P1.4 MEASUREMENTS OF BERYLLIUM-7 AND OZONE AT DEER PARK DURING THE TEXAS 2000 AIR QUALITY STUDY

Jeffrey S. Gaffney* and Nancy A. Marley
Argonne National Laboratory

1. INTRODUCTION

During the past few years, Houston, Texas, has surpassed Los Angeles in having the highest levels of ozone in an urban area. The Texas 2000 Air Quality Study was conducted during the summer of 2000 to assess the reasons for this high ozone production. One possible source is ozone transported from aloft. Natural radionuclides have been proposed for use in monitoring the transport of ozone and aerosols in the troposphere (Gaffney et al. 1994, 1995). For example, ^{7}Be is known to be produced in the upper troposphere and lower stratosphere by interactions with cosmogenic particles. Beryllium-7 has a 53.28-day half-life and is a gamma emitter that attaches itself to fine particles in the atmosphere once it is formed. Indeed, in tropospheric aerosol samples ^{7}Be is typically found in association with aerosol particles that are 0.3 μm in diameter. Some investigators have asserted that ozone from aloft can be transported into rural and urban regions during stratospheric-tropospheric folding events, leading to increased background levels of ozone.

2. EXPERIMENTAL METHODS

During the Texas 2000 Air Quality Study, aerosol samples with a 2.5-μm cutoff were collected at the Deer Park, Texas, site during 12-hr cycles (day/night) for a 30-day period in August-September 2000.

High-volume samples were collected on glass fiber filters to monitor ^{7}Be levels at the field site on Julian days 225-259. The site, located near a city park and at a distance from traffic, is under routine operation by the Texas Natural Resource and Conservation Commission. Instruments operated at this site during the study period included an ozone monitor (Dasibi), a nitrogen oxides instrument (API), a CO instrument (API), a nephelometer, an ultraviolet-B peroxyacetyl nitrate (PAN) measurements were made by using a fast gas chromatograph with luminol detection (described in another presentation at this meeting). This paper focuses on the ozone and ^{7}Be data.

Air samples were collected on filters for analysis with a high-volume air sampler. The system incorporated a Sierra cascade impactor with only the stage two inlet, which has a nominal 2.5-μm cutoff for the sample aerodynamic diameter. Thus, the air samples were less than 2.5 μm in size. Whatman glass fiber filters (8 in. x 10 in.) were used to collect the samples in approximately 12-hr cycles with a General Motor Works Model 2000 pump. Sampling rates were 720 m^{3} per day.

The filters containing the aerosol samples were folded once and placed in labeled manila envelopes that were then put into sealable plastic storage bags. Gamma counting was performed by using a EG&G Ortec 92x Spectrum Master System with a high-purity germanium (HPGe) coaxial detector (GEM-115220-P-S). This system was operated with EG&G Ortec software and a Gateway 386 personal computer. The HPGe crystal detector, 82.7 mm in diameter and 92.2 mm in length, was operated with a positive-bias voltage of 3,000 V. Under these conditions the resolution of the system was 1.81 keV. Lead and steel bricks were used to shield the detector from background radiation. Background counting rates, taken during the entire measurement period, were 3.1 counts per minute. After samples were received for counting, each filter was folded twice and placed in a glass petri dish to establish consistent geometry for the gamma measurements. Under these conditions the 477.6-keV peak was easily measured.

Samples were corrected for system background, for the 53.29-day half-life decay of the ^{7}Be, and for the 10.39% gamma emission rates for the beryllium activity in disintegrations per minute (Browne and Firestone 1986). Data were then converted to mBq m^{-3} by using the sampled air volume and converting to the Bq units (disintegrations per second).

* Corresponding author address: Jeffrey S. Gaffney, Environmental Research Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439. email: gaffney@anl.gov.
meter (Richardson-Berger), and a multifilter rotating shadow band radiometer (Yankee Environmental Systems). In addition, modified fast-response NO_2 and

Samples of ^{7}Be with known activity, obtained from the Argonne's Environment, Safety, and Health Division (ESH/ANL), were run on the system as secondary calibration standards. The original high-volume air analyses were performed by ESH/ANL against standards from the National Institute of Standards and Technology (NIST). Thus, the secondary standards were traceable to NIST standards. Samples were also allowed to decay, and the decay rate was noted to back-calculate ^{7}Be activity measured with the Environmental Research Division (ER/ANL) HPGe detector. These analyses enabled determination of a geometry factor of 7% for the samples analyzed in petri dishes. Comparison of Argonne standards measured in this way demonstrated good agreement between our calibrated system with the 7% correction factor and the secondary standards (see Table 1). A least-squares fit to the data set yields

(ER/ANL result) = 1.047(ESH/ANL result) – 0.014 ,

with an R^2 value of 0.9896.

