

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

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 groundwater 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.

			Dissolved	Total Sulfide
Well Screen	Date	ORP (mV)	Oxygen (mg/L)	(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-162	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.