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Author(s): Craig F. Eberhart

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Using Absolute Humidity and Radiochemical Analyses of Water Vapor Samples to Correct Underestimated Atmospheric Tritium Concentrations

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Craig F. Eberhart

Air Quality Group, MS J978, Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

Los Alamos National Laboratory (LANL) emits a wide variety of radioactive air contaminants. An extensive ambient air monitoring network, known as AIRNET, is operated on-site and in surrounding communities to estimate radioactive doses to the public. As part of this monitoring network, water vapor is sampled continuously at more than 50 sites. These water vapor samples are collected every two weeks by absorbing the water vapor in the sampled air with silica gel and then radiochemically analyzing the water for tritium. The data have consistently indicated that LANL emissions cause a small, but measurable impact on local concentrations of tritium. In early 1998, while trying to independently verify the presumed 100 percent water vapor collection efficiency, I found that this efficiency was normally lower and reached a minimum of 10 to 20 percent in the middle of summer. This inefficient collection was discovered by comparing absolute humidity (g/m^3) calculated from relative humidity and temperature to the amount of water vapor collected by the silica gel per cubic meter of air sampled. Subsequent experiments confirmed that the elevated temperature inside the louvered housing was high enough to reduce the capacity of the silica gel by more than half. In addition, our experiments also demonstrated that, even under optimal conditions, there is not enough silica gel present in the sampling canister to absorb all of the moisture during the higher humidity periods. However, there is a solution to this problem. Ambient tritium concentrations have been recalculated by using the absolute humidity values and the tritium analyses. These recalculated tritium concentrations were two to three times higher than previously reported. Future tritium concentrations will also be determined in the same manner. Finally, the water vapor collection process will be changed by relocating the sampling canister outside the housing to increase collection efficiency and, therefore, comparability to the true ambient concentrations of tritium.

INTRODUCTION

The LANL sampler uses silica gel to collect samples of atmospheric water vapor. Water vapor samples are collected in vertically mounted canisters containing about 135 grams of silica gel with a volume of 220 milliliters. This silica gel is dried in a drying oven before use in the field to remove most residual water. This material is used as a desiccant to remove moisture from the air, followed by distillation, condensation, collection as a liquid, and analysis for tritium. According to the Department of Energy[1], this process is recognized as a method for collecting essentially all of the atmospheric moisture. The airflow rate through our silica gel canisters is typically 200 ml/min or about 4 cubic meters per two-week sampling period. Historically, the water mass has been determined by the difference in the start and ending weights of the silica gel canisters or by measuring the water collected through condensation of the distillate.

Two factors are needed to estimate ambient levels of tritium as an oxide: water vapor concentrations in the air and tritium concentrations in the water vapor. Both of these need to be representative of the true concentrations to obtain an accurate estimate of the ambient tritium concentrations. This paper primarily addresses the first issue: the accuracy of the water vapor concentrations.

THE PROBLEM - WATER VAPOR COLLECTION EFFICIENCIES

There has always been an implicit assumption that silica gel penetration by water vapor was relatively small unless breakthrough occurred. In *The Procedures Manual of the Environmental Measurements Laboratory*[2], it stated that the water vapor absorption capacity of silica gel could be as small as five percent of the silica gel mass under low humidity conditions. With about 135 g of silica gel in an AIRNET canister, the water vapor collection capacity could be less than seven grams of water for some of the two-week collection periods in Los Alamos. Manufacturer data also show that capacity decreases with decreasing relative humidity (Figure 1). These sources of information indicate that the capacity of the silica gel can be a factor at both low and high water vapor concentrations dependent on the mass of silica gel used as a collection media.

In addition to measuring water vapor concentrations by using silica gel, we operate a network of meteorological towers primarily for use in air dispersion modeling. Relative humidity and temperature are measured continuously at each of these sites. These measurements are collected using calibrated instruments traceable to NIST standards. The data are stored in a database as 15-minute averages and can be subsequently used to calculate absolute humidity concentrations, in grams of water per cubic meter, by using the Clasius-Clapeyron[3] equation. For this paper, these NIST-traceable measurements are considered to be correct and unbiased values.

