

Use of Laser Technology to Monitor Ammonia Emissions from Dairy Lagoons

Prepared by

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CSU/ARI Project

- California State University (CSU)
- Agricultural Research Initiative (ARI)

Monitoring Ammonia, Methane and Other Emissions In Real Time At Dairies and Other Agricultural Operations
Principal Investigators: Dave Goorahoo and Charles Krauter,
Begun 7/1/02, to be completed 12/31/06

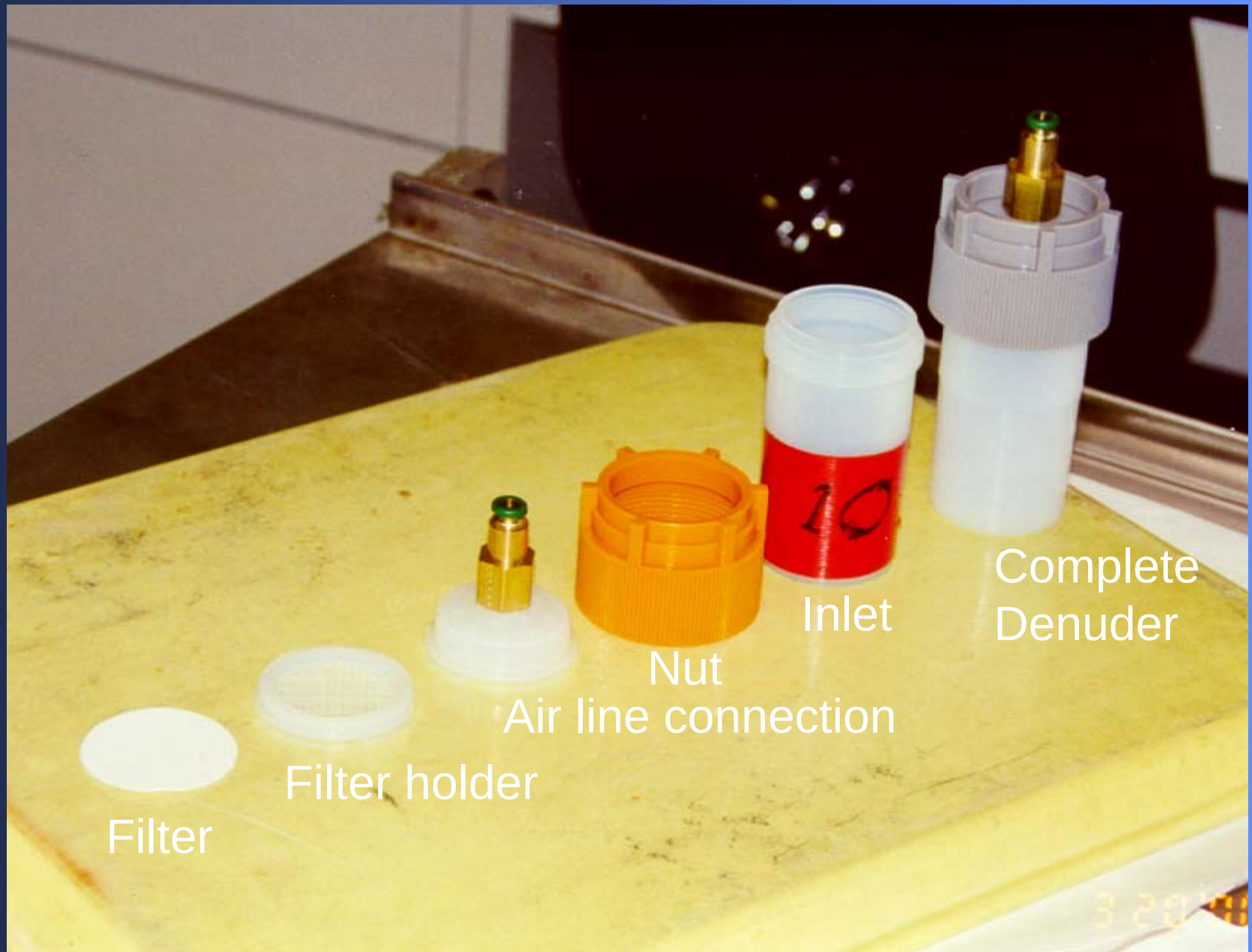
- California Air Resources Board (CARB)
- California Dairy research Foundation (CDRF)
- California Water Institute (CWI)
- Numerous Dairy Cooperators and Growers

Background

- **Over the past five years we have been monitoring ammonia emissions from various agricultural operations in the San Joaquin Valley, CA.**
- **Use of “Active” sampling filter packs, sometimes referred to as “denuders”**
- **The filter packs require several hours of sampling to acquire sufficient NH_3 for detection in the laboratory**

Ammonia Filter Packs

- Filter disks are impregnated with a reacting substance, (5% citric acid in 95% ethanol).
- Air is pumped through the filter, NH_3 is scrubbed out, forming ammonium citrate that stays on the filter paper
- Lab analysis determines micrograms of NH_3 on the filter disk.



Filter

Filter holder

Air line connection

Nut

Inlet

Complete
Denuder

3 20 11



***Citrate
impregnated
filter***

Field Monitoring of Ammonia Emissions

- NH_3 was sampled in the field with active denuders on a portable tower at 1, 2, 5, 10 and 18 meters elevation.
- Samples taken continuously from 2 days before to 5 days after the fertilizer application.
- Wind speed was monitored at each sample height to calculate NH_3 fluxes and gradients





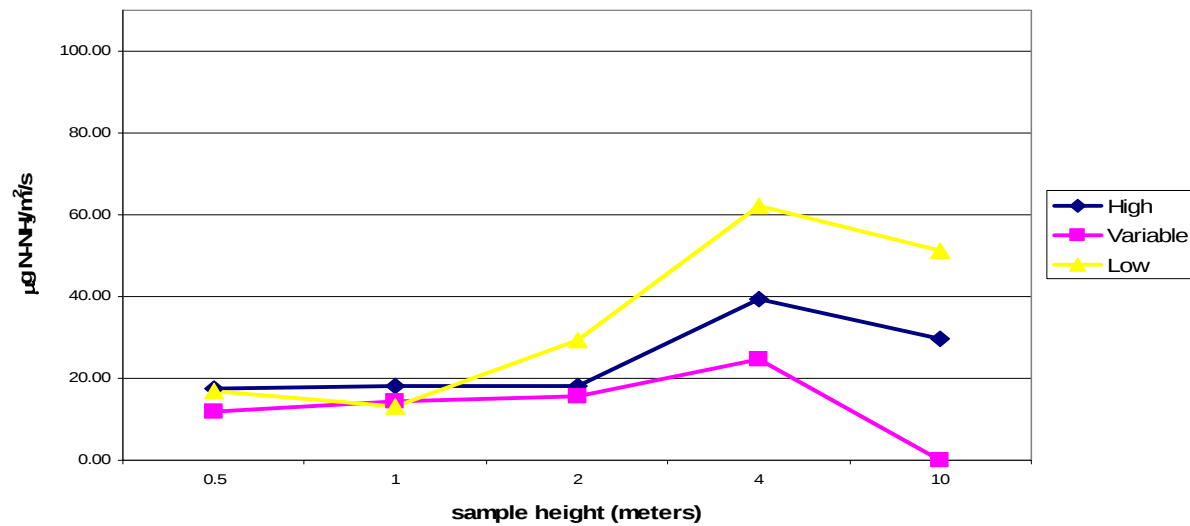
Determination of NH_3 in the sample

- Air pulled through the filters
- Filters were changed diurnally.
- Flow rate through the denuders recorded for each sampling period.
- Lab analysis of NH_3 on the denuder disk multiplied by the volume of air determined concentration $\text{NH}_3/\text{meter}^3$ of sampled air.

