General

# Los Alamos National Laboratory

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Date: April 3, 1998
Refer to: ESH-17:98-179

Mr. John Parker, Chief
DOE Oversight Bureau
New Mexico Environment Department
P.O. Box 26110
Santa Fe, NM 87502

entered

LANL - ES - Air

Dear Mr. Parker:

As part of our continuing effort to improve the Laboratory's environmental surveillance program, Craig Eberhart, an environmental scientist in our Air Quality Group, has been evaluating the air samplers used to collect water vapor and particulate matter from ambient air. From this evaluation, Craig has found a way to improve the accuracy and to simplify the methodology for determining atmospheric tritium concentrations by using meteorological measurements to calculate water vapor concentrations.

Water vapor and particulate matter samples as collected by our surveillance system are analyzed radiochemically and combined with flow rate information to determine concentrations of various radionuclides in ambient air, including tritium present as tritiated water. Our air monitoring network, known as AIRNET, meets the substantive DOE requirements for environmental surveillance (DOE Order 5400.1 - General Environmental Protection Program, DOE Order 5400.5 - Radiation Protection of the Public and the Environment, and DOE/EH-0173T - Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance). These requirements include guidelines suggesting that silica gel "... collects essentially all of the moisture." As such, we have used silica gel for many years. However, Craig's review of water vapor collection efficiency, which is attached, indicates that this is probably not the case for our AIRNET samplers.

Mr. Eberhart compared water vapor concentrations from meteorological measurements (traceable to NIST standards) to water vapor collected by the AIRNET silica gel as an independent and effective method of verification. Basically, the AIRNET system collects a maximum of two to three grams of water per cubic meter of air sampled, even when concentrations are as high as ten grams per cubic meter. Since the collection mechanisms of silica gel are very complex and only generally predictable, correction for silica gel collection efficiencies would not be accurate or easy. Instead, we intend to use water vapor concentrations, as determined by the meteorological measurements, along with the radiochemical analysis of the water vapor collected on the silica gel to determine ambient concentrations of tritium.

There are data that indicate the concentration of tritium in the water vapor samples are representative of the concentrations in the atmospheric water vapor, but the data are not as definitive as the data for water vapor collection efficiency. Craig has initiated a series of relatively simple tests to determine if the samples are representative. If the samples are not representative, other collection methods will be evaluated and considered for possible use, but this is a longer term issue.

Since we will be calculating current and future ambient concentrations of tritium using a more accurate method of determining atmospheric water vapor than used in the past, it is appropriate to re-evaluate historical data. Recalculated ambient tritium concentrations, including the effective dose equivalents, will generally increase by a factor of two to three with a possible worst case scenario of five. If this worst case five-fold increase were applied, for example, to the 1996 tritium doses from the 17 AIRNET compliance stations employed by the Laboratory and specified by the FFCA, the maximum dose would increase from 0.013 millirems to 0.065 millirems. Even if these five-fold increases in dose were realized, the total AIRNET-measured doses from tritium, uranium, plutonium, and americium would still be less than two percent of the EPA National Emission Standard that limits public exposures from DOE facilities to a maximum of 10 millirems (40 CFR Part 61 Subpart H).

We have notified the US Department of Energy as to possible broader application of these conclusions. We are providing similar notifications to the US Environmental Protection Agency and various stakeholders about this issue.

Please contact Craig Eberhart (505-667-2917) or myself (505-665-8855), if any additional information is required.

Sincerely,

Douglas Stavert
for Group Leader

Att.: ESH-17:98-142, "Water Vapor and Tritium Collection Efficiency of Silica Gel"

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NATIONAL LABORATORY
# memorandum
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ESH-17 Air Quality Group

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## WATER VAPOR AND TRITIUM COLLECTION EFFICIENCY OF SILICA GEL

### Summary

Recent data analyses indicate that the AIRNET silica gel canisters are not collecting all of the water in the air being sampled. If 100 percent of the water is not collected, then atmospheric water vapor, and therefore tritiated water, will be underestimated because the amount of water collected on the silica gel is used to measure water vapor concentrations. This memorandum discusses these analyses, potential causes and proposes to use meteorological humidity measurements to calculate ambient water vapor concentrations and ambient tritium concentrations.

### Introduction

The LANL AIRNET 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 $cm^3$. This silica gel is dried in a drying oven before use in the field to remove any 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 various DOE documents, such as the Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance (DOE/EH-0173T), this process is recognized as a method for collecting essentially all of the atmospheric moisture. The air flow rate through our silica gel canisters is typically 200 $cm^3$/min. The water mass is determined by the difference in the start and ending weights of the silica gel canisters or by measuring the water collected by condensation of the distillate. Before late 1992, when new AIRNET samplers were deployed, the silica gel canisters were located outside the sampler housing. Since late 1992 the canisters have been located inside the housing.

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 memorandum does not evaluate the radiochemical analysis process, but the radiochemical analyses are used in calculations to demonstrate the effects of water vapor measurements on ambient tritium concentrations.

**Water Vapor Collection**

As part of my recent efforts to develop an integrated plan for characterizing the AIRNET samplers, I have been evaluating some possibilities for testing the water vapor collection efficiency of the silica gel. I had planned to serially connect two silica gel canisters to estimate the penetration and breakthrough of water vapor. Penetration is water vapor that is not collected for whatever reason. Breakthrough is caused by the silica gel water absorption capacity being depleted which will increase penetration to 100 percent. Water vapor that penetrates the first canister will probably not be collected on the second canister *unless* this penetration is caused by breakthrough. Therefore, this experiment would not measure the penetration that occurs before breakthrough.

There has always been an implicit assumption that silica gel penetration was relatively small unless breakthrough occurred. In *The Procedures Manual of the Environmental Measurements Laboratory* (HASL-300), it stated that the water vapor absorption capacity of silica gel could be as small as five percent under low humidity conditions. This means that the AIRNET water vapor collection capacity could be less than seven grams for many of the two-week collection periods in Los Alamos. Manufacturer data also indicate that capacity decreases with relative humidity (see Figure 1). In addition to breakthrough occurring earlier than expected, I also became concerned that the last few percentage points of atmospheric moisture may not be collected at all unless the contact time with the silica gel is greatly increased. For example, if silica gel does not collect water vapor below 5% relative humidity the negative bias would be 6.25% for 80% relative humidity. If the relative humidity was only 10%, and the collection capability did not change, the negative bias would be 50%. In both cases, air with 5% relative humidity would be exiting the silica gel canister, but the percent underestimate during low humidity conditions would be much greater.

These thoughts led me to compare of the AIRNET water vapor collection numbers to the meteorological measurements of humidity. With the assistance of Ernie Gladney, Jeff Baars, and Jake Martinez, I was able to collect the data necessary for comparing water vapor data for 1990 and 1994 through 1997. Figure 2 is a comparison of the White Rock AIRNET stations and the TA-54 meteorological tower data. The meteorological data used in this comparison were fifteen minute data averaged over the actual two-week sample period for the Nazarene Church AIRNET sampler (Site #32) during 1997. The White Rock data were used for several reasons: They were all relatively close to the TA-54 meteorological tower; the 1997 data reflect our current operating practices; and there are several other White Rock sites with similar collection schedules, elevations, and weather conditions.

