ABSTRACT

Peterson, Barry Todd. AN EXPERIMENTAL STUDY OF THE VERTICAL EDDY DIFFUSIVITY AND DRY DEPOSITION OF AMMONIA ON A NATURAL GRASSY SURFACE. (Under the direction of S. Pal Arya and Viney Aneja.)

Until recently ammonia has been relatively ignored as a primary pollutant in the United States. Due to the rapid growth of animal (hog) farms, eastern North Carolina experiences higher levels of ambient ammonia and ammonium concentrations. The primary focus of this work was on the eddy diffusivity and the dry deposition velocity of ammonia over a natural grassy surface downwind of some typical natural/anthropogenic sources in eastern North Carolina.

All Data was collected on a 7m aluminum walk-up tower. Temperature, wind speed, wind direction and ammonia/ammonium concentrations were collected at two different heights (2m and 6m). Citric acid coated annular denuders with filter packs were used to measure the ammonia and ammonium concentrations. The tower was located at the NADP site NC41 in Raleigh, NC. The tower is located 300-400m from a small waste lagoon used by the NCSU Educational Swine Unit. The fetch is undisturbed in all quadrants except for the northeast. The northeast quadrant is disturbed by a group of small trailers, greenhouses and swine houses. The remaining quadrants are grassy fields used for grazing approximately 100 head of cattle

Hourly-averaged measurements of temperatures, wind speeds and concentrations of ammonia and ammonium are made. We assume a horizontally-homogeneuous atmospheric surface layer. Surface-layer similarity relations were used for estimating the

vertical fluxes of momentum and heat. The modified Bowen ratio and gradient method were used for estimating the vertical flux and the deposition velocity of ammonia.

AN EXPERIMENTAL STUDY OF THE VERTICAL EDDY DIFFUSIVITY AND DRY DEPOSITION OF AMMONIA ON A NATURAL GRASSY SURFACE

by

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BIOGRAPHY

Barry Todd Peterson was born in North Carolina. He has a younger and older brother. His family moved to Michigan when he was three and he continued to live there until 1989, when he moved to Raleigh, NC.

He initially was in the hydraulic and pneumatic industry and became the branch manager of a hydraulic and pneumatic distributor in Raleigh, NC. After moving to Raleigh he decided that he wanted to pursue a career in air quality/pollution.

In October of 1991 he was married to Elizabeth Marie Mark. She is also from Michigan and moved to North Carolina with him.

He obtained his Bachelor of Science in Meteorology from North Carolina State University in May 1997. In the spring semester of 1998 he began his pursuit of a Master of Science in Atmospheric Science.

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I. A REVIEW OF ATMOSPHERIC MEASUREMENT METHODS AND RESULTS OF FIELD EXPERIMENTS AND OBSERVATIONS OF AMMONIA AND AMMONIUM CONCENTRATIONS AND DRY DEPOSITION ON NATURAL SURFACES

INTRODUCTION:

Ammonia is one of the most abundant reducing species and reactive component of the atmosphere. As a pollutant, it has been largely ignored in the United States. Recently Europe has shown an increasing interest in atmospheric ammonia (NH_3) and ammonium (NH_4^+), (NH_x=NH_3 + NH_4^+). There have been some recent advances in the ambient concentration measurement technology, specifically continuous flow denuders (ECN, The Netherlands; Wyers *et al.,* 1993), that have recently made it possible to accurately determine dry deposition rates of ammonia and ammonium . There have been some studies done in the Netherlands which has experienced higher concentration levels of NH_3 and NH_4^+ than other parts of Europe. Due to the rapid growth of animal (hog) farms, Eastern North Carolina also experiences higher levels of NH_3 and NH_4^+ (see Appendix 2-5). This similarity of ammonia concentrations and terrain makes it imperative for us to review the recent studies of ammonia concentrations and deposition/emission rates in the Netherlands and other parts of Europe for developing similar methods to be used in Eastern North Carolina.

DRY DEPOSITION:

Dry deposition is defined as the downward exchange of trace gases and aerosols from ambient air to any natural or man-made surface. The processes involved are gravitational settling of particulate matter, transport by turbulent eddies, molecular diffusion, inertial impaction or absorption at the surface (Aneja *et al.,* 1994) (see Figure 1).

The dry deposition of NH_3 is important close to the source with wet deposition of NH_4^+ being more important at some distance downwind from the source (Asman, 1995, 1998). Dry deposition of NH_3 can vary greatly in an area of scattered local sources. NH_3

is different from many pollutants in that in the presence of significant liquid phase concentrations (e.g., lagoons handling animal waste and sprayed fields), it can allow an upward flux, while away from surface sources the flux is downward resulting in dry deposition. The flux is dependent upon the relative magnitude of the surface NH_3 concentration and that of the environmental concentration (C_e). The ammonia compensation point (C_{cp}) is the gas phase concentration at equilibrium with the liquid NH_3 concentrations in plants. When $C_e = C_{cp}$ there is no net flux. The consumption of NH_3 by plants is in equilibrium with their emissions due to biological processes (Farquhar *et al.*, 1980).

NH_3 concentrations depend on spatial distribution of emission sources, as well as near-surface winds, atmospheric stability, temperature, moisture and pH. An increase in surface temperature can cause a shift from deposition to emission. Atmospheric humidity, roughness and wetness of surface, and near-surface winds also influence the dry deposition rate. Through the use of an appropriate air quality and dispersion model, it is possible to quantify these effects and obtain some general relationships between ammonia flux and environmental and surface variables.

Due to the large number of meteorological and surface characteristics involved and the chemical reactivity of NH_3, it is rather difficult to parametize NH_3 exchange between the surface and the atmosphere (primarily the atmospheric boundary layer). Micrometeorological flux measurements or estimates based on the gradient or modified Bowen ratio methods are used to determine dry deposition or emission rates. An indirect method that is used frequently to parameterize the deposition velocity (V_d) utilizes the resistance analogy or approach (Aneja *et al.*, 1986; Hicks *et al.*, 1987).

$$V_d = (R_a + R_b + R_c)^{-1} \qquad (1)$$

Here R_a is the aerodynamic resistance, R_b is the quasi-laminar boundary layer resistance, and R_c is the surface/canopy transfer resistance. This method has been used to adequately describe the dry deposition to surfaces where emission is rare or negligible. While it does ignore compensation point estimates, it has been widely used in the estimation of NH_3 fluxes. The most uncertain term in the above parameterization is the surface/canopy resistance (R_c) (e.g., Aneja *et al.*, 1994; Duyzer, 1994; Erisman *et al.*, 1988; Fowler *et al.*, 1998; Wyers *et al.*, 1998).

INTERACTION OF GASEOUS AMMONIA AND AEROSOL AMMONIUM:

Aerosol $NH_4^+$is the primary atmospheric reaction product of NH_3. Ammonium particles can be either in the solid and/or aqueous phase. NH_4^+ can be produced by the sublimation or condensing of NH_3 gas onto particles forming solid ammonium compounds (Wexler and Seinfeld, 1990) and by the atmospheric reactions involving NH_3 and acid gases (see Appendix 1). Ammonia can dissolve in water forming an NH_4^+ that has been found to be one of the major ion constituents in clouds (Saxena and Lin, 1990; Li and Aneja, 1992). There is also the molecular diffusion of background ammonia onto particle surfaces. Ammonia is a highly reactive gas component in the atmosphere. It exists in the atmosphere in three phases: gas, aqueous and particle (see Appendix 1). It is this reactivity between phases that has made it difficult to accurately measure atmospheric ambient concentrations used in the estimation of fluxes (Jaeschke *et al.*, 1998).

MEASUREMENT TECHNIQUES AND METHODS:

CONTINUOUS WET-FLOW DENUDER

The continuous flow denuder (ECN, The Netherlands; Wyers *et al.*, 1993) consists of a rotating annular denuder, a pump, a detector unit and a data logger. The denuder is rotated at a speed of 30 rotations per minute. Air is sampled through the denuder at 30 liters per minute. Sodium hydrogen sulfate ($NaHSO_4$) is used as the absorption solution. This solution coats the walls of the denuder as it rotates. The absorption solution is monitored and kept at a constant level in the denuder. NH_3 is absorbed in the solution with an efficiency > 99%. The solution is pumped out and replaced with fresh solution continuously at certain intervals. After the absorption solution is pumped out it is mixed with 0.5 M sodium hydroxide (NaOH) containing 60 ppb NH_4^+. The two solutions are merged in a mixing chamber/debubbler at a rate of 0.08 ml/min. The result is the formation of gaseous ammonia. Approximately 30% of the ammonia will permeate a semi-permeable PTFE membrane and is dissolved into a stream of double-demineralized water. The demineralized water has had all the carbonates

removed from it by an ion exchange column. The ammonium concentration in the stream is determined conductometrically. The temperature of the stream is measured by a thermistor. This temperature is used to correct the analysis for temperature effects. The data logger registers all the data which can be analysed to determine average concentrations.

VANADIUM(V) OXIDE (V_2O_5)-COATED THERMODENUDER

The thermodenuder (ECN, The Netherlands; Keuken *et al.*, 1989) consists of a V_2O_5-coated annular denuder, a pump, a transportable oven, a NO_x monitor and a data logger. Air is pumped through the annular denuder and is adsorbed in the coating solution with an efficiency > 99%. After sampling, the oven is heated to 700°C and transported over the last 10 cm of the denuder. This section of the denuder is heated for 5 min. The oven is then transported over the entire denuder and again heated for 5 min. The adsorbed NH_3 is converted to NO_x and then pumped into the NO_x monitor using the ambient air as the carrier gas. The signal from the first 10 s of sampling is used for the baseline calculation. The NO_x concentration is sampled for both 5 minute intervals and integrated by the data logger. The NH_3 concentration is determined by the difference in the integrated peaks (this assumes that all the NH_3 is adsorbed in the first part of the denuder, while any possibly interfering N-containing compounds are equally adsorbed in the whole denuder), the gas flow and a calibration constant. (Mennen *et al*., 1996).

TUNGSTEN(VI) OXIDE (WO_3)-COATED THERMODENUDER

This thermodenuder (Romer *et al.*, 1994; Braman *et al.*, 1982) consists of two WO_3 coated denuders, a tube that has a gold foil serving as a catalyst, a pump, a NO_x monitor and a computer that controls the instruments and stores the collected data. To heat the denuders and the catalyst tube they are wrapped in heating wire. Air is pumped through one of the denuders for 15 minutes. NH_3 and NO_y (reactive oxidized nitrogen species = $NO + NO_2 + HNO_3 + HNO_2 + PAN + \cdots$) are chemisorbed on the coating with an efficiency > 98%. After the 15 minutes of sampling the tube is heated to 400° C and flushed with helium and oxygen (He/O_2) . While this tube is heated and flushed the other tube is sampling the air. This provides a continuous measurement. NH_3 and NO_y desorb in the heated tube and are pumped through the catalyst and heated to 800° C. At this temperature they are converted into NO. This NO containing gas is diluted with clean air

and then drawn into the NO_x monitor. The NO signal is measured and then integrated in the computer. This integration is done in such a way that the NO_y is not calculated as NH_3.

DYNAMIC FLOW THROUGH CHAMBER FLUX METHOD

This open bottom cylindrical chamber (diameter = 27 cm, height = 42 cm, and volume = 25 liters) is constructed from polycarbonate material and is held in place by a stainless steel frame driven into the ground to a depth of ~ 10 cm. The inner chamber wall is coated with five mil thick flourinated ethylene propylene (FEP) Teflon® to reduce the loss to the walls. Air is pumped through the chamber. The internal air volume is well mixed by a motorized teflon stirrer. The collection procedure can vary. The outlet port can be connected by PFA teflon tubing directly to an analyser or the air sample can be collected in a teflon bag and then immediately (< 1min) analysed to determine concentrations (Kim *et al*., 1994; Sullivan, 1995). A mass balance method is used to determine the flux of the trace gas.

DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY (DOAS)

The DOAS consists of a high pressure Xenon lamp, a receiver, a detection system and a computer (Mennen *et al*., 1996). Light is generated between 200-1000 nm. A concave mirror is used to collimate the light. The receiver is placed at the other side of the light path. The received light is then transmitted through a fiber optic cable to the detection system. The detection system is a 0.5-m Czerny-Turner spectrometer with a rapid scanning device (a rotating disk with a 200-mm diameter that has 20 slits of 0.4 mm width), a photo multiplier tube (PMT), a 12-bit ADC and a computer. The computer analyzes the measured spectra. The main absorption peak of NH_3 is between 200-220nm. NH_3 concentrations are determined by the measured spectra and then stored in the computer.

PHOTOACOUSTIC MONITOR

This instrument (Rooth *et al.*, 1990) uses a CO_2 laser, a photoacoustic cell, a series of four microphones, a lock-in amplifier and a computer. Chopped infra-red light is transmitted through the photoacoustic cell that is continuously flushed with the ambient air. The chopper frequency is tuned to the resonance of the cell. Different species absorb the light at different wavelengths. This absorbed energy is released as heat. This heat

produces a pressure wave. The microphones detect the acoustic signal that is generated. This signal is then amplified. The signal is corrected for the background absorption of water and CO_2. CO2 and water concentrations are determined from the photoacoustic signal that is generated using 9.23 μm wavelength. NH_3 does not absorb light at this wavelength. NH_3 molecules are excited by the photons in the 9.22 μm wavelength. The concentrations of NH_3, carbon dioxide (CO_2) and water are determined and stored by the computer.

ANNULAR DENUDER (CAD/IC) SYSTEM

To collect NH_3 the denuder is coated with citric acid. There is a filter pack attached to the end of the denuder. The filter pack contains a Teflon filter. This collects the particulate matter that flows through the denuder. The Teflon filter is followed by a nylon filter that collects gaseous nitric acid (HNO_3) that may be released from the Teflon filter due to dissociation of ammonium nitrate, or any nitric acid in the ambient air stream. The samples from the denuder and filter pack are extracted by using de-ionized water. The anions in this solution are analyzed by ion chromatography and the NH_4^+ by colorimetric method. Atmospheric concentrations are determined from this analysis by measuring the flow rates. (Aneja and Murthy, 1994; Wiebe *et al*., 1990).

PASSIVE SAMPLERS

The passive sampler consists of 4 pairs of 10 cm long glass tubes with the inner walls coated with oxalic acid (inner dia. 0.7 cm). The two tubes are connected in series. One end of the tube has a stainless steel disc inserted to reduce the air flow inside the tubes. The reduced flow speed increases the NH_3 collection efficiency and helps to establish a low friction resistance. The pairs of tubes are mounted so that a set of tubes is facing in the north, south, east and west directions. Anemometers measure the wind speed. The average horizontal NH_3 flux (F_{hz}) is calculated. The F_{hz} is then divided by the mean wind speed (m/s) at the same height as the sampler. The result is the wind speed weighted NH_3 concentration (Schoerring, 1995; Hansen *et al.*, 1998).

COMPARISON OF AMMONIA MEASURING METHODS:

The following results are from a field study conducted in Bilthoven, Netherlands. (Mennen *et al.*, 1996) It was found that overall the ECN continuous-flow denuders provided the fastest response time. It can measure fluctuations in ammonia concentrations with a characteristic time of 1.5 min. It has a low detection limit, high precision, linear range up to at least 300 μgm^{-3} with a linearity < 1%, nearly no interferences, high accuracy and a fast response. It is highly suitable for measuring NH_3 concentrations in areas that have rapidly varying concentrations, such as in areas with high emissions. Most importantly it can be used to determine deposition fluxes using the gradient method. It does have the disadvantage that because it is positioned horizontally the sedimentation of particles may affect the separation procedure. (Wyers *et al.*, 1993)

The vanadium(V) oxide (V_2O_5) thermodenuder responded much slower to rapid concentration variations than the continuous denuder. It demonstrated a linear range up to 200 μgm^{-3}. There were frequent problems with the oven and datalogger. The tungsten(VI) oxide (WO_3) also experienced trouble in the field. The instrument tended to drift consistently and there was a continued problem of a constant value given. It also had a linear range up to 200 μgm^{-3}. The DOAS system did not suffer from problems in the field and as long as the concentrations are not too low it could be used over open fields. It does require constant attention. The receiver needed frequent aligning with the light path. The photo-acoustic monitor is not suitable for measuring ambient field concentrations. It was not able to provide useful data. The annular denuder showed good results and had a linear range up to 300 μgm^{-3} but it cannot provide continuous or short-time averaged concentration measurements.

