring program. The results may then be used to help evaluate the need for additional studies or well installations at other locations. One possible location for additional study is near well R-22 which demonstrates impacts from polymer-based additives. Comparisons of aqueous chemistry between R-22 and a new well cluster combined with the results of studies such as analyses of altered minerals from microcosms, analysis of aquifer materials extracted from well screens that are too impacted to meet DQOs, and push-pull tracer tests may provide much insight into the magnitude and long-term impacts of the problems associated with residual additives at other locations.

9. The proposed criteria did not specify specific actions to be taken, other than flagging of data, if evaluations indicated impacts due to drilling additives. It is recommended that the criteria be expanded to specify precisely what flagging the data means with respect to data limitations, usability, and corrective actions such as well re-development or replacement, given the DQOs for each monitoring location.

Issue 2: Will the use of commercial drilling fluids and bentonite clay preclude any contaminants from being accurately sampled even after well cleanup? If so, which ones?

Site-specific contaminants of concern include isotopes of americium, cesium, iodine, plutonium, strontium, technetium, and uranium, as well as chlorinated solvents, perchlorate, and others. Whether samples obtained from the hydrogeologic characterization wells following re-development are representative of aquifer conditions will depend on the degree to which residual drilling fluids and altered aquifer materials have been removed or returned to their unaltered states. This question can only be answered following demonstration that the geochemical properties of the aquifer materials surrounding the well screen have not been altered with respect to sorption characteristics for the contaminants for which sorption or geochemical environment is a significant concern. Studies such as those discussed above will be necessary to validate predictions made based on aqueous chemistry.

Other issues affecting whether samples from the hydrogeologic characterization wells are representative of aquifer conditions include the design and construction of these wells. Many of the wells, particularly those constructed at the top of the regional aquifer, use screens as long as approximately 60 ft. This type of construction can result in significant dilution of any contaminants that may be present unless the contaminant is pervasive throughout the entire screened interval, regardless of the location of the contaminated zone within the screened interval. In some instances, interval sampling using a pump/packer or other discrete interval

sampling system may provide information concerning differences in water chemistry within the screen and the possible effects of dilution. Although the use of long screens may extend the useful life of the well in a setting where the regional water table is declining and may offer an opportunity to sample a larger portion of the aquifer than possible with a more conventional monitoring well design, it may render early detection of contaminants more uncertain. It is recommended that the DQOs for this type of well be reviewed to determine whether the long-screened construction and associated possibility of significant dilution are acceptable before incorporation into a detection monitoring program.

In addition, the use of a long screen increases the risk of cross connection of different hydrostratigraphic units. Cross connection of different units may result in significant vertical flow within the well and the transport of contaminants, if present, to other parts of the aquifer system. The existence of a vertical flow field within the well may be characterized using a sensitive electromagnetic or heat-pulse borehole flowmeter as described in Young *et al.* (2000). Additional information and advice regarding design and use of borehole flowmeter surveys to characterize both the vertical flow within a well and the zones from which water enters a long-screened well during purging and sampling can be provided, if desired.

Of even greater importance is the choice of screened intervals within the target hydrostratigraphic section. As the focus of the issues raised by the NNMCAB concerned the effects of drilling additives, a detailed evaluation of the individual well constructions and screened intervals was not performed. However, it is recommended that such an analysis be performed before wells are determined to meet criteria normally applied in a detection monitoring program. In summary, factors other than the effects of drilling additives may have a greater impact on whether ground-water samples are suitable for the purpose of early detection of contaminant releases or migration and should be considered during specification of a detection monitoring network.

Issue 3: In public reports, LANL indicates that contamination from LANL operations has not reached certain ground-water regions. LANL bases these statements on analytical results which show that certain fast-moving contaminants, such as tritium, that are not affected by drilling fluids or clays have not been detected in concentrations above background in samples from the wells. Are tritium and other mobile constituents suitable indicators of possible impacts for the entire suite of site-specific constituents at LANL?

The contaminants of concern vary in their mobility in the environment due to differences in their physical/chemical properties. In principle, accurate knowledge of the concentrations of the most mobile contaminants, particularly tritium, can be used as an indicator of the maximum extent of the less mobile contaminants of concern, such as the isotopes of plutonium. However, this type of evaluation assumes that all of the contaminants of concern in a given area were disposed at approximately the same time and location and that the concentration and mass of the mobile contaminant were sufficiently high to allow detection at a given distance from the disposal point. Documents provided for this review did not include information concerning the analyses of historical waste streams or sufficient details concerning site hydrogeology to estimate potential migration pathways and the effects of dispersion. Therefore, this potential use of tritium data at LANL could not be evaluated in detail. Based on experience at other sites, it is

quite possible that the available information may only allow a screening-level evaluation to be performed.

Tritium activity is also used as an indicator of the ground-water age or elapsed time since the water entered the subsurface. This evaluation should be useful at LANL in assessing the potential for contaminants of concern to be present based on whether the water entered the subsurface before or after disposal activities began. However, care must be exercised in the interpretation of these data due to the effects of dilution within long-screened wells, uncertainty with respect to the effects of biological processes in impacted well screens sampled using a no-purge technique, and related factors.

It is further noted that Bitner *et al.* (2004) also consider nitrate and perchlorate to be conservative environmental tracers that travel at the speed of the ground water. However, these constituents may be subject to removal under certain conditions, such as in a reducing environment surrounding well screens impacted by polymer-based additives. Therefore, well-specific evaluations using these compounds may be useful at LANL but should be performed with care.

Issue 4: (a) Can LANL derive an independent estimate of background concentrations of potential contaminants from accumulated ground-water data without using analytical results from the wells associated with the Hydrogeologic Work Plan? (b) Would such data constitute reliable criteria for judging when wells are suitable as monitoring wells?

An evaluation of "background" ground-water chemistry is provided in LANL (2005a). In this study, sources for background data determined to reflect conditions in the regional aquifer were limited to a few springs and long-screened water production wells located at significant distances from many of the characterization wells. These types of sources generally produce water that is a mixture of contributions from different lithologic units and different areas. This type of study may provide useful information concerning "background" constituent concentrations for the purpose of siting a water supply well. However, it does not appear to be appropriate for detailed comparisons with water samples obtained from monitoring wells that provide samples from discrete zones and likely represent much smaller volumes of the aquifer and different flow paths within the aquifer. Although the information in LANL (2005a) provides insight into the possible range of "background" conditions, data from monitoring wells located upgradient of waste management units/disposal areas would be needed to allow more reliable comparisons with wells located downgradient of these units. Therefore, the current "background" data should not be used as the sole indicator of whether samples are representative of aquifer conditions.

Summary

Most of the hydrogeologic characterization wells at LANL appear to have been installed using drilling additives that have the potential to impact the quality of data obtained from the affected well screens. Some of these impacts have been documented in various LANL publications. A systematic study to identify impacted screens based on aqueous chemistry has recently been performed (LANL, 2005c) and will be reviewed under separate cover. In general,

it is likely that many of these screens may not produce representative samples for constituents that strongly sorb to clays or whose fate in the environment is sensitive to changes in redox conditions for some period of time. In particular, the constituents of concern that may be most affected by the residual drilling additives are certain radionuclides (*e.g.*, isotopes of americium, cerium, plutonium, radium, strontium, uranium), many stable metal cations, and organic compounds that may be degraded in the impacted environment near the well screen.

