A Study of Atmosphere-Forest Exchange of Reactive Nitrogen Via Measurements of Nitrate in Canopy Top Leaves
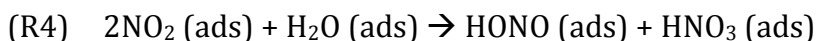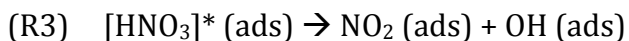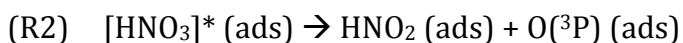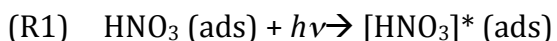
Michaela TerAvest, Xianliang Zhou

Abstract:

Nitric acid deposited on leaf surfaces may be an important player in the atmospheric nitrogen balance in the deciduous forest environment near the University of Michigan Biological Station. Levels of nitrate deposited on leaf surfaces at the top of the canopy were measured at different times of day to determine when the canopy was a source and when it was a sink of atmospheric nitrogen. Data was also analyzed in conjunction with precipitation and tree species recordings to determine whether these have an effect on deposited nitrogen and, in turn, on atmospheric nitrogen. A significant trend in nitrate concentrations throughout the day was found and involved decrease of leaf nitrate in the morning, changing to accumulation in the afternoon. This is suspected to be due to photolysis rates and the conversion of nitric acid to nitrous acid and subsequent volatilization of nitrous acid.

Introduction:

Nitrogen oxides are important atmospheric pollutants and are a result of the combustion of fossil fuels and the oxidation products thereof (e.g. Kato and Akimoto, 2007; Olivier, et. al., 1998; Penner, et. al., 1991). Released nitric oxide (NO) is quickly oxidized to NO_2, which goes through many further reactions in the atmosphere and is a key factor in the production of tropospheric ozone (e.g. Finlayson-Pitts and Pitts, 1993). In the atmosphere nitric acid (HNO_3) is formed through the reaction $NO_2 + OH + M \rightarrow HNO_3 + M$. HNO_3 is a "sticky" species and undergoes both wet and dry deposition. Thus, HNO_3 deposition has been thought of as an important pathway for removing reactive nitrogen from the atmosphere (e.g., Dollard, et. al., 1987; Penner, et. al., 1991; Sirois and Barrie, 1998). However, a new mechanism involving HNO_3 adsorbed on surfaces reacting to form HONO, which could be released into the atmosphere, has been proposed by Zhou et al (2003):

(R1) HNO_3 (ads) + $h\nu \rightarrow$ [HNO_3]* (ads)

(R2)   [HNO_3]* (ads) $\rightarrow$ HNO_2 (ads) + $O(^3P)$ (ads)

(R3)   [HNO_3]* (ads) $\rightarrow$ NO_2 (ads) + OH (ads)

(R4) $2NO_2$ (ads) + H_2O (ads) $\rightarrow$ HONO (ads) + HNO_3 (ads)

This mechanism was proposed to explain field measurements showing significantly higher daytime HONO mixing ratios than predicted by gas-phase reactions alone in rural areas (Zhou, et. al., 2002), and was later supported by laboratory tests (Zhou, et. al. 2003). Results from several field measurements (e.g.

Alicke, et. al., 2002; Volkamer, et. al., 2007; Zhou, et. al. 2002, 2003) have shown that HONO is an important precursor for OH radicals, a strong oxidizer responsible for oxidizing and removing pollutants from the atmosphere (e.g. Anderson and Hites, 1996; Volkamer, et. al., 2007).

This above-described photochemical process has also been proposed as a source of HONO from arctic snowpack. Measurements of HONO above the snowpack in the spring in Alert, Canada showed a distinct diurnal cycle with a maximum at solar noon and a minimum at midnight. This supports the proposed mechanism because it would be dependent on sunlight to drive photolysis and would show this type of pattern (Zhou, et. al., 2001). Deposited nitrogen was also studied in Antarctica with a focus on the atmospheric effects and showed that it might be playing an important role in recent changes in Antarctic ozone (Mayewski and Legrand, 1990).

