Measurements of Dry Deposition
for Deposition Velocity Model Evaluation

Peter L. Finkelstein
John F. Clarke
Atmospheric Sciences Modeling Division
Air Resources Laboratory
National Oceanic and Atmospheric Administration
Research Triangle Park, NC 27711
(On assignment to Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency)

Thomas G. Ellestad
Atmospheric Characterization and Modeling Division
Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

INTRODUCTION

The U.S. Environmental Protection Agency's (EPA) nationwide network to monitor dry deposition of gases and particles, the National Dry Deposition Network (NDDN), measures not deposition, but concentration of pollutants and meteorological variables relevant to deposition processes. The amount of pollutant being deposited per unit area and time, the flux, is computed as the product of the measured concentration and calculated deposition velocity. Deposition velocity is estimated using an inferential model developed by NOAA's Atmospheric Turbulence and Diffusion Division.[1,2,3] The model simulates the physical and chemical processes of pollutant transfer and absorption by plants and surfaces using measured meteorological and site vegetation variables as input. Annual and seasonal dry deposition as derived from the inferential model and concentration measurements are reported for the 50 site EPA NDDN.[4]

We have recently begun an independent effort to evaluate deposition velocity models by making direct flux measurements and concurrent meteorological measurements needed for the models at several NDDN sites, which differ in terrain, climate, soil, and vegetation cover. The measurement system, instrumentation, and sampling protocol are described briefly herein, along with some preliminary data from our 1994 field program. More detailed analyses are currently underway.

MEASUREMENT SYSTEMS

The system has three major instrument groups; one to measure trace gas fluxes by eddy correlation or gradient techniques, one to measure the components of the energy balance, and one to measure the variables needed by the deposition velocity models; as well as a data acquisition system.

Eddy Correlation Measurements

Fluxes of ozone, sulfur dioxide, carbon dioxide, water vapor, heat, and momentum are measured by eddy correlation. For the gases, ambient air is pulled from the vicinty of (4 cm) a three axis sonic anemometer array ($\simeq$ 5m above ground) through a draft tube and filter to the fast response instruments that are housed in a temperature controlled box at the base of the tower. The fast ozone analyzer, based on the work of Ray et al.[5], employs the chemiluminescent reaction of ozone with eosin-Y dye, which is borne in a carrier of ethylene glycol. Sulfur dioxide is measured by a fast response Meloy model SA-285 flame photometric analyzer operated with a direct inlet line and hydrogen fuel that is spiked with 70 ppb SF_6. Fast response data for water vapor and carbon dioxide are produced by a LICOR model 6262 infrared absorption analyzer.

Draft Tube Considerations.
A key feature of our system is the location of the fast response instruments at the base of the tower in a temperature-controlled box and the use of a draft tube (a 9 m length of Teflon tubing) to draw air from the sonic array to the fast analyzers. We feel that this design represents the best compromise between locating the instruments on the tower and locating them in the support trailer some 50 meters away. The advantages of this approach are: 1) no flow distortion caused by bulky instruments mounted on the tower, 2) minimal sample separation distance for wind speed, temperature, and gases, 3) lighter and smaller towers may be used, 4) easier installation and removal of equipment, 5) more accessible gas analyzers for maintenance and calibration, and 6) corrections for heat flux are not necessary. The disadvantages include: 1) a time delay between the sampling of the wind velocity and the gas concentration (which can be evaluated),

2

2) some loss of high frequency response, and 3) possible draft tube contamination. Locating the instruments in the support trailer would solve some problems, but would require a large flow rate through the draft tube, which might distort the flow field in the vicinity of the sonic array. It may also be untenable for more adsorptive gases such as sulfur dioxide.

Our draft tube is an FEP Teflon™ tube of 0.95 cm inside diameter, 9 m in overall length, with a Teflon filter located 1.5 m from the tube's inlet, and a flow rate of about 20 L/min. These conditions result in a Reynolds number of 3000 and a length/radius ratio of 1900, in accord with the recommendations of Massman[6]. The Teflon filter is used to keep the tube's inner wall from becoming contaminated with particles. As a direct test of the high frequency loss caused by our draft tube, we used our fast response ozone analyzer, which has an inherent response of 5-6 Hz, and sampled a step change in ozone through various configurations. The analyzer's response degraded to about 3 Hz, which is corrected as noted below. About half the attenuation is due to the tube and half to the filter and its holder. Responses for the other analyzers are similarly degraded. The degraded response, with correction, is still sufficient to perform eddy correlation measurements during most atmospheric conditions.

To test the response of the system in the field, and derive the correction for high frequency loss, we examined the co-spectra of the gases with vertical velocity. Figure 1 presents the normalized co-spectra for four gases and the heat flux, $\overline{w'T'}$ taken during mid-day at the Beaufort site. It can be seen that the energy in the co-spectra (the area under the co-spectral curve) for the gases is indeed lower than that for the heat flux at the high frequency end of the spectrum, and that it also falls off more rapidly. This occurs because the frequency response of the gas instruments is not quite as high, as the temperatuare (1 to 3 Hz vs. 10 Hz); and because some high frequency information is lost due to mixing in the draft tube. To see that the heat flux spectrum is reasonable we compare the average of six heat flux spectra taken under good conditions with that proposed by Moore[7] based on Kaimal's Kansas experiment (Figure 2). The agreement at the high frequency end is excellent. An average gas co-spectra, (averaged over the same six cases and four gases) in the figure shows more clearly the area of high frequency loss.

