

**Response to the “Review of Periodic Monitoring Report for Pajarito Watershed;
December 2–December 18, 2008, Los Alamos National Laboratory,
EPA ID No: NM0890010515, HWB-LANL-09-018”
Dated July 29, 2009**

INTRODUCTION

To facilitate review of this response, the New Mexico Environment Department’s (NMED’s) comments are included verbatim. Los Alamos National Laboratory’s (LANL’s or the Laboratory’s) responses follow each NMED comment

SPECIFIC COMMENTS

NMED Comment

1. *Section 4.2 (Analytical Data) of the PMR indicates that United States Environmental Protection Agency (EPA) Region 6 tap water screening levels were used for constituents having no other regulatory standard and for which toxicological information is published. EPA now uses Regional Screening Levels (RSLs) which have replaced the EPA Region 3 RBC Table, the Region 6 HHMSSL Table and the Region 9 PRG Table. The most recent version of the RSL table is available at http://www.epa.gov/reg3hwind/risk/human/rbconcentration_table/index.htm. Text, affected tables and appendices in future Pajarito and other watershed PMRs must reference the most recent RSL tap water values where appropriate.*

LANL Response

1. Beginning with the monthly groundwater data review report for July 2009 data, the Laboratory is using the regional screening levels (RSLs) for screening. The group of periodic monitoring reports (PMRs) to be submitted in November 2009 will use the RSLs, as will all future PMRs.

NMED Comment

2. *The listing for well 03-B-9 (sic) in PMR Table 3.4-1 (Observations and Deviations) indicates that only water level measurements were obtained at the well due to well casing damage. The table's comment column for the well indicates the location will be checked again during the next sampling period. Table 5.4-1 (page 57) of the 2008 Interim Facility-Wide Groundwater Monitoring Plan (2008 IFGMP) notes that the well casing is damaged and that only water level measurements are collected at that location. Unless other types of deviations occur at this location, it would be appropriate to remove the listing as a deviation for this well in future Pajarito Watershed PMRs.*

LANL Response

2. The comment column in Table 3.4-1 was in error in indicating that the location will be checked again during the next sampling period because only water-level measurements are collected from that location. In September 2009, well 03-B-09 was plugged and abandoned and will be removed completely from the annual Interim Facility-Wide Groundwater Monitoring Plan.

NMED Comment

3. Section 4.2.2.1 (Previously Unreported Results) indicates 1,4-dioxane was present in September 2008 at regional aquifer well R-20 at a concentration greater than the EPA tap water screening level used for comparison (see also Comment 1. above). The Permittees indicated the volatile organics method for this compound was ". . . unreliable" and noted that the sample was analyzed after the sample holding time had expired for that method. They further noted that the ". . . more precise semi-volatile organic method" also used for analyses of the compound indicated 1,4- dioxane was not present in the sample. The Permittees did not provide documentation or further explanation for either assertion relative to selection of appropriate laboratory methodologies.

Since the semi-volatile method has a lower reported detection limit compared to the volatile method, it could be viewed as being more precise in that regard. At the same time, it can be argued that analysis of the sample (typically, immediately acid-preserved [or with mercuric chloride] with subsequent refrigeration in zero headspace sample containers) past its accepted holding time (14 days using the volatile methodology) could result in some sample volatilization losses or microbial degradation of the compound and understate the compound concentration relative to what it might have been if analyzed within the accepted holding time. By contrast, the semi-volatile method requires unpreserved samples (other than refrigeration), a seven day holding time for sample extraction and a 40 day holding time for the extracts. Filled sample containers for semi-volatile analysis typically contain headspace from the time of sample collection until sample extraction. Since the Permittees did not include paper or electronic copies of the laboratory reports for the September samples, NMED cannot determine when the samples were analyzed relative to accepted holding times for volatiles or when the samples were extracted and analyzed for semi-volatiles.

Electronic copies of laboratory data for previously unreported results must be provided in future Pajarito Watershed PMRs and must be included in all other future watershed PMRs submitted by the Permittees.