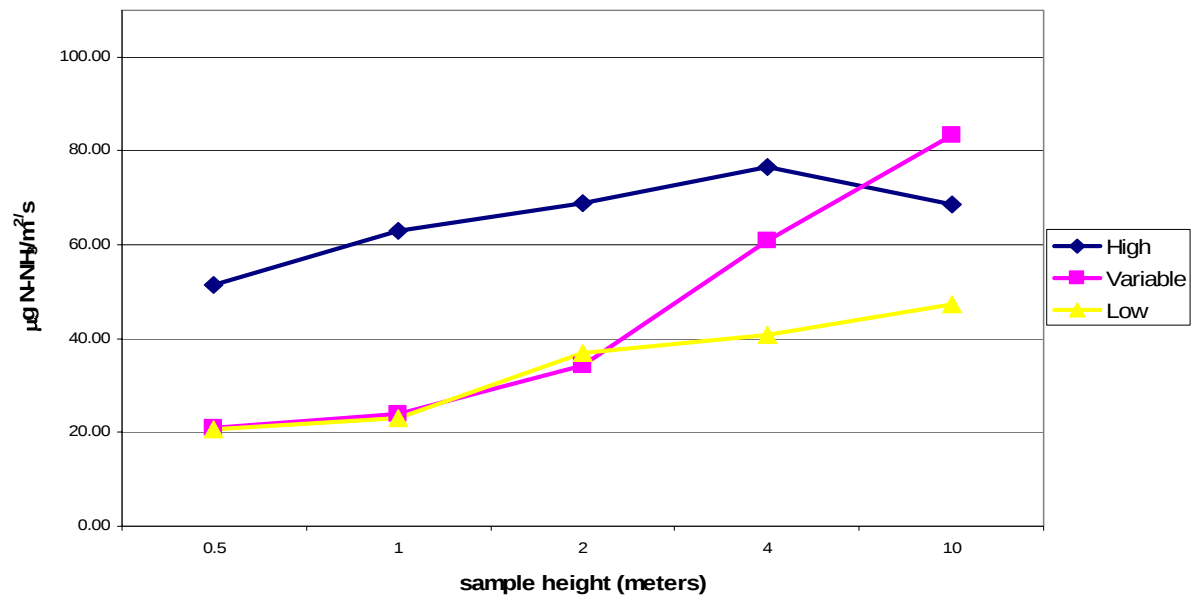
Ammonia Emissions from Site-Specific Variable Rate Nitrogen Applications in Cotton

- **Refer to poster by Beene et al.**
- **Major objective was to determine the ammonia emissions from fields fertilized with high, low and variable rates of anhydrous ammonia**

June 4th to 5th (night) pre-application



June 6th to 7th (night) - night after application



Results from Variable Rate study

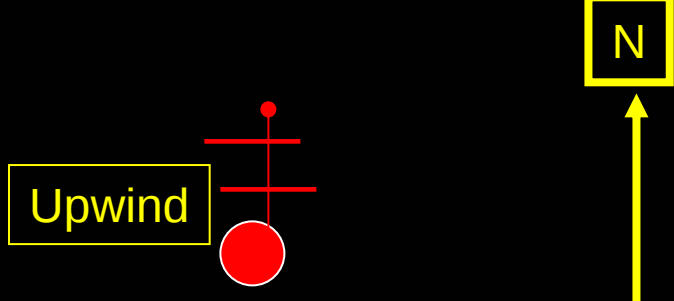
- **Levels of NH_3 in all three treatment plots increased after application of anhydrous fertilizer**
- **Highest levels of NH_3 monitored during the day after application**
- **Two days after application, levels of ammonia were back near pre-application levels**

Objectives of Dairy Research

The overall goal of the study is to contribute to on going efforts to make dairy operations sustainable by: (a) identifying probable areas that contribute to environmental degradation; and, (b) recommending management practices to mitigate these adverse effects.

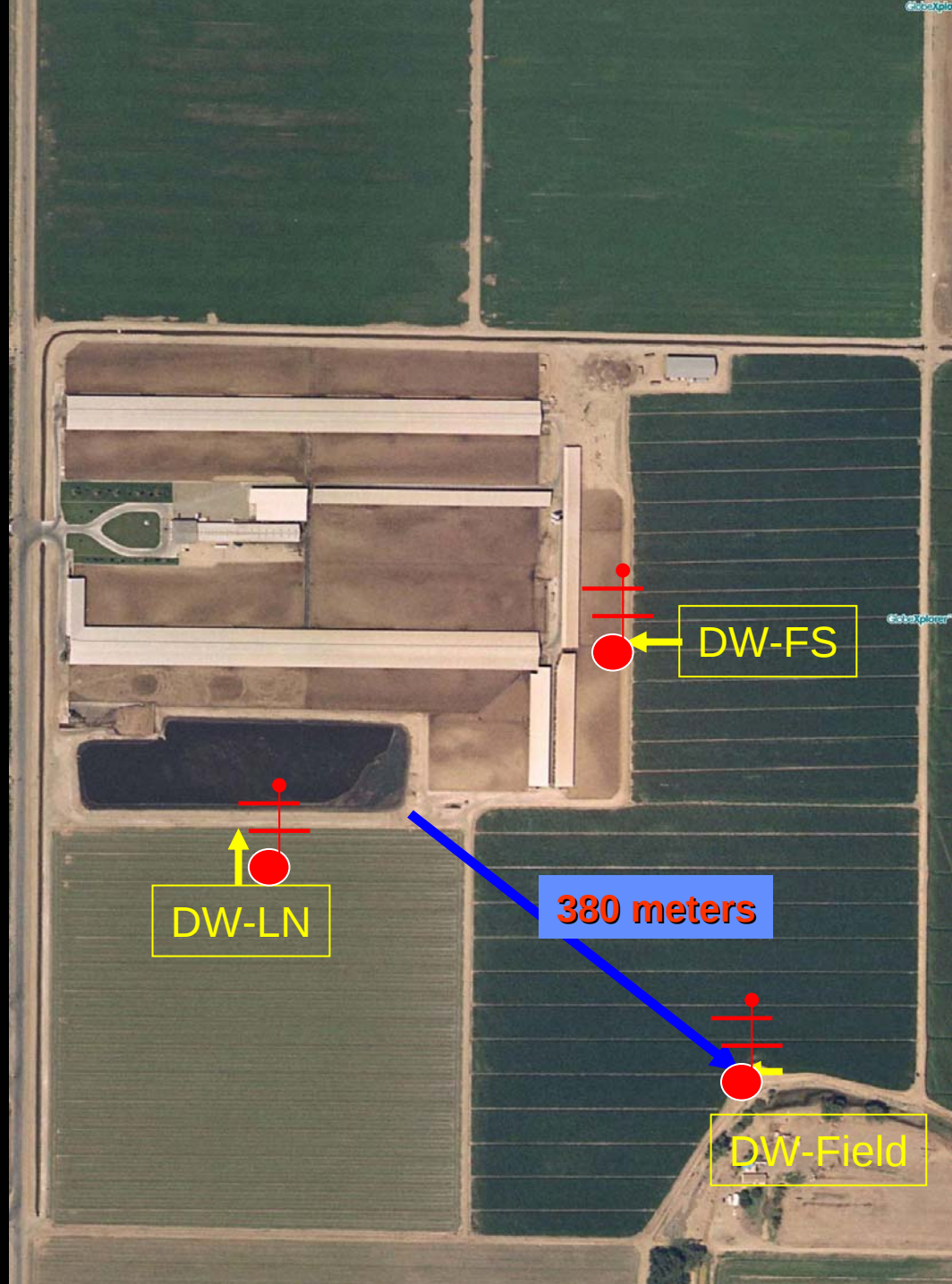
The objectives are:

- (1)Quantify spatial and temporal variability NH_3 emissions on dairy;
- (2) Correlate emissions with climatic, soil, water and livestock parameters; and,
- (3) Evaluate the influence of management practices on the gas emissions.



Generally, Data collected when wind was from NW

Denuder sample collection ranged from as short 2 hours to as long as 72 hours



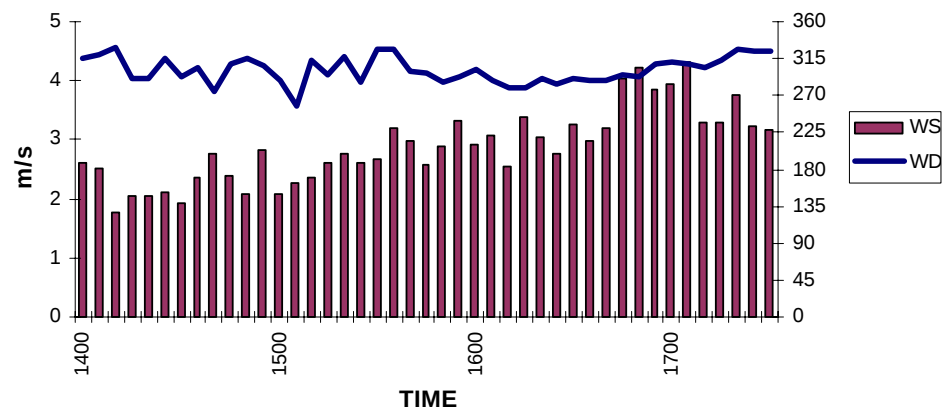
Sampling over 3hrs.