Predictions of the time frames for the impacted intervals to return to natural conditions are uncertain. It is also likely that the inability to fully remove the additives which were used during drilling has reduced the hydraulic conductivity of many of the impacted screened zones. Due to the difficulty in assessing the damage that may be caused by the presence of residual drilling additives in the screened zone of a well, it is recommended that the need for continued use of additives within the screened interval of monitoring wells be reassessed. The following recommendations for improvement during the drilling and construction of future monitoring wells may allow installation of wells that provide the most representative samples possible for all of the contaminants of concern at LANL. It is noted that many of these techniques are successfully used at the Idaho National Laboratory (INL) to avoid the use of drilling additives, other than water to control heaving, in the screened zone. Although the drilling conditions at no two sites are identical, similar problems, such as heaving materials, consolidated and unconsolidated formations, and depths in excess of 1000 ft are also encountered at INL and successfully drilled using techniques similar to those described below.

1. Strive to drill boreholes using no bentonite or organic additives within screened intervals. Additives may be used in intervals above the target monitoring zone if telescoping casing constructions are used and the hole is adequately cleaned before drilling the final footage within the interval to be screened. Targeting of monitoring intervals prior to drilling should be possible at locations where data from the existing characterization wells are available.

2. Use screen types and well designs that maximize the open area of the screen and allow for the most uniform and effective well development. Use aggressive development methods that result in water movement into and out of the well screen.

3. Minimize the time between drilling and well development, particularly if additives have been used within the screened zone. As indicated in Table 1, many of the hydrogeologic characterization wells were not developed in a timely fashion following well completion. It should be noted that the time between the drilling of any given interval in a multi-completion well and the development of that interval is often longer than the time lag calculated in this table. This time lag will often exacerbate the difficulties in removing residual drilling fluids.

4. At locations determined to be critical to the detection monitoring program, consider replacement of wells that were drilled using bentonite or that exhibit impacts due to organic additives with wells installed without additives in the screened zones, if needed to meet the DQOs for that monitoring location.

The path for resolution of issues concerning the impacts of drilling additives on the quality of ground-water samples should include identification of all well screens impacted by

drilling additives, specification of the corrective actions to be taken, and field studies performed to verify these evaluations. Based on the uncertainty in characterizing the condition of aquifer materials adjacent to the well screens and the potentially long time frames that some impacts may last, installation of replacement wells at critical locations should also be considered.

If you have any questions concerning this review, please do not hesitate to call us (Acree: 580-436-8609; Ford: 580-436-8872; Ross: 580-436-8611) at your convenience. We look forward to future interactions with you concerning this and other sites.

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References

Benner, S.G., C.H. Hansel, B.W. Wielinga, T.M.Barber, and S. Fendorf, 2002. Reductive dissolution and biomineralization of iron hydroxide under dynamic flow conditions. Environmental Science & Technology, 36: 1705-1711.

Bitner, K., D. Broxton, P. Longmire, S. Pearson, and D. Vaniman, 2004. Response to Concerns About Selected Regional Aquifer Wells at Los Alamos National Laboratory, LA-UR-04-6777. Los Alamos National Laboratory, Los Alamos, NM.

Hansel, C.M., S.G. Benner, and S. Fendorf, 2005. Competing Fe(II)-induced mineralization pathways of ferrihydrite. Environmental Science & Technology, 39: 7147-7153.

Hansel, C.M., S. Benner, P.S. Nico, and S. Fendorf, 2004. Structural constraints of ferric (hydr)oxides on dissimilatory iron reduction and the fate of Fe(II). Geochimica et Cosmochimica Acta, 68: 3217-3229.

Hansel, C.M., S. Benner, A. Dohnalkova, P.K. Kukkadapu, and S. Fendorf, 2003. Secondary mineralization pathways induced by dissimilatory iron reduction of ferrihydrite under advective flow. Geochimica et Cosmochimica Acta, 67:2977-2992.

Istok, J.D., J.A. Field, M.H. Schroth, T.E. Sawyer, and M.D. Humphrey, 1999. Laboratory and field investigation of surfactant sorption using single-well, “Push-Pull” tests. Ground Water, 37:589-598.

Kukkadapu, R.K., J.M. Zachara, J.K. Fredrickson, and D.W. Kennedy, 2004. Biotransformation of two-line silica-ferrihydrite by a dissimilatory Fe(III)-reducing bacterium: Formation of carbonate green rust in the presence of phosphate. Geochimica et Cosmochimica Acta 68: 2799-2814.

Longmire, P., 2002. Characterization Well R-22 Geochemistry Report, LA-13986-MS. Los Alamos National Laboratory, Los Alamos, NM.

LANL, 2005a. Groundwater Background Investigation Report, LA-UR-05-2295. Los Alamos National Laboratory, Los Alamos, NM.

LANL, 2005b. Screening Tables Template. Draft well assessment criteria provided by electronic mail, dated September 6, 2005, Los Alamos National Laboratory, Los Alamos, NM.

LANL, 2005c. Well Screen Analysis Report, LA-UR-05-8615. Los Alamos National Laboratory, Los Alamos, NM.

Poulton, S.W., M.D. Krom, and R. Raiswell, 2004. A revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulfide. Geochimica et Cosmochimica Acta, 68: 3703-3715.

Wersin, P., P. Hohener, R. Giovanoli, and W. Stumm, 1991. Early diagenetic influences on iron transformations in a fresh-water lake sediment. Chemical Geology, 90: 233-252.

Young, S.C., H.E. Julian, H.S. Pearson, F.J. Molz, and G.K. Boman, 1998. Application of the Electromagnetic Borehole Flowmeter, EPA/600/R-98/058, U.S. Environmental Protection Agency, Cincinnati, OH.

Zachara, J.M., R.K. Kukkadapu, J.K. Fredrickson, Y.A. Gorby, and S.C. Smith, 2002. Biomineralization of poorly crystalline Fe(III) oxides by dissimilatory metal reducing bacteria (DMRB). Geomicrobiology Journal, 19: 179-207.

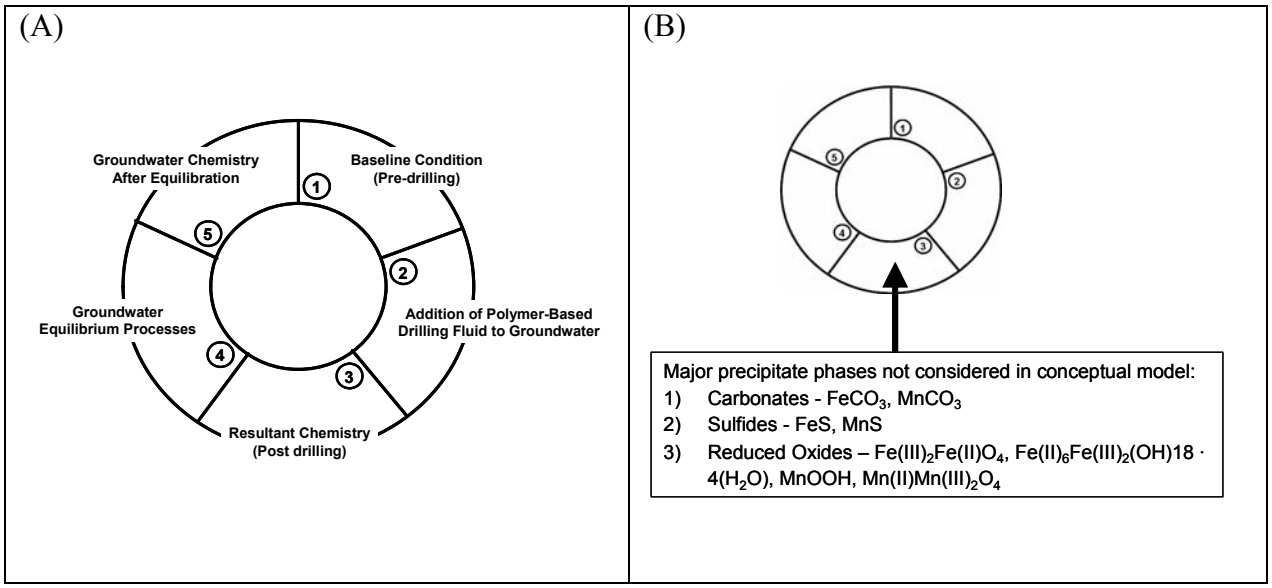

Figure 1. Illustration of certain aspects of solid phase chemistry not considered in the Bitner *et al.* (2004) conceptual model describing the evolution of aqueous and solid phase chemistry at well screens impacted by biodegradation of polymer-based drilling fluids. (A) Simplified depiction of the LANL conceptual model relative to the various stages of geochemical evolution in the impacted zone adjacent to the well screen. (B) Precipitation of major solid phases that can occur during Stage 3 reduction processes.

