General

ENTERED

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

OFFICE OF
RESEARCH AND DEVELOPMENT

March 30, 2009

MEMORANDUM

SUBJECT: Los Alamos National Laboratory (LANL), Los Alamos, NM (09RC06-001)
Well Screen Analysis Report (WSAR), Rev. 2 (LA-UR-07-2852)
Groundwater Background Investigation Report (GBIR), Rev. 3 (LA-UR-07-2853)

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

Richard T. Wilkin, Ph.D., Environmental Scientist
Subsurface Remediation Branch

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

As requested, the referenced documents have been reviewed by the above named staff of the National Risk Management Research Laboratory (NRMRL) – Ground Water and Ecosystems Restoration Division. Additional review was provided by Dr. Bruce Pivetz of Shaw Environmental, Inc. Shaw is an on-site contractor providing technical support services to this laboratory. The review focused on the methods and conclusions of the WSAR. The GBIR was reviewed in the context of its use in the WSAR. 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.

As in the review of previous versions of these documents (Ford and Acree to Mayer, 2/16/06), this review is focused on the evaluation of the effects of drilling additives on the collection of representative samples from wells installed under the hydrogeologic characterization program. It is noted that factors other than the effects of drilling additives (*e.g.*, screen length, position within the hydrostratigraphic section, location with respect to potential contaminant source areas, groundwater sampling methods) may have a greater impact on whether groundwater samples are suitable for the purpose of early detection of contaminant releases or migration. Such location-specific issues are beyond the scope of this review.

Although the current versions of the documents attempt to address several of the issues raised during the previous reviews, there is still a relatively high degree of uncertainty in the results reported in the WSAR. For example, additional species indicative of a range of contaminant reactivity have been incorporated into the evaluations. However, several potential indicators are

34091

not routinely measured or available. The uncertainty related to this issue is illustrated by the following example. At locations where bentonite additives were used, the WSAR (Section 4.11) concludes that indicators suitable for directly evaluating the reliability of non-detects of highly adsorbing radionuclides are not available. Consequently, this section of the document concludes that it was not possible to evaluate the affected well screen intervals for detections of strongly adsorbing radionuclides. The document appears to modify this conclusion in later sections and indicates that these non-detect results would be accepted as representative of actual conditions if the well passed all other applicable criteria. Regardless of the conclusion stated in Section 4.11, the WSAR ultimately determines that some well screens drilled using bentonite, such as well R-32, screen 1 (Table 4-5) produce reliable samples for highly sorbing constituents such as plutonium (Table 6-4). Such assessments appear to be contradictory and are, at best, confusing. Given the lack of appropriate indicators, a more conservative and defensible approach would appear to be the one advocated in Section 4.11 rather than the approach ultimately used. Many similar issues contribute to the uncertainty inherent in the screening results.

In general, the criteria used to evaluate wells in the WSAR are complex and may ultimately prove to be unreliable. The most significant concerns noted in review of the current versions of the WSAR and GBIR are related to three areas:

- The results of the WSAR and related assessments have not been fully validated using site-specific data from laboratory and field studies.

- The criteria rely heavily on "background" data obtained from long-screened production wells and springs that do not necessarily represent water quality upgradient of the hydrogeologic characterization monitoring wells.

- The reliability of criteria used to evaluate the representativeness of groundwater samples from well screens following transformations of residual organic drilling additives and the return of groundwater samples to oxidized conditions is uncertain due to a lack of direct assessments of the site-specific mineralogical transformations and the reliance on groundwater sampling data.

Each of these issues increases the uncertainty in the conclusions of the WSAR and is discussed in detail below.

Validation of the Screening Results

As noted by the National Research Council (2007: National Research Council, Plans and Practices for Groundwater Protection at the Los Alamos National Laboratory, Final Report), evidence regarding the conditions surrounding the monitoring well screens is indirect. Additional laboratory and field investigations to better determine the nature and evolution of the interactions between the drilling, well construction, and aquifer materials; quantify sorption parameters; and to demonstrate the accuracy of the screening results presented in the WSAR are

recommended to validate the results. Without such validation, assessments of the impacts on the representativeness of groundwater samples should be considered to be of uncertain quality.