Desirable wind speed
and direction.

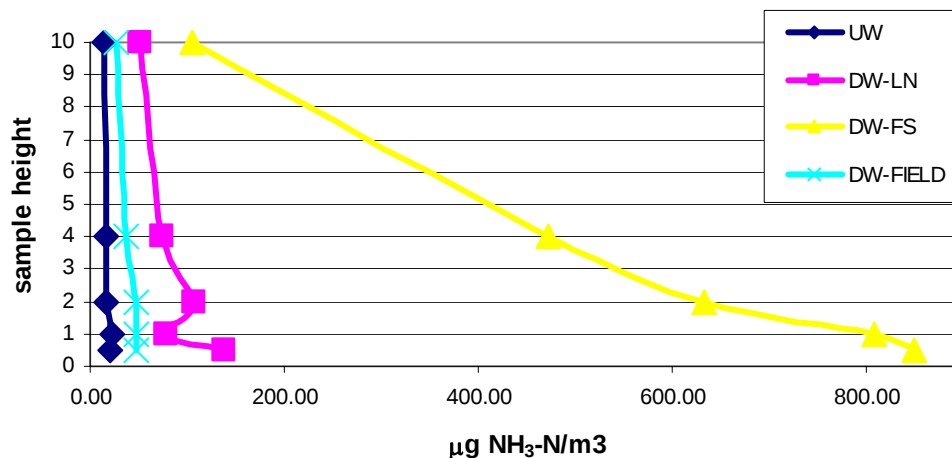
Fallow field.

WIND SPEED & DIRECTION

September 15 (1400-1730)



AMMONIA CONCENTRATIONS SEPTEMBER 15 (1400-1730)



Meteorological Conditions

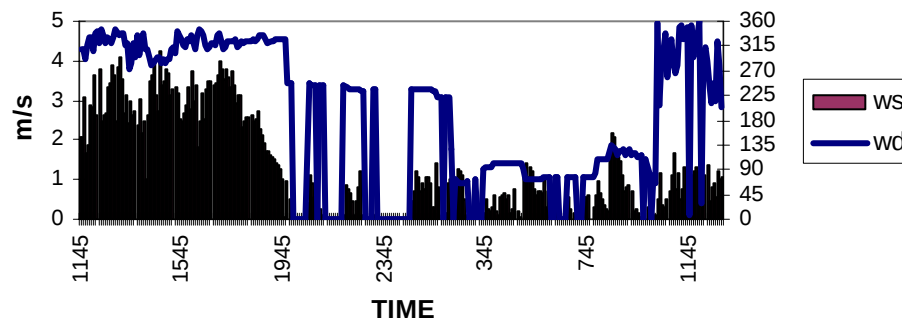
wind speed (m/s)	wind direction	temperature (F)	RH
2.9	301.0	92.2	21.3

Sampling over 24 hrs.

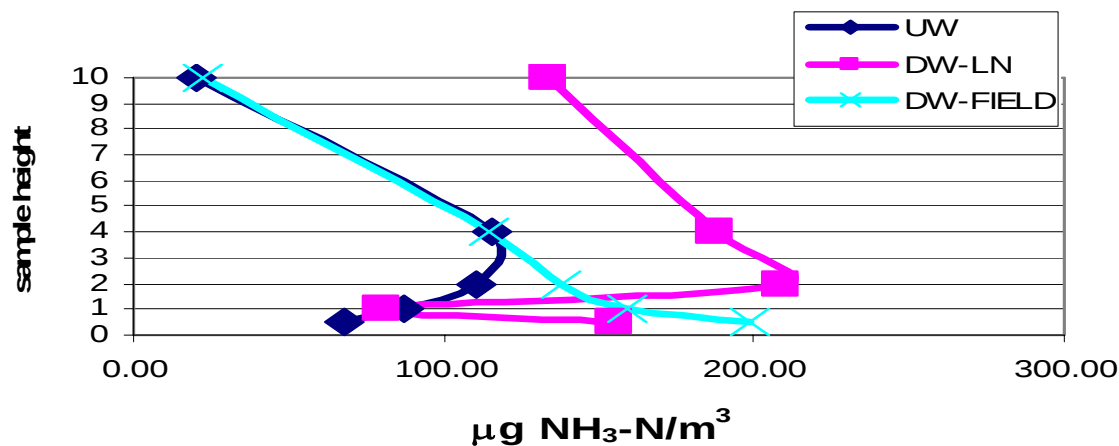
Variable wind speed and direction.

Fallow field.

WIND SPEED & DIRECTION
Sept 10 (1145) - Sept 11 (1305)



AMMONIA CONC. SEPTEMBER 10-11



Meteorological Conditions

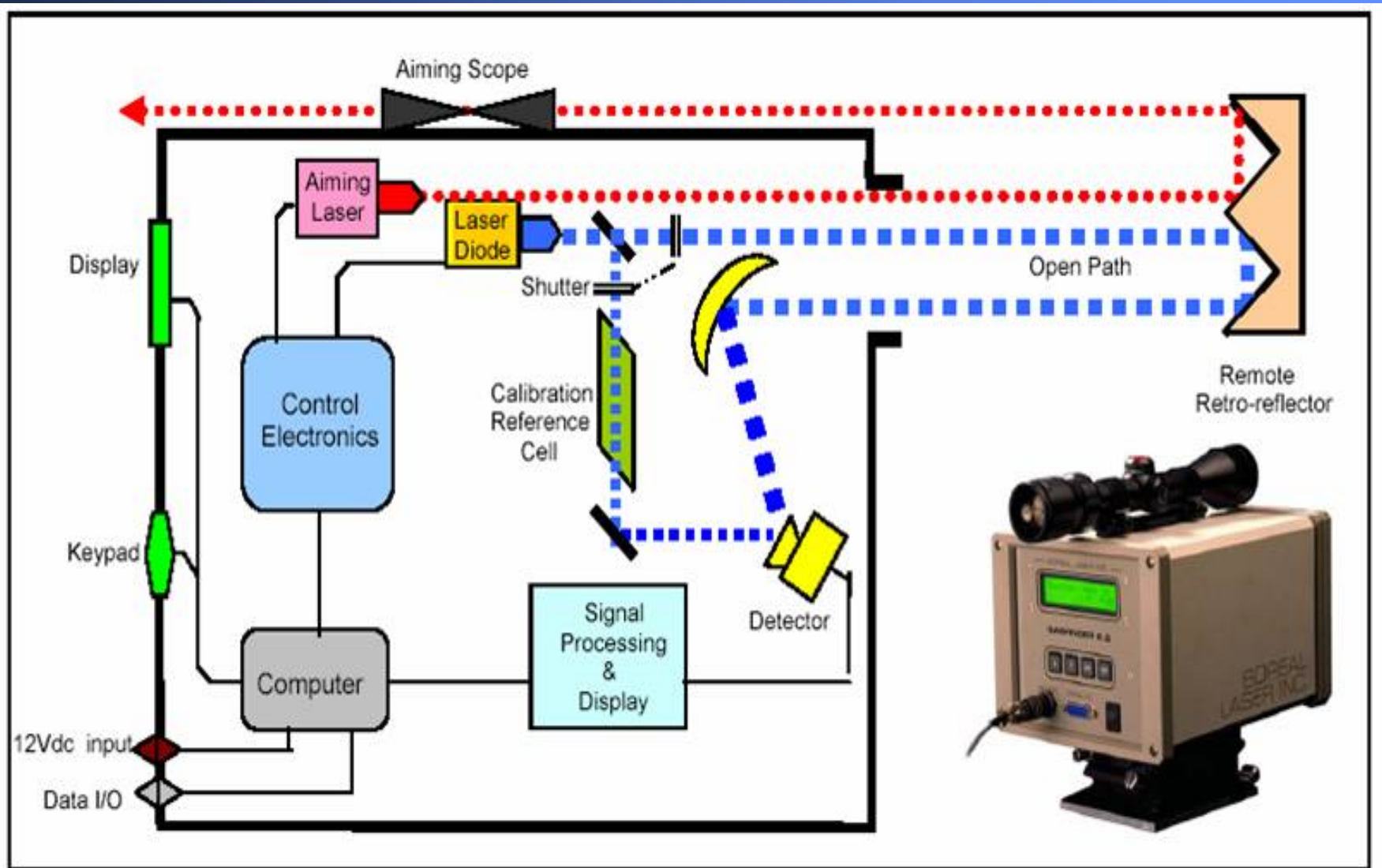
wind speed (m/s)	wind direction	temperature (F)	RH
1.2	variable	71.4	55.14344