Another study (Williams *et al.*, 1992) also had good results with the citric acid coated denuders (CAD/IC) in comparison to the photo-fragmentation/laser-induced flourescence (PF/LIF) instrument, Molybdenum oxide (MoO_3) annular denuder sampling/chemiluminescence detection (MOADS) technique, a tungsten oxide denuder sampling/chemiluminescence detection (DARE) system and an oxalic acid coated filter pack sampling/colorimetric analysis (FP/COL) method. The CAD are a good choice when continuous measurements are not required or desired. The sample times are

typically around 2 hours. This method is labor intensive but it offers good results at a modest cost.

It was found that with the passive flux samplers the estimated vertical flux will differ from the true flux because wind-weighted concentrations are used instead of time-weighted, no stability correction is used and the averaging rules in measurements are neglected. Errors of 10-50% can be expected in the calculation of annual ammonia flux (Hansen *et al.*, 1998). This system might provide sufficient results for long-term flux determination but it is not suitable for rapidly changing NH_3 concentration areas and continuous measurements.

The dynamic flow-through chamber has been used for determining the NO_x and NH_3 soil fluxes (Kim *et al*., 1994; Sullivan, 1995; Aneja *et al*., 2000). It has been used primarily for measuring soil emissions.

MICROMETEOROLOGICAL FLUX METHODS:

MASS BALANCE METHOD

The flux is determined by calculating the amount of NH_3 that crosses a plane through the whole boundary layer of the area of interest. The following formula is used (Denmead, 1983; Wilson and Shum, 1992):

$$F_{NH3} = \frac{1}{X}\int_0^{Z_{bl}} u(z)[C_{a(z)} - C_{ao(z)}]dz \qquad (2)$$

X is the upwind distance between the edge of the plot and the mast (m), Z_{bl} is the height of the internal boundary layer (m), u(z) is the wind speed at height z and $C_{a(z)}$ and $C_{ao(z)}$ are the concentrations of NH_3 at height z measured on the mast and upwind of the experimental plot. Measurements are usually made at 5-6 heights from the soil surface to the height Z_{bl}.

EDDY CORRELATION METHOD

This method uses the direct measurements of the turbulent exchanges to determine the flux. It requires fast-response instrumentation to measure the fluctuations of velocity, temperature and trace concentration that contribute to the momentum and other fluxes. The covariance can then be computed by averaging the products of the

fluctuations over any chosen time interval. For example, vertical fluxes of momentum (τ) and heat (H) are given by the following formulas (Arya, 1988):

$$\tau = -\rho\overline{uw} \quad (3)$$

$$H = \rho C_p \overline{\theta w} \quad (4)$$

with x axis oriented along the mean wind.

These fluxes approximate the surface fluxes, if it is assumed that the fluxes remain constant, independent of height in a horizontally homogeneous surface layer (Arya, 1988). The mass flux of NH_3 cannot be measured using this method, until a suitable fast response sensor for measuring concentration fluctuations becomes available.

M-O SIMILARITY THEORY

From the M-O similarity relations the friction velocity (u_*) and friction temperature (θ_*) can be estimated. These can then be used to estimate the dimensionless wind shear (ϕ_m) and potential temperature gradient (ϕ_h):

$$(kz / u_*)(\partial U / \partial z) = \phi_m(\zeta) \quad (5)$$

$$(kz / \theta_*)(\partial \Theta / \partial z) = \phi_h(\zeta) \quad (6)$$

k is the von karman constant. These are the basic similarity functions that can relate the constant fluxes to the mean gradients in the surface layer (Arya, 1988; 1999).

$$\tau = \tau_o = \rho u_*^2 \quad (7)$$

$$H = H_o = -\rho C_p u_* \theta_* \quad (8)$$

They can also be used to determine the eddy diffusivities or exchange coefficients of momentum (K_m) and heat (K_h) (Arya, 1988, 1999).

$$K_m = (kzu_*) / \phi_m(\zeta) \quad (9)$$

$$K_h = (kzu_*) / \phi_h(\zeta) \quad (10)$$

GRADIENT METHOD

Measurements of mean wind speed and temperature are made at two heights. Finite difference approximations can used for the gradients in the surface layer. These approximations can be used for computing the Richardson number (Ri) and the corresponding Monin-Obukhov stability parameter z/L. Using the exchange coefficients of heat and momentum these fluxes can be calculated using the gradient transfer relations (Arya, 1988, 1999):

$$\tau_o = \rho K_m (\partial U / \partial z) \tag{11}$$

$$H_o = -\rho C_p K_h (\partial \Theta / \partial z) \tag{12}$$

MODIFIED BOWEN RATIO

The basic assumption of this method is the equality among the exchange coefficients. If the flux and concentration at two heights is known for one scalar (e.g., temperature) then the exchange coefficient is known. Using this assumption the flux of another constituent can be determined by measuring it's concentration at the same heights.

$$F_2 = F_1 \frac{\Delta C_2}{\Delta C_1} = k_1 \Delta C_2 \tag{13}$$

Where F_1 and F_2 are the fluxes, ΔC_1 and ΔC_2 are the differences in the concentrations (of the two species between the two heights) and k_1 is an exchange or transfer coefficient. Temperature or water vapor is considered as a reference scalar whose flux is measured either using the eddy correlation method or estimated from the gradient method.

COMPARISON OF MICROMETEOROGICAL METHODS:

The mass balance method (MBM) has been shown to be useful for small areas with limited fetch. It is best used for measuring the initial emissions after slurry spreading in a field (Genermont *et al.*, 1998).

The eddy correlation method has the least assumptions and measures the turbulent exchanges directly but it requires expensive fast response instruments. The lack of

suitable fast-response sensor for ammonia makes this method impractical for field studies.

The gradient method has been used successfully in many studies (Erisman and Wyers, 1993, Hansen *et al*., 1998, Schonburg and Stobel, 1989). The difficulty lies in determining the appropriate eddy diffusivities. In strongly stratified conditions the gradient method may become invalid due to the uncertainties in the M-O flux profile relations (Arya, 1988).

The use of the modified Bowen-Ratio technique has been made to measure fluxes of trace gases (Duyzer, 1994, Huebert and Robert, 1985, Meyers *et al.*, 1996). The results showed that the exchange coefficients were not statistically different. This supports the assumption that once trace gases enter the atmosphere they are mixed indiscriminately due to atmospheric turbulence. The use of this method alone with a reactive species such as NH_3 would not be advisable. It could be used in conjunction with gradient method (and M-O Similarity Theory) because they are related by eddy diffusivities. Using these two methods together has the benefit of not requiring expensive instrumentation. They are not as sensitive to errors in sampling and difference measurements like that of the eddy correlation method (Businger, 1986). They have been used successfully in many studies of other trace gases.

RESULTS OF FIELD EXPERIMENTS:

Erisman and Wyers, (1993) studied the surface exchange properties of NH_3 over two heathland sites. The sites were *Leender Heide* and *Elspeetsche Veld* in the Netherlands. The undisturbed fetch was from 500 to 1000m extending from southeastern to northern directions for *Leender Heide* and from 400 to 1000m extending from the southeastern to western directions for *Elspeetsche Veld*. Winds from other directions are disturbed by forests and farms. The dominant species on these sites is heather with an average height of 25-30 cm. These two heathland sites are located in an area that has extensive livestock production. Three continuous wet-denuders were placed at 1, 2 and 4 m above the canopy surface. The NH_3 concentrations were measured continuously and stored as 30 minute averages. These were used with the micrometeorological gradient method to determine deposition parameters. During dry environmental conditions with

relative humidity below 60%, the surface/canopy resistance (R_c) varies from 500 to 1000 s/m. Emission fluxes of NH_3 (0-0.5 µg/m²/s) were observed when a low ambient concentration of NH_3 existed during these dry conditions. During wet environmental conditions with the relative humidity above 80% or during rain the R_c becomes negligible. It was observed that during wet fog conditions the R_c would vary from 0 in low pH to 200-800 s/m in high pH conditions. Deposition fluxes of (0-0.30 µg/m²/s) were observed during wet conditions. The average deposition velocity (V_d) during this study was 2.2 (± 2.2) cm/s. It was noted that there were no differences in these deposition parameters between the two sites. It was found that during small gradients when V_d is small the error in the estimation of R_c increases. This increase in error might be overcome if enough continuous data sets are available to allow the data to be analysed using error-weighting in a time series analysis.

In another study Duyzer (1994) found that over the heather/purple moor grass vegetation of the Netherlands NH_3 is deposited more rapidly than ozone, sulfur dioxide (SO_2) or nitrogen dioxide (NO_2). During this study more than 100 measurements of the dry deposition flux of NH_3 and NH_4^+ were made at four different heathland locations. The sites were the similar in that they were homogeneous for least 500 m upwind fetch. There was no ammonia source within a few kilometers of any of these sites. The NH_3 concentration was measured with oxalic acid coated denuders (50 cm long glass tubes; inner dia. 3 mm; flow rate 3 l/m). Three denuders were used at each height logarithmically spaced between 0.6 m and 7.5 m above the canopy surface. Most of the measurements were taken during the daytime. The measurements that were taken at night did not vary much from those taken during the day. The average daytime flux of NH_3 was 3.7 µgm^{-3} with a standard deviation of 4.8 µgm^{-3} and the average daytime flux of NH_4^+ was 6.6 µgm^{-3} with a standard deviation of 6.4 µgm^{-3}. These rates suggest that deposition to the leaf surfaces are important as well as the stomatal uptake. Compensation point effect did not play a role in this study. It is estimated that the compensation point for the Dutch heathland would lie below 1 µgm^{-3}. It was found that wet surfaces are more efficient at absorbing NH_3 than dry surfaces. The wet surface median canopy resistance (R_c) was found to be 15 s/m compared to that of 40 s/m for dry surfaces. There also appears to be no influence by season, time of day or NH_3

concentration on the values of surface/canopy resistance (R_c) and the deposition velocity (V_d). Duyzer *et al*., (1989) also found that there is a correlation between air temperature and NH_3 concentrations. This was explained on the basis that with increased temperatures there will be increased emissions from animal wastes. It should be noted that at one site that is near important source regions the deposition was notably less efficient. Duyzer offered no explanation other than possibly due to the long term exposure to high concentrations the surface at this site had become saturated. An average deposition velocity of 1.9 cm/s was observed during the measurements for all four heathland locations used in this study. Due to the small number of flux measurements over the detection limit for NH_4^+ an estimated deposition velocity of 0.18 cm/s was used. The annual average flux from this study is approximately 10 kg/ha/yr with dry deposition being around 50% of the wet deposition. It is estimated that the input from NH_4^+ does not exceed 20%.

A similar study was conducted over heather and wavy grass in Denmark (Hansen *et al*., 1998). The site was a mostly flat plain with a fetch varying between 200 and 500 m. This study used wind-vane samplers and the micro-meteorological gradient method to calculate the vertical fluxes of NH_3. The ammonia deposition calculated from 5 weekly periods varied from 6.0 to 10.5 kg N /ha/yr with an estimated error of 10-50%. The corresponding deposition velocities varied from 1.0 to 2.9 cm/s. This is of the same order of magnitude found in other studies that used different techniques (e.g. Duyzer, 1994; Erisman and Wyers, 1993).

Continuous wet-denuders and the aerodynamic flux-gradient method were used to measure the ammonia exchange over the moorland of southern Scotland (Fowler, *et al*., 1998). Three denuders were placed at different heights (0.4, 1.4, and 3.4 m) above the moorland to obtain continuous vertical gradients of NH_3 concentrations. Thirty minute mean profiles were used in the calculations of fluxes. The site provided an undisturbed fetch between 1 and 3 km in the directions of 70-190° from the north. The site is pre-dominately grasses, sedges, and mosses with a height variation of 25 to 55 cm. It was found that during the winter months this area was an efficient sink for NH_3 with a deposition velocity range of 1.5 to 3.0 cm/s and a surface/canopy resistance close to zero.

During the summer it experiences significant change. The deposition velocity drops from a February median of 2.5 cm/s to 0.5 cm/s in August as a result of an increase in the surface/canopy resistance due to the dryer and warmer conditions of summer. Its typical daytime value during the summer was 100 s/m. This study did find significant diurnal variation in the summer months. The surface/canopy resistance increased to a maximum by mid-day, which during low ambient concentrations (< 0.2 μgm^{-3}) represented an emission flux of NH_3. This diurnal and seasonal trend was not evident in the Netherlands (Duyzer, 1994). The annual estimate of the dry deposition of NH_3 to this site is approximately 2 kg N/ha with an annual approximation of 3 kg N/ha from wet deposition.

Aneja and Murthy, (1994) conducted a study that included the determination of the dry and wet deposition of NH_3 and NH_4^+, respectively, to high elevation (~ 2006 m) spruce-fir forests. This site was located at Mt. Mitchell State Park in North Carolina. The site consisted mainly of Fraser Firs with a height of 6-7 m. The study was conducted from May through September for 1988 and 1989. Citric acid coated annular denuders with a constant flow rate of 16.5 l/m were used with micrometeorological measurements to determine the deposition parameters. A deposition velocity of 0.8 cm/s was used to estimate fluxes (Aneja *et al*., 1986). Based on concentration measurement above the canopy, the seasonal (May-Sept.) dry deposition estimate of gaseous NH_3 for 1988 was 0.55 (±0.41) kg/ha/season and that of 1989 was 0.21 (±0.72) kg/ha/season. The contribution of aerosol NH_4^+ by dry deposition was much less only 0.16 (±0.11) and 0.12 (±0.05) kg/ha/season, respectively. The estimated wet deposition for 1988 was 0.6 kg/ha/season and 1989 was 1.7 kg/ha/season. The increase in wet deposition in 1989 is probably due to the increase in the ambient concentration level of ammonia in 1989. The ambient concentration measured varied from 0.62 μgm^{-3} in 1988 to 1.47 μgm^{-3} in 1989.

Anderson *et al*., (1993) conducted a similar study on a spruce stand in Denmark. They used oxalic acid coated denuders (glass tubes 50 cm in length; 3 mm dia.; flow rate of 3 l/m) and the gradient method to determine deposition parameters. The site is located in Ulborg Forest and is 40 m above sea level. The site is surrounded by agricultural activities. There is no industry in the area and the nearest town is 15 km away. The site consisted mainly of Norway spruce with a mean height of 10 m. Three denuders were

placed at each height (18 and 36 m) above the forest floor. Two one week sampling periods were conducted, one in the spring and one in late summer. The estimated mean deposition velocity was 2.6 cm/s with the largest value being observed in the afternoon. It is estimated that the average flux for a growing season (25 april-30 sept.) is 87 µg $N/m^2/h$.

Wyers and Erisman, (1998) conducted a study of the ammonia exchange over a Douglas-Fir forest for a 2 year period (1993-1994) using continuous wet-denuders and the gradient method. This area was surrounded by more forest consisting of mainly oak and larch. The mean tree height was 20 m with an estimated stem density of 800/ha. Three denuders were used one placed at each height of 24.5, 28, and 34 m above the forest floor. Thirty minute mean averages were stored. A canopy water storage (CWS) value is calculated from total measured rainfall and total evaporation. This CWS value was used as a means of describing the canopy surface as saturated. When CWS is greater than 2 mm it is considered saturated. The canopy is considered completely dry when the CWS is below 0.25 mm. It was observed that the surface/canopy resistance (R_c) experienced a diurnal trend. During the day R_c was negligible and at night increased to 300 s/m. This trend was not evident when the canopy was saturated. The R_c remained essentially zero both during the day and night. During a dry period in this study there was a clear daily cycle of net deposition at night and net emission during the day that cannot be explained by the shift of aerosol-gas equilibria. This alternating cycle continued until the surface became saturated with water from a rain shower. This cycle was observed to last for 5 days before the rain shower. Overall the study shows that during dry or drying periods the deposition is less efficient than during wet conditions and that the infrequent occurrence of emissions does not influence the overall annual deposition flux.