Figure 2 compares meteorological data from one tower (TA-54) to nearby AIRNET sites that are at similar elevations and to the most distant tower location (TA-49). The TA-54 tower is at a lower elevation than the TA-49 tower and therefore in an area with less annual precipitation, but Figure 2 shows that water vapor concentrations are slightly, but consistently higher at TA-54 because they are calculated on an actual cubic meter basis. However, these differences indicate that two-week averages for humidity are more of a regional phenomenon and do not show much spatial variation within or near LANL boundaries. It also indicates that a day or two difference in sampling periods is small to insignificant. The big disparity is between the water collected by the AIRNET samplers and the water measured by the meteorological instruments. During the winter, the measurements are roughly comparable, but during the summer the efficiency was normally lower and reaches a minimum of 10 to 20 percent in the middle of summer. A wide variety of comparisons were made between the fifty plus AIRNET samplers and the meteorological towers, but the same pattern always emerges: the water vapor concentrations, as measured by site-wide averages, are consistently higher using the meteorological measurements than the mass collected by the AIRNET samplers especially in the summer.

POTENTIAL CAUSES AND EXPERIMENTAL RESULTS

When this inefficient collection of water was first discovered, a wide variety of potential causes were identified including capacity, airflow rate, penetration before reaching capacity, the type of silica gel in use, and temperature. Since heat is used to remove water from the silica gel, it was identified as a likely factor in collection efficiency and/or capacity.

A limited series of field tests were designed to evaluate these factors by operating a series of samplers in various configurations. For each test, timer readings, airflow measurements using a bubble meter, and weight increases were recorded daily except for some weekends. Ambient concentrations of water vapor were calculated from these data. In addition, ambient water vapor concentrations were calculated for every fifteen minutes of meteorological data. These absolute humidity concentrations were then averaged for the same time intervals represented by the AIRNET measurements.

Although a variety of tests were conducted, data from one experiment are sufficient to illustrate how water vapor is collected by silica gel. The results of this experiment are shown in Figure 3 which compares the calculated water vapor concentrations for silica gel canisters deployed in the open air to those within closed louvered AIRNET housings. The absolute humidities calculated from the meteorological measurements are also shown. Temperatures inside the AIRNET housings were collected during the experiments and generally ranged from about 35°C to 50°C depending on the time of day, the location within the housing, and the meteorological conditions. Ambient temperatures during this test ranged from 7°C to 31°C.

This test clearly demonstrates that the canisters in closed AIRNET samplers collect at reduced efficiencies within several days after deployment and reached capacity, or no net weight gain, in about 6 days. The graph also shows that capacity varies with absolute humidity. For example, around September 9, some canisters lost weight as the absolute humidity dropped indicating a reduction in capacity. Two days later, when the absolute humidity increased, the same canisters increased in weight indicating an increase in capacity. The open air canisters worked much better than the ones in the closed housings, but their collection efficiency also decreased near the end of the sampling period because they were approaching capacity. Other experiments produced similar patterns with the capacity being dependent on relative humidity, temperature, and/or the combination of the two measurements (absolute humidity).

EFFECTS ON AMBIENT TRITIUM CONCENTRATIONS

If the amount of water vapor collected on the silica gel is used as the measurement of atmospheric water vapor, any collection rate less than 100 percent will introduce a negative bias by underestimating ambient concentrations of water vapor. However, using absolute humidity, as calculated from temperature and relative humidity, can eliminate this systematic bias in our measurements. The absolute humidity can also be used to reconstruct historical ambient tritium concentrations since its use corrects this bias by eliminating the amount of water collected from the calculations.

Since 100 percent, or a consistent percentage, of the water vapor is not collected, samples may not be representative of ambient concentrations especially for short-term releases. Even if one two-week sample is not representative of the entire two weeks, a larger group of samples, such as the 26 samples used for calculating annual averages, will generally be representative of the annual concentrations. If there is a change in collection efficiency within a two-week sampling period one could argue that a short-term release of tritiated water is not representatively sampled. This would be true, but somewhat disingenuous because random errors are associated with all sampling activities. Collecting less than 100 percent of the water present in the air passing through the silica gel will not provide as good an estimate as a complete sample, but water absorption into and out of the silica gel will continue throughout the sampling period. As such,

the water that is collected should provide a representative random sample.

