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Corrections for Measurements of Tritium in Subterranean Vapor using Silica Gel

Jeffrey J. Whicker
Jean M. Dewart
Shannon P. Allen
William F. Eisele
Michael C. McNaughton
Andrew A. Green

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Introduction

Background

Los Alamos National Laboratory (LANL) performs environmental sampling to ensure public and environmental health and to demonstrate compliance with existing regulations (LANL 2007). One part of these efforts includes extraction of soil gas from subterranean monitoring wells (LANL 2008). These monitoring wells are used as access ports to sample bedrock and soil gas at different depths within the vadose zone where samples are taken for measurement of a variety of chemical and radiological contaminants, including tritium. Extraction and measurement of tritium in these samples presents numerous technical challenges regarding the sampling, measuring, and reporting of tritium concentration measurements in the subterranean soil gas.

Though tritiated water and vapor in the vadose zone does not represent a direct ingestion or inhalation dose pathway for humans or other biota, sampling of soil gas is performed for several important reasons. First, contamination from most spills and buried waste first enters the vadose, and measurement of contamination in the soil gas is one of the first indicators of a breach of containment. Second, and important for risk assessment, the soil gas concentration data at different well depths is used to identify and establish temporal and spatial patterns in concentrations and to investigate plume transport dynamics. The major concern is to assess the potential for the plume to reach groundwater, which increases its hazard to people. Finally, the measurements can be also used to test and calibrate migration models, the main tool used to predict migration of contaminants to groundwater (Till and Grogan 2008).

Measurement Procedure and Calculations

A procedure (LANL 2009a) has been developed to ensure consistency in vadose sampling for tritium. The procedure generally follows the standard protocol for soil gas monitoring found in ASTM D5314-92 (ASTM 2006). The general sampling process includes using air pumps to purge sampling lines, extraction of the soil gas from the bed rock, and then to pass the pore gas through about 135 g of prebaked silica gel packed into a sampling tube. The sampling continues until about 5 g (i.e., 5 mL) of moisture in the soil gas is collected. The sampling tubes are immediately sealed and sent to an analytical laboratory where the collected moisture is driven off the silica gel by heating. The collected moisture is analyzed for tritium content using liquid scintillation counting (LSC) and the results reported in units of Bq/L_{water}. This value represents the amount of tritium in the extracted vapor at a particular depth in the vadose. Eqn. 1 shows the calculation for tritium concentration from the extracted vapor:

$$C(Bq/L) = \frac{A}{V} = \frac{A}{M_E \div \rho_{water}} \quad \text{(Eqn. 1)}$$

where: A is the amount of radioactivity of tritium in the moisture (units of Bq), and

V is the volume of the liquid in the sample analyzed (unit of L),

M_E is the mass of the liquid extracted (unit of g), and

ρ is the density of water (i.e., 1 g cm^{-3}).

There are several sources of potential error associated with these measurements, as described in Eqn. 1. There is random error in the radioactivity measurements (A) that

are included in the laboratory reports, the error of the measurements of mass of the sampled moisture (M_E) is a few percent, and the density of water (ρ) is considered to be a constant. However, the largest potential error is less obvious and is based on the assumption that the mass of the water extracted during laboratory analysis is solely from the vapor sampled, that is, that there is no bound water in the prebaked silica gel. This assumption has been shown to not be valid despite prebaking of the silica gel. Patton et al. (1997) found that silica gel baked in an oven at over $\geq 100^{\circ}$ C for extended time periods still contained substantial amounts of tightly bound water. The amount of residual moisture depends on the nature of the silica gel, but the amount is large enough to significantly impact the accuracy of the results (Rosson et al. 2000, Guthrie et al. 2001) and underestimate tritium releases to the environment (Simpkins and Hamby 1997). The error occurs when the HTO in the sample undergoes isotopic exchange, or mixing, with the bound H_2O in the silica gel. This "dilution" effectively biases the concentration measurements low.