In light of the fact that 1,4-dioxane is completely water miscible, quite soluble in water, very mobile in soils, and has been reported present previously at very high (greater than 2,000 and 4,500 parts per billion) concentrations in shallow wells 03-B- 10 and 03-B-13 respectively, that are located northwest of and potentially hydraulically upgradient of R-20, its apparent presence at regional well R-20 is a matter of concern to NMED. Review of available data in the RACER database indicates that 1,4-dioxane is also reported present at concentrations which exceed current screening levels in three intermediate perched wells located within the Mortandad watershed (MCOI-4, -5 and -6). A potential source (or sources) of this compound, within either watershed, has not been identified by the Permittees.

A related area of concern to NMED, with respect to specific analysis of 1,4-dioxane by either volatile or semi-volatile methodologies, is the appropriateness of continued use of either of the two methods currently used by the Permittees' contract laboratories. According to PMR Table E-4, the Permittees' contract laboratory uses U.S. Environmental Protection Agency (EPA) methods SW-846 8260B and SW-846 8270C for analyses of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), respectively.

NMED believes the Permittees need to research the current status of EPA method development efforts underway for analyses of 1,4-dioxane. As a starting point, http://www.tallevast.info/pdfs/dioxane_may19.pdf provides a summary of a comparative analysis study performed by a private contractor for a former industrial facility located in Tallevast, Florida. The study compares analytical results for 1,4- dioxane using EPA methods 8260B, 8270C and 8270 with

isotope dilution. The Permittees are encouraged to review the methods discussed in the Tallevast comparative study and to consider other available and potentially appropriate methods.

After reviewing available methods for analyses of 1,4-dioxane, the Permittees must propose future use of a method (or methods) that will result in reliable sample to sample and quarter to quarter detection capabilities for 14-dioxane at concentrations below applicable screening levels for the compound, that minimizes sampling and analytical constituent losses and provides the best possible accuracy, precision and reproducibility by the Permittees' contract laboratories.

The Permittees' completed evaluation of proposed methods must be submitted on or before November 1,2009.

LANL Response

3. The Laboratory is investigating the potential sources and explanations for detection of 1,4-dioxane at R-20 and a number of other wells, and is following 1,4-dioxane trends at R-20. Sources were evaluated as part of the revised Pajarito Canyon investigation report (LANL 2009, 106771). The Laboratory will provide electronic copies of laboratory data for previously unreported results in future watershed PMRs. The rest of NMED's comment focuses on evaluation of analytical methods for detection of 1,4-dioxane and selection of the most appropriate method. A summary of our evaluation follows.

1,4-Dioxane by SW-846 EPA Method 8260B, Purge and Trap Gas Chromatography Mass Spectroscopy (GCMS) Volatile Organic Analytes

Analyzing 1,4-dioxane by SW-846 EPA Method 8260B (Volatiles) is not effective. As a purgeable compound, 1,4-dioxane is a mid-eluting analyte with an extremely poor purging efficiency. Other nontarget compounds and internal standards in this elution range may cause interference with the analysis, resulting in highly biased results.

1,4-Dioxane was removed from our volatile organic target analyte list.

1,4-Dioxane by SW-846 EPA Method 8270C, GCMS Semivolatile Organic Analytes

For General Engineering Laboratories (GEL), SW-846 EPA Method 8270C, the 1,4-dioxane method detection limit (MDL) is 1 µg/L and practical quantitation limits (PQL) is 10 µg/L.

The continued analyses of 1,4-dioxane by U.S. Environmental Protection Agency (EPA) Method 8270C (Semivolatiles) is effective and should be continued for the following reasons.

- The analyte is chromatographically well separated from the extract solvent peak.
- The PQL adjusted for the *worst* case extraction efficiency (laboratory control sample recovery lower acceptance range of 30%) would be 33.3 (MDL 3.3) µg/L; this is approximately one-half of the 61.1 µg/L EPA RSL tap water screening level (at 10^{-5} excess cancer risk) for 1,4-dioxane.
- The PQL adjusted for the *average* extraction efficiency (laboratory control sample recovery mean of 55%) would be 18.2 (MDL 1.8) µg/L; this value is approximately one-third of the 61.1 µg/L tap water screening level for 1,4-dioxane.