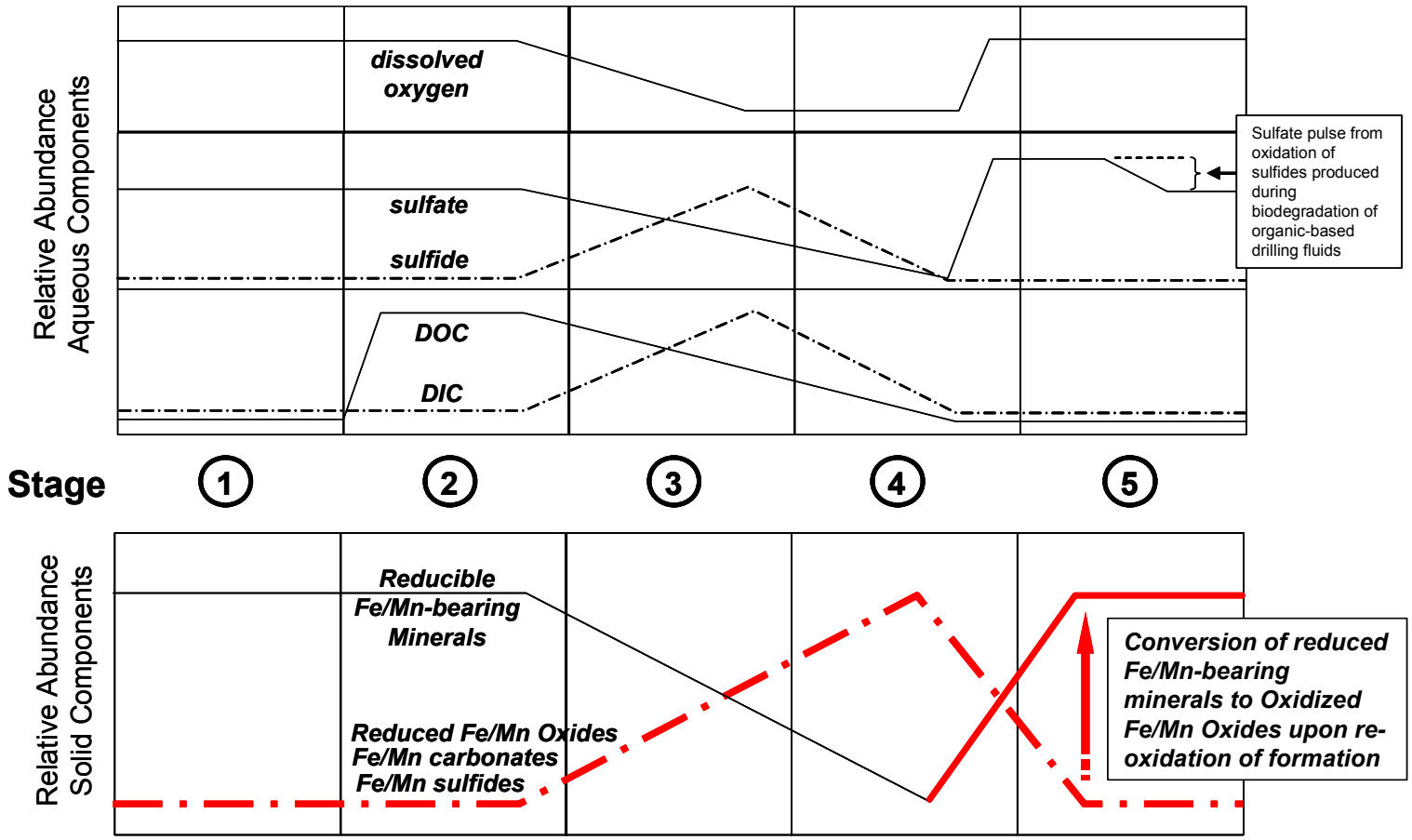

Figure 2. Schematic diagram depicting the evolution of aqueous and solid phase chemical components within the impacted zone of the aquifer adjacent to well screens impacted by the biodegradation of organic-based polymer drilling fluids. Changes in relative abundance of individual chemical components are depicted based on the current state-of-knowledge of mineral alterations that accompany organic biodegradation reactions (*i.e.*, microbially-driven iron-, manganese-, and sulfate-reduction) in subsurface environments.