CONCLUDING REMARKS:

It was not the purpose of this paper to quantify the environmental impact that the deposition of NH_3 and NH_4^+ might have on vegetation and water resources. This is an area that requires continued studies to ascertain the full impact that ammonia is having on the nitrogen loading of soil and surface water.

It has been shown that there is an agreement about the strong influence on the deposition parameters by surface wetness, temperature, pH and humidity. With wet conditions being more efficient at deposition than during dry or drying conditions.

The relative importance of stomatal intake is still a topic of debate. There is a general agreement that it does play a role during the day but it alone does not explain the deposition rates that have been measured. The emissions that are sometimes measured during the day are believed not to influence the annual average deposition rate. There is some disagreement on whether there is a diurnal trend in the deposition parameters. Some studies found none while others did.

The deposition velocity (v_d) decreases in the presence of weak winds. The v_d of ammonia is less over water surfaces than over land (Businger, 1986; Duyzer, 1994; Lee *et al.*, 1998) This suggests a direct relation of roughness length (z_o) to deposition velocity. An increase in z_o will correspond to an increase in the v_d (i.e. Cities and forests have higher deposition velocities than shrub or grass covered surfaces)(Businger, 1986).

In areas of low ambient ammonia concentrations it is generally agreed that the compensation point plays a major role and must be considered in the estimation of deposition velocities. In the Netherlands the compensation point has been found not to play a role due to their higher ammonia concentrations.

With the limited studies that have been done on the dry deposition of NH_3 and NH_4^+ these differences are not surprising. As more studies are done many of the uncertainties that exist today will be resolved.

ACKNOWLEDGEMENTS:

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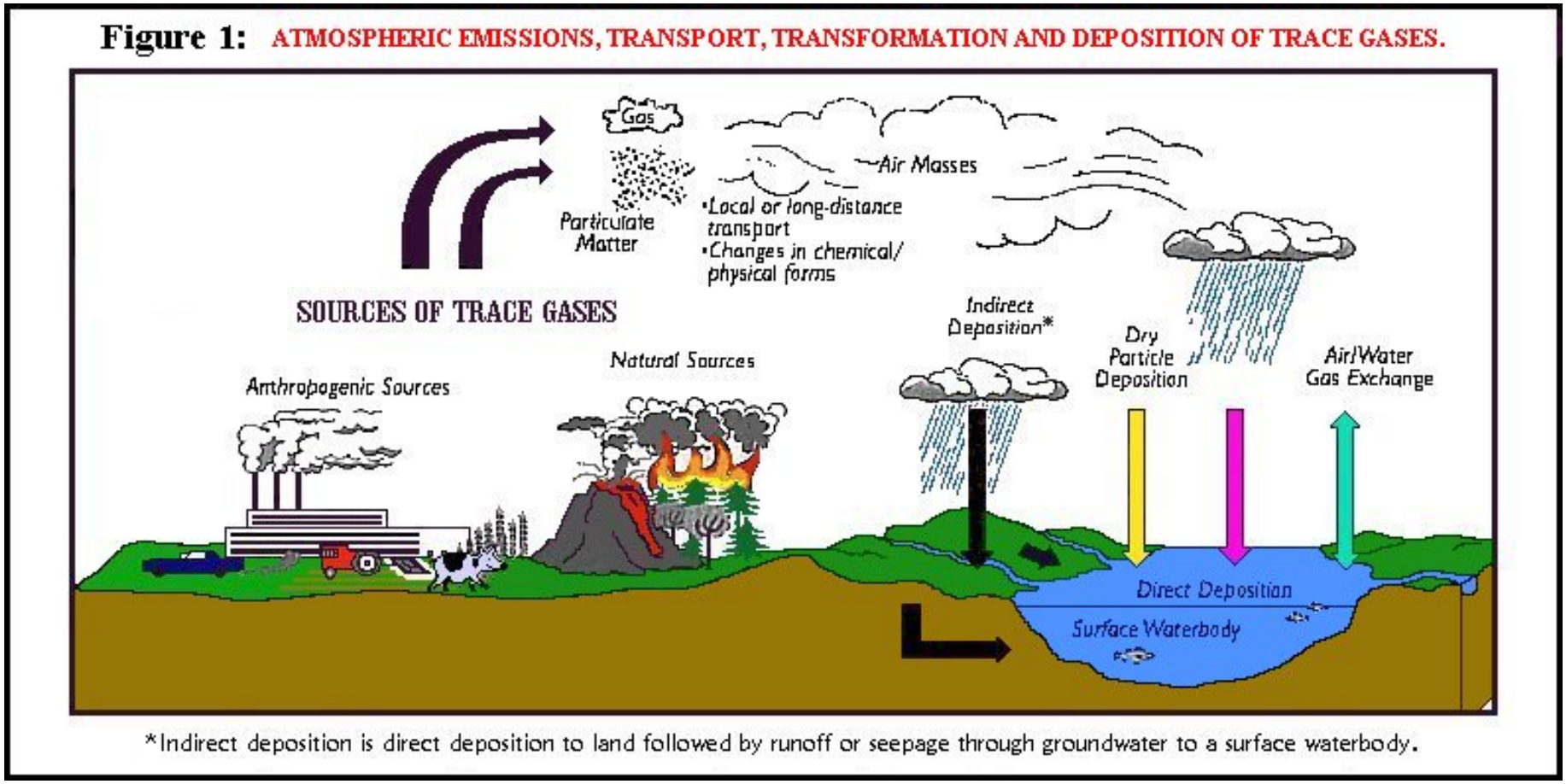


Figure 1. Deposition processes of anthropogenic and natural sources of trace gases.

REFERENCES/BIBLIOGRAPHY

Andersen Helle Vibeke, Hovmand Mads F., Hummelshoj Poul and Jensen Niels Otto (1993) Measurements of ammonia flux to a spruce stand in Denmark. *Atmospheric Environment* **27A**, 189-202.

Aneja Viney P., Rogers H. H., and Stahel E. P. (1986) Dry deposition of ammonia at environmental concentrations on selected plant species. *Journal Air Pollution Control Association* **36**, 1338.

Aneja Viney P. and Murthy Anuradha B. (1994) Monitoring deposition of nitrogen-containing compounds in a high-elevation forest canopy. *Air & Waste Management Association* **44**, 1109-1115.

Aneja Viney P., Malik Brahm P., Tong Quan Sang, Kang Daiwen, Overton, John H. (2000) Measurement and Modeling of NH_3 Emissions at Waste Treatment Lagoon-Atmospheric Interface. *Water, Air & Soil Pollution* **Focus 1**, 177-188.

Arya S. P. (1988) Introduction to Micrometeorology. Academic Press, San Diego.

Arya S. P. (1999) Air Pollution Meteorology and Dispersion. Oxford University Press, New York.

Asman Willem A. H. (1995) Parameterization of below-cloud scavenging of highly soluble gases under convective conditions. *Atmospheric Environment* **29**, 1359-1368.

Asman Willem A. H. (1998) Factors influencing local dry deposition of gases with special reference to ammonia. *Atmospheric Environment* **32**, 415-421.

Asman Willem A. H., Sutton Mark A. and Schorring Jan K. (1998) Ammonia: emission, atmospheric transport and deposition. *New Phytol.* **139**, 27-48.

Braman R. S., Shelley T. J., and McClenney W. A. (1982) Tungstic acid for preconcentration and determination of gaseous and particulate ammonia and nitric acid in ambient air. *Analyt. Chemistry* **54**, 358-364.

Businger J. A. (1986) Evaluation of the accuracy with which dry deposition can be measured with current micrometeorological techniques. *Journal of Climate and Applied Meteorology* **25**, 1100-1124.

Chimka Cassie T., Galloway James N. and Cosby Bernard J. (1997) Ammonia and the Chesapeake Bay airshed. *Stac Publication* **97-1**, 1-49

de Arellano Jordi Vila-Guerau and Duynkerke Peter G. (1995) Atmospheric surface layer similarity theory applied to chemically reactive species. *Journal Geophysical Research* **100**, 1397-1408.

Denmead O. T. (1983) Micrometeorological methods for measuring gaseous losses of nitrogen in the field. In *Gaseous Loss of Nitrogen from Plant-Soil Systems* (edited by Freney J. R. and Simpson J. R.), pp. 133-157. Martinus Nijhoff/dr. W. Junk, The Hague.

Duyzer J. H., Verhagen H. L. M., Erisman J. W. (1989) The deposition of acidifying substances at the Asselsche Heide (in Dutch), *MT-TNO Rep. R 89/029*, Delft, The Netherlands, 1989.

Duyzer Jan (1994) Dry deposition of ammonia and ammonium aerosols over heathland. *Journal of Geophysical Research* **99**, 18,757-18,763.

Erisman Jan Willem, Vermetten Aart W.M., Asman Willem A. H., Wauers-Ijpelaan Anita, Slanina, Jacob (1988) Vertical distribution of gases and aerosols: The behavior of ammonia and related components in the lower atmosphere. *Atmospheric Environment* **22**, 1153-1160.

Erisman Jan Willem and Duyzer Jan (1991) A micrometeorological investigation of surface exchange parameters over heathland. *Boundary-Layer Meteorology* **57**, 115-128.

Erisman Jan Willem and Wyers G. Paul (1993) Continuous measurements of surface exchange of SO_2 and NH_3; Implications for their possible interactions in the deposition process. *Atmospheric Environment* **27A**, 1937-1949.

Erisman Jan Willem, Bleeker Albert and Jaarsveld Hans Van (1998) Atmospheric deposition of ammonia to semi-natural vegetation in the Netherlands-methods for mapping and evaluation. *Atmospheric Environment* **32**, 481-489.

Farquhar G. D., Firth P. M., Wetselaar R. and Weir B. (1980) On the gaseous exchange of ammonia between leaves and the environment: Determination of the ammonia compensation point. *Plant Physiology* **66**, 710-714.

Ferm M., Areskoug H., Hanssen J. E., Hilbert G. and Lattila H. (1988) Field intercomparison of measurement techniques for total NH_4^+ and total NO_3^- in ambient air. *Atmospheric Environment* **22**, 2275-2281.

Fowler D., Flechard C. R., Sutton M. A. and Storeton-West R. L. (1998) Long term measurements of the land-atmosphere exchange of ammonia over moorland. *Atmospheric Environment* **32**, 453-459.

Galperin M. V. and Sofiev M. A. (1998) The long-range transport of ammonia and ammonium in the Northern Hemisphere. *Atmospheric Environment* **32**, 373-380.

Genermont S., Cellier P., Flura D., Morvan T. and Laville P. (1998) Measuring ammonia fluxes after slurry spreading under actual field conditions. *Atmospheric Environment* **32**, 279-284.

Genfa Zhang, Uehara Tomoe, Dasgupta Pumendu K., Clarke Antony D. and Winiwarter Wilfried (1998) Measurement of diffusive flux of ammonia from water. *Analytical Chemistry* **70**, 3656-3666.

Hansen Birgitte, Nornberg Per and Rasmussen Keld Romer (1998) Atmospheric ammonia exchange on a heathland in Denmark. *Atmospheric Environment* **32**, 461-464.

Herrmann Uwe and Jaeschke Wolfgang (1989) Determination of dry deposition of gases over tree tops by measured data and numerical model. *Mechanisms and Effects Of Pollutant-Transfer into Forests*, 13-20.

Hicks B. B., Baldocchi D. D., Meyers T. P., Hosker R. P. and Matt R. P. (1987) A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. *Water, Air and Soil Pollution* **36**, 311.

Huebert B.J. and Robert C. H. (1985) The dry deposition of nitric acid to grass. *Journal of Geophysical Research* **90**, 2085-2090.

Huebert B. J., Luke W. T., Delany A. C. and Brost R. A. (1988) Measurements of concentrations and dry surface fluxes of atmospheric nitrates in the presence of ammonia. *Journal of Geophysical Research* **93**, 7127-7136.

Huebert Richard A., Delany Anthony C. and Huebert Barry J. (1988) Numerical modeling of concentrations and fluxes of HNO3, NH3 and NH4NO3 near the surface. *Journal of Geophysical Research* **93**, 7137-7152.

Jaeschke W., Dierssen J. P., Gunther A. and Schumann M. (1998) Phase partitioning of ammonia and ammonium in a multiphase system studied using a new vertical wet denuder technique. *Atmospheric Environment* **32**, 365-371.

Keuken M. P., Wayers-Ijpelaan A., Mols J. J., Otjes R. P. and Slanina J. (1989) The determination of ammonia in ambient air by an automated thermodenuder system. *Atmospheric Environment* **23**, 2177-2185.

Kim Deug-Soo, Aneja Viney P. and Robarge Wayne P. (1994) Characterization of nitrogen oxide fluxes from soil of a fallow field in the central piedmont of North Carolina. *Atmospheric Environment* **28**, 1129-1137.

Lee D. S., Halliwell C., Garland J. A., Dollard G. J., and Kingdon R.D. (1998) Exchange of ammonia at the sea surface-a preliminary study. *Atmospheric Environment* **32**, 431-439.

Lekkerkerk L. J. A., Heij G. J. and Hootsmans M. J. M. (1995) Ammonia: the facts *Dutch priority programme on acidification*. **Report no. 300-06**

Li Z. and Aneja V. P. (1992) Regional analysis of cloud chemistry at high elevations in the Eastern United States. *Atmospheric Environment* **26A**, 2001-2017.

Mennen M. G., Van Elzakker B G., Van Putten E. M., Uiterwijk J. W., Regts T. A., Van Hellemond J., Wyers G. P., Otjes R. P., Verhage A. J. L., Wouters L. W., Heffels C. J. G., Romer F. G., Van Den Beld L. and Tetteroo J. E H. (1996) Evaluation of automatic ammonia moniters for application in an air quality monitoring network. *Atmospheric Environment* **30**, 3239-3256.

Meyers Tilden P., Hall Mark E., Lindberg Steven E. and Kim Ki (1996) Use of the modified Bowen-Ratio technique to measure fluxes of trace gases. *Atmospheric Environment* **30**, 3321-3329.

Michaelis W., Schonburg M. and Stobel R. P. (1989) Deposition of atmospheric pollutants into a North German forest ecosystem. *Mechanisms and Effects Of Pollutant-Transfer into Forests*, 3-12.

Oss R. Van, Duyzer J. and Wyers P. (1998) The influence of gas-to-particle conversion on measurements of ammonia exchange over forest. *Atmospheric Environment* **32**, 465-471.

Romer F. G., Beld L. van den, Elzakker B. G. van and Mennen M. G. (1994) Automated thermodenuder system for continuous measurement of atmospheric ammonia concentrations. In: *Physico-chemical Behavior of Atmospheric Pollutants*, EC Air Pollution Research Report **50**, 755-760.

Rooth R. A., Verhage A. J. L. and Wouters L. W. (1990) Photoacoustic measurement of ammonia in the atmosphere: Influence of water vapor and carbon dioxide. *Appl. Opt.* **29**, 3643-3653.

Rosenberg Ch Puxbaum H. and Gregori M. (1989) Occurrence of HNO_3, NH_3 and NH_4NO_3 in two forested regions in Austria. *Mechanisms and Effects Of Pollutant-Transfer into Forests*, 97-107.

Saxena V. K., Stogner R. E., Hendler A. H., DeFelice T. P., Yeh R. J. and Lin N. H. (1989) Monitoring the chemical climate of the Mt. Mitchell State Park for evaluation of its impact on forest decline. *Tellus* **41B**, 92-109.

Saxena V. K. and Lin N. H. (1990) Cloud chemistry measurements and estimates of acidic deposition on an above cloudbase coniferous forest. *Atmospheric Environment* **24A**, 329-352.

Schonburg W. Michaelis and Stobel R. P. (1989) Deposition of atmospheric pollutants into a north German forest ecosystem. In *Mechanism and Effects of Pollutant-Transfer into Forests* (edited by Georgii H.W.), pp. 3-12. Kluwer Academic Publishers.

Schjoerring Jan K. (1995) Long-term quantification of ammonia exchange between agricultural cropland and the atmosphere-I. Evaluation of a new method based on passive flux samplers in gradient cofiguration. *Atmospheric Environment* **32**, 885-893.

Seinfeld J. H. (1986) Atmospheric Chemistry and Physics of Air Pollution. Wiley-Interscience Pub., New York.

