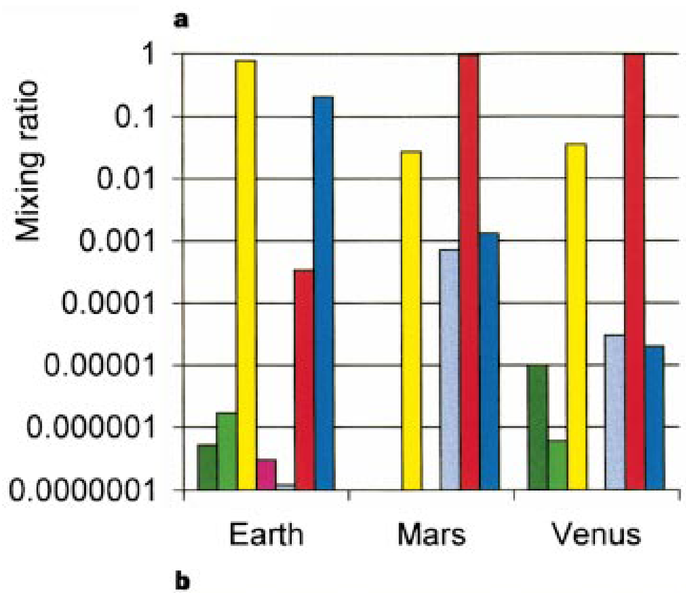
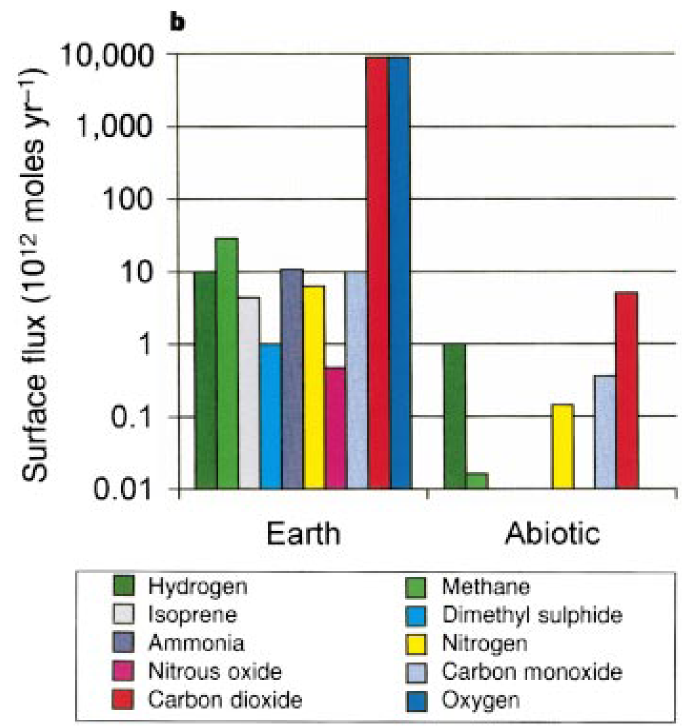
Lecture on Trace Gas Emissions

Dennis Baldocchi
ESPM
University of California, Berkeley
Spring 2012

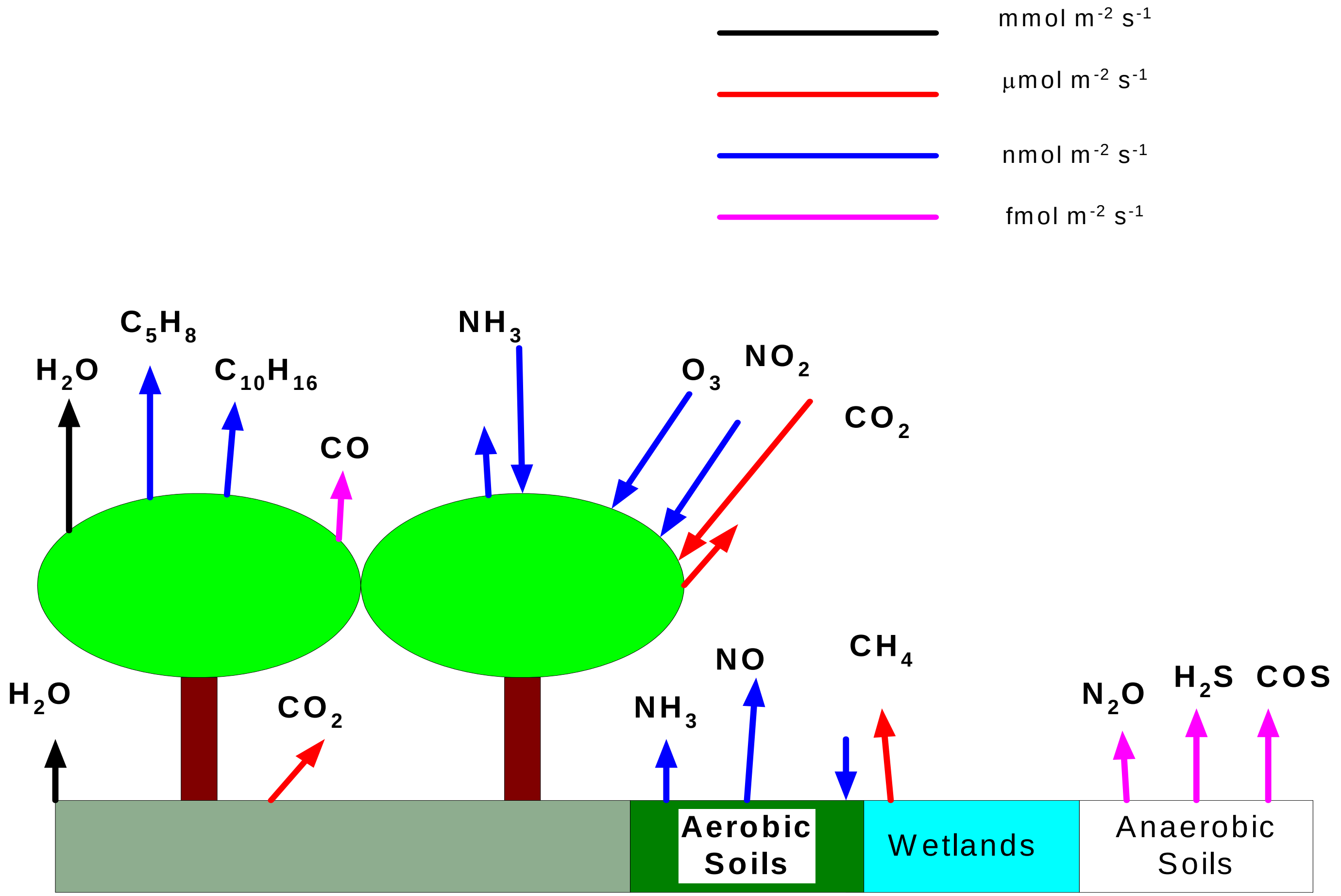
Mixing Ratios and Fluxes





Lenton, 1998 Nature

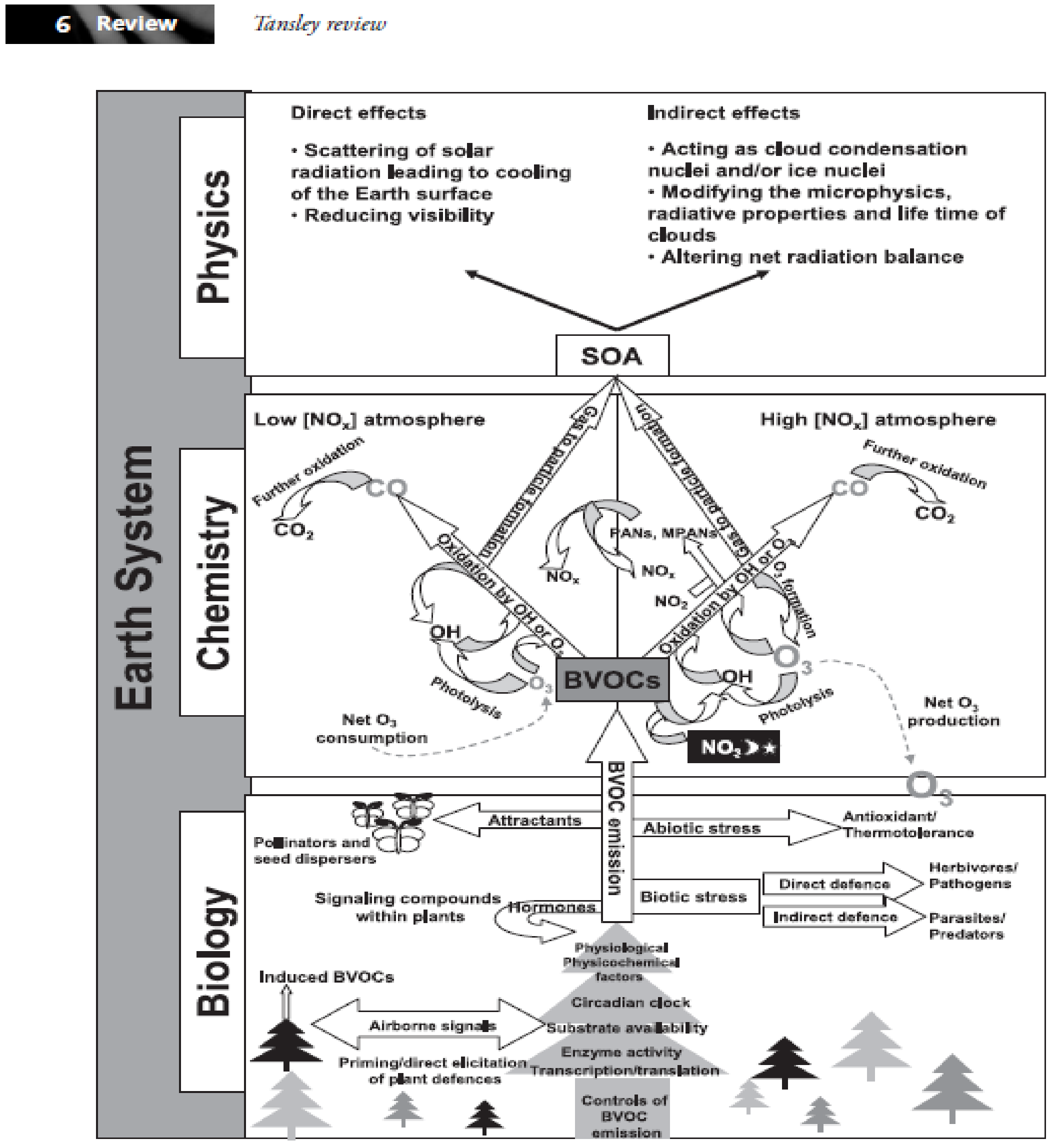
Trace Gas Exchange



Trace Gas Stoichiometry: A Flux Redfield ratio for the Biosphere

ESPM 228 Adv Biomet & Micromet

Biogenic Hydrocarbons



Laothawornkitkul et al New Phytologist Tansley review .pdf

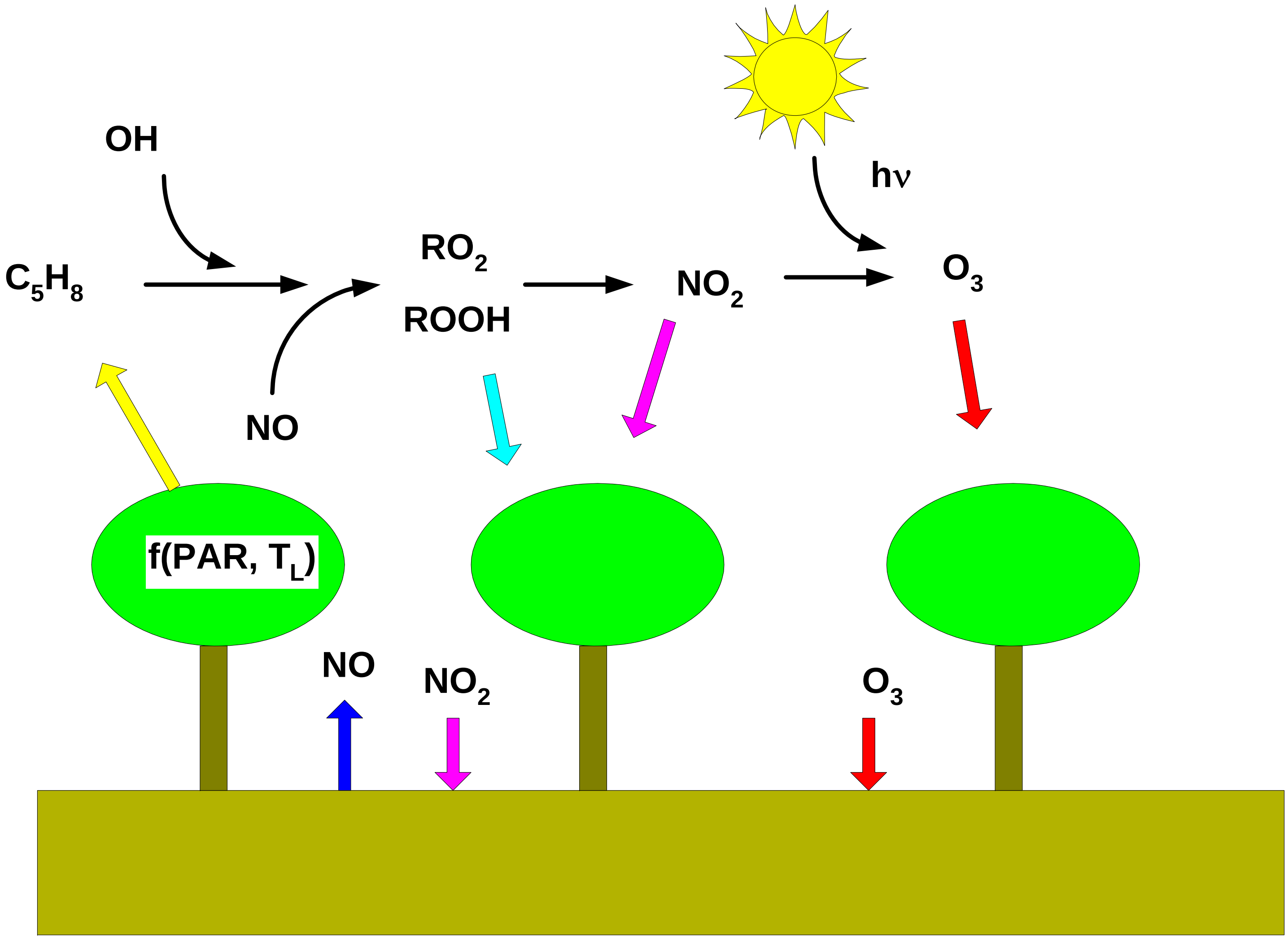
Visibility

Air Pollution

Stress Signal
l
Plant Protection

Carbon Loss

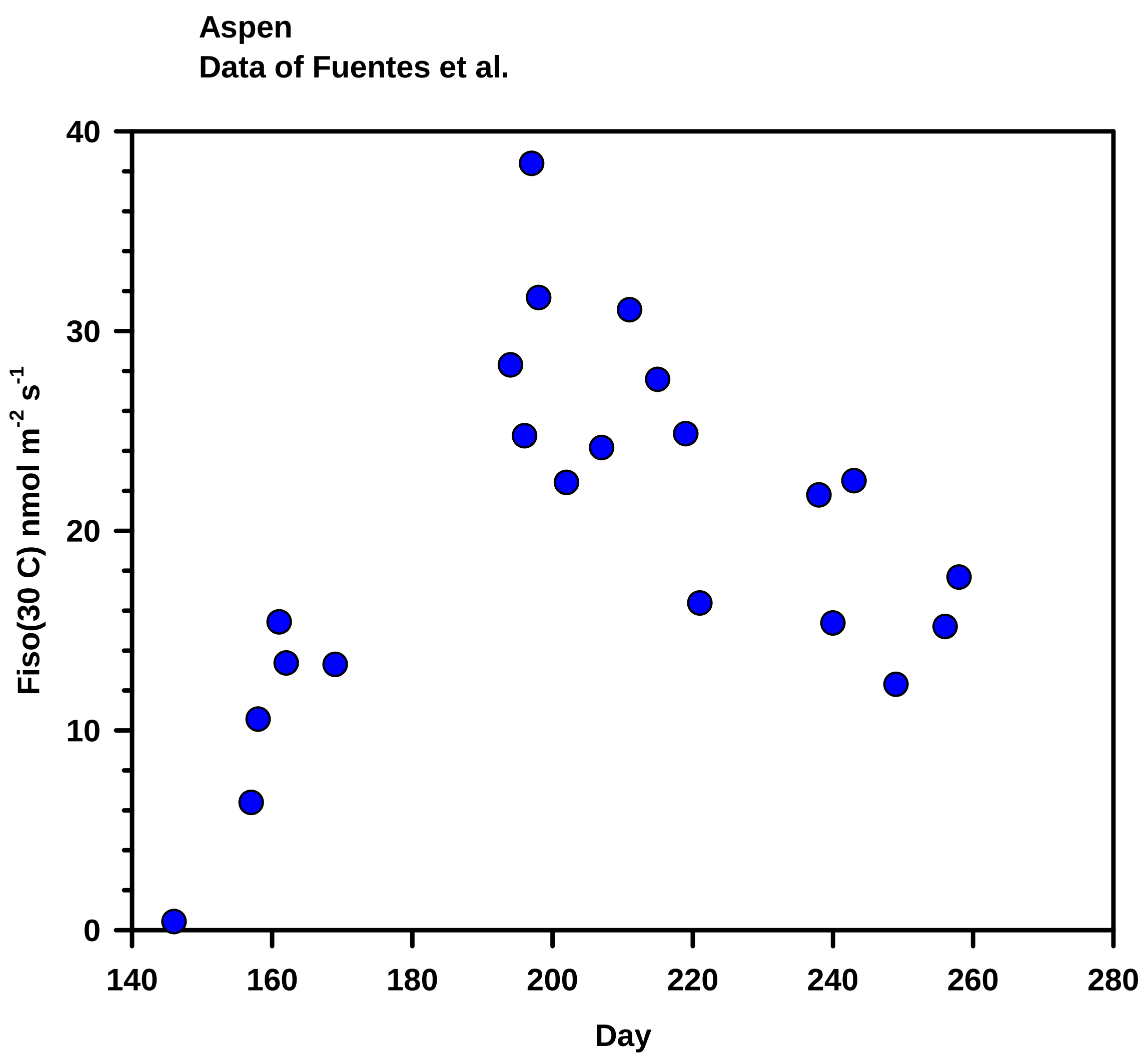
VOC produce O_3 in high NOx state



Global budget

Global Isoprene Emissions: 400 to 600 Tg y-1
~ 40% of non-methane biogenic hydrocarbon emissions

Stand Scale Isoprene Flux Measurements: Monospecies Stand



Revolution in Sensors
Proton Transfer Reaction- Mass Spectrometer

COMPOUNDS IN THE EARTH'S ATMOSPHERE

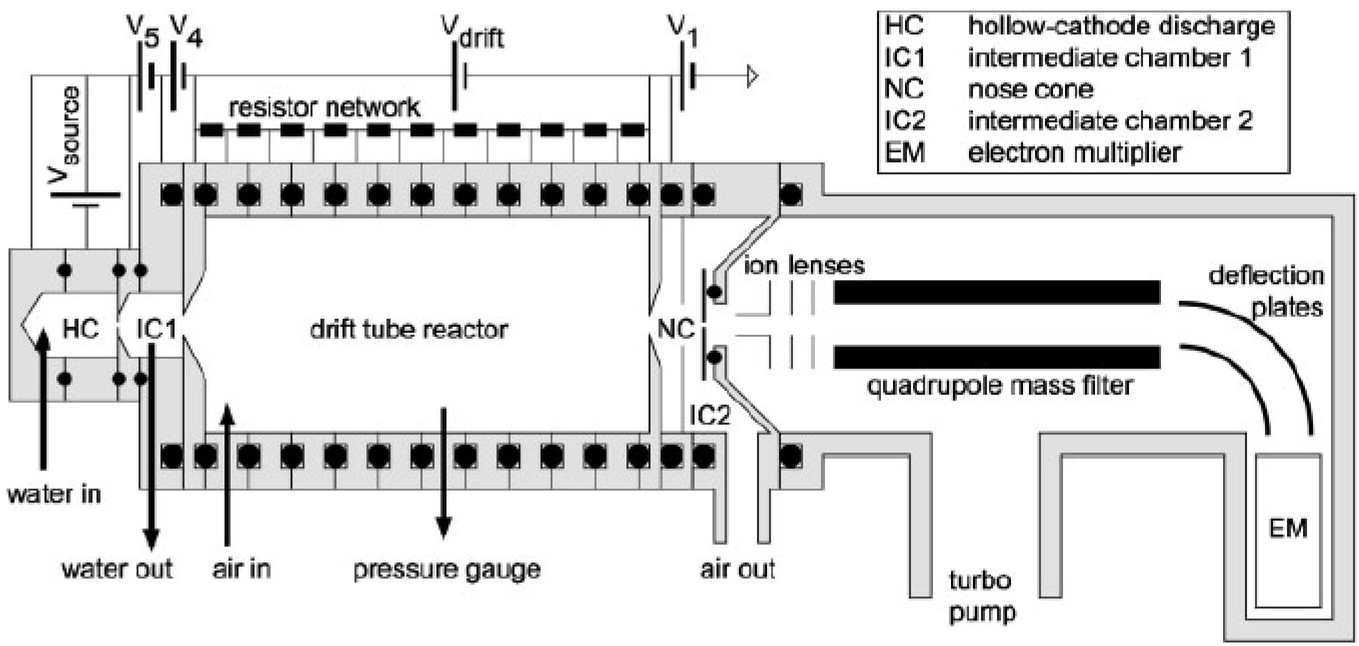
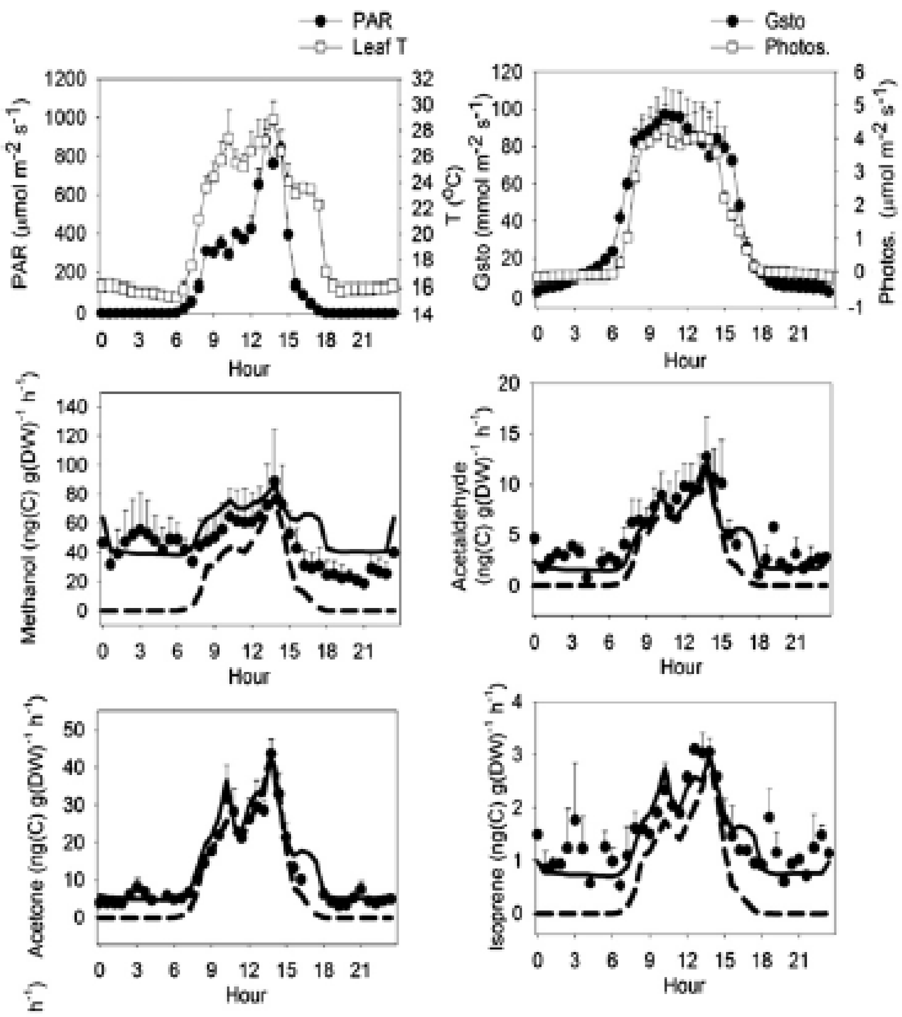