Three sites were selected for comparing the two ways of calculating atmospheric tritium concentrations: Santa Fe, Eastgate in the Los Alamos townsite, and an onsite location known as Area G. These three sites were chosen as examples because they represent background or regional concentrations (Santa Fe, site #3); the public receptor site with the highest dose caused by LANL emissions (Eastgate, site #10); and an on-site location in a radioactive waste disposal with controlled access (Area G - site #35). The Area G location has the highest measured concentrations of tritium in the network due to evaporation and transpiration of tritiated water from nearby buried radioactive waste. Tritium concentrations for these three sites, calculated using absolute humidity and water collected by the silica gel, are shown in Figures 4 through 6 with a summary of the data in Table 1.

For Santa Fe, the estimated concentrations and doses were 2.4 times higher using the meteorological measurements, but most of the values are below the Minimum Detectable Activities (MDA). The Santa Fe measurements are primarily a function of the analytical process variability and the water vapor concentrations. Had the random variation in the analytical process occurred in a different pattern, the calculated concentrations may have actually decreased because some of the analyses were less than zero.

The Eastgate site does show significantly elevated concentrations of tritium when compared to Santa Fe using either method for calculating air concentrations. Estimated concentrations increased from 1.9 pCi/m^3 to 3.9 pCi/m^3. The estimated dose increased at the same rate, 2.1 times, to .026 mrem. This dose is still low, but it represents a reasonable estimate because most of the these analyses are above the MDA.

The Area G concentrations increased from 281 to 755 pCi/m^3. The calculated ambient concentrations at this site increased more than the concentrations at the Eastgate site (2.7 vs. 2.1) because the primary source, diffusion and transpiration from the buried radioactive waste, increases greatly during the warm months of the year when the silica gel collects a much smaller percentage of the water vapor in the sampled air. The estimated dose increased from 1.9 to 5.0 millirems. Even though this dose is almost half of the maximum allowable NESHAP standard, it is an on-site location with controlled access where worker standards, not NESHAP requirements, apply.

CONCLUSIONS

Absolute humidity, as calculated from the meteorological measurements of percent relative humidity and temperature, is a better measurement of water vapor concentrations than measuring the amount of water collected per cubic meter of air by silica gel because it does not appear to be negatively biased. We have recalculated historical concentrations of tritium and have now switched to using meteorological measurements for future calculations. In addition, our data have shown that the silica gel capacity to collect water vapor increases if the gel is at a lower temperature and the absolute humidity remains constant. Therefore, we are in the process of relocating our silica gel to a cooler location outside the AIRNET housing to increase the efficiency and capacity of the gel while also the comparability to the true ambient concentrations of tritium.

ACKNOWLEDGEMENTS

BIBLIOGRAPHY

1. *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance*, U.S. Department of Energy: Washington D.C., January 1991.

2. *The Procedures Manual of the Environmental Measurements Laboratory*, 28th Ed., U.S. Department of Energy, February 1997.

3. Iribarne, J.V.; Godson, W.L. *Atmospheric Thermodynamics*, 2nd Ed.; D. Reidel Publishing Company, 1991.

Table 1. Average Tritium Concentrations[1] and Estimated Dose[2]

Sampling Site	Water Vapor Data Source		Ratio
	AIRNET	Met Data	
Santa Fe (#3)	0.10 pCi/m^3	0.24 pCi/m^3	2.4
	0.00067 mrem	0.0016 mrem	
Eastgate (#10)	1.9 pCi/m^3	3.9	2.1
	.013 mrem	0.026 mrem	
Area G (#35)	281	755	2.7
	1.9 mrem	5.0 mrem	

[1]As calculated from the data graphed in Figures 4 through 6 (This includes most of the 1997 and 1998 data)

[2]Using the Appendix E value from 40 CFR Part 61 where an annual concentration of 1500 pCi/m^3 is equal to 10 millirems.