Table 1. Comparison of results for high-volume air filter samples, as measured by ER/ANL and ESH/ANL (NIST-traceable standard).

Sample	ESH/ANL (mBq m^{-3})	ER/ANL (mBq m^{-3})
1	2.17	1.92
2	1.97	1.65
3	5.35	5.40
4	1.57	1.65

Errors in the analysis are expected to be less than 5%, on the basis of this analysis and the calibration for the counting portion of the work. The results reported here are the corrected activity, specifically the ^{7}Be concentration at the time of the sampling, calculated by taking into account the measured activity and the time lag between sampling and counting for the 53.28-day half-life of ^{7}Be. These data can be converted to pCi m^{-3} by multiplication by the conversion factor 0.4509. During this study, we also obtained a number of samples taken by others at sites in the region at approximately the same time. Samples were obtained at the Clinton site at Galveston, CAMS-34; Harris Co. NW, CAMS-26; and Harris Co., CAMS-8. These data indicate that the Deer Park values are in good agreement with the other values and are representative of the regional ^{7}Be levels for this time period. Details have been reported elsewhere (Gaffney et al. 2001).

3. RESULTS AND DISCUSSION

To identify correlations, we compared the results for ^{7}Be with ozone maxima and average ozone levels at the site during 12-hr periods. Figure 1 shows the raw ozone data taken during the field study at 1-min intervals. A number of very high levels of ozone formation were observed, with four periods exceeding 150 ppb and one exceeding 200 ppb.

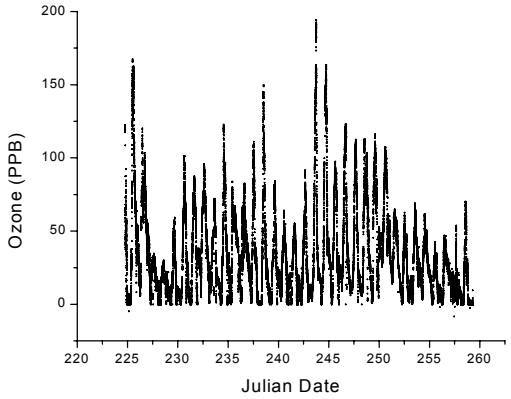

Figure 1. Ozone data taken at 1-min intervals at Deer Park during the Texas 2000 Air Quality Study.

Because the ^{7}Be data were taken over 12-hr periods, we used the ozone data set in Figure 1 to calculate average ozone levels for 12-hr periods for temporal comparison of average ozone (ppb) and ^{7}Be (mBq m^{-3}). The results are in Figure 2.

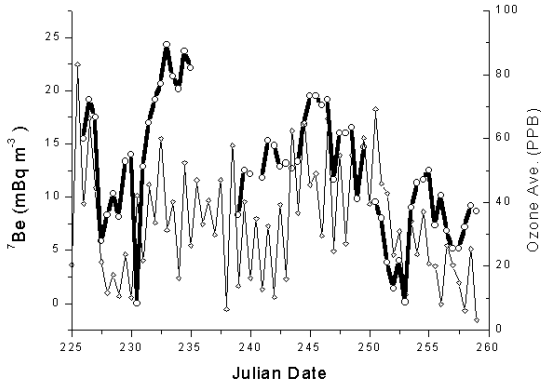

Figure 2. Temporal comparison of ^{7}Be (bold line) in 12-hr samples with ozone averages for the same time periods at the Deer Park site.

For comparison, we plotted the same temporal variation of ^{7}Be with the maximum ozone values during the 12-hr sampling periods (Figure 3).

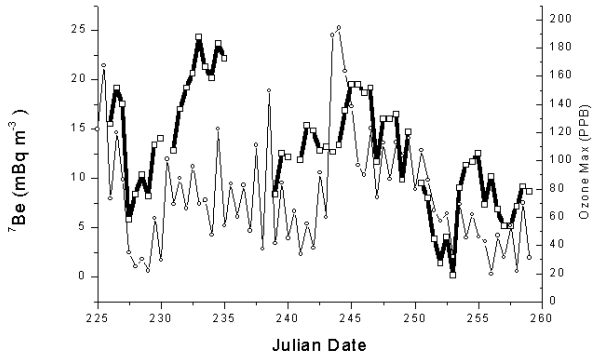

Figure 3. Temporal comparison of ^{7}Be (bold line) in 12-hr samples with ozone maxima for the same time periods at the Deer Park site.