To determine whether or not the assumption that the loss is due in part to the draft tube is reasonable, we consider the transfer function for draft tubes developed by Massman. It is

$$T(\omega) = \exp[-\omega^2 \lambda La/u^2] \tag{1}$$

where

> ω is in rad/sec,
> λ is an experimentally derived coefficient which is a function of Reynolds number,
> $'L'$ is the length of the tube,
> $'a'$ is the radius of the tube, and
> $'u'$ is the mean velocity in the tube.

Using the appropriate tube measurements, one can calculate that a "T" of .5 falls near 9 rad/sec, or about 1.25 Hz. This is in excellent agreement with the frequency at which energy loss occurs. With some confidence, we can now explain the difference in the areas under the heat flux and gas flux curves. The difference in areas, which equals the required correction, is about 17%. This correction,

which is consistent with that suggested by Moore (op cit), is applied to the computed gas fluxes in this study.

Data Quality for Eddy Correlation Flux Measurements. In our measurements of the fluxes of O_3, SO_2, H_2O, CO_2, heat, and momentum using eddy correlation techniques we are concerned that the measurements be as accurate as possible, and not be simply a fortuitous measurement of co-variance without physical significance. Businger[8] presents an excellent review of the theory and practice of trace-gas flux measurements. In that review he lists a number of possible sources of error which should be considered in flux measurements. Among them are: 1) concurrent heat and water vapor fluxes, 2) sampling duration 3) instrument system response time, 4) instrument separation, 5) random noise, 6) entrainment, advection, and non-stationarity, 7) height of sampling above the surface, 8) irregular fetch, and 9) flow distortion near the sampling system. We have attempted to take each of these potential problem areas into consideration, either in the design of the monitoring system, in the field set-up, or in the analysis and correction of the data. Frequency corrections are discussed above. We also examined selected spectra for indications of problems.

Spectral analysis of high frequency data collected by the sonic anemometers and fast gas analyzers can be a good source of information on data quality. Kaimal[9] shows idealized spectra (his Figs 2.1 and 2.4) with regions of energy production, dissipation, and the inertial subrange. Analysis of data by spectral decomposition allow us to observe whether or not problems of advection or non-stationarity, or problems with fetch, flow distortion, or electronic noise are impacting a particular sampling period. Advection and non-stationarity will affect the lower frequencies, causing much higher energy levels than expected in this range. Unusual levels of high frequency turbulence caused by flow distortion or uneven fetch may show up in the inertial sub-range, while electronic noise will usually be seen as a continuously increasing energy with increasing frequency in the inertial sub-range and dissipation ranges. Lack of instrument response will be evident by lack of expected energy at the high frequency end of the spectrum, assuming there isn't compensating noise.

As a further check on data quality, we examine the net energy balance for each half-hour period, to be sure that the flux measurements were reasonable. The net flux balance was computed as the difference of net radiation minus the fluxes of sensible and latent heat, heat fluxes into the ground, and soil heat storage. If any of the systems is not working properly, it is highly likely that it will be obvious in this computation. No time period with a net energy imbalance of >150 w/m^2 were included in the final data base.

Gradient System for Nitric Acid Flux

Nitric acid flux is determined from a two-hour measurement of concentration gradient combined with a vertical exchange coefficient calculated from the temperature gradient and heat flux, similar to the work of Huebert and Robert[10]. Concentration measurements are made using filter packs. They are loaded with Zefluor™ fluorocarbon and Nylasorb™ nylon filters at an analytical laboratory, shipped to the site, sampled at a flow rate of 15 L min^{-1}, and returned to the laboratory. Analysis of the nylon filters for nitrate is usually completed within one to two weeks of sampling. In sampling, the lower units are placed 1-2 m above the vegetation, while the upper units are 7-8 m above the lower units. For quality control purposes, two filter packs were used at each of the two heights. Periodically, we ran all four filter packs at one height to check the precision of the overall sampling and analysis system. During this experiment only one two-hour sample could be collected per day,

4

usually during periods of maximum convective activity and other favorable meteorology. Consequently, the number of valid samples is small.

PRELIMINARY DATA ANALYSIS

Initial results are presented here. While having received scrutiny, these should be considered preliminary.

Sites
Two sites were studied in the summer and fall of 1994. The first, a coastal site (34.91°N, 76.59°W) near Beaufort, North Carolina, was on the property of The Open Grounds Farm, a very large, extremely flat farm which raises corn, soybeans, hay, and cattle. Most of the measurements were over short grass, but winds sometimes blew over a growing stand of corn. All measurements had an unobstructed fetch of several kilometers. This site is characterized by strong winds (the sea breeze), high moisture flux, and low pollutant concentrations. This site was studied during June and July 1994.

The second site was at the Bondville, Illinois, research station (40.05°N, 88.37°W) operated by the Illinois State Water Survey. This area is also very flat, with excellent fetch. Our measurements were exclusively over corn. They began in August and extended past the corn's senescence in October. This site was characterized by moderate winds and moderate pollutant concentrations with occasional plumes of sulfur dioxide.

Ozone Deposition Velocity
Figure 3, a time series of half-hour fluxes of O_3, CO_2, and latent heat for a six day period at the Bondville site, is an example of data collected at the two sites. Negative values reflect flux to the surface. A multiplicative factor of -0.005 for latent heat was used to scale the output for graphical purposes. Several points are evident from this figure. The daytime fluxes increase rapidly to a maximum and then decrease just as rapidly, while the nighttime fluxes are relatively constant. The shape of the three curves is self-consistent for each day, showing the same small scale variation. The relative magnitude of the peaks of the three gases does not remain constant. Ozone uptake does occur at night, at about 1/10 the peak value during the day. CO_2 fluxes are positive at night, consistent with surface sources. Small scale variations at night are reflected in both the ozone uptake and carbon dioxide emissions, while the nocturnal water vapor flux is almost zero.