FIGURE 1. Schematic drawing of the PTR-MS instrument.

deGouw and Warneke 2007 Mass Spectometer Reviews

BVOC Fluxes from Citris



Fares et al 2011 Atmos Environ

Biochemistry of Isoprene Production

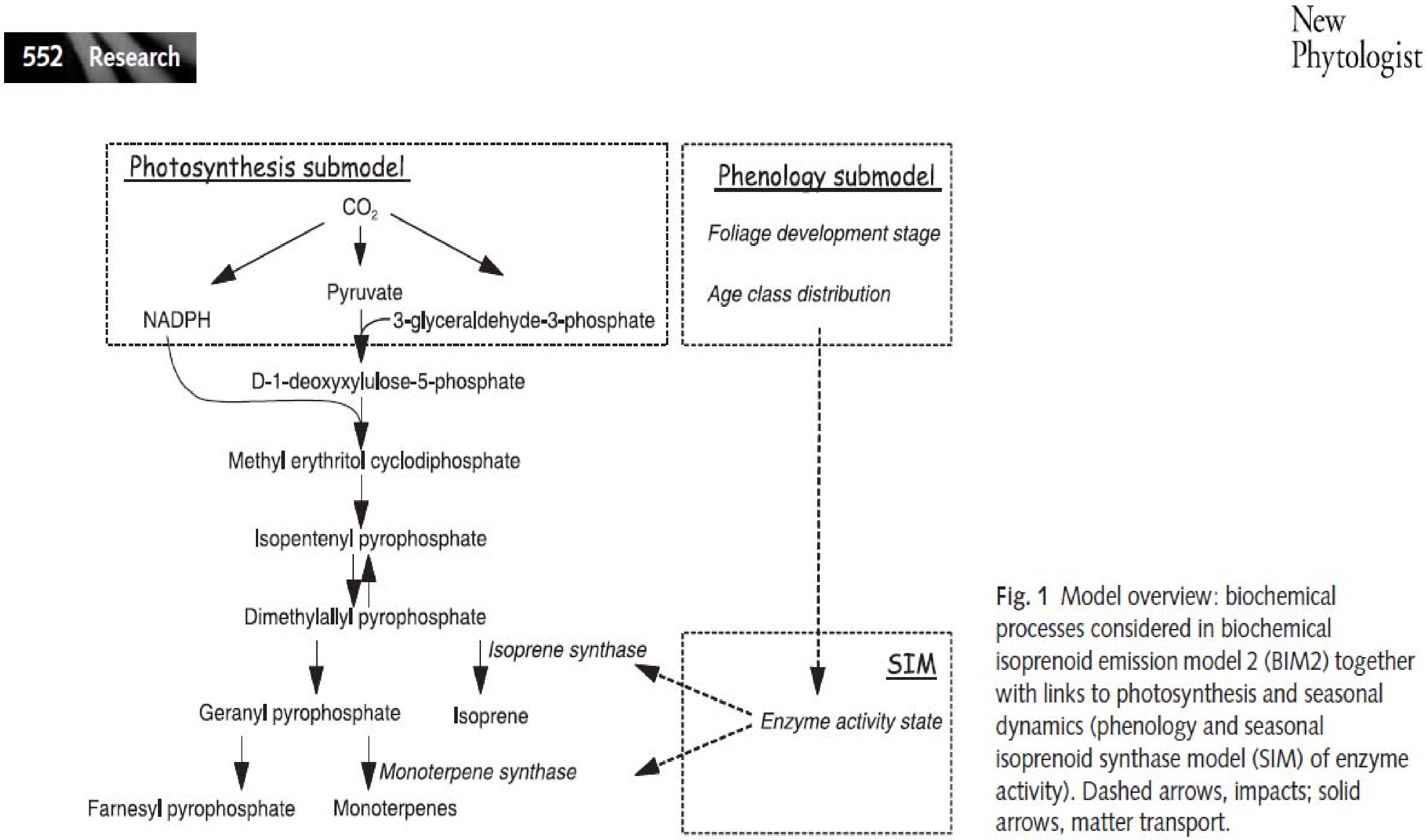
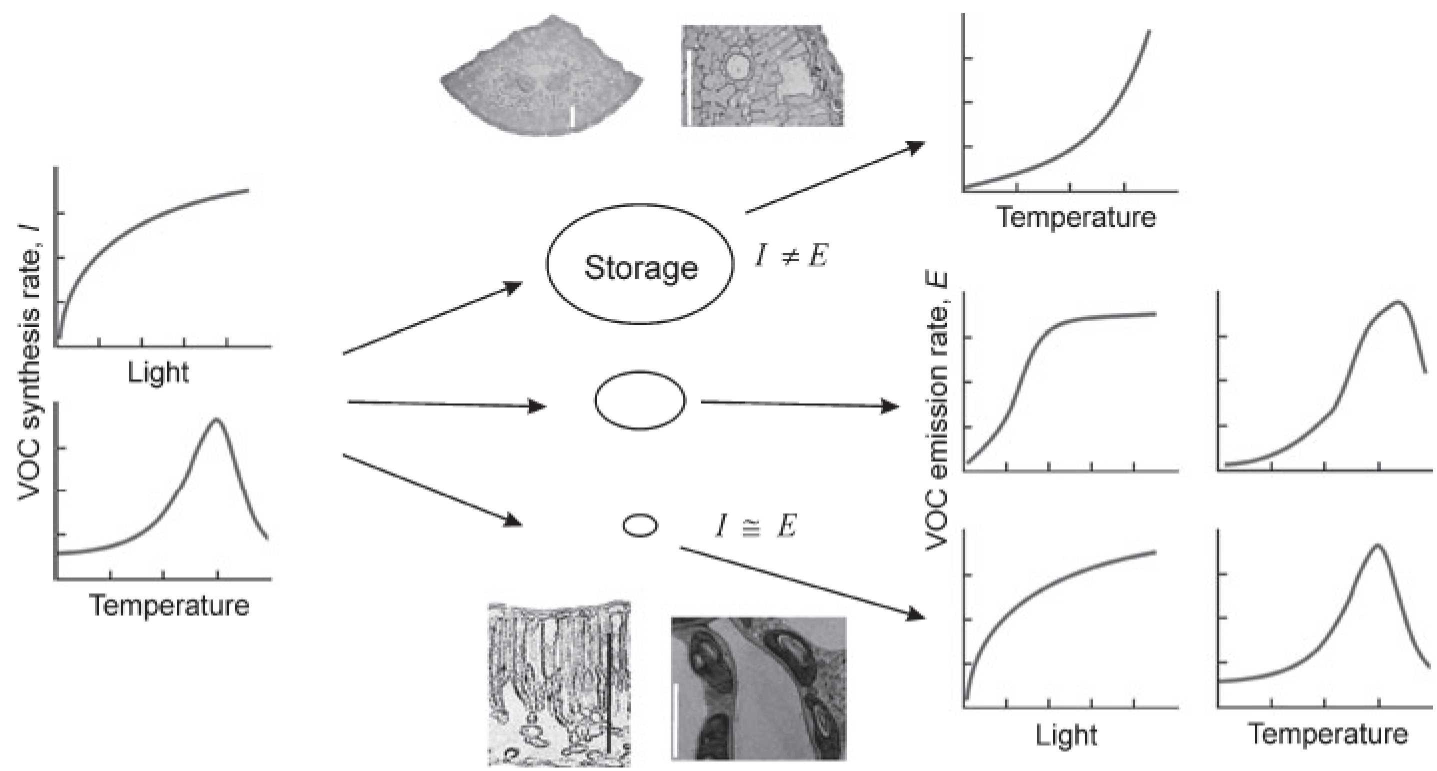


Fig. 1 Model overview: biochemical processes considered in biochemical isoprenoid emission model 2 (BIM2) together with links to photosynthesis and seasonal dynamics (phenology and seasonal isoprenoid synthase model (SIM) of enzyme activity). Dashed arrows, impacts; solid arrows, matter transport.

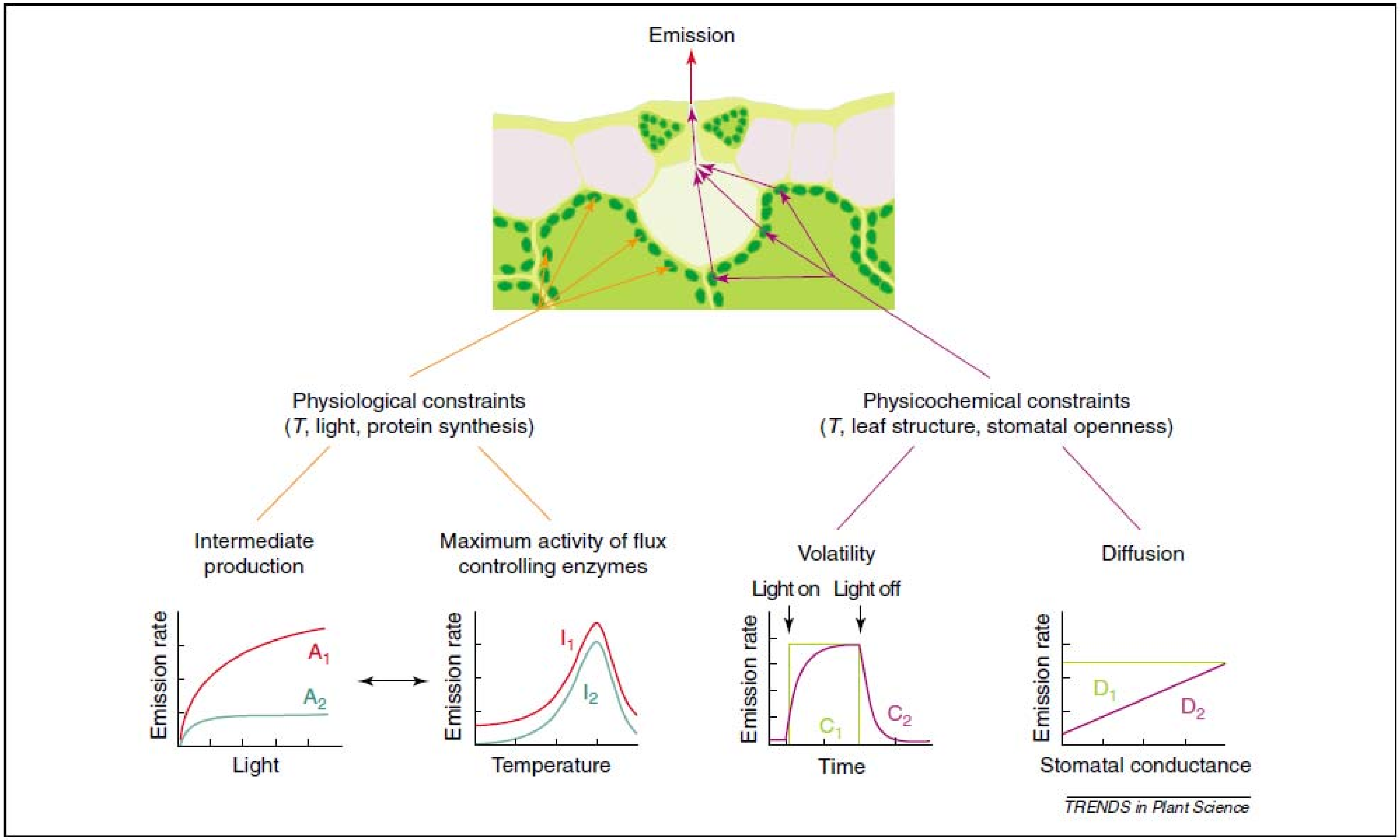
Grote, 2007 New Phytologist

Synthesis (I) vs Emission (E)

Modeling Volatile Isoprenoid Emissions – A Story with Split Ends R. Grote & Ü Niinemets



Grote and Niinemets



Niinemets et al, Trends in Plant Science 2004

Guenther-Monson-Fall Isoprene Emission Model

$$F_{isoprene} = S_I \cdot f(Q_p) \cdot f(T_l)$$

S_I is a species specific, standardized emission factor (nmol m^{-2} s^{-1}) at a specified leaf temperature (T_l) and photon flux density (Q_p).

Functions in the Guenther-Monson-Fall Model

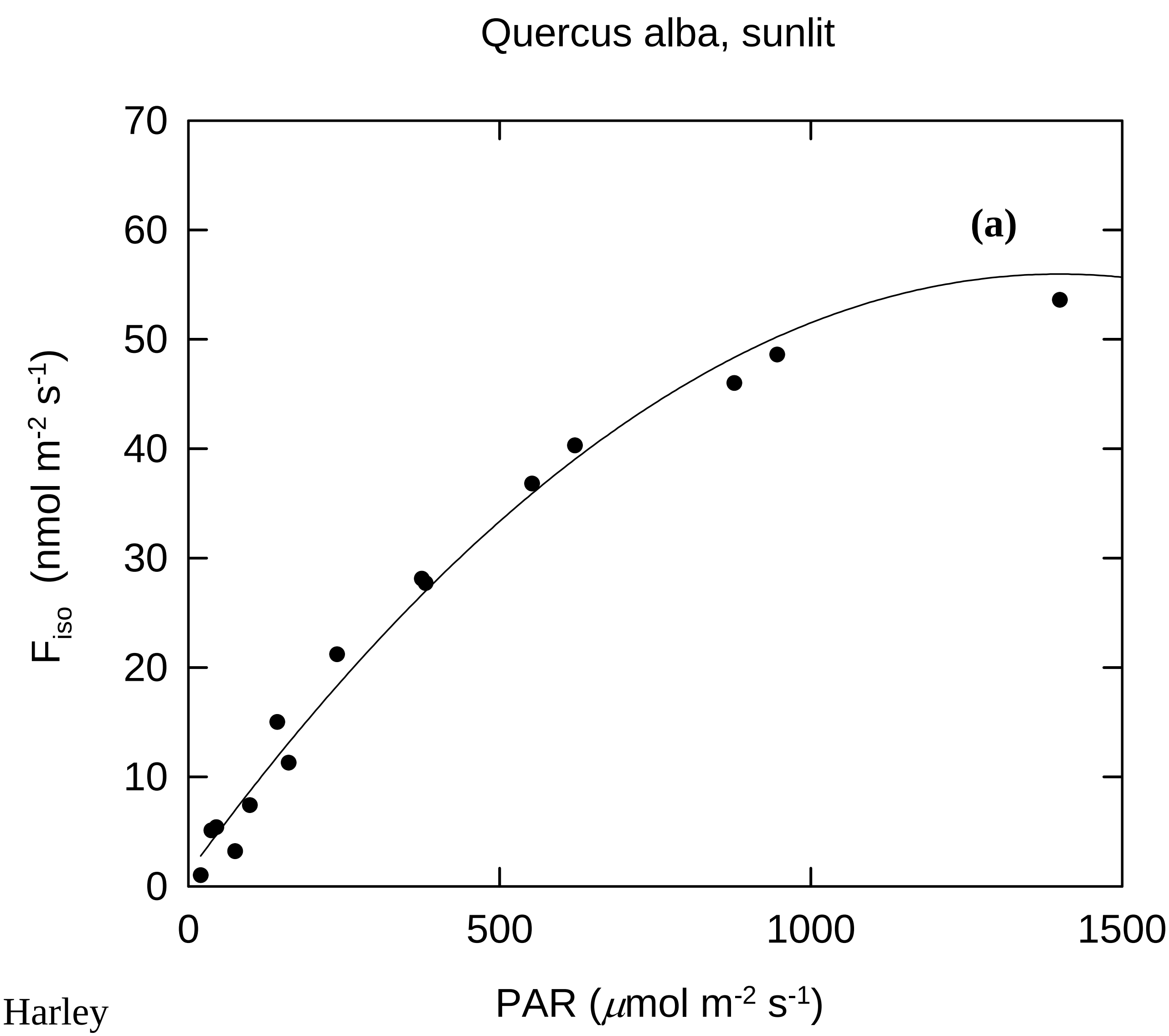
$$f(Q_p) = \frac{\alpha \cdot C_L \cdot Q_p}{\sqrt{1 + \alpha^2 \cdot Q_p^{\,2}}}$$

$$f(T) = \frac{exp\left(\dfrac{C_{T1} \cdot (T_k - 303)}{R \cdot 303 \cdot T_k}\right)}{1 + exp\left(\dfrac{C_{T2} \cdot (T_k - T_{opt})}{R \cdot 303 \cdot T_k}\right)}$$

(m^2 s^1 $mmol^{-1}$(quanta)) and *CL* are empirical constants

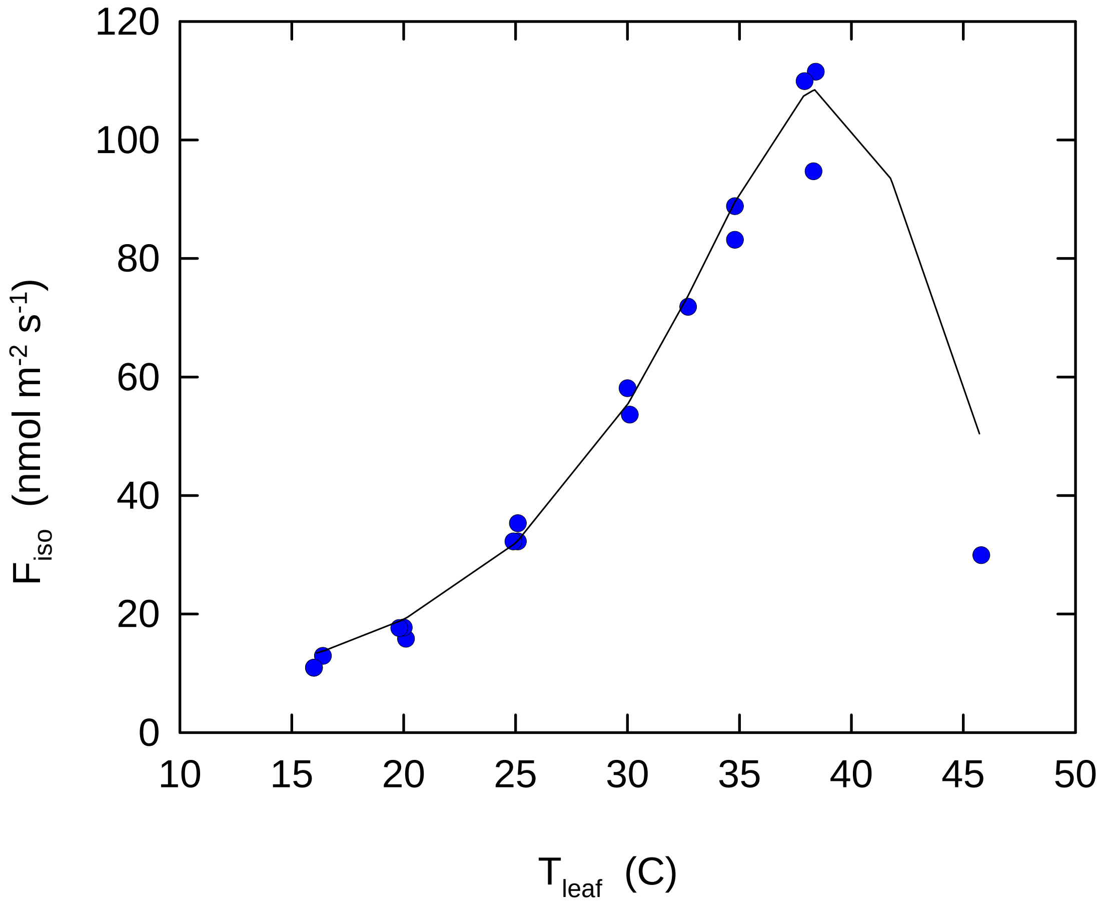
R is the universal gas constant (8.314 J K^{-1} mol^{-1}), *CT1* and *CT2* are coefficients and *Topt* is the optimum temperature and T_k is the leaf temperature, in Kelvin

