Aerosol Nutrient Deposition Measured by Eddy-Correlation Mass Spectrometry

Daniel A. Gonzales and Jonathan O. Allen, Chemical and Materials Engineering, Arizona State University, Mail Stop 876006, Tempe, AZ 85287-6006 daniel.gonzales@asu.edu

Background and Motivation

Dry deposition of aerosols contributes to the nutrient loading of urban ecosystems and surrounding areas. Gaseous nitrogen species include oxides (NO_X) from fossil fuel combustion and ammonia (NH_3) from agricultural activities. These species are important in the chemistry of the atmosphere (Figure 1), contributing to ozone formation, acid-base chemistry, and aerosol formation.

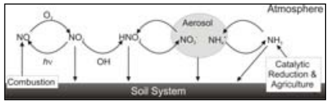

Figure 1: Simplified diagram of anthropogenic N species.

In urban areas, such as the Phoenix metro, high emissions of reactive nitrogen species cause an increase in atmospheric aerosol formation and dry deposition. Baker et al. have estimated an N dry deposition flux of 18.5 kg ha^{-1} y^{-1} to the Central Arizona-Phoenix area (2001). Other research has resulted in much lower estimates of about 6.7 kg ha^{-1} y^{-1} (Baker, 2001). The wide range of values show the need for improved estimates of N dry deposition flux and this is a key goal of the CAP-LTER biogeochemical research program.

Methods

Time series measurements of a scalar, such as temperature (θ) or three-dimensional wind velocities (u, v, w), can be split into a mean part (denoted by brackets) and a turbulent part (denoted by a prime). The turbulence, or "gustiness" of the wind, can be visualized as irregular motions called eddies.

If we consider an idealized eddy in a nearly adiabatic atmosphere, eddies will cause warm air from below to move upward (w' > 0, θ' > 0) and cool air from above to move downward (w' < 0, θ' < 0). The net motion from this turbulence is zero, [w'] = 0, but the product w'θ' is positive for both upward and downward turbulent motions. The average heat flux [w'θ'] is positive for small eddy mixing and the same procedure applies to other scalar fluxes. This average of the product of turbulent scalars (covariance) is the eddy-correlation method. Thus the deposition flux, F, of a scalar can be calculated from the covariance of the vertical wind, w, with a scalar, S,

$$F = [w'S'] \quad (1)$$

and the deposition velocity, v_d, of an aerosol species can be calculated from

$$v_d = -F/[S] = -[w'S']/[S] \quad (2)$$

PROPHET 2001

A co-located sonic anemometer and Aerosol Mass Spectrometer (AMS) were used to determine the fluxes during the PROPHET 2001 field study in a mixed hardwood forest in northern Michigan. In the AMS (Figure 2) aerosol particle size is determined from the time-of-flight in a chamber of known length. The composition of the aerosol is then determined using a quadrupole mass spectrometer.

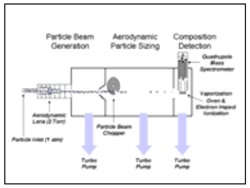

Figure 2: Schematic of the Aerosol Mass Spectrometer.

Typical Deposition Velocities

Gallagher et al. calculated the deposition velocities as a function of particle size to a forest canopy (1997). Their results are shown in Figure 3. Typical deposition velocities for sub-micron particles expected during PROPHET 2001 are about 0.1 cm/s.

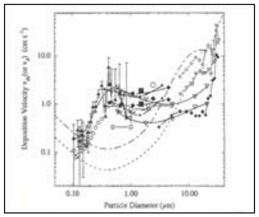

Figure 3: Deposition velocities to forest canopy (Gallagher et al., 1997).

Results and Discussion

Momentum Flux

The vertical flux of u-momentum is expected to be negative, transporting momentum to the surface from aloft. Night time fluxes are often weaker than day time fluxes, due to decreased turbulence at night, creating a diurnal pattern of the momentum flux time series.

The eddy-correlation method (Equation 1) is used to calculate the momentum flux from the covariance of u and w. Figure 4 shows 15-minute averaged momentum fluxes (blue circles) and the 3-hour average of the 15-minute fluxes (solid line) for August 6, 2001. The night time results are in the same range as published results (McMillen, 1988), however, positive day time fluxes were caused by unstable atmospheric conditions.

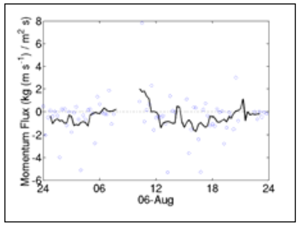

Figure 4: Momentum flux data for 15-minute averaging periods on August 6, 2001.

Sensible Heat Flux

The sensible heat flux also has a noticeable diurnal cycle. Day time values are expected to be positive because solar heating of the earth's surface transfers heat to the atmosphere. Without solar heating, the night time fluxes are near zero.

Temperature and vertical wind data are used to calculate the sensible heat flux from Equation 1. Figure 5 shows the sensible heat fluxes over 15-minute averaging periods (blue circles) and the 3-hour average of the 15-minute fluxes (solid line). Similar results have been obtained by Schmid et al. (2001).