Figure 1. Collection Capacity of Silica Gel versus Relative Humidity
(at 25 ^{o}C)
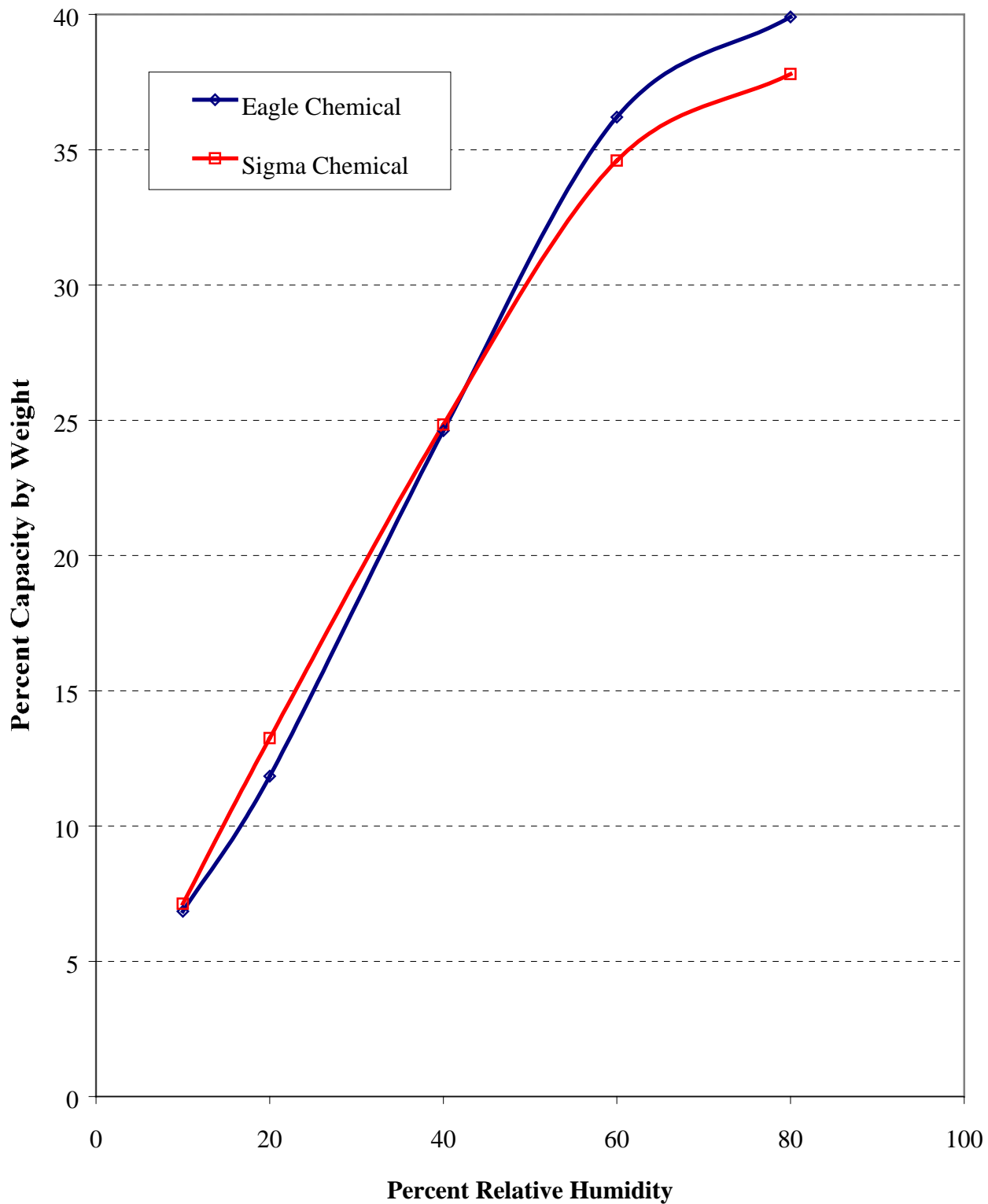
