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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
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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

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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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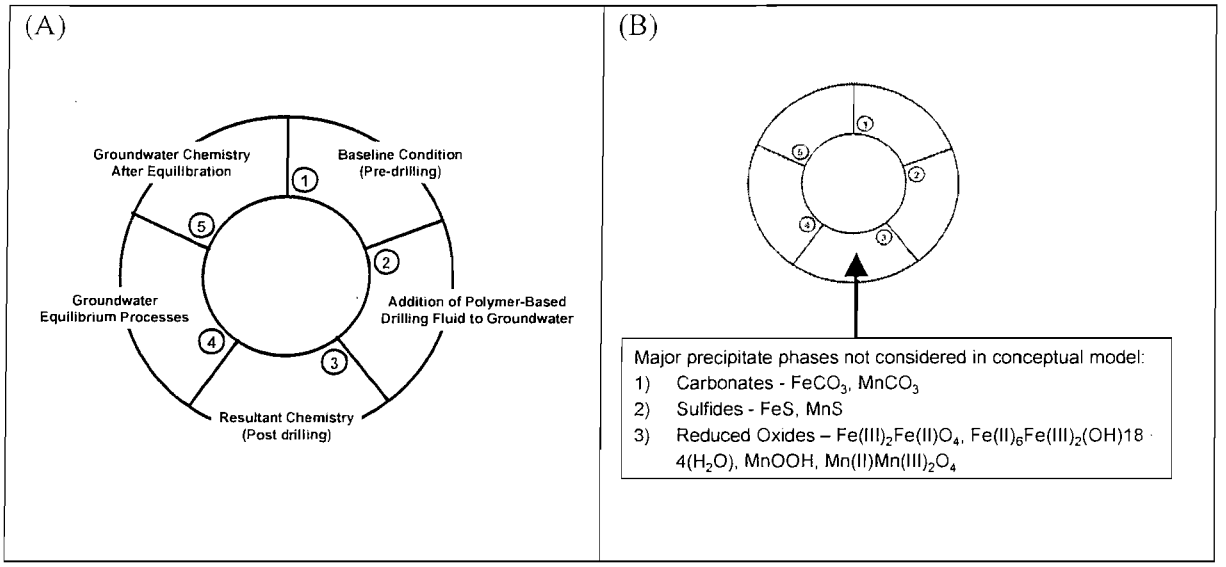

Figure 1. Illustration of certain aspects of solid phase chemistry not considered in the Bitner *et al.* (2004) conceptual model describing the evolution of aqueous and solid phase chemistry at well screens impacted by biodegradation of polymer-based drilling fluids. (A) Simplified depiction of the LANL 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.