In this study, we propose to quantify nitrate loading on tree leaves at the canopy top in a Northern Michigan forest at the University of Michigan Biological Station (UMBS), as a function of the time of day, meteorological conditions, and tree species. The information will later be used along with other parameters that are being measured concurrently at the PROPHET (Program for Research on Oxidants; Photochemistry, Emissions and Transport) tower, including HONO, OH, and NO_x, to examine HONO chemistry in the rural and forested environment, especially its source from surface HNO_3 photolysis from forest canopy.

Factors that are suspected to play a role in the leaf surface nitrate concentrations include those affecting deposition and those affecting loss. Deposition might be influenced by weather conditions, such as precipitation, fog, dew, relative humidity, wind direction, wind speed, origin of air parcel, cloudiness and perhaps others. The leaf properties, such as species, albedo, roughness and quickness of drying; weather changes such as cloudiness and precipitation; solar radiation, and perhaps others could affect the rate of loss of nitrate on the leaf surfaces. This study will focus on effects of solar radiation (represented by time of day), tree species and precipitation.

Materials and Methods:
Leaves were collected from the top of the canopy using a cherry picker; the leaves collected were in the top layer and were the first exposed to sunlight and passing air parcels (see Figure 1). The canopy was composed mainly of bigtooth aspen, red maple, red oak, red pine and white pine (see Figure 2). Samples were taken at different times throughout the day to assess changes in concentration of leaf-surface nitrate throughout the day. The sampling regime included days with 1-3 samples, with collections

Figure 1. Photo of cherry-picker used for leaf sampling.

at varying times throughout the day. Samples were collected from three different tree species; bigtooth aspen, red maple and red oak. These species were chosen because they were common in the canopy and easily accessible from the location of the cherry picker. Tree species, location, time, geographic direction the leaves face and meteorological data were

Figure 2. Photo of the canopy at sampling height.

recorded for the time and location of sampling. One-leaf samples were placed in 25mL tubes in the field then taken back to the lab. Three separate samples for each species at each time were taken as replicates.

In the lab, 20 mL of Milli-Q purified H_2O (18.2 Ω) were added to each sample tube and inverted ~20 times and shaken vigorously for ~10 s to rinse the leaf. The leaf was removed, photographed and scanned with a surface area analyzer to obtain the area of each leaf. The resulting solution was kept at ~4°C in vials with no air bubbles until analysis. Samples were analyzed by azo-dye derivatization and detection of the dye by absorbance at 540 nm, see Figure 3 (method of Yao, et. al., 1998).

A Bran Luebbe Auto Analyzer 3 segmented flow analyzer was used to make nitrate (NO_3^-) measurements. The calibration curve was linear over the range 7 to 53 µg NO_3^--N/L. Control samples were measured repeatedly and measurements fell within 2 standard deviations of the stated concentration of the control sample. The Environmental Resource Association was the source of the control samples. The practical quantitation limit (determined by EPA method) was 0.81 µg NO_3^--N/L with 96.8% accuracy.
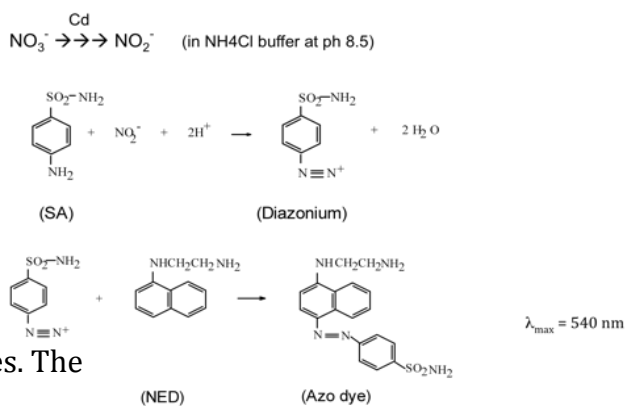

Figure 3. Azo-dye derivatization of nitrite.