Simply stated, the White Rock data indicate that the AIRNET samplers appear to be collecting as little as 20 percent of the total moisture during the summer months when the water vapor concentrations are highest. This result was so unexpected that I did the same comparison for the TA-49 meteorological tower versus the AIRNET samplers on the west side of the Laboratory. Again, the AIRNET results, as shown in Figure 3, were much lower than the meteorological data.

There was one anomalously high value of about 13 g/m$^3$ at Site 77, but the amount of air sampled was only slightly more than one cubic meter (about 25% of the normal volume).

Figure 4 compares the two sets of meteorological data. The TA-54 tower near White Rock is at a lower elevation than the TA-49 tower and therefore in an area with less annual precipitation, but the water vapor concentrations are slightly, but consistently higher because they are calculated on an a actual cubic meter basis. However, this comparison indicates that two-week averages for humidity are relatively constant within and near LANL boundaries. It also indicates that a day or two difference in sampling time is insignificant. Therefore, I averaged the AIRNET data across all of the sites and compared it to the average of the TA-49 and TA-54 data (Figure 5). Once again the same pattern emerges: the water vapor concentrations as measured by meteorological data are higher especially in the summer.

## Potential Causes

As noted above, the highest calculated concentration of water vapor in 1997 White Rock sample was for a sample associated with a small air volume. Having the highest vapor concentration associated with the lowest air sampling volume when the number of samples is 226 is probably more than coincidence. This anomaly could be due to a wide variety of factors including data entry errors, water already resident on the sample, water collection during sample handling, etc. However, I decided to explore the possibility that capacity is low and/or is reached early in the sampling process by plotting the distribution of water weight gains by year. These data are plotted in Figure 6 for 1990 and 1994 through 1997. If the amount collected levels off, as it does for 1994 through 1997, capacity may be a problem.

The data for 1990 do not appear to level off like the later years possibly due to the silica gel canister being located outside the AIRNET housing, where the temperature would be lower, or due to the longer sampling period (one month). These1990 data are plotted in Figure 7. As with later years, the AIRNET water vapor collection efficiency appears to be low during the summer months even though the mass of water collected is approximately double that collected for 1994 through 1997. This indicates that sampling time may be a factor.

The 1990 AIRNET data has not been through the rigorous data review that is now used to accept or reject all ambient monitoring data. There are some problems with this data. For example, December and October are the two most humid months for 1990 according to the AIRNET data, but the meteorological measurements indicate below average absolute humidity (g/m$^3$) and below average relative humidity. This particular problem may have been caused by a change in field personnel in the Fall of 1990.

Since heat is used to remove water from the silica gel, it's clear that the temperature can be a major factor in capacity. However, ambient temperatures and even temperatures in the housing may not be high enough to greatly affect water vapor collection. Figure 8 is a plot of average temperature versus the calculated water vapor concentration for 1997. It does appear that there could be a small decrease in collection capability in the warmest part of the year, but the decrease is not dramatic.

**Tritium Concentrations in the Water Vapor Samples**

Even though it appears that we are not getting an accurate estimate of the ambient water vapor concentrations, it is possible to use humidity measurements to reconstruct ambient concentrations if the tritium measurements in the distilled water samples are representative of the ambient proportions. The extensive quality assurance process in place for analytical chemistry indicates that the analysis for tritium in the water sample is a good estimate. Two other factors could prevent accurate estimates: water vapor collection for only part of the sampling period or residual water when the sample is deployed.

As previously noted, the silica gel may not be collecting a sample throughout the sampling period, but diffusion into and out of the silica gel may make it representative of the two week period. Our current data do not provide enough information to evaluate this issue. Even if the two-week sample is not representative of the entire two weeks, a larger group of samples, such as the 26 two-week samples used for calculating annual averages will be representative of the annual concentrations. If there is a change in collection efficiency within a two-week sampling period and there is not significant water exchange between the air and the silica gel, one could attempt to argue that a short-term release of tritiated water is not representatively sampled. This would be true but disingenuous because <u>any</u> sampling activity is subject to the same criticism. 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 it should represent a random sample because the diffusion rates and the frequency of changing the silica gel should not be related to releases from LANL.

Residual water on the sample can be evaluated. Fifty-two trip blanks were "collected" and analyzed in 1997. These trip blanks are spiked with about 10 grams of well water per sample. The amount of water recovered in the distillation process is normally within a gram of the spike amount indicating that there is little or no water present when the sample is deployed. Very low tritium concentrations are present in the recovered water which would indicate that any residual water, if it present, is not a significant source of tritium. Using a water sample spike with a tritium spike might provide more definitive information about the presence of residual water.

**Recalculating Ambient Tritium Concentrations and Doses**

Three sites were selected for recalculating atmospheric tritium concentrations: Santa Fe (#3), Eastgate (#10), and Area G (#35). Ambient concentrations of tritium for most of 1997 were calculated using AIRNET water volumes and meteorological measurements of humidity. These three sites were chosen as examples because they represent background or regional concentrations (Santa Fe, site #3), the MEI site impacted by LANL emissions (Eastgate, site #10), and an on-site location with controlled access that has the highest AIRNET-measured concentrations of tritium due to evaporation and transpiration of tritiated water from buried radioactive waste (Area G - site #35). These recalculated values are shown in Figures 9 through 11 with a summary of the data in Table 1.

For Santa Fe, the estimated concentrations and doses were 31 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 1.88 pCi/m$^3$ to 4.23 pCi/m$^3$. The estimated dose increased at the same rate, 2.25 times, to .028 mrem. This dose is still low, but it represent a reasonable estimate because most of the these analyses are above the MDA.

The Area G concentrations increased from 231 to 701 pCi/m$^3$. The calculated ambient concentrations at this site increased more than the concentrations at the Eastgate site (3.04 times vs. 2.25 times) 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 1.5 to 4.7 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

It's clear that we underestimate water vapor concentrations in the summer due to higher temperatures, higher water vapor concentrations, and/or low silica gel absorption capacity. The causes and mechanisms are still being evaluated and will probably require some limited testing. However, if the meteorological measurements of ambient water concentrations are valid, we will only need to determine if the tritium measurements in the collected water are representative of the concentrations in the ambient water vapor. Even though we underestimate water vapor concentrations, our data indicate that we do see definite patterns in ambient tritium concentrations such as the high values at site 35 (TA-54, Area G-2, back fence) and higher concentrations at Eastgate than in Santa Fe which indicates that we are collecting comparable samples. I propose to lead the efforts to address the following technical issues: testing the silica gel; implementing a process to calculate ambient tritium concentrations using meteorological measurements; and evaluating the need to recalculate historical tritium data.