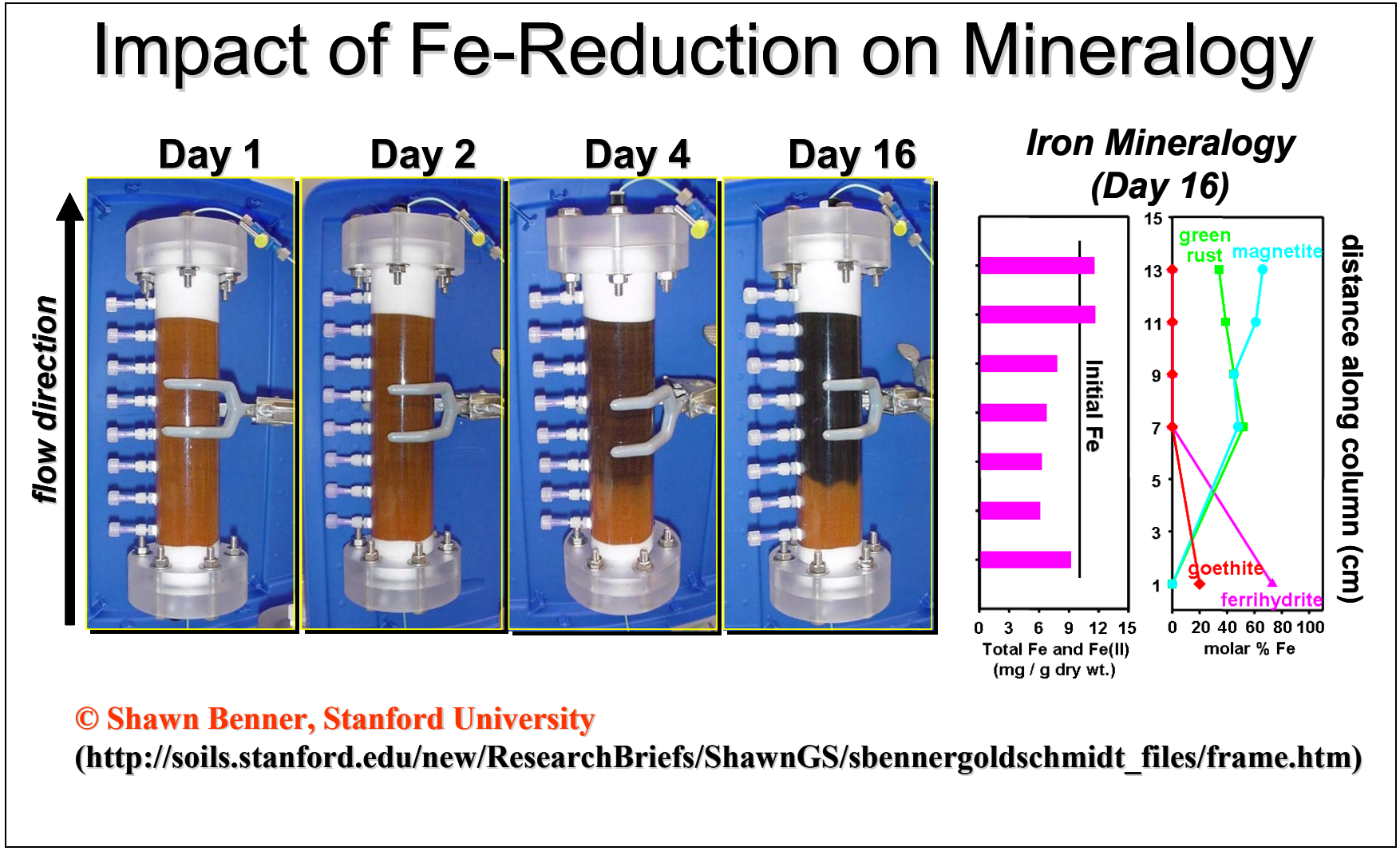

Figure 3. Illustration of transformations in iron oxide mineralogy induced by microbial processes that generate iron-reducing conditions. The starting Fe-bearing mineral was ferrihydrite, which was transformed to a mixture of ferrihydrite, goethite, magnetite, and green rust by day 16. The details of this experimental research are documented within Benner *et al.* (2002).

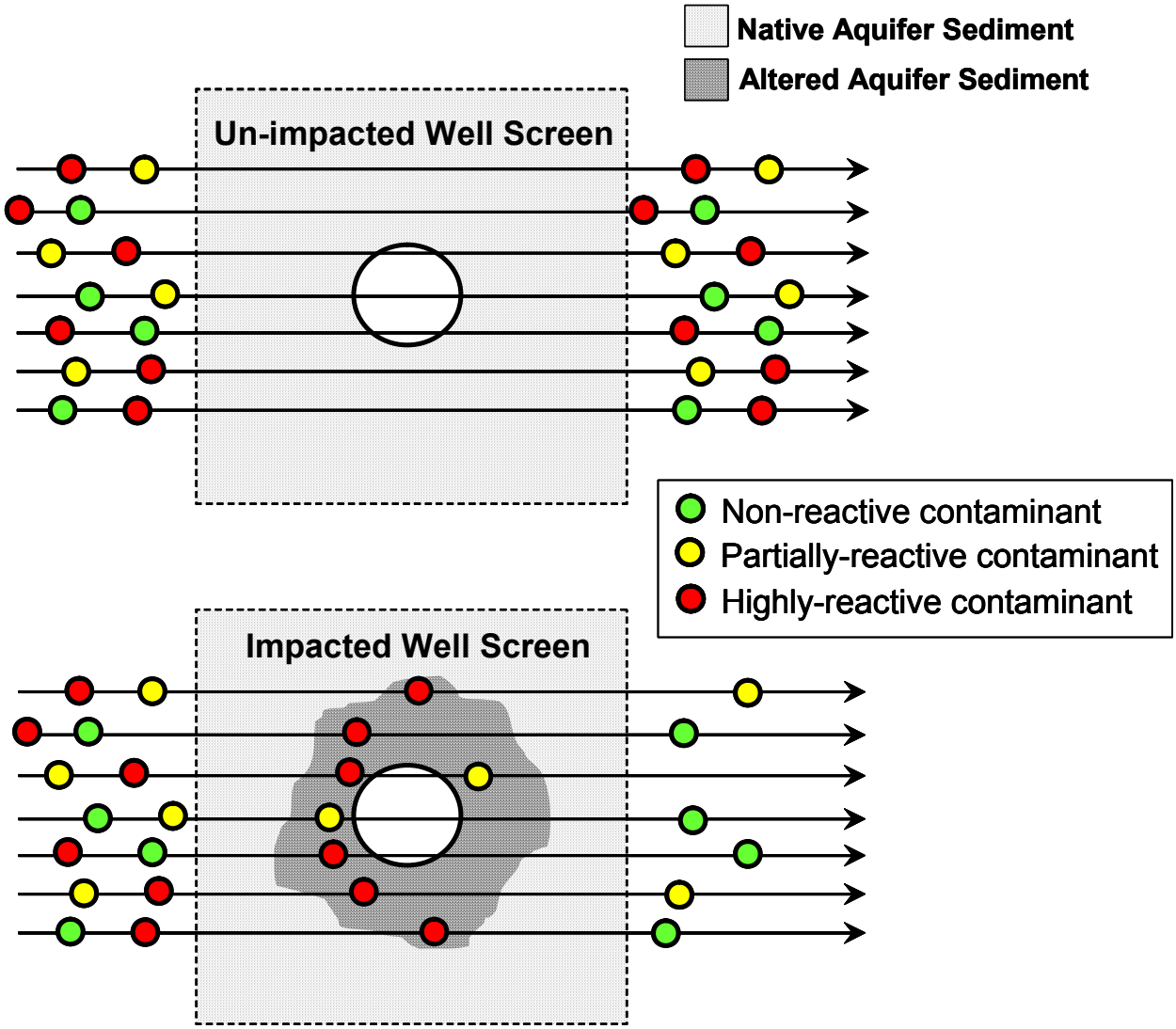

Figure 4. Conceptual schematic illustrating differential transport behavior of contaminants within the impacted zone adjacent to a well screen influenced by biodegradation of organic-based drilling fluids.

Table 1. Listing of drilling additives employed during implementation of the hydrogeologic characterization program at LANL.

		Drilling Fluid *										Impact Category		
Well	**Elapsed Time Before Development (Days) ****	EZ-MUD	QUIK-FOAM	TORKEASE	LIQUI-TROL	PAC-L	Bentonite	QUICK-GEL	N-SEAL	Magma Fiber	Soda Ash	Biodegradation	Bentonite	Both
		Polymer-based					**Bentonite-based**		**Other**					
R-1	11													
R-2	7													
R-4	10													
R-5	12													
R-7	16													
R-8	11													
R-9	115													
R-11	No report													
R-12	26													
R-13	33													
R-14	17													
R-15	Chrono uncertain													
R-16	16													
R-19	Chrono uncertain													
CdV-R-15-3	~92													
CdV-R-37-2	~25													
R-20	9													
R-21	8													
R-22	~40													
R-23	20													
R-25	64													
R-26	12													
R-28	30													
R-31	~31													
R-32	11													
MCOBT-4.4	~23													
MCOBT-8.5	No well													
R-9i	Chrono uncertain													
CdV-16-1(i)	No report													
CdV-16-2(i)	No report													
CdV-16-3(i)	No report													

* Based on information presented in Table 1 of Bitner *et al.* (2004).
** Determined as the time from completion of the entire borehole to initiation of development activities.

Table 2. Documented examples where microbial degradation of organic compounds resulted in alteration of iron mineralogy under iron- and sulfate-reducing conditions.

Starting Mineralogy	Reducing Conditions	Resultant Mineralogy	Reference
ferrihydrite	Iron-reducing	lepidocrocite, goethite, magnetite	Hansel *et al*., 2005
ferrihydrite	Iron-reducing	magnetite, green rust, vivianite	Kukkudapu *et al*., 2004
ferrihydrite	Iron-reducing	goethite, hematite, lepidocrocite, siderite, vivianite, magnetite, green rust	Zachara *et al*., 2002
goethite, hematite	Iron-reducing	Fe(II) sorbed to goethite/hematite	Hansel *et al*., 2004
poorly crystalline Fe(III) oxide	Iron- & sulfate-reducing	iron sulfide	Wersin *et al*., 1991
ferrihydrite, lepidocrocite, goethite, magnetite, hematite	Abiotic reaction with dissolved sulfide	Fe(II) sorbed to iron oxide surface, FeS	Poulton *et al*., 2004

Table 3. Listing of water-leachable chemical constituents present in drilling fluids employed during implementation of the hydrogeologic characterization program at LANL.