Sullivan Lee Jay (1995) Biogenic nitric oxide emissions: trends, seasonal variations and interpretations (Under the direction of Viney P. Aneja). Masters thesis, Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, North Carolina.

Sutton M. A., Burkhardt J. K., Guerin D., Nemitz E. and Fowler D. (1998) Development of resistance models to describe measurements of bi-directional ammonia surface-atmospheric exchange. *Atmospheric Environment* **32**, 473-480.

Sutton M. A., Lee D. S., Dollard G. J. and Fowler D. (1998) Introduction atmospheric ammonia: emissions, deposition and environmental impacts. *Atmospheric Environment* **32**, 269-271.

Van Hove L.W. A., Vredenberg W. J. and Adema E. H. (1990) The effect of wind velocity, air temperature and humidity on NH_3 and SO_2 transfer into bean leaves (Phaseolus Vulgaris L). *Atmospheric Environment* **24A**, 1263-1270.

Warneck Peter (1988) Chemistry of the Natural Atmosphere. Academic Press, San Diego.

Wexler Anthony S. and Seinfeld John H. (1990) The distribution of ammonium salts among a size and composition dispersed aerosol. *Atmospheric Environment* **24A**, 1231-1246.

Wiebe H. A., Anlauf K. G., Tuazon E. C., Winer A. M., Biermann H. W., Appel B. R., Solomon P. A., Cass G. R., Ellestad T. G., Knapp K. T., Peake E., Spicer C. W. and Lawson D. R. (1990) A comparison of measurement of atmospheric ammonia by filter packs, transition-flow reactors, simple and annular denuders and Fourier-transform infrared spectroscopy. *Atmospheric Environment* **24A**, 1019-1028.

Williams E. J., Sandholm S. T., Bradshaw J. D., Schendel J. S., Langford A. O., Quinn P. K., LeBel P. J., Vay S. A., Roberts P. D., Norton R. B., Watkins B. A., Buhr M. P., Parrish D. D., Calvert J. G. and Fehsenfeld F. C. (1992) An intercomparison of five ammonia measurement techniques. *American Geophysical Union* paper number 92JD00721 0148-0227.

Wilson J. D. and Shum W. K. N. (1992) A re-examination of the integrated horizontal flux method for estimating volatilisation from circular plots. *Agric. For. Met.* **57**, 281-295.

Wyers Paul G., Oties R. P. and Slanina J. (1993) A continuous-flow denuder for the measurement of ambient concentrations and surface-exchange fluxes of ammonia. *Atmospheric Environment* **27A**, 2085-2090.

Wyers Paul G. and Erisman Jan Willem (1998) Ammonia exchange over coniferous forest. *Atmospheric Environment* **32**, 441-451.

APPENDIX 1:

ATMOSPHERIC TRANSFORMATIONS OF NH_x

Atmospheric transformations of NH_3 are relatively straightforward and are essentially acid base reactions. The following reactions may occur:

1. $NH_3(g) + H_2O(l) \rightarrow NH_4^+ + OH^-$
2. $NH_3(g) + HNO_3(g) \leftrightarrow NH_4NO_3(s)$
3. $NH_3(g) + H_2SO_4(s) \rightarrow NH_4HSO_4(s)$
4. $NH_4HSO_4(s) + NH_3(g) \rightarrow (NH_4)_2SO_4(s)$
5. $NH_3(g) + HCl(g) \leftrightarrow NH_4Cl(s)$

Langford et al (1992) state that the nitrate reaction is more prevalent in western cities where NO_x/SO_2 emissions ratio is larger than in the eastern United States and that the HCl reaction occurs mainly in coastal areas.

Given the speed of the reactions and the solubility of the products, the residence times of NH_3 (Table 3.1) and NH_4^+ (Table 3.2) are in the order of hours to days.

Table 3.1 Residence Times of NH_3 (adapted from Fangmeier et al, 1994)

Residence Time	Source
3-5 days or less	NAPAP, 1990
2.8 hours (day) and 5 hours (night)	Erisman et al, 1988
0.8 days	Moller & Schieferdecker, 1985
1-4 days	Soderklund & Svensson, 1976
4 days	Dawson, 1984

Table 3.2 Residence Times of NH_4^+ (adapted from Fangmeier et al, 1994)

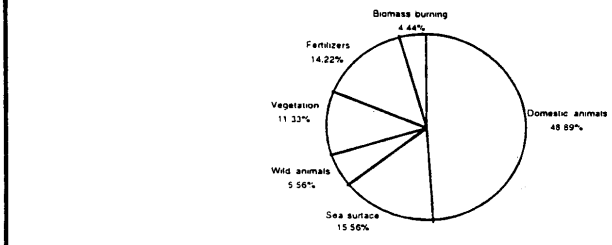
Residence Time	Source
4-7 days	Bonis et al,
7.7 days	Moller & Schieferdecker, 1985
7-19 days	Soderklund & Svensson, 1976
15 ± 9 days	Bottger et al, 1978

Source: Chimka et al (1997)

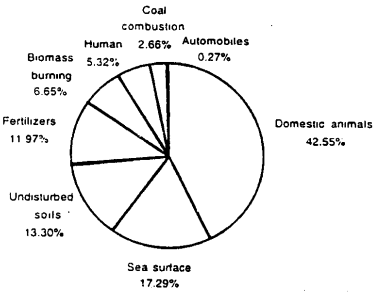
APPENDIX 2:

Estimated global ammonia emissions by source (Tg N per year)

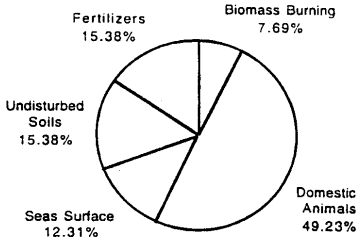
Source	Schlesinger & Hartley, 1992	Dentener & Crutzen, 1994	Galloway et al, 1996
Domestic animals	32.0 (24-40)	22.0	32
Sea surface	13.0 (8-18)	7.0	8 (3-13)
Undisturbed soils	10.0 (6-45)		10
Wild animals		2.5	
Vegetation		5.1	
Fertilizers	9.0 (5-10)	6.4	10
Biomass burning	5.0 (1-9)	2.0	5
Human	4.0		
Coal combustion	2.0		
Automobiles	0.2		
Total	**75.2 (50-128)**	**45.0**	**65 (60-70)**



Dentener & Crutzen, 1994



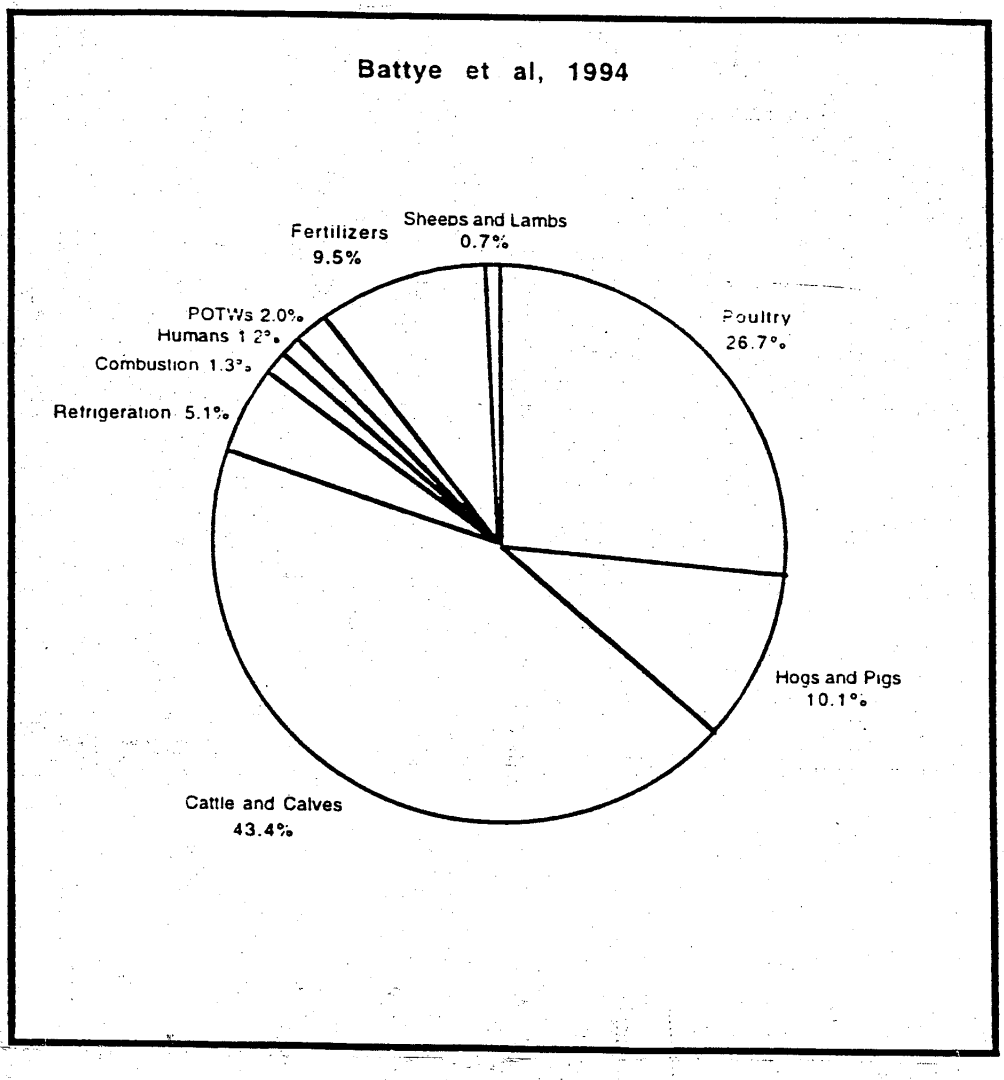
Schlesinger & Hartley, 1992



Galloway et al, 1996

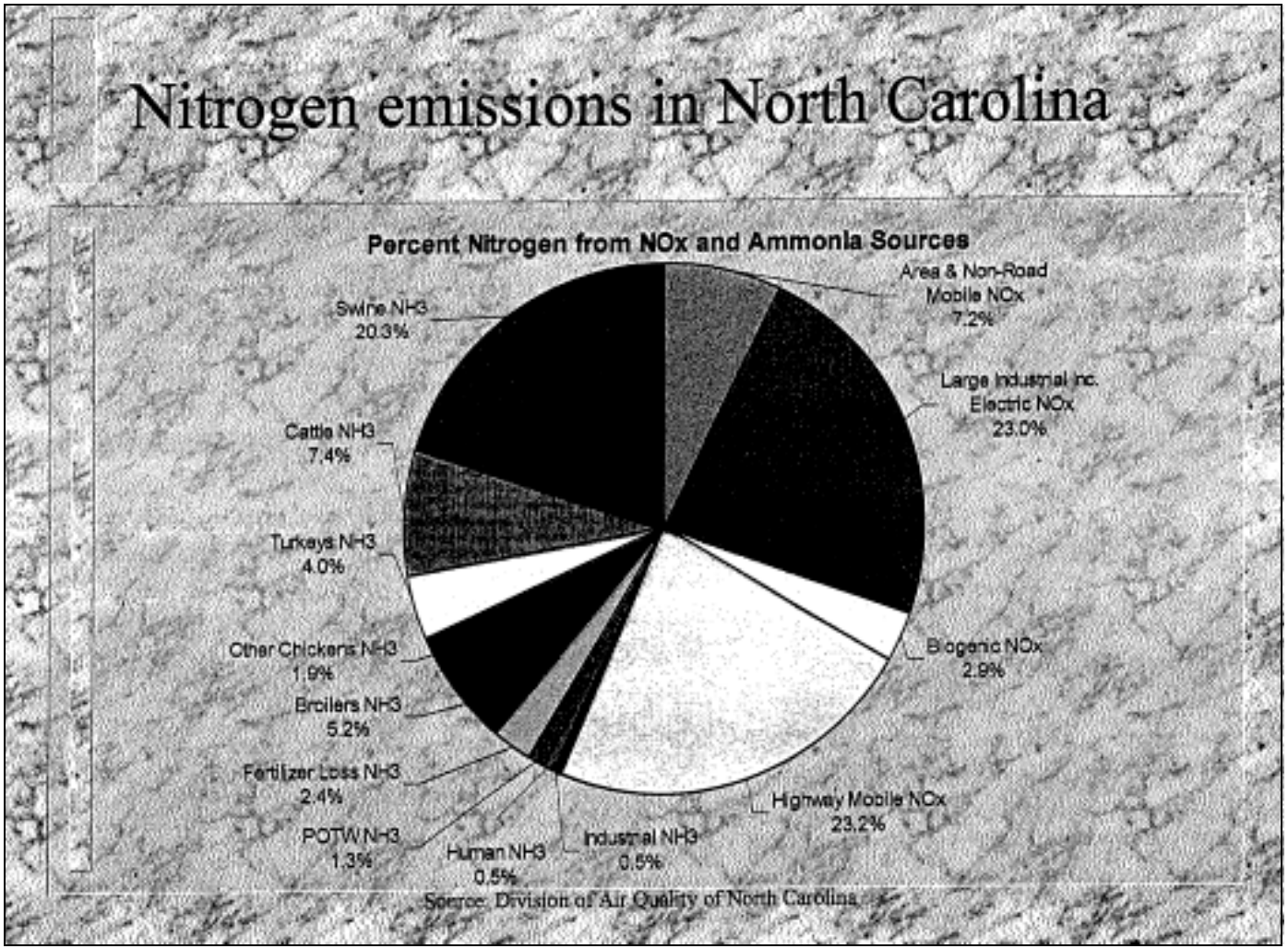
Pie graphs of estimated global emissions by source
Source: Chimka et al. (1997)

APPENDIX 3:



Pie graph of estimated United States emissions by source
Source: Chimka et al. (1997)

APPENDIX 4:


Nitrogen emissions in North Carolina
Percent Nitrogen from NOx and Ammonia Sources
Area & Non-Road Mobile NOx 7.2%
Large Industrial Inc. Electric NOx 23.0%
Biogenic NOx 2.9%
Highway Mobile NOx 23.2%
Industrial NH3 0.5%
Human NH3 0.5%
POTW NH3 1.3%
Fertilizer Loss NH3 2.4%
Broilers NH3 5.2%
Other Chickens NH3 1.9%
Turkeys NH3 4.0%
Cattle NH3 7.4%
Swine NH3 20.3%
Source: Division of Air Quality of North Carolina

APPENDIX 5:

Average wet (W), dry (D) and total NH_x deposition in the Netherlands in the period 1980-1993 (mol $ha^{-1}yr^{-1}$)

	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993
N	0640	0640	0630	0680	0660	0710	0730	0750	0620	0620	0680	0540	0670	0680
D	1565	1660	1690	1630	1710	1700	1710	1710	1610	1560	1560	1650	1300	1320
Tot	2205	2300	2320	2310	2370	2410	2440	2460	2230	2180	2240	2190	1970	2000

Ammonia emissions in the Netherlands in 1980, 1990 and 1993 (million kg NH_3)

Source	1980	1990	1993
Manure	224	222	181
Housing and stores	*82*	*94*	*98*
Fields	*31*	*15*	*15*
Manure application	*111*	*113*	*68*
Artificial fertilizer	10	10	9
Industry	10	6	6
Households	10	11	11
Total	254	249	208

Critical levels for O_3, SO_2, NO_x and NH_3 in the atmosphere to components of forest ecosystems in the Netherlands.

Substance	Vegetation	Effects/criteria	Critical level
O_3	Trees in stands	10% growth reduction	AOT40=10 ppm.h[1]
SO_2	Plants in forests or natural vegetation	Damage, reduced growth	Annual av. 20 $\mu g/m^3$
	Lichen	Change in species composition	Annual av. 10 $\mu g/m^3$
NO_x[2]	Plants	Adverse impact on physiological processes	Annual av. 30 $\mu g/m^3$
NH_3	Natural vegetation	Adverse impact on physiological processes, change in species composition[3]	Annual av. 8 $\mu g/m^3$

1) AOT40 is the hourly concentration exceeding 40 ppb, calculated as the total during the exposure period.

2) Both NO_2 and NO have phytotoxic effects, when determining critical levels it is assumed effects are additive, interaction effects between NO_2 and SO_2 and/or O_3 are also included.