CFE:db

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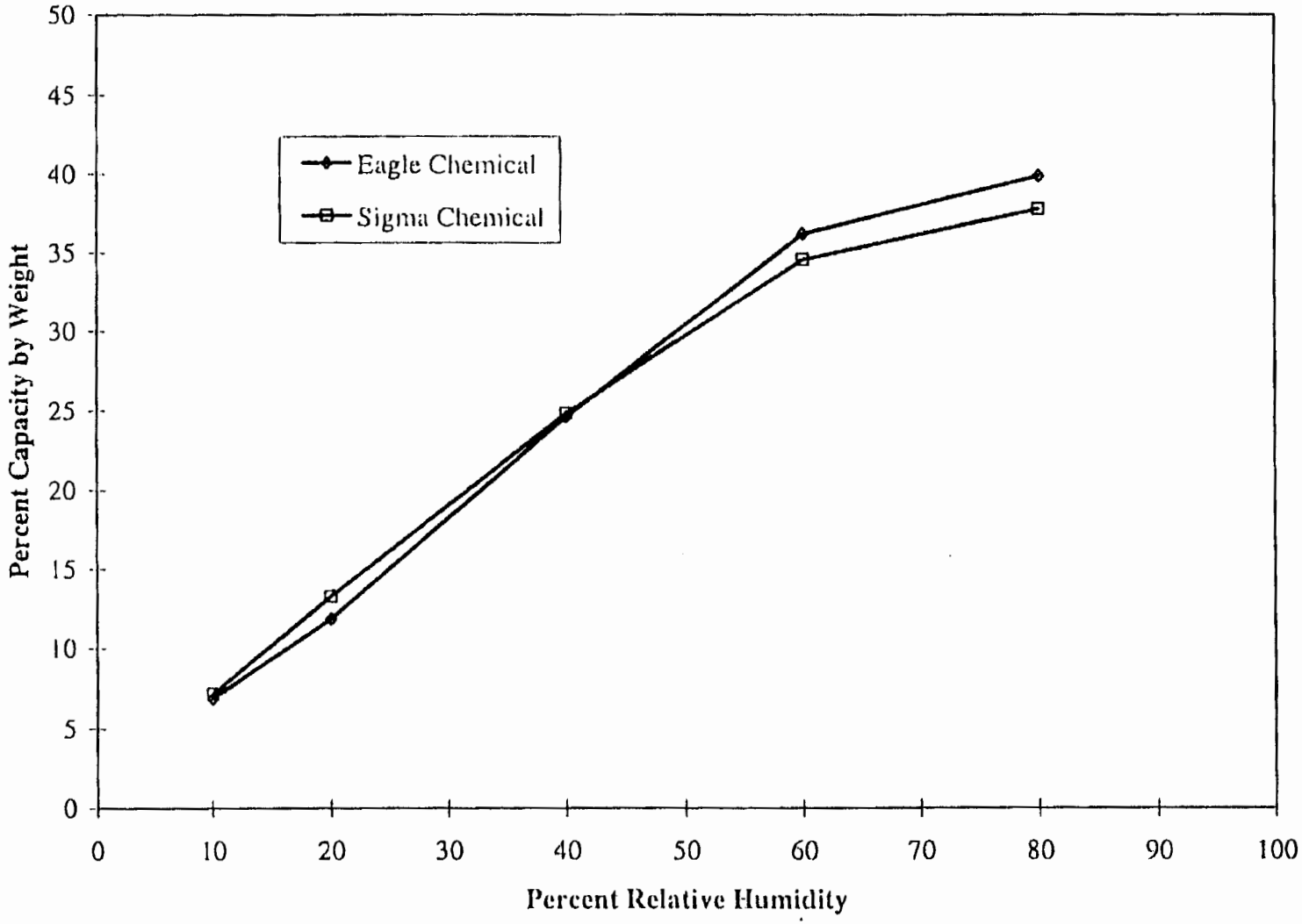
ESH-17 File

Figure 1. Collection Capacity of Silica Gel versus Relative Humidity



# Figure 2. Atmospheric Moisture in White Rock

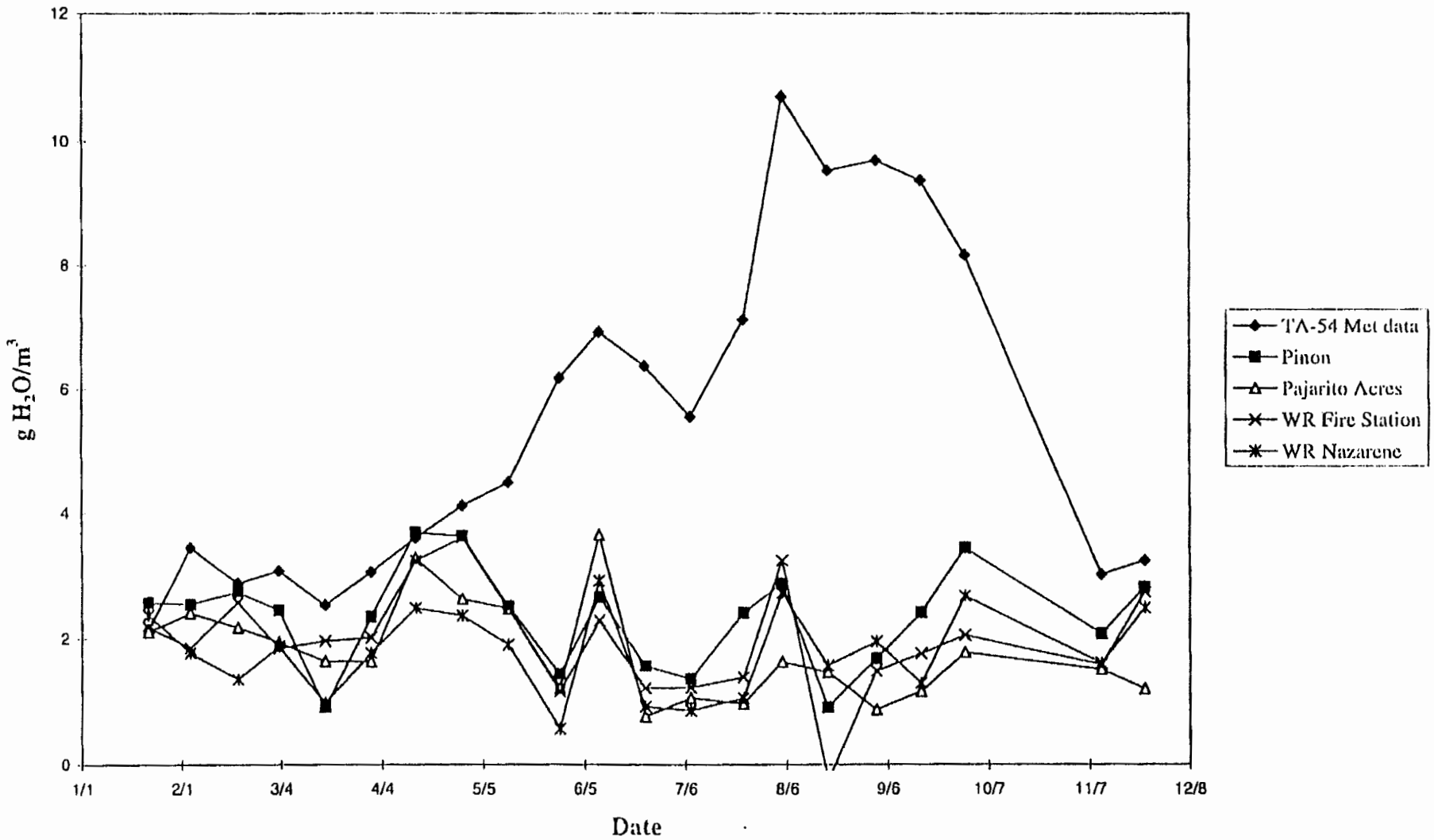


Figure 3. LANL-West Water Measurements
(>2m$^3$ sampled)