Light Response Function



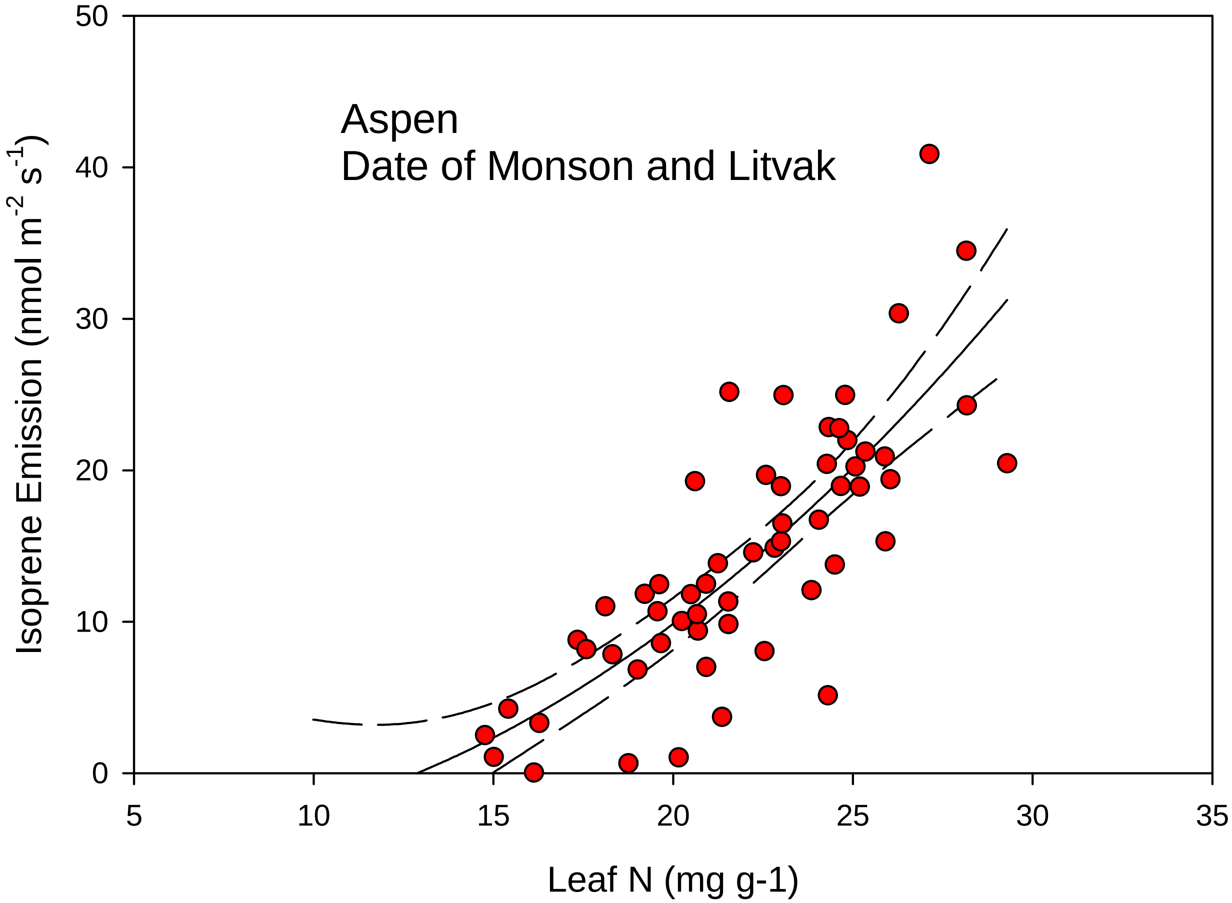
Data of Peter Harley

Temperature Response Function

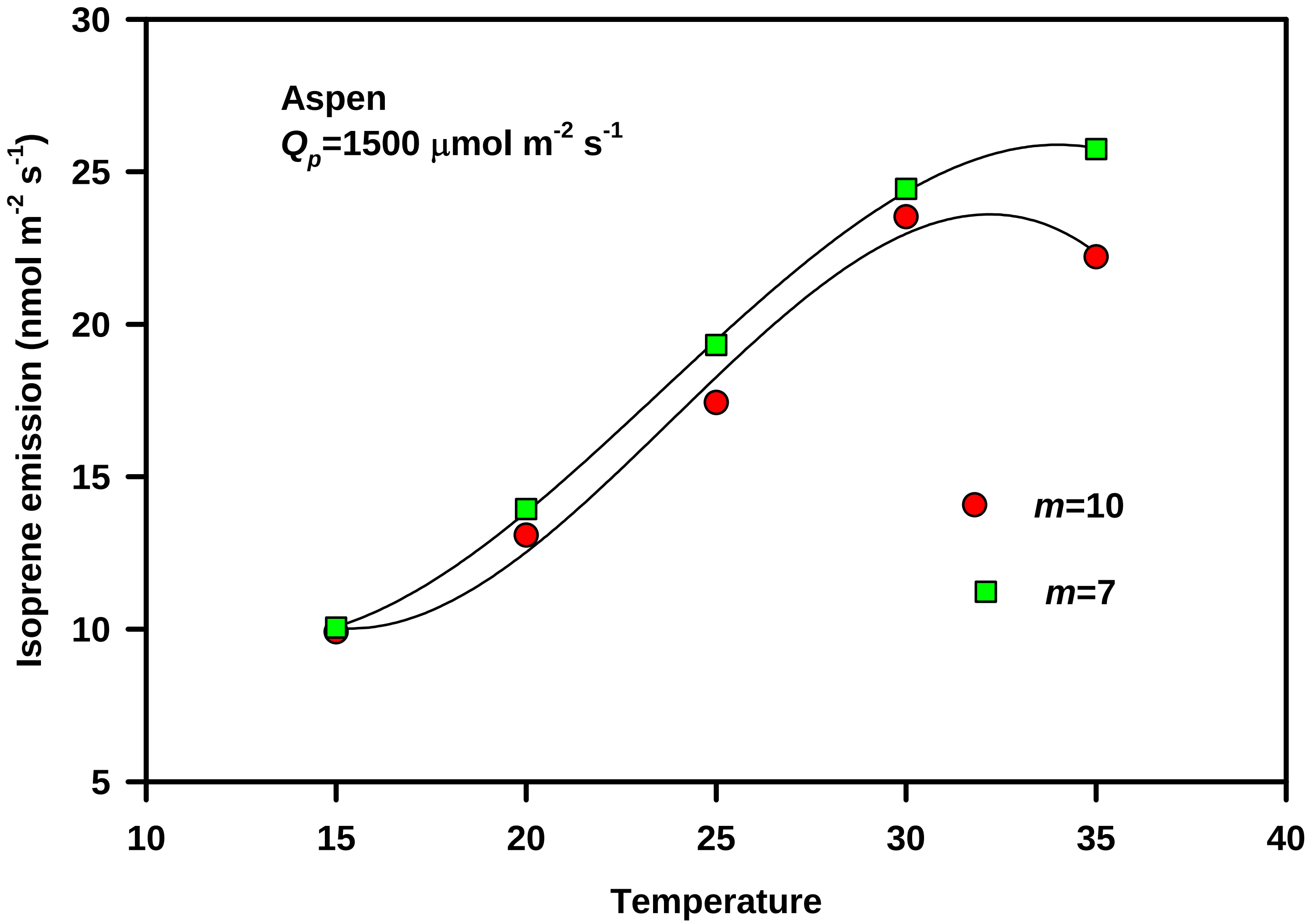


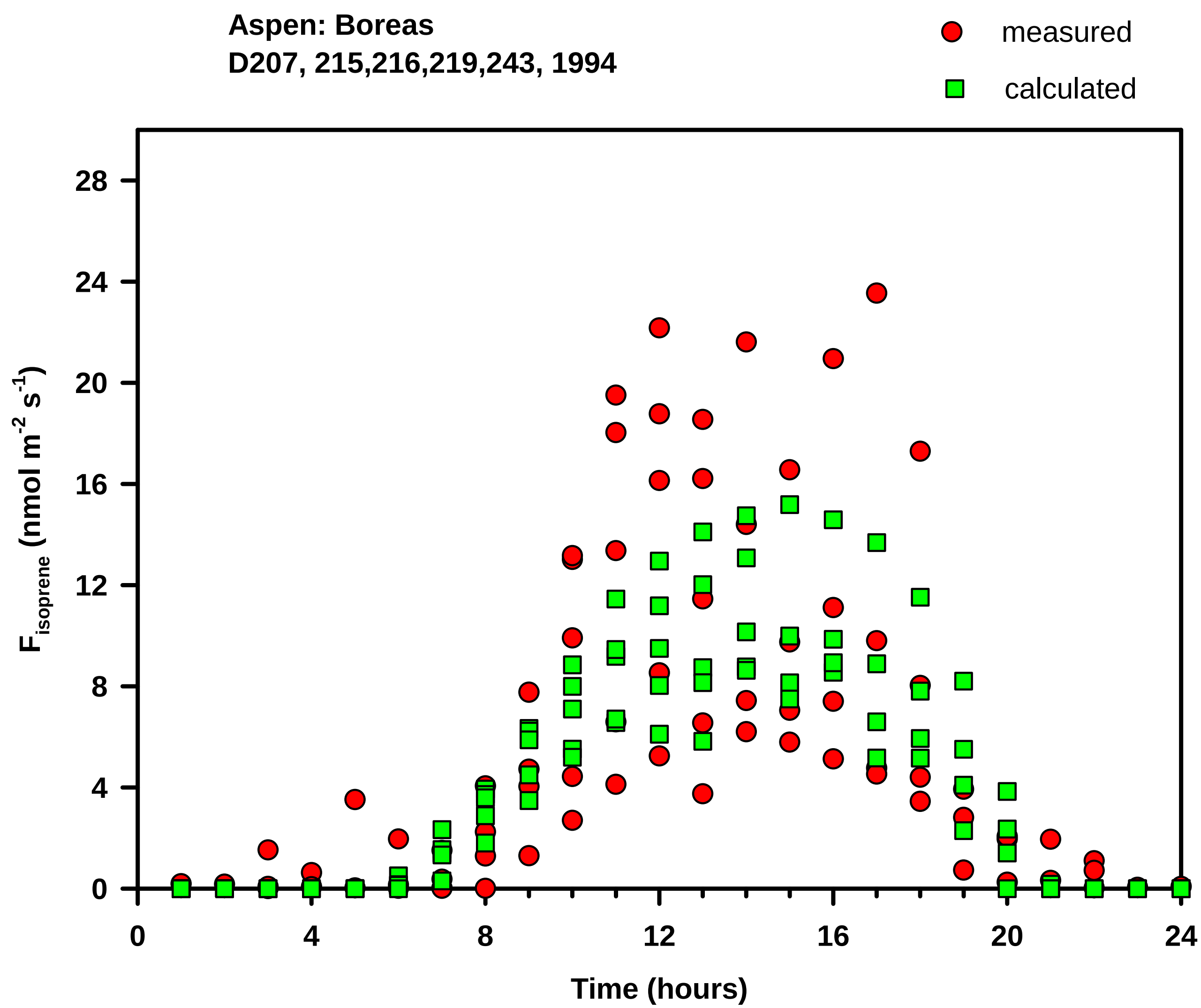
Data of Peter Harley

Isoprene Emission Scales with Leaf Nitrogen



Isoprene and Drought:Theory
Assuming Stomatal Closure Leads to Greater Leaf Temperature





Baldocchi et al 1999 JAM

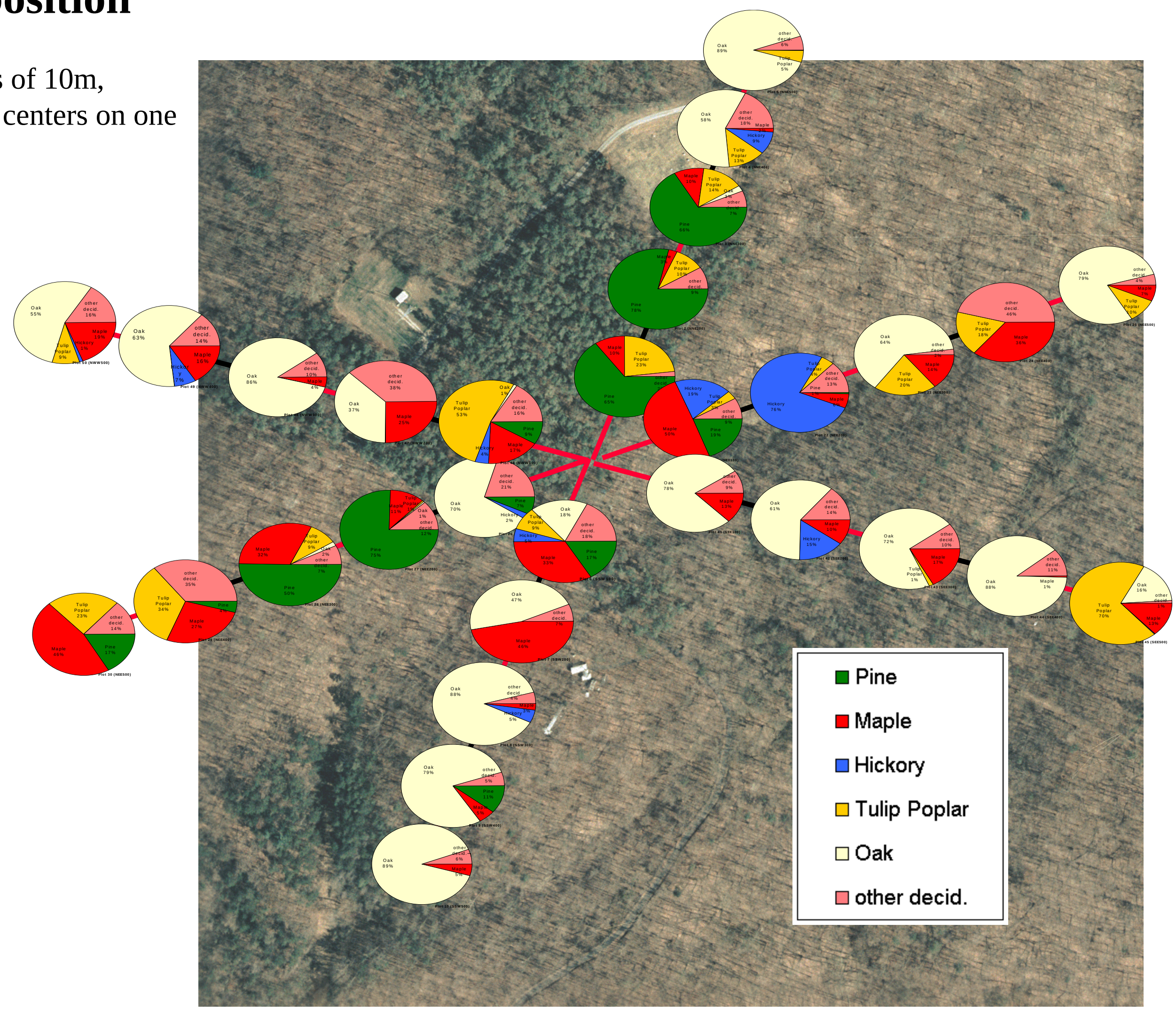
Walker Branch 1999 Species Composition

Mixed Forests Contain Isoprene Emitters and non Emitters

(each plot has a radius of 10m, distance between plot centers on one transect is 100m)

N

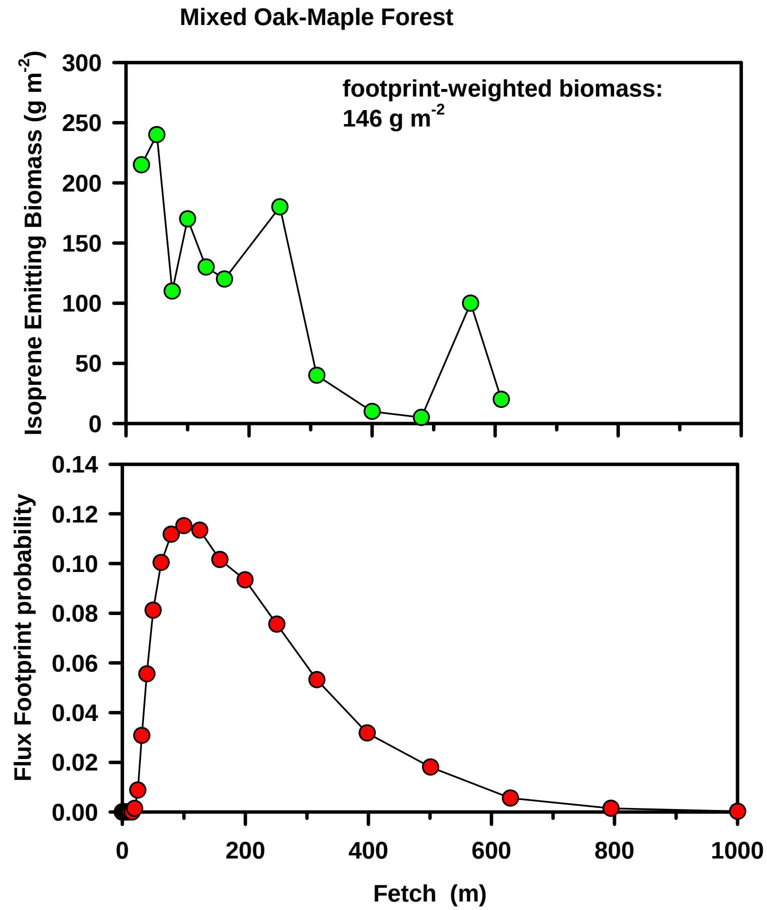
500m



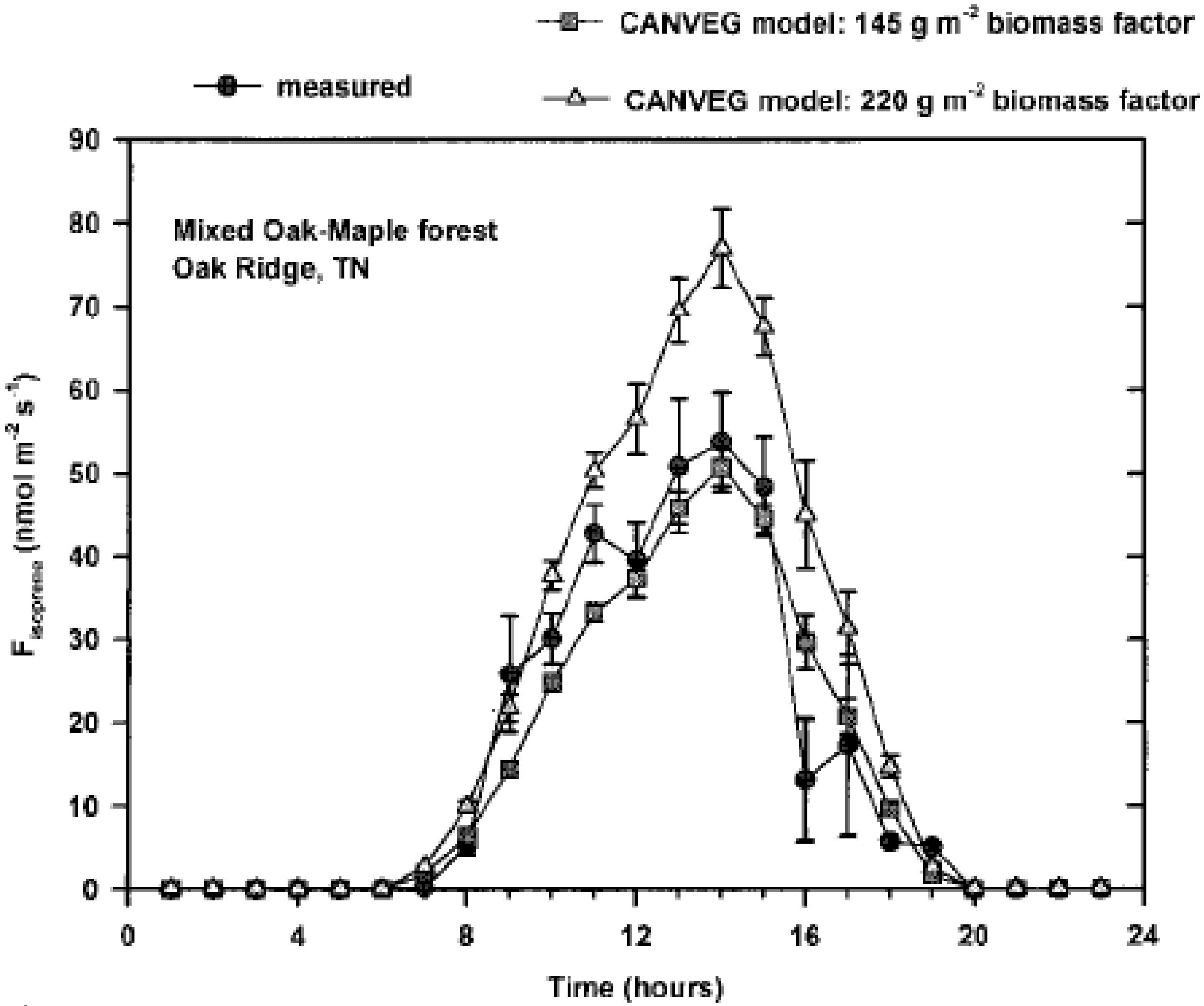
Data of Eva Falge

$$b_I = \int_0^\infty b_I(x)\,p(x)\,dx$$

isoprene emitting biomass (b_I), sensed by a micrometeorological flux measurement system, along the wind-blown axis (x) is a function of the flux footprint, defined by the probability distribution p(x)

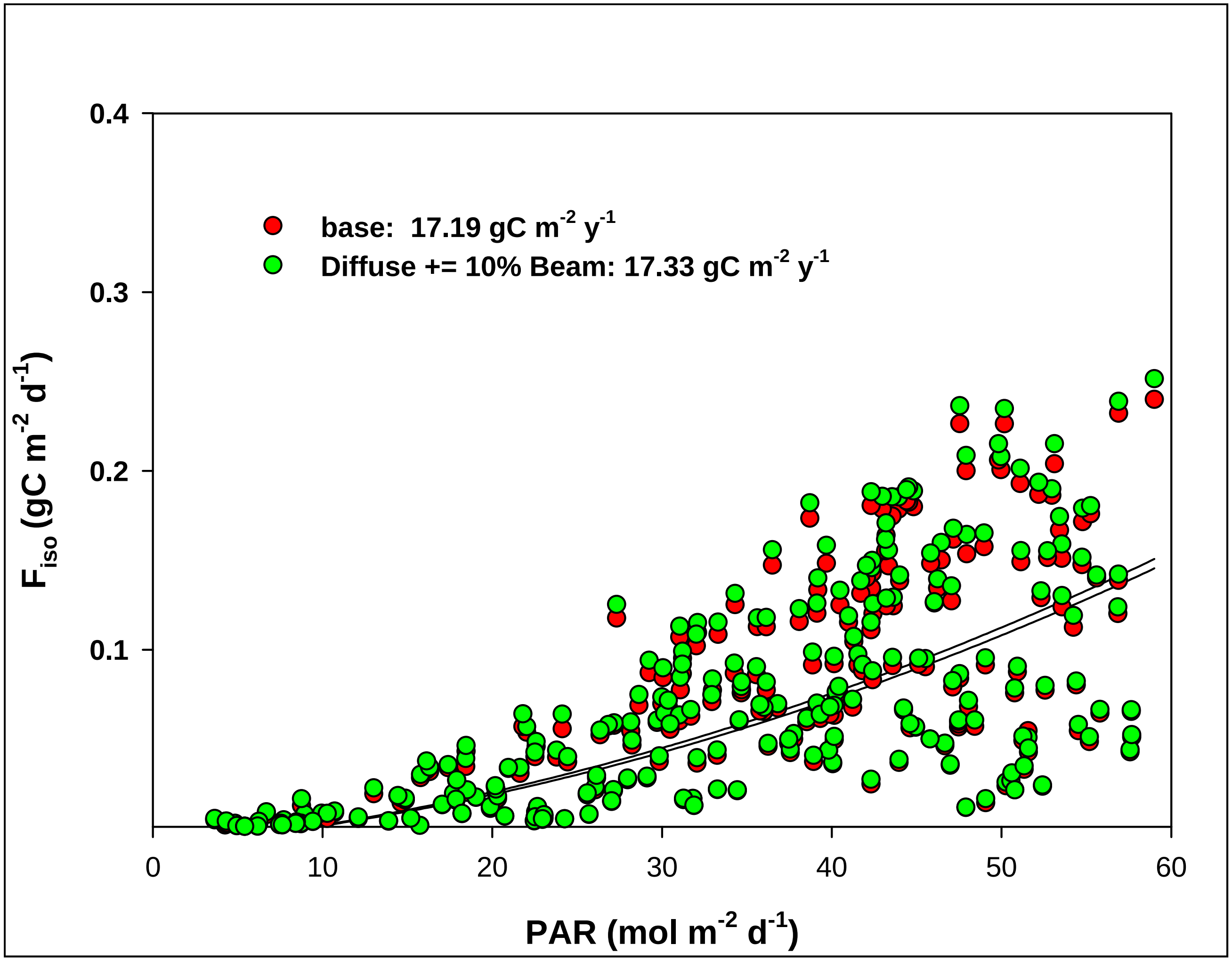


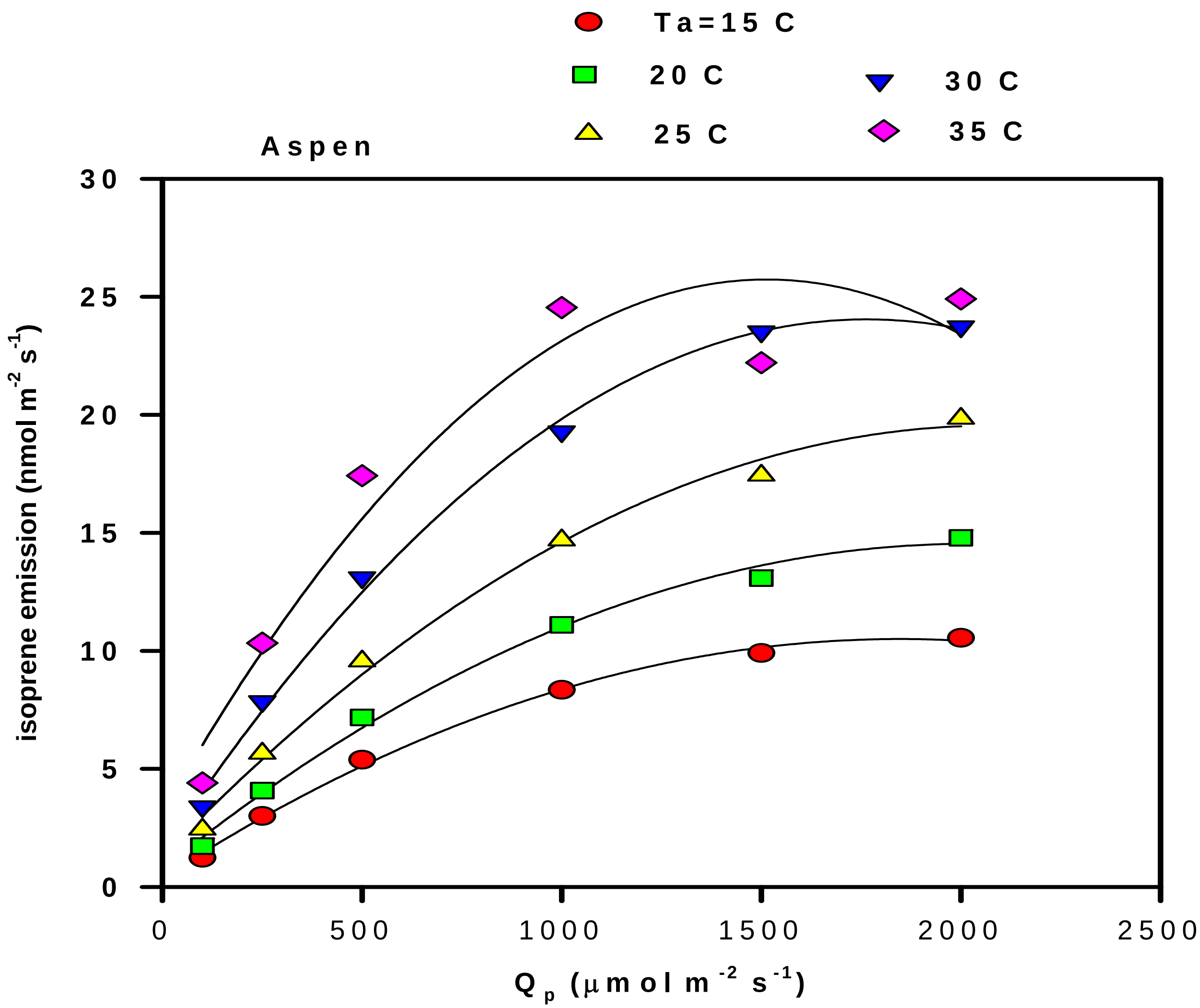
Model in Mixed Forest with and without Flux Footprint



