A Passive Monitoring Technique for Measuring Ammonia Fluxes

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INTRODUCTION

- Ammonia is an Important Pollutant Because:
  - Forms fine particulate by reaction with nitric acid
  - Formation of ammonium sulfate by reaction with sulfuric acid
- Emission Inventories are Difficult to Determine Because:
  - Emissions are largely fugitive (domestic animal waste)
  - difficult to measure due to the equilibrium with ammonium nitrate

Emission Factor Determination

- Upwind-Downwind Measurements
- Meteorological Measurements
- Concentration Measurements
  - Open path FTIR (real time)
  - Heated converter-chemiluminescent detection
  - Filter pack (integrated sample)
  - Diffusion denuder (integrated sample)
- Dispersion Modeling

Objective

- Develop a passive sampler that will directly measure ammonia flux
- Evaluate by determining emissions at a dairy and comparing with active sampling

APPROACH

- Use a Fabric Diffusion Denuder as a Collection Substrate
- Mount the Denuder in an Open Tube
- Test Flow Difference from Outside to Inside of the Tube
- Evaluate at a Dairy and Compare Flux Measurements

Fabric Denuder

- Developed to Actively Sample Nitric Acid and Ammonia
- Consists of a Fabric Coated with an Adsorbent Collects the Target Gas From Flow Around a Fiber
- Allows Particles to Pass Unattenuated
- Evaluated Under Both Laboratory and Ambient Conditions

Theoretical Basis

- Selectively adsorb gases around a fiber rather than a long channel
- Approach is based on diffusion batteries used to collect fine particles
- Diffusion batteries progressed from single channels, to multiple channels, to honeycomb, and ended with wire screens

Efficiency Calculation

- An empirical equation was used to describe particle penetration through a wire mesh: P=exp (-AnP*e* $^{-2/3}$)

$$A = \frac{2bah}{p\,(1-a)r}$$ where:

ß = 2.7
a = solid surface fraction (volume solid/total volume ≈ 0.3 by geometry)
r = fiber radius, cm
h = screen thickness, cm
n = number of screens

P*e* = Peclet number = 2r U_0/D

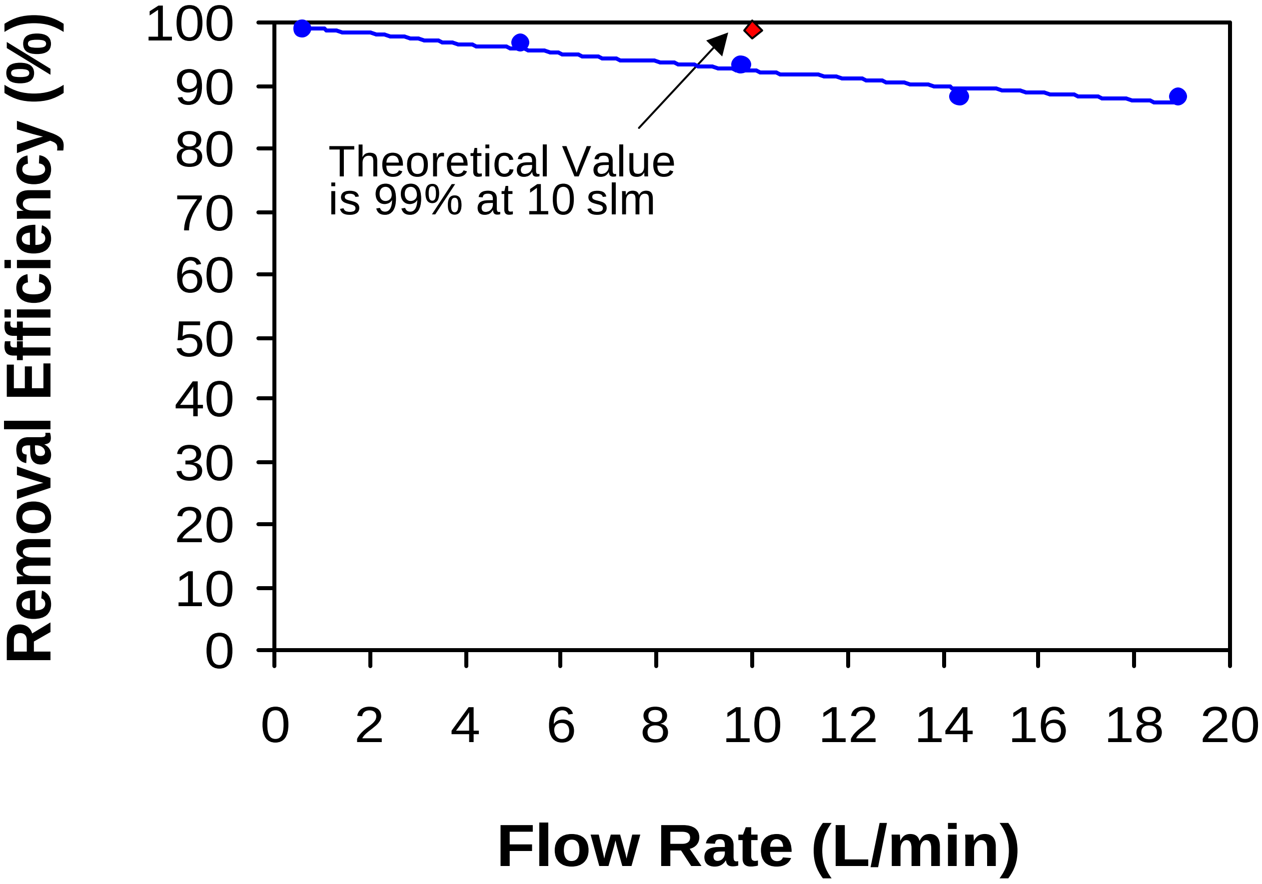
where:

U_0 = undisturbed flow velocity, cm sec^{-1}
D = Diffusion coefficient, cm^2 sec^{-1}

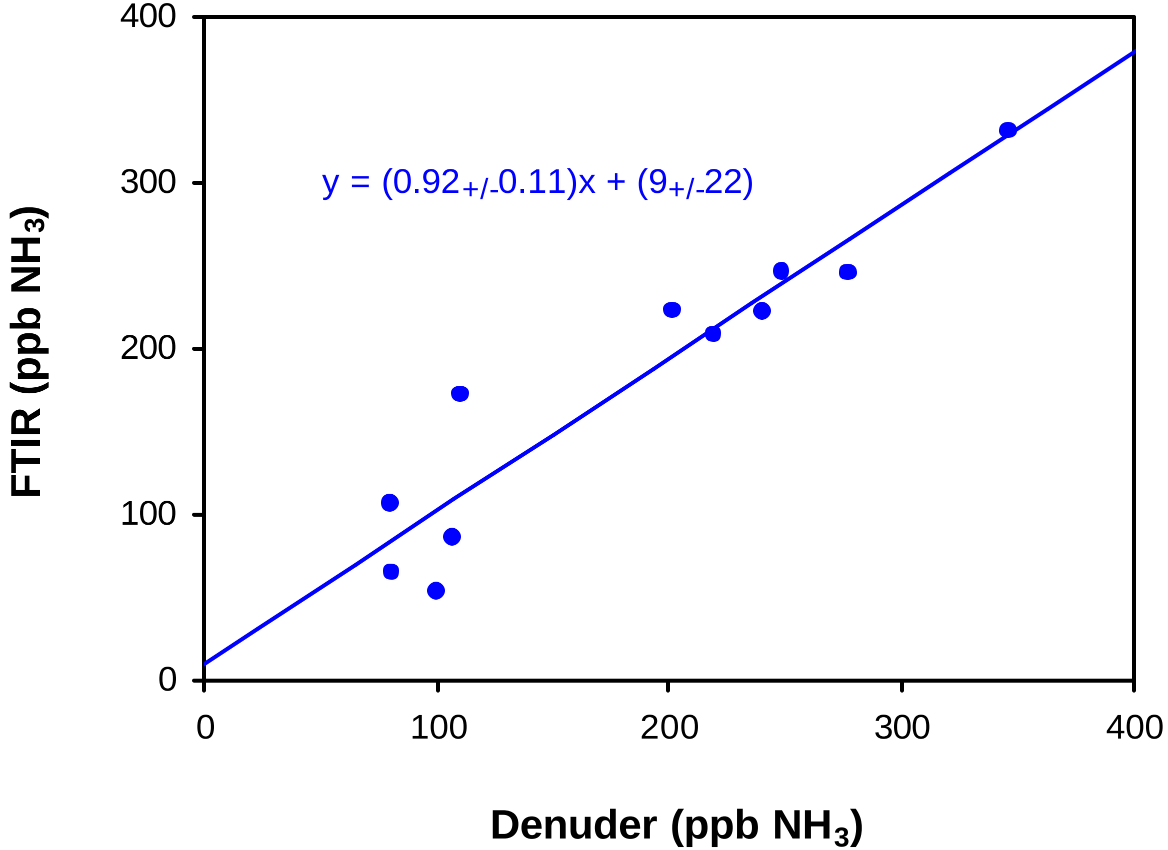
Penetration Calculation Parameters

- **Fabric grid cell is 100 µm on 250 µm centers**
- **4.0 cm diameter fabric @ 10 L/min**
- **Nitric acid (D = 0.12 cm^2/sec)**
    - **P = 0.02**
- **0.1 µm Particle (D = 6 x 10^{-6} cm^2/sec)**
    - **P > 0.99**