Mathematical correction of the tritium concentration measurements accounting for the residual moisture in the prebaked silica gel is required, as derived beginning with Eqn. 2. First, the mass of the liquid extracted from the silica gel (M_E) will be a combination of the sampled mass (M_S) and the residual moisture (M_R) in the silica gel, as shown in Eqn. 2.

$$M_E = M_s + M_R \qquad \text{(Eqn. 2)}$$

Ideally, M_E would equal M_S. However, if one makes the reasonable assumption that M_R contains a relatively small amount of tritium [background tritium concentrations in air are about 1 Bq L^{-1} (NCRP 1979, UNSCEAR 2000)], and that the tritium in the sample mixes thoroughly with the residual moisture, then Eqn. 3 shows how any residual moisture can dilute the sample with "clean" water and result in an estimate of the tritium concentration that is biased low.

$$C(Bq/L) = \frac{A}{V} = \frac{A}{M_E \div \rho_{water}} = \frac{A}{(M_s + M_R) \div \rho_{water}} \quad \text{(Eqn. 3)}$$

To correct for residual moisture in the sample, the mass of the residual water needs to be determined. The mathematical corrections are shown in Eqns. 4 and 5.

$$C(Bq/L) = \frac{A}{(M_S + M_R) \div \rho} \times \frac{(M_S + M_R)}{M_S} \quad \text{(Eqn. 4)}$$

$$C(Bq/L) = \frac{A}{(M_S + M_R) \div \rho} \times CF \quad \text{(Eqn. 5)}$$

Here, CF is the correction factor adjusting measured tritium concentrations accounting for residual moisture in the silica gel. The mass of the sampled water, M_S, is measured as the difference in masses of the cartridge containing the silica gel before and after sample collection. The mass of the residual moisture can be determined by knowing the fraction of residual water by mass in the preheated silica gel prior to sampling.

$$M_R = M_{SilicaGel} \times F_{M-R} \qquad \text{(Eqn. 6)}$$

$F_{M\text{-}R}$ is the fraction of mass of the prebaked silica gel due to residual moisture. The correction factor, CF, then becomes:

$$CF = \frac{\left(M_{SilicaGel} \times F_{F-R}\right) + M_S}{M_S}, \qquad \text{(Eqn. 7)}$$

which is substituted into Eqn. 5 to correct samples for the dilution due to residual moisture. $M_{SilicaGel}$ and M_S are measured in the laboratory per procedure, but measurement of the fractional mass of the moisture is needed for the correction.

Purpose of Study

The LANL AIRNET program currently corrects for changes in humidity and for residual moisture in the silica gel in measurement of tritium in the atmosphere (Eberhart 1999), but a correction factor has not been determined for subterranean soil gas measurements. Other studies have shown that this correction can be significant and can vary with silica gel type, amount of moisture collected, and laboratory procedures (Eberhart 1999, Rosson et al. 2000). The primary purpose of this study was to determine the correction factor (i.e., Eqn. 7) and investigate its uncertainty. This is required for accurate measurement of tritium concentrations in subterranean soil gas at LANL and allows for a more accurate representation of the tritium levels in the vadose zones.

METHODS

Determination of Residual Moisture (F_M) in Silica Gel

A series of measurements (n = 18) were made of the residual moisture mass in silica gel that is used to collect soil gas vapor for tritium analysis. Soil gas measurements of tritium are made by the two main LANL environmental contractors, and because each contractor uses a different silica gel, 9 measurements were conducted on each type using the same protocol.

The following procedure was used for these measurements. First, silica gel from both contractors was preheated at a temperature of 105° C for over two days, per procedure. The preheated silica gel from both contractors was quickly separated into individual samples with masses of approximately 1, 2, 3, and 5 g. These preheated masses (M_{before}) were recorded before complete denaturing. For denaturing, all samples were placed into a furnace at a temperature of 1000° C for 2 hours, and the final mass of the denatured gel (M_{final}) was recorded. The residual/bound moisture fraction by mass was calculated as shown in equation 8.

$$F_M = \frac{m_{before} - m_{final}}{m_{before}} \qquad \text{(Eqn. 8)}$$

Uncertainty Analysis for correction for residual moisture in silica gel

Analysis of the uncertainty of the correction factor, *CF*, was done using Monte Carlo simulation techniques (Till and Grogan 2008) using Crystal Ball software[1]. The Monte Carlo technique allows propagation of errors from each variable through the final