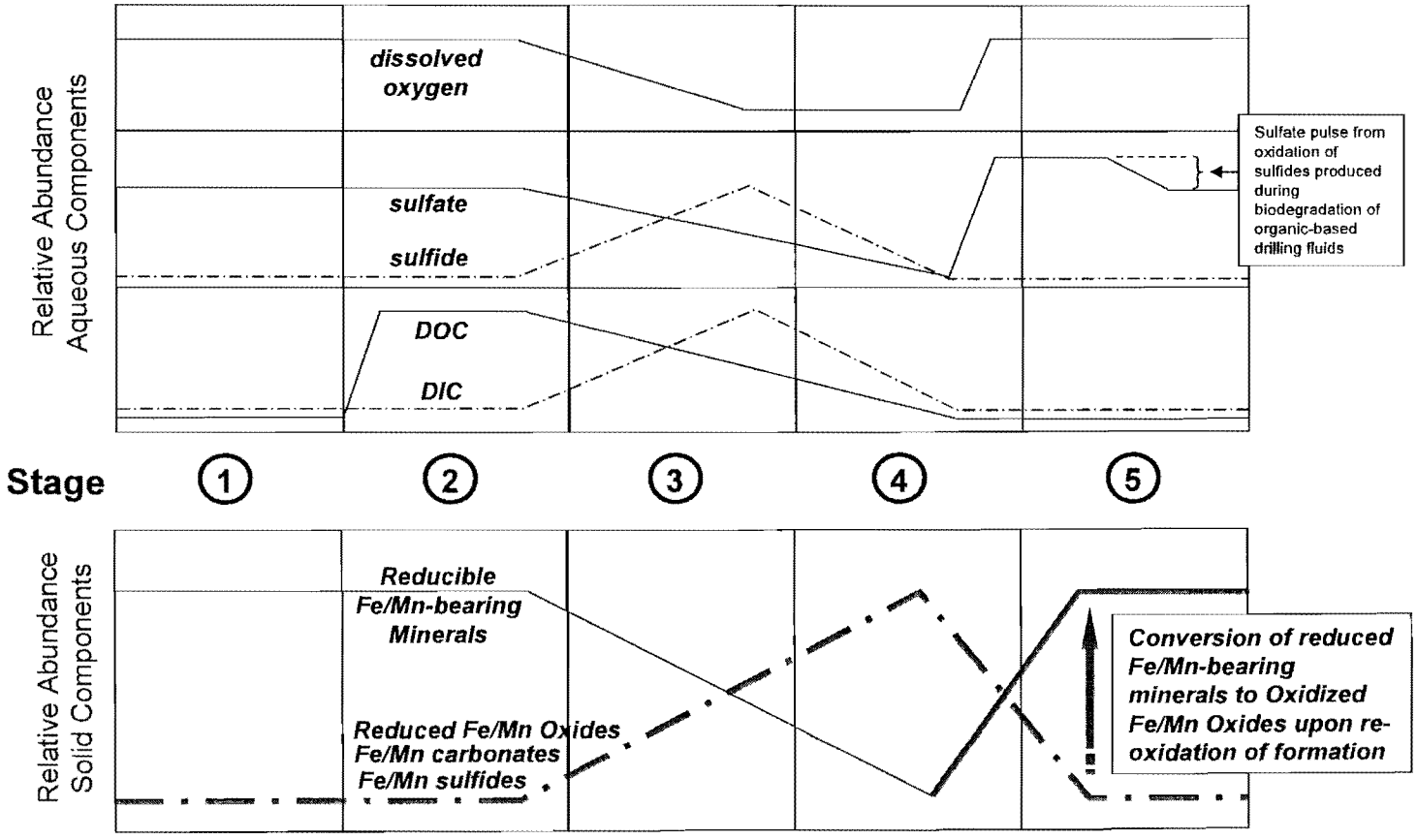

Figure 2. Schematic diagram depicting the evolution of aqueous and solid phase chemical components within the impacted zone of the aquifer adjacent to well screens impacted by the biodegradation of organic-based polymer drilling fluids. Changes in relative abundance of individual chemical components 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.

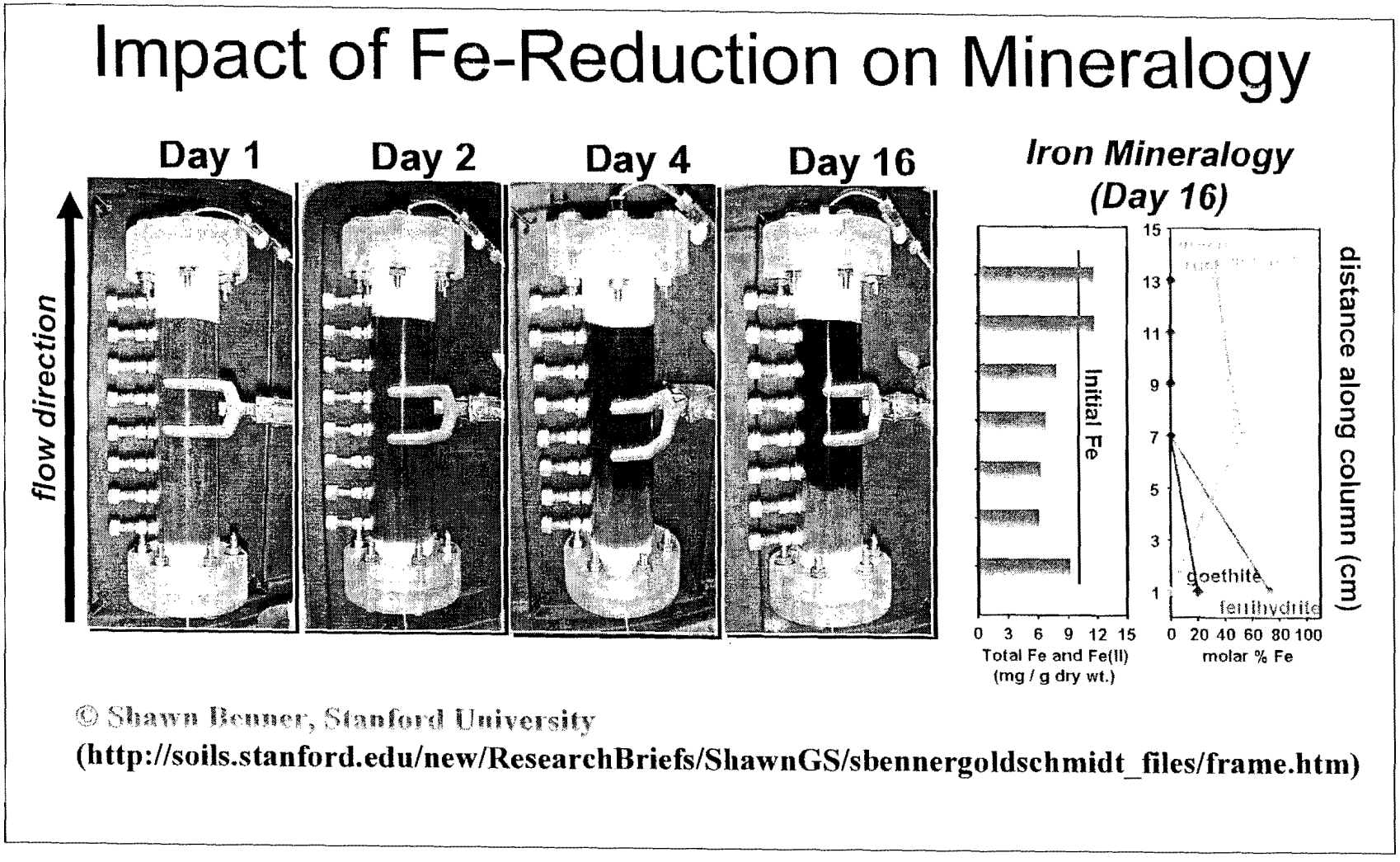

Figure 3. Illustration of transformations in iron oxide mineralogy induced by microbial processes that generate iron-reducing conditions. The starting Fe-bearing mineral was ferrihydrite, which was transformed to a mixture of ferrihydrite, goethite, magnetite, and green rust by day 16. The details of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