Laboratory Testing
47mm - Sodium Carbonate Coating
Nitric Acid Removal Efficiency-35ppb



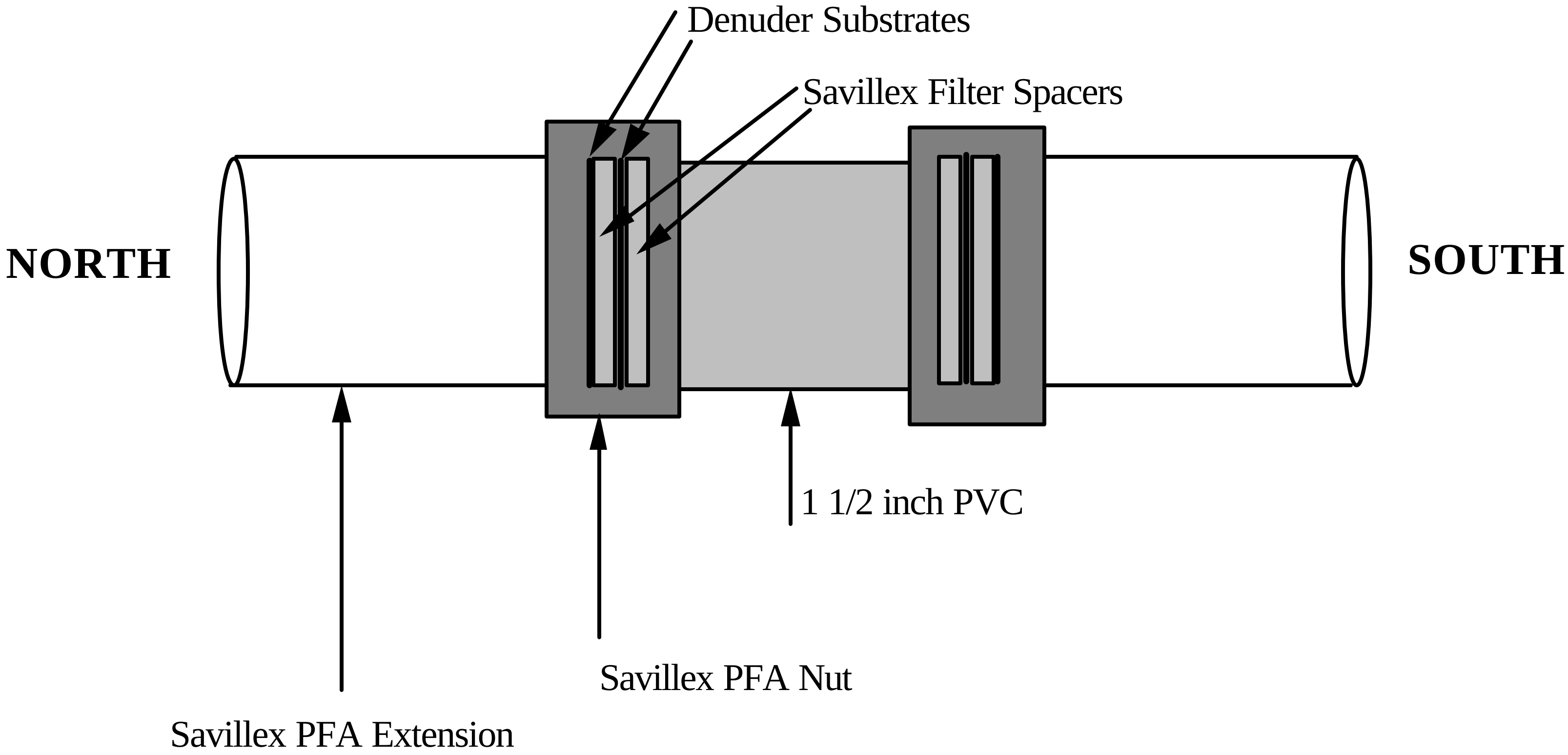
Ammonia Measurement with Fabric Denuder (H_3PO_4-Coated) Compared to Open-Path FTIR