Analyte *	Concentration Unit	Bentonite	EZ-MUD	Quik-FOAM	TORKEASE	LIQUI-TROL	PAC-L	Soda Ash	Quick-gel	magma-fiber	n-seal	Regional Aquifer**	Intermediate Perched Zones**
Ag	ppm	<0.009					<0.2		<0.01		<0.01		
Al	ppm	0.229					3.860		1.006		5.971		
Alk(Lab)	ppm CaCO3	---					85557.377	1052213.087	17595.519		75253.552	150.000	65.000
As	ppm	1.374					<0.2		0.091		<0.01	<0.007	<0.007
B	ppm	1.008					<2		0.302		0.379		
Ba	ppm	0.018					1.103		0.101		0.209		
Be	ppm	<0.009					<0.2		<0.01		<0.01		
Br	ppm	0.275					<4		6.336		<0.2		
C DIC	ppm	---					295.915		156.886		25.779		
C DOC	ppm	---					196663.745		94.232		30.423	<12	<12
C TIC	ppm	---					---		---		---		
C TOC	ppm	---					---		---		---		
Ca	ppm	9.984					115.793		137.778		593.288	38.000	16.000
Cd	ppm	<0.009					<0.2		<0.01		<0.01		
Cl	ppm	116.332					20769.162		65.067		3.981	9.100	71.000
ClO3	ppm	<0.09					<4		<0.2		<0.2		
ClO4	ppm	1.191					---		---		---		
Co	ppm	<0.009					<0.2		<0.01		<0.01		
CO3	ppm	---					0.000	602459.000	886.000		910.000		
Cond.(F)	µS/cm	---					---		---		---		
Cond.(L)	µS/cm	---					---		---		---		
Cr	ppm	0.082					2.941		0.070		0.009		
Cs	ppm	<0.009					<0.2		0.020		<0.01		
Cu	ppm	0.062					3.492		0.131		0.171		
F	ppm	7.236					1630.287		10.560		16.017		
Fe	ppm	<0.09					5.514		0.503		<0.1		
Hardness	CaCO3 ppm	---					---		---		---		
HCO3	ppm	---					104380.000	58700.000	19665.000		89959.000		
Hg	ppm	0.002					<0.02		<0.001		<0.001		
I	ppm	---					---		---		---		
K	ppm	6.046					33.084		15.387		80.084	5.100	7.500
Li	ppm	0.247					<0.2		0.704		0.265		
Mg	ppm	1.282					16.542		13.778		0.853		
Mn	ppm	0.016					0.368		0.080		<0.01		
Mo	ppm	2.473					<0.2		0.825		<0.01		
Na	ppm	1346.520					93553.127		5390.440		64.162	31.000	36.000
NH4	ppm	---					---		---		---		
Ni	ppm	0.016					0.368		0.040		0.019		
NO2	ppm	0.183					<4		<0.2		<0.2		
NO3	ppm	196.940					<4		237.340		<0.2	0.910	0.500
OH	ppm	---					---		---		---		
Oxalate	ppm	4.855					<4		<0.2		<0.2		
Pb	ppm	<0.0009					0.368		<0.01		<0.01		
pH	Lab	---					7.970	11.380	9.090		9.470		
PO4	ppm	6.504					10586.759		<0.5		<0.5		
Rb	ppm	0.011					<0.2		0.040		0.171		
Sb	ppm	0.056					<0.2		<0.01		0.020		
Se	ppm	0.092					<0.2		0.191		0.066		
Si	ppm	204.268					110.279		159.903		211.347		
SiO2	ppm calc	437.134					235.996		342.192		452.283		
SO4	ppm	1007.600					<4		9483.553		95.722	17.200	11.300
S2O3	ppm	---					---		---		---		
Sn	ppm	<0.009					<0.2		<0.01		<0.01		
Sr	ppm	0.030					0.551		2.011		1.137		
Th	ppm	<0.009					<0.2		<0.01		0.023		
Ti	ppm	<0.009					<0.4		<0.02		<0.02		
Tl	ppm	<0.009					<0.2		<0.01		0.023		
U	ppm	0.070					<0.2		0.040		0.023		
V	ppm	0.128					<0.4		<0.02		0.152		
Zn	ppm	<0.009					<0.4		<0.02		<0.02		
TDS	ppm	---					231339.313		36259.586		92184.026		
Acetate	ppm	++					+		-		-		
Formate	ppm	++					+		-		-		

No data reported for these analytes.

Indicates analyte with elevated concentration that may serve as a useful indicator for water quality in impacted well screens.

* Data were copied from Excel file (Drilling_Additives.xls) provided by Patrick Longmire/LANL to Richard Mayer/R6 via e-mail on April 19, 2005.

** Maximum background concentration; data were derived from Table 4.3-1 (LANL, 2005b) and/or LANL (2005a), Appendix C.

Appendix A

Screening Tables Template
(LANL, 2005b)

The following tables were provided by LANL via electronic mail and dated September 6, 2005.

Table 4.3-1

Background Values for Key Indicator Species Used in this Assessment

Analyte	Units	Regional Aquifer			Intermediate Perched Zones			Tier criteria
		Minimum	Maximum	Mean	Minimum	Maximum	Mean	
Field parameters								
Field alkalinity (as HCO_3)	mg/L	65	150	103	34	65	54	2.2-3, 2.2-5
Field pH	SU	6.5	8.3	7.6	6.7	8.0	7.4	2.2-3, 2.2-5
Turbidity (nonfiltered)	NTU	0	5.4	2.0	0	27	7.3	2.1-1, 2.1-6
General Inorganics								
Calcium	mg/L	9.1	38	16	5.8	16	9.4	*not used*
Chloride	mg/L	1.7	9.1	3.2	0.53	71	6.9	*not used*
Magnesium	mg/L	0.23	8.4	2.7	1.2	6.1	2.8	*not used*
Nitrate and Nitrite (NO_3+NO_2-N)	mg/L	0.025	0.91	0.32	0.001	0.5	0.3	2.2-4, 2.2-5
Potassium	mg/L	1.4	5.1	2.4	1.5	7.5	3.5	*not used*
Sodium	mg/L	9.4	31	18	4.4	36	9.2	2.1-1, 2.1-6
Sulfate	mg/L	1.8	17.2	4.7	0.95	11.3	4.4	2.1-1, 2.1-6 2.2-2, 2.2-5
Metals								
Barium	µg/L	1.9	110	36	5	110	29	*not used*
Boron	µg/L	4.6	51	23	1	13	7.4	2.1-1, 2.1-6
Iron	µg/L	3.65	131	27	3.65	1560	170	2.2-3, 2.2-5
Manganese	µg/L	0.025	57	4.7	0.05	9	2.4	2.2-3, 2.2-5
Strontium	µg/L	42	510	192	42	164	76	2.1-2, 2.1-6
Uranium	µg/L	0.195	2.8	0.88	0.11	0.84	0.31	2.1-1, 2.1-2, 2.1-6
Zinc	µg/L	0.26	80	13	0.26	33	5.3	2.1-2

SU=standard units, pH=-log[H+]