[1] Oracle Software, 1515 Arapahoe St. Suite 1300, Denver, CO 80202

calculations of CF. The distribution of each parameter in Eqn. 7 was determined based either on actual measurements or an assumed distribution. The first parameter is the mass of the sample collected (M_S). Over 150 measurements of Ms collected from 2007 and 2008 field logbooks were analyzed and M_S ranged from about 2 g up to 46 g with a median of 15. Therefore, in the Monte Carlo simulations we assumed a triangular distribution with 2 g, 15 g, and 46 g as the minimum, most likely, and maximum masses of collected samples. For the second parameter, the mass of the silica gel ($M_{SilicaGel}$), we assumed the typical amount of 135 g ± 13.5 g. This amount is based on the typical mass in a cylinder, as written in the procedure (LANL 2009b), with a 10% error. A normal distribution of fractional moisture content by mass (F_M) was assumed and was based on the mean and standard deviations measurements made during the denaturing process. The values for distribution of F_M were 6.3% ± 0.3% (further details are in the Results section). Ten thousand Monte Carlo calculations were run and the final distribution for CF was determined from these results.

Results

The percent bound moisture for the silica gel used by Apogen and LATA were similar with means and standard deviations of 6.5 ± 0.25% and 6.3 ± 0.14%, respectively (Table 1). The combined mean and standard deviation was 6.4 ± 0.3 %. Figure 1 shows the results in terms of water loss as a function of the amount of the initial mass of the silica gel. There was no statistically significant difference between the two types of silica gels used by the contractors, so both sets of data were combined in the statistical analysis and

all data are shown in Figure 1. The regression slope was slightly over 6% residual moisture mass per gram of silica gel. This means that for a sample canister with say 100 g of silica gel, that there will be about 6 g of residual moisture in the canister. Given that sampling of vapor stops when about 5 g of vapor moisture is collected, the relative amount of residual moisture in the silica gel is enough to dilute the sample resulting in concentration measurements that are biased low. Thus, the residual moisture, combined with a small sample amount, could result in biases that are significant enough to require correction.

The correction factor (*CF*) can be estimated using Eqn. 7. An average *CF* can be calculated using values from measurements assuming that the initial mass of the silica gel was 135g, the fractional amount of moisture in the silica gel was 0.064, and the mass of the sampled vapor was 15 g. The correction factor becomes 1.57, as shown below.

$$CF = \frac{(135g \times 0.064) + 15g}{15g} = 1.57 \qquad \text{(Eqn. 9)}$$

However, each variable used to calculate has uncertainty, which was propagated in the calculation to produce a distribution of values for the *CF* using Monte Carlo simulations from Crystal Ball, as described in the Methods section. The resulting distribution of values for *CF* is presented in Figure 2. The mean and standard deviation of the distribution of *CF* values in Figure 2 was 1.53% ± 0.36%, and the minimum, median, and maximum values were 1.14, 1.43, and 5.27, respectively. Ninety-five percent of the values were less than about 2.

Discussion and Conclusions

Correction factors for subterranean measurements of tritium in soil gas were determined. Though vapor measurements are currently used for qualitative assessment, application of these corrections would improve their accuracy and could increase the inherent value of this data for future uses. At a minimum, corrections for the residual moisture in the silica gel should be made. The measurements of moisture in silica gel reported here resulted in a median correction factor of 1.43. This correction factor is similar to that found by Rosson et al. (2000) and Guthrie et al. (2001). We recommend that historical tritium soil gas measurements be corrected by this factor. Corrections for future measurements can be done individually using Eqn. 7.

For future modeling efforts, it is best to use the full distribution of values to provide a distribution of probabilities and concentrations that would be predicted to reach the groundwater and describe the range of potential impact. For worst case scenarios, the higher values of the *CF* could be used such as the 95% value of 2.

There are several important assumptions that are made that impact the correction factor, as described in this report. The first is that it is assumed that the tritium in the sampled HTO is fully mixed with the residual moisture in the silica gel. That is, the isotopic exchange is complete. Rosson et al. (2000) showed that this is a reasonable assumption though they found that amount of exchangeable water in the silica gel could be slightly higher (about 10%) than the mass of water content in the silica gel (determined through denaturing) possibly due to unaccounted alterations in hydroxyl groups or residual moisture even after denaturing. A second assumption is that there is

no isotopic difference in the concentrations of HTO and H_2O in the water evaporated during the processing of the sample in the laboratory. Rosson et al. (2000) showed that this is a reasonable assumption, especially with the higher heats used to drive the moisture off the silica gel, and the impact of the isotope effect for this process is only a few percent. The isotope effect for evaporation is much larger at lower temperatures (e.g., 10° C) and needs to be accounted for when calculating concentrations in soil water from subterranean soil gas measurements (Price 1958).