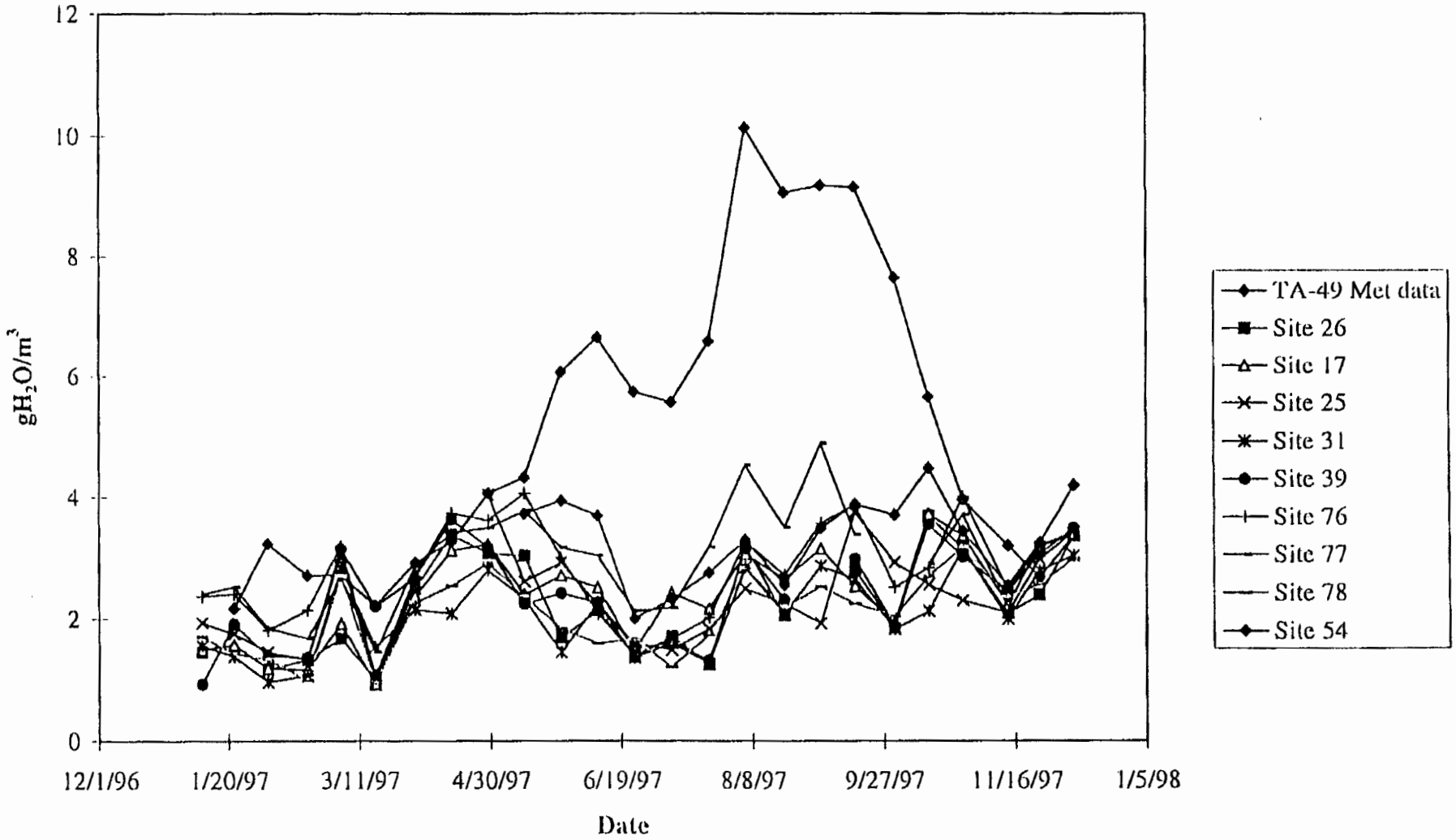


Figure 4. Comparison of TA-54 and TA-49 Meteorological Water Vapor Concentrations