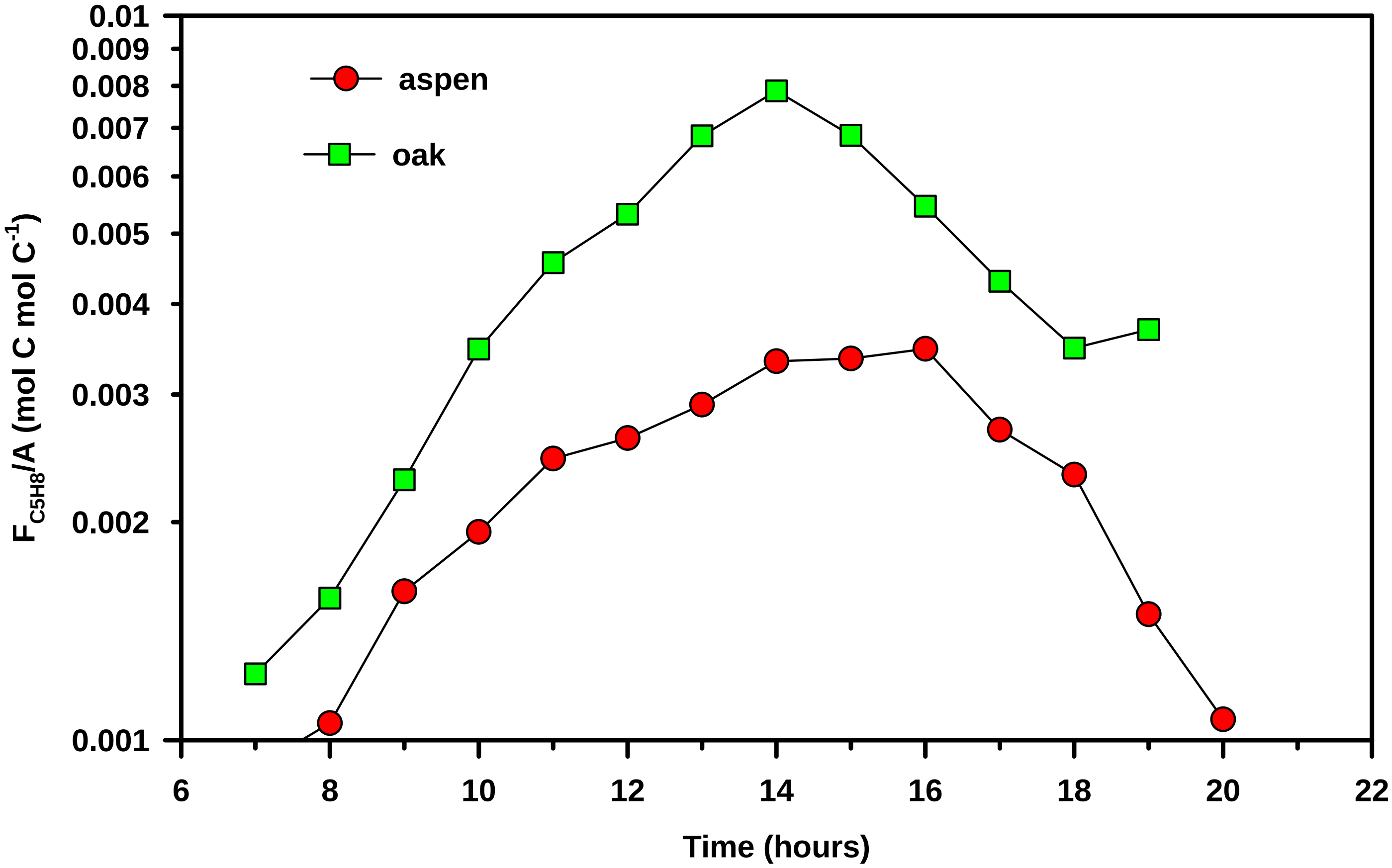
Baldocchi et al 1999 JAM

Canopy Isoprene Emission and Diffuse Radiation

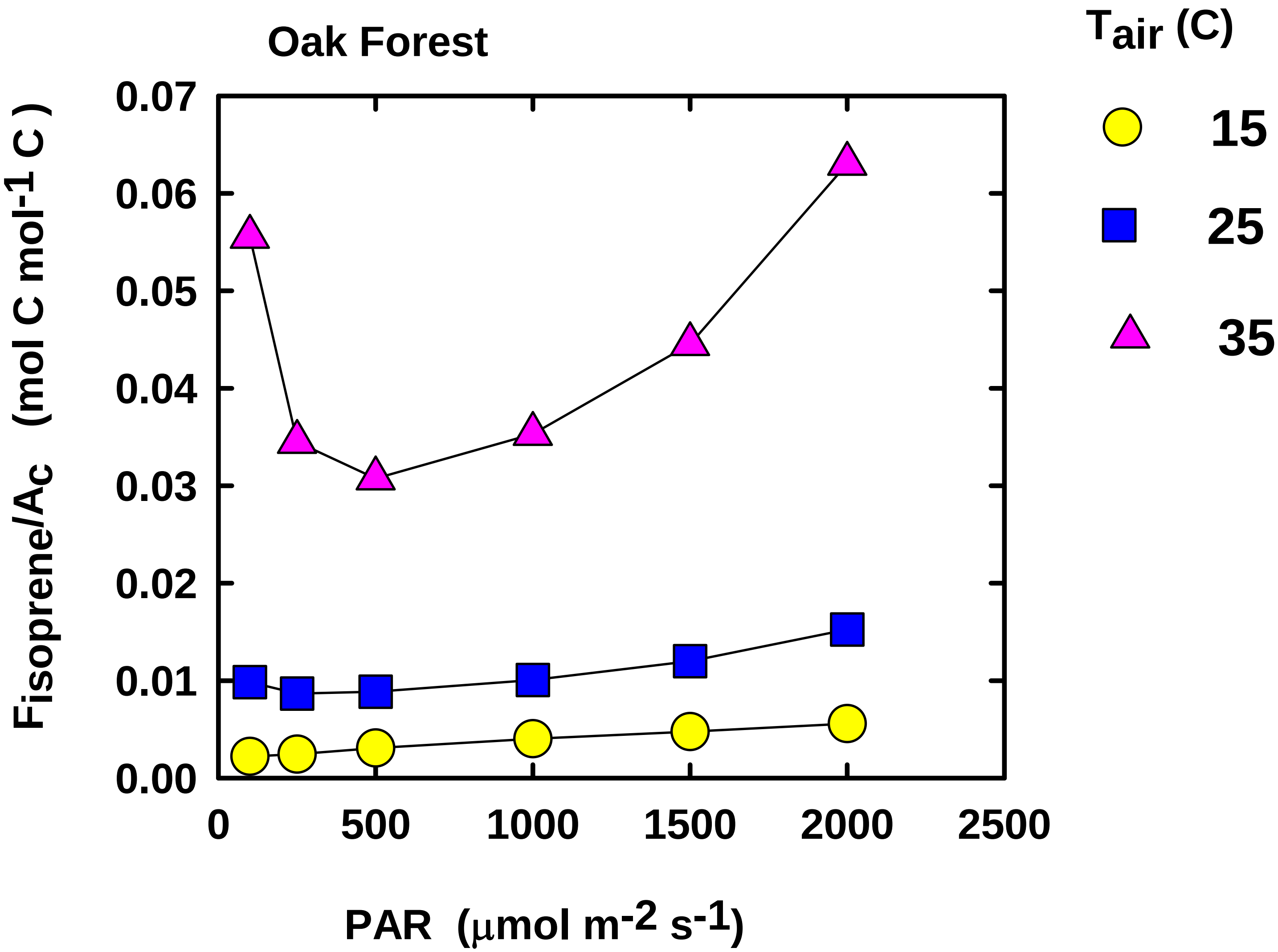



Ta=15 C
20 C
25 C
30 C
35 C
Aspen
isoprene emission (nmol m^{-2} s^{-1})
0
5
10
15
20
25
30
0
500
1000
1500
2000
2500
Q_p (μmol m^{-2} s^{-1})

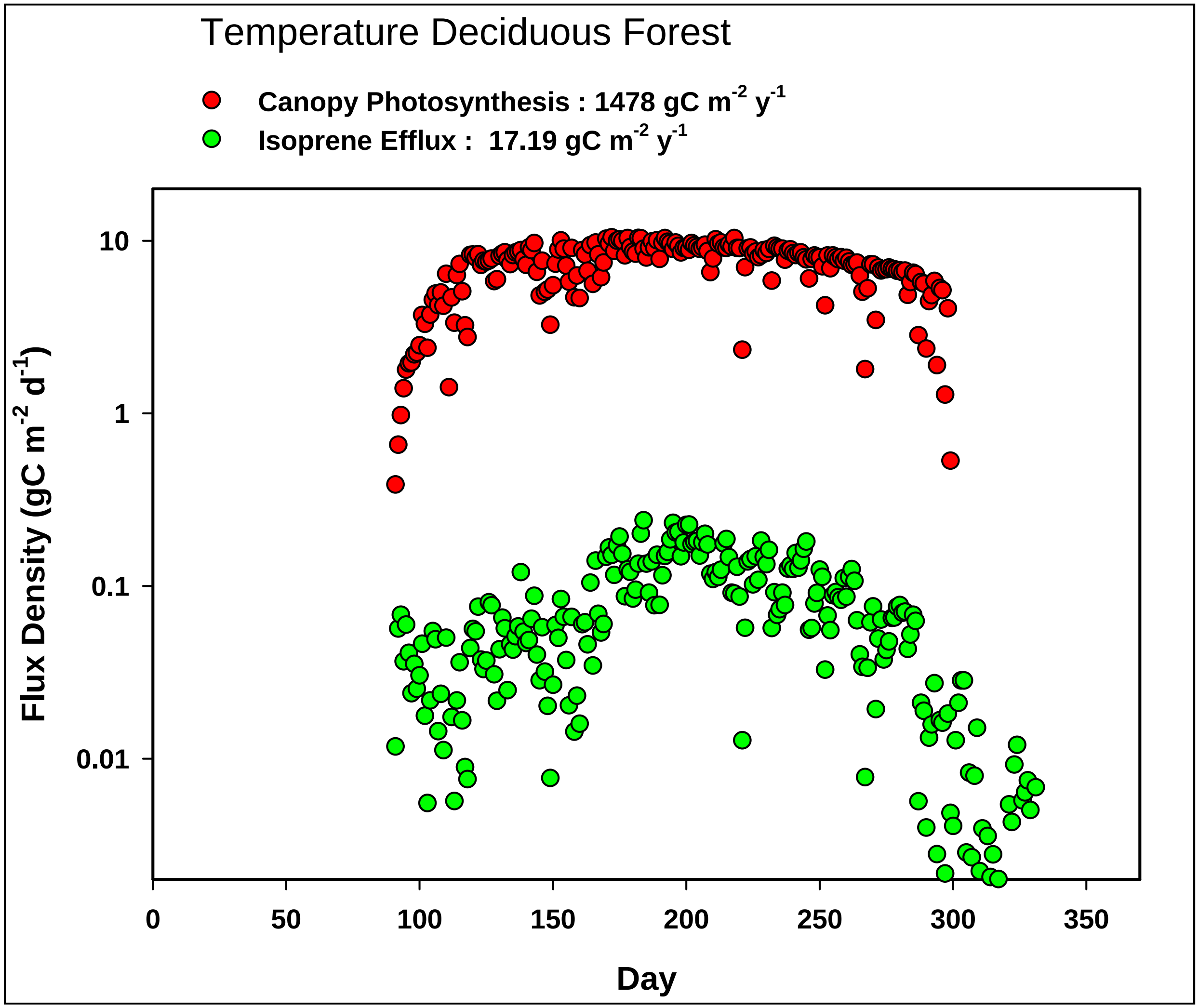
Diurnal Pattern of Photosynthesis and F_I



Fraction of Assimilated C lost by Hydrocarbon emission is a function of T



Annual C budgets



Niinemets Model, adapted by Arneth et al.

The supply of DMAPP for isoprene synthesis
and isoprene synthase activity exert the primary control on production (Niinemets et al., 1999).

DMAPP levels are affected by the photosynthetic electron transport rate, which supplies the required ATP and NADPH for carbon reduction from CO2 to isoprene.

Two major assumptions underlie this Approach:

(i) a certain fraction of electrons is available for isoprene synthesis

(ii) the competitive metabolic strength of isoprene synthesis pathway is proportional to the total activity of isoprene synthase in the leaves.

Niinemets Model, adapted by Arneth et al.

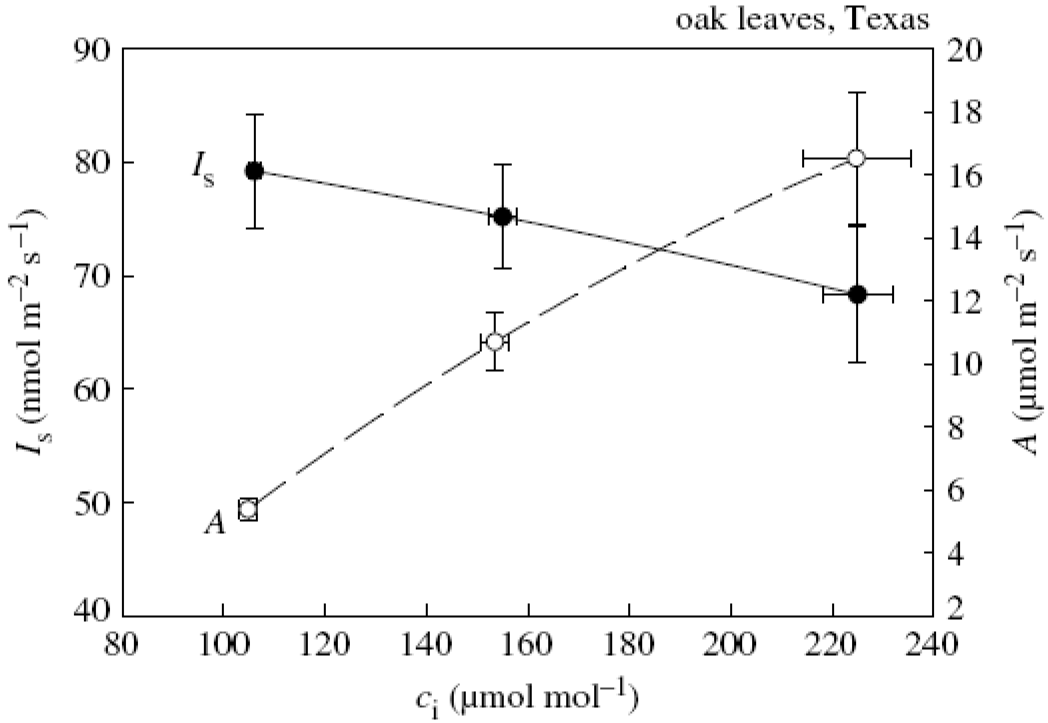
$$I = \varepsilon J \alpha$$

$$\alpha = \frac{C_i - \Gamma_*}{6(4.67C_i + 9.330\Gamma_*)}$$

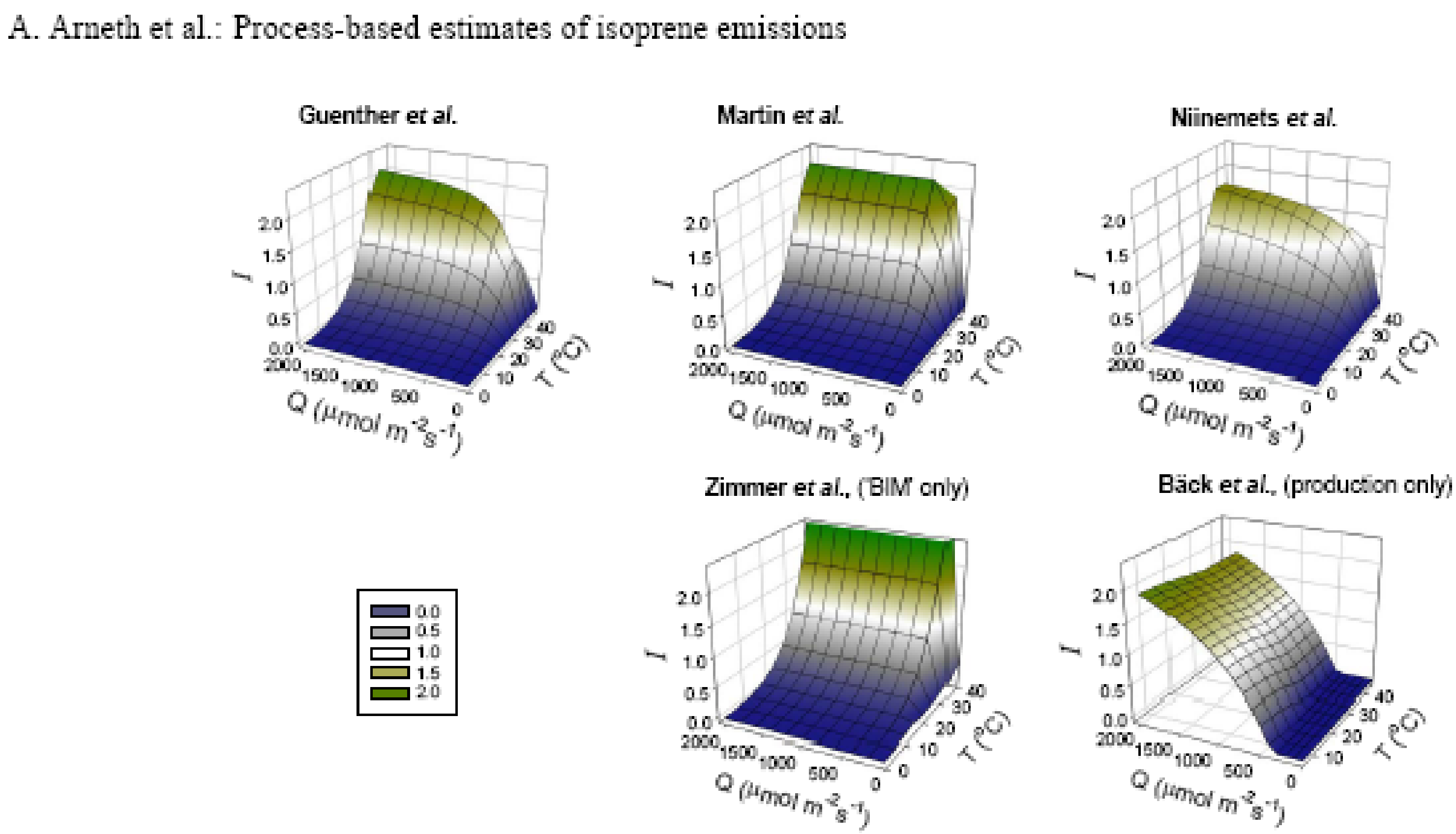
ε is fraction of electrons for Isoprene production
J is electron transport rate
Ci is internal CO2
Γ* is CO2 compensation point

Isoprene Emissions Decreases with CO_2 And is a function of CO2 Exposure

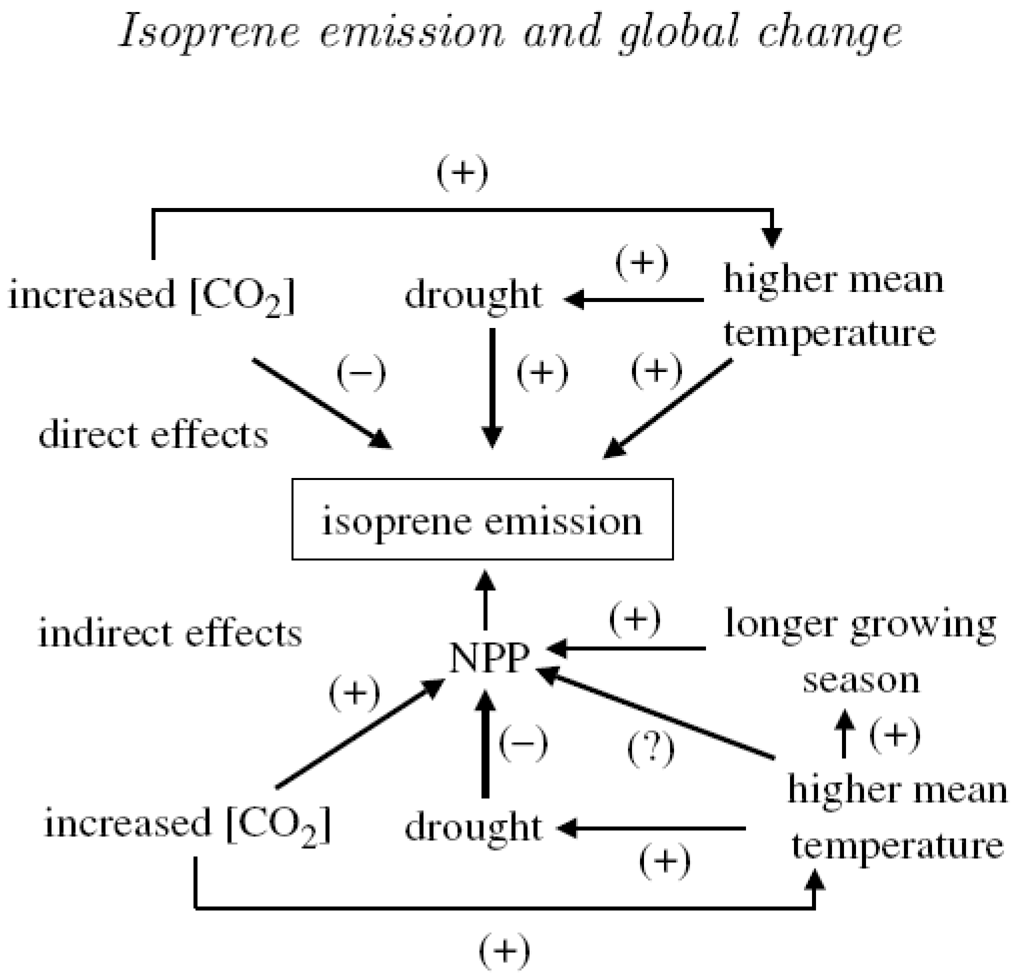
R. K. Monson et al.