3) Both enhanced and reduced growth are considered; effects of combinations of pollutan considered.

Source: Final report APV III, 1995

II. AN EXPERIMENTAL STUDY OF THE VERTICAL EDDY DIFFUSIVITY AND DRY DEPOSITION OF AMMONIA ON A NATURAL GRASSY SURFACE

INTRODUCTION:

Until recently ammonia has been relatively ignored as a primary pollutant in the United States. Due to the rapid growth of animal (hog) farms, eastern North Carolina experiences higher levels of ambient ammonia and ammonium concentrations (Aneja *et al.*, 2001). The primary focus of our work was the vertical flux of ammonia and dry deposition velocity over a natural grassy surface downwind of some typical natural/anthropogenic sources in eastern North Carolina.

This study was initiated to address the lack of data and knowledge of the ammonia and ammonium deposition in eastern North Carolina. This information is important, as pointed out in North Carolina Department of Environment and Natural Resource's Assessment Plan for Atmospheric Nitrogen Compounds (NCDENR, 1997). It will provide useful insight into the growing problem of nitrogen over-enrichment in the Neuse River watershed and other watersheds in North Carolina. It will also aid in the development of suitable parameterizations of dry deposition velocities of ammonia and ammonium for use in regional air quality models, such as RADM, or EPA's Models-3/CMAQ.

EXPERIMENT:

SITE DESCRIPTION

The site is located at the National Acid Deposition Program's (NADP) Site NC41 near Raleigh, NC (Finley Farm). A seven-meter walk-up tower was erected approximately 300-400 meters from a small waste lagoon used by the North Carolina State University's (NCSU) Educational Swine Unit. This lagoon is located in the northeast quadrant from the tower location. There are also poultry houses located approximately 800 meters due west of the tower. Photographic views of the surrounding terrain and farm facilities in different directions from the tower are shown in Figures

1(a)-(d). There is undisturbed fetch in all quadrants except for the northeast. The northeast quadrant is disturbed by a group of small trailers, greenhouses, swine barns and the lagoon. The remaining quadrants are grassy fields used for grazing approximately 150 head of cattle.

MEASUREMENT TECHNIQUES

The micrometeorological equipment attached to the tower measured the temperature, horizontal wind speed and direction at 2m and 6m (see Figure 2). Fifteen minute averages were stored in a Campbell Scientific data logger. The temperature was measured using two Campbell Scientific Model ASPTC Aspirated Shielded Fine Wire Thermocouples. The horizontal wind speed and direction were measured with two Young Model 05305-5 Wind Monitors. These wind monitors have an accuracy within ± 0.3 m/s and ± 2 degrees.

Ammonia concentrations were measured at 2m and 6m using a citric acid coated annular denuder system, as shown in Figure 3 (Aneja and Murthy, 1994; Wiebe *et al*., 1998). To collect NH_3 the denuder was coated with citric acid. There is a filter pack attached to the end of the denuder. The filter pack contains a Teflon filter. This collects the particulate matter (NH_4^+) that flows through the denuder. The Teflon filter is followed by a nylon filter that collects gaseous nitric acid (HNO_3) that may be released from the Teflon filter due to dissociation of ammonium nitrate, or any nitric acid in the ambient air stream. The citric acid coated denuder was extracted with 10 ml of de-ionized water.

The teflon filter was extracted with 0.2 ml Methanol and 6 ml 0.0001 N. Perchloric Acid. The samples were analyzed by a QuickChem 8000 using the colorimetric procedure (Indophenol blue method). This method has a detection limit of 50 μg N/L of solution.

Three hour sampling times were used. The ambient air was drawn through the denuder at a flow rate of 10 l/min. The atmospheric concentrations were determined using the sample analysis, flow rate and sampling time.

An inter-comparison of the denuders was conducted. Samples were taken with the denuders at the same height in an attempt to determine if any instrument bias existed.

In most cases, the denuders were in good agreement. No pattern emerged of one denuder returning consistently higher concentrations, however there were several instances of significant differences in their concentration measurements. Figure 4 shows the 3-hour averaged concentration comparison of the samples taken by the denuders at the same height. Ensuring that each denuder has the same flow rate of ambient air passing through them is the only calibration that can be done when using these annular denuders. Flow rate through the denuders was the same, therefore it was not the source of the large measurement differences. A regression analysis shows the correlation between the two denuders was still reasonable with $R^2 = 0.77$ (see Figure 5). A comparison of the denuders to the mean resulted in $R^2 = 0.95$ and $R^2 = 0.93$, respectively (see Figures 6 & 7). However, these comparisons indicated that measurements of concentration gradients using two separate denuders might have large errors.

METHODOLOGY

Hourly-averaged measurements of temperature and wind speed and three-hour averaged concentrations of ammonia were made. It was assumed that a horizontally-homogeneuous atmospheric surface layer exists. Surface-layer similarity relations were used for estimating the vertical fluxes of momentum and heat. The modified Bowen ratio and gradient method were used for estimating the vertical flux and the deposition velocity of ammonia and ammonium. The following flux-gradient relations, based on the gradient- transport (K) theory, are commonly used in the surface layer (Arya, 1999, 2001):

$$\overline{u'w'} = -u_*^2 = -K_m \frac{\partial \bar{u}}{\partial z} \tag{1}$$

$$\overline{\theta'w'} = -u_*\theta_* = -K_h \frac{\partial \bar{\theta}}{\partial z} \tag{2}$$

$$\overline{c'w'} = -K_z \frac{\partial \bar{c}}{\partial z} \tag{3}$$

where $\overline{u'w'}$, $\overline{\theta'w'}$, and $\overline{c'w'}$ are the covariance or turbulent fluxes of momentum, sensible heat and tracer gas, respectively, $\bar{u}$, $\bar{\theta}$, and $\bar{c}$ denote the mean horizontal wind

speed, potential temperature, and concentration, and K_m, K_h, and K_z are the eddy diffusivities of momentum, heat, and a tracer gas.

Assuming $K_z = K_h$, from the above relations,

$$\overline{c'w'} = \overline{\theta'w'}\frac{\Delta\bar{c}}{\Delta\bar{\theta}} \tag{4}$$

where $\Delta\bar{c}$ and $\Delta\bar{\theta}$ are the differences between mean concentrations and potential temperatures between the same two heights (i.e., z_1 and z_2). This method of determining the vertical scalar (e.g., ammonia) flux is known as the modified Bowen ratio method.

Estimation of vertical gradients and stability are commonly made using the following logarithmic finite-difference approximations (Arya, 2001):

$$\frac{\partial\bar{u}}{\partial \ln z} \cong \frac{\Delta\bar{u}}{\Delta \ln z} = \frac{\Delta\bar{u}}{\ln(z_2/z_1)} \tag{5}$$

$$\frac{\partial\bar{\theta}}{\partial \ln z} \cong \frac{\Delta\bar{\theta}}{\Delta \ln z} = \frac{\Delta\bar{\theta}}{\ln(z_2/z_1)} \tag{6}$$

The gradients are estimated at the geometric mean height, $z_m = \sqrt{z_1 z_2}$, using the following approximations:

$$\frac{\partial\bar{u}}{\partial z} \cong \frac{\Delta\bar{u}}{z_m \ln(z_2/z_1)} \tag{7}$$

$$\frac{\partial\bar{\theta}}{\partial z} \cong \frac{\Delta\bar{\theta}}{z_m \ln(z_2/z_1)} \tag{8}$$

The gradient Richardson number at the height z_m can also be estimated as

$$Ri = \frac{g}{T_0}\frac{\partial\bar{\theta}}{\partial z}\left(\frac{\partial\bar{u}}{\partial z}\right)^{-2} \cong \frac{g}{T_0} z_m \left(\ln\frac{z_2}{z_1}\right)\frac{\Delta\bar{\theta}}{(\Delta\bar{u})^2} \tag{9}$$

The fluxes of momentum and heat and the scaling parameters can be determined from the following Monin-Obuhkov similarity relations:

$$\frac{kz}{u_*}\frac{\partial\bar{u}}{\partial z} = \phi_m(\zeta) \tag{10}$$

$$\frac{kz}{\theta_*}\frac{\partial \bar{\theta}}{\partial z} = \phi_h(\zeta) \tag{11}$$

where u_* is the friction velocity, θ_* is the temperature scale, k ≅ 0.4 is the von Karman constant, and $\phi_m(\zeta)$ and $\phi_h(\zeta)$ are the empirical similarity functions of the M–O stability parameter $\zeta = z/L$, which is uniquely related to the gradient Richardson number, i.e., $\zeta = f(Ri)$.

Eddy diffusivities of momentum and heat can be expressed as

$$K_m = \frac{kzu_*}{\phi_m} \; ; \; K_h = \frac{kzu_*}{\phi_h} \tag{12}$$

which may differ, especially under daytime unstable conditions.

Using the relationship $\zeta = f(Ri)$, we can estimate $\zeta_m = z_m / L$ and hence, the Obukhov length L. Then , from the M-O similarity relations (Arya, 2001),

$$u_* \cong k\Delta\bar{u} \Big/ \phi_m(\zeta_m)\ln(z_2 / z_1) \tag{13}$$

$$\theta_* \cong k\Delta\bar{\theta} \Big/ \phi_h(\zeta_m)\ln(z_2 / z_1) \tag{14}$$

which can be used to verify the earlier estimate of L, using it's definition

$$L = u_*^2 \Big/ \left(k\frac{g}{T_0}\theta_* \right) \tag{15}$$

Using the estimated M-O scaling parameters, the sensible heat flux can be computed as

$$\overline{\theta w'} = -u_*\theta_* \qquad \text{or,} \quad H_0 = -\rho C_p u_*\theta_* \tag{16}$$

The eddy diffusivity of heat at the height z_m, can be expressed as

$$K_h = kz_m u_* / \phi_h(\zeta_m) \tag{17}$$

All the gradients, similarity scales, sensible heat flux, and eddy diffusivity of heat are estimated or computed for each hourly/averaging period from wind and temperature measurements.

Assuming that the vertical eddy diffusivity of ammonia is equal to that of heat, i.e., $K_z = K_h$, the ammonia flux at $z = z_m = (z_1 z_2)^{1/2}$ can be estimated as

$$\overline{c'w'} = -K_z \Delta\bar{c} \Big/ \left(z_m \ln \frac{z_2}{z_1} \right) \tag{18}$$

in which the eddy diffusivity is the average of K_h over the longer (e.g., 3 hr) sampling period for concentration measurements by the annular denuders.

The deposition velocity is estimated or computed from it's defining expression (Arya, 1999)

$$V_d = -\frac{Flux}{Concentration} = K_z \Delta\bar{c} \big/ \bar{c}\, z_m \ln \frac{z_2}{z_1} \tag{19}$$

where $\bar{c}$ is the average concentration near the surface (say at z_1).

RESULTS:

VERTICAL EDDY DIFFUSIVITY

The fifteen (15) minute averages of temperature and wind speed at heights, z_1 = 2m and z_2 = 6m were collected from the datalogger. These 15-minute measurements were then averaged to compute hourly mean wind speeds and temperatures at both heights. The temperature at z_1 was used as T_o. These hourly mean wind speeds and temperatures were then used in the equations presented in the Methodology section to compute or estimate the variables needed to determine the potential temperature gradient ($\frac{\partial\bar{\theta}}{\partial z}$), heat flux ($H_o$), and eddy diffusivity of heat (K_h) for each hour. The hourly eddy diffusivities of heat corresponding to each hour during the 3-hour sampling events were averaged to compute a 3-hour average K_h to be used in equations (18) and (19).

The diurnal variations of the potential temperature gradient, heat flux, and eddy diffusivity of heat during wintertime sampling are shown in Figures 8-10. It can be seen that on cloudy days (Feb. 5-7) the diurnal variations were rather small in comparison to those on clear sunny days (Feb. 2-3). These results are what would be expected due to solar heating on clear days and the insulating effect of clouds during cool winter days. In the springtime, the variation of these parameters are not as pronounced as those found in

the wintertime. The diurnal variations during springtime sampling are shown in Figures 11-13.

AMMONIA FLUX AND DRY DEPOSITION VELOCITY

Sampling was conducted at various times from February 1999 through May 1999. NH_3 fluxes in the range of -0.5 to 0.5 μg of $N/m^2/s$ and deposition of velocities of -0.14 to 0.4 m/s were estimated using this experimental method.

It is possible to estimate the maximum expected deposition velocity using the following widely used parameterization or expression for deposition velocity of a gaseous substance (Arya, 1999).

$$V_d = (r_a + r_s + r_t)^{-1} \tag{20}$$

where r_a is the aerodynamic resistance to transfer through the turbulent surface layer, r_s is the resistance associated with the molecular sublayer adjacent to the deposition surface, and r_t represents the combined resistance of the surface and transfer to the substrate. An upper bound on the deposition velocity or it's maximum expected value V_{dmax} can be estimated by assuming that the gas is readily absorbed at the surface, i.e., $r_t = 0$. Thus,

$$V_{dmax} = (r_a + r_s)^{-1} \tag{21}$$

using the Reynolds analogy between the mass and the momentum transfers to the surface,

$$r_a = \frac{\bar{u}_r}{u_*^2} \tag{22}$$

where u_r is the mean velocity at the reference height z_r for deposition velocity. An approximate expression for r_s is (Weseley *et al*., 1977),

$$r_s = \frac{c}{u_*} \tag{23}$$

in which the empirical constant is estimated to lie between 5 and 6.5.

Wyers and Erisman (1998) defined the maximum velocity (Vmax) and the maximum possible flux (Fmax) based on aerodynamic resistance only, i.e.,

$$Vmax = \frac{1}{r_a} = \frac{u_*^2}{\bar{u}_r} \tag{24}$$

$$F_{max} = - V_{max} \bar{c}_r = - u_*^2 \frac{\bar{c}_r}{u_r} \qquad (25)$$

They compared their measured (estimated) ammonia fluxes with the maximum possible fluxes. A few cases of |F| >|Fmax| are attributed to the scatter in their data. A comparison of the measured (estimated) fluxes and deposition velocities from this experiment to maximum values calculated using Wyers and Erisman's method are shown in Figures 14 and 15. It can be seen in these figures that many of the measured values exceed the maximum possible value. These values cannot be dismissed as scatter in the data.

As mentioned before, samples were taken with the denuders at the same height in an attempt to determine if any instrument bias existed. While no bias was indicated, it was shown that it was possible to have significant differences in the concentration measurements between the two denuders.

No explanation for the large disparity could be found due to any sampling techniques or procedures used in the field. This left only the possibility of contamination during the coating of the denuders before sampling and/or during sample extraction.

Due to logistical and financial reasons the denuder preparation and sample extractions were done by a third party. This experiment had no control over lab conditions or operating procedures. The lab was a small trailer located just off-site of a large hog farming operation in Faison, North Carolina. Due to it's close proximity to hog waste lagoons the ambient air concentrations of NH_3 would likely be higher than what could be considered normal for our measurement site. This would make it difficult to prep and extract the denuders in what can be considered "clean room" conditions. This was confirmed by the results of the trip blanks that were sent with the samples. These denuders were never opened to the atmosphere. They simply were taken to the site and returned to the lab with sample I.D.'s. The method detection limit was <50 μg of N / L of solution. The results from these blanks ranged from <50 to 230 μg of N / L of solution. Table 1 presents the concentration results of the trip blanks. All of these blanks should have been below the detection limit.

Due to the frequency of high concentrations in the blanks it is very likely the explanation for the measured values of deposition velocity and flux being greater than the calculated maximum values, and the disparity in the denuder concentrations when we took samples at the same height. While the results presented in this paper are suspect due to the apparent problem of contaminated tubes they can still provide some insight into the deposition of NH_3. Not all of the measured values exceeded the maximum possible. Some of these may not have been influenced by contaminated tubes and represent valid values of NH_3 deposition velocity and flux at this site.

The range of precision in the meteorological instruments measuring the wind speed and temperature is another potential source of error in the estimated NH_3 deposition velocity and flux. Incorrect temperature or wind speed measurements by the instruments will influence the gradient estimates, which can lead to a larger or smaller eddy diffusivity of heat being estimated than actually existed during the sampling event.

