

## **Dry Air-Surface Exchange**

Goal: To develop improved methods to estimate air-surface exchange rates of energyrelated sulfur and nitrogen compounds and atmospheric oxidants.

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## Air-Surface Exchange of Peroxyacetyl Nitrate at a Grassland Site

Measurements of the dry deposition velocity of peroxyacetyl nitrate (PAN) were made during the daytime above a grassland surface by a modified Bowen ratio technique from July through October of 1996. Differences in the air temperature, water vapor content, and PAN concentration were measured between the heights of 3.0 m and 0.92 m. Although the measurement uncertainties were large, the cumulative data indicated a slight downward flux of PAN with an average and standard error of 0.13±0.08 cm s for the dry deposition velocity. Theoretical calculations showed that thermal decomposition of PAN at surfaces heated to temperatures above the ambient air levels would contribute less than 15% of the total PAN flux at the elevations of the PAN measurements for leaf and soil surface temperatures of 30-40°C and heat fluxes of 100-200 W m<sup>-2</sup>. A theoretical evaluation of the transfer of PAN through leaf stomata and the plant cuticular membrane indicated that uptake of PAN by vegetation is controlled by transfer through the leaf stomata rather than the cuticular membrane. The stomatal resistance for PAN is a factor of 1.6 greater than the value for  $O_3$  and the mesophyll resistance for  $O_3$ is also expected to be less than the value for PAN because O<sub>3</sub> has more reaction sites within plant cells and reacts with protein thiols of the cell membranes at a faster rate than PAN. Measurements from other studies indicate that the dry deposition velocity of PAN above a vegetated surface during the daytime is a factor of 0.5-0.3 lower than that of O<sub>3</sub>. Our measurements of the PAN deposition velocity agree with the previous studies and the theoretical calculations based upon the physicochemical properties of PAN and the grassland surface. These measurements indicate that removal of PAN from the daytime atmospheric boundary layer by thermal decomposition is more important than dry deposition.



PAN concentrations measured on two days.



Frequency distribution of concentration differences seen during mornings.



Frequency distribution of concentration differences seen during afternoons.



## Flux Divergences of Nitrogen Dioxide and Ozone in the Atmospheric Surface Layer

Eddy correlation measurements of the vertical fluxes of nitrogen dioxide and ozone were measured at heights of 5 m and 10 m above a short maize canopy in 1995 and above a soybean canopy in 1996. In 1995, the molar rate of ozone destruction in this layer appeared to greatly exceed the molar production rate of nitrogen dioxide. This imbalance suggests that the reactions involving only nitric oxide, nitrogen dioxide, and ozone were insufficient to describe the destruction rate of ozone. In 1996, somewhat similar conditions were found at times, although the changes with height of nitrogen dioxide and ozone fluxes were relatively small, apparently because the rate of nitric oxide emissions was much smaller from the field, which had been planted to soybeans. The reverse case of ozone production and nitrogen dioxide destruction was seen on several days in 1996, starting during midmorning and continuing through the afternoon. The supply of excess nitrogen dioxide by vertical mixing in the planetary boundary layer or by horizontal advection might have caused this reverse in chemical production versus destruction. Major questions exist on the effects of interference by ozone and PAN on the nitrogen dioxide signals.

Comparison of ozone fluxes measured at a height of 10 m by two independent systems, one from the Atmospheric Turbulence and Division (ATDD) and one from Argonne National Laboratory (ANL). The horizontal separation was about 30 m. Each point represents a half-hour average.



Ozone fluxes measured at heights of 10 m and 5 m on the same mast. Each point represents a half-hour average.



Ozone fluxes measured at two levels and, for the 10-m level, at both the ATDD and ANL locations. The tendency for fluxes of a larger magnitude at 5 m indicates ozone production in the layer.



Fluxes of nitrogen dioside measured at two levels on one mast. No corrections for interference by ozone have been applied here.



Estimates of nitrogen dioxide fluxes afer a first-order adjustment to account for the effects of interference by ozone. Larger flux values at 5 m than at 10 m indicates destruction of nitrogen dioxide in the layer.



Ozone fluxes on a day when ozone destruction appeared to dominate until mid-morning, followed by ozone production.



## Use of Satellite Observations to Estimate Vegetative Conditions for Atmosphere-Biosphere Exchange of Chemical Substances

An algorithm consisting several modules was developed to use satellite remote sensing data to describe vegetative conditions for estimating atmospherebiosphere exchange of atmospheric trace gases. The algorithm uses several simplified approaches so that it can be easily coupled with the archived Pathfinder AVHRR data sets available for describing global terrestrial biosphere. The simplification was made to adjust raw NDVI data by a linear scaling to account for the reduction in NDVI by atmospheric effects. A relatively simple model for radiation transfer within a plant canopy was used with a simple inversion technique that involves only one unknown, LAI, for every single input but other model parameters have to be predetermined from existing experimental data. The LAI and APAR values estimated from satellite data with the algorithm were evaluated with the data from ground measurements made at several different locations. Spatial, seasonal, and annual variations in LAI and APAR can be closely described by calculations by the algorithm using the AVHRR NDVI satellite-derived data. The modules in the algorithm can be updated and replaced with improved or problem-specific ones if needed. For example, the algorithm was designed for use not only with processed AVHRR data but can also be used with real-time AVHRR data at a higher spatial and temporal resolution. The inversion method is simple in the present version and can be replaced with a more advanced automatic inversion technique when it is improved. In addition, the module for biogenic emission described here needs to be coupled with more widely-used emission models such as **BEIS model**.