Because of its low molecular weight, 1,4-dioxane elutes immediately after the solvent front, which lowers the chances of potential interference. For the GEL data, the 1,4-dioxane peak is eluting

between 6–12 s after the solvent front (depending on the instrument). This separation is consistently achieved in GEL's instrument calibrations, laboratory control samples, and client samples.

Since 1,4-dioxane may be lost when concentrated to the method-prescribed 1 mL volume, it is necessary to assess extraction efficiency. The best method to assess target analyte recoveries after concentration to 1 mL is with laboratory control sample recoveries, which directly measure extraction efficiency. GEL's laboratory control sample recovery range for 1,4-dioxane acceptance range is 30% to 80% with a mean of 55%.

1,4-Dioxane by SW-846 EPA Method 8270, GCMS Semivolatile Organic Analytes with Isotopic Dilution

SW-846 EPA Method 8270, GCMS Semivolatile Organic Analytes with Isotopic Dilution, would provide a MDL about an order of magnitude lower than EPA Method 8270C (Semivolatiles). However, it is not necessary to use SW-846 EPA Method 8270, GCMS Semivolatile Organic Analytes with Isotopic Dilution, because GEL consistently achieves a PQL below the tap water screening level for 1,4-dioxane of 61.1 µg/L with the standard (nonisotopic dilution) 8270C method.

NMED Comment

- 4. PMR Appendix B (Field Parameter Results) indicates that some surface water sampling locations (Bulldog Spring, Kieling Spring, and Pajarito below confluences of South and North Anchor East Basin) are somehow "purged" of various volumes of water prior to sample collection while other surface water sampling locations are not "purged". The PMR does not provide discussion about how locations are selected for the "purging" process or about how and why any purging is done at the selected sampling locations. Future Pajarito Watershed PMRs (and other affected watershed PMRs as applicable) must discuss the purging methodology, including a description of how, when and why the "purging" process is done and assess the validity of the process in terms of how and whether the process affects the representativeness of collected surface water samples at a given sample location, particularly in regard to sampling for VOCs.*

LANL Response

4. The use of the term "Purge Volume" in Appendix B of the PMR is a misnomer; flow rates were measured. The 2009 Interim Facility Wide Groundwater Monitoring Plan (LANL 2009, 106115) indicates on p. C-4 of Appendix C that at the time of sampling, surface water (including flowing springs) will have flow rates measured or estimated according to Standard Operating Procedure 5224, Spring and Surface Water Sampling. These flow rates have been tabulated in Table 2.0-1 of the reports.

NMED Comment

- 5. PMR Appendix D-1, page D-1 indicates that the 'J' qualifier signifies "(Organic/Inorganic). The required extraction or analysis holding time for this result was exceeded." This may be a cut and paste error since the same qualifier description was used for the 'H' qualifier (also for sample holding time exceeded) on the same page. The 'J' qualifier is typically used by the Permittees to denote estimated concentration values for analytes which are greater than the method detection limit but less than the practical quantitation limit (see also, PMR, Appendix E, page E-7, Lab Qualifier Code J). Future Pajarito Watershed PMR data qualifier listings should be reviewed for completeness and accuracy prior to submittal of the documents to NMED.*

LANL Response

5. The “J” qualifier was mistakenly noted as “exceeded holding time” when it actually denotes an estimated value. All future PMRs will contain revised and updated laboratory qualifier descriptions.

REFERENCES

LANL (Los Alamos National Laboratory), May 2009. “2009 Interim Facility-Wide Groundwater Monitoring Plan,” Los Alamos National Laboratory document LA-UR-09-1340, Los Alamos, New Mexico. (LANL 2009, 106115)

LANL (Los Alamos National Laboratory), August 2009. “Pajarito Canyon Investigation Report, Revision 1,” Los Alamos National Laboratory document LA-UR-09-4670, Los Alamos, New Mexico. (LANL 2009, 106771)