Interesting, a tropical depression affected the Houston area on Julian days 227-228. Initially hurricane and then tropical storm warnings were given for the nearby coastal area, but the storm hit to the west of Houston and Deer Park. However, very clean air was brought into the area, as indicated by the very low ozone levels observed (Figure 1). Concentrations of other trace gas species such as NO_X, CO, and PAN were also very low during this period. Note that the ^{7}Be levels were low during the clean-air episode and higher on the days preceding and following. Figures 2 and 3 demonstrate that local ozone observations were not well correlated with the ^{7}Be increases and decreases. The ozone levels observed during this period were approximately 25 ppb, consistent with background concentrations anticipated for an air mass over the Gulf of Mexico.

To address the potential for transport of ozone into the area from the stratosphere or upper troposphere, we plotted the ^{7}Be data against the ozone averages and ozone maxima for the entire time period. These correlations are shown in Figures 4 and 5, respectively. The figures show that for the entire data set, the correlations are weak, indicating that little ozone was being brought into the area from the upper air masses.

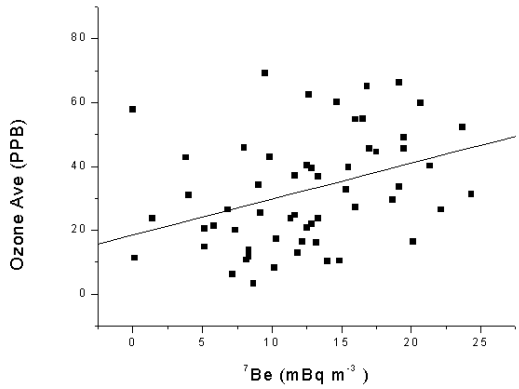

Figure 4. Correlation of ozone averages and ^{7}Be during the 12-hr periods. Linear least-squares analysis gives the following fit: O_3 ave = (1.1 $\pm$ 0.4) [^{7}Be] + (18 $\pm$ 5), R^2 = 0.13.

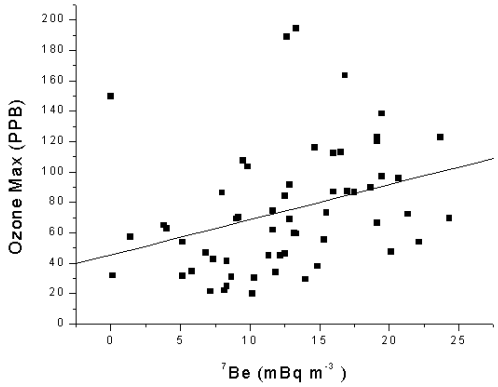

Figure 5. Correlation of ozone maximum values and ^{7}Be during the 12-hr periods. Linear least-squares correlation best-fit equation: O_3 max = (2.3 $\pm$ 0.9) [^{7}Be] + (45 $\pm$ 12), R^2 = 0.10.

Better mixing would be expected during daytime than during nighttime, when the nocturnal boundary layer is established. To test this prediction, we examined the correlation of average ozone values and ozone maxima with ^{7}Be during daytime and nighttime periods in the same time frame. These correlations with ^{7}Be are shown in Figure 6 (daytime ozone averages), Figure 7 (daytime ozone maxima), Figure 8 (nighttime ozone averages), and Figure 9 (nighttime ozone maxima).

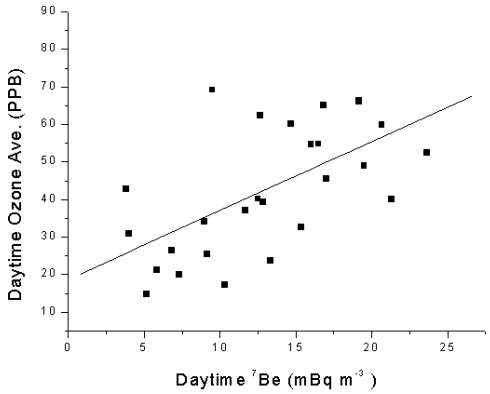

Figure 6. Correlation of daytime ozone averages with ^{7}Be at the Deer Park site: O_3 ave = (1.8 ± 5) [^{7}Be] + (19 ± 7), R^2 = 0.37.

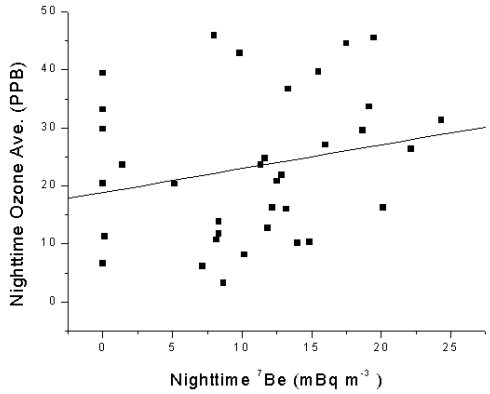

Figure 8. Correlation of nighttime ozone averages with ^{7}Be at Deer Park site: O_3 ave. = (0.4 ± 0.3) [^{7}Be] + (19 ± 4), R^2 = 0.05.