CONCLUDING REMARKS

While it is highly probable that the estimated range in NH_3 fluxes of -0.5 to 0.5 μg of $N/m^2/s$ and deposition of velocities of -0.14 to 0.4 m/s is too large for the grassy surface measured in this study, it can provide a source of values for comparison by other studies conducted in similar environments on grassy surfaces.

With the advent of reliable chemiluminescence ambient ammonia analyzers the continued use of annular denuders to measure ambient NH_3 concentrations is uncertain. In the event that someone is considering using annular denuders, this study could provide valuable insight into the problems that could be encountered in the use of annular denuders in the measurement of NH_3 concentrations.

Figure 1a. Area North of Tower

Figure 1b. Area West of Tower

Figure 1c. Area South of Tower

Figure 1d. Area East of Tower

Figure 2. Tower with instruments.

Figure 3. Annular Denuder System used to measure ambient ammonia concentrations at 2m and 6m.

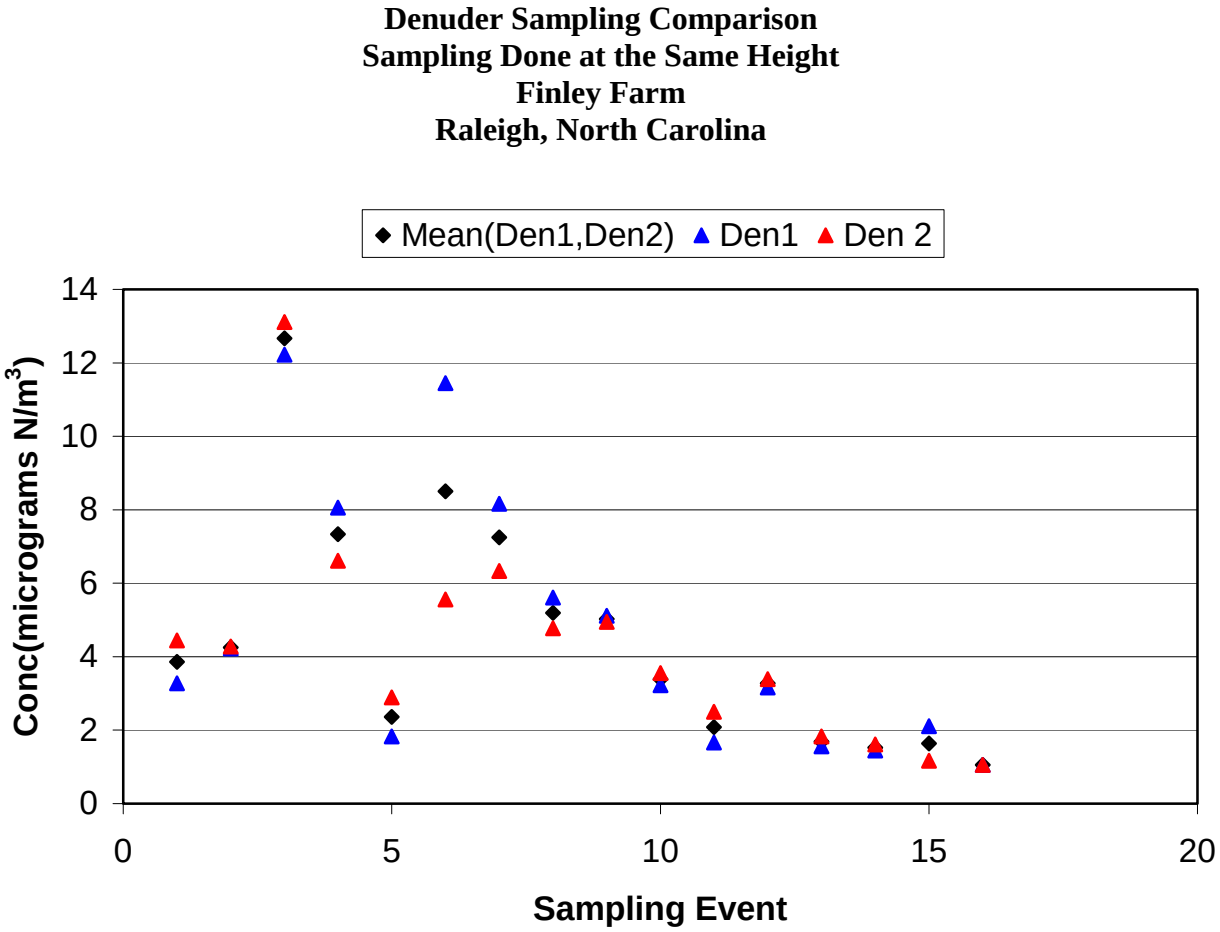


Figure 4. Comparison of concentration measurements of two denuders used in this study at the same height.

Denuder Sampling Comparison
Sampling Done at the Same Height
Finley Farm
Raleigh, North Carolina

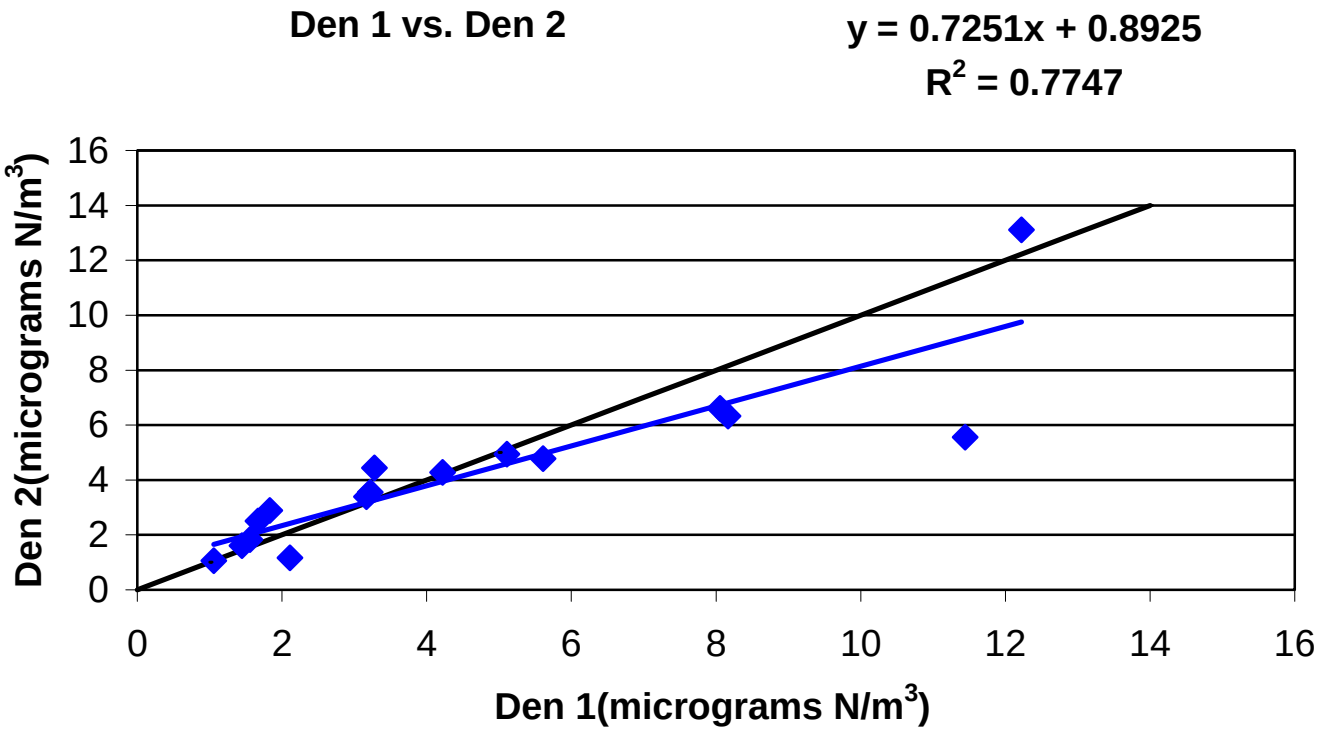


Figure 5. Regression analysis of concentration measurements of two denuders at the same height.

Denuder Sampling Comparison
Sampling Done at the Same Height
Finley Farm
Raleigh, North Carolina

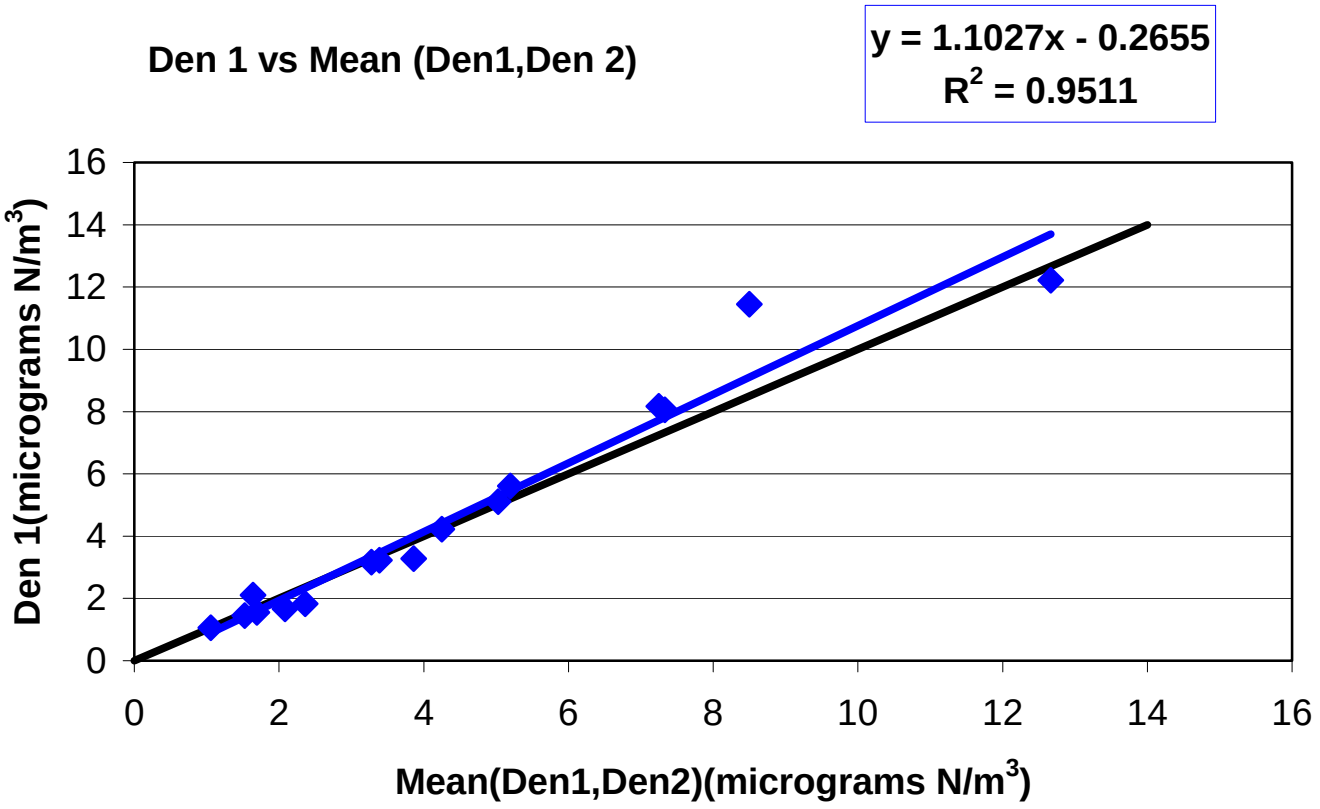


Figure 6. Regression analysis of denuder 1 with the mean of denuders 1 and 2.

Denuder Sampling Comparison
Sampling Done at the Same Height
Finley Farm
Raleigh, North Carolina

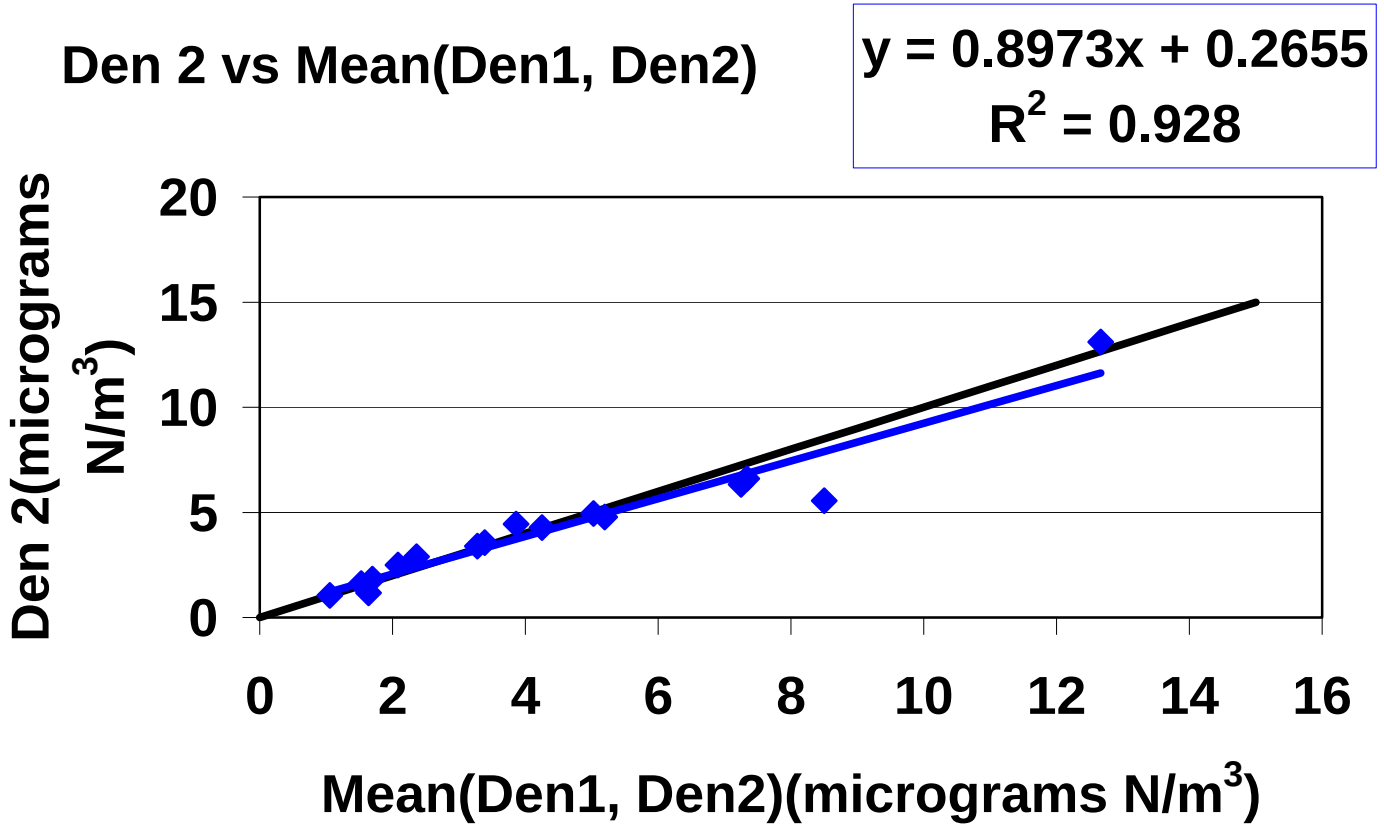


Figure 7. Regression analysis of denuder 2 with the mean of denuders 1 and 2.