Table 4.4-1

Tier 1 Questions and Criteria for Effects of Residual Drilling Materials

Tier 1 Issue:	**Does the screen interval produce groundwater samples that are free of any residual effects from drilling fluids or muds, and that are reliable and representative of the groundwater*?** Note: The assessment criteria in this table are applicable to the three most recent characterization and/or surveillance samples for the screen. If less than three samples are available for this purpose, then the outcome is considered "Preliminary."		
Tier	**Screening Question**	**Assessment Criteria**	**Consequence of "NO" response**
1-1	Is residual bentonite mud known to be absent from the screen interval?	• If the well was not drilled using bentonite mud, answer YES. • If the well was drilled using bentonite mud, answer NO.	If NO, then tier 2.1 questions are applicable to identify the extent to which analytes or PCOCs may be affected by residual bentonite.
1-2	Is residual organic drilling fluid known to be absent from the screen interval?	• If the well was not drilled using organic drilling fluids, answer YES. • If the well was drilled using organic drilling fluids, answer NO.	If NO, then tier 2.2 questions are applicable to identify the extent to which analytes or PCOCs may be affected by residual organic drilling fluids or reducing conditions.
If the answer is YES for both questions, then it is concluded that the screen interval produces groundwater samples that are representative of predrilling conditions for all analytes and PCOCs. **It is not necessary to proceed to either of the Tier 2 sets of questions.**			

* In this report, "groundwater" refers only to water from perched intermediate zones or the regional aquifer. The methodology used in this report is not applicable to water from alluvial zones.

Table 4.5-1

Tier 2.1 Questions and Criteria for Residual Bentonite

Tier 2.1 Issue: Has residual bentonite been sufficiently removed such that it does not interfere with transport of contaminants into the screen interval[a]?

Note: The assessment criteria in this table are applicable to the three most recent characterization and/or surveillance samples for the screen. If less than three samples are available for this purpose, then the outcome is considered "Preliminary."

Tier	Screening Question	Assessment Criteria[b]	Consequence of "NO" response
2.1-1	Evaluation of bentonite as a potential source term: Have all indicators of bentonite mud been removed from the screen interval?	2.1-1a Are concentrations of the following species all within the upper range of background concentrations in groundwater? For well screens in the regional aquifer: – Is B < 0.051 mg/L? – Is SO_4 < 17 mg/L? – Is Na < 31 mg/L? – Is U < 0.0028 mg/L? For well screens in intermediate perched zones: – Is B < 0.013 mg/L? – Is SO_4 < 11 mg/L? – Is Na < 36 mg/L? – Is U < 0.0008 mg/L?	If NO for any analyte, then flag any detections of the following analytes as possibly elevated above predrilling concentrations due to desorption from residual bentonite: General inorganic analytical suite: Alkalinity, K, Mg, Na, Br, Cl, F, NO_3, Total P, SO_4 Metals analytical suite: As, Ba, B, Cr, Cu, Hg, Mn, Mo, Ni, Sb, Se, U, V Radionuclide analytical suite: U-234, U-235, U-238
2.1-2	Evaluation of bentonite as a potential sink: Are water-quality data reliable and representative for general inorganics, metals, and radionuclides that would adsorb onto residual bentonite if present?	2.1-2a. Is the concentration of dissolved Sr > 0.042 mg/L (the minimum background concentration for groundwater)?	If NO, then flag the following analytes as possibly less than predrilling concentrations due to adsorption onto residual bentonite: Ca, Mo, Sr, V Sr-90
		2.1.2b. Is the concentration of dissolved U above the minimum background concentration for groundwater? For screens in the regional aquifer: – Is U > 0.0002 mg/L? For screens in intermediate perched zones: – Is U > 0.0001 mg/L?	If NO, then flag the following analytes as possibly less than predrilling concentrations due to adsorption onto residual bentonite: U, U-234, 235, 236, 238

Tier 2.1 Issue: Has residual bentonite been sufficiently removed such that it does not interfere with transport of contaminants into the screen interval[a]?

Note: The assessment criteria in this table are applicable to the three most recent characterization and/or surveillance samples for the screen. If less than three samples are available for this purpose, then the outcome is considered "Preliminary."

Tier	Screening Question	Assessment Criteria[b]	Consequence of "NO" response
		2.1.2c. Is the concentration of dissolved Zn above the instrument detection limit? Note: Zn is considered here to be an appropriate indicator species for the adsorption behavior of metal cations and Cs-137, Co-60, Eu isotopes, and Nd-147.	If NO, then flag any nondetects of the following analytes as possibly less than predrilling concentrations due to adsorption onto residual bentonite: Metals: Ag, Be, Cd, Cr, Cs, Co, Cu, Fe, Pb, Hg, Mn, Mo, Ni, Sb, Tl, Zn Radionuclides: Cs-137, Co-60, Eu-152, Eu-154, Eu-155, La-140, Nd-147
		2.1.2d. Some radionuclides adsorb so strongly to clays, including bentonite, that they are rarely detected in groundwater. As a result, we are not aware of any suitable indicator species that are routinely measured and that can be used to evaluate whether or not the nondetects are representative of groundwater concentrations.	Flag any nondetects of the following analytes as possibly less than predrilling concentrations due to adsorption onto residual bentonite: Am-241, Ce-139, Ce-141, Ce-144, Pu-238,239,240, Ra-226, Ra-228
2.1-3	Are water-quality data reliable and representative for HE and HE degradation products?	NO for HE and HE degradation products with an adsorption coefficient (Kd) greater than 1 mL/g. YES for all other relevant HE and HE degradation products because these do not adsorb or partition onto bentonite.	Flag the following HE and HE degradation products: *{to be determined following literature review}*
2.1-4	Are water-quality data reliable and representative for Herbicides, Pesticides, PCBs, Dioxins, and Furans?	NO for herbicides, pesticides, PCBs, and dioxins. These species are assumed to partition or adsorb strongly onto bentonite, with Kd values much greater than 1 mL/g. YES for furans. These species adsorb poorly onto bentonite, with Kd values less than 1 mL/g.	Flag all herbicides, pesticides, PCBs, and dioxins.
2.1-5	Are water-quality data reliable and representative for SVOAs/VOAs (LANL Specific)?	NO for SVOAs/VOAs that have an adsorption coefficient (Kd) greater than 1 mL/g. YES for all other SVOAs/VOAs because these adsorb poorly onto bentonite, with Kd values less than 1 mL/g.	Flag the following SVOAs/VOAs: – Xylene[1,3-] [meta] – Trichlorobenzene[1,2,4-] – Trichlorobenzene[1,2,3-] – Dioxins, PCBs, and pesticides – Polynuclear aromatic hydrocarbons (PAHs)
2.1-6	Are water-quality data reliable and representative for Diesel Range Organics (DROs)?	NO for DRO species. These long-chain aliphatic hydrocarbons are assumed to adsorb or partition strongly onto bentonite, with Kd values greater than 1 mL/g.	Flag all DRO analytes.

[a] In this report, "groundwater" refers only to water from perched intermediate zones or the regional aquifer. The methodology used in this report is not applicable to water from alluvial perched zones.

[b] Responses should be based on analytical results obtained for filtered samples.