Tunable Diode Laser (TDL) Systems

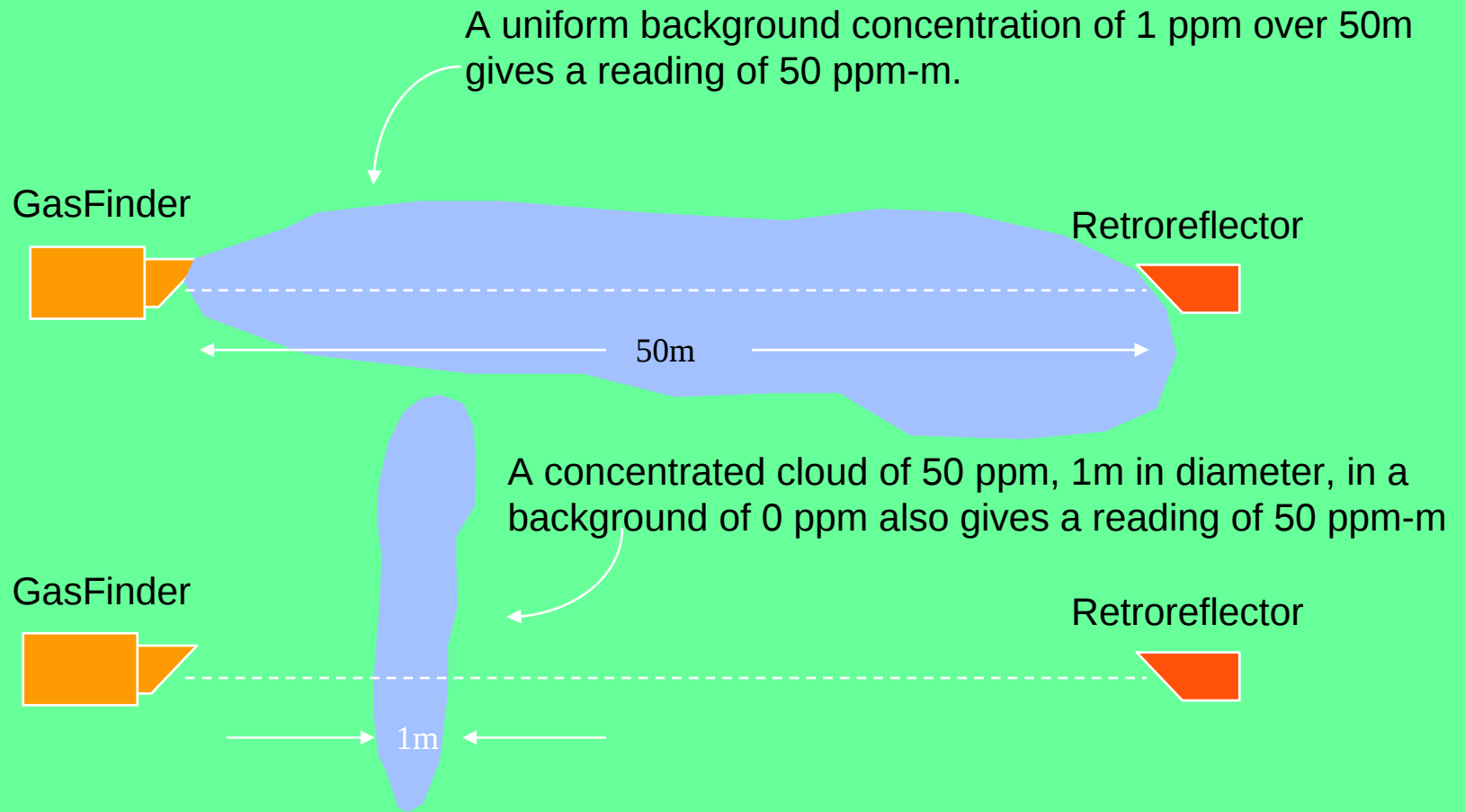
- **The filter pack method for collecting atmospheric NH_3 requires several hours to collect a sample in most instances.**
- **Time period may be too long to characterize short term operations.**
- **The TDL system measures Real Time gas concentration over an open path.**



Tunable Diode Laser (TDL)- Principle of Operation



GasFinder measures ppm-metres



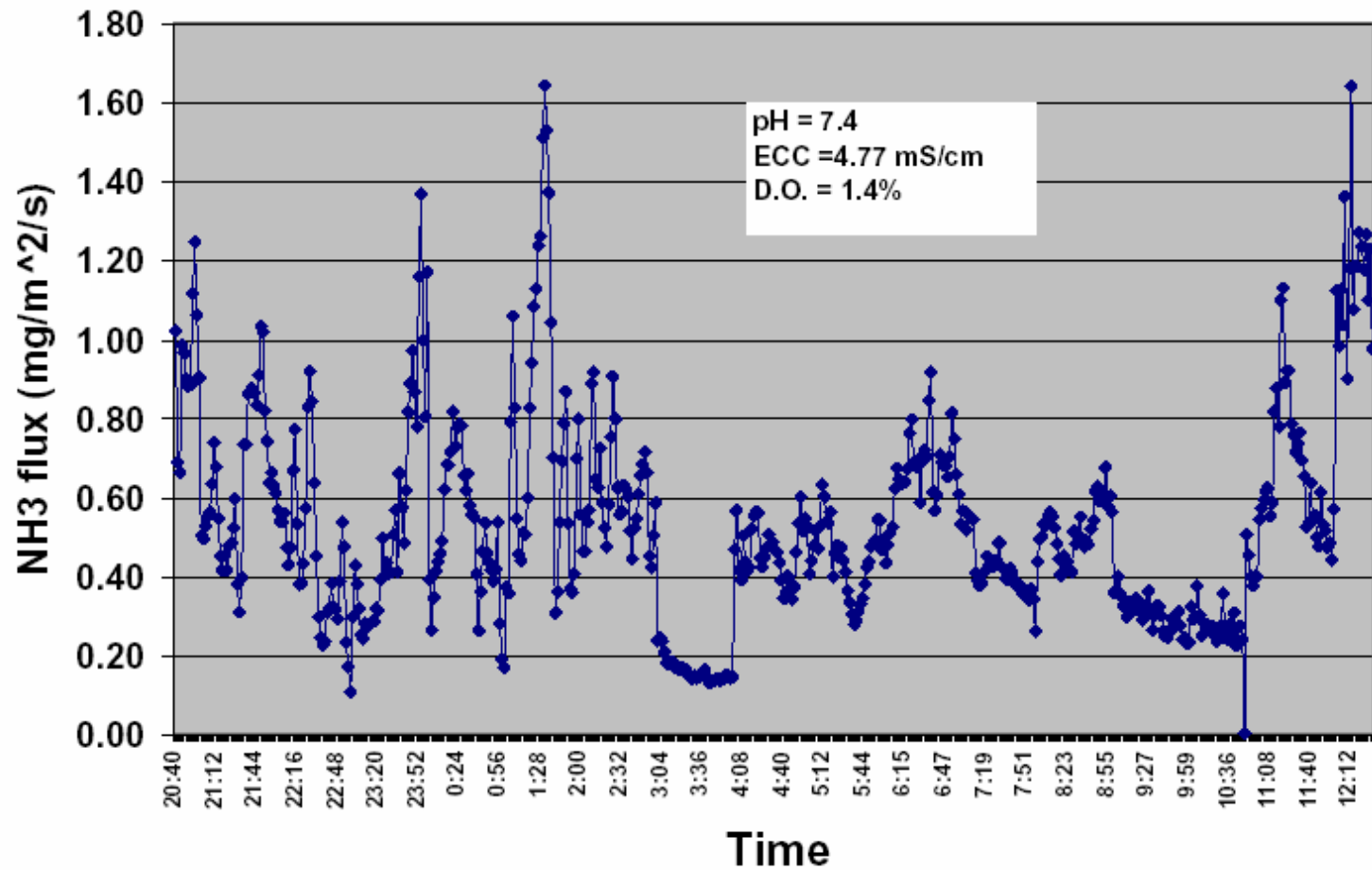
GasFinder Gases and Sensitivities

Gas	Sensitivity (ppm-m)	1m path (ppm)	10m path (ppm)	100m path (ppm)
HF (high)	0.1	0.1	0.01	0.001
HF (low)	1	1	0.1	0.01
NH3	5	5	0.5	0.05
H2S	20	20	2	0.2
CH4	1	1	0.1	0.01
CO2	1000	1000	100	10
HCN	1	1	0.1	0.01
HCl	1	1	0.1	0.01