Model Hierarchy Testing

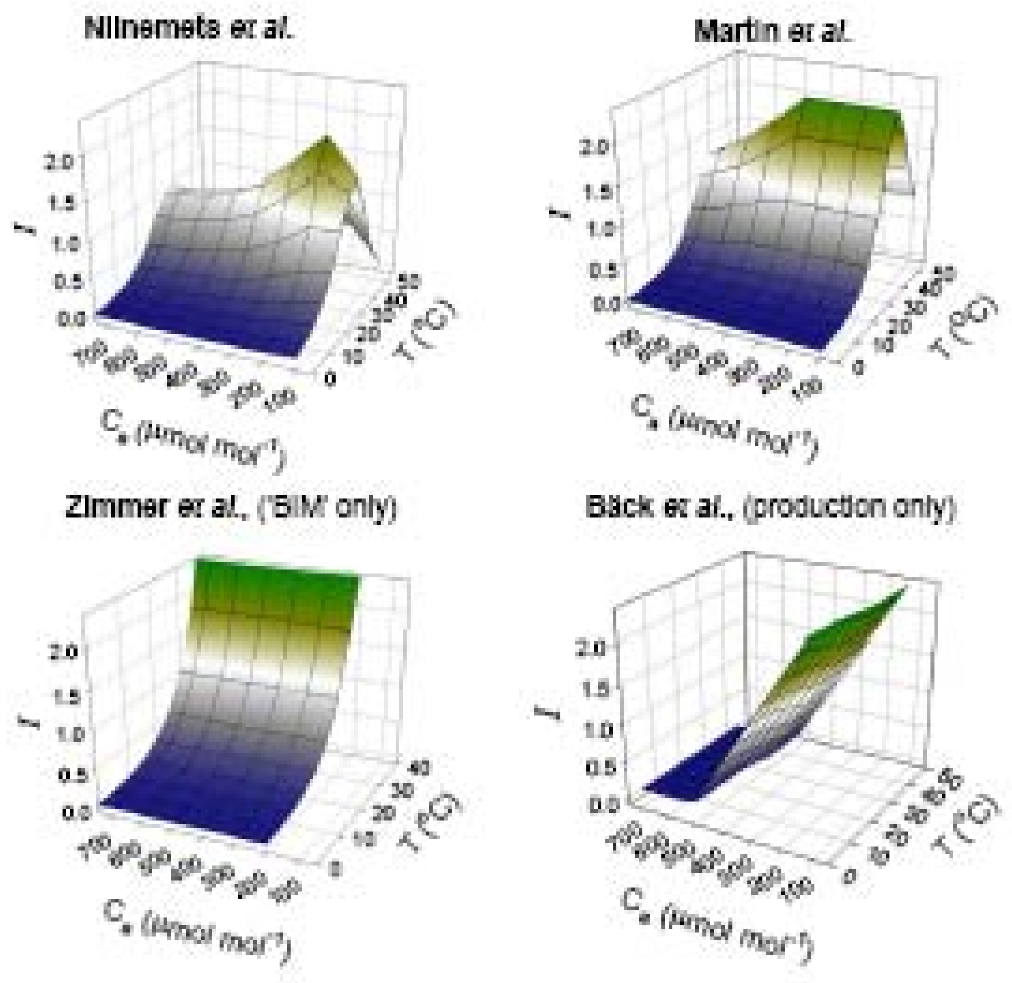


Arneth et al. 2004 ACP

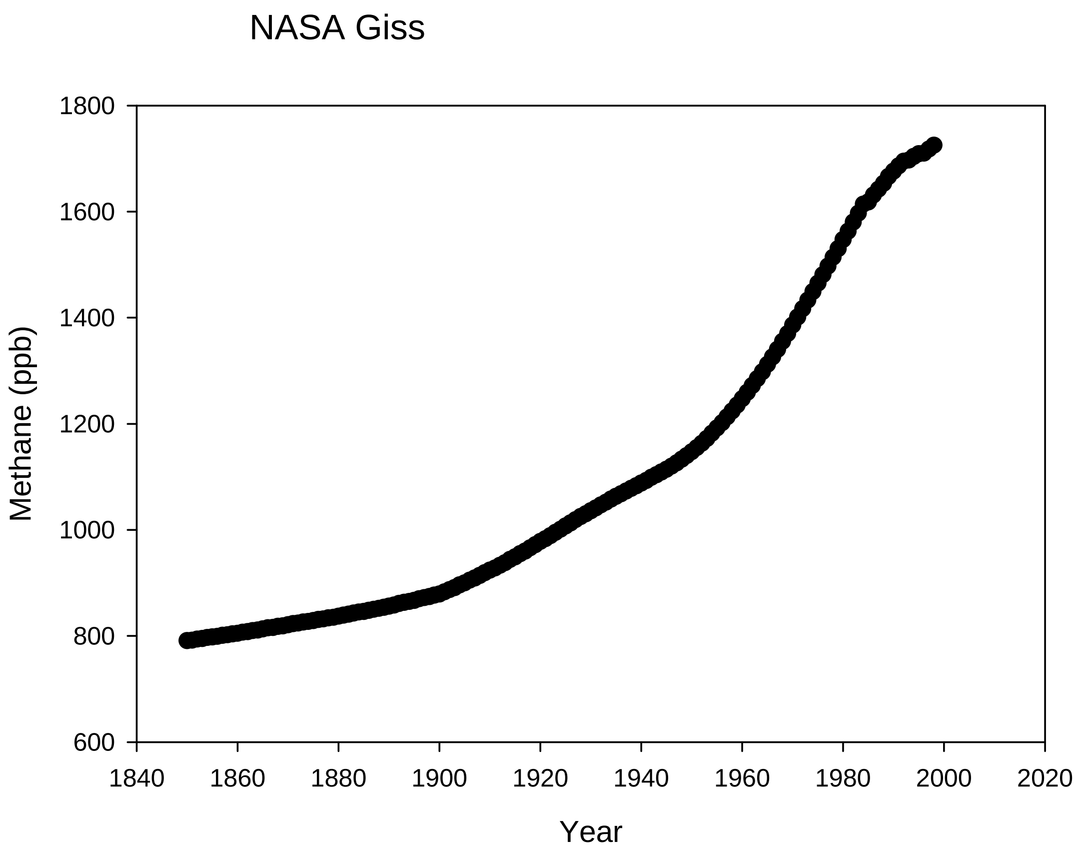


Monson et al 2007

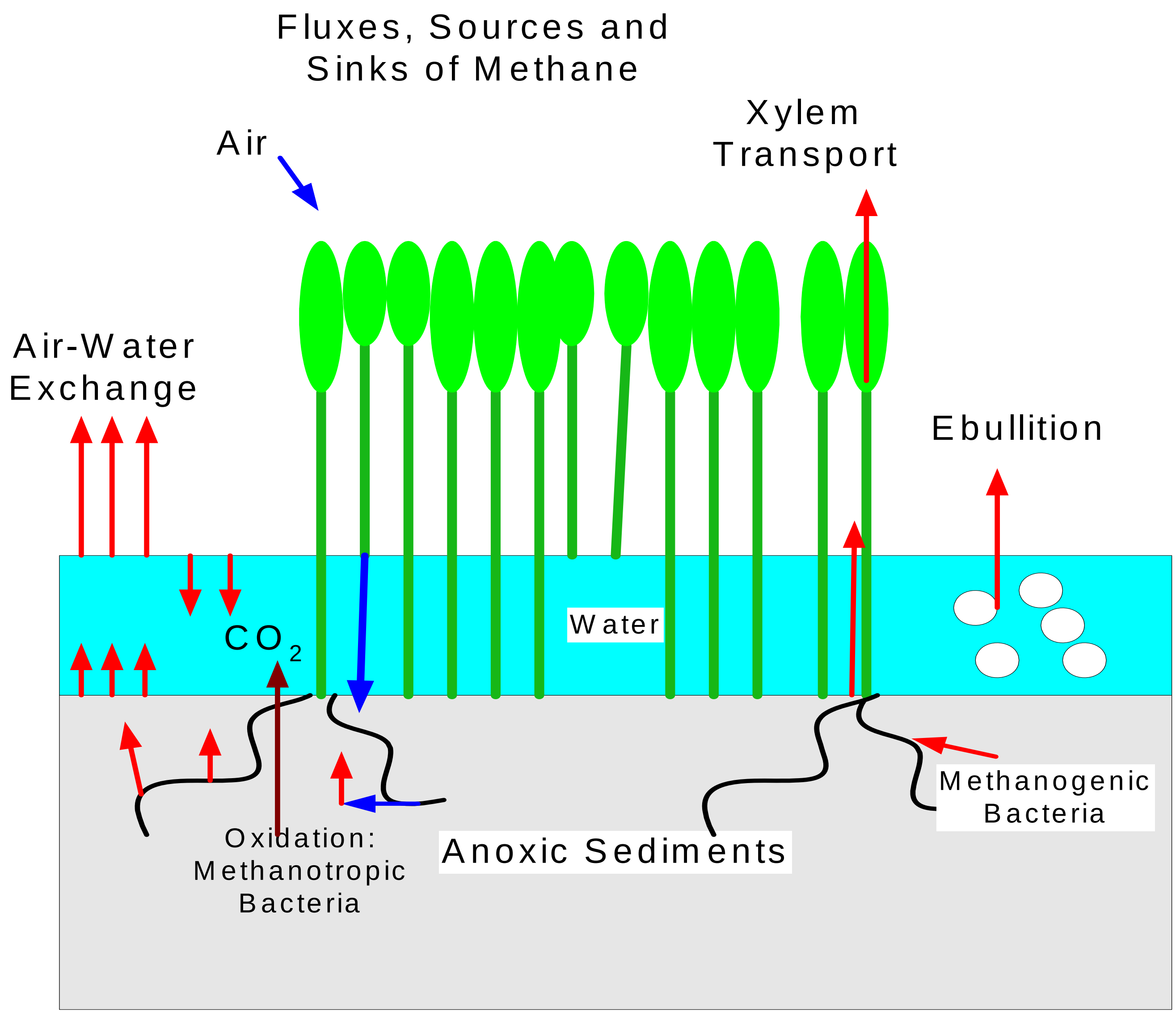
Isoprene Emissions with T and CO2



Contemporary Record in Methane, CH_4

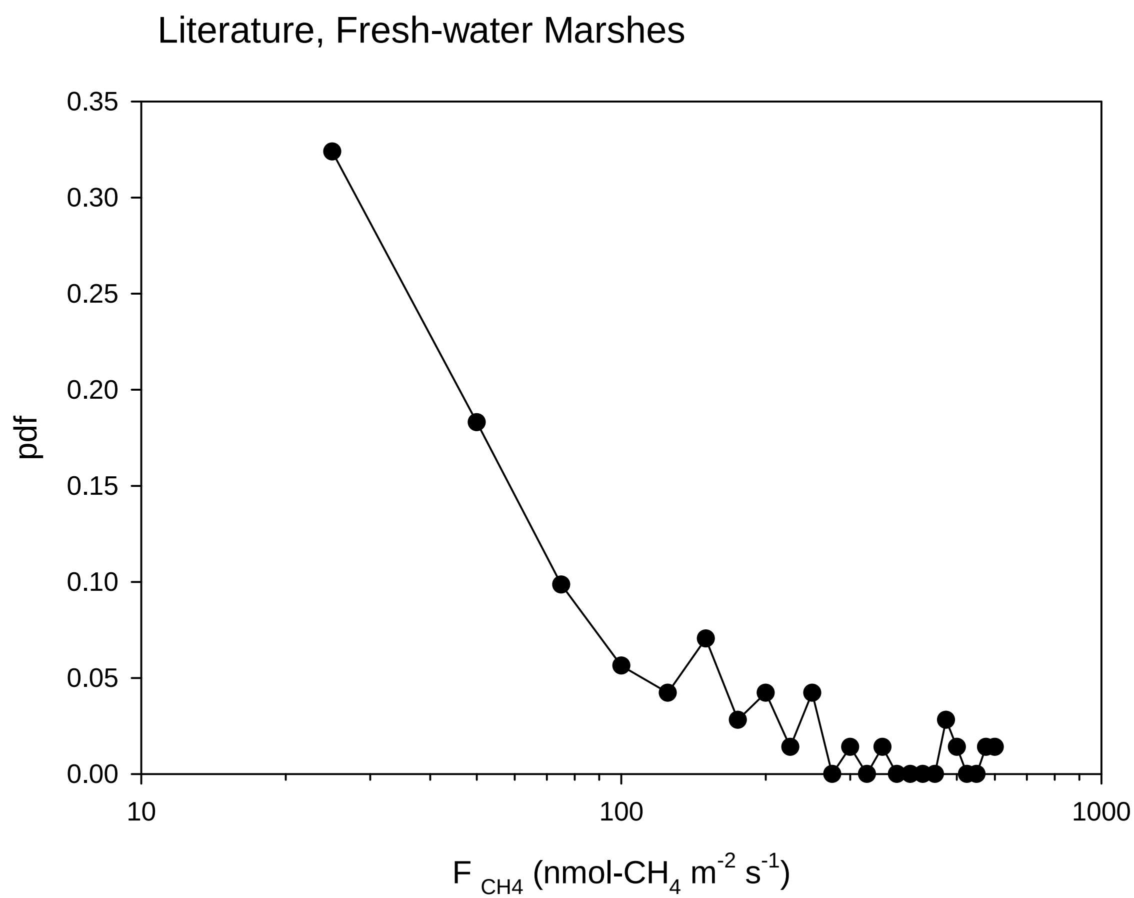


- Sources: fermentation by methanogenic archaea in anaerobic environments
  - Cows
  - Termites
  - Rice
  - Wetlands
- Sinks
  - Oxidation by OH by aerobic soils


Fluxes, Sources and Sinks of Methane
Air
Xylem Transport
Air-Water Exchange
Ebullition
CO_2
Water
Oxidation: Methanotropic Bacteria
Anoxic Sediments
Methanogenic Bacteria

Histogram of Published Methane Fluxes

50% of Fluxes < 32 nmol m^{-2} s^{-1}, but fluxes up to 600 nmol m^{-2} s^{-1} are possible



Methane Production is limited by the presence of alternative electron acceptors

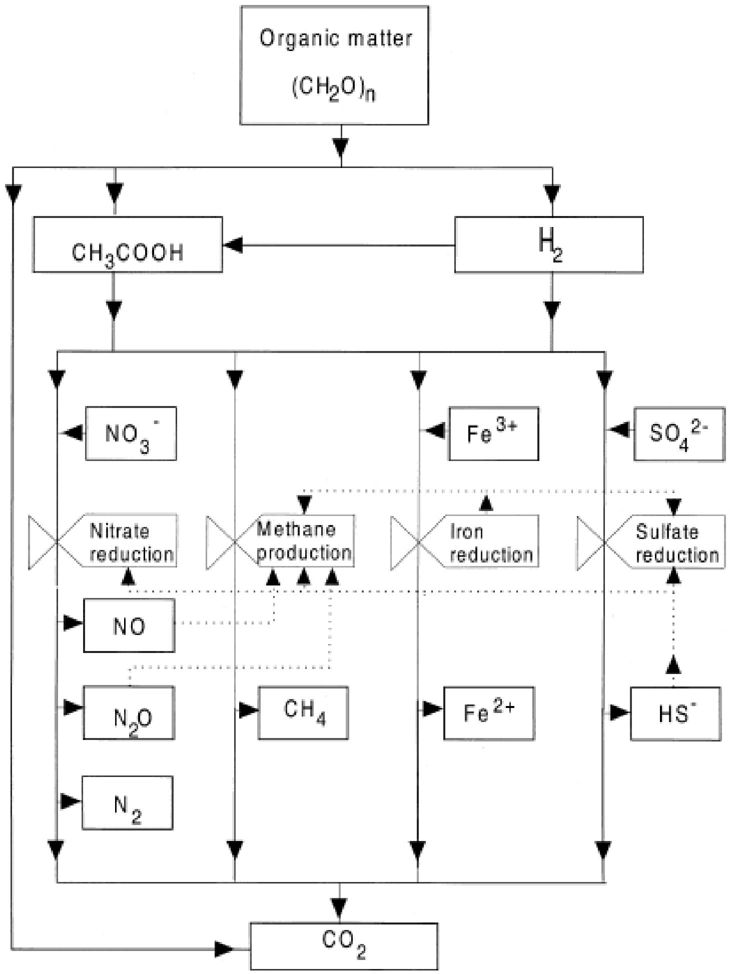
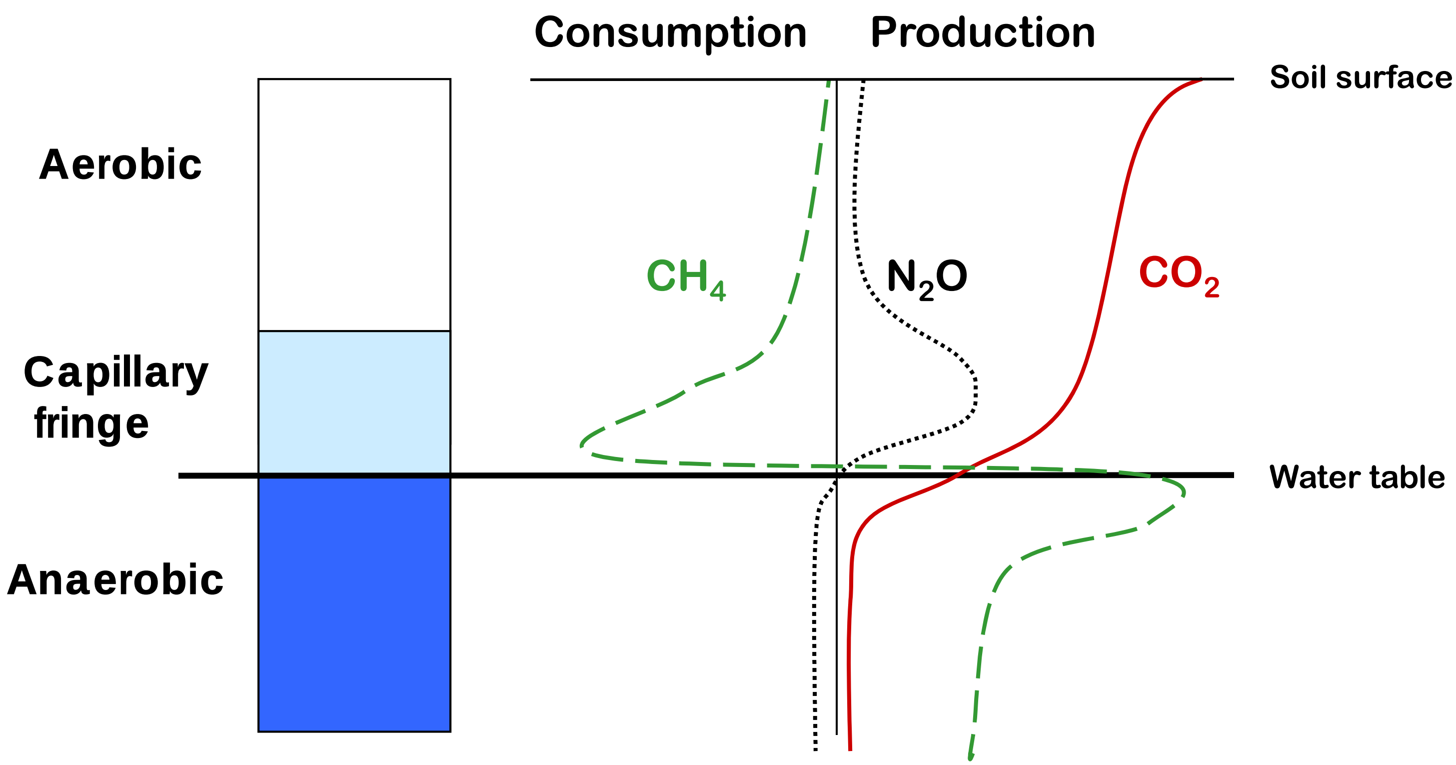


Fig. 1. Schematic representation of the interactions accounted for in the model. Lines indicate compounds flows and dashes indicate inhibitory effects. Chemolithotrophic reactions are not indicated separately in this scheme.

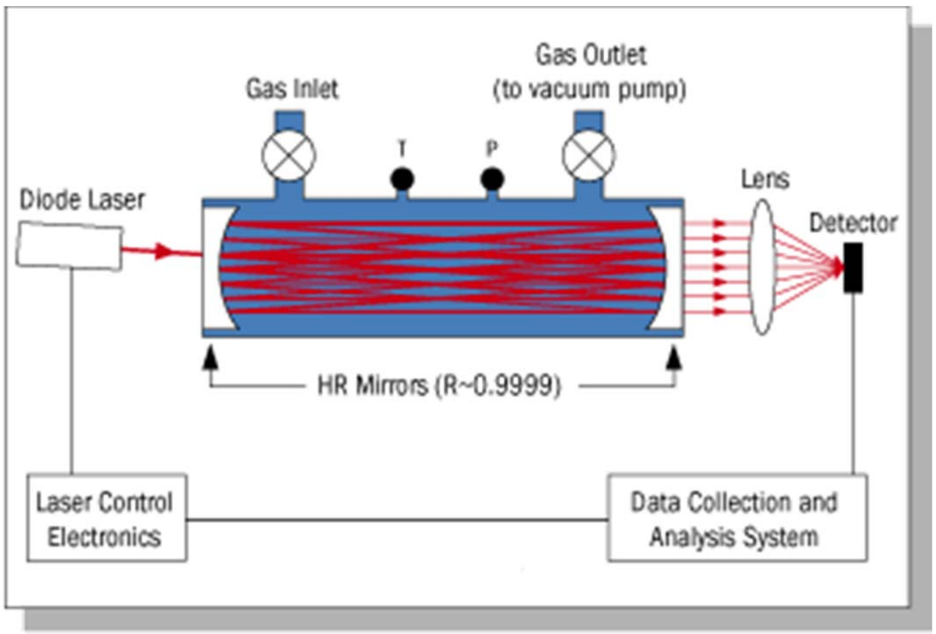
Van Bodegom and Scholten, 2001 Geochemica Cosmochemica