An important goal of this program is to understand the performance of the inferential model of deposition velocity under various conditions of ambient concentration, meteorology, and vegetation. A preliminary analysis of model performance is given in Figures 4 and 5 where modeled and measured O_3 deposition velocity, averaged over all days to give an average diurnal cycle, are compared for both Beaufort and Bondville. Both include only data when the winds were less than 10 m/s. Model results are for the 1993 version of the NOAA multilayer inferential model.[11]

Several features stand out. Average afternoon measured deposition velocities are slightly higher for Beaufort than for Bondville, while nighttime values are lower. Modeled afternoon deposition velocities, however, are nearly twice as high at Beaufort than Bondville. The model underestimates the afternoon measurements at Bondville and overestimates at Beaufort. The model underestimates

5

nighttime deposition of O_3 at both sites. We have not yet attempted to account for these differences.

Figure 6 shows the maximum half-hour average ozone flux for each day that had a valid mid-day set of measurements from August 17 to October 1 at Bondville. These peak values vary considerably from day to day, depending on the general meteorology of the day. However, it can be seen that there is a general trend toward smaller peak flux as the season progresses. Also shown is a measure of the viability of the corn plants, in this case the average number of completely green leaves on each plant. As corn matures, the leaves brown one by one, first from the bottom up to the ear leaf, then from the top down to the ear leaf. The variety of corn in this field has a uniform 21 leaves per plant. It can be seen that the corn plants matured from maximum capability for photosynthesis at the beginning of the study, to almost none at the end. The reduction in maximum ozone flux seems to be reflected in the reduced capacity for uptake of ozone by the corn as the season progressed.

Nitric Acid Deposition Velocity
For nitric acid, the precision (as the coefficient of variation) achieved for a pair of collocated filter packs averaged 5.1% at Beaufort and 3.1% at Bondville. The multilayer inferential deposition velocity model[11] was run for comparison with measured results (Figure 7). Through the model and measurements do not show order-of-magnitude differences with each other, there are frequent cases of differences with each other, there are frequent cases of differences exceeding 25%. In general the model appears to have more serious overestimates of deposition velocity than underestimates. One interesting note is the marked difference in the two sites' results. At Beaufort, the model predicts values in a fairly narrow range of 1 to 2.5 cm's^{-1}, while the measured values go much lower, although the lower measured values had increased uncertainly because the gradients were very small (<5%) in those four cases. In contrast, at Bondville, the measurements ere in a more narrow range than the model predictions. At this point in our analysis, we do not know the reasons for this difference. An important part of our work will be examining such cases of poorer agreement, with the goal of finding patterns of atmospheric or surface conditions when disagreement occurs, which may lead to improvements in the model or in the measurement network. Most of our runs were made in the mid-day period when maximum flux and nitric acid concentrations are expected. In subsequent studies we plan to extend sampling into earlier and later periods and look at diurnal cycles.

CONCLUSIONS

We have constructed and operated a mobile trace gas flux monitoring system. Data is being collected over a variety of vegetative covers, land-use characteristics, and climatic regimes. The complete data set will be used to evaluate and improve deposition velocity models and to study the mechanisms of gas transfer between the atmosphere and biosphere. Preliminary analysis of the first year's data shows that the 1993 version of the NOAA multi-layer deposition velocity model is giving reasonable values, on average, but there are site to site differences, and time of day differences that need to be understood. These discrepancies tend to confirm the advisability of testing such models under many different conditions.

ACKNOWLEDGEMENTS

REFERENCES

1. B.B. Hicks, R.P. Hosker, Jr., T.P. Meyers and J.D. Womack, "Dry deposition inferential measurement techniques - I. Design and tests of a prototype meteorological and chemical system for determining dry deposition," Atmos. Environment, 25A(10):2345-2359 (1991).

2. T.P. Meyers, B.B. Hicks, R.P. Hosker, Jr., J.D. Womack and L.C. Satterfield, "Dry Deposition inferential measurement techniques - II. Seasonal and annual deposition rates of sulfur and nitrate," Atmos. Environment, 25A(10):2361-2370 (1991).

3. B.B. Hicks, D.D. Baldocchi, R.P. Hosker, Jr., B.A. Hutchinson, D.R. Matt, R.T. McMillen and L.C. Satterfield, On the Use of Monitored Air Concentrations to Infer Dry Deposition, NOAA Technical Memorandum ERL/ARL-141, 1985, 65pp.

4. J.F. Clarke and E.S. Edgerton, Dry Deposition Flux Calculations for the National Dry Deposition Network, EPA-600/R - 93/065, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1993, 91pp.

5. J.D. Ray, D.H. Stedman and G.J. Wendel, "Fast chemiluminescent method for measurement of ambient ozone," Anal. Chem., 58:598-600 (1986).

6. W.J. Massman, "The attenuation of concentration fluctuations in turbulent flow through a tube," JGR, 96(D8):15269-15273 (1991).

7. C.J. Moore, "Frequency response corrections for eddy correlation systems," Bound.-Layer. Meteor., 37:17-35 (1986).

8. J.A. Businger, "Evaluation of the accuracy with which dry deposition can be measured with current micrometeorological techniques," J. Clim. and Appl. Meteor., 25:1100-1124 (1986).

9. J.C. Kaimal and J.J.Finnigan, Atmospheric Boundary Layer Flows, Their Structure and Measurement. Oxford University Press, New York, 1994, 290pp.