Conversion of ppm- m data

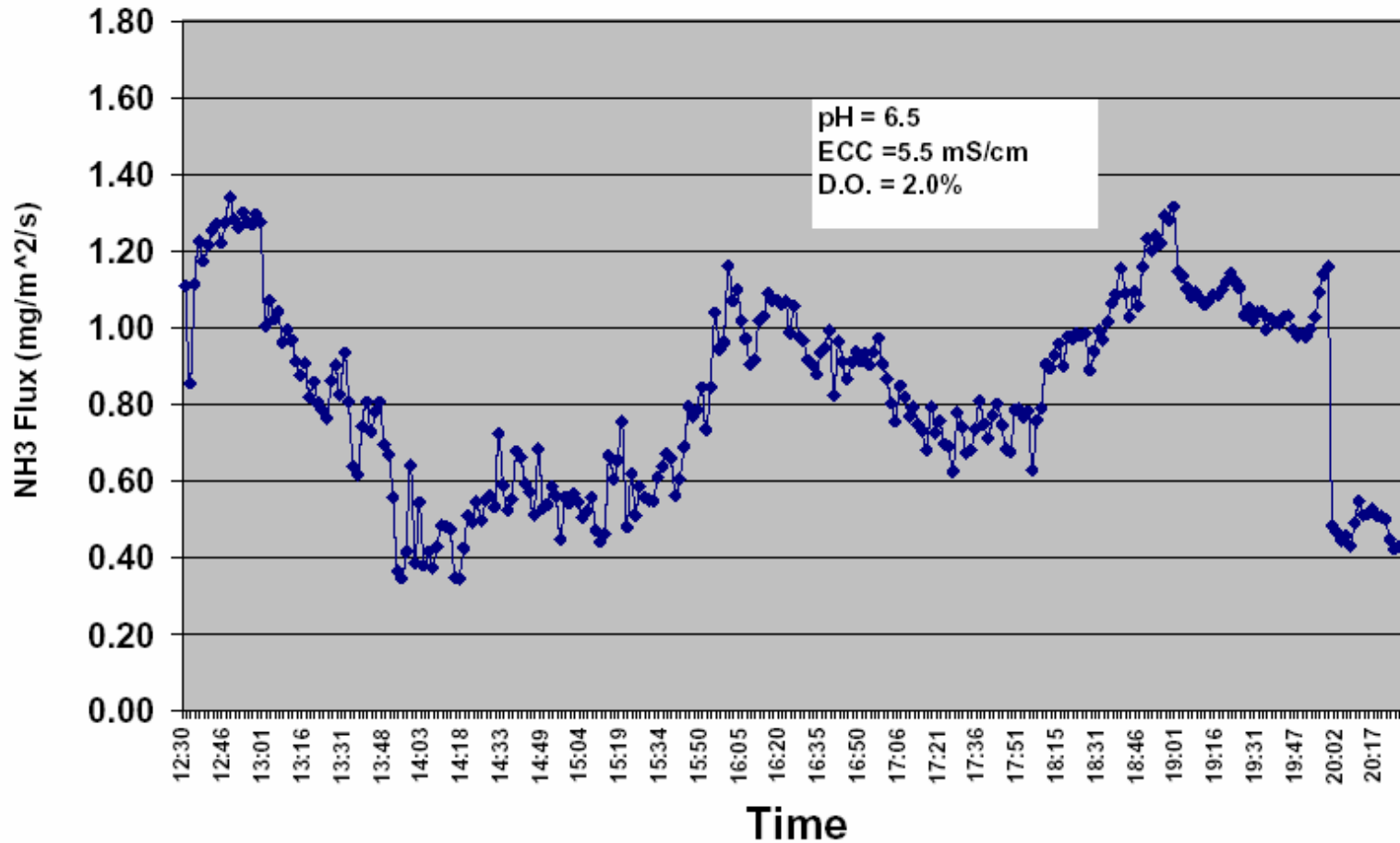
- Divide by path length to get ppm
- Use molecular weight, Universal gas constant, pressure and temperature to convert ppm to mg per m³ of gas
- Use wind speed to convert mg per m³ to horizontal flux at a given height in mg/m³/s

Ammonia flux at 1.5m above "Large" Lagoon Prior to Acidification
Monitoring period : July 20th to July 21st 2003