In summary, the impact of residual bound moisture on tritium measurements in soil vapor is sufficient to warrant correction. This paper shows that the magnitude of this dilution is on-the-order of about a factor of two, biasing the results low. The calculations also show that the correction factor is largest for samples with the least amount of collected moisture and will approach one as more sample mass is collected, but the realistic amounts of moisture collected under normal sampling times require correction. This correction will provide more accurate data for measurement interpretation and risk assessment for public exposures.

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Table 1. Results of measurements made to determine the percent of residual, bound moisture in silica gel following prebaking. Results include samples from both LANL contractors APOGEN and LATA.

Crucible	Mass Empty Crucible (g)	Mass of Crucible w/pre-denatured gel (g)	Net Mass of gel (g)	Cruc. w/ denatured gel (g)	Mass of Water lost (g)	Percent bound water
			APOGEN Contractor			
1	49.3912	50.4388	1.0476	50.3682	0.0706	6.739213
2	48.4071	49.4224	1.0153	49.3522	0.0702	6.914213
3	52.2148	53.2605	1.0457	53.1904	0.0701	6.703643
4	52.7999	55.8038	3.0039	55.6114	0.1924	6.405007
5	51.6778	54.6539	2.9761	54.4636	0.1903	6.394274
6	51.845	54.8281	2.9831	54.6384	0.1897	6.359157
7	51.7259	56.7239	4.998	56.413	0.3109	6.220488
8	49.3898	54.3796	4.9898	54.069	0.3106	6.224698
9	48.4061	53.3839	4.9778	53.0701	0.3138	6.30399
			LATA Contractor			
1	52.2133	53.2349	1.0216	53.1747	0.0602	5.892717
2	52.7987	53.7927	0.994	53.7314	0.0613	6.167002
3	51.6764	52.6739	0.9975	52.6126	0.0613	6.145363
4	51.8433	54.8441	3.0008	54.6586	0.1855	6.181685
5	51.7246	54.7121	2.9875	54.5259	0.1862	6.232636
6	49.3912	51.3687	1.9775	51.2461	0.1226	6.199747
7	48.4074	53.3855	4.9781	53.0817	0.3038	6.10273
8	52.2141	57.2201	5.006	56.921	0.2991	5.97483
9	52.7997	57.7492	4.9495	57.4605	0.2887	5.832912