Uncertain Background Conditions

The WSAR criteria rely heavily on comparisons between data obtained from the impacted well screens and data reported in the GBIR. The data used to characterize "background" conditions is sparse, derived mainly 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 and residence times within the aquifer. Actual background values at the locations of the individual characterization well screens may be significantly different from the proposed values.

As noted many times in the GBIR, water chemistry is determined by the lithologies of aquifer materials through which the water migrates and the residence time. Data from springs near the Rio Grande and the long-screened production wells does not necessarily represent the flowpaths monitored by the individual short-screened characterization wells. The GBIR recognizes this limitation. However, it indicates that the appropriate data (*i.e*, data from similarly screened wells immediately upgradient of the regulated units) may never be available. This approach introduces unavoidable uncertainty in evaluations of screens with residual effects because it does not allow for spatially distinctive geochemical zones or variability in groundwater chemistry in different aquifer lithologies.

It is quite possible that constituent concentrations observed in unimpacted monitoring wells may be significantly different from the data provided in the GBIR. For example, it appears the well R-35B was recently installed near the top of the regional aquifer without the use of harmful drilling additives within the screened interval. Concentrations of zinc measured in filtered groundwater samples have varied from approximately 40 ug/l to 60 ug/l. This range is above the maximum value of approximately 32 ug/l reported in Table 4.2-3 of the GBIR and is at or above the maximum value reported in Table 4-3a of the WSAR. This example illustrates the uncertainty inherent in using "background" data obtained from sources that are not constructed to monitor the same flowpaths as the monitoring wells in question.

It is also noted that the current evaluation methods may not fully identify conditions representative of the unimpacted regional aquifer. Footnote K in Table E2 indicates that although screens 6, 7, and 8 of well R-25 had a perfect score in the evaluation, the screens may still be impacted by water from perched zones above the regional water table.

Continuing Impacts to Aquifer Materials after Return to Oxidizing Conditions

The geochemical analysis appears to rely heavily on a determination of the overall redox status of groundwater as inferred from water quality parameters, such as dissolved oxygen, oxidized forms of nitrogen (nitrate) and sulfur (sulfate), low dissolved concentrations of iron and manganese, and detection of contaminants in oxidized forms. Part of the analysis includes an

evaluation of potential solid-phase processes (modification of surface-active minerals, changes to carbonate mineral stability) based upon the groundwater chemistry. Modification of in situ redox conditions is clearly an important aspect of the problem being dealt with here. As pointed out, the organic drilling fluids provide a source of carbon for native microbial populations in the aquifer. These organisms can have long-term impacts on water chemistry and aquifer mineralogy in the vicinity of the well screen. In general, anaerobic conditions resulting from the respiration of microbes shift the types of minerals and contaminant-reactivity of mineral surfaces that may be in equilibrium or near equilibrium with the specific water chemistry.

Using criteria established in this report, an undesirable component of uncertainty will persist regarding screen impacts because it is not possible to understand all possible mineral-contaminant interactions solely by evaluating water chemistry. As an example, consider a well that shows redox-status evolution from iron-reducing conditions, linked to residual drilling fluids, to oxidizing conditions comparable to the targeted background conditions. In this case, the geochemical criteria would suggest that water chemistry has achieved or is approaching pre-drilling conditions and, furthermore, that contaminant species can be monitored accordingly for their presence or absence. During the evolution of this system, when native microbes supported mobilization of ferrous iron, it is possible that reactive Fe(II)-bearing minerals formed in the available pore spaces adjacent to the well screen. As portrayed in the conceptual model presented in the WSAR (*e.g.*, Figure 4-9), possible phases include ferrous carbonate, ferrous sulfide (in sulfate-reducing compartments or micro-environments), but also could include green rust minerals, ferrous hydroxycarbonate, and magnetite. These Fe(II)-bearing phases are all known to interact with and possibly sequester potential contaminants of concern (*i.e.*, nickel, cadmium, cobalt, arsenic, zinc, americium, technetium, chromium, uranium). In this scenario, as organic carbon is consumed and levels of dissolved oxygen begin to increase, these previously formed Fe(II)-bearing minerals would be anticipated to undergo oxidative transformation to hydrous ferric oxide or iron oxyhydroxides. It might be further anticipated that these newly formed Fe(III)-bearing phases would be very fine-grained and highly sorbent, again with the ability to sequester contaminant species of concern. So along with the shift to oxidizing conditions, as indicated in water chemistry parameters, comes an anticipated shift in reactive iron mineralogy. Based on the criteria proposed, it is not possible to clearly assess: i) how long reduced, Fe(II)-bearing minerals might persist, and ii) what type of mineral phase or assemblage would result as a consequence of the return to more oxidizing conditions.