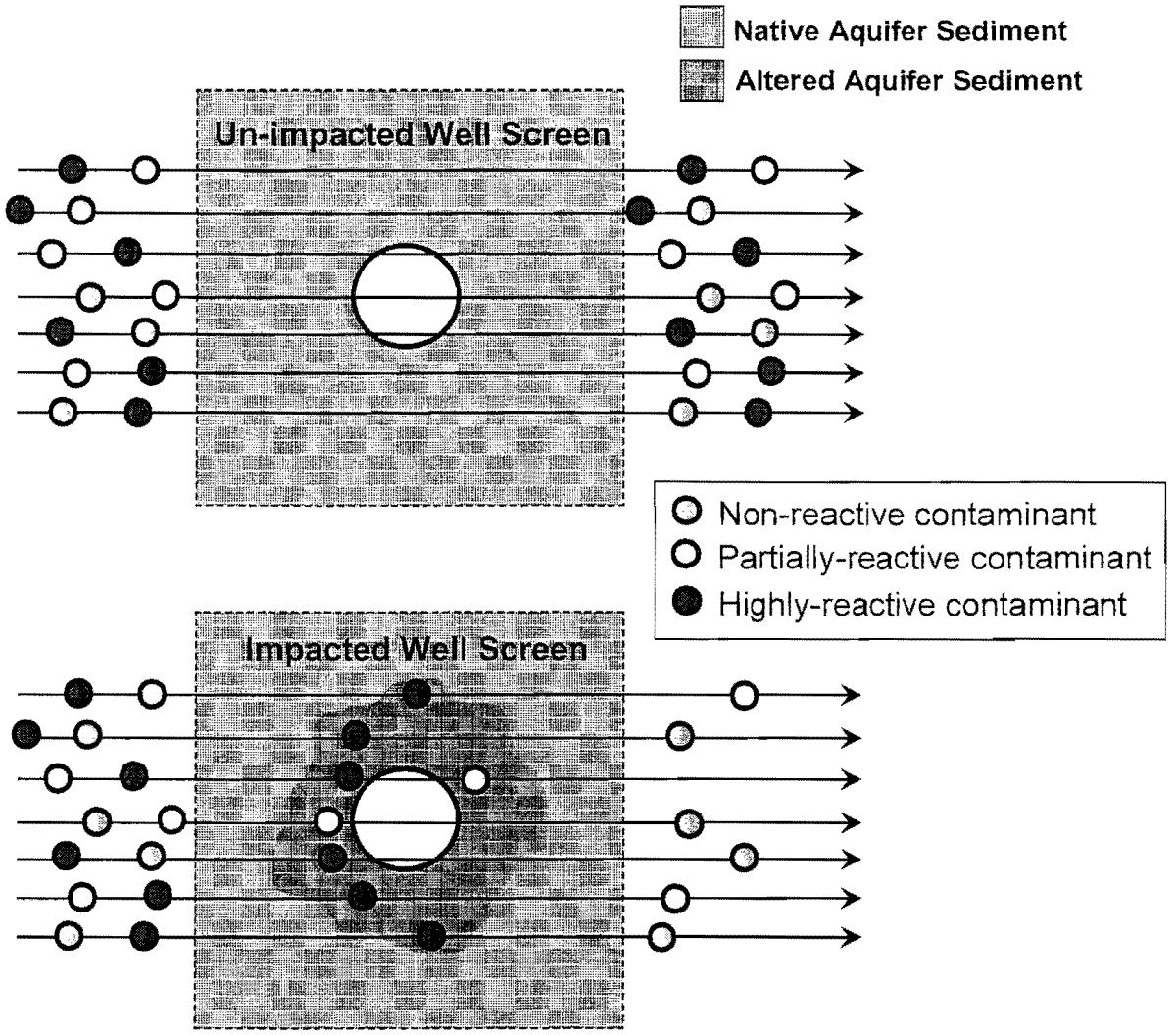

Figure 4. Conceptual schematic illustrating differential transport behavior of contaminants within the impacted zone adjacent to a well screen influenced by biodegradation of organic-based drilling fluids.

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

Well	Elapsed Time Before Development (Days) **	Drilling Fluid *										Impact Category		
		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)	uS/cm	---					---		---		---		
Cond.(L)	uS/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 <u>detections</u> 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 <u>all</u> 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 <u>all</u> 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.			