Soil profile

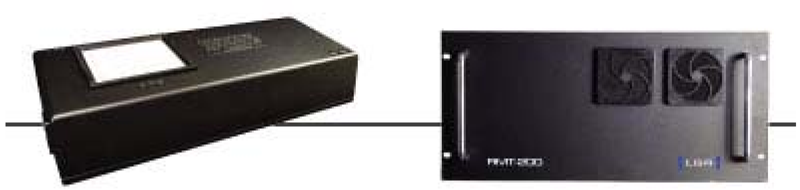


From Annette Friebauer

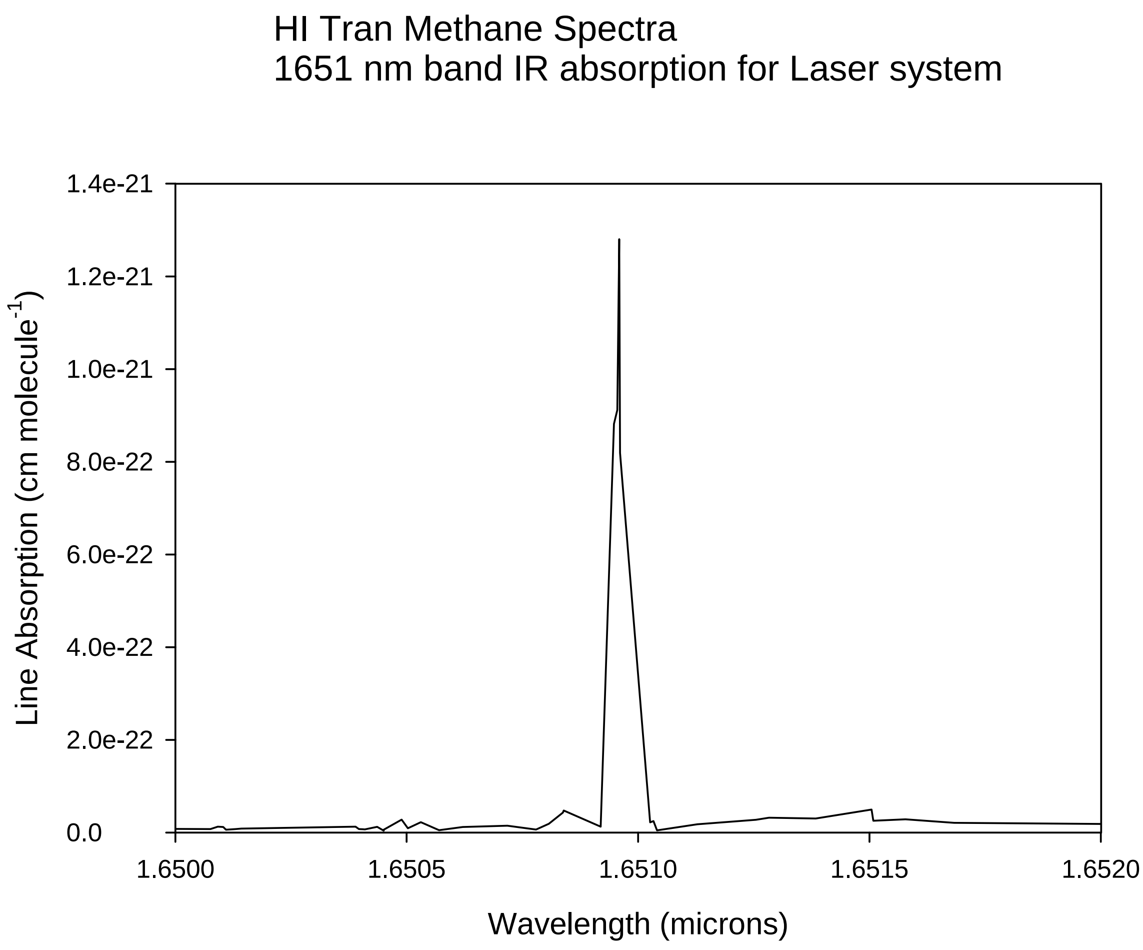
Measuring Methane with Off-Axis Infrared Laser Spectrometer



Closed path
Moderate Cell Volume, 400 cc
Long path length, kilometers
High power Use:
Sensor, 80 W
Pump, 1000 W; 30-50 lpm
Low noise: 1 ppb at 1 Hz
Stable Calibration



Los Gatos Research


HI Tran Methane Spectra
1651 nm band IR absorption for Laser system
Line Absorption (cm molecule-1)
1.4e-21
1.2e-21
1.0e-21
8.0e-22
6.0e-22
4.0e-22
2.0e-22
0.0
1.6500
1.6505
1.6510
1.6515
1.6520
Wavelength (microns)

Boreal Fen, Finland

86 nmol m^{-2} s^{-1} =
5 mg m^{-2} h^{-1}

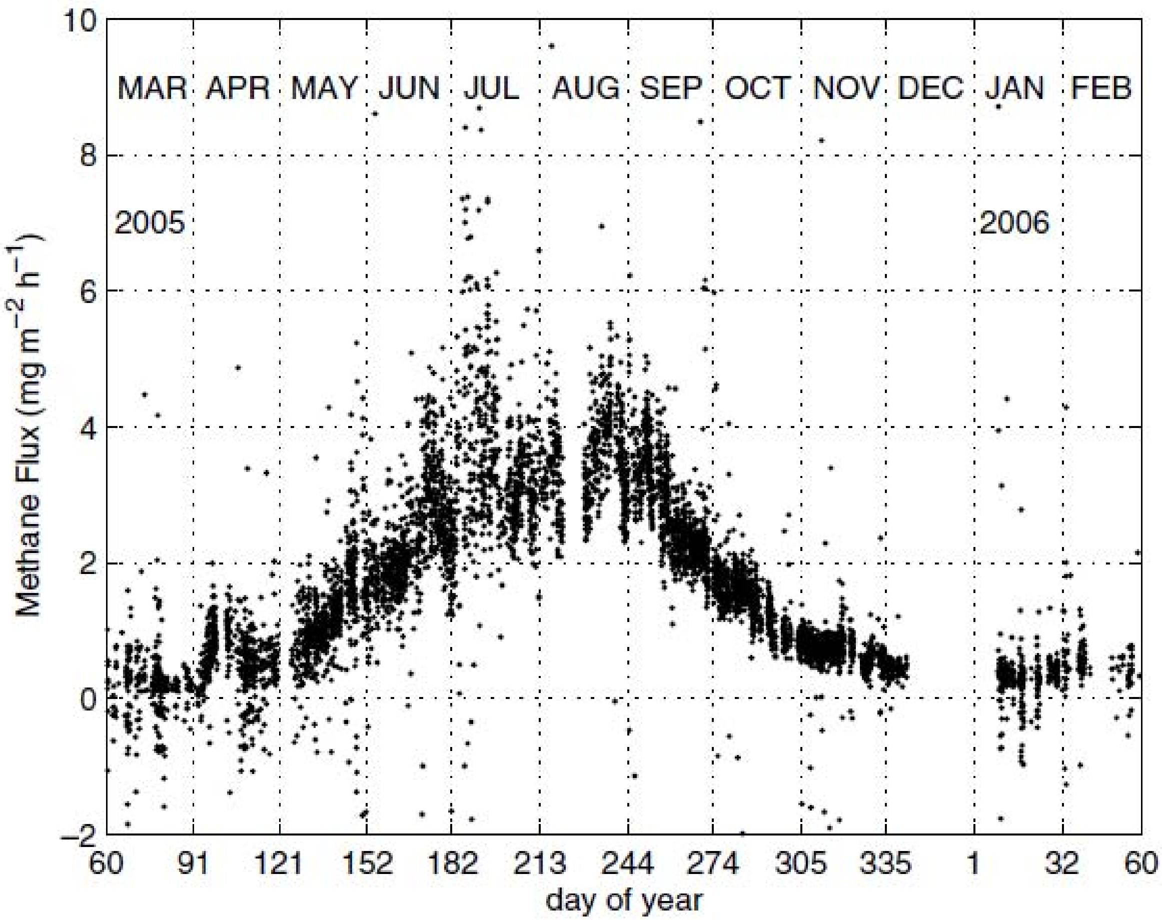
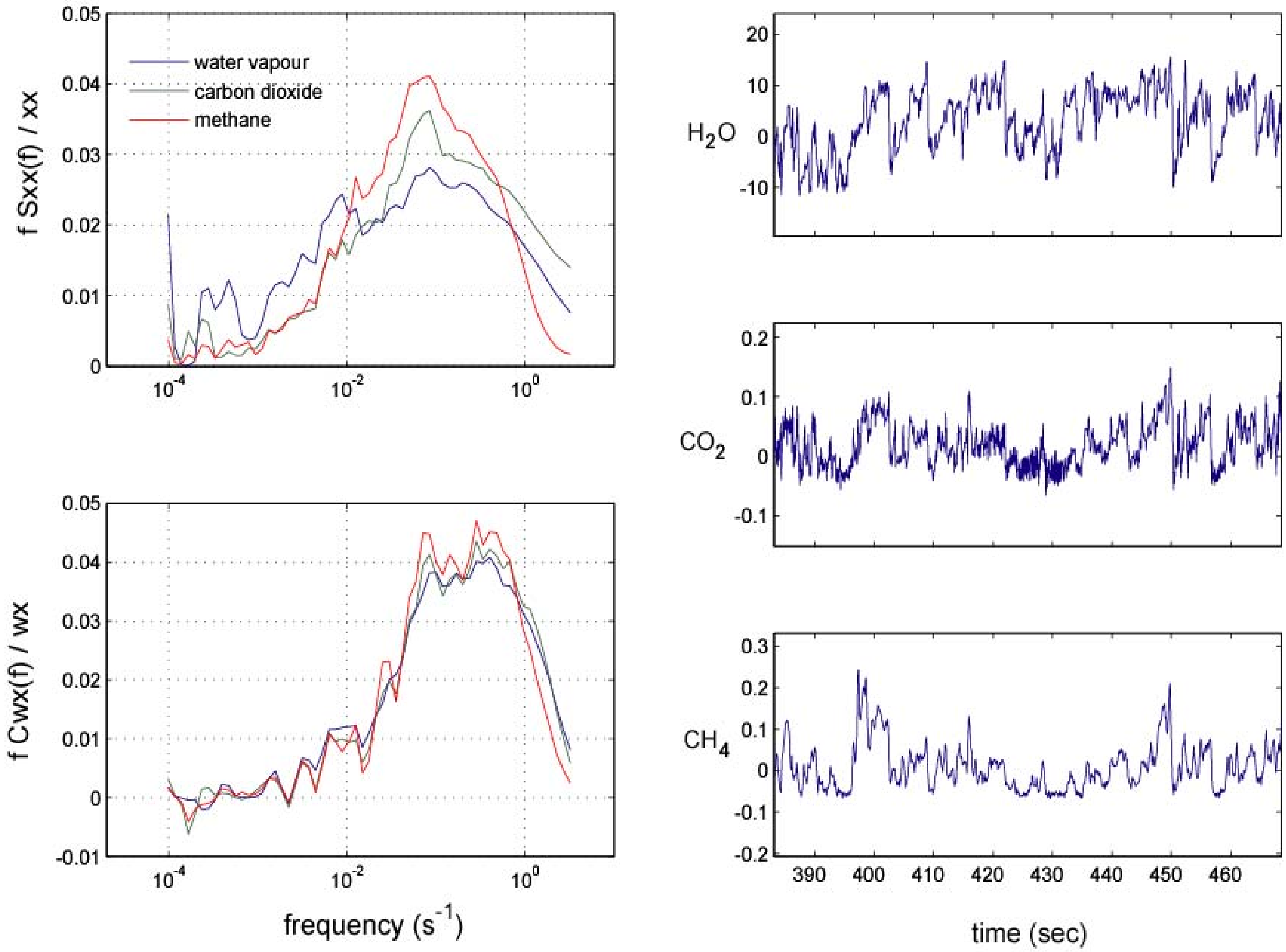


Fig. 3. Annual cycle of measured half-hourly methane fluxes. Positive sign indicates upward flux, i.e. emission from the fen.

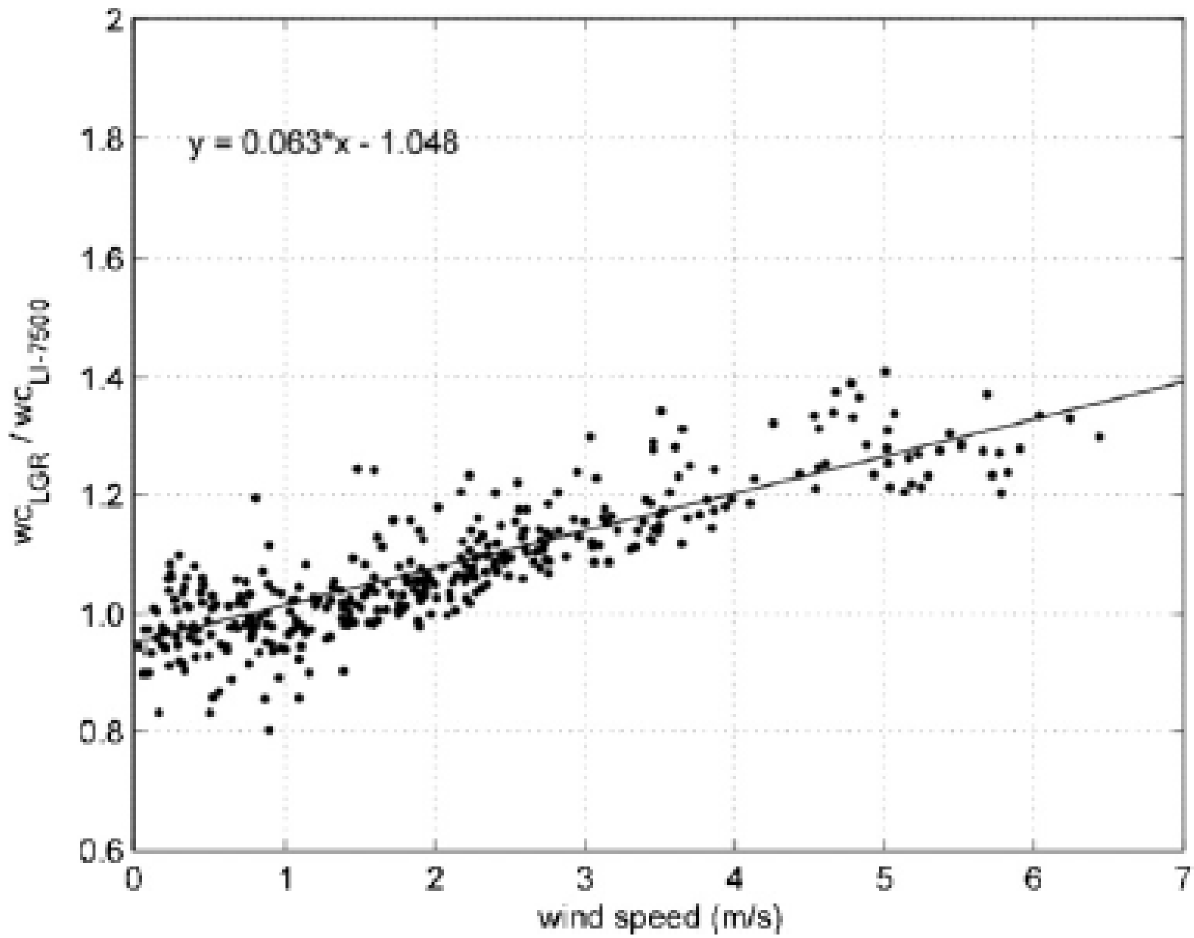
Rinne et al 2007 Tellus

Spectral Performance of Gas Sensors



Detto et al., BLM 2010

Attenuation of Closed Path Methane Flux with Wind Speed

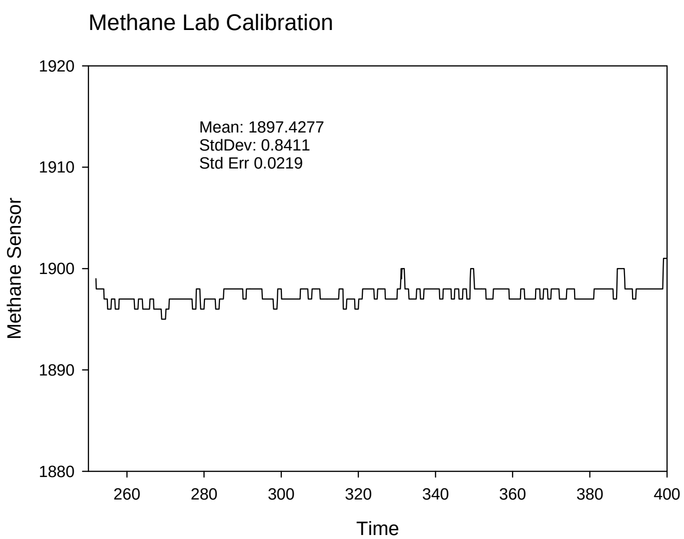


Detto et al. 2011 AgForMet

Zero-Flux Detection Limit, Detecting Signal from Noise

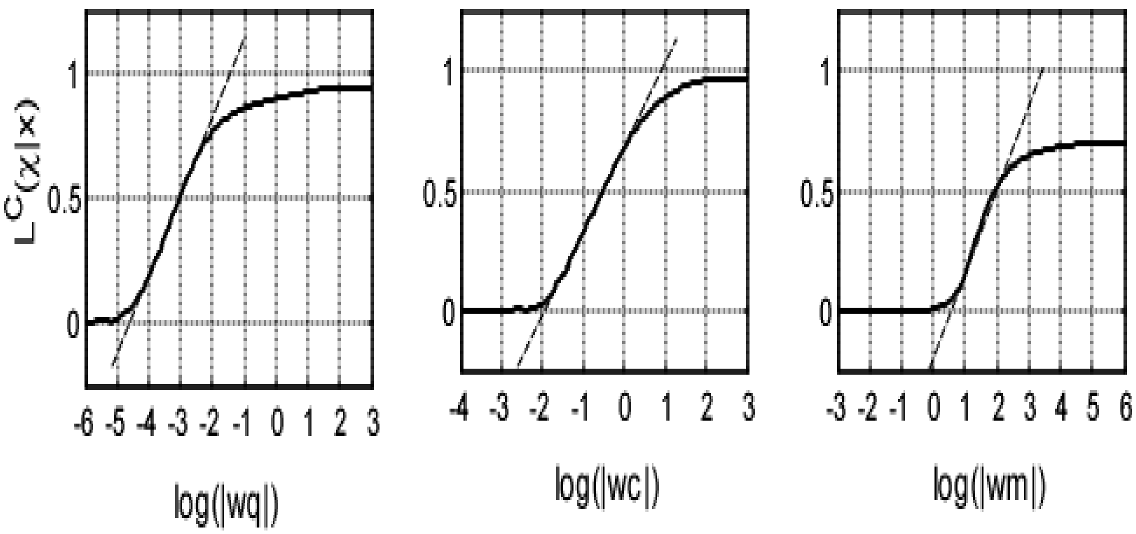
$$F = \overline{w'c'} \approx r_{wc}\sigma_w\sigma_c$$

r_{wc} ~ 0.5
σ_{ch4} ~ 0.84 ppb @ 1 Hz sampling rate
σ_{co2} ~ 0.11 ppm



U* m/s	σ_w m/s	$F_{min,}$ CH_4 nmol m^{-2} s^{-1}	$F_{min,}$ CO_2 µmol m^{-2} s^{-1}
0.1	0.125	2.1	0.275
0.2	0.25	4.2	0.55
0.3	0.375	6.3	0.825
0.4	0.5	8.4	1.1
0.5	0.625	10.5	1.375

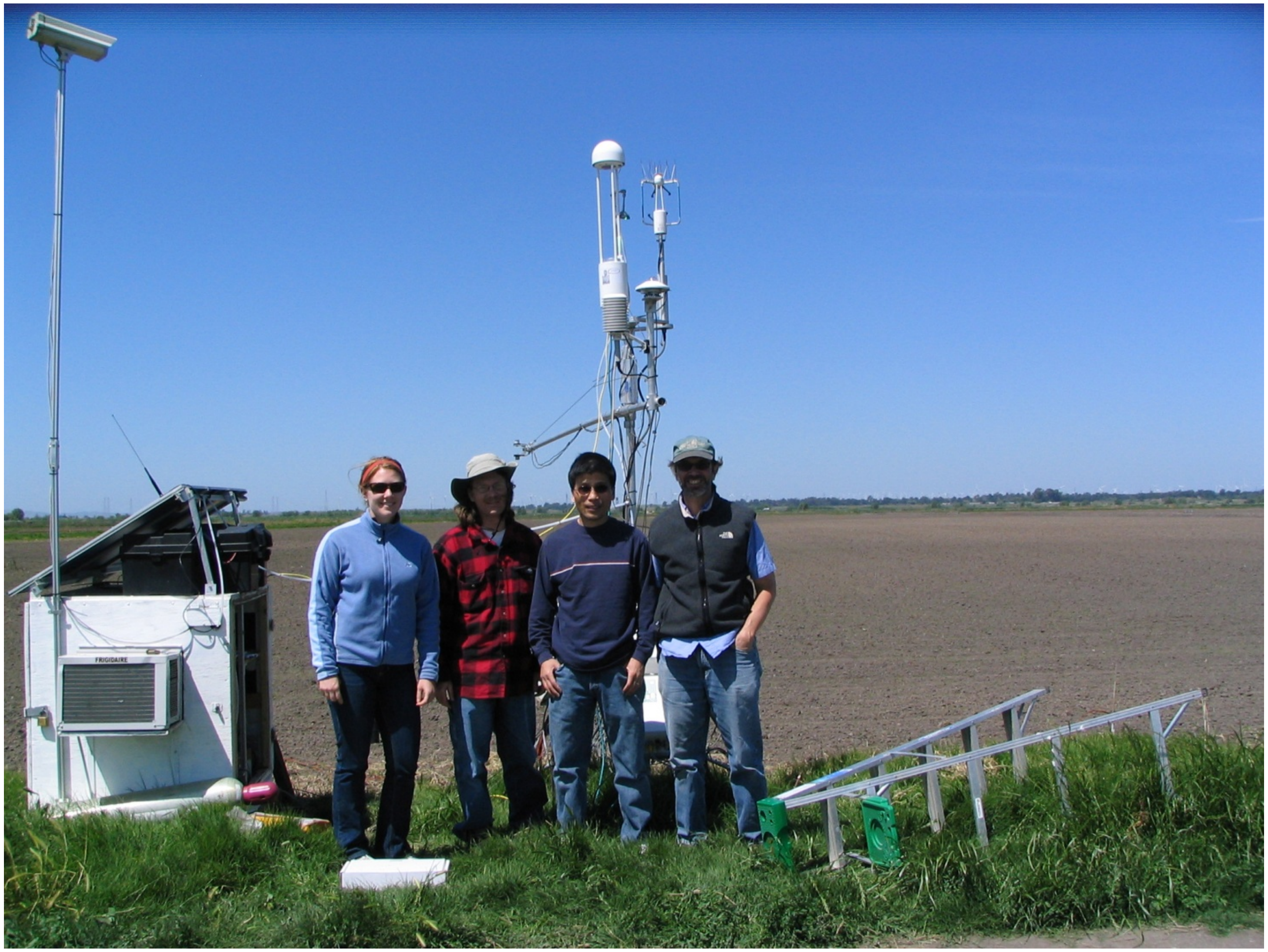
Flux Detection Limit, based on 95% CI that correlation between W and C that is non-zero



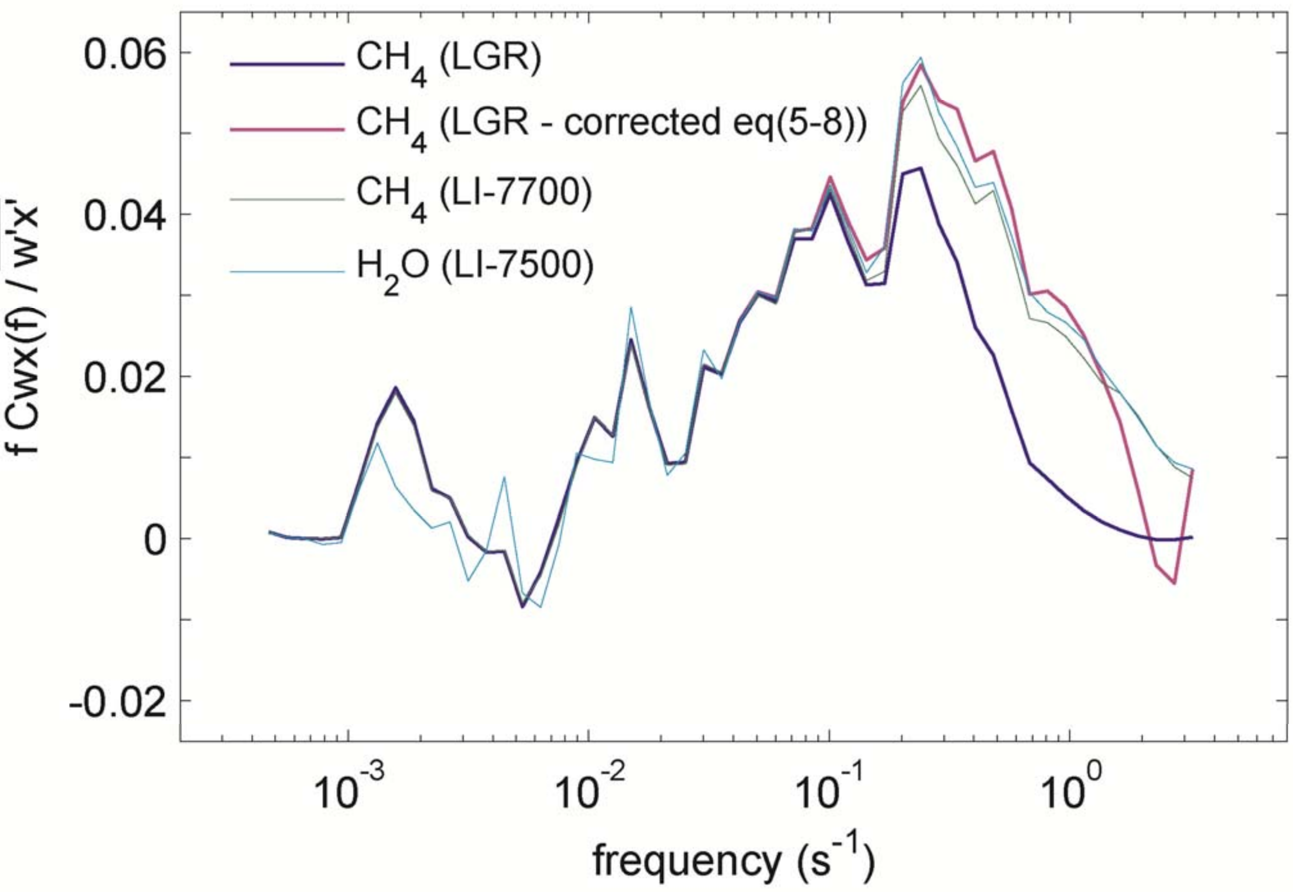
0.035 mmol m^{-2} s^{-1}, 0.31 mmol m^{-2} s^{-1} and 3.78 nmol m^{-2} s^{-1} for water vapour, carbon dioxide and methane flux,