10. B.J. Huebert and C.H. Robert, "The dry deposition of nitric acid to grass," JGR, 90(D1):2085-2090 (1985).

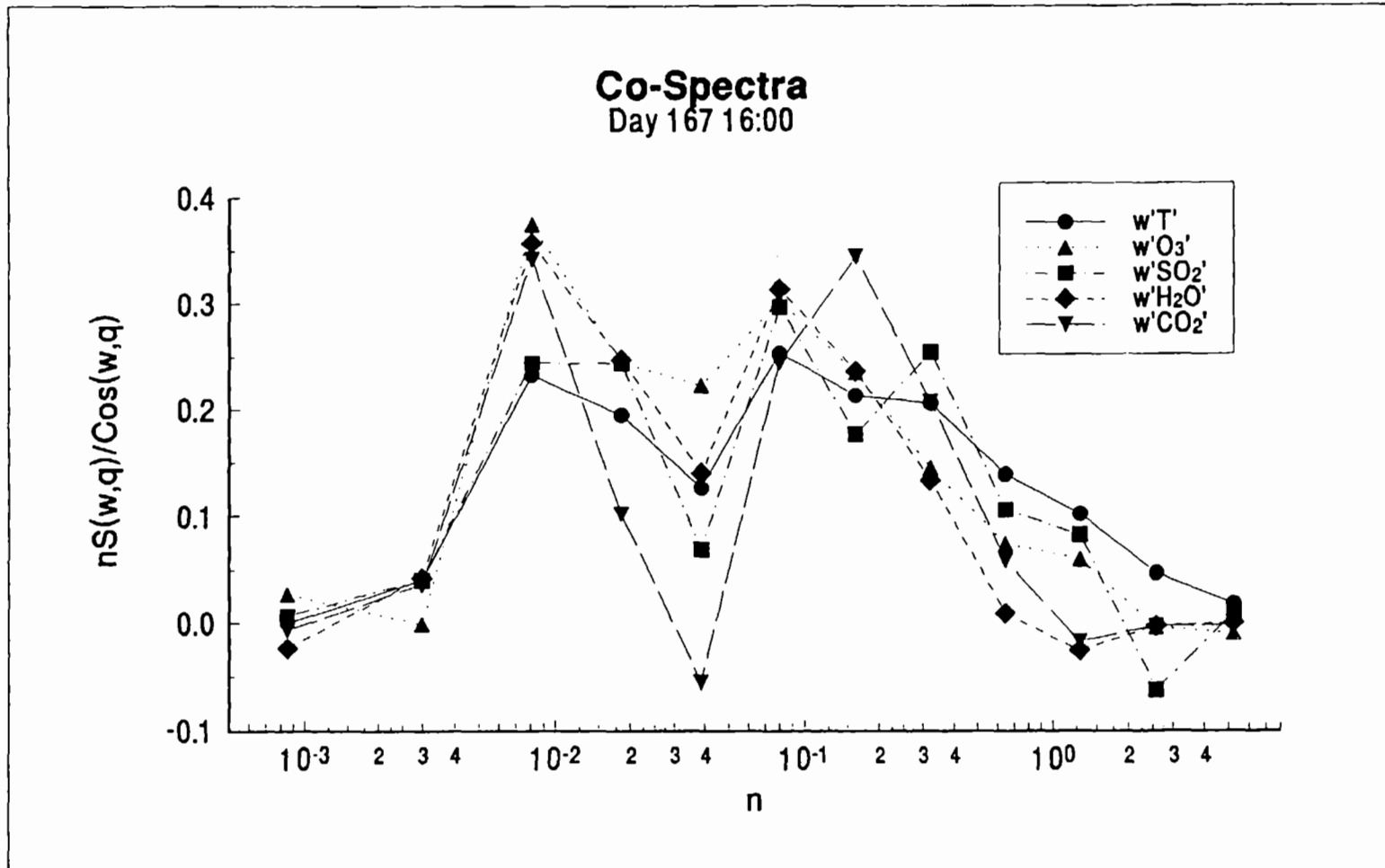11. T.P. Meyers, NOAA ATDD, Oak Ridge TN., Personal Communication, 1994.