Table 4.5-2

Tier 2.2 Questions and Criteria for Residual Organic Drilling Fluids

Tier 2.2 Issue: Have the effects of residual organic drilling fluids been sufficiently removed such that groundwater samples are reliable and representative of the groundwater[a]? Note: The assessment criteria in this table are applicable to the three most recent characterization and/or surveillance samples for the screen. If less than three samples are available for this purpose, then the outcome is considered "Preliminary."			
Tier	**Screening Question**	**Assessment Criteria[b]**	**Consequence of "NO" response**
2.2-1	Have residual organic drilling fluids been removed from the screen interval?	Are all of the following conditions met the last 3 times that these analytes were measured? – Are DOC/TOC < 2 mg/L? – Is TKN < 0.4 mg/L? – Is Ammonium (as N) < 0.07 mg/L? – Are concentrations of acetone and/or isopropyl alcohol below the detection limit?	If NO, flag any detected concentrations of the following analytes as possibly greater than predrilling concentrations due to the presence of residual organic fluids: – DOC, TOC, TKN, Ammonia (as N) , acetone, isopropyl alcohol Note: This flag is not applicable to any non-detects for these analytes.
2.2-2	Is sulfur present in its oxidized (SO_4) form?	Is SO_4 detected?	If NO, then flag the following analytes as possibly less than predrilling concentrations due to chemical transformation, desorption from Fe/Mn (oxy)hydroxides, or mineral precipitation under sulfate-reducing conditions. General inorganic analytical suite: Alkalinity, Ca, NO_3+NO_2-N, SO_4, ClO_4 Metals analytical suite: Ag, As, Ba, B, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, U, V, Zn Radionuclide analytical suite: Am-241, Ce-139, Ce-141, Ce-144, Cs-137, Co-60, Eu-152, Eu-154, Eu-155, La-140, Nd-147, Pu-238,239,240, Ra-226, Ra-228, Sr-90, U-234,235,236,238 All HE and HE degradation products All herbicides, pesticides, PCBs, dioxins, and furans All Diesel Range Organics All SVOAs and VOAs
If YES for question 2.2-2, then continue to the next question. If NO, there is no need to proceed further.			

Tier 2.2 Issue: Have the effects of residual organic drilling fluids been sufficiently removed such that groundwater samples are reliable and representative of the groundwater[a]?

Note: The assessment criteria in this table are applicable to the three most recent characterization and/or surveillance samples for the screen. If less than three samples are available for this purpose, then the outcome is considered "Preliminary."

Tier	Screening Question	Assessment Criteria[b]	Consequence of "NO" response
2.2-3	Have redox conditions been restored to oxidizing conditions with respect to SO_4, Fe and Mn?	**If YES for 2.2-2 (above),** then are all of the following conditions also met? – Is field pH between 6.5 and 8.3? – Is dissolved Fe < 130 µg/L? – Is dissolved Mn < 60 µg/L? – Is field alkalinity (as HCO_3) < 150 mg/L (for well screens in the regional aquifer) or < 65 mg/L (for well screens in intermediate perched zones)?	If NO, then flag the following analytes as possibly not reliable or representative of predrilling concentrations due to chemical transformation, desorption from Fe/Mn (oxy)hydroxides, or mineral precipitation under reducing conditions. General inorganic analytical suite: Alkalinity, Ca, NO_3+NO_2-N Metals analytical suite: Ag, As, Ba, B, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, U, V, Zn Radionuclide analytical suite: Am-241, Ce-139, Ce-141, Ce-144, Cs-137, Co-60, Eu-152, Eu-154, Eu-155, La-140, Nd-147, Pu-238,239,240, Ra-226, Ra-228, Sr-90, U-234,235,236,238 All SVOAs and VOAs
If YES for question 2.2-3, then continue to the next question. If NO, there is no need to proceed further.			
2.2.4	Have redox conditions been restored to oxidizing conditions with respect to NO_3 and dissolved oxygen (DO)?	**If YES for 2.2-2 and 2.2-3 above**, then are both of the following conditions also met? – Is NO_3+NO_2-N detected? – Is field DO > 0.1 mg/L?	If NO, then flag the following analytes as possibly not reliable or representative of predrilling concentrations: General inorganic analytical suite: Alkalinity, Ca, NO_3+NO_2-N All SVOAs and VOAs
If YES for all of the above criteria, then it is concluded that residual organic drilling fluids have been sufficiently removed, and that redox conditions have been restored, such that there are no residual impacts of these products on analytes in this screen interval.			

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OFFICE OF
RESEARCH AND DEVELOPMENT

February 16, 2006

MEMORANDUM

SUBJECT: Los Alamos National Laboratory, Los Alamos, NM (05RC06-001)
Well Screen Analysis Report (LA-UR-05-8615)

FROM: Robert Ford, Ph.D., Environmental Scientist
Subsurface Remediation Branch

Steven D. Acree, Hydrologist
Applied Research & Technical Support Branch

TO: Richard Mayer
U.S. EPA, Region 6

As requested, the referenced document has been reviewed by the above named staff of the National Risk Management Research Laboratory (NRMRL) – Ground Water and Ecosystems Restoration Division. The review and recommendations contained in this memorandum represent a technical evaluation of site-specific conditions based on the current state of the science and are neither policy nor prescriptive guidance. In general, the criteria used to evaluate the representativeness of ground-water samples from well screens installed under the hydrogeologic characterization program still fail to consider impacts that may be present following biodegradation of residual organic drilling additives and the return of oxidizing conditions. This issue and other concerns regarding the evaluation criteria proposed by LANL are discussed in detail below.

1. Tier 2.2 screening analysis for impacts from organic drilling additives focused on assessing removal of organic compounds and the return of oxidizing conditions.

The current focus of the screening process for assessing impact of organic drilling fluids is directed towards determining the persistence of the organic additives and reducing conditions resulting from biodegradation of these compounds. While this is an important objective for the screening analysis, it should not be the sole objective. Specifically, this analysis approach does not address the potential impact of changes to aquifer mineralogy adjacent to the well screen. The changes in aquifer mineralogy resulting from iron- and sulfate-reducing conditions established by biodegradation of

organic drilling additives can significantly alter the sorption characteristics for reactive site contaminants. The changes in aquifer sorption properties and, therefore, reactive contaminant movement to impacted well screens will not be adequately reflected by the LANL criteria. It is recommended that this potential impact be evaluated through expansion of the current approach. One possible tool that could be used is expansion of the list of input parameters employed in the principal component analysis (PCA) (Section 5 of the Well Screen Analysis Report) to capture a more representative range of sorption reactivity for site contaminants, as discussed below.

2. Issues concerning the use of multivariate statistical analysis as a screening tool to assess the return of ground-water chemistry to pre-drilling conditions for well screens impacted by residual drilling fluids.

The application of multivariate statistical analysis provides a very useful tool to screen comparability of water chemistry data obtained from characterization wells and from appropriate background locations. However, it needs to be recognized that the ability of this tool to evaluate potential impacts of residual drilling fluids is predicated on the use of a suite of input parameters that captures all potential impacts. In this regard, the current choice of input parameters appears to be sufficiently comprehensive to capture comparative patterns in components that may be leached from residual drilling fluids as well as the persistence of reducing conditions resulting from biodegradation of organic drilling fluids. However, the input parameters do not sufficiently represent the range of sorption characteristics associated with potential contaminants of concern. Thus, the analysis fails to capture the potential impact of changes in aquifer mineralogy that may alter the transport characteristics of potential contaminants of concern adjacent to impacted well screens.

This limitation may be addressed through expansion of the list of input parameters that are implemented in the principal component analysis (PCA). Based on evaluation of data presented in the Groundwater Background Investigation Report (LANL, 2005), there are several analytes that could be added to this list to provide more comprehensive coverage of contaminant reactivity. These candidate analytes include: europium, thorium, and uranium. These analytes provide more comprehensive coverage of sorption affinity for site contaminants (*e.g.*, Bradbury and Baeyens, 2005). Of these three analytes, insufficient or no data currently exist to include europium and thorium into the PCA. It is recommended that consideration be given to the routine inclusion of these analytes for ground-water trace element analyses. Based on analysis of existing ground-water data, it is unclear why uranium was not included in the list of 'metals/trace elements' considered for statistical analysis. Uranium meets the criterion of having less than 50% nondetects for alluvial, intermediate, and regional ground-water samples collected thus far. In addition, while vanadium was included in the list of 'metals/trace elements' input into the PCA, no information is provided to explain why this trace element was not listed in the principal components identified in Table 5-1.

