Reply to Comments of Mr. Donivan Porterfield on "Groundwater Contamination in the Regional Aquifer Beneath the Los Alamos National Laboratory," Version June 26, 2004 by Robert H. Gilkeson

Reply by Robert H. Gilkeson (Version Dec. 15, 2004)

The Northern New Mexico Citizens Advisory Board (NNMCAB) requested Mr. Porterfield to review the Gilkeson report. Mr. Portefield is a member of the EMSR Committee of NNMCAB. Mr. Porterfield is employed at the Los Alamos National Laboratory (LANL) as a radiochemist. In this document I reply to the five specific comments by Mr. Porterfield.

1. **Comment by Mr. Porterfield**:
   "I think his citations (citations in the Gilkeson report) from EPA guidance and EAG reports does raise the presence of drilling fluids as an issue worthy of a formal response as to its potential impact on completed wells and its continued use." (The EAG reports referred to by Mr. Porterfield are the written reports of the group of consultants known as The External Advisory Group who advised LANL on activities in the Hydrogeologic Workplan).

Reply by Mr. Gilkeson:
I agree with Mr. Porterfield's recommendation for a formal response concerning the effects of drilling fluids (including the biodegradable fluids and -foams, and the bentonite clay muds) on the reliability of analytical data from the impacted LANL monitoring wells. In Gilkeson (2004) I recommend that an external group of experts review <u>all</u> of the activities of the LANL Hydrogeologic Workplan.

2. **Comment by Mr. Porterfield**:
   "Also, Mr. Timm's comments also point out a lack of consistency in how well reports address the issue of equilibrium, i.e. how do we know when its in equilibrium." (Mr. Timm is a member of the NNMCAB who has written a report titled "Review Comments on Geochemistry Reports for Characterization Wells R-7, R-9, R-9i, R-15, and R-22".)

Reply by Mr. Gilkeson:
Mr. Porterfield and Mr. Timm have identified a very serious issue concerning the ability to determine that the groundwater samples collected from a monitoring well impacted by the use of drilling fluids have returned to equilibrium. I agree with their concern. However, a more important issue is the determination whether the groundwater samples collected from the impacted wells are <u>representative</u> of the contaminant chemistry of groundwater in the aquifer outside of the zone of aquifer strata that have been altered by the use of biodegradable polymer-based drilling fluids, biodegradable foams, and bentonite clay drilling muds.

A study of trends in pH, specific conductance, oxidation-reduction potential (Eh), and major ions can be used to indicate that the groundwater may have returned to an oxidized

stable condition, that is to equilibrium. Nevertheless, this judgment would not prove that groundwater samples collected from the impacted well are representative of the contaminant chemistry in the regional aquifer or in a perched zone of saturation. My analysis is that many of the impacted LANL monitoring wells may be irreparably damaged for contaminant chemistry,

The irreparable damage is because the invasion of the aquifer strata by the biodegradable drilling fluid and foams, and the bentonite clay drilling muds has introduced materials into the aquifer strata at many of the monitoring wells that have strong, selective sorption properties for many radionuclide contaminants (Langmuir, 1997, Stumm and Morgan, 1996, LANL, 2000).

An example of the irreparable damage to the contaminant chemistry in water samples that are collected from the impacted LANL monitoring wells is screen # 1 in LANL monitoring well R-7. The aquifer strata that surround screen #1 were invaded with biodegradable, polymer based drilling fluids and biodegradable foam. Nevertheless, the staff of LANL and NMED conclude that the oxidizing chemistry of groundwater samples collected from screen # 1 is proof that the samples are representative of the contaminant chemistry in the aquifer. This conclusion by NMED and LANL is wrong as shown by the anomalously low dissolved uranium concentrations that are present in the quarterly samples collected from screen #1. The chemical processes that are removing uranium from the groundwater will also remove other contaminants of concern.

3. **Comment by Mr. Porterfield**:
   "If the cited drilling fluids were indeed capable of removing strontium, including strontium-90, then I would expect the kinetics of that reaction would be pretty quick, i. e. there would be no consistent decline but it just wouldn't be there, unless there is some very rate limiting aspect to this."

Reply by Mr. Gilkeson:
The biodegradable polymer-based drilling fluids and the biodegradable foams that were used in the borehole for monitoring well R-7 are the cause of a large change in the aqueous geochemistry of the aquifer strata in the impacted zone surrounding the monitoring well. There are rate limiting aspects for the interaction of the geochemical processes.