Co-Spectra
Day 167 16:00

Figure 1. Normalized co-spectra, showing a rapid fall off at high frequency for all gases. N is normalized frequency (f·z/u). The abscissa is n times the cospectra normalized by the covariance.
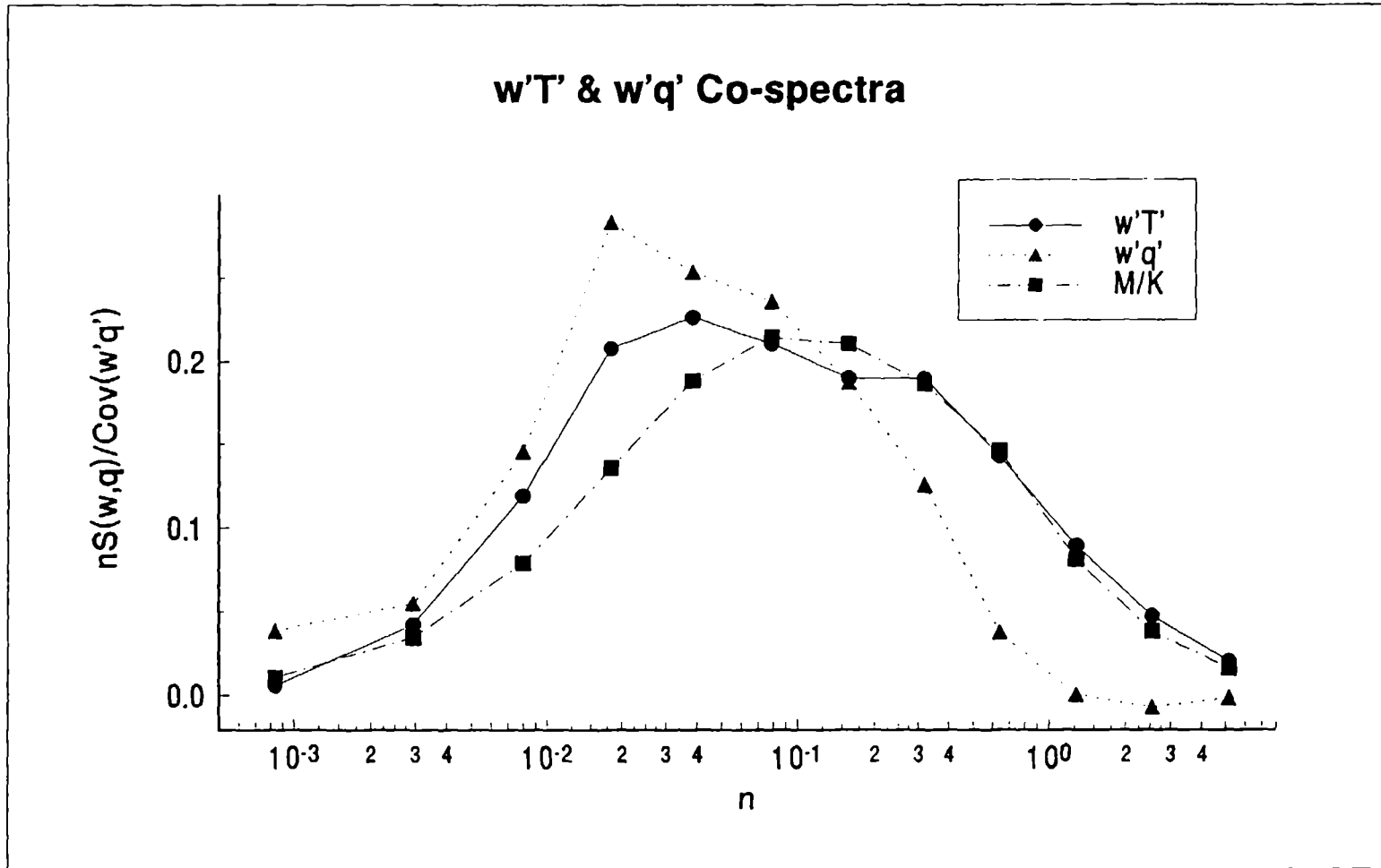
w'T' & w'q' Co-spectra

Figure 2. Co-spectra averaged over 6 cases and all gases, compared with measured heat flux and results from Moore/Kaimal. An integration under the $\overline{w'T'}$ and $\overline{w'q'}$ curves shows the energy in the gas spectra to be 17% low due to high frequency losses. The M/K curve is the best fit to the co-spectra presented by Moore.