A preliminary study was performed to assess the precision of the measurement process and the stability of samples of a period of ten days after sampling. Figure 4 shows that there was no significant trend in the measurements made over the first 250 hours following sampling. Each measurement was within 10% of the average of all measurements. Based on this study samples were considered to be stable when stored at 4°C for ten days or less.
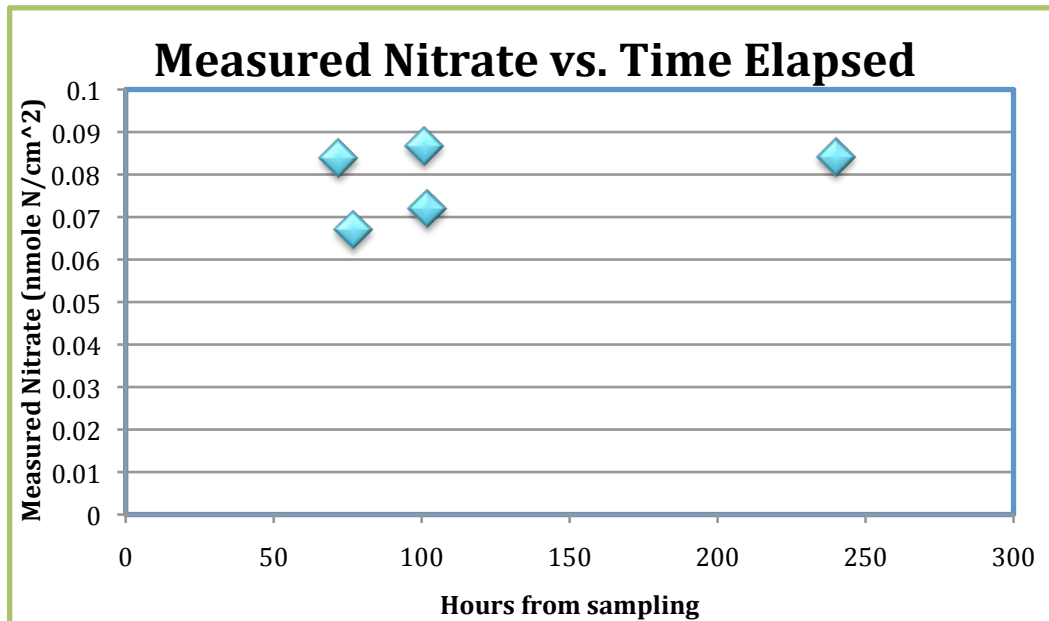
Measured Nitrate vs. Time Elapsed

Figure 4. Time series measurements of a nitrate sample.

Results and Discussion:

The results of this preliminary study show that nitrate concentration on leaves in the canopy varied throughout the day. Based on the proposed chemical mechanism, a decrease of leaf nitrate throughout the day was expected due to photolysis to HONO, if depsotion over this period is not s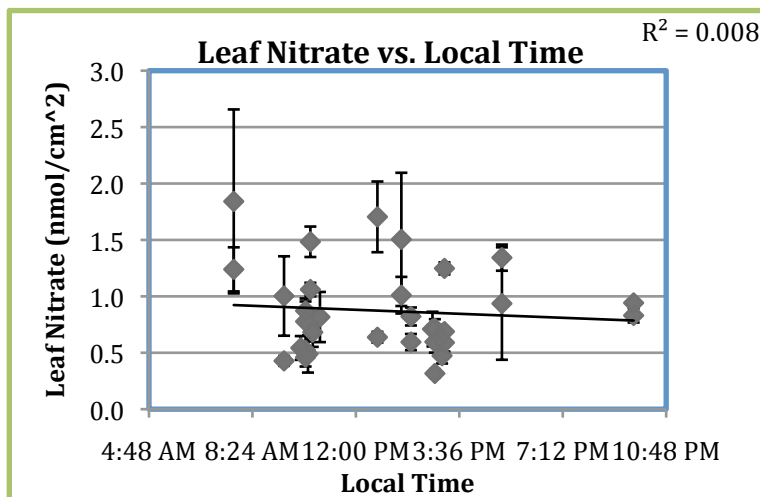ignificant. Figure 5 shows all data collected and does not show any significant pattern. The data is highly variable and in the future could be improved by collecting more samples each day and plotting differences between the first sample of each day and following samples. To reduce the effect of variability three-hour averages were plotted. Figure 6 shows the average relationship between nitrate on the leaf and time of sampling. The points of the graph follow a trend of decrease in the morning yet the high standard deviations of each point show that the data is simply too variable to show any significant trend.