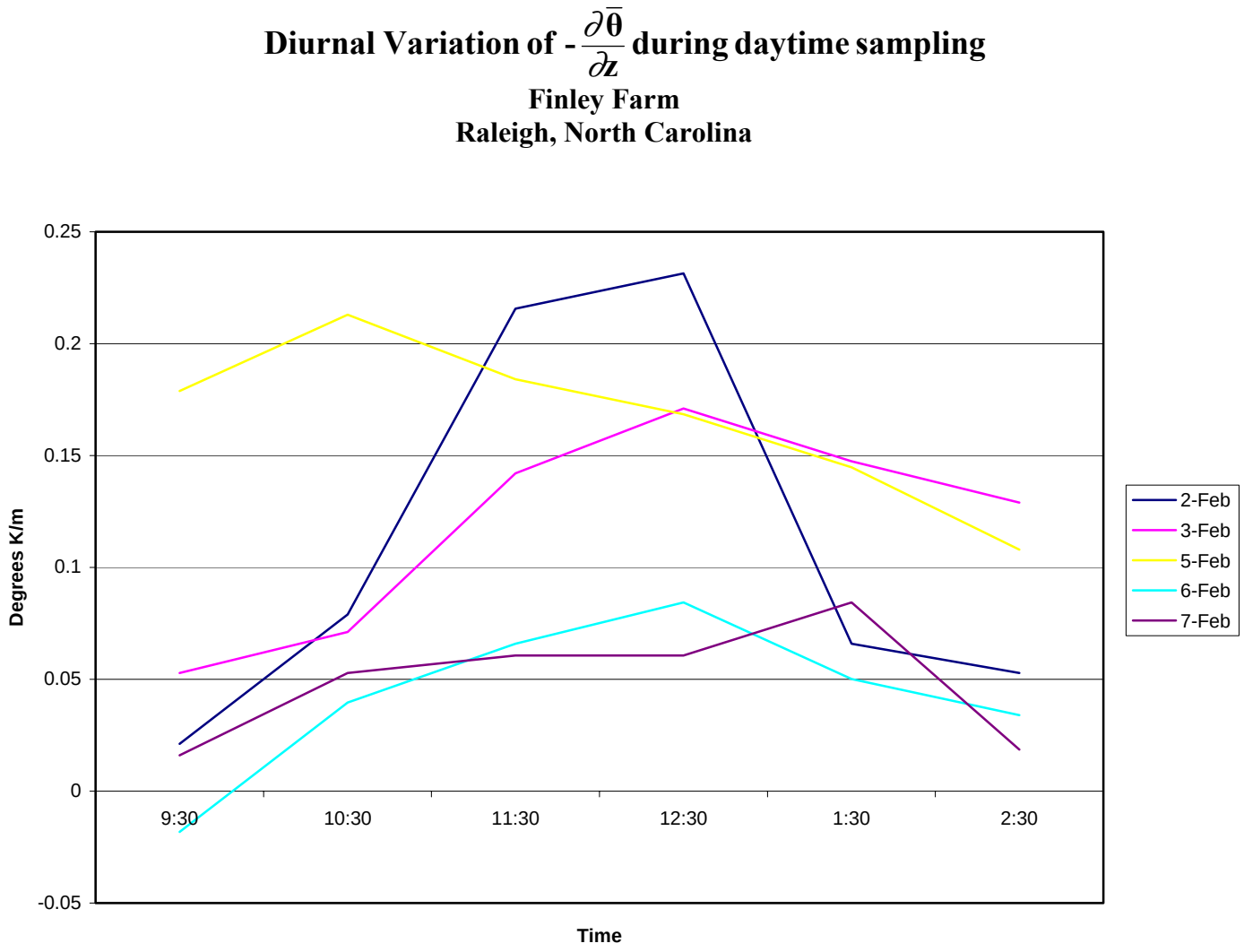


Figure 8. Diurnal variation of potential temperature gradient during wintertime sampling.

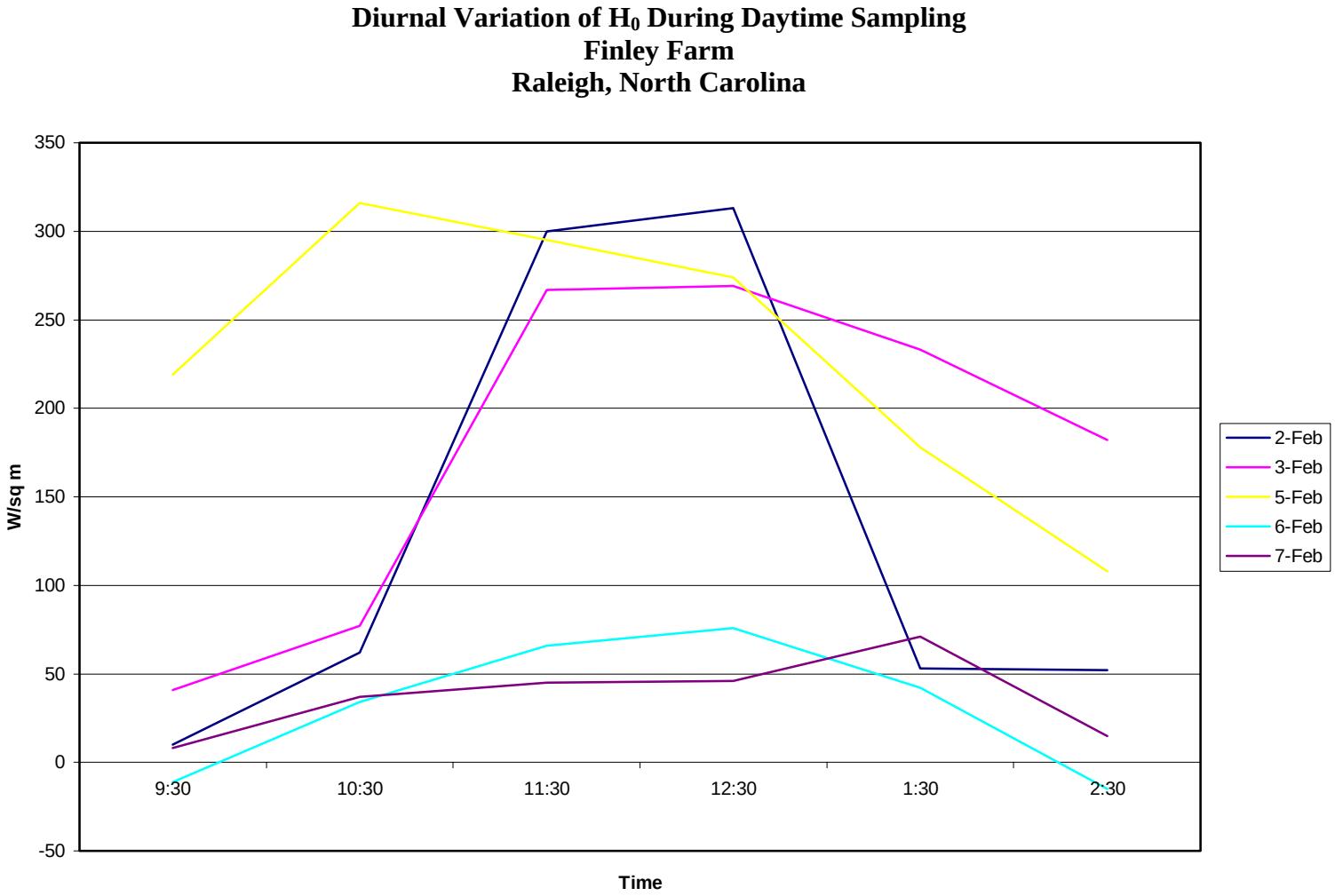


Figure 9. Diurnal variation of heat flux during wintertime sampling.

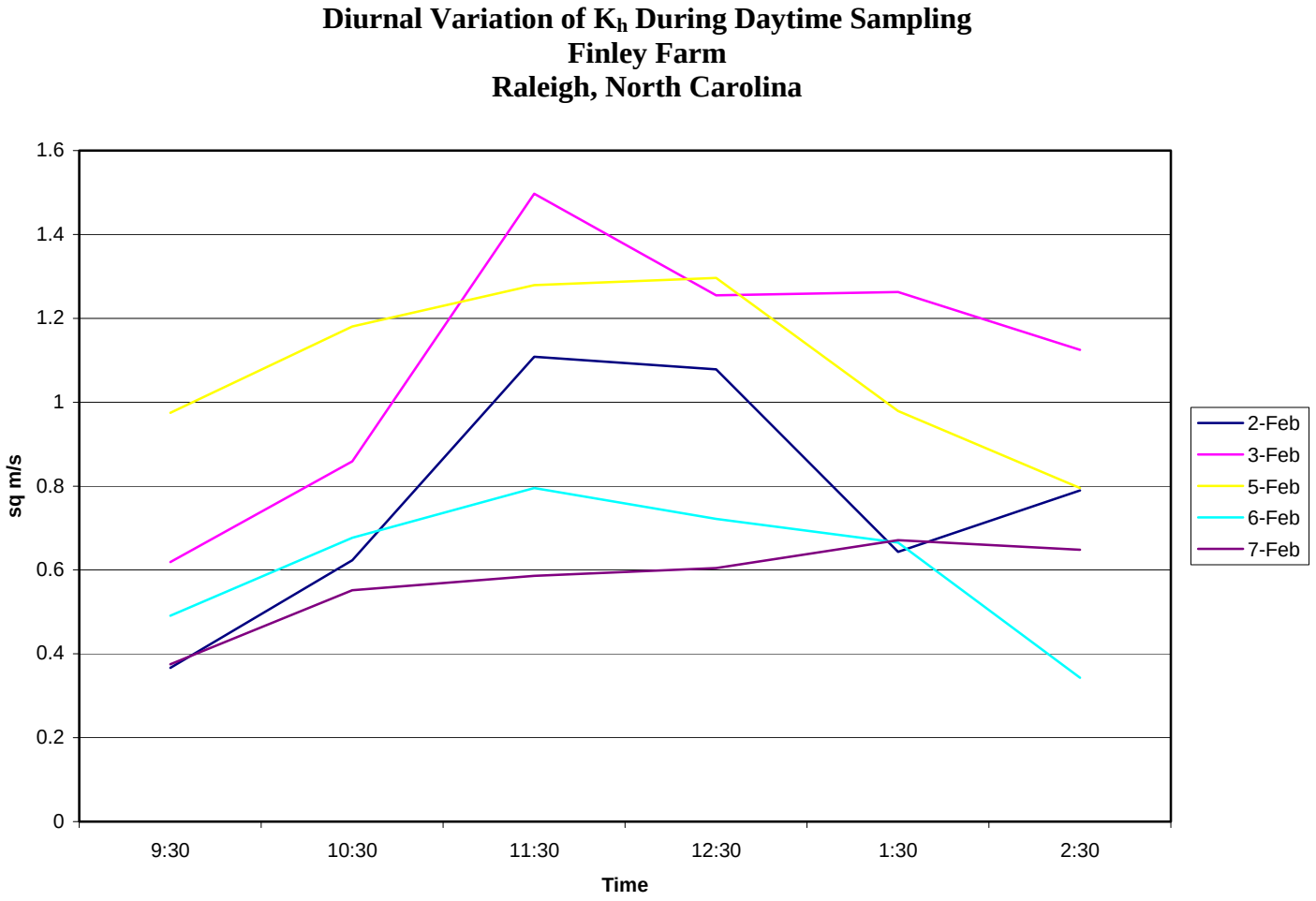


Figure 10. Diurnal variation of eddy diffusivity of heat during wintertime sampling.

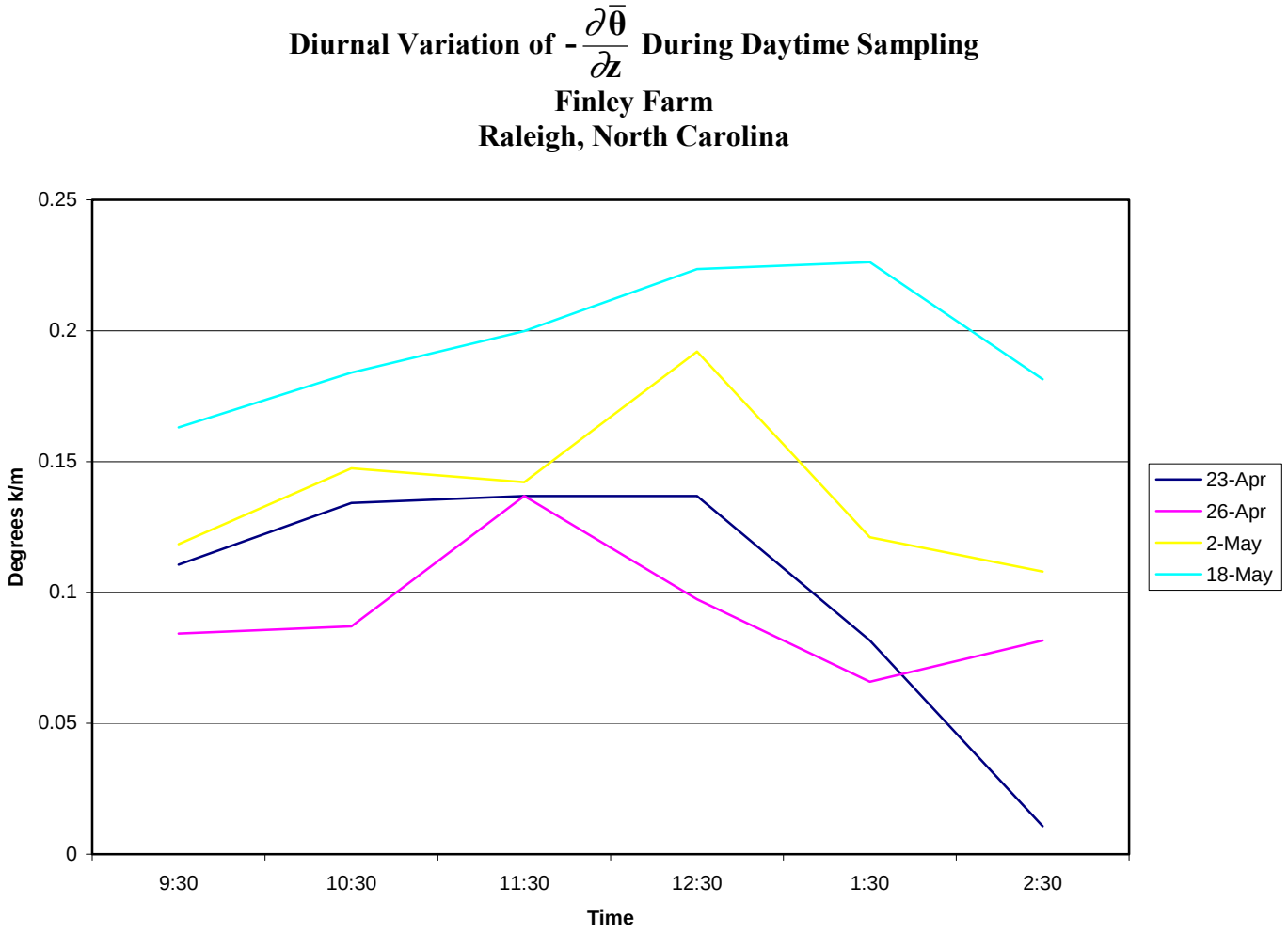


Figure 11. Diurnal variation of potential temperature gradient during springtime sampling.