FLUX TIME SERIES
BONDVILLE
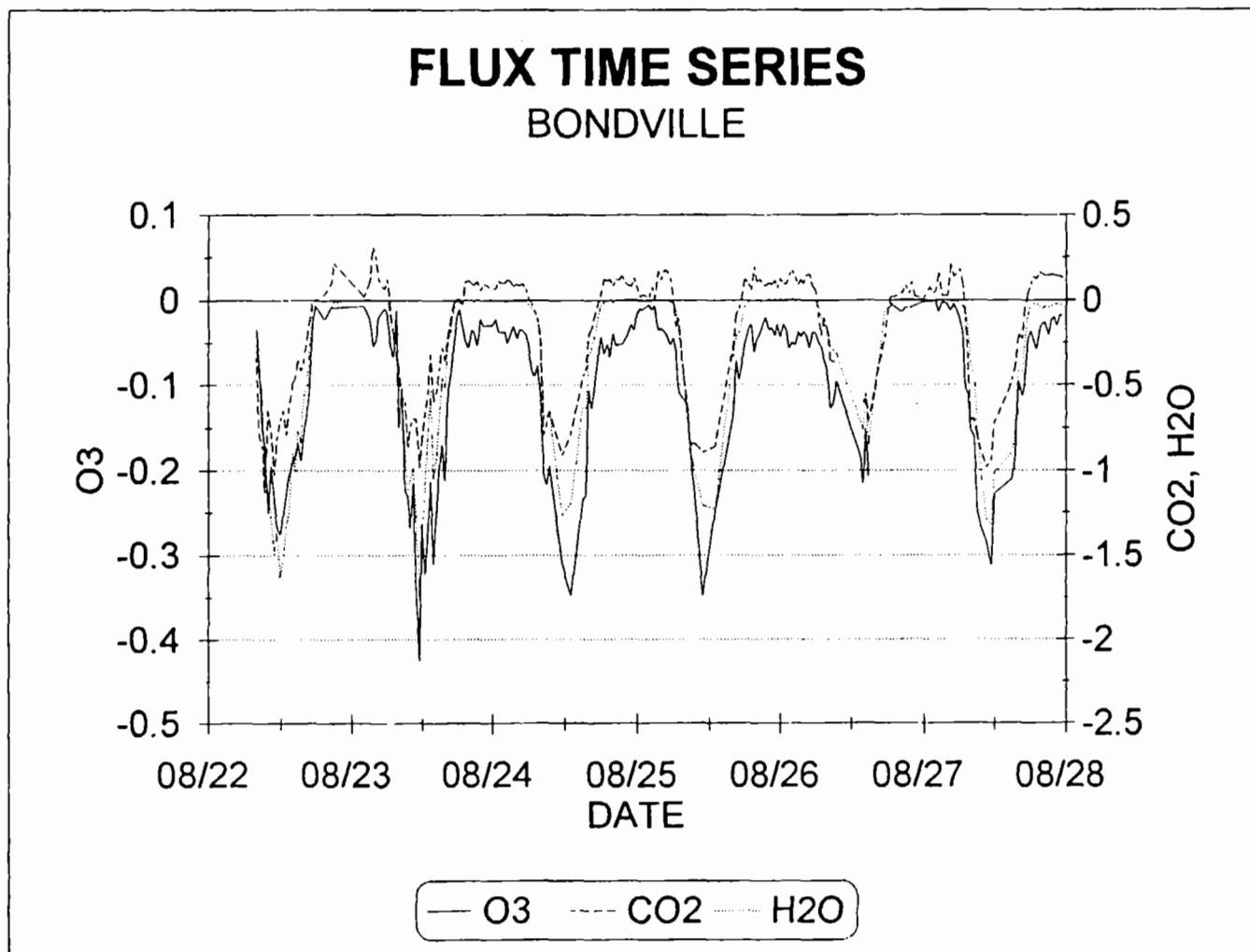
Figure 3. Time series of 30 min. average fluxes for O_3, CO_2, and latent heat at Bondville, IL. Some data are missing. The O_3 units are ppb m s^{-1}, the CO_2 units are ppm m s^{-1}, and the latent heat units are -0.005 watts m^{-2}.
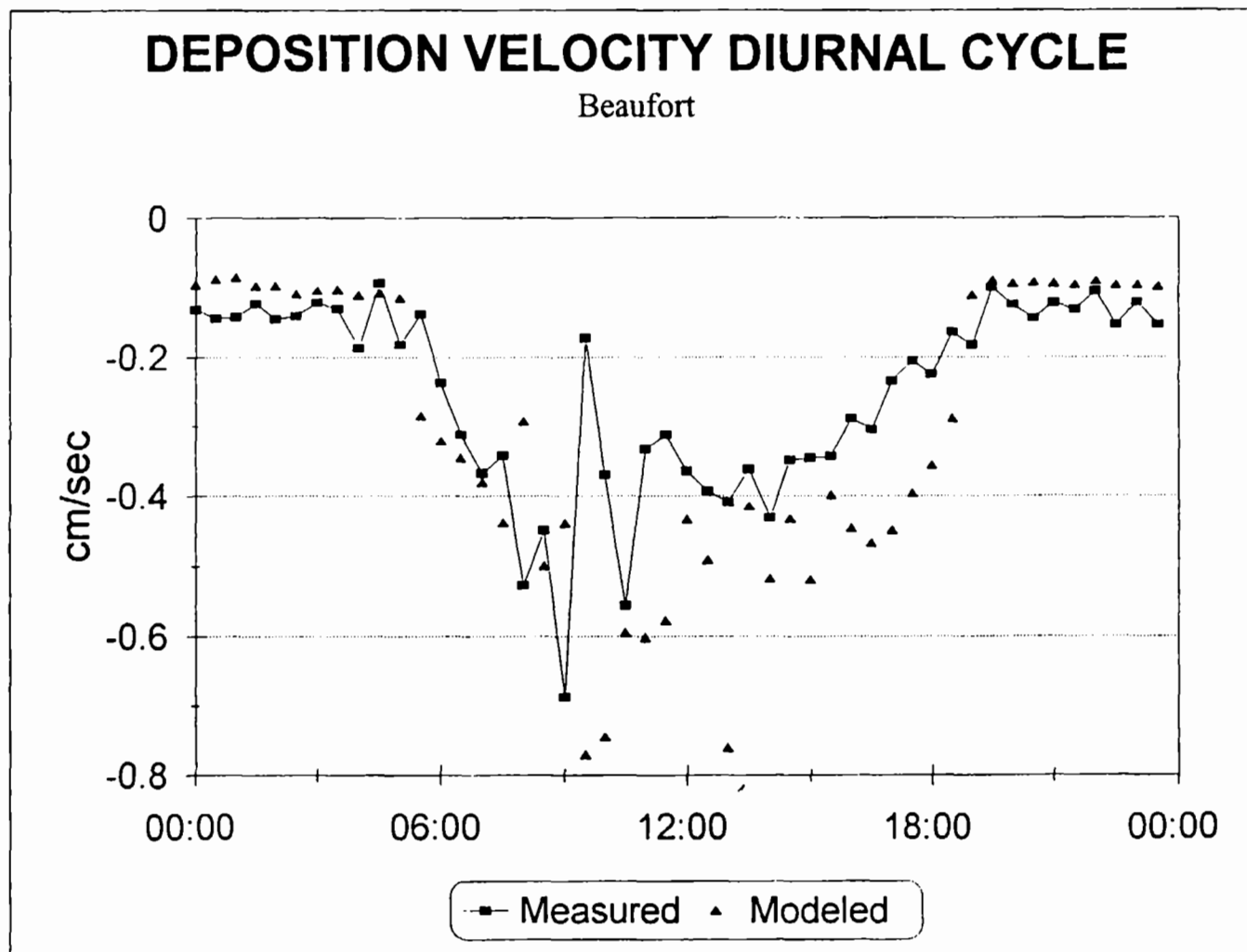
DEPOSITION VELOCITY DIURNAL CYCLE
Beaufort