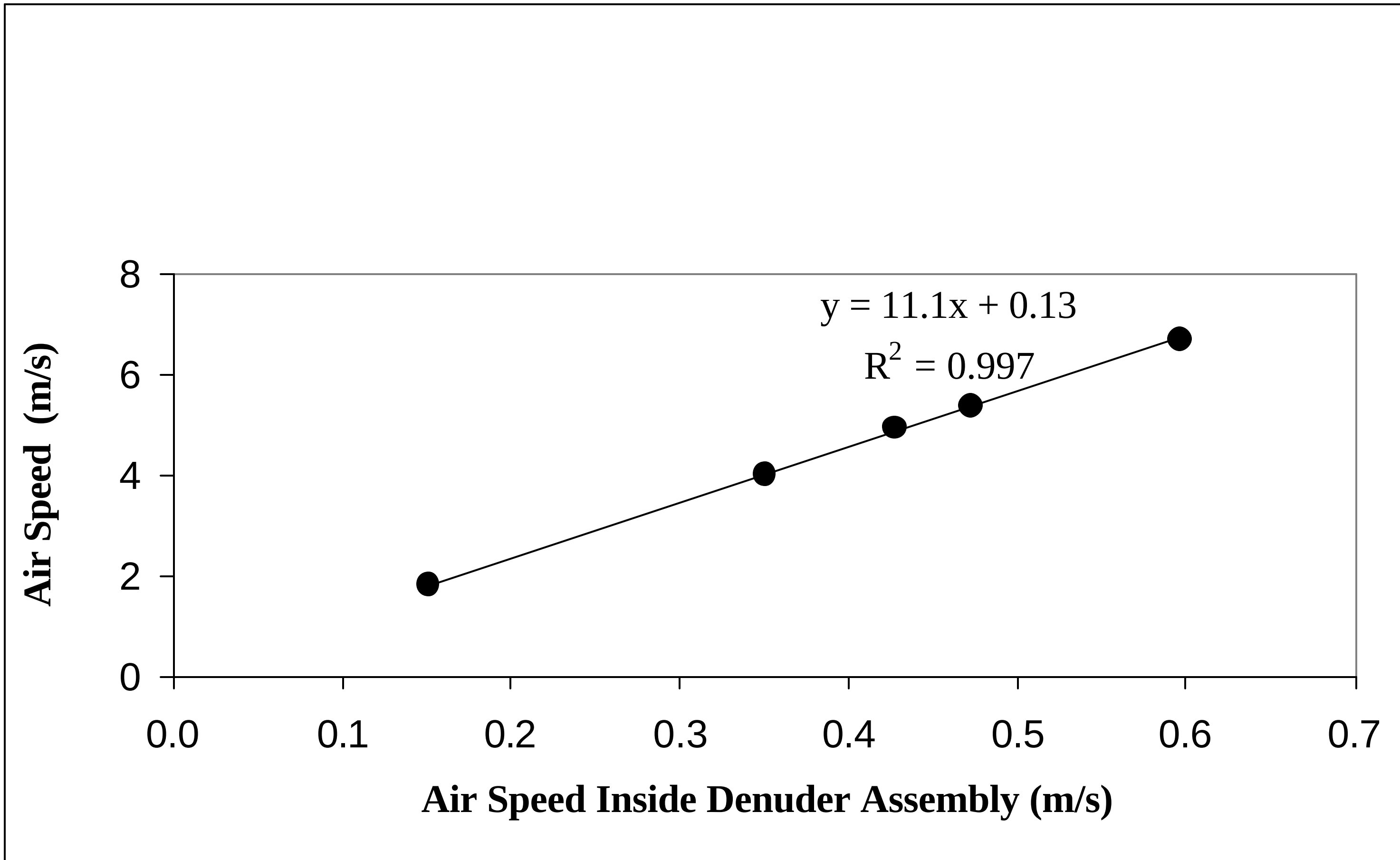
Flux Denuder Construction

- Based on Passive Tubular Denuder
- Open face Teflon Filter Holders Joined with a PVC Pipe
- Two Assemblies Used:
  - Sample north-south
  - Sample east-west