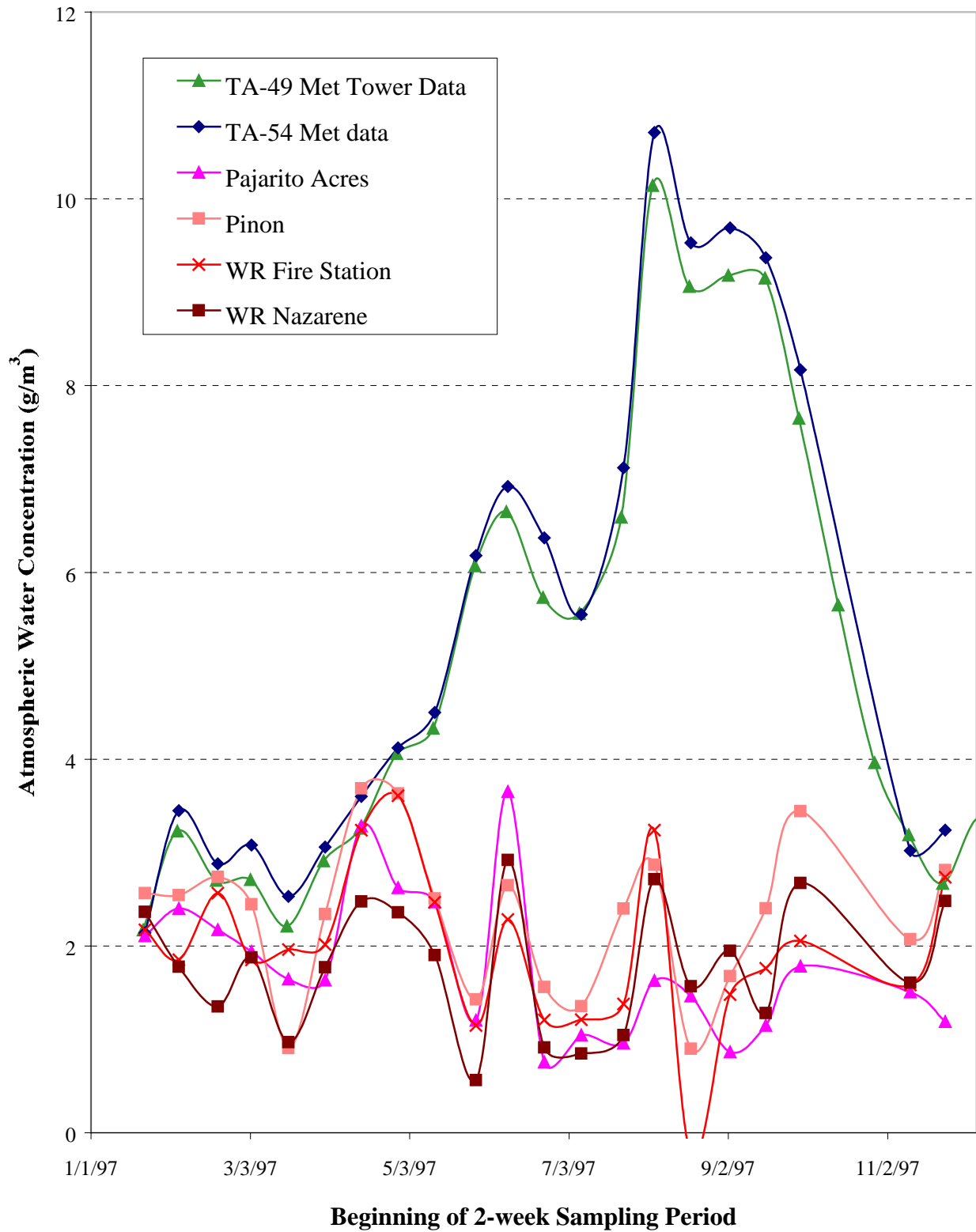**Figure 2.** Atmospheric Moisture in White Rock