3. Issues concerning the use of only the most recent analytical data in the tiered analysis.

The well screen assessment only utilizes data from the most recent sampling rounds. This approach is appropriate for determining whether oxidizing conditions have been restored but, as noted above, may not be a good indicator of the representativeness of the sample for reactive constituents that may sorb to the minerals formed when reducing conditions were present. For wells that passed the Tier 2.2 evaluation, it is recommended that this assessment also be applied to data obtained soon after well installation to determine whether previous geochemical conditions may have resulted in continuing sorption of contaminants.

There is an additional concern regarding the use of only the three most recent measurements in these assessments without examination of trends that may be present. As noted on page 23 of the Well Screen Analysis Report, well R-16 Screen 3 passed the test criteria but exhibited a declining sulfate trend that clearly indicated continuing impact. Examination of trends provides another line of evidence regarding the condition of impacted well screens and should be formally included in these evaluations.

4. **Issues regarding the strong reliance on uncertain background conditions.**

The LANL criteria rely heavily on comparisons between data obtained from the potentially impacted well screens and data obtained from the Groundwater Background Investigation Report (LANL, 2005). The data used to characterize background conditions appear to be sparse, derived from sources representing mixtures of water that are significantly different from the samples obtained from the hydrogeologic characterization wells, and are representative of significantly different flow paths within the aquifer. Actual background values at the locations of the individual characterization well screens may be significantly different from the proposed values. Therefore, the strong reliance on these uncertain background conditions for the evaluation of the impacts of residual drilling additives increases the uncertainty in these assessments.

5. Inclusion of analogs that represent the full range of contaminant reactivity.

Where applicable, comparison of chemistry data for suspected well screens impacted by bentonite and/or organic polymers to background concentrations should include constituents that represent the full range of reactivity for potential site contaminants of concern. Examples of inorganic constituents that may be anticipated in background ground-water samples that represent a useful range of sorption reactivity (and mechanism) with respect to potential site contaminants of concern include zinc (Zn), strontium (Sr), molybdenum (Mo), cesium (Cs), barium (Ba), europium (Eu), thorium (Th), and uranium (U). The current criteria are structured to make use of comparisons between background values and data obtained from characterization wells for some but not all of these constituents. It is recommended that the utility of the constituents not currently used in the well assessment criteria be considered.

6. Issues related to sample collection and preservation.

Both approaches (the tiered analysis and the principal component analysis) used to evaluate the recovery of well screens to pre-drilling conditions are predicated on the accuracy of field and/or laboratory measurements. The overall accuracy of these measurements relative to representing the water chemistry adjacent to the sample well screen is dependent on two primary factors:

1) the accuracy of instrumental performance relative to quantitation of a given analyte, and
2) the reliability of sample collection and preservation methods to prevent alteration of the chemical conditions of collected ground-water samples.

Validation of achieving the first factor is insufficient to insure that the second factor has been appropriately addressed. Failure to address both factors can ultimately result in water chemistry data that are not representative of the aquifer conditions adjacent to the well screen.

As stated on pg. 4 of the Well Screen Analysis Report, field data 'are not currently subjected to the same level of qualification, beyond verification of instrument calibrations and checks.' This statement is made relative to the level of qualification applied to assessment of laboratory data reliability. This is an important consideration given the stated assumption (Section 3.0, pg. 8) that 'field-based measurements…provide reliable qualitative indicators for the presence of sulfate-reducing conditions…'. For the purpose of this review, it is assumed that field data presented in Table C-4 were derived from instruments that passed verification of instrument calibrations and checks. However, there appear to be significant inconsistencies in the reported field data that bring into question the adequacy of methods employed for water sample collection and preservation to insure that changes in water chemistry have not occurred prior to laboratory analyses. In particular, reported values for ORP, dissolved oxygen, and total sulfide (or combinations thereof) at some well locations conflict with general patterns observed for oxidized or reduced ground water. Two example screen intervals that illustrate this situation are provided in Table 1.

These two examples may provide 'worst case' situations relative to other screened intervals. However, they are not isolated situations. Data from many of the well screens appear to be inconsistent or suspect. The concern is not simply that a given screen was appropriately identified to have 'failed' or 'passed' a specified tier criterion. Rather, these data comparisons raise serious concerns relative to the accuracy of the field data for use in the screening process (even in a qualified sense) and, more importantly, the degree to which laboratory measurements were made on water samples that were no longer representative of the condition that existed within the aquifer adjacent to the well screen. This latter concern would impact the reliability of both the tiered analysis and the multivariate statistical analysis performed by LANL.

Table 1. Comparison of measured ORP, dissolved oxygen, and total sulfide for ground-water samples collected from two screened intervals. Red shading indicates measurements for a given sampling date that are in conflict, while green shading indicates measurements which appear to be internally consistent. Data were obtained from Table C-4 of the Well Screen Analysis Report.

Well Screen	Date	ORP (mV)	Dissolved Oxygen (mg/L)	Total Sulfide (mg/L)
CdV-R-15-3 5	20-Oct-04	--	13	0.232
	5-Apr-05	-99	7.4	0.290
	20-Apr-05	--	6.1	0.118
	12-Jul-05	-59	4.2	--
R-16 2	18-May-04	-65	9.9	0.473
	13-Oct-04	--	13	0.567
	2-Dec-04	--	13	0.564
	13-Jun-05	-75	5.3	--

7. Use of dissolved zinc as the sole analog for evaluations in LANL criterion 2.1-2c.

It is important to identify analytes that are transported less conservatively than the contaminants of concern. Dissolved zinc is proposed for screening the condition of wells impacted by bentonite relative to the possible loss of cesium-137, cobalt-60, europium isotopes, and neodymium-147 onto residual bentonite solids adjacent to the impacted well screen (LANL criterion 2.1-2c). One significant limitation to this approach is that zinc has not been universally detected in site ground water. LANL (2005) reports non-detectable zinc in about 56% of the samples evaluated. Thus, non-detectable zinc at a given well screen could indicate either sorption onto residual bentonite or the lack of this constituent at measurable concentration in the native ground water at the interval sampled by the well screen. In addition, there are some published ion exchange selectivity series that indicate cobalt partitions more strongly than zinc to clay minerals (including bentonite). Thus, detection of zinc would not preclude loss of cobalt-60 on residual bentonite. LANL criterion 2.1-2 should be re-evaluated in an effort to identify a more reliable replacement or supplemental candidate to zinc. Barium presents a potential alternative/additional candidate (99% detect in area ground water), although it is unclear how prevalent this metal may be as a site contaminant of concern.

8. Inclusion of technetium-99.

It is noted that technetium-99 is not mentioned in Table 4-8. It appears that this potential contaminant should be included. As noted in Table 4-7, samples for technetium-99 obtained from screens impacted by reducing conditions may not be representative of pre-drilling conditions.

9. Criteria validation.

Due to uncertainties in the utility of aqueous chemistry assessments for the determination of whether samples are fully representative of aquifer conditions, it is recommended that laboratory and field studies be designed to validate these or similar criteria.

If you have any questions concerning this review, please do not hesitate to call us (Acree: 580-436-8609; Ford: 580-436-8872) at your convenience. We look forward to future interactions with you concerning this and other sites.

cc: Mike Fitzpatrick (5303W)
Rafael Gonzalez (5204G)
Vince Malott, Region 6
Terry Burton, Region 6

References

LANL, 2005. Groundwater Background Investigation Report, LA-UR-05-2295. Los Alamos National Laboratory, Los Alamos, NM.

Bradbury, M. H. and Baeyens, B. 2005. Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metal and actinides. Geochimica et Cosmochimica Acta, 69: 875-892.