Figure 5. All nitrate measurements versus time of sampling.

To minimize the effects of meteorological differences between days differences between matched samples (same location, same species, same day) were taken and plotted against the midpoint time between the two points. This resulted in a graph showing how much nitrate decreased relative to the first
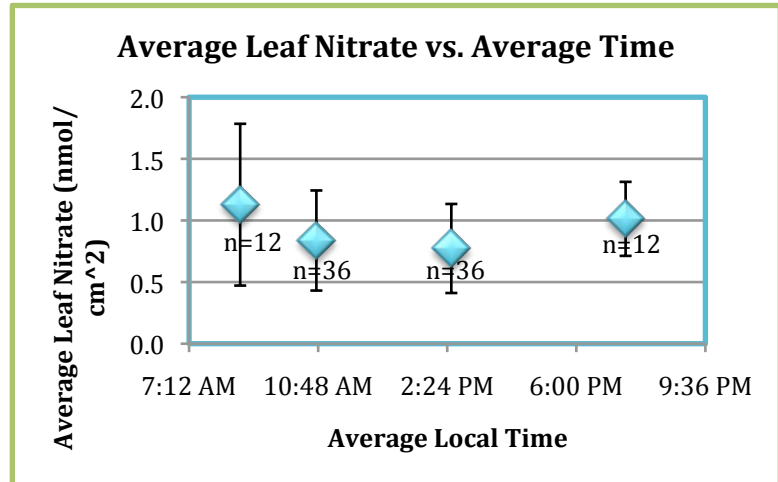
Average Leaf Nitrate vs. Average Time

Figure 6. Three-hour averages of nitrate data.

measurement of each day. A second-order polynomial was fit to this data with an R^2 value of 0.55, which indicates a significant relationship at p<0.01 (see Figure 7). This shows that nitrate on the leaves was decreasing throughout the morning, with the rate dropping off around noon, and then changing to accumulation in the afternoon.

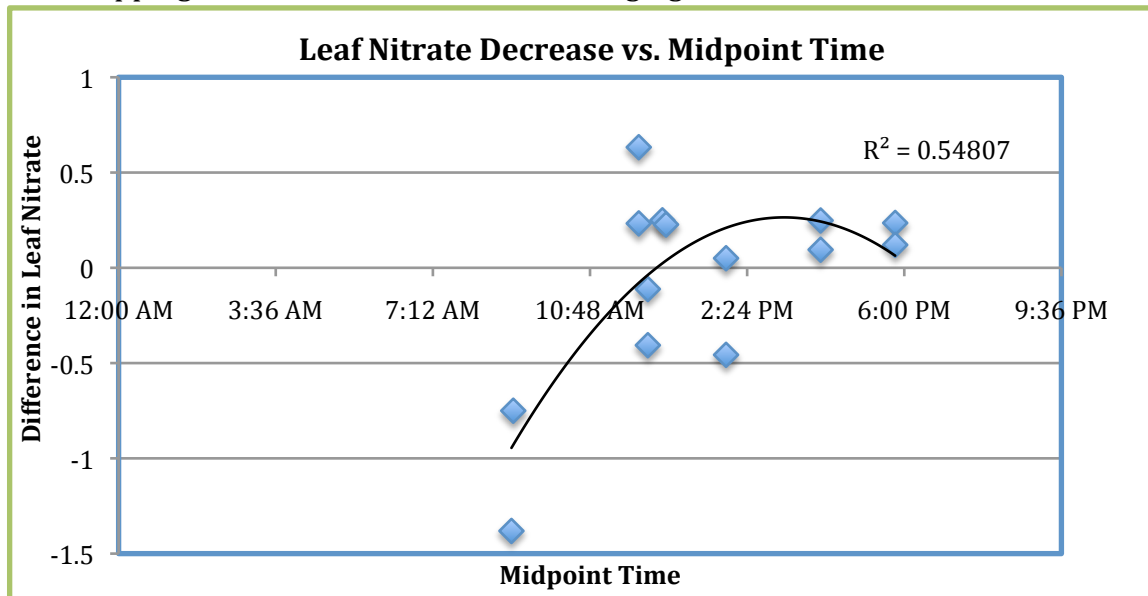**Leaf Nitrate Decrease vs. Midpoint Time**

$R^2 = 0.54807$

Figure 7. Differences between consecutive points.