The EZ-MUD* drilling fluid that has invaded the aquifer strata has a negative charge density of 30% which may enhance the polymers ability to adsorb the cations Sr^{2+}, PuO_2^{1+}, UO_2^{2+}, and $AmCO_3^{1+}$ (LANL, Oct., 2000). It is important to note that the drilling of the borehole for LANL monitoring well R-7 with the use of EZ-MUD* began after LANL released the information on the adsorption properties of the drilling fluid for contaminants of concern. It was inappropriate for LANL to use drilling fluids that have sorption properties for many contaminants of concern in groundwater.

In addition, the drilling fluids and foam contain organic carbon that resulted in a "bloom" of bacteria. The enhanced respiration of the bacteria greatly increased the level of carbonic acid in groundwater with a corresponding dissolution of the alkaline earth metals from the aquifer strata. The alkaline earth metals include strontium, calcium, magnesium, and barium.

The enhanced bacterial respiration also created an anaerobic environment that resulted in high levels of dissolved iron and manganese in groundwater while causing the precipitation of dissolved uranium and some other radionuclide contaminants (if present in the groundwater). The high concentrations of dissolved iron listed in the LANL well R-7 Geochemistry Report for the four quarterly samples of 17.0, 14.0, 12.4, and 8.75 mg/L, respectively, are direct evidence that the precipitation of hydrous ferric oxides (HFO) and iron oxyhydroxides is occurring (Driscoll, 1986, Langmuir, 1997).

From Driscoll, (1986):

> "If the dissolved iron content of the groundwater exceeds 0.5 mg/L, precipitation of iron is likely, although some precipitation may begin at concentrations as low as 0.25 mg/L."

From Langmuir (1997):

> "Crystallization of hydrous ferric oxide (HFO) takes years in water low in iron, but may occur in a few hours or days in the presence of several mg/L of dissolved iron."

> "They (the iron precipitates) can cause a loss of up to 90% in the productivity of a well."

The precipitation of iron as HFO and iron oxyhydroxides is important as these "fresh coatings" as blanket deposits on the aquifer strata and even on the filter pack sediments have strong sorption properties for many radionuclide contaminants including the actinides and uranium (Langmuir, 1997). The precipitates greatly lower the permeability of the aquifer strata with the result that groundwater samples are collected from the stagnant groundwater that is in the immediate vicinity of the well screen.

An important feature in the first three quarters of analyses in the LANL Well R-7 Geochemistry Report is the little change in dissolved concentrations of magnesium compared to the large decline in dissolved calcium. The decline in bacterial respiration that is occurring over the four quarters resulted in lower levels of dissolved carbon dioxide. The decline in dissolved carbon dioxide has little control on the concentration of dissolved magnesium but a large control on the concentration of dissolved calcium (Langmuir, 1997, Driscoll, 1986). This is important information as it indicates that the decline in concentrations of calcium, strontium, and strontium-90 is primarily because of precipitation, coprecipitation, and sorption instead of dilution.

Furthermore, the declining trend for dissolved uranium concentrations in the quarterly groundwater samples collected from monitoring well R-7 is important evidence that chemical processes are removing constituents from groundwater. Uranium is a natural constituent in groundwater. However, uranium is also a contaminant of concern in groundwater because of its extensive use in LANL activities. For the LANL monitoring wells, there is a need for accurate knowledge of the level of dissolved uranium in perched zones of saturation and in the regional aquifer.

The LANL well R-7 reports show that a uranium concentration of 0.0021 mg/L was measured in a groundwater sample collected at the top of the regional aquifer from the borehole for well R-7 and significantly lower dissolved uranium concentrations of 0.000084 and 0.000051 mg/L were measured in the first two quarterly samples collected from the top of the regional aquifer in well R-7. Uranium was "not detected" in the groundwater samples collected in the third and fourth quarter from well R-7. LANL does not have accurate knowledge of the levels of dissolved uranium in the regional aquifer beneath Los Alamos Canyon at the location of LANL monitoring well R-7.