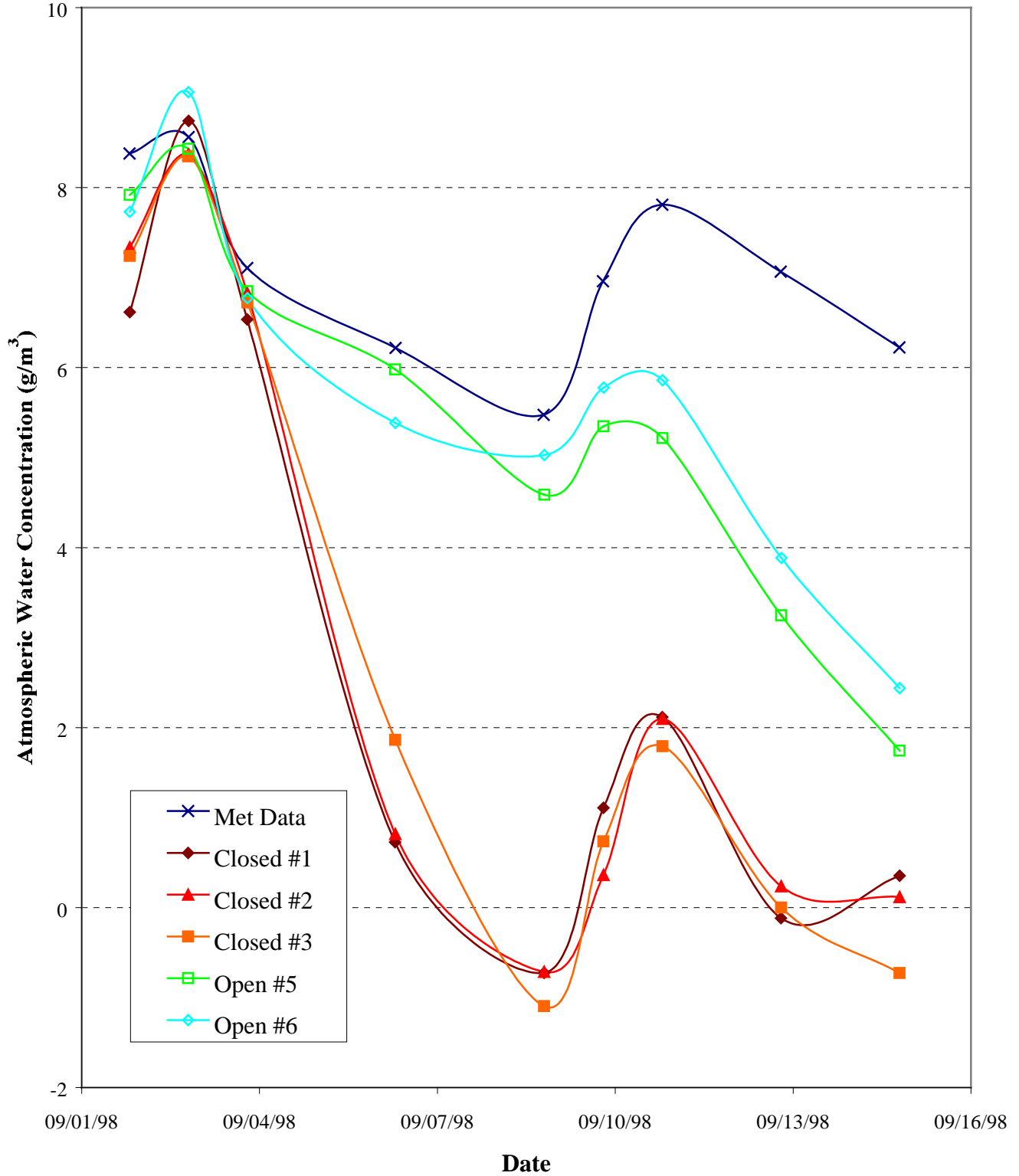**Figure 3.** Closed vs. Open Air Sampling of Water Vapor
(200cc/min)