To investigate the role of nitrate deposition in determining the level of nitrate on the leaf, observed points were plotted alongside predicted values of nitrate excluding effects of deposition. The predicted values were estimated by calculating the approximate photolysis rate of nitrate on the leaves for every half hour throughout the sampling period. The photolysis rate constant was approximated using the following equation:

$$J \sim J^{max} * (UV/UV^{max})$$

The predicted value of nitrate was calculated by the following equation:

$$[HNO_3]^t = [HNO_3]^o * e^{-Jt}$$

where $[HNO_3]^t$ is the predicted nitric acid concentration at time t, $[HNO_3]^o$ is the initial nitric acid concentration, J is the calculated photolysis rate constant at time t and t is the amount of time that has passed between $[HNO_3]^o$ and $[HNO_3]^t$. Each point was calculated by using the previous point as the initial value, the corresponding J and 1800 s as t.

Further analysis shows that there is variability in the rate of dry deposition throughout the day. Figure 8 shows the predicted concentrations (based on the first sample of each day) and the measured concentrations plotted against time. Assuming changes in leaf surface nitrate are due to only photolysis, observed concentrations that fall above the predicted concentrations indicate deposition, those on the line indicate no deposition and those below indicate little or no deposition with non-photolytic processes removing nitrate. There are obviously many factors affecting the

Figure 8. A sample of photolysis prediction graphs. Diamonds represent predicted values, squares represent observed values.

deposition of nitrate, but what is indicated from these graphs is that in the afternoon deposition is occurring at a rate high enough to cause a net accumulation even with photolytic loss occurring.

There seems to be an opposite trend in the morning. There may be less deposition in the morning because the air is low in nitrate due to most of it being deposited on surfaces during the night. In the one day where this is shown (July 29), the measured concentration actually goes below the prediction by photolytic loss. This means that at least on that day there was another mechanism contributing to loss of nitrate from the leaf surface. This could be explained by nitrate simply revolatilizing back to the atmosphere (Honrath, et. al.), or could be caused by other chemical reactions that are more prevalent in the first light hours of the day.

When viewed in conjunction with flux measurements of total reactive nitrogen (NO_y) obtained above the canopy, there is more that this data can say about the fate of reactive nitrogen. In the summer of 2005 reactive nitrogen measurements taken at the PROPHET tower show that in the net NO_y flux was always negative, reaching a maximum deposition rate of approximately -1.4 $\mu mole/m^2/h$ at ~10:30 AM, for averaged measurements from August 9 to September 2 (Hogg, 2007). At this same time, calculated flux from 3-hour averaged

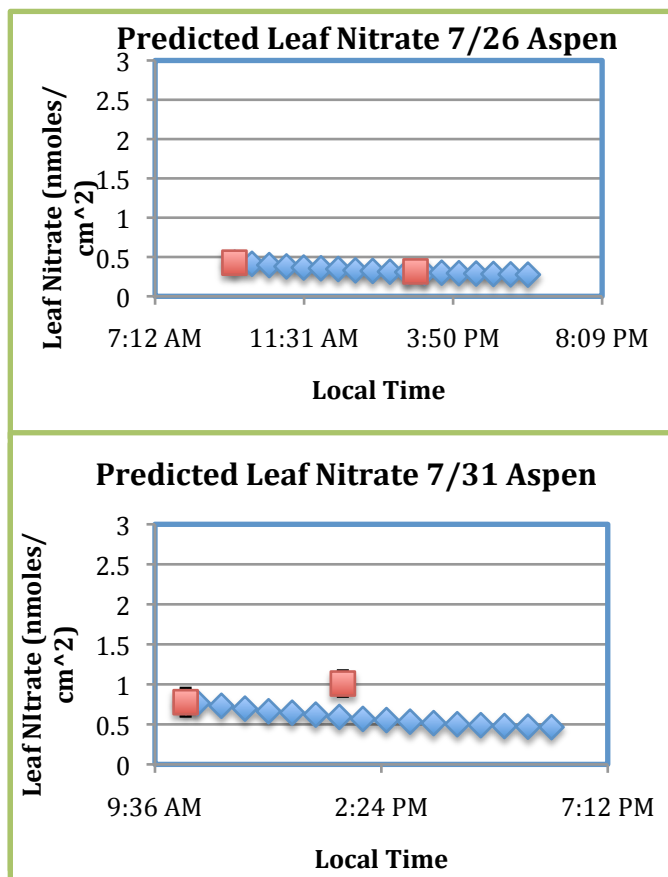leaf measurements show a flux of HNO_3 from the leaf to be approximately 1.35 µmole/m^2/h. If the relationship between these fluxes is assumed to be
net flux= up flux (from surfaces/transport) + down flux (deposition, values are negative), then dry deposition is 2.75 µmole/m^2/h. This means that deposition can be twice as high or higher than net flux and therefore net flux of NO_y is, by itself, not an accurate representation of deposition.