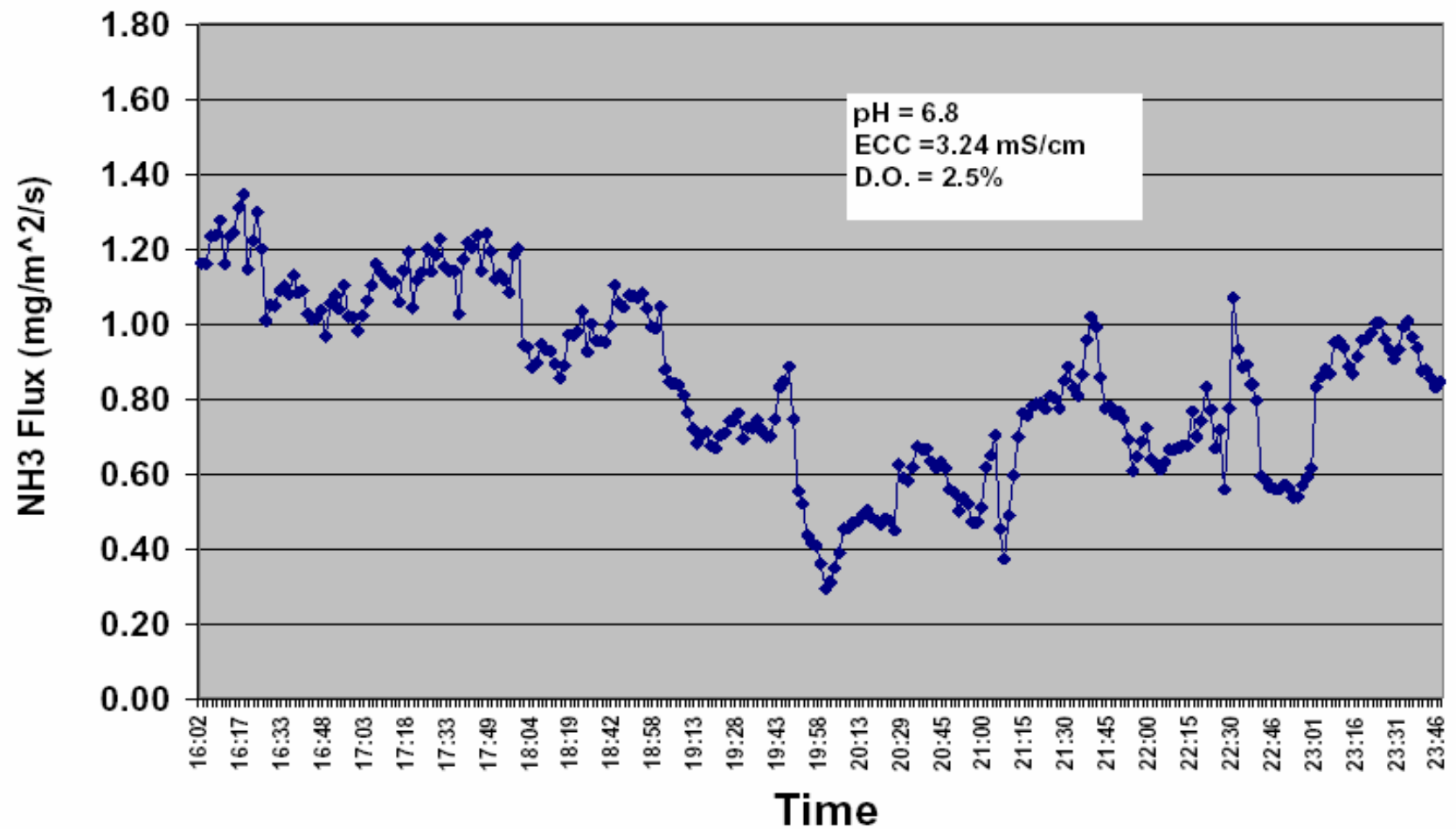


Ammonia Flux at 1.5m above "Large" Lagoon During Acidification

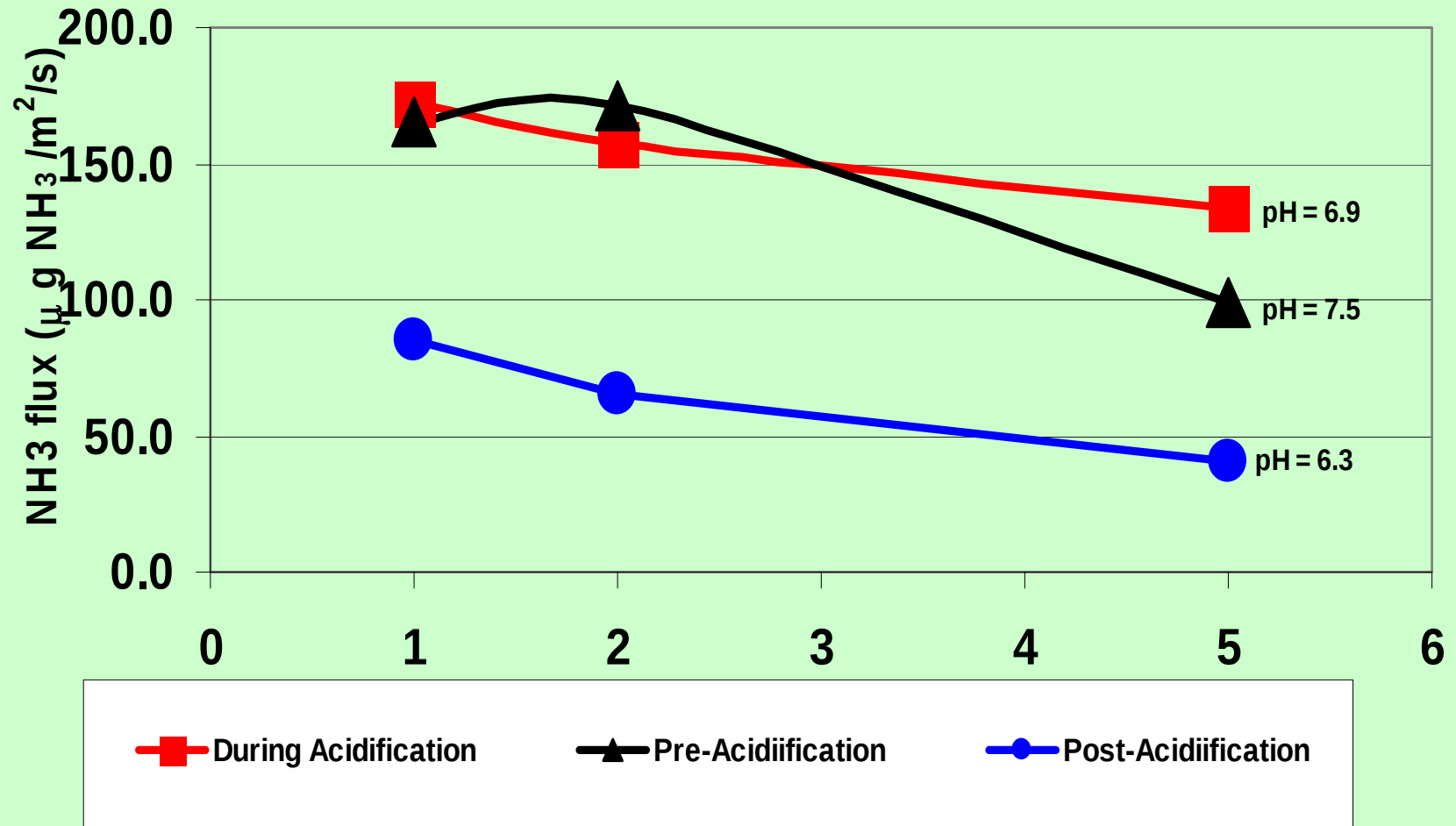
Monitoring period : July 21st Noon to July 21st Evening



Ammonia Flux at 1.5m above "Large" Lagoon During Aeration and Agitation
Monitoring period : July 22nd Evening to July 22nd Night



Ammonia fluxes measured with active samplers before, during and after acidification of Lagoon at CSUF dairy



Generic Benefits of TDL

- **Very high resolution - about 0.003 cm^{-1}**
 - Enables measurement of individual spectral lines
 - No spectral interference from other gases
 - Linear over wide dynamic range
- **Very sensitive - ppm to ppb levels**
- **Fast response times – typically 1 second**
- **High reliability - no moving parts**
- **Non-contact method - suitable for corrosives**
- **Amenable to fiber optics - multiple path capability**
- **Widely applicable - many species absorb in NIR**
- **Potential for multiple species**





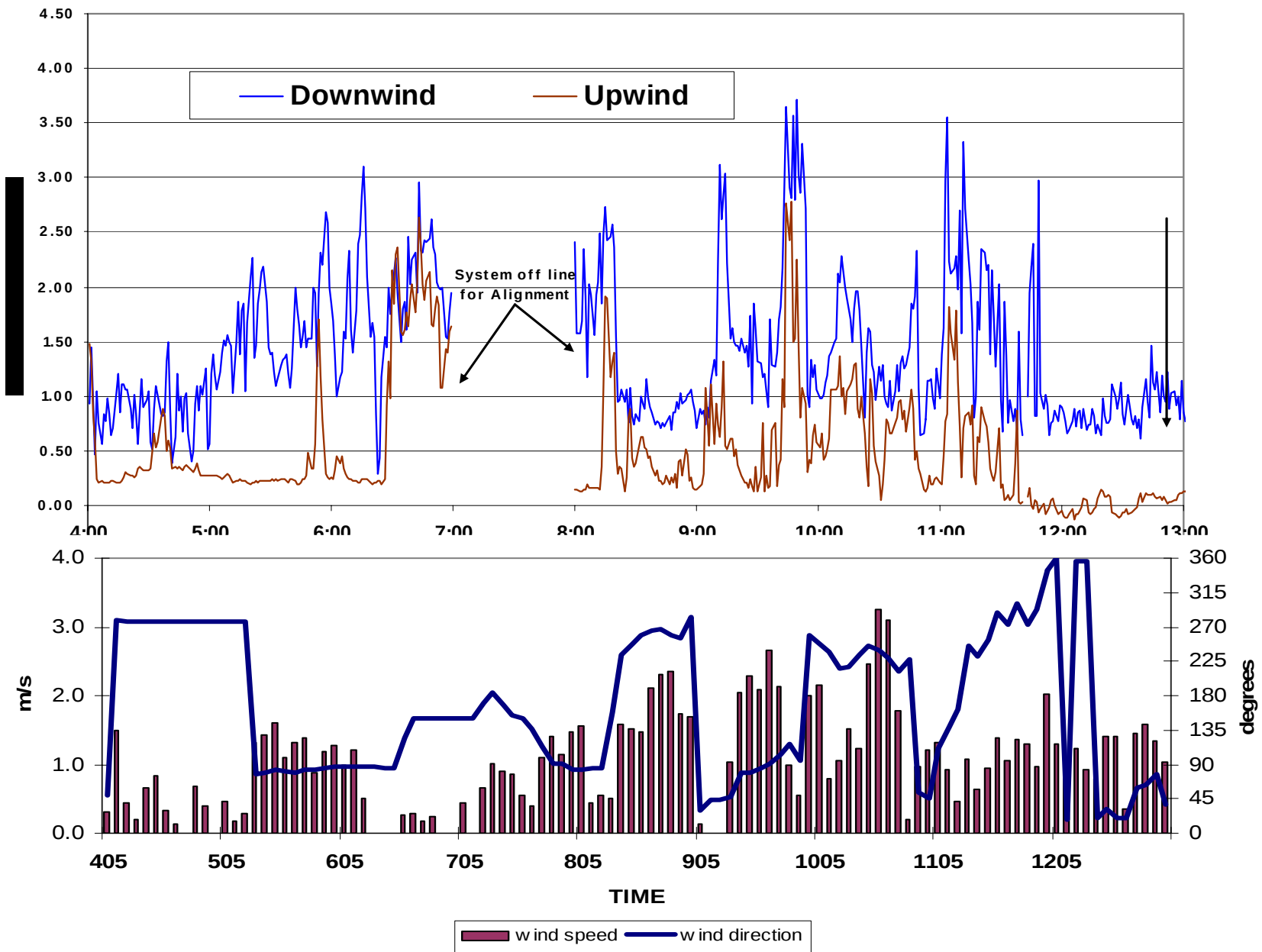
Using TDL Data for Modeling Emission rates