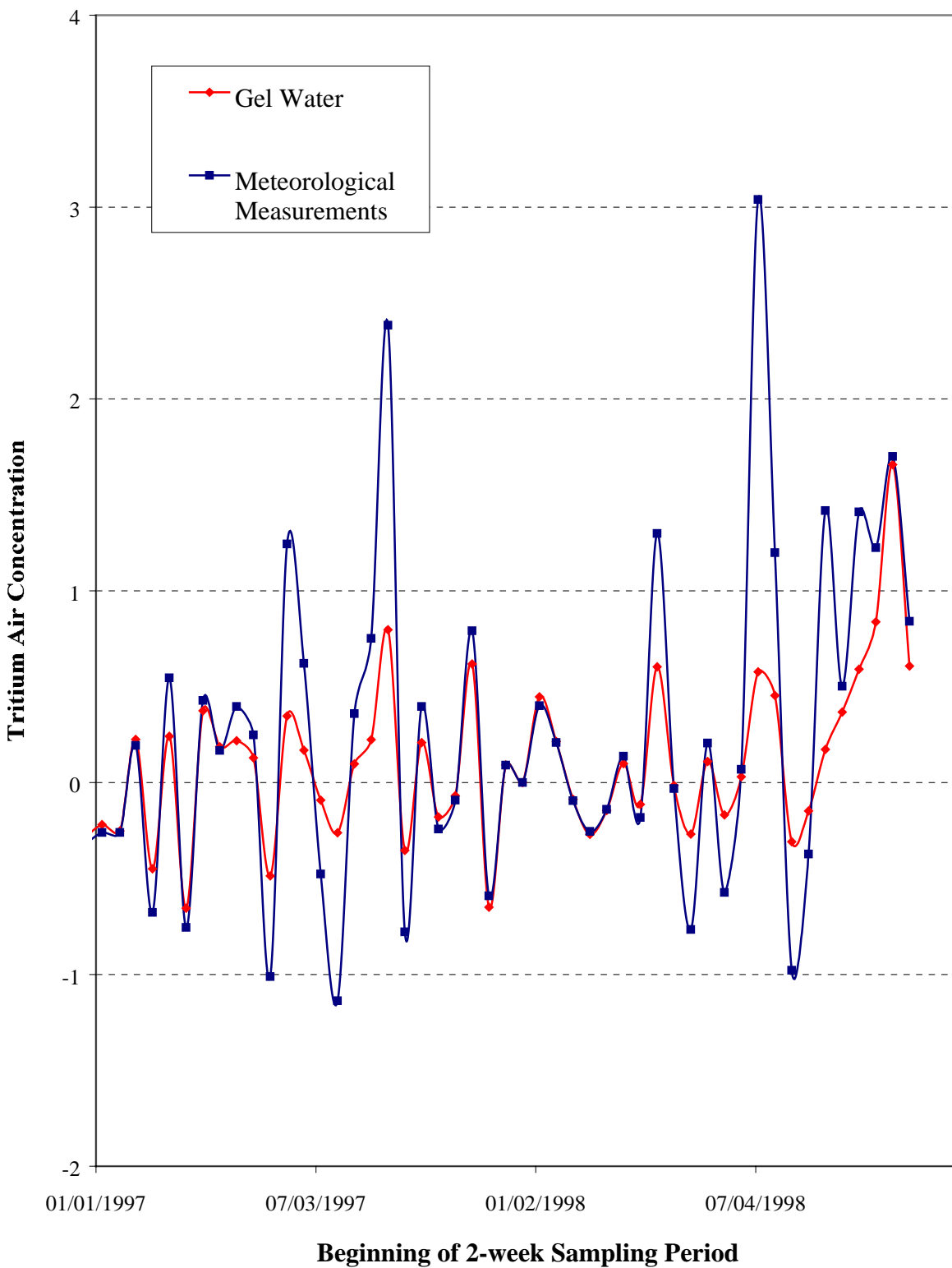**Figure 4.** Tritium Measurements in Santa Fe, NM
(1997-1998)