The variation between replicates in this study was high. This is attributed to the high number of factors affecting the amount of nitrate on each leaf and the relatively low precision of the measurement process.

One of the major sources of variation was the occurrence of rain within 24 hours before the sampling. Qualitative measurements of rain nitrate showed that concentrations were above 3 µM, which is much higher (over 1000x) than any concentration measured on the leaves. There are many possible effects on the leaves from the rain. Since it was so high in nitrate it could add nitrate to the leaves, or the rain could take more leaf nitrate with it as it washes over the leaves.

Following a rain event or dew formation, it was observed that aspen leaves dried much more quickly than maple or oak leaves. Although the type of leaf was not expected to show a significant difference in general, how quickly each leaf dries after the rain event could also effect how much nitrate is on it at the time of sampling. All of these factors could cause high variability in samples taken within a day after a rain event. Figures 9 and 10 show the marked decrease in variability when samples with rain and without rain in the previous 24 hours are separated.
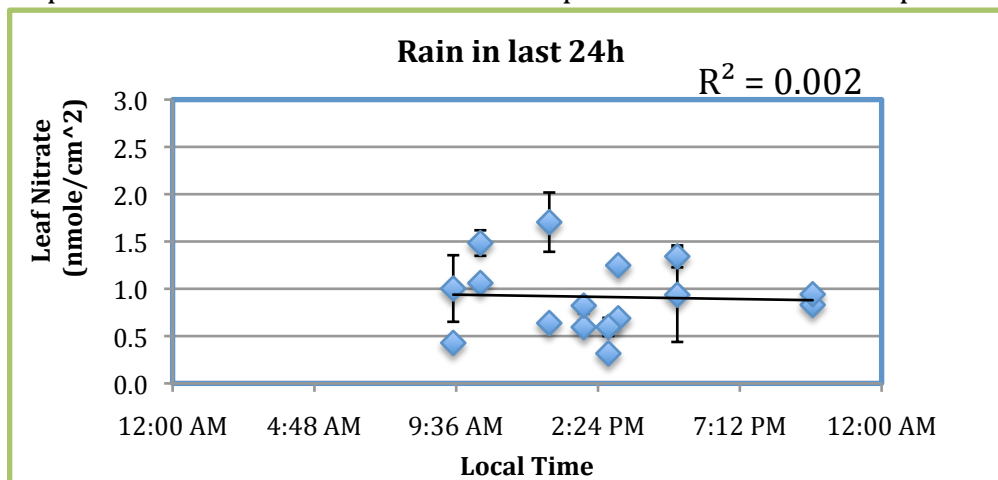