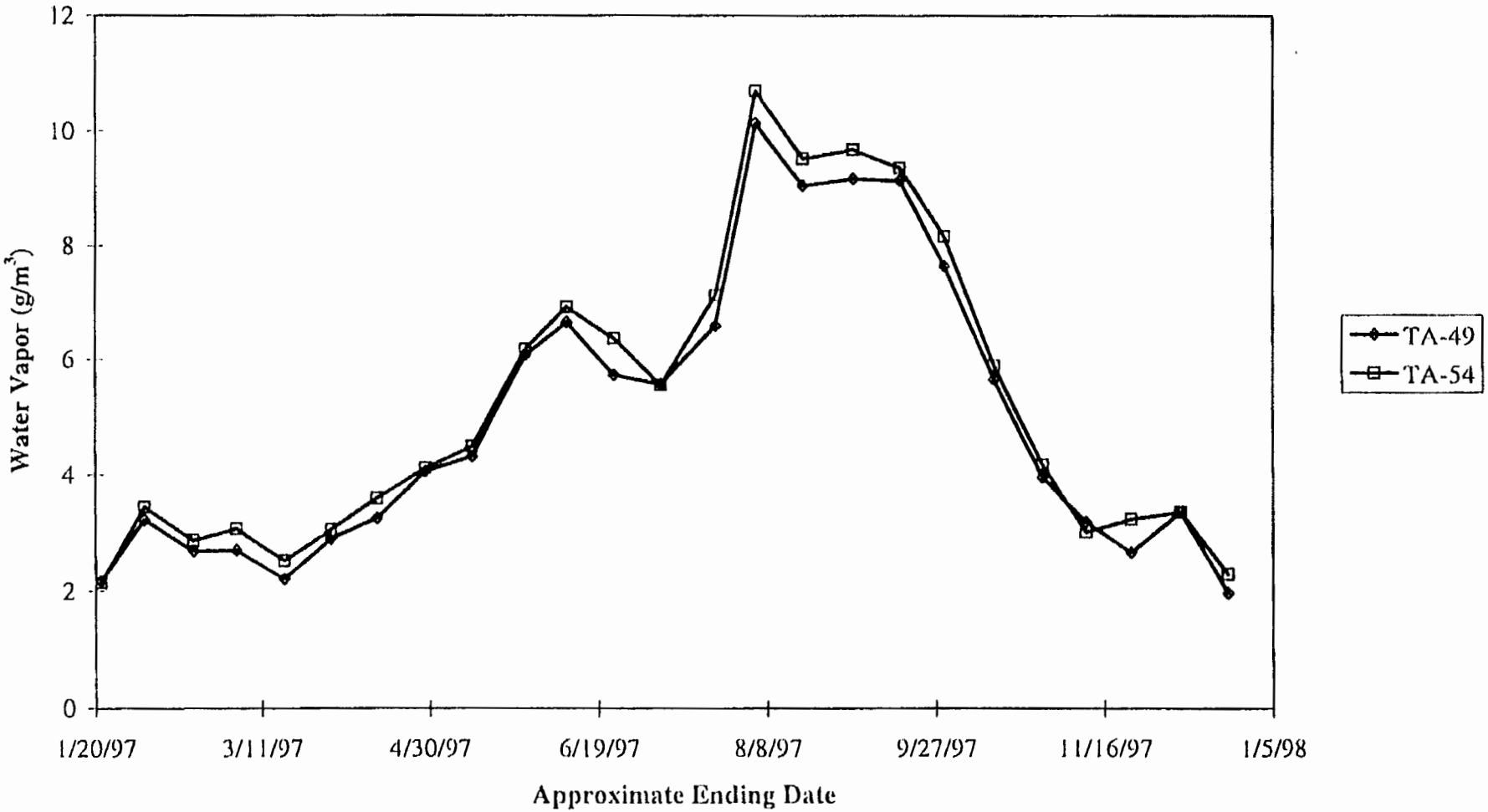
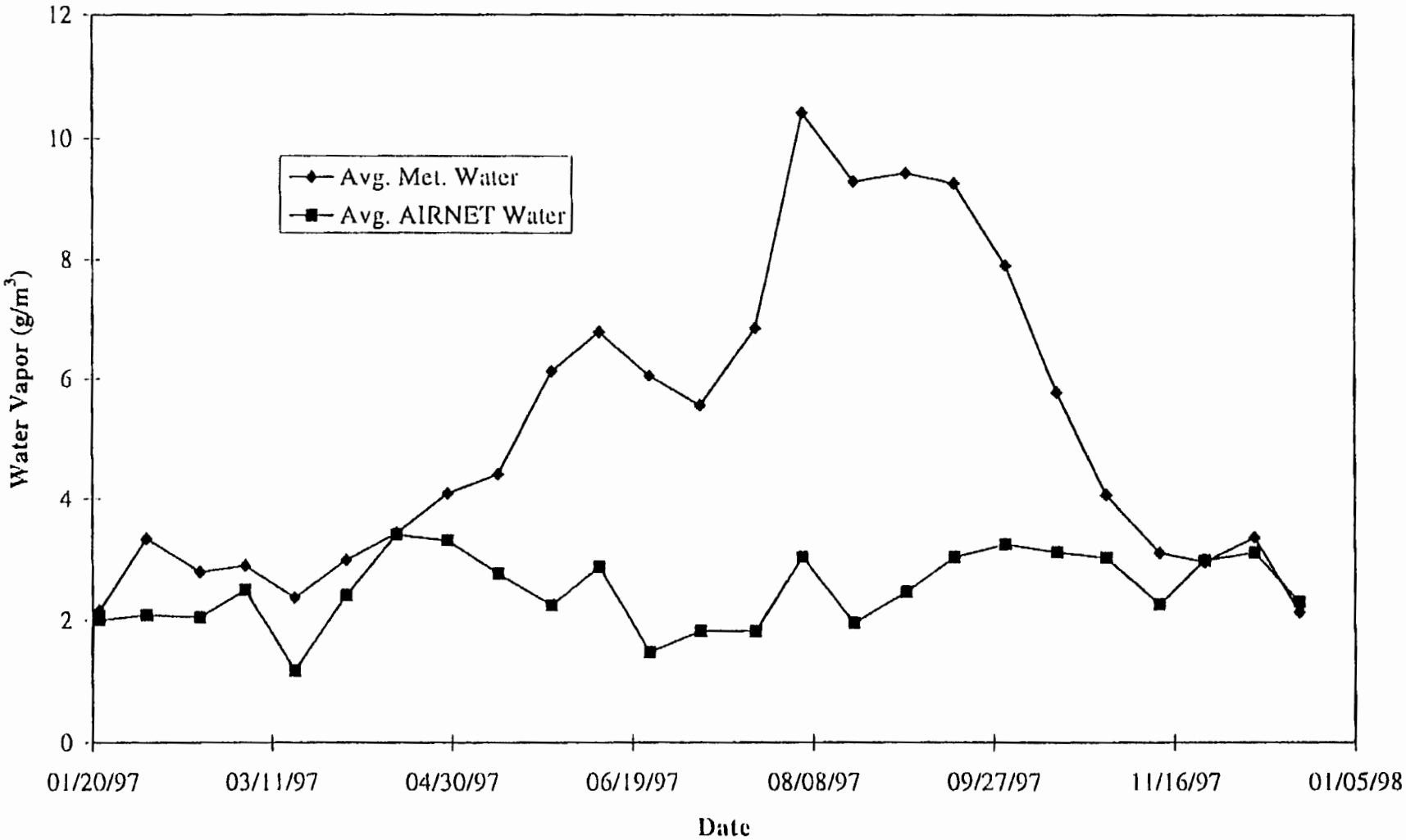