Figure 5. Tritium Measurements in Los Alamos, NM
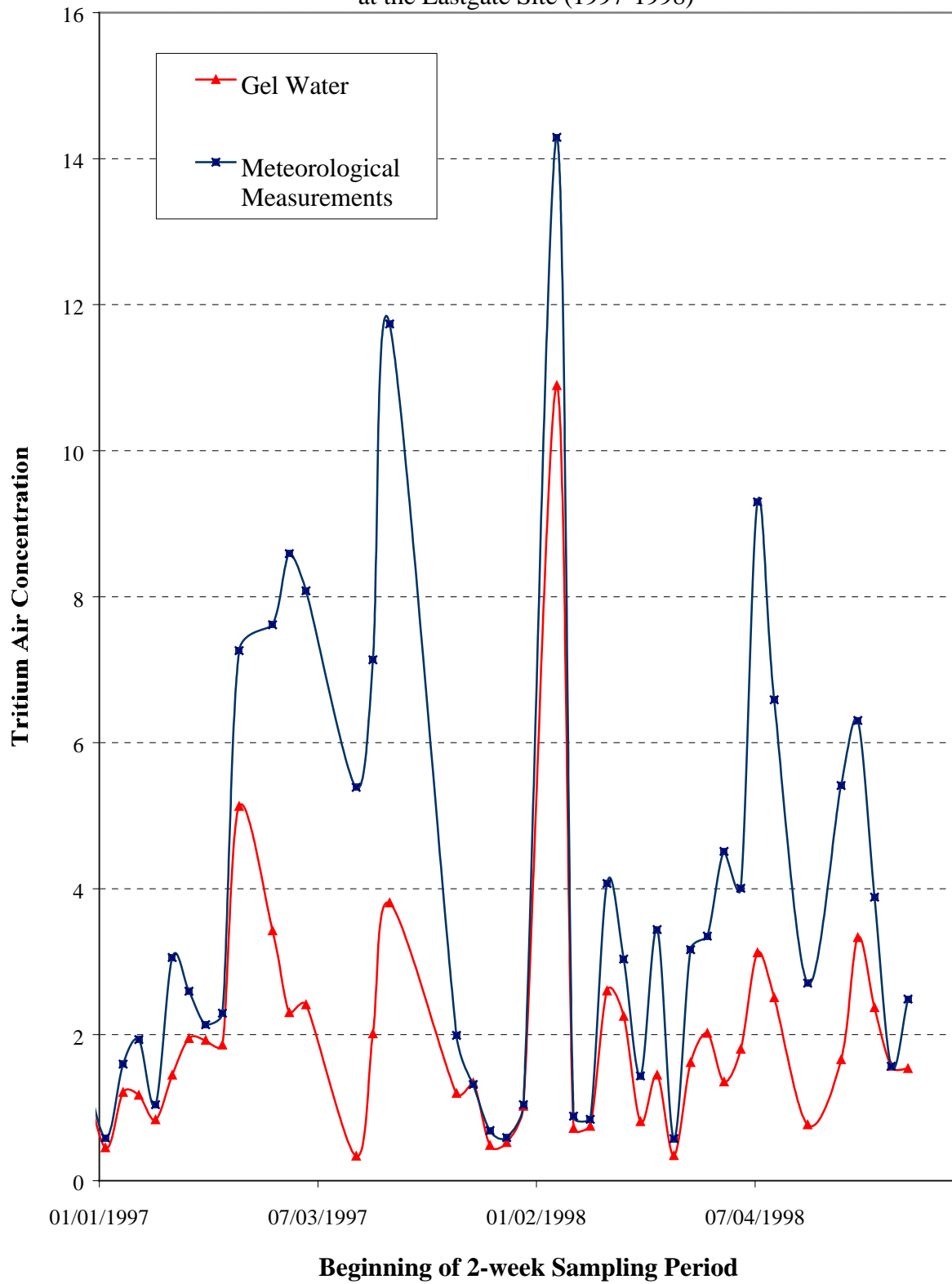at the Eastgate Site (1997-1998)

Figure 6. Tritium Measurements at Los Alamos National Laboratory within Area G an Active Radioactive Waste Disposal Site (1997-1998)