Figure 9. Nitrate measurements versus sampling time when there was rain within 24 hours before sampling.
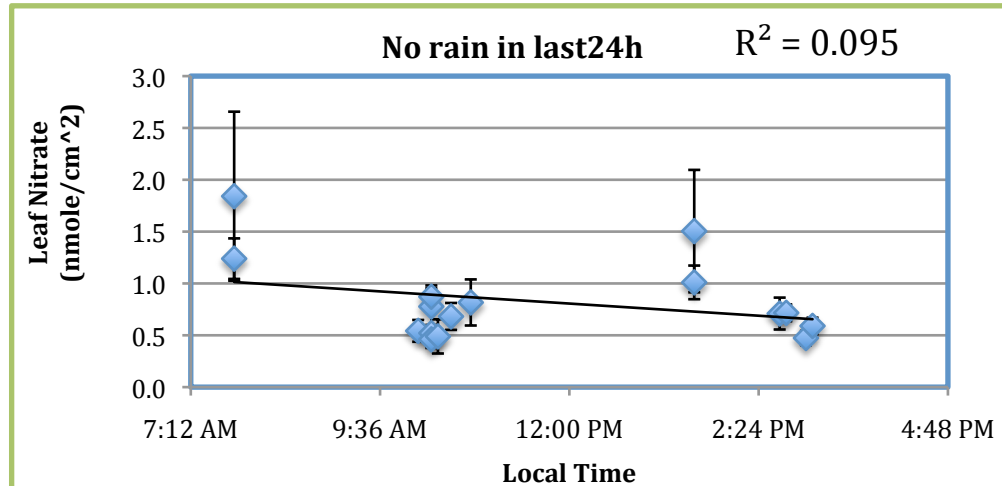
Figure 10. Nitrate measurements versus sampling time when there was no rain within 24 hours before sampling.

One factor that does not seem to be a major source of variation between samples is the species of leaf. Figure 11 shows the samples separated by species of leaf and qualitatively there does not appear to be a significant difference between red maple, bigtooth aspen and red oak. Figure 12 shows the differences between aspen and maple and aspen and oak. Differences between matched samples (same date and time) were taken and averaged. The difference between maple and aspen was not significant but the difference between oak and aspen was significant at $p=0.05$. This difference may be due to the larger size and more brittle condition of the oak as compared with leaves of the other two species. It is also possible that oak leaves, being fairly brittle, sustained more damage upon being inserted into the sample tubes. This may have resulted in some nitrate from inside the leaf tissue being released into the wash solution.
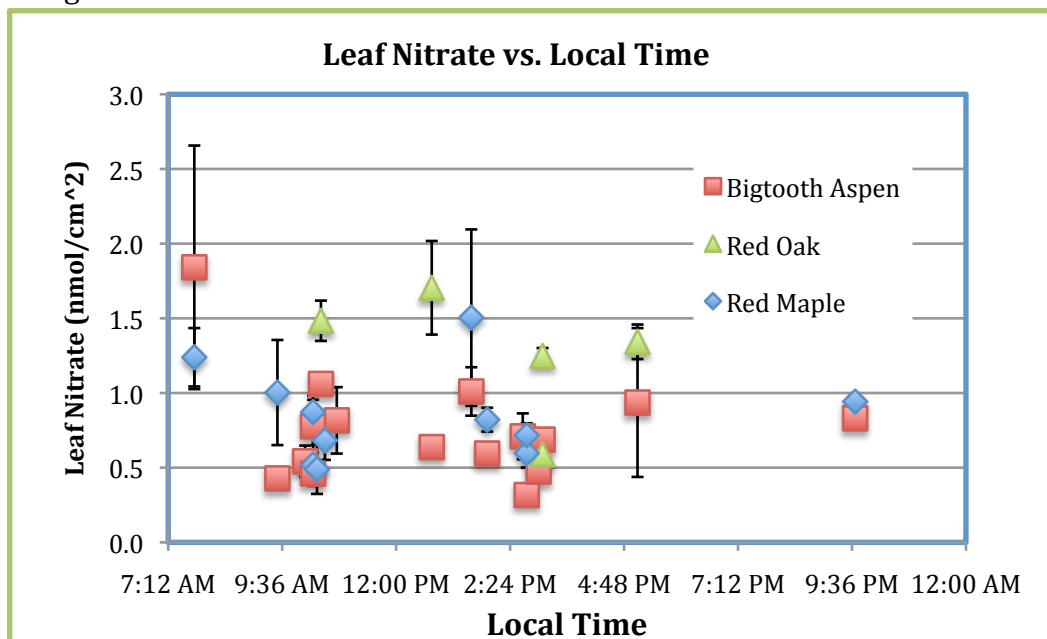