Figure 5. Comparison of Water Vapor Concentrations - 1997



# Figure 6. Water Vapor Collection Data by Year

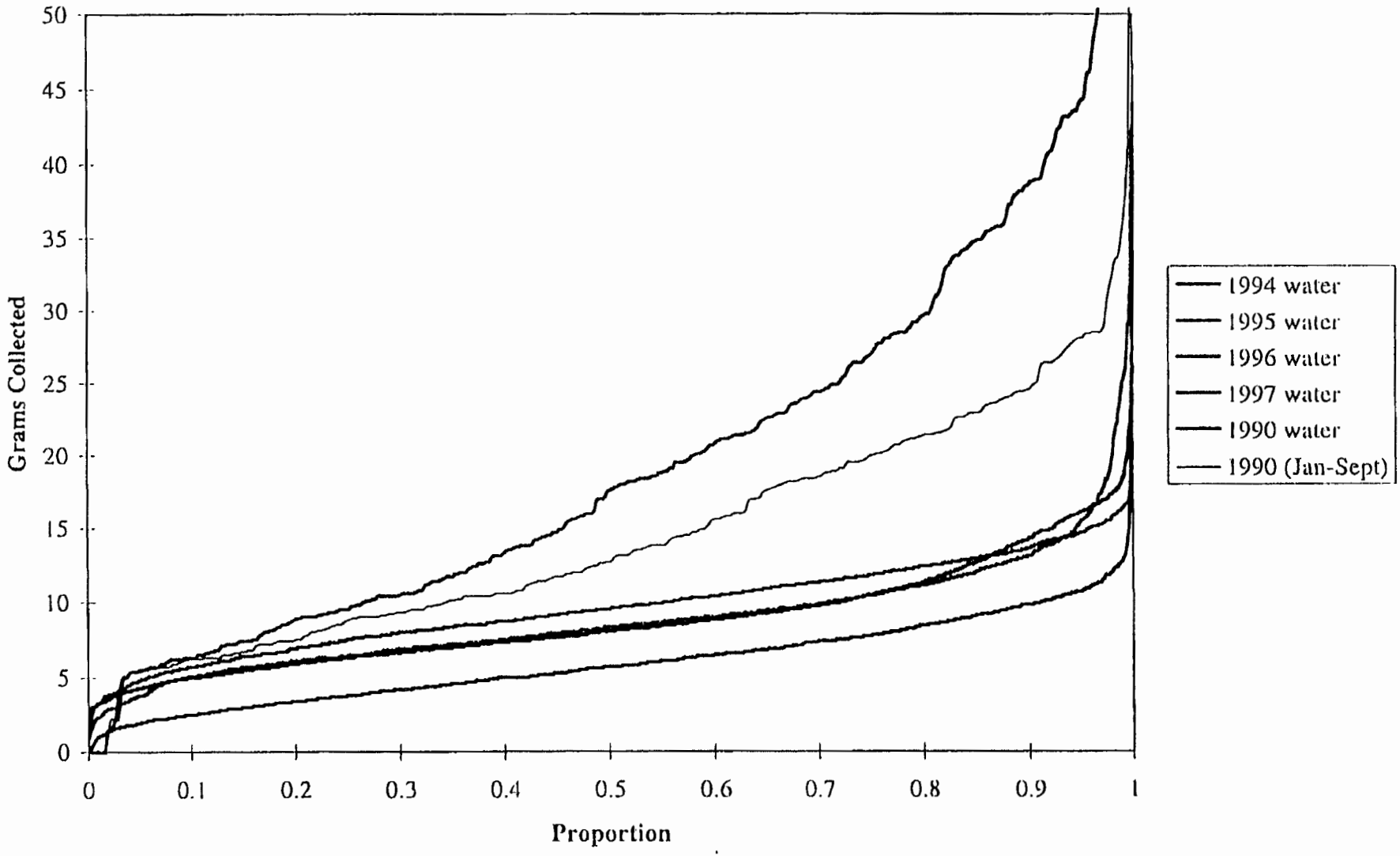


Figure 7. Water Vapor Measurements for 1990

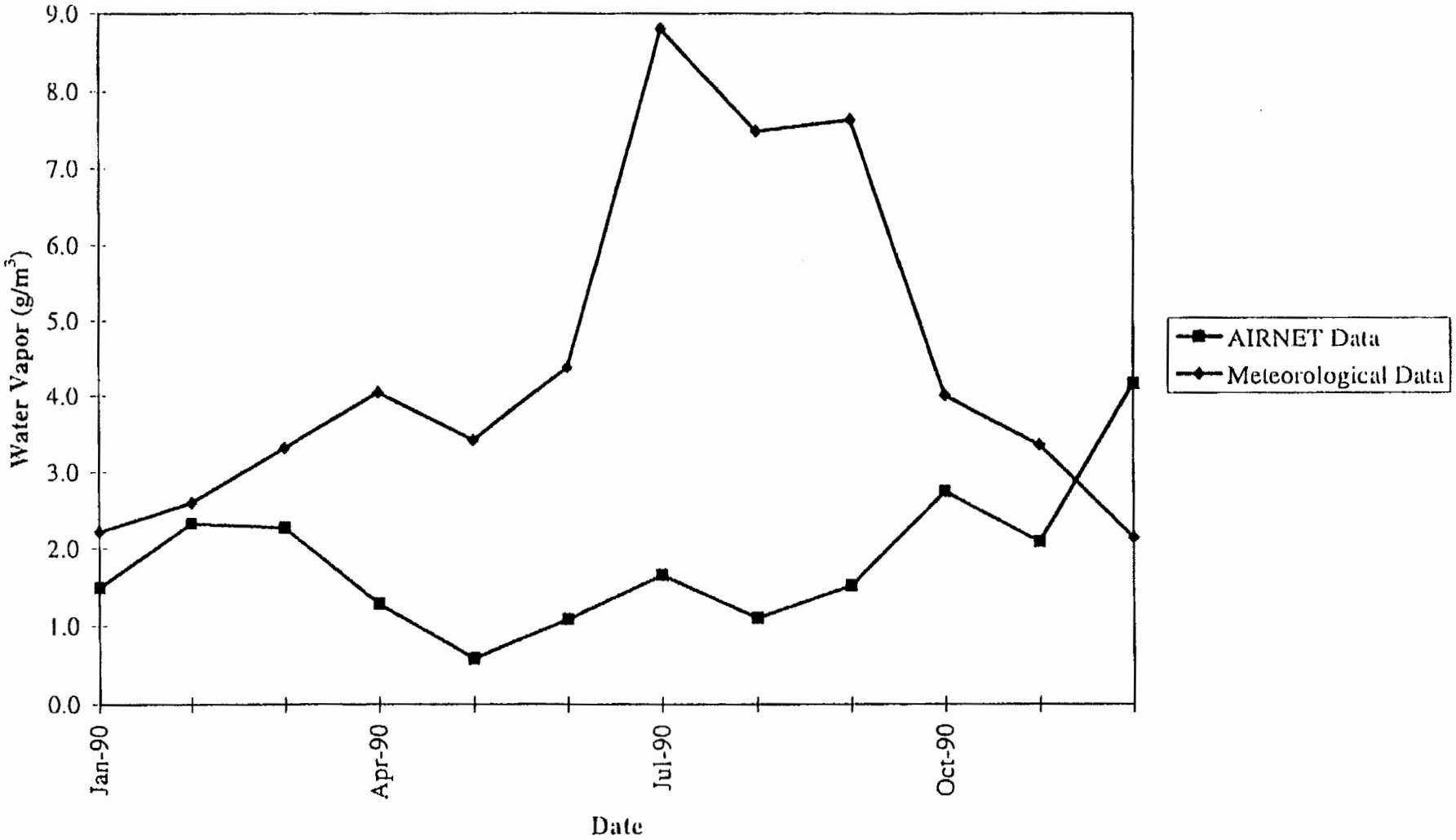


Figure 8. Temperature and Water Vapor from Meteorological and AIRNET Sampler Data (1997)