- **Attempt to do inverse dispersion modeling using the EPA approved model: Industrial Source Complex Short Term version 3 (ISC-STv3).**
- **Due to the limited number of laser units available we were unable to obtain simultaneous upwind and downwind concentrations**
- **This presents the problem of determining what portion of the measured concentration downwind of a source is attributable to that source.**

Using a 3-phased sampling scheme

- Laser path is placed upwind (**phase 1**) in order to characterize the background concentration of the target pollutant.
- After approximately 1 hour the (based on concentration trend) the laser path is moved to downwind of the target source (**phase 2**).
- Once sufficient data is collected in the downwind location, the path is replaced in the original location (**phase 3**) in order to verify that there are no significant changes in the background concentration.
- Any significant difference in concentration between **phase 1** and **phase 3** is determined.
- **Phase 3** typically consists of leaving the lasers in the upwind location for an extended period of time in order to determine if there is a trend in the upwind concentration.
- The duration of the three phase process is based on relatively steady state atmospheric conditions.

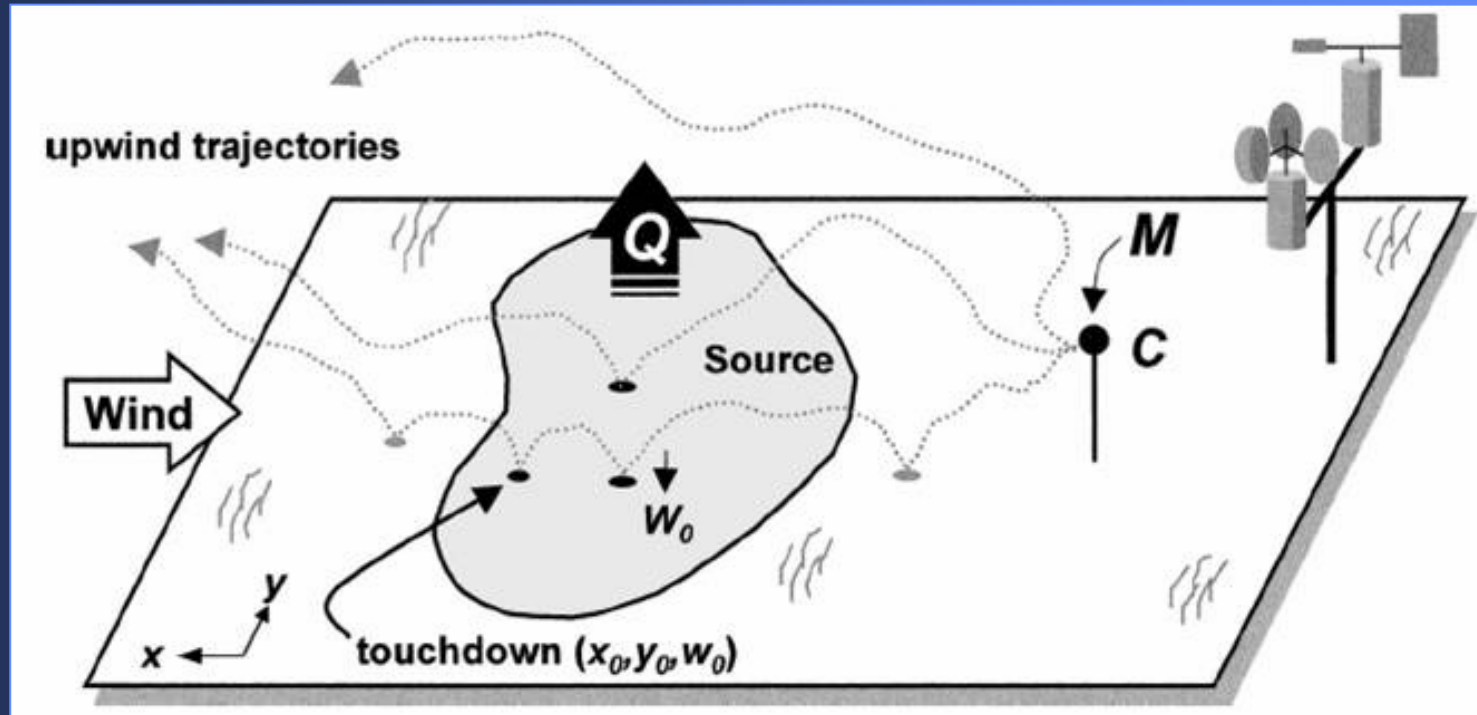
Ammonia Concentrations for two paths over an open lot



Backward Lagrangian Stochastic Model

- **The BLS approach by Flesch et al (1995).**
- **Lagrangian stochastic (LS) model calculates the paths of a large number of individual particles as they travel with the local wind field.**
- **The basic assumption made is that the particles have only limited memory of their previous state.**

Backward Lagrangian Stochastic Model



(From Flesch et al. 2004)

Basis for Windtrax v1.0 Software

BLS versus Gaussian Model

- Personal communication with group in Canada (Windtrax) and at TAMU
- Refer to work by:
Jacqueline E. Price *et al* (2004)
Center for Agricultural Air Quality
Engineering and Science – Texas A&M
University
- Presented at : 2004 ASAE/CSAE Annual
International Meeting – Ottawa, ON, Canada

Windtrax vs ISC-ST3

Jacqueline E. Price *et al* (2004)

- ERs from the models vary by a factor of 10!
- WindTrax predicted ER 10 times that of the ISC – downwind concentration would be 10 times more than the actual!
- Regulatory impact
- Back-calculated pollutant ERs are extremely model dependent

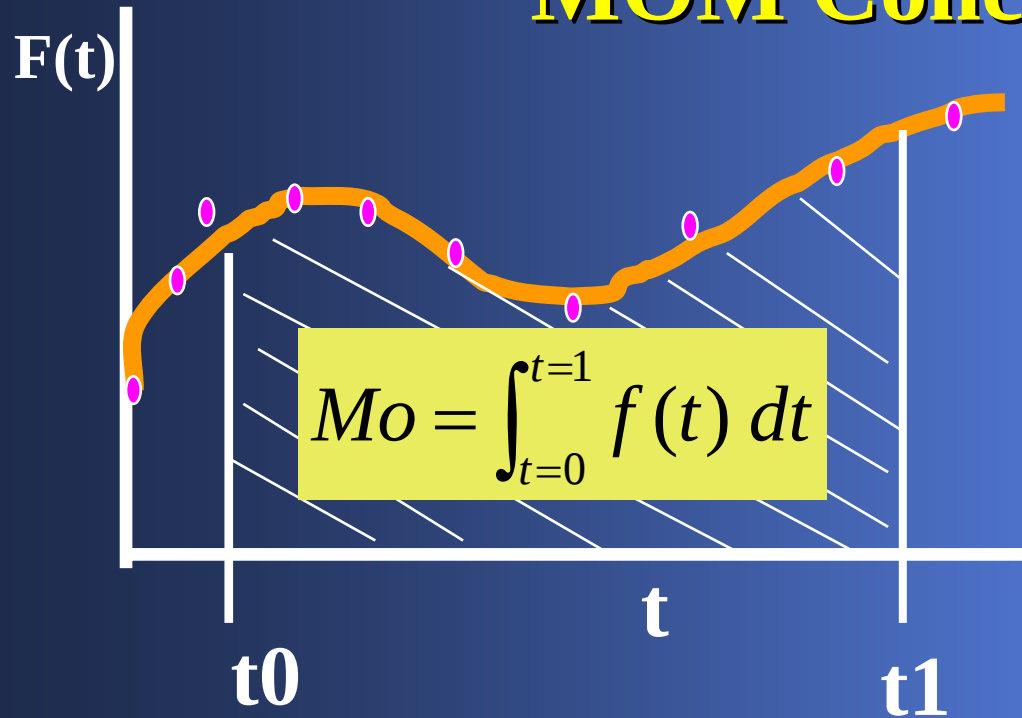
Method of Moment (MOM) Analysis

- **Curve fit the data using Mathcad 2000**
- **Method of Moment Analysis (MOM) for assessing the relative amount of gas emitted from area covered by path length**
- **Assumptions in this approach:**
 - Constant area (fetch) is monitored by TDL
 - Wind pattern is consistent