Passive Denuder Flux Sampler



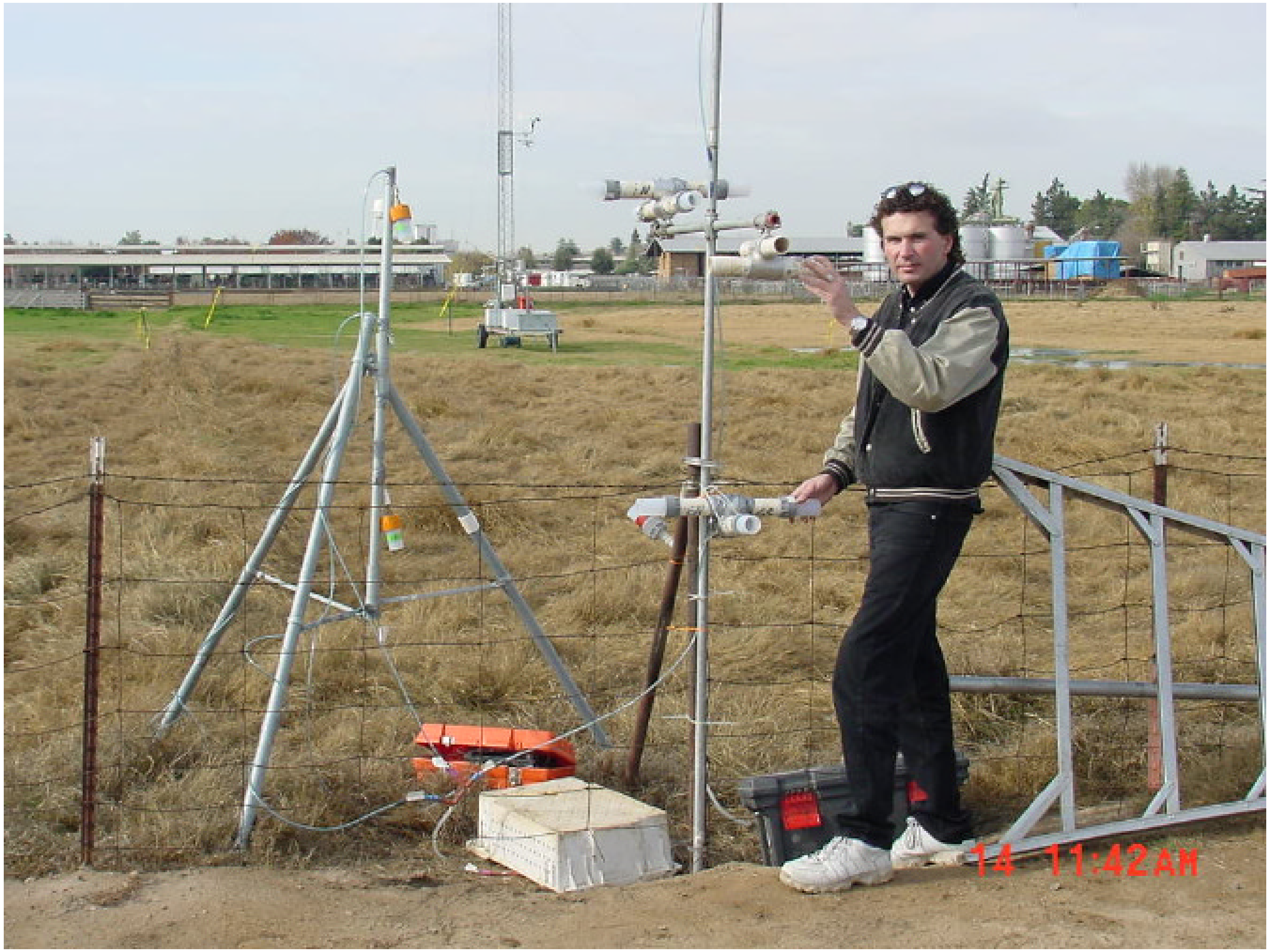
Comparison of Air Speed Outside and Inside the Passive Denuder Assembly



SAMPLE COLLECTION

- Small Dairy (500 head)
- Prevailing Northwest Afternoon Wind
- Passive Samplers at Lagoon
  - 1 Upwind at 2m
  - 1 Downwind at 1m
  - 2 Collocated downwind at 2m
  - 1 Downwind at 5m
- Five Sets of Collocated Filter Pack Samplers
- Meteorological Measurements