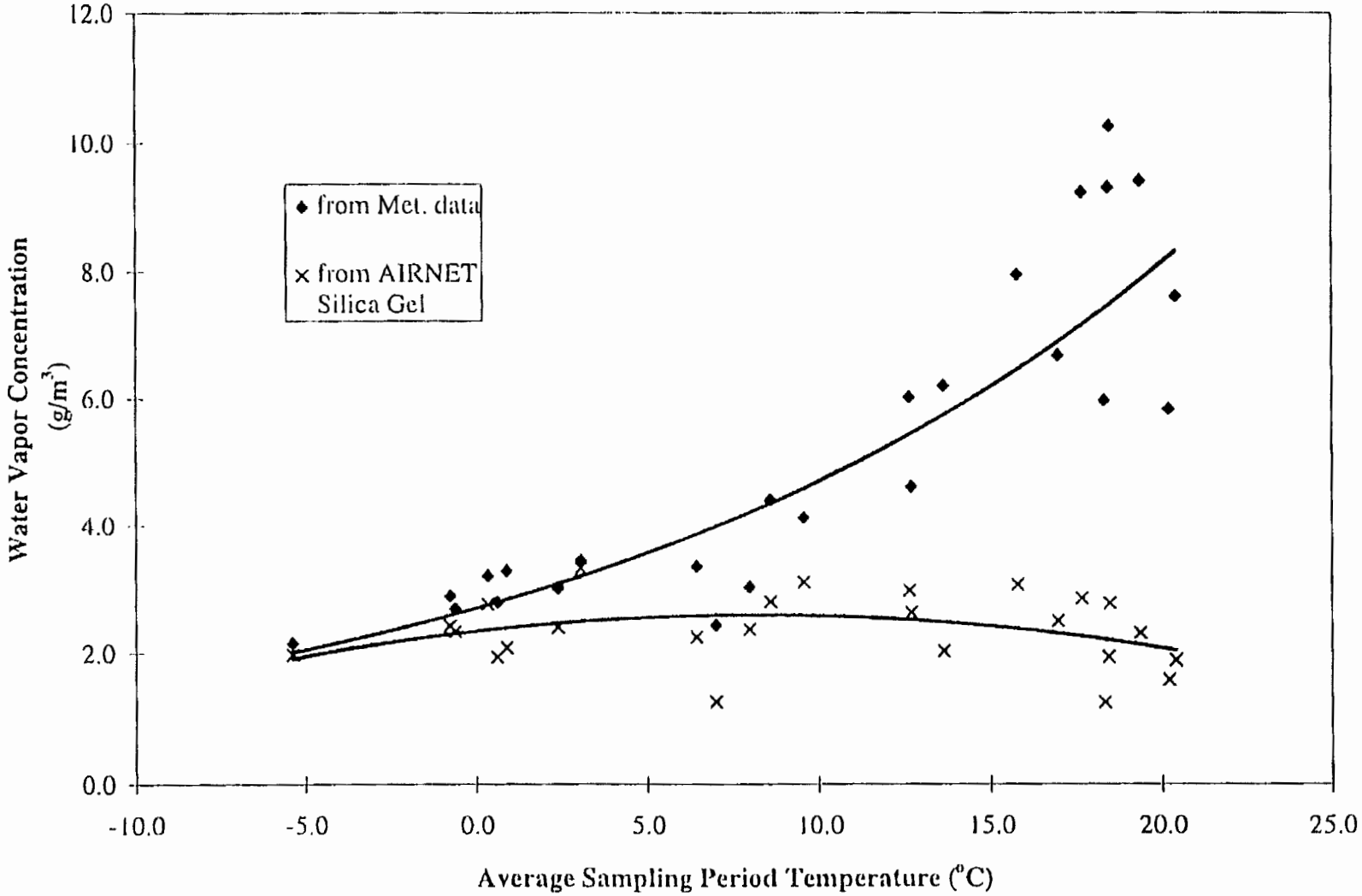


Figure 9. Tritium Concentrations Using AIRNET and Meteorological Water Measurements - Santa Fe

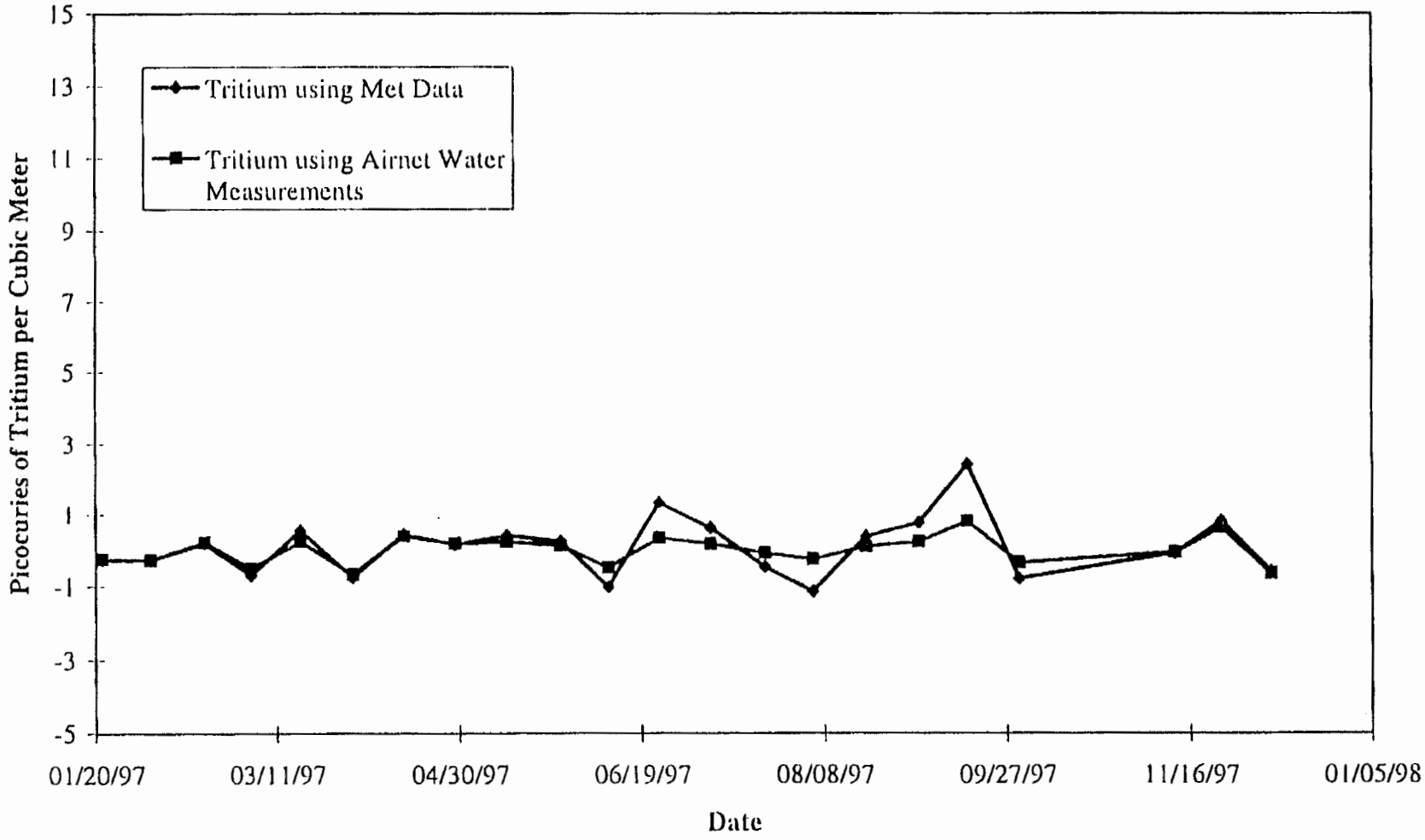


Figure 10. Tritium Concentrations Using AIRNET and Meteorological Water Measurements - Eastgate