Figure 11. Each measurement plotted versus sampling time and separated by species.
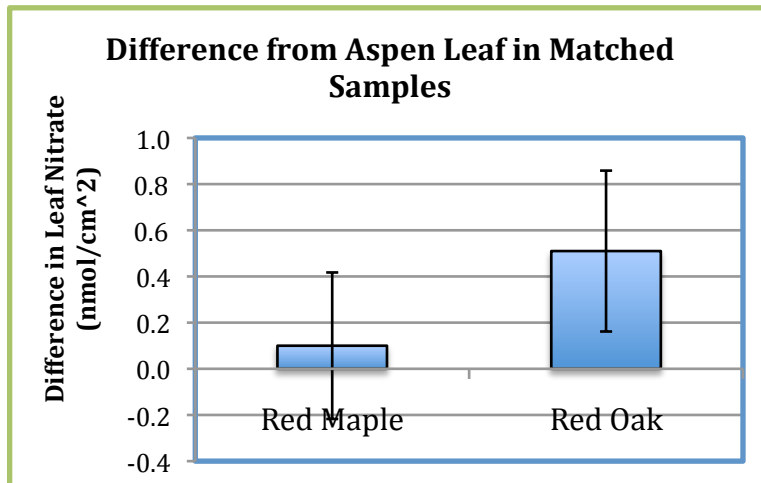
Difference from Aspen Leaf in Matched Samples

Figure 12. Differences between species.

Conclusion:

The results of this study show that leaf surface nitrate varies throughout the day. Plotting differences between each two values of each day showed that there was a significant relationship between time of day and leaf nitrate, with nitrate decreasing through the morning and accumulating in the afternoon. For other factors examined, rain increased random variability and oak leaves showed significantly higher nitrate concentrations than aspen leaves. Analysis of the data in comparison with photolysis rates and measured NO_y flux data suggested that nitrate deposition to the forest may be almost twice as high as the net flux of NO_y and that it also varied throughout the day. In the future, more effective studies could be performed by taking more data points in each day in order to obtain a better assessment of changes in nitrate concentration throughout the day. Future studies may also include a more in depth investigation of higher nitrate levels measured on oak leaves.

Recommendations for Future Work:

Future studies on leaf surface nitrate levels should include a more rigorous sampling regime, with more samples collected on each sampling day and more sampling days. Increasing the size of the data set will allow more significant conclusions do be drawn in the future. Unless study is being done explicitly on the effects of rain, samples should not be collected within 24 hours after a rain event because this will only increase random variability in the sample set. Samples throughout each day should be matched as well as possible with regard to all other factors being tested to ensure that temporal differences are not due to other differences between samples.

References:

Alicke, et. al., *Journal of Geophysical Research*, **107**, LOP 9-1 (2002).

Anderson and Hites, *Environmental Science and Technology*, **30**, 1756-1763 (1996).

Dollard, et. al., *Nature*, **326**, 481-483 (1987).

Finlayson-Pitts and Pitts, *Journal of the Air and Waste Management Association*, **43**, 1091-1100 (1993).

Hogg, Alan. Stomatal and Non-Stomatal Fluxes of Ozone, NOx, and NO_y to a Northern Mixed Hardwood Forest, University of Michigan Doctoral Thesis (2007).

Honrath, et. al., *Atmospheric Environment*, 36, 2629-2640 (2002).

Kato and Akimoto, *Atmospheric Environment*, **41**, 171-191 (2007).

Mayewski and Legrand, *Nature*, **346**, 258-260 (1990).

Olivier, et. al., *Environmental Pollution*, **102**, 135-148 (1998).

Penner, et. al., *Journal of Geophysical Research*, **96**, 959-990 (1991).

Sirois and Barrie, *Tellus,* **40B**, 59-80 (1988).

Volkamer, et. al., *Atmospheric Chemistry and Physics Discussions*, **7**, 5365-5412 (2007).

Yao, et. al., *Environmental Science and Technology*, **32**, 2646-2649 (1998).

Zhou, et. al., *Geophysical Research Letters*, **28**, 4087-4090 (2001).

Zhou, et. al., *Journal of Geophysical Research*, **107**, 4590-4600 (2002).

Zhou, et. al., *Geophysical Research Letters*, **30**, 2217-2220 (2003).