My review of the LANL Geochemistry Reports has determined that the methods that are used to collect groundwater samples from the multiple-screened wells are inappropriate for measurement of unstable properties of the groundwater and for collection of samples for the analytical suite. Presently, LANL collects groundwater samples from the multiple-screen monitoring wells by deploying an evacuated container (the Westbay* MOSDAX tool) to collect water samples from the discrete sampling ports in the Westbay* sampling systems. Several trips with the container may be necessary to collect the volume of groundwater required for the analytical suite. For the LANL multiple-screen monitoring wells, no volume of groundwater is purged from the screened intervals prior to the measurement of groundwater parameters and the collection of groundwater samples. In addition, the field-measured parameters including temperature, specific conductance, dissolved oxygen, and turbidity were measured when the groundwater was in contact with the atmosphere (LANL Well R-7 Geochemistry Report, 2002). The inappropriate methods used at LANL for measurement of important field parameters and collection of analytical samples compromise data quality and prevent accurate knowledge of aquifer chemistry.

The EAG (2001) recognized the need to use a low-flow pumping system for the collection of groundwater samples from the multiple-screen monitoring wells as follows:

> "The presence of residual drilling additives is disappointing, but not surprising; it is both difficult (perhaps impossible) and expensive to develop wells at this depth sufficiently to completely remove such materials. The Westbay* tool (MOSDAX) currently being used for sampling provides no capability for avoiding sample contamination with the residual drilling additives; in fact, it probably maximizes it. This is because the tool almost passively collects the groundwater from the immediately adjacent zone of the sandpack/borehole

wall/formation. In the absence of drilling additive contamination, this would be a desirable outcome, but not when it is present. Since the additives are impacting the samples and their subsequent evaluation, the EAG has one recommendation for altering the manner in which samples are being collected until the additives are no longer an issue.

RECOMMENDATION:
Temporarily discontinue use of the measurement port and MOSDAX probe in the Westbay* wells. Instead, collect samples with the pump and the Westbay* pumping port via low-flow sampling techniques with equilibration of indicator parameters using a flow-through cell.

This sampling approach would increase the likelihood that groundwater from outside the borehole zone contaminated with drilling additives could be acquired. Observation of the stabilization of purging indicator parameters, such as dissolved oxygen, Eh, and conductivity, during the low-flow purging process can be used to detect this continuity with the aquifer water. Although the acquired water would still have to travel through the additive contaminated zones (the zones of altered chemistry that are contaminated with residual drilling fluids), the amount of contamination imparted to the samples during this brief contact should be minimal relative to the MOSDAX samples that have set in this zone for some time."

LANL has not followed the advice of the EAG for using a low-flow pumping system for collection of groundwater samples. Concerning the present practice at LANL of not purging a volume of groundwater for monitoring of field parameters before the collection of groundwater samples for contaminant analyses, an EPA Superfund Forum Guidance document by Puls and Barcelona (1989) contains the following guidance:

- Use a positive displacement pump to pump groundwater from the screened interval.
- Groundwater samples should be collected in such manner to eliminate O_2 and CO_2 exchange with the atmosphere.
- Use a flow-through type cell to monitor the pumped groundwater. Monitoring for dissolved oxygen, temperature, conductivity and pH (also monitoring Eh and turbidity) aids in the interpretation that representative groundwater samples are collected for contaminant analyses.
- Before collection of groundwater samples for the analytical suite, continue low-flow pumping and monitoring of groundwater parameters for a sufficient period of time to ascertain that the groundwater parameters have stabilized. The time of pumping necessary to collect representative water from the aquifer strata is around two times the time required to get plateau values for the above parameters.

- For analysis of metals (and radionuclides), routinely collect both filtered and unfiltered samples. Filtration should be performed in the field with no air contact. In-line pressure filtration is best with as small a filter pore size as practically possible (e.g., 0.05, 0.10 micron). The prevention of air contact during the filtration process is very important for anoxic groundwater (e.g., well R-7, R-22, and other impacted LANL monitoring wells). Air contact of anoxic ground-water during filtration will result in iron oxidation and colloid formation and a removal during filtration of previously dissolved species in the anoxic groundwater.

There is an obvious need to use a low-flow pumping system for the collection of groundwater samples from the LANL multiple-screen monitoring wells. The monitoring of groundwater samples in a flow-through cell during an appropriate period of pumping will help determine the future value of the screened intervals that are impacted by the biodegradable drilling fluids and foams. Unfortunately, the collection of groundwater samples with a low-flow pumping system will not provide a remedy for the need to replace the LANL monitoring wells that are irreparably damaged.

4. Comment by Mr. Porterfield

"I could hypothesize that the consistent decline he (Mr. Gilkeson) observes is the result of mixing of water in that particular well zone with water from a higher zone, which was more contaminated."