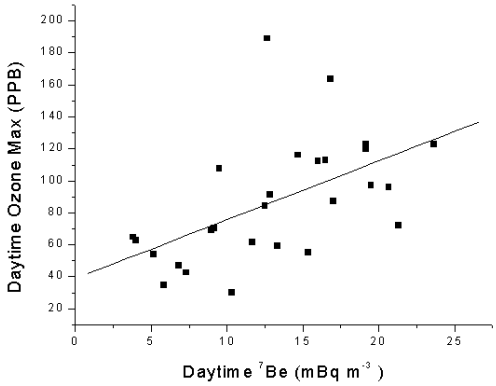

Figure 7. Correlation of daytime ozone maxima with ^{7}Be at the Deer Park site: O_3 max = (3.7 ± 1.1) [^{7}Be] + (38 ± 16), R^2 = 0.29.

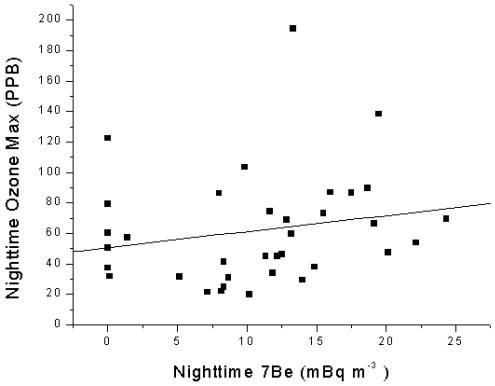

Figure 9. Correlation of nighttime ozone maxima with ^{7}Be at the Deer Park site. Best linear fit: O_3 max = (1 ± 0.9) [^{7}Be] + (51 ± 12), R^2 = 0.04.

The correlations are somewhat better in the daytime data set, as one would expect with better mixing of the upper air masses. However, for both the ozone average and ozone maximum correlations, the linear fits are still not very significant, because the R^2 values are less than 0.4.

The data for the correlations of nighttime ozone with ^{7}Be are consistent with the reduced mixing from aloft expected when the nighttime boundary layer is established. Essentially no correlation is observed. This is also probably tied to the loss of ozone by deposition and its titration at night by NO from local vehicle and industrial sources. Indeed, the Deer Park area, one of the largest industrial and petrochemical industrial areas in the nation and world, has considerable sources of NO and hydrocarbons.

To summarize, we found no significant correlation between the observed ^{7}Be levels at the Deer Park site and either the 12-hr ozone maxima or the 12-hr ozone averages. Although the correlation for ozone and ^{7}Be is slightly better in the daytime than during nighttime, neither correlation is significant. At best, 30% of the ozone variance can be explained by the ^{7}Be correlation (i.e., R^2 ~ 0.3, see Figures 6 and 7). This result is not inconsistent with the intercept values observed and the low ozone levels during the tropical storm event. That is, ozone background levels are 15-40 ppb in this area.

These analyses indicate that ozone exceedances observed during this study at the Deer Park site and at nearby Houston sites are much more likely to have been due to local photochemical formation of ozone than to upper air transport. Indeed, some evidence suggests two possible causes for the very rapid formation of ozone and peroxyacyl nitrates observed in

the Deer Park and Houston region in general: (1) the high levels of reactive hydrocarbons observed in the area and (2) the release of molecular chlorine from local sources, leading to rapid formation of peroxy radicals by the reaction of photochemically produced Cl radicals, which will react with alkanes hundreds of times faster than the rate of the normal OH chemistry.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research, Atmospheric Chemistry Program, and by the Texas Natural Resource and Conservation Commission via the University of Texas, Austin, under contract W-31-109-Eng-38. This work was performed at Argonne National Laboratory.

REFERENCES

Browne, E., and R.B. Firestone, 1986: *Table of Radioactive Isotopes*. V.S. Shirley, Ed., John Wiley and Sons, New York.

Gaffney, J.S., K.A. Orlandini, N.A. Marley, and C.J. Popp, 1994: Measurement of ^{7}Be and ^{210}Pb in rain, snow, and hail. *J. Appl. Meteorol.* **33** 869-873, and references therein.

Gaffney, J.S., K.A. Orlandini, N.A. Marley, and C.J. Popp, 1995: Reply to comments on "Measurement of ^{7}Be and ^{210}Pb in rain, snow, and hail." *J. Appl. Meteorol.* **34** 2106-2109.

Gaffney, J.S., N.A. Marley, K.A. Orlandini, and P.J. Drayton, 2001: *Validation Measurements of Tropospheric ^{7}Be Levels during the Texas 2000 Houston Air Quality Study*. ANL/ER/TR-01/001, prepared for the University of Texas, Austin, by Argonne National Laboratory, Argonne, Illinois, March.