Detto et al, AgForestMet, 2011

New Licor 7700 Open Path Methane Spectrometer: Low Power, NO PUMPS

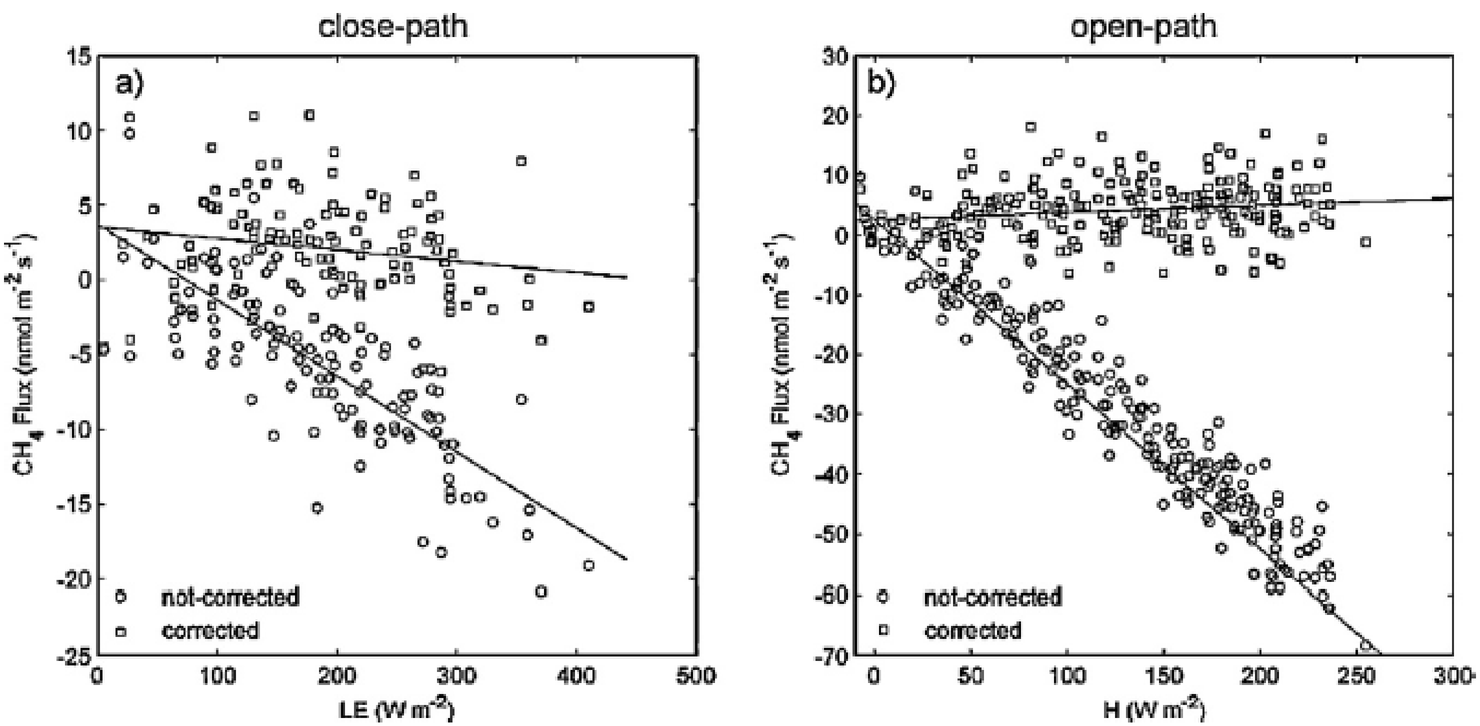


CoSpectra Open Vs Closed Path Methane Sensors



Detto et al. 2011 AgFormet

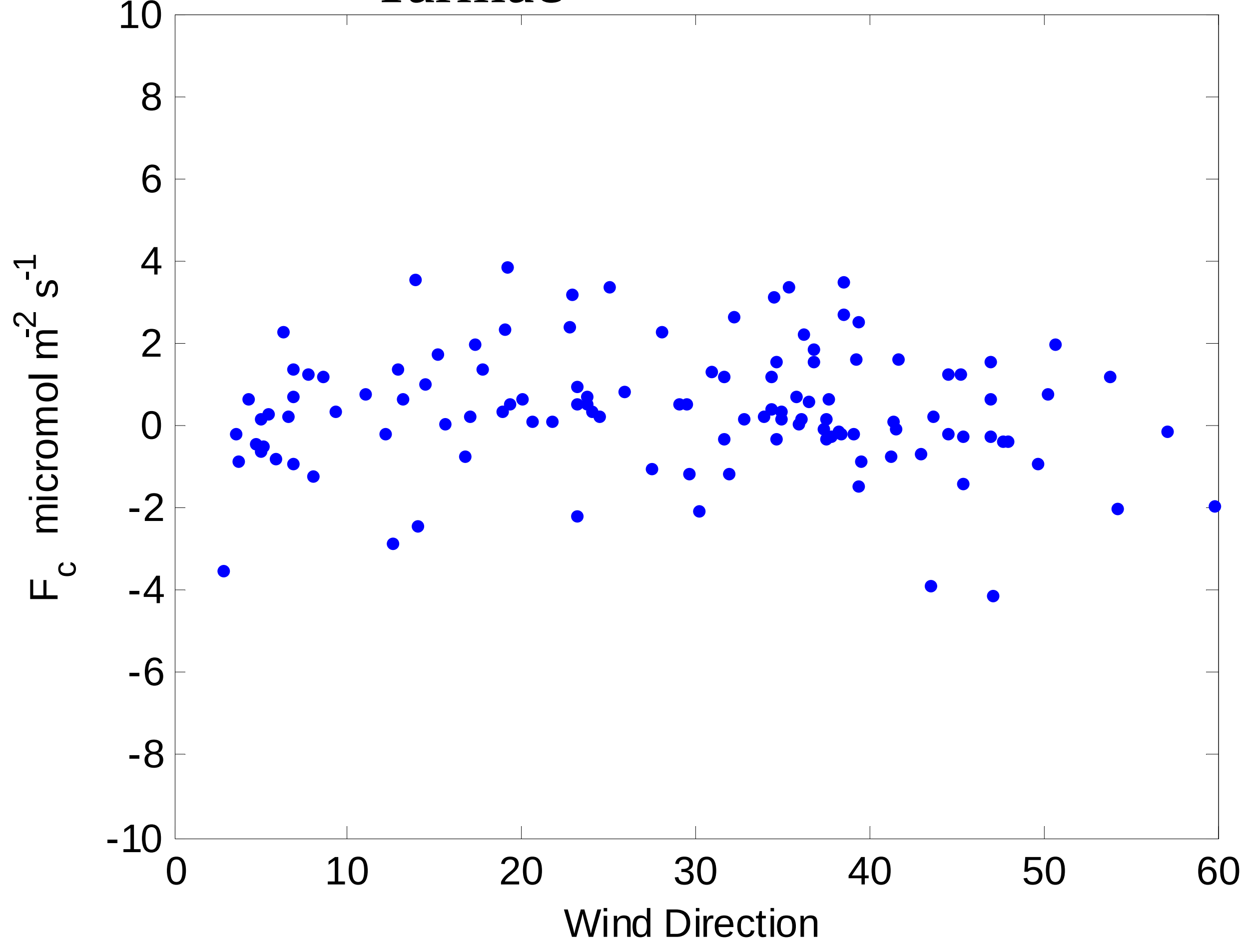
Density Corrections Open Vs Closed Path Methane Sensors



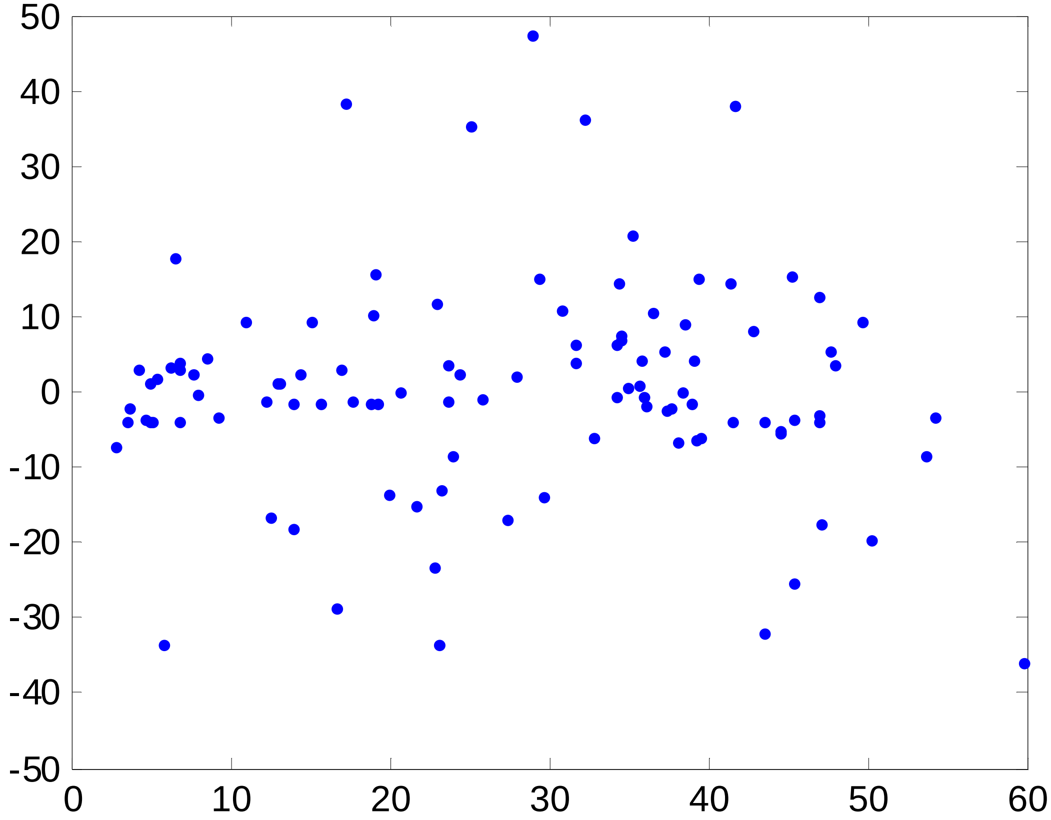
Detto et al. 2011 AgFormet

Testing Density Fluctuation Corrections at Moffatt Field

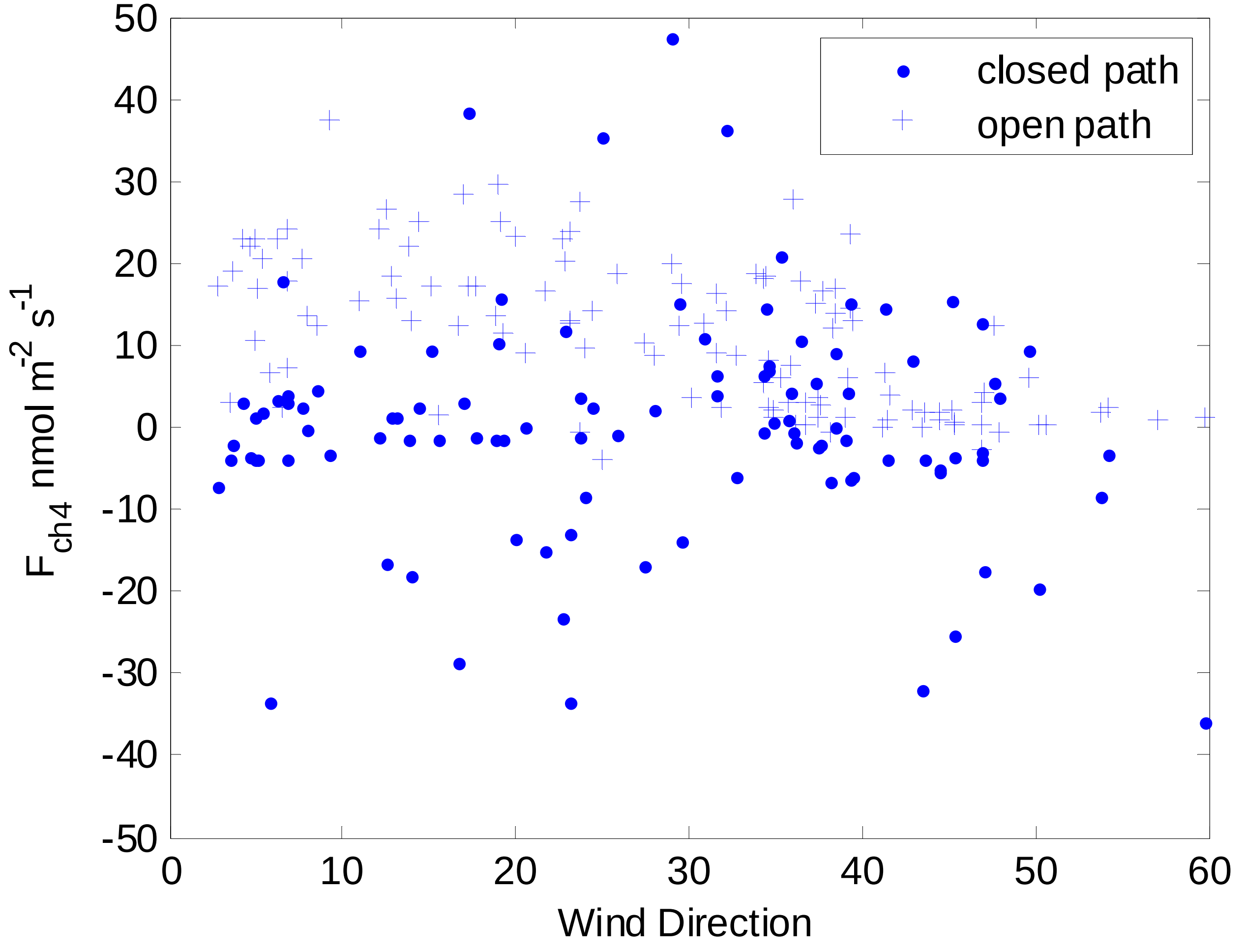
CO2 Flux Over the Tarmac



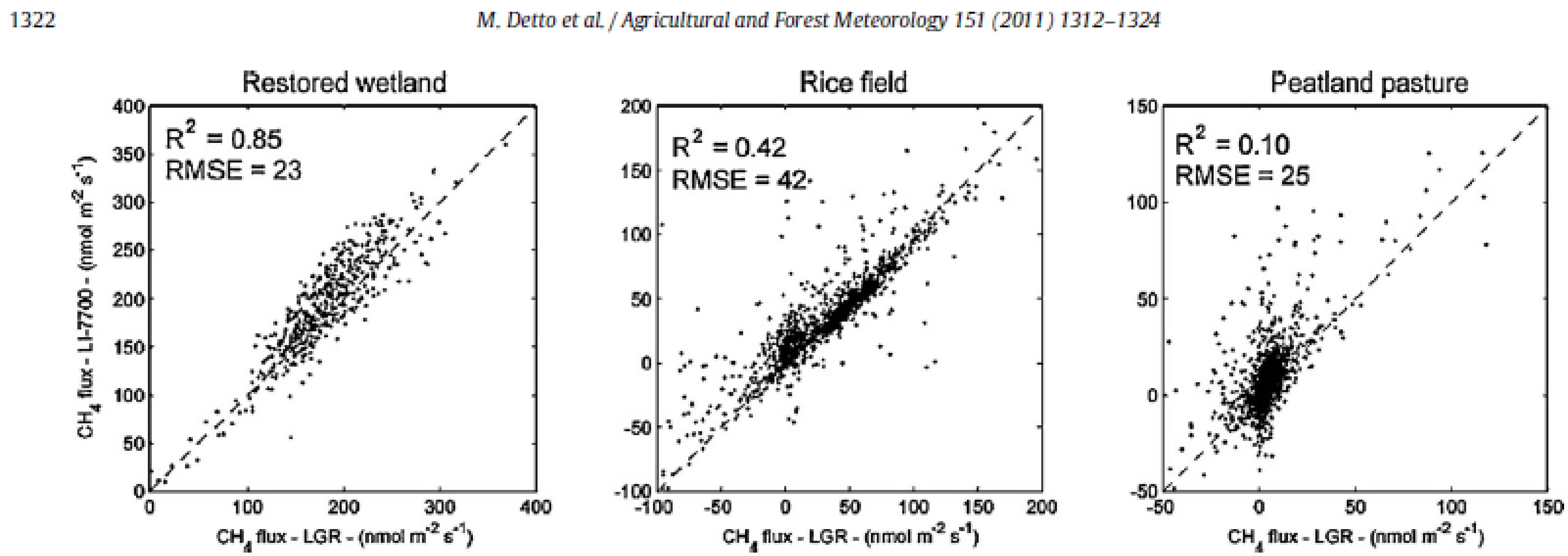
Methane Fluxes over the Tarmac, LGR Closed Path



Methane Fluxes over the Tarmac



Open vs Closed Path Methane Sensor Flux Measurements



Detto et al. 2011 AgFormet

Methane Fluxes Experience Much Seasonality and transcend several Orders of Magnitude

78 WHALEN

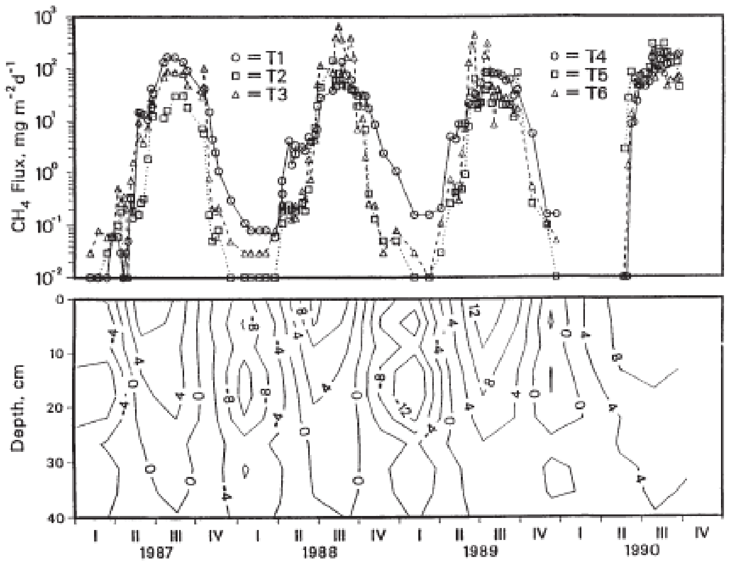
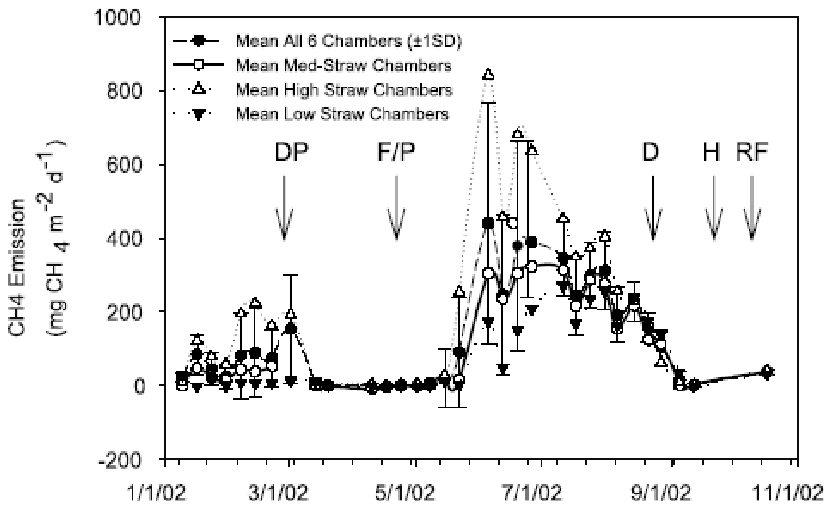


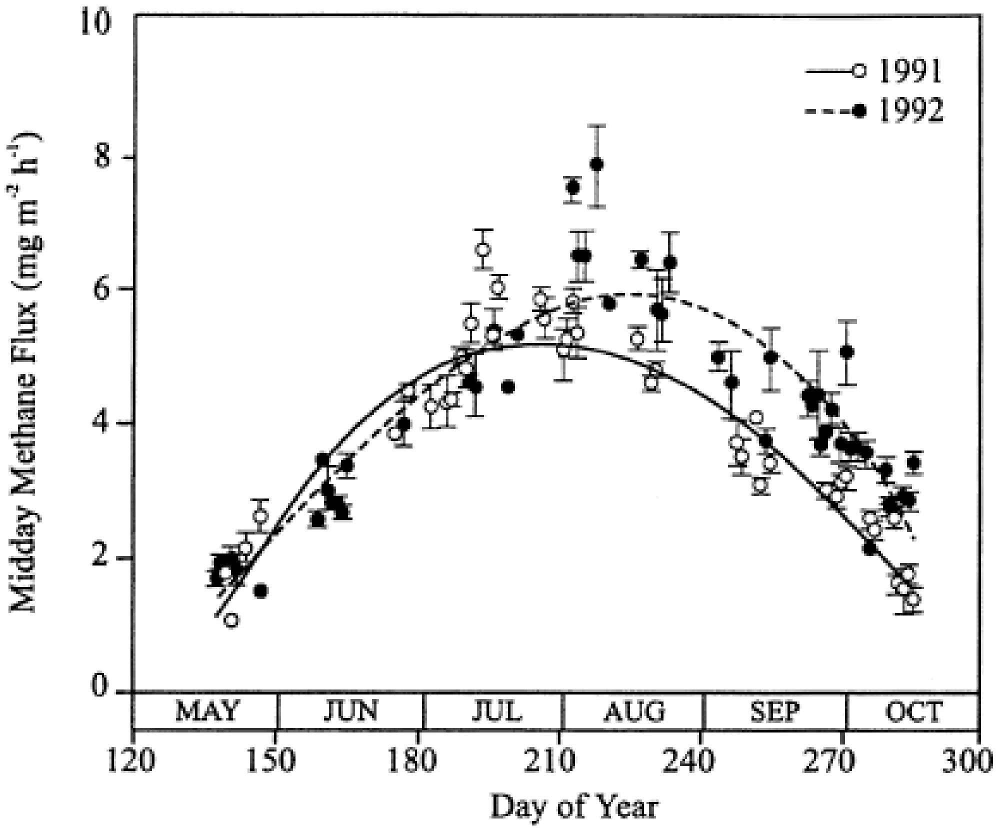
Figure 2. Four-year time series of net CH_4 fluxes to the atmosphere (top) and soil isotherms (bottom) at fixed sites in a sub-arctic Alaskan bog. Flux determinations were made using a static chamber technique. (From Whalen and Reeburgh, 1992, with permission of American Geophysical Union.)



