Attachment 1

Correction of Tritium Pore-Vapor Concentrations for the Impacts of Silica Gel–Bound Water

Summary

As part of a review of the environmental sampling procedures, Los Alamos National Laboratory (LANL) identified a low bias in the tritium pore-vapor concentration data caused by the inherent properties of silica gel, the sampling medium. The bias can be corrected through the use of field data collected for each sample. Standard Operating Procedure 5074, Sampling of Sub-Atmospheric Air, has been revised to ensure the collection of the field data required the correction. The LANL environmental database has been updated to use the field data to correct for the low bias. All tritium pore-vapor concentration data, including pre-July 2009 samples, have been corrected in the LANL environmental database. Corrected tritium pore-vapor concentration data are available to the New Mexico Environment Department (NMED) and the public through the RACER database. Reports submitted to NMED after July 26, 2009, include corrected data.

This letter provides the documentation of the low bias, the method for correction, the corrections for pre-July 2009 data, updates to databases, and a list of reports submitted to NMED before July 26, 2009, that include uncorrected data. Also attached are the two technical documents referenced in this letter.

Low bias in tritium pore-vapor concentrations

Pore gas samples are pulled through a canister containing silica gel, a desiccant that absorbs water vapor from the pore-gas sample. At the end of sampling, water is distilled from the silica gel at the analytical chemistry laboratory. The sample water is analyzed for tritium using liquid scintillation counting techniques.

Silica gel contains water bound to the silica gel molecules at the beginning of sampling, which cannot be removed from the silica gel by drying before sampling. As the pore-vapor sample is pulled through the silica gel, the tritium in the pore-vapor sample is diluted by the "nontritiated" (or almost nontritiated) bound water of the silica gel (Whicker et al. 2009). Thus, the water sample distilled from the silica gel by the analytical laboratory at the end of sampling has a lower tritium concentration than the original pore-vapor sample.

A correction factor (CF), accounting for the dilution by silica gel bound water, can be determined on a sample-by-sample basis from the weight of the initial silica gel sample medium, the amount of moisture collected in the sample, and the bound water percentage of the silica gel (Whicker et al. 2009). The pore-vapor sample tritium concentration received from the analytical laboratory is then multiplied by the correction factor to account for the dilution by silica gel bound water.

$$CF = \frac{[SGi * BW] + MS}{MS} \qquad \textbf{Equation 1}$$

SGi = weight of dry silica gel in grams

BW = silica gel–bound water fraction

MS = weight of sample moisture water collected in grams

Correction of tritium pore-vapor concentrations (July 2009 and after)

For each tritium pore-vapor sample, the initial weight of the silica gel, the initial weight of the sample canister, and the final weight of the sample canister (following sampling) are measured. These data are entered into the database along with the fraction of bound water. Silica gel is routinely tested to determine the bound-water fraction. Typical bound-water values found in the literature are 0.05 to 0.07. The mean bound-water fraction in silica gel used in LANL tritium pore-vapor monitoring is 0.064 (Whicker et al. 2009). The database calculates the correction factor for each sample based on these parameters and then calculates a corrected tritium pore-vapor concentration using the correction factor and the tritium pore-vapor concentration result from the analytical laboratory. The individual sample uncertainty value and minimum detectable activity are also corrected using this same method.

This method of correction assumes the water bound to the silica gel before sampling contains no tritium. In fact, naturally occurring tritium can be detected in water of about 27 pCi/L (NCRP 1979; UNSCEAR 2000). For tritium pore-vapor sample values at or near background levels, the correction factor overestimates the true concentration.

Correction of pre-July 2009 data

Tritium pore-vapor data have been collected routinely since 2001. To provide a consistent set of tritium pore-vapor data (pre and post July 2009 data) for use in potential data assessment tasks (e.g., contaminant transport and diffusion modeling), LANL has corrected all tritium pore-vapor data collected before July 2009. To correct pre-July 2009 data, LANL used the percent moisture values available from the analytical chemistry laboratory, since the field data were not required to be collected and hence is not available. Analytical laboratory percent moisture data are available for more than 90% of pre-July 2009 data.

The analytical laboratory reports a percent moisture value for each tritium pore-vapor sample (Marczak 2009). The percent moisture value is calculated by the analytical laboratory as the moisture collected from the sample divided by the weight of the dry silica gel plus the moisture collected from the sample (i.e., MS/(SGi+MS)). Using the percent moisture value, expressed as a fraction, Equation 1 can be transformed to

$$CF = [(1/\%\ \text{Moisture}) - 1] * BW + 1 \qquad \textbf{Equation 2}$$

Some pre-July 2009 samples have no analytical laboratory percent moisture values. An estimate of the distribution of correction factors has been calculated (Whicker et al. 2009). Based on a review of 2 yr of tritium pore-vapor sample field data, the minimum, median, and maximum values of the correction factor are 1.14, 1.43, and 5.27, respectively (Whicker et al. 2009). Ninety-five percent of the correction factor values were less than about 2. Thus, when analytical laboratory percent moisture values were not available, tritium pore-vapor concentrations were corrected using a factor of 2 for pre-July 2009 data.

Updates to LANL environmental database

The LANL environmental database has been updated to store silica gel field data and to calculate corrected tritium pore-vapor concentrations following Equation 1. The database also calculates the corrected individual sample uncertainty and minimum detectable activity values using this same method.

The corrected tritium pore-vapor concentration is uploaded into the RACER database. The original analytical laboratory tritium pore-vapor concentration (uncorrected value) remains in the LANL environmental database and is available upon request.

To document the method of correction used for individual tritium pore-vapor samples, qualifier reason codes have been added to the environmental database and/or comments have been added to the environmental database Chemical Analysis Result (CAR) table.

Method for Calculating Correction Factor	Validation Reason Code	Qualifier Reason Code	Comment in CAR table (appended to existing comment)
Silica gel field weights for the individual sample	No change from original sample	No change from original sample	No comment code related to tritium correction factor
Percent moisture value from analytical laboratory for the individual sample	No change from original sample	No change from original sample	R17A = data have been recalculated to reflect bound water using percent moisture
Silica gel field weights and analytical laboratory percent moisture are not available. Correction factor of 2 is used.	"J" added to existing qualifier	R17	R17B = data have been recalculated to reflect bound water using factor of 2

Reports submitted to NMED before July 26, 2009

LANL has submitted a number of reports to NMED between 1994 and 2009 that include tritium pore-vapor data, which are not corrected. These reports are listed in the attached table. None of these uncorrected data were used in making regulatory decisions (e.g., no further action). All the data published in these reports are now corrected and available through the RACER database.

References

Marczak, S., October 2009. "Technical Implementation of the Correction Factor Calculation for Tritium in Pore-Gas Data, Revision 1," Los Alamos National Laboratory document LA-UR-09-6972, Los Alamos, New Mexico. (Marczak 2009)

NCRP (National Council on Radiation Protection). 1979. Tritium in the Environment. NCRP Report no. 62.

UNSCEAR (United Nations Scientific Commission on the Effects of Atomic Radiation). 2000. Report of the United Nations Scientific Committee on the Effects of Atomic Radiation to the General Assembly.

Whicker, J.J., J.M. Dewart, S.P. Allen, W.F. Eisele, M.C. McNaughton, and A.A. Green, September 2009. "Corrections for Measurement of Tritium in Subterranean Vapor Using Silica Gel," Los Alamos National Laboratory document LA-UR-09-6230, Los Alamos, New Mexico. (Whicker et al. 2009)