Reply by Mr. Gilkeson:

The cross-contamination of groundwater in the regional aquifer at LANL monitoring well R-7 with overlying groundwater contaminated with strontium-90 is possible because of the drilling of an open borehole that allowed downward flow of groundwater from perched zones of saturation to mix with groundwater in the regional aquifer. The downward flow of groundwater from perched zones was also allowed to occur for approximately a one-month period of time in the multiple-screen monitoring well that was installed.

However, the analytical data for groundwater samples collected from the screened perched zone that yields water samples show that strontium-90 was "not detected" with recorded values for the four quarterly samples ranging from 0.5 to -0.0499 pCi/L. Nevertheless, it is possible that the low values of strontium-90 in groundwater samples collected from the perched zone are because of the effect of the drilling fluids. The drilling fluids have introduced chemical processes that are responsible for anomalously low values for dissolved uranium in the quarterly water samples collected from screen # 1 that is installed in the perched zone.

The fact that the presence of strontium-90 in groundwater samples collected from the regional aquifer at monitoring well R-7 may be because of cross-contamination does not change the responsibility of LANL and DOE to determine the source of the strontium-90 in the regional aquifer. The strontium-90 contamination in the regional aquifer may be

from the downward travel of strontium-90 through the unsaturated zone from the known contamination sources in groundwater in the alluvial sediments that are present at a shallow depth along the valley landscape of Los Alamos Canyon.

It is very important to gain knowledge of where strontium-90 recharge to the regional aquifer is occurring because of the detection of strontium-90 in groundwater samples collected from the public supply well Otowi-1. For groundwater samples collected in June and August of 2000, the measured activities with 3-sigma validation were 0.19 pCi/L and 0.23 pCi/L, respectively (NMED, 2002). This supply well is located downgradient of LANL monitoring well R-7. The NMED has expressed the following concern for strontium-90 contamination in the regional aquifer:

> "The extent of strontium-90 contamination at the LANL facility has not been fully investigated. Moreover, the levels of strontium-90 detected in the drinking water supply wells are likely to have been substantially diluted. The rate of groundwater withdrawal in municipal water supply wells often exceeds one thousand gallons per minute, and the screened interval is typically hundreds of vertical feet across multiple producing zones, resulting in a high degree of dilution."

"The Environment Department believes that this evidence is sufficient to support its finding that there may be an imminent and substantial endangerment to health and the environment from strontium-90 contamination at the LANL facility." (NMED, 2002).

5. **Comment by Mr. Porterfield**:
   "I think an important aspect would be the presence of tritium. -- So if it (tritium) is not present that suggests that other possible radionuclides are also not present and not just being masked by drilling fluid impact as Gilkerson (the correct spelling is Gilkeson) suggests."

Reply by Mr. Gilkeson:
The presence of low activities of tritium in groundwater does not automatically exclude the possibility for the presence of other contaminants. It is important to note that the tritium levels in the regional aquifer are not accurately known because of the improper methods that are used for the collection of the quarterly samples. The improper sampling methods are discussed in my reply to comment #3. In addition to the "not detected" recorded values for strontium-90, the LANL Well R-7 Geochemistry Report shows that several semi-volatile contaminants and volatile organic contaminants (solvents) were detected at validated levels in groundwater samples from the regional aquifer. The improper construction of the monitoring well prevents accurate knowledge of the types and levels of SVOC's and VOC's that are in groundwater. The unnatural chemistry in the immediate vicinity of LANL monitoring well R-7 will degrade and transform the VOC and SVOC contaminants in the groundwater samples that are collected from the stagnant body of water that surrounds the well screen (Pankow and Cherry, 1996). The

presence of VOC and SVOC contaminants in the regional aquifer beneath Los Alamos Canyon is a serious issue that requires careful study.

My point is this: The improper installation of LANL monitoring well R-7 prevents knowledge of the presence of many contaminants in the regional aquifer and in the perched aquifer beneath Los Alamos Canyon at the present time and for an unknown period of time into the future. The correct action by LANL and DOE is to replace the damaged multiple-screen well with monitoring wells that are properly constructed for monitoring of contamination in the perched zone, at the top of the regional aquifer, and in the highly permeable river gravel aquifer strata that are present at the total depth of the borehole for monitoring well R-7. It is important to understand that many of the LANL monitoring wells are improperly constructed and require replacement.

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