The critical point is that the nature of the reactive iron mineralogy cannot be assessed by examining water chemistry alone. In order to have a sense of the reactive nature of the aquifer solids, other testing would be required. At some point, it would be expected that any reactive minerals present in the system may become saturated or modified to the extent that they would no longer influence water chemistry in regions adjacent to the well screen. However, there are no compelling lines of evidence provided in the report that would indicate when this desired point is ultimately reached.

Recommendations to Reduce Uncertainty

Due to uncertainties in the mineralogical alterations induced by the drilling additives, uncertainty in the utility of aqueous chemistry assessments for the determination of whether samples are fully representative of aquifer conditions, and the lack of appropriate data for the assessment of water quality immediately upgradient of the impacted characterization wells, it is recommended that additional laboratory/field studies be designed to reduce uncertainty and validate the results of the WSAR. In this regard, the following studies may significantly improve the understanding of the site-specific impacts of the drilling additives and the potential time frames over which the impacts may be expected to continue.

1. **Upgradient Well Installations.** Install wells immediately upgradient of the regulated units of most concern, screening intervals equivalent to those of monitoring wells located downgradient of the regulated units. If such wells were installed without the use of harmful drilling additives in the screened zone, the data should be useful in better defining pre-drilling conditions within the particular hydrostratigraphic units of interest. The data would also provide insight into the representativeness of the "background" ranges used in the WSAR.

2. **Laboratory Investigations.** Laboratory studies could be performed to more fully understand impacts of the drilling additives on the evolution of redox conditions and secondary mineral formation. Subsequently, impacted materials from the studies could be subjected to redox conditions representative of the unimpacted aquifer allowing investigation of the evolution of mineral phases. Aquifer materials obtained during these studies could be used to quantify interactions with contaminants of concern. The results could be used as a baseline to understand the geochemical behavior of subsurface materials and validate conceptual models for the transformations that are occurring as well as aid in the validation of the criteria proposed in the WSAR. It is noted that similar studies were recommended by the National Research Council (2007: National Research Council, Plans and Practices for Groundwater Protection at the Los Alamos National Laboratory, Final Report). Laboratory studies could also be performed to quantify sorption of the inorganic constituents of concern onto the materials used during well construction at LANL.

3. **Field Studies**. Ultimately, lines of evidence from field studies will be needed to reduce uncertainty in the validation of criteria used in the WSAR. Useful lines of evidence would include: characterization of aquifer solids obtained from impacted wells, evaluation of the effects of well purging prior to sampling of impacted wells, and push-pull tests to directly examine sorption properties at impacted wells. A primary line of evidence would also be the installation of new well(s) drilled without the use of additives in the screened zone near impacted well(s). A comparison of water quality data from the two wells would provide direct evidence of the degree of impact and the effects on water quality. Such installations could be performed near regulatory units of greatest concern to maximize the benefits of the data.

If you have any questions concerning this review, please do not hesitate to call us (Acree: 580-436-8609; Wilkin: 580-436-8874) at your convenience. We look forward to future interactions with you concerning this and other sites.

cc: Mike Fitzpatrick (5303W)
Vince Malott, Region 6
Terry Burton, Region 6