Figure 4.   Average diurnal cycle of modeled and measured O_3 deposition velocity at the Beaufort site.
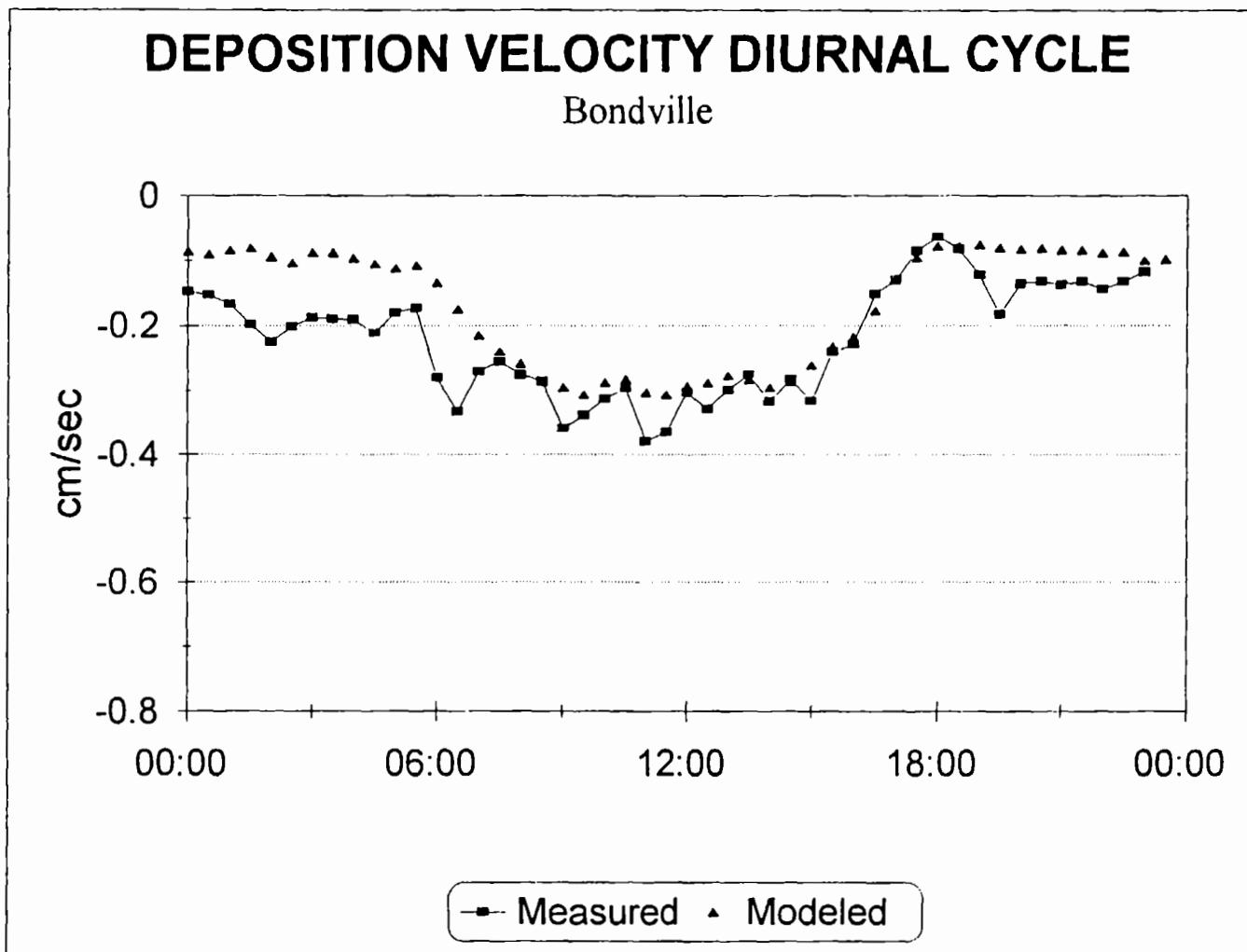
Figure 5. Average diurnal cycle of modeled and measured O_3 deposition velocity at the Bondville site.