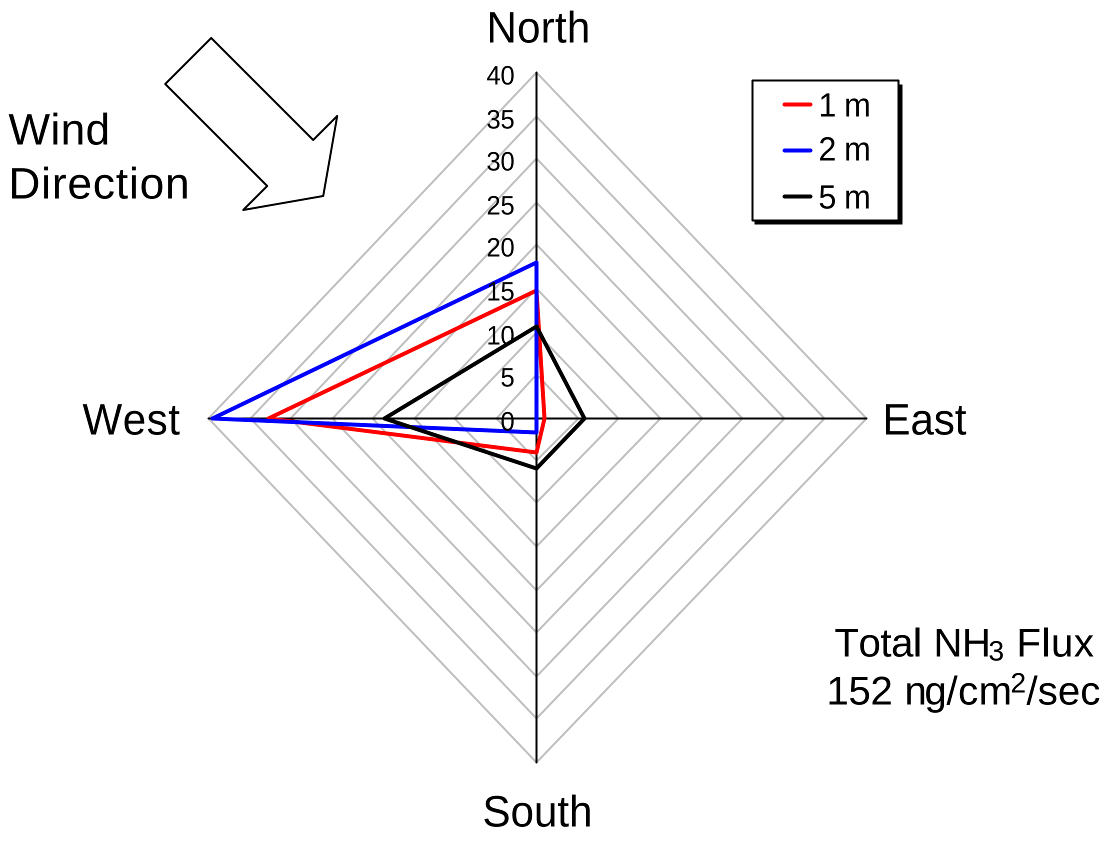
Sample Collection



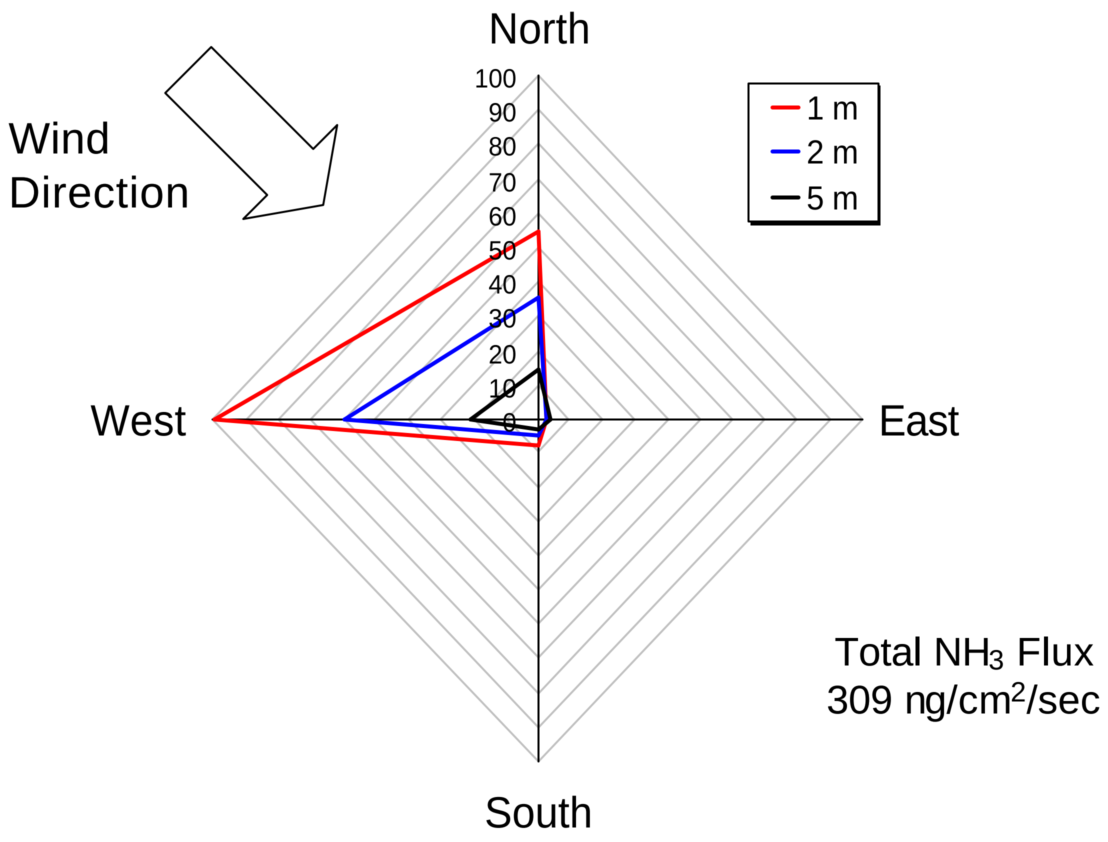
RESULTS

- Samples Extracted with Water and Ammonium Measured via Indolephenol Blue
- Subtracted Background