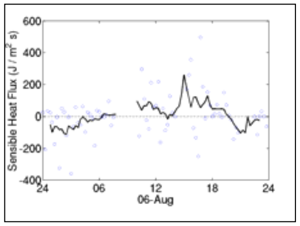

Figure 5: Sensible heat flux for 15-minute averaging periods on August 6, 2001.

Nitrate Deposition

Aerosol fluxes are expected to be low during the night time and increasing during the day, with a noticeable diurnal pattern. This is due to increased atmospheric turbulence and increased aerosol formation during the day time.

Aerosol nitrate fluxes are calculated from Equation 1 and deposition velocities are calculated from Equation 2. The 30-minute averaged deposition velocities (blue circles) and 2.5 hour averages (solid line) for August 6, 2001, are shown in Figure 6. Gallagher et al. obtained similar results for the particle size range measured (1997).

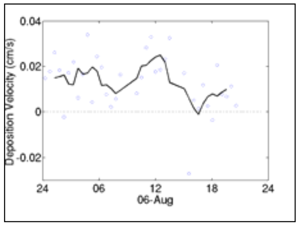

Figure 6: Nitrate deposition velocity for August 6, 2001.

Sulfate Deposition

Aerosol sulfate flux data are calculated using the eddy-correlation method from Equations 1 & 2. The 30-minute averaged sulfate deposition velocities (blue squares) for August 4, 2001, are shown in Figure 7. These results are also consistent with those of Gallagher et al. (1997).

Sulfate deposition velocities are about an order of magnitude higher than those for nitrate. Although the deposition velocities are calculated for different time periods, such a large difference is not expected. Additional analysis of the deposition data is needed.

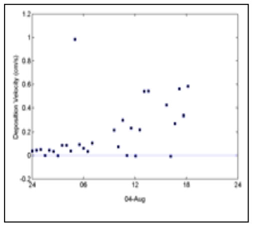

Figure 7: Sulfate deposition velocities for August 4, 2001.

Conclusions

Flux data calculated for the PROPHET 2001 field study show good agreement with expected values and exhibit a strong diurnal cycle. Unstable atmospheric conditions caused a positive momentum flux during the morning of August 6, 2001. The sensible heat flux behaves as expected and aerosol deposition velocities are reasonable. The unstable conditions during the morning of August 6, 2001, may have caused the decrease in nitrate deposition velocity during the same time period.

Average nitrate deposition velocities calculated for the sub-micron particles measured during PROPHET 2001 are in the range of 0.02 to 0.03 cm/s. Sulfate deposition velocities are in the range of 0.2 to 0.6 cm/s. These deposition velocities are within experimental error of those found by Gallagher et al. for the same size range (~0.1 cm/s). The sulfate deposition velocities are about an order of magnitude higher than nitrate deposition velocities. The cause of this is unknown and further analysis is needed to explain this result.

The results indicate that the eddy-correlation is applicable for measurement of aerosol fluxes over a forest. Using the same analysis eddy-correlation can also be used for simpler terrains, such as deserts or croplands, to estimate deposition fluxes of aerosol species.

Future Work

We have completed some of the analysis of the PROPHET 2001 data. Initial flux calculations show that our data is in good agreement with expected values. We plan to complete analysis of this data set by calculating fluxes for the various aerosols monitored during the PROPHET 2001 field study.

Plans are currently underway to conduct a field study in the Phoenix, Arizona metropolitan area. We plan to deploy the Aerosol Mass Spectrometer (AMS) and sonic anemometer in an area of simple terrain within the urban landscape to collect eddy-correlation mass spectrometry data. Nitrate data from this study can be used to improve upon N dry deposition estimates for the CAP biogeochemical research program.

In the long term we hope to conduct collaborative research with ecologists and soil biologists to refine estimates of nitrogen dry deposition and simultaneously determine soil response.

References

Baker, L.A., Hope, D., Xu, Y., Edmonds, J., and Lauver, L., 2001. Nitrogen Balance for the Central Arizona-Phoenix (CAP) *Ecosystems*. Ecosystems, 4, 582-602.

Gallagher, M.W., Beswick, K.M., Duyzer, J., Westrate, H., Choularton, T.W., and Hummelshoj, P., 1997. Measurement of Aerosol Fluxes to Speulder Forest Using a Micrometeorological Technique. Atmospheric Environment, 31, 359-373.

McMillen, R.T., 1988. An Eddy Correlation Technique with Extended Applicability to Non-Simple Terrain. *Boundary-Layer Meteorology*, 43, 231-245.

Schmid, H.P., Grimmond, C.S.B., Cropley, F., Offerle, B., and Su, H.-B., 2000. Measurements of CO_2 and energy fluxes over a mixed hardwood forest in the mid-western United States. *Agricultural and Forest Meteorology*, 103, 357-374.

ASU Arizona State University
CHEMICAL AND MATERIALS engineering