McMillan et al 2007 JGR

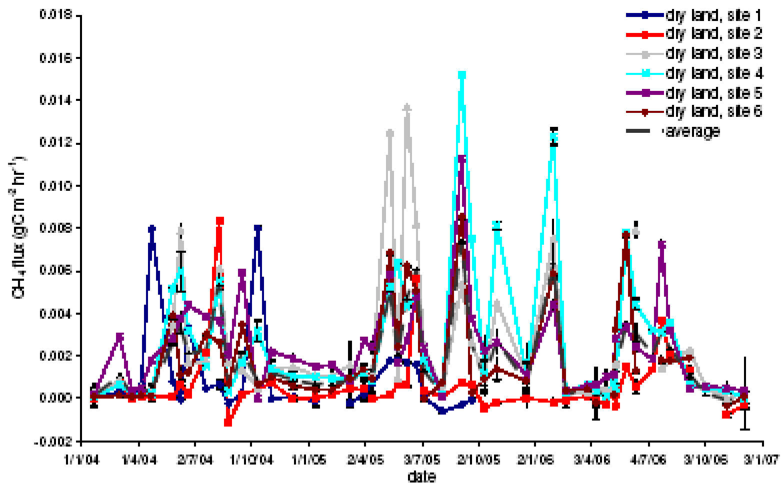
Whalen 2005 Env Eng Sci

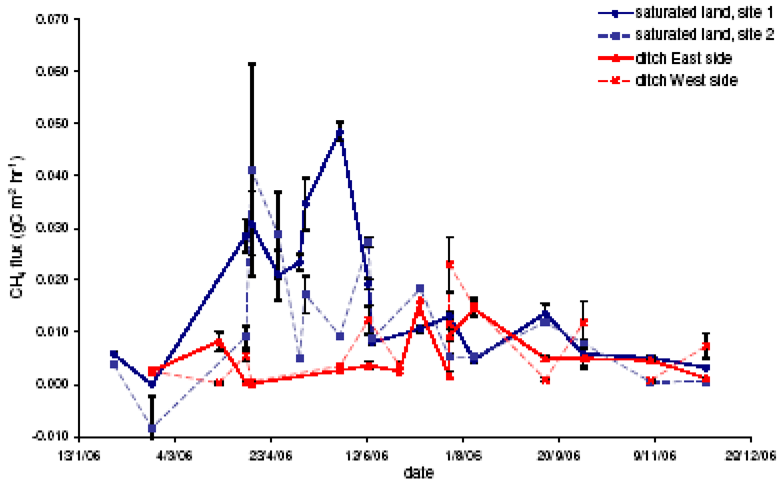
Interannual Variation in Methane Fluxes due to Water Table



Shurpali and Verma, 1998

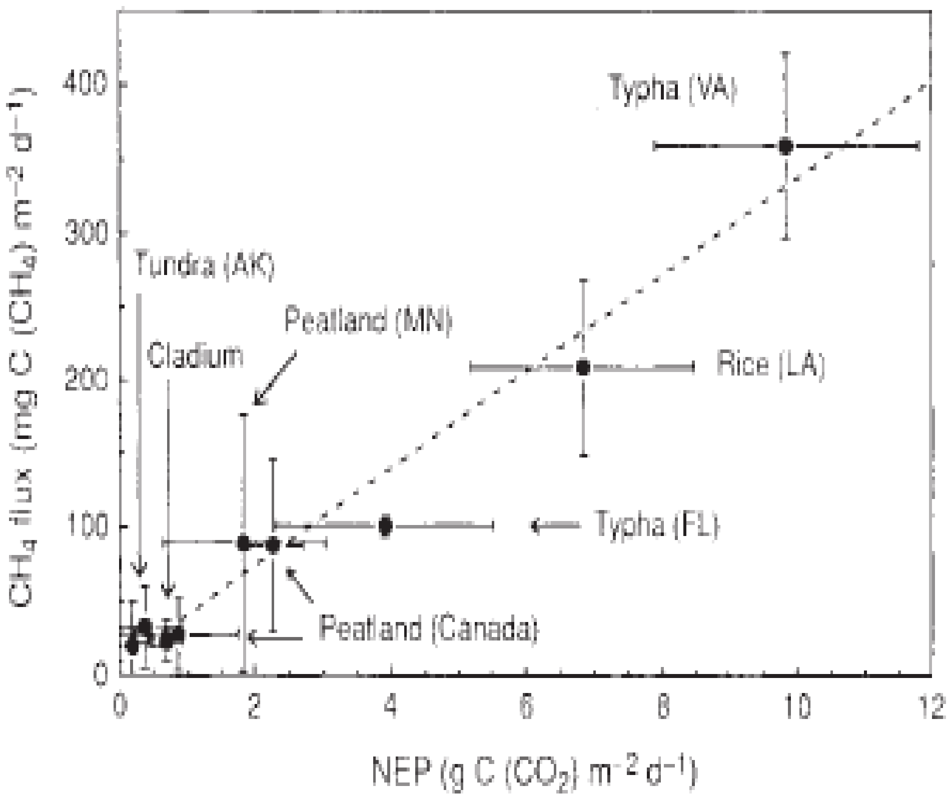
Role of Landscape in Holland





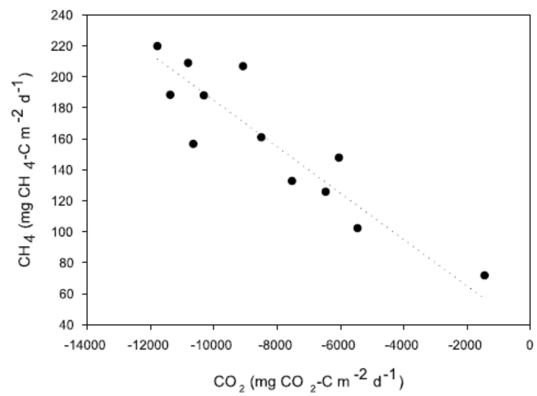
Hendricks et al 2007 Biogeoscience

Methane Efflux Scales with NEP

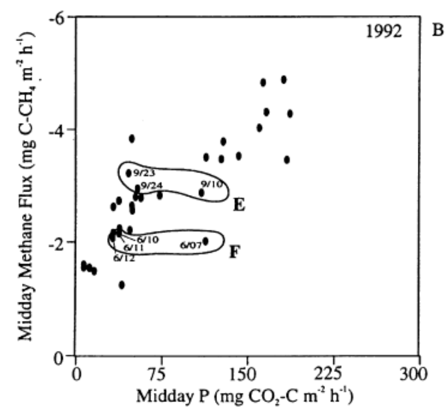


Whiting and Chanton, 1993 Nature

Rice in Ca



McMillan et al 2007 JGR



Shurpali and Verma, 1998

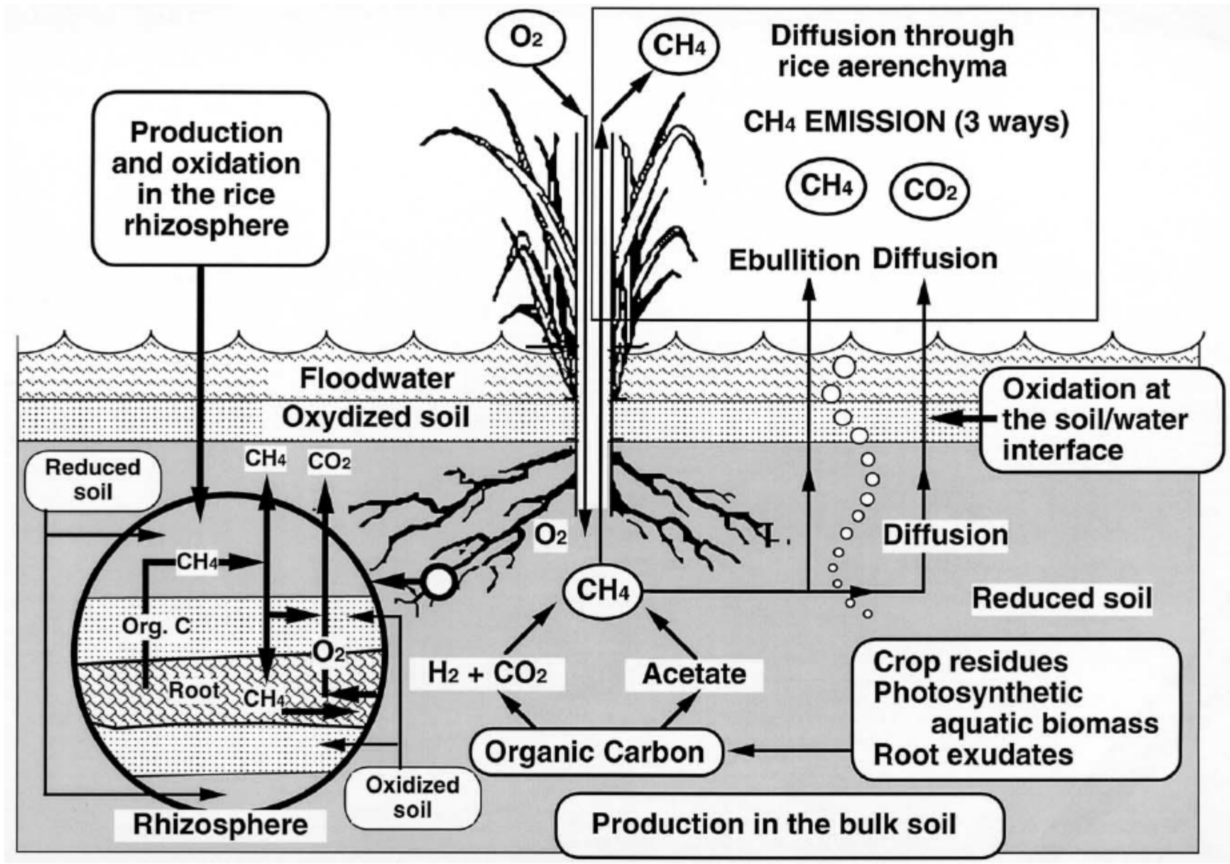
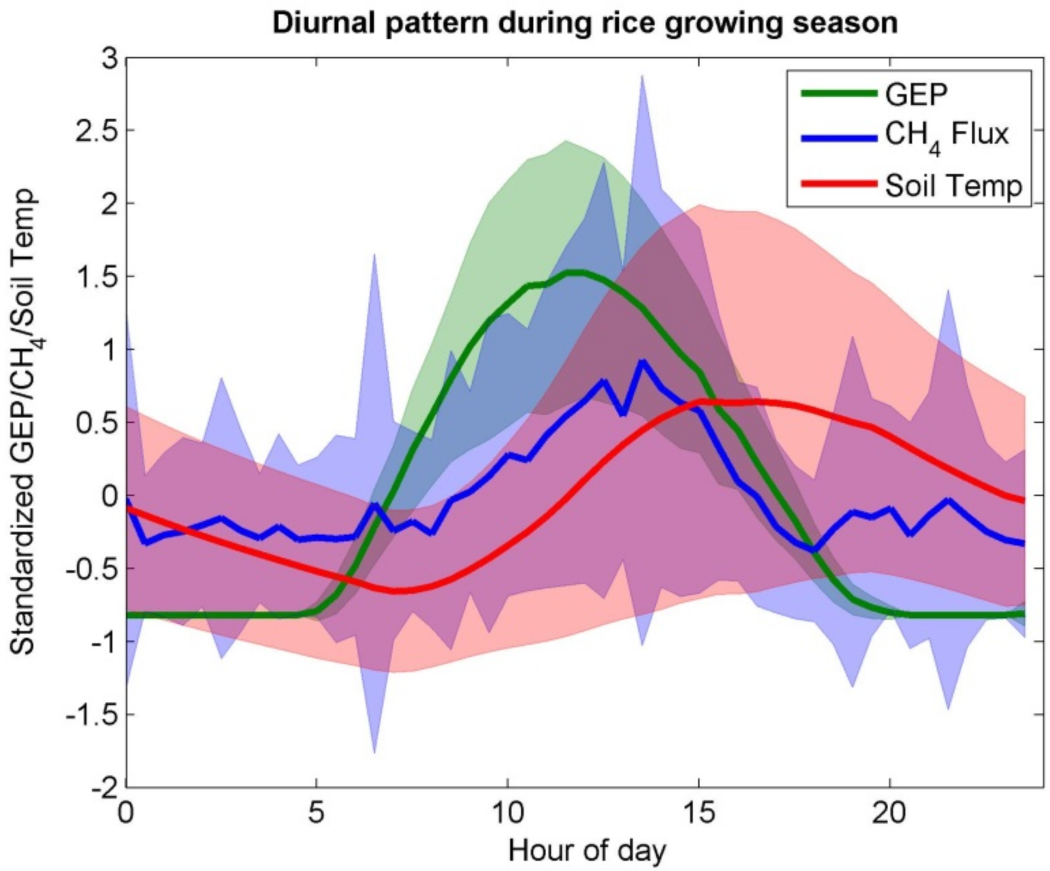


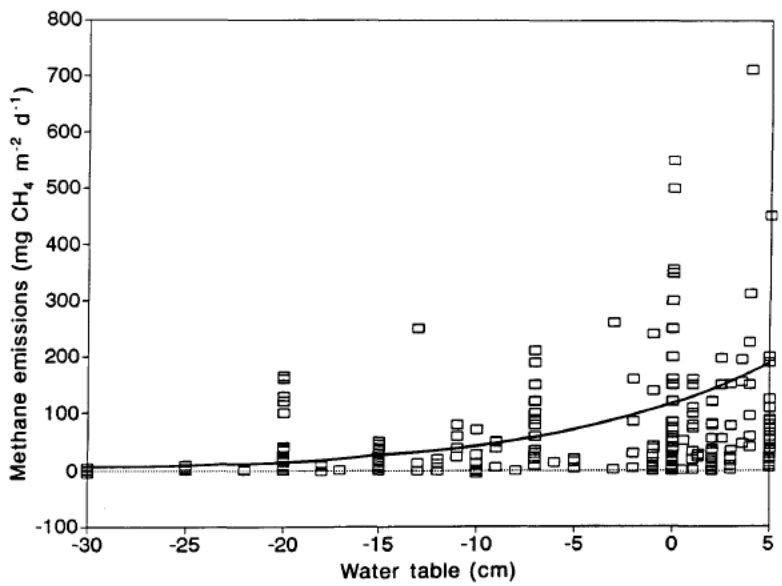
Figure 1. Production, consumption and transfer of CH_4 to the atmosphere in ricefields.

Photosynthesis leads Methane Fluxes, which lead Temperature

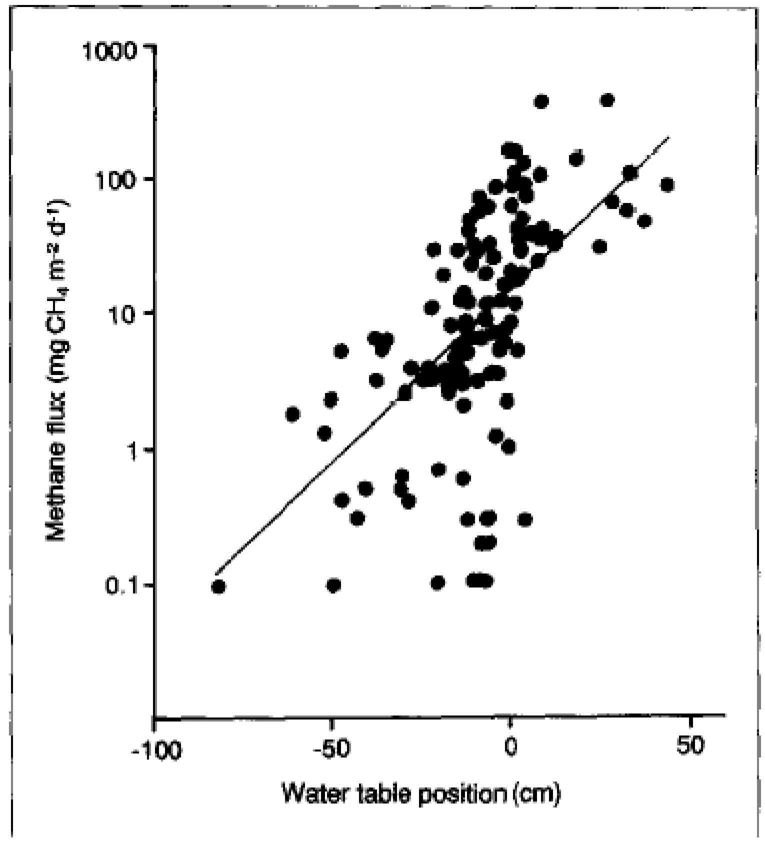


Hatala et al, GRL 2012

Methane Emission and Water Table

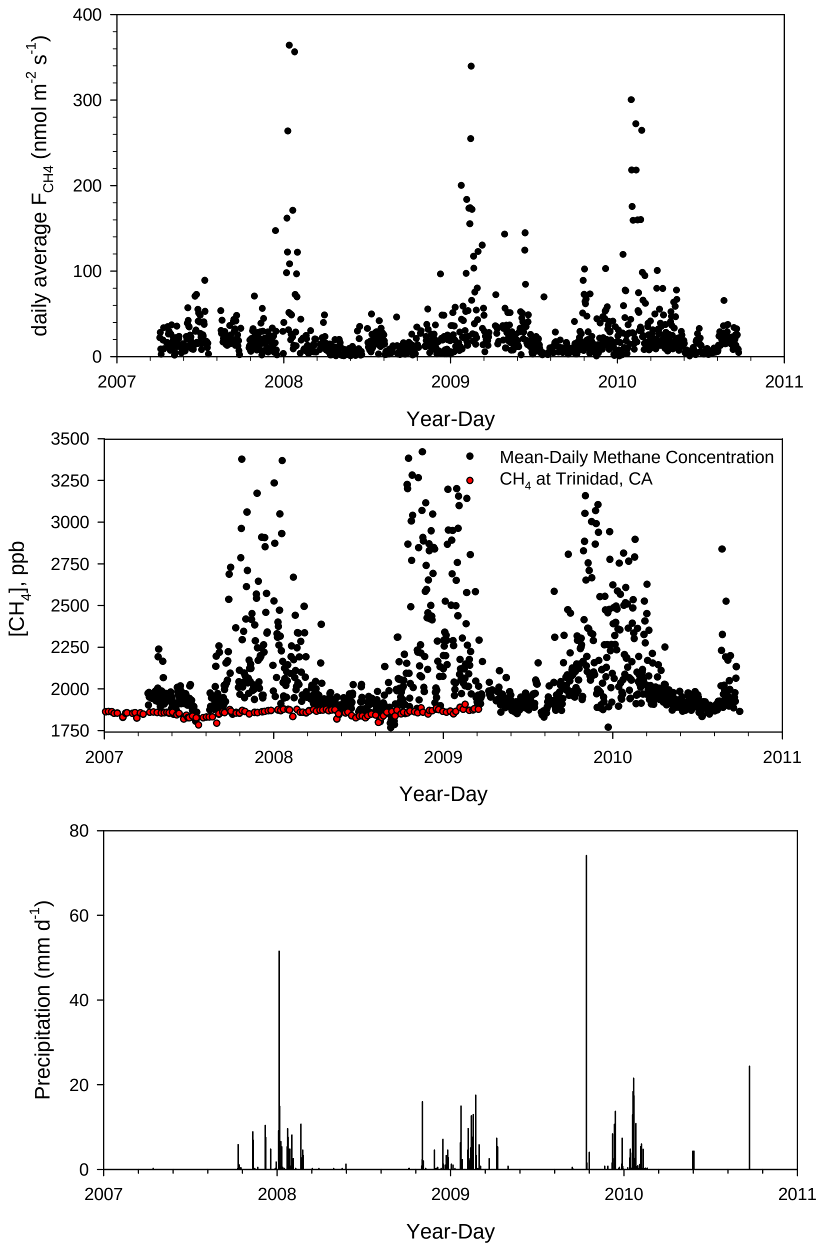


Roulet et al, 1992 Tellus



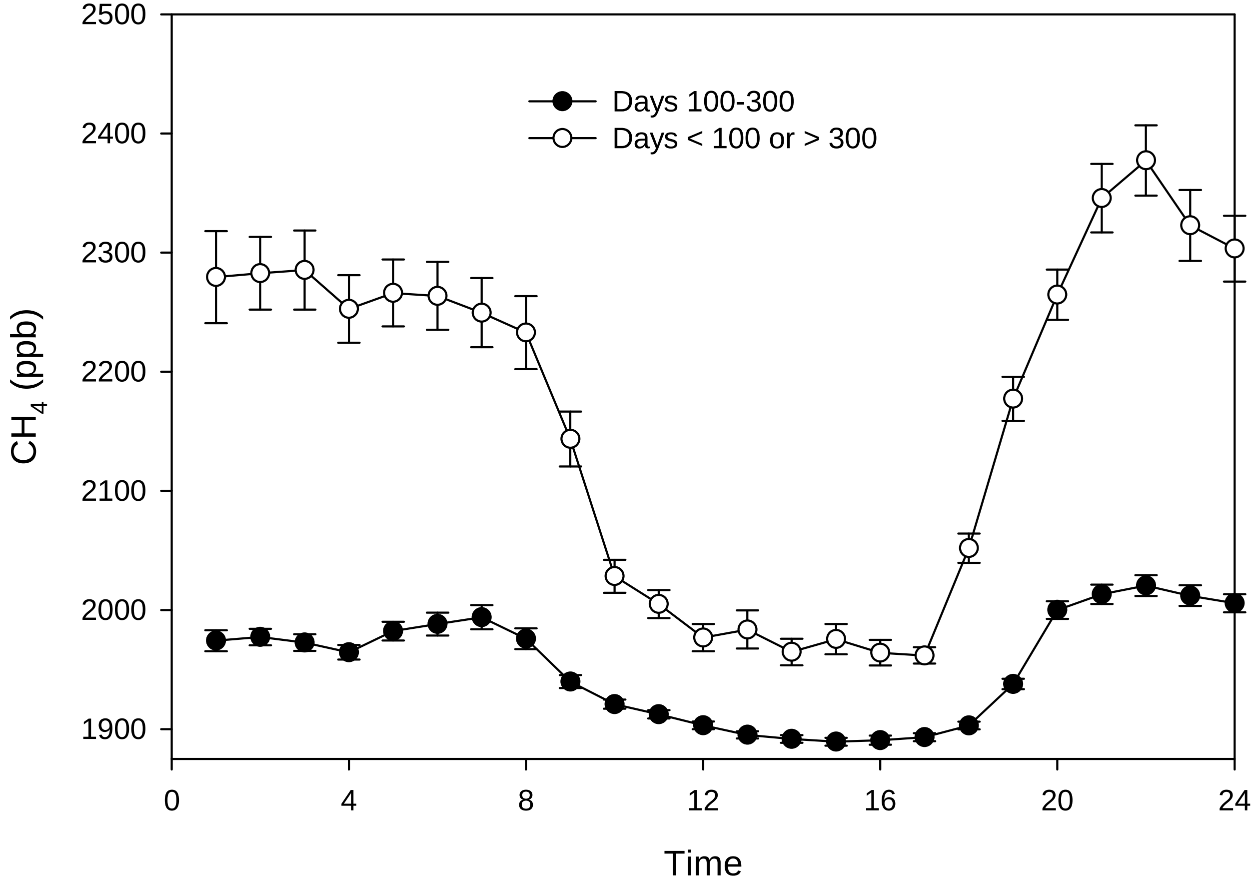
Bubier and Moore, TREE, 1994

3 Years of Methane Flux Data from Sherman Island



Baldocchi et al AgForMet, 2012

Methane Concentrations Experience Nocturnal Maximum