- Calculated Flux by Holder Dimensions and Sampling Time Only
- Plotted with Respected to Orientation (north, south, east, west)

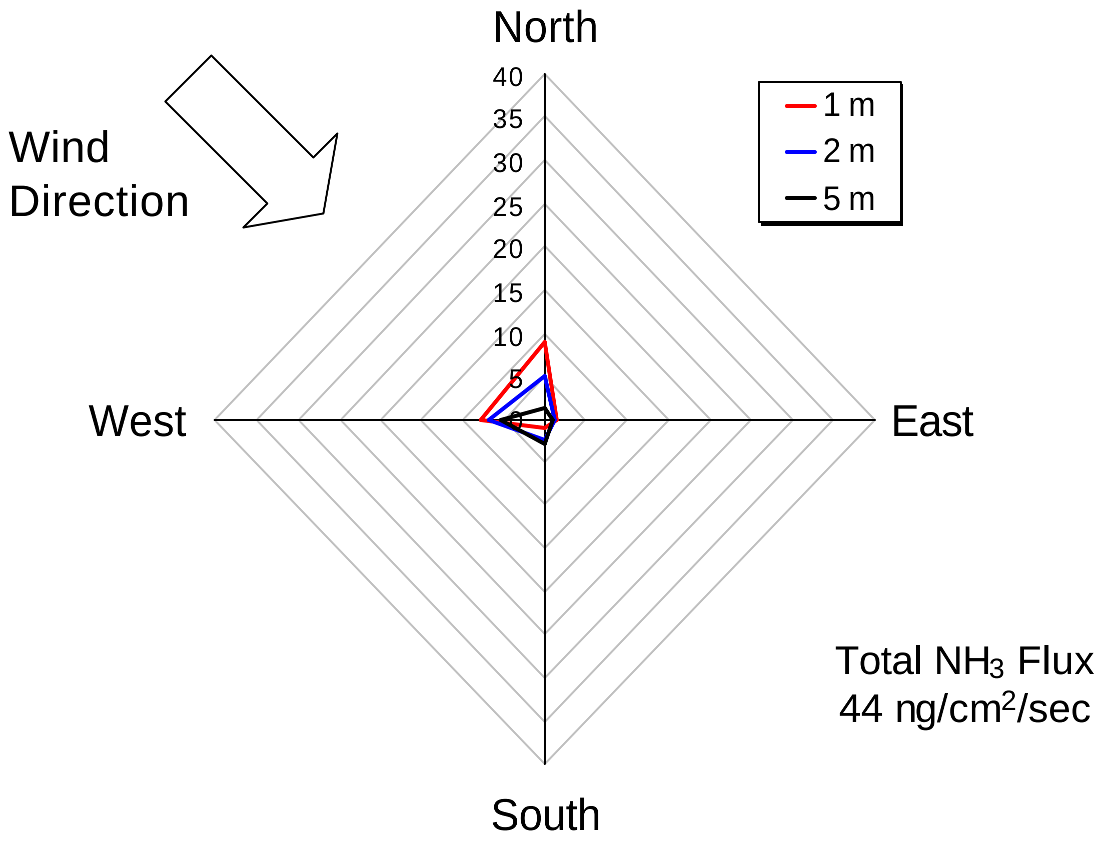
NH_3 Flux vs. Denuder Direction at a Dairy Lagoon the Day Prior to H_2SO_4 Acidification