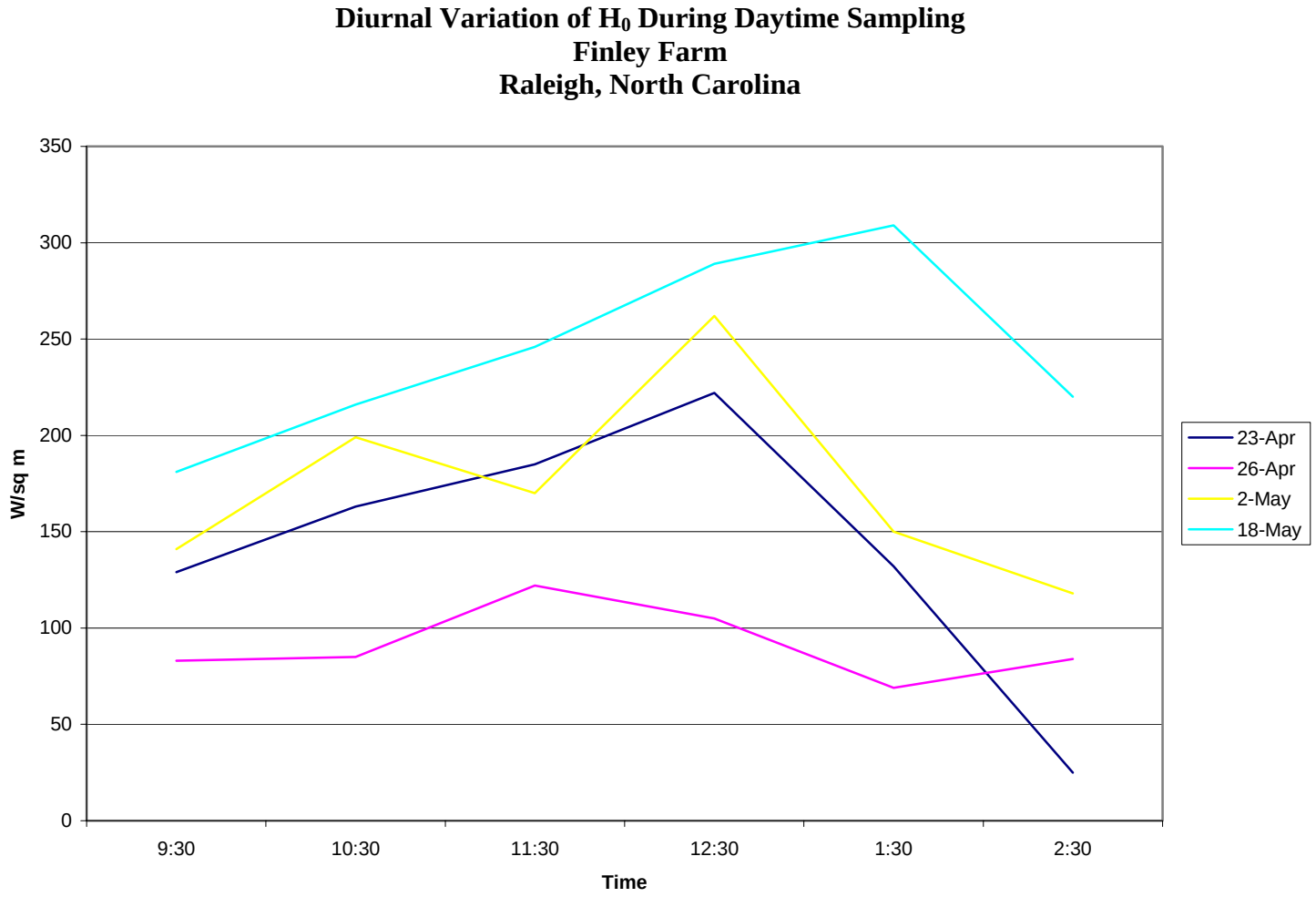


Figure 12. Diurnal variation of heat flux during springtime sampling.

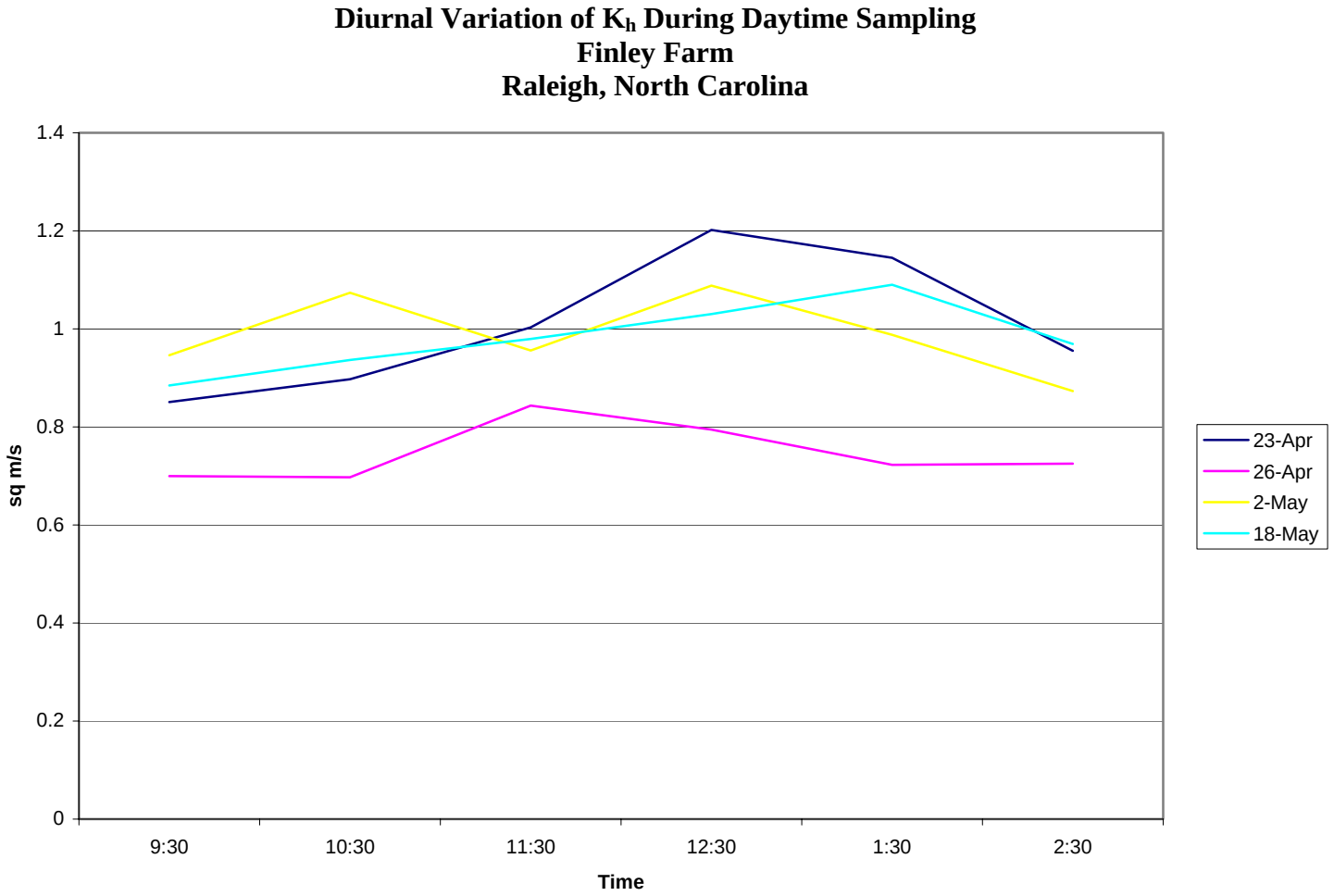


Figure 13. Diurnal variation of eddy diffusivity of heat during springtime sampling.

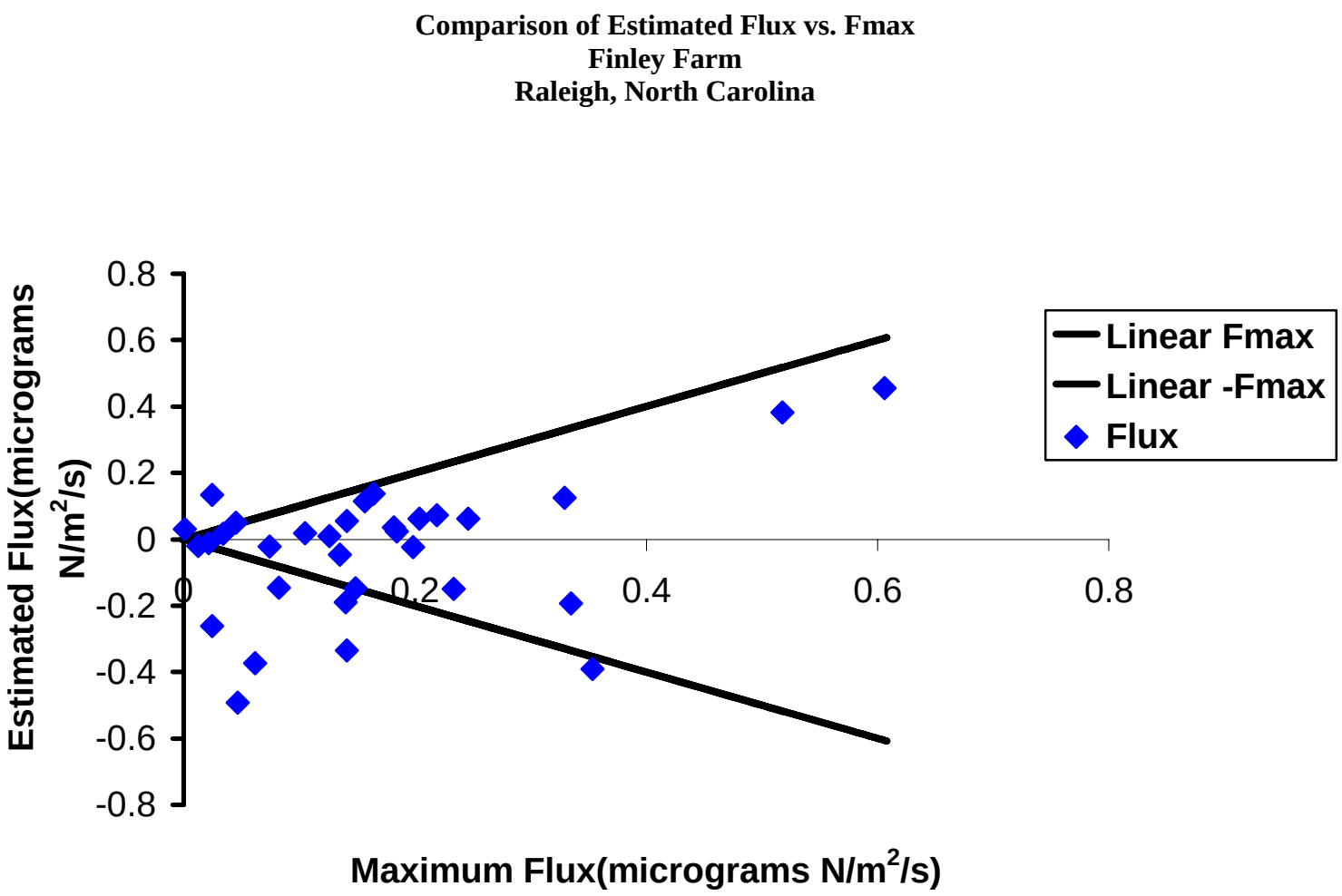


Figure 14. Comparison of estimated (measured) NH_3 flux and the computed maximum Flux during each sample period.

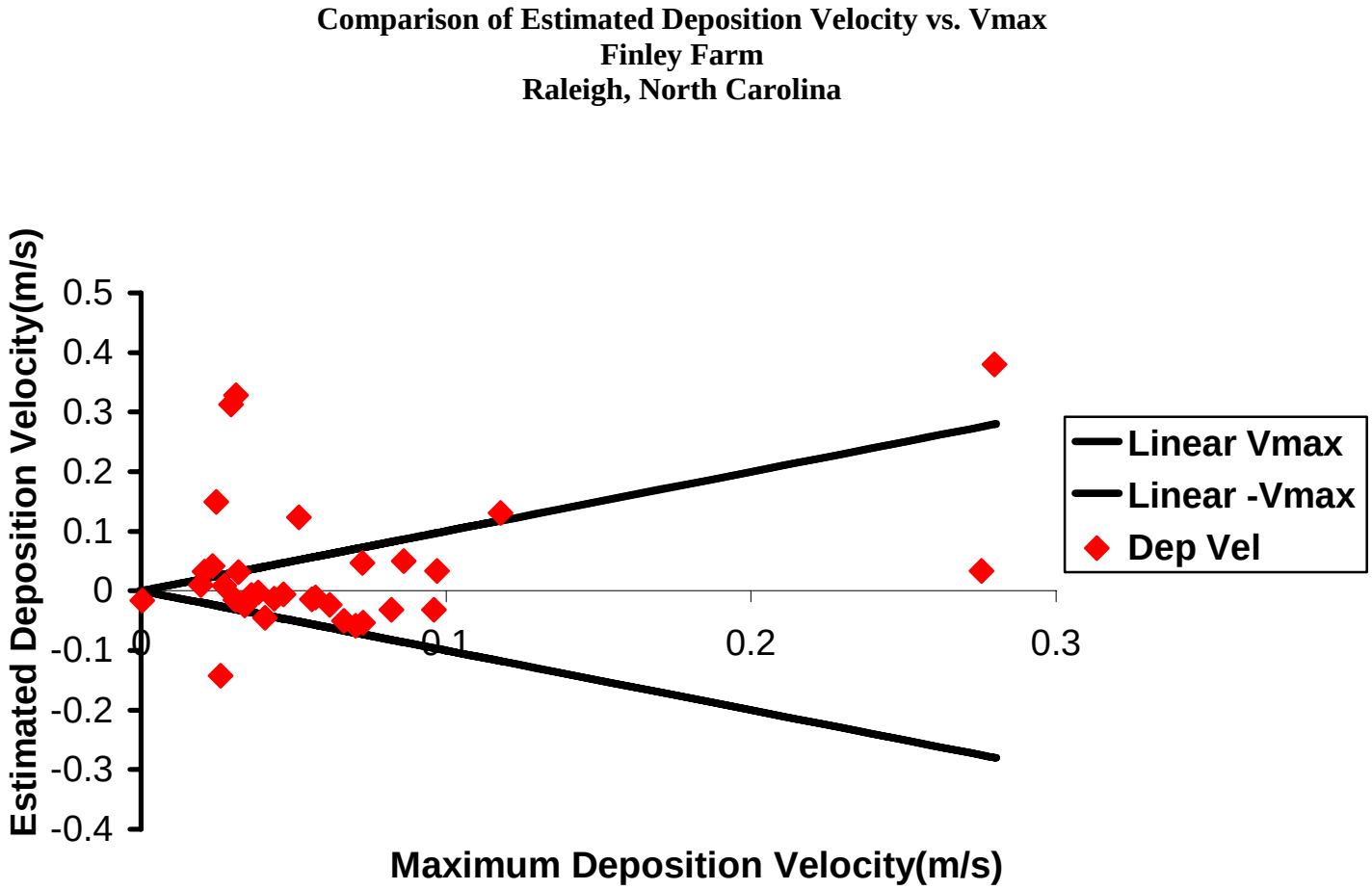


Figure 15. Comparison of estimated (measured) deposition velocity and the computed maximum velocity during each sample period.

Table 1
Trip Blank NH_3 Concentration Results
Finley Farm
Raleigh, North Carolina

TRIP BLANKS	CONCENTRATION (µg of N / L of solution)
1	<50
2	<50
3	230
4	<50
5	<50
6	<50
7	<50
8	<50
9	140
10	<50
11	100
12	<50
13	70
14	<50
15	90
16	<50

REFERENCES/BIBLIOGRAPHY

Aneja Viney P. and Murthy Anuradha B. (1994) Monitoring deposition of nitrogen-containing compounds in a high-elevation forest canopy. *Air & Waste Management Association* **44**, 1109-1115.

Aneja Viney P., Roelle Paul A., Murray George C., Southerland James, Erisman Jan Willem, Fowler David, Asman Willem A. H., Patni Naveen (2001) Atmospheric Nitrogen Compounds II: Emissions, Transport, Transformation, Deposition & Assessment. *Atmospheric Environment* **35**, 1903-1911.

Arya S. P. (2001) Introduction to Micrometeorology, Second Edition. Academic Press, San Diego.

Arya S. P. (1999) Air Pollution Meteorology and Dispersion. Oxford University Press, New York.

NCDENR, (1997) Assessment Plan for Atmospheric Nitrogen Compounds: Emissions, Transport, Transformation, and Deposition, Division of Air Quality, North Carolina Department of Environment and Natural Resources.

Weseley M. L., Hicks B. B., Dannevik W. P., Frisella S. (1977) An Eddy-Correlation Measurement of Particulate Deposition from the Atmosphere. *Atmospheric Environment* **11,** 561-563**.**

Wiebe H. A., Anlauf K. G., Tuazon E. C., Winer A. M., Biermann H. W., Appel B. R., Solomon P. A., Cass G. R., Ellestad T. G., Knapp K. T., Peake E., Spicer C. W. and Lawson D. R. (1990) A comparison of measurement of atmospheric ammonia by filter packs, transition-flow reactors, simple and annular denuders and Fourier-transform infrared spectroscopy. *Atmospheric Environment* **24A**, 1019-1028.

Wyers Paul G. and Erisman Jan Willem (1998) Ammonia exchange over coniferous forest. *Atmospheric Environment* **32**, 441-451.