MOM Concepts

- **Spline fit the data using Mathcad 2000**
- **Zeroth moment, M_0 = mass under curve**
- **Ist moment = M_1 can be used to obtain mean time for center of mass**
- **2nd moment = M_2 for variance or spread around center of mass**

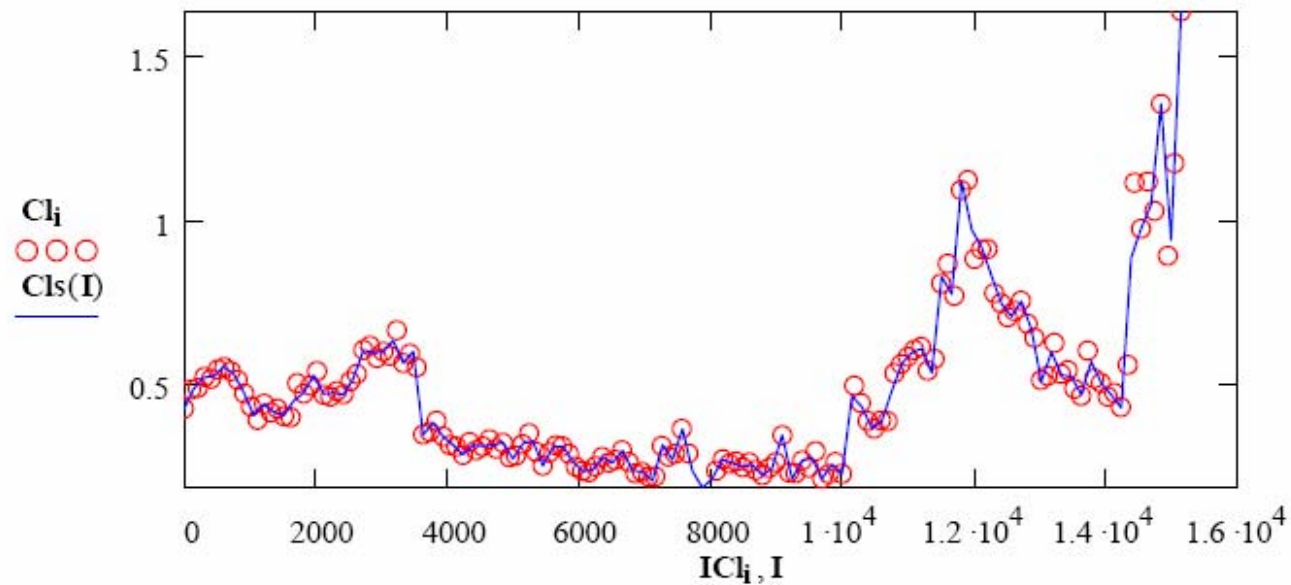
MOM Concepts cont'd



$$M_1 = \int_{t=0}^{t=1} t f(t) dt; \quad \text{Mean} = \frac{M_1}{M_0}$$

$$M_2 = \int_{t=0}^{t=1} \left(t - \frac{M_1}{M_0} \right)^2 \frac{f(t)}{M_0} dt; \quad \text{Variance} = M_2$$

MOM during Pre- acidification



$$CIMA := \int_0^{\max(ICl)} Cls(I) dI$$

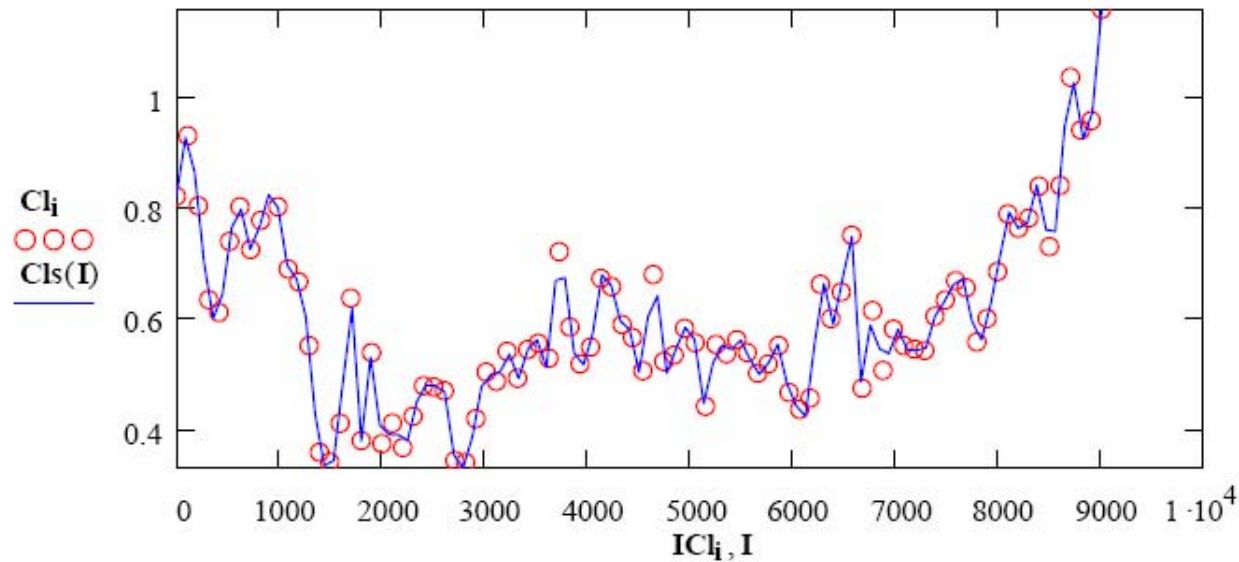
$$CIMA = 7.252 \times 10^3 \quad \text{zeroth moment}$$

Summary for MOM results for Lagoon

TRT = Preacid

Mean	Variance	Skewness	Total Amount
$ECI = 8.467 \times 10^3$	$VarCI = 2.362 \times 10^7$	$SKCI = -0.268$	$CIMA = 7.252 \times 10^3$

MOM during acidification



$$CIMA := \int_0^{\max(ICl)} Cl_s(I) dI$$

$$CIMA = 5.415 \times 10^3 \quad \text{zeroth moment}$$

Summary for MOM results for Lagoon

TRT = acid

Mean	Variance	Skewness	Total Amount
$ECl = 4.678 \times 10^3$	$VarCl = 7.771 \times 10^6$	$SKCl = -0.097$	$CIMA = 5.415 \times 10^3$

Comparison MOM Results

Treatment	Total x10 ³	Mean x 10 ³	Variance x 10 ⁷	Skewness
Pre acid	7.252	8.467	2.362	-0.268
Acid	5.415	4.678	0.7771	-0.097
Ratio of Acid: PreAcid	74.7	55.2	32.9	36.2
Relative change	25.3	44.8	67.1	63.8

Summary

- Assuming that the TDL instruments are kept within optimum operating temperature conditions, the TDL technology is suitable for detecting the gas concentrations from dairy lagoons during the summer temperatures in SJV, California.
- During intense fog condition observed during the Fall season, the lasers fail

Summary (Cont'd)

- Data collected with the TDL depict the periods of relatively higher diurnal emissions which generally go undetected with the filter pack sampling
- It is essential to conduct monitoring during the fall, winter and spring seasons to assess the performance of the TDL system under these conditions, while at the same time examining any seasonal variability in the gaseous emissions.
- At least one more set of each lasers are needed if we are to obtain simultaneous upwind and downwind concentrations data necessary for validation of EPA model.

Summary (Cont'd)

- Potential use of the data from the TDL for modeling:
 - EPA approved ISC-ST3
 - Windtrax
- Using Mathcad curve fitting and method of moment analysis approach (WITH ACKNOWLEDGEMENT OF SIMPLIFYING ASSUMPTIONS) may be useful for comparing relative amount of gas emitted over a given area covered by TDL path length

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THANK YOU