NH_3 Flux vs. Denuder Direction at a Dairy Lagoon During H_2SO_4 Acidification



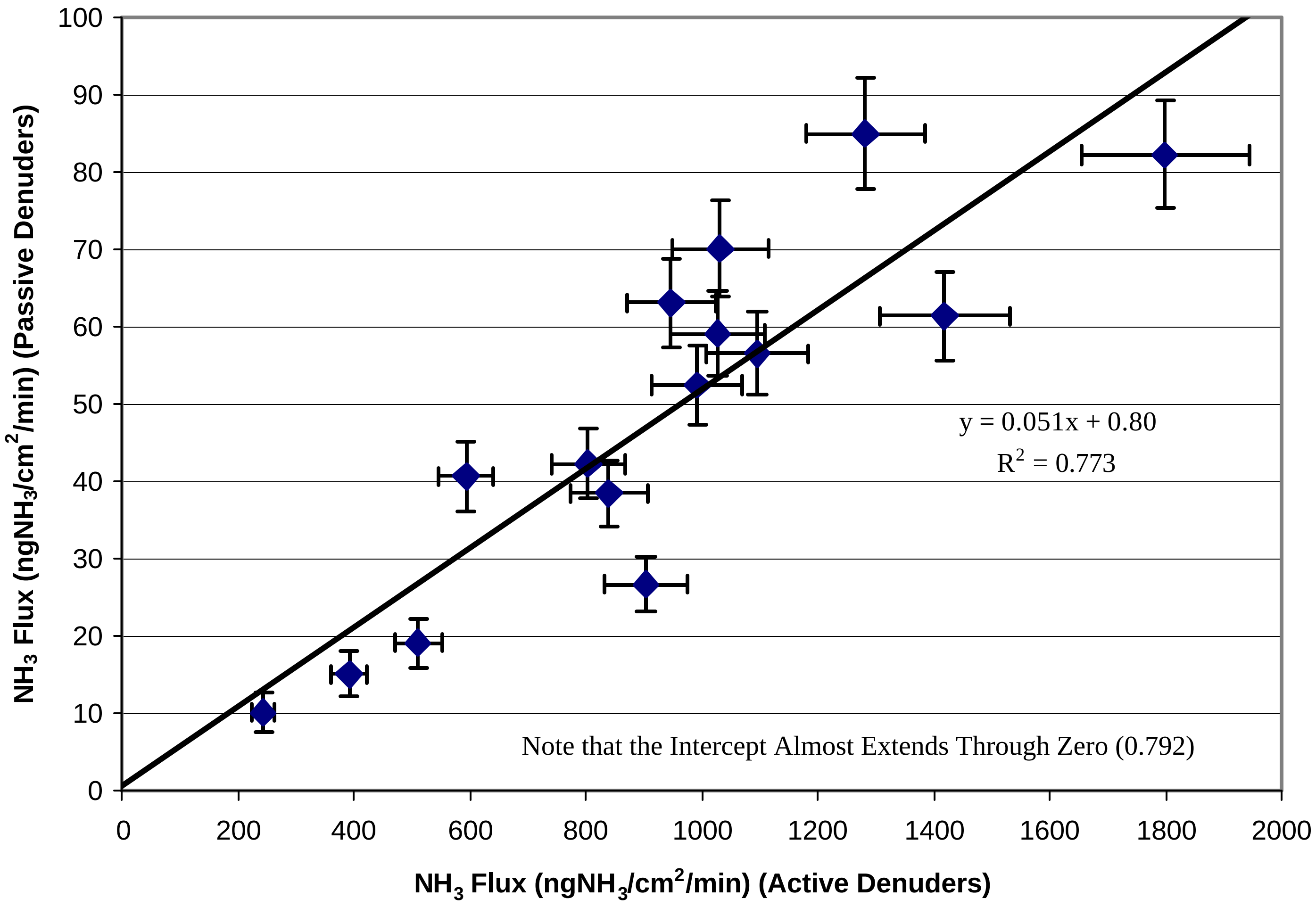
NH_3 Flux vs. Denuder Direction at a Dairy Lagoon the Day After H_2SO_4 Acidification



Comparison With Filter Pack Measurements

- Multiplied Filter Pack Concentration by Average Wind Speed
- Summed Passive Flux Directions
- Compared Noting That:
  - Measurements are inherently different
  - No correction was made for wind velocity difference between inside and outside of the denuder tube

Ammonia Flux Regression Plot Between Filter Pack and Passive Flux Sampler



CONCLUSIONS

- Passive Flux Sampler Compares Favorably with Active Samplers
- Advantages
  - Low Cost
  - No Power Requirements
  - Easy to Install on a Pole