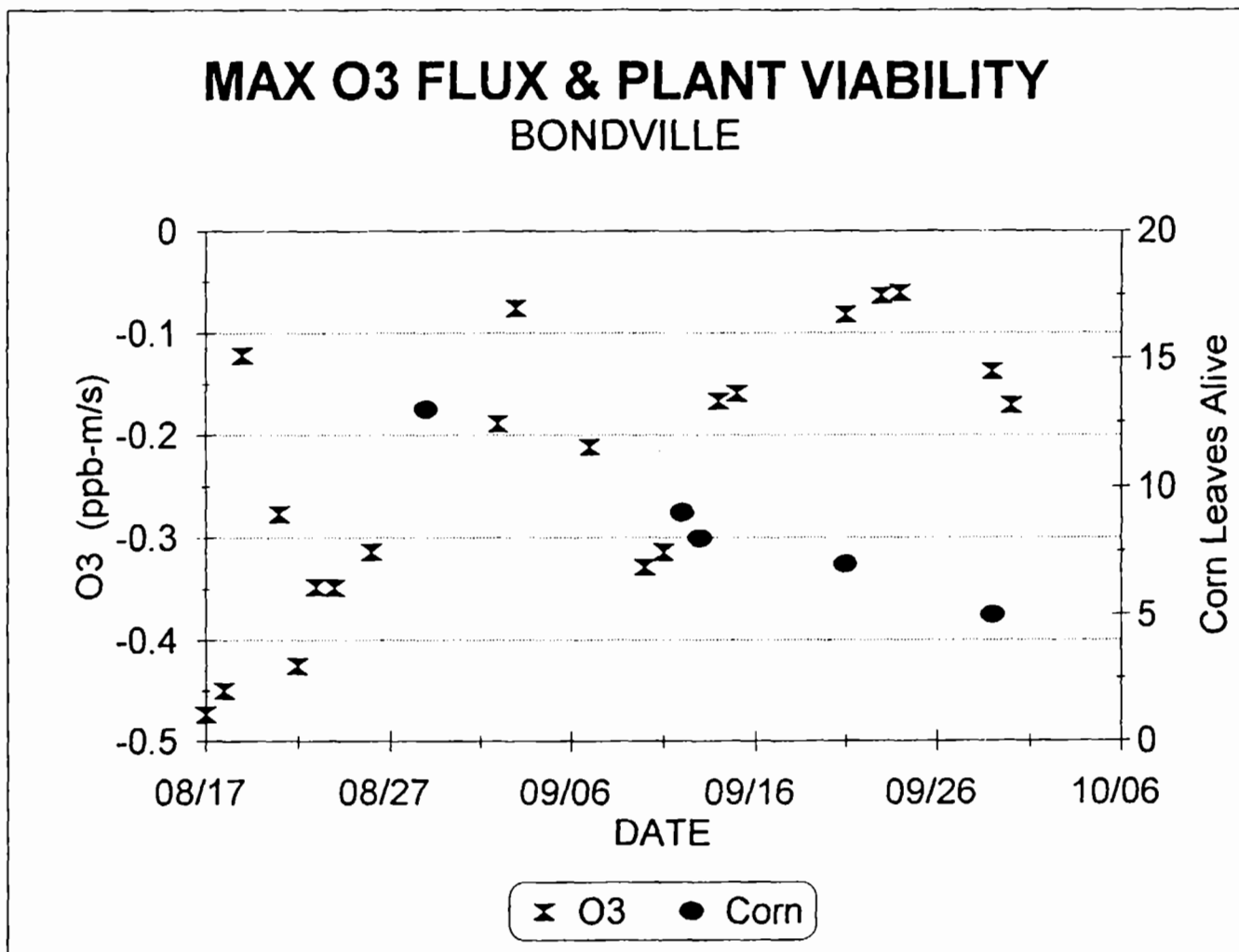
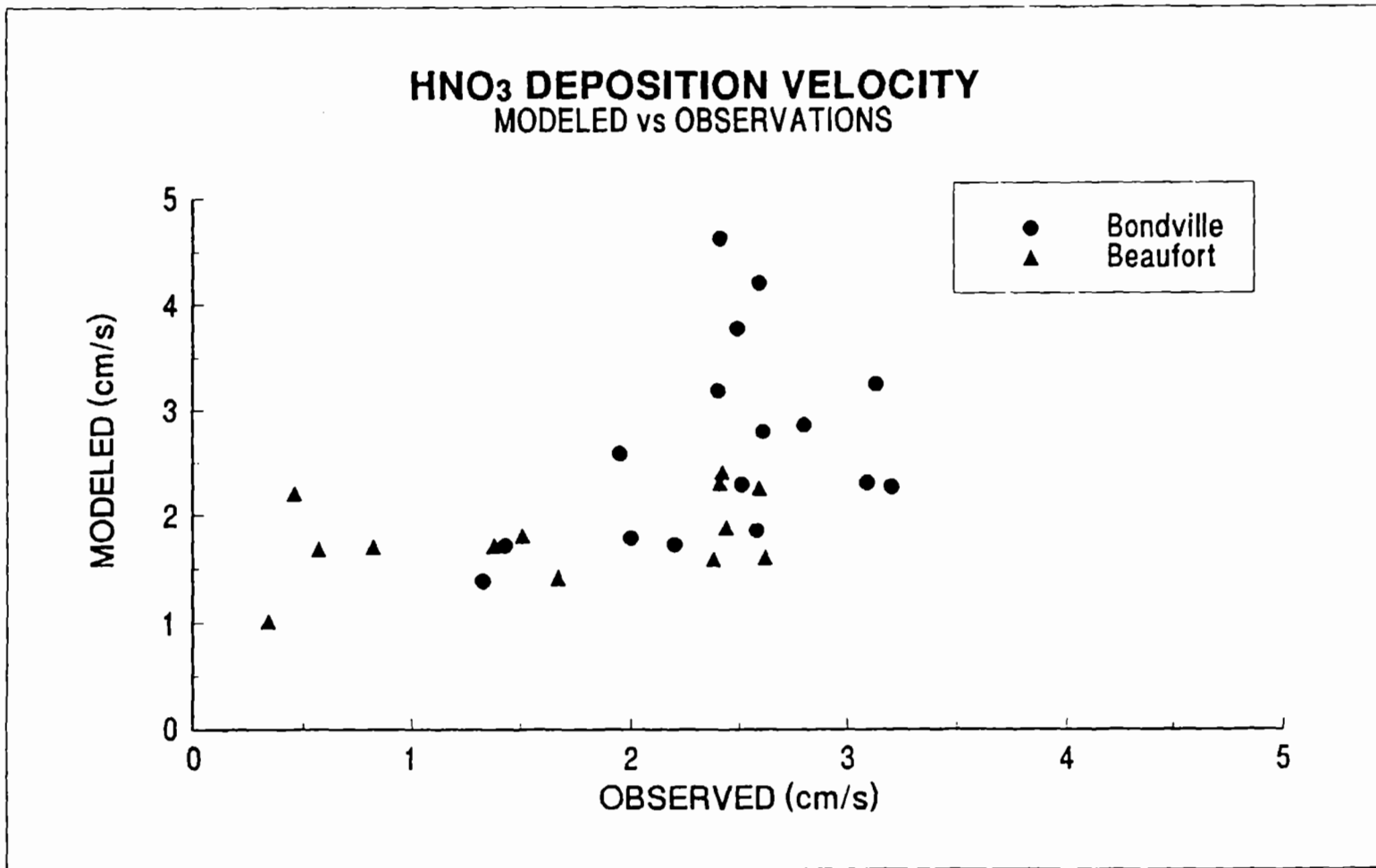Figure 6. Time series of daily maximum O₃ flux and plant viability at Bondville.

Figure 7.   Measured and modeled deposition velocity for HNO₃.