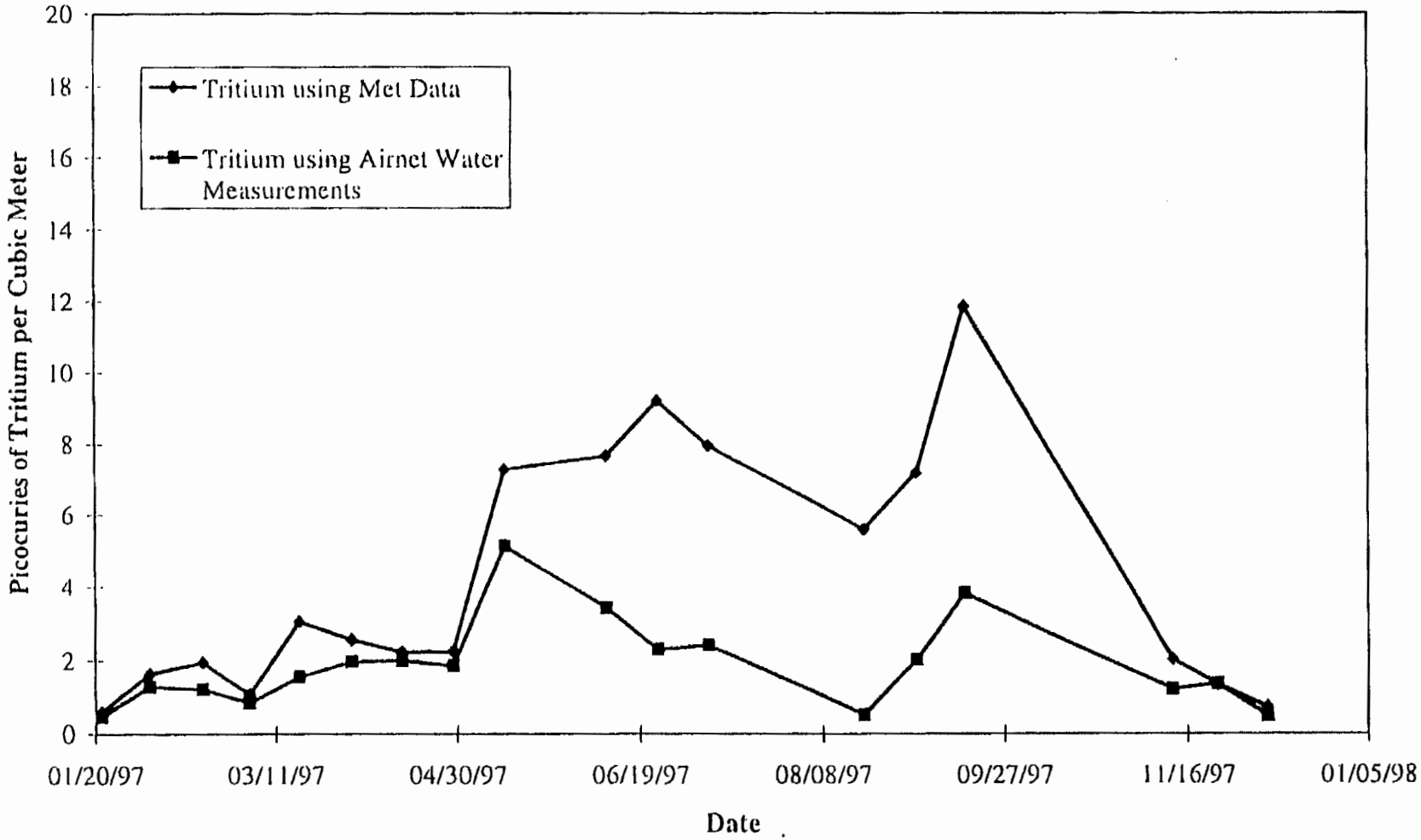


Figure 11. Tritium Concentrations Using AIRNET and Meteorological Measurements - Area G (site 35)

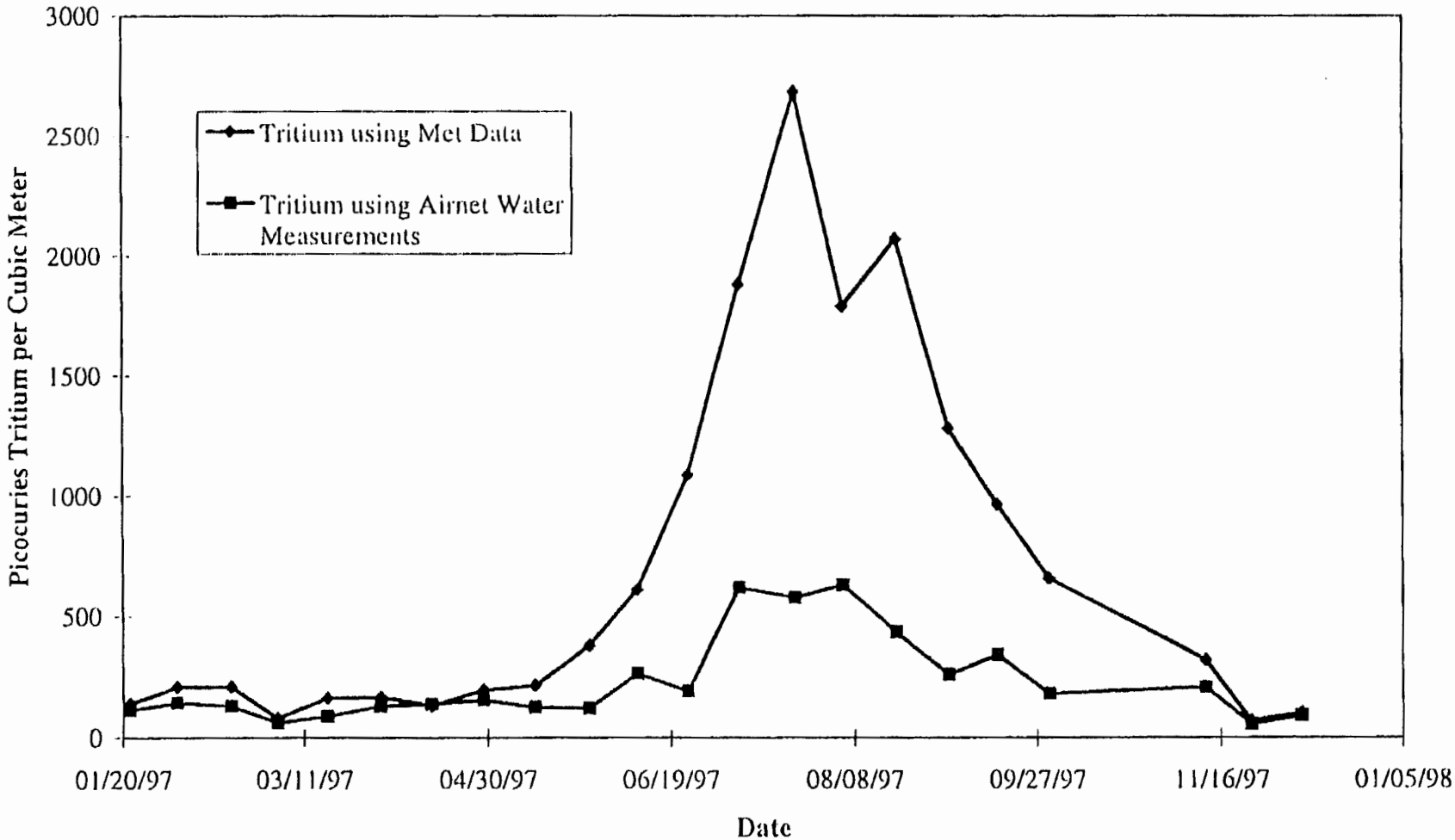


Table 1. Average Tritium Concentrations[1] and Estimated Dose[2]

| Sampling Site | Water Vapor Data Source | | Ratio |
|---|---|---|---|
| | AIRNET | Met Data | |
| Santa Fe (#3) | 0.003 pCi/m$^3$<br>.000021 mrem | 0.098 pCi/m$^3$<br>.00066 mrem | 31. |
| Eastgate (#10) | 1.88 pCi/m$^3$<br>.013 mrem | 4.23 pCi/m$^3$<br>.028 mrem | 2.25 |
| Area G (#35) | 231 pCi/m$^3$<br>1.5 mrem | 701 pCi/m$^3$<br>4.7 mrem | 3.04 |

[1]As calculated from the data graphed in Figures 9 through 11 (This includes most, but not all 1997 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 mrem