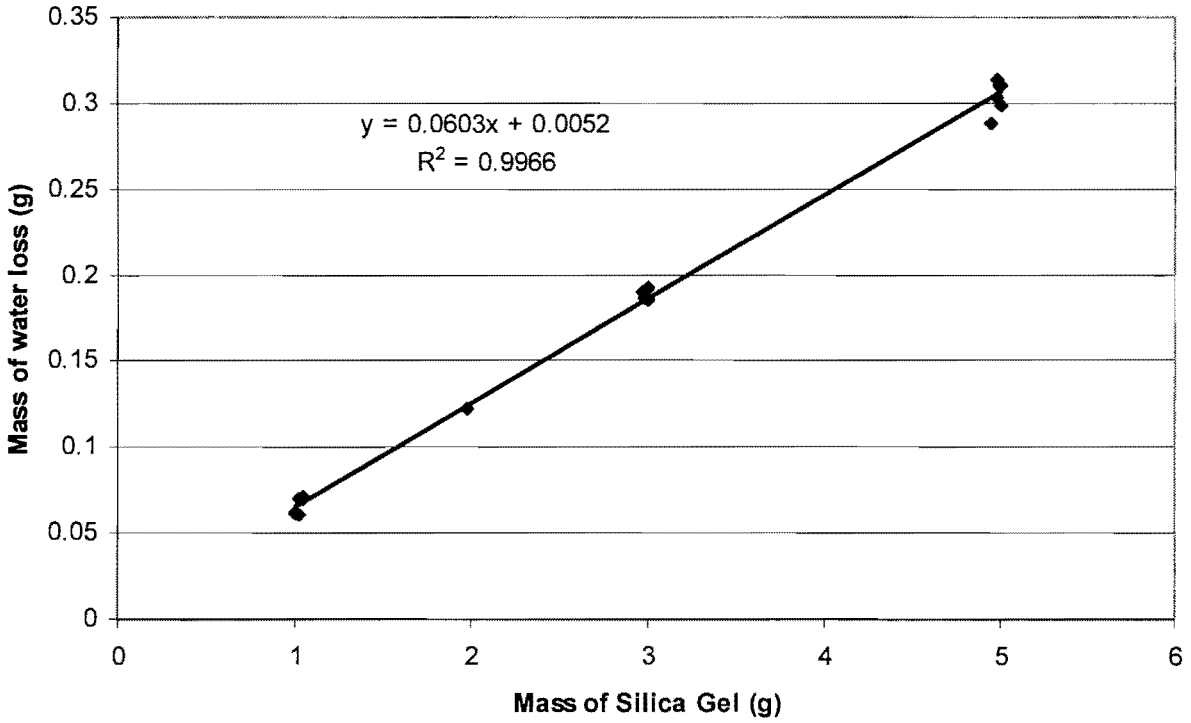

Figure 1. Decrease in water mass as a function of amount of silica gel in sample before denaturing in the high temperature oven.

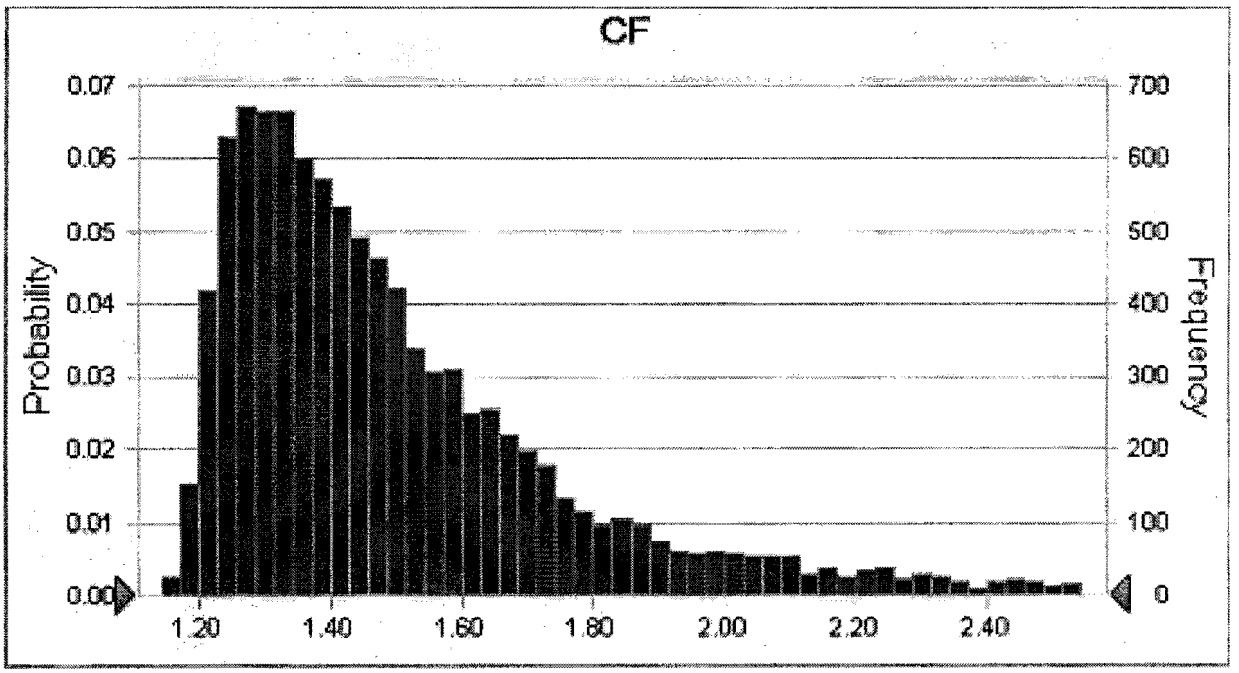

Figure 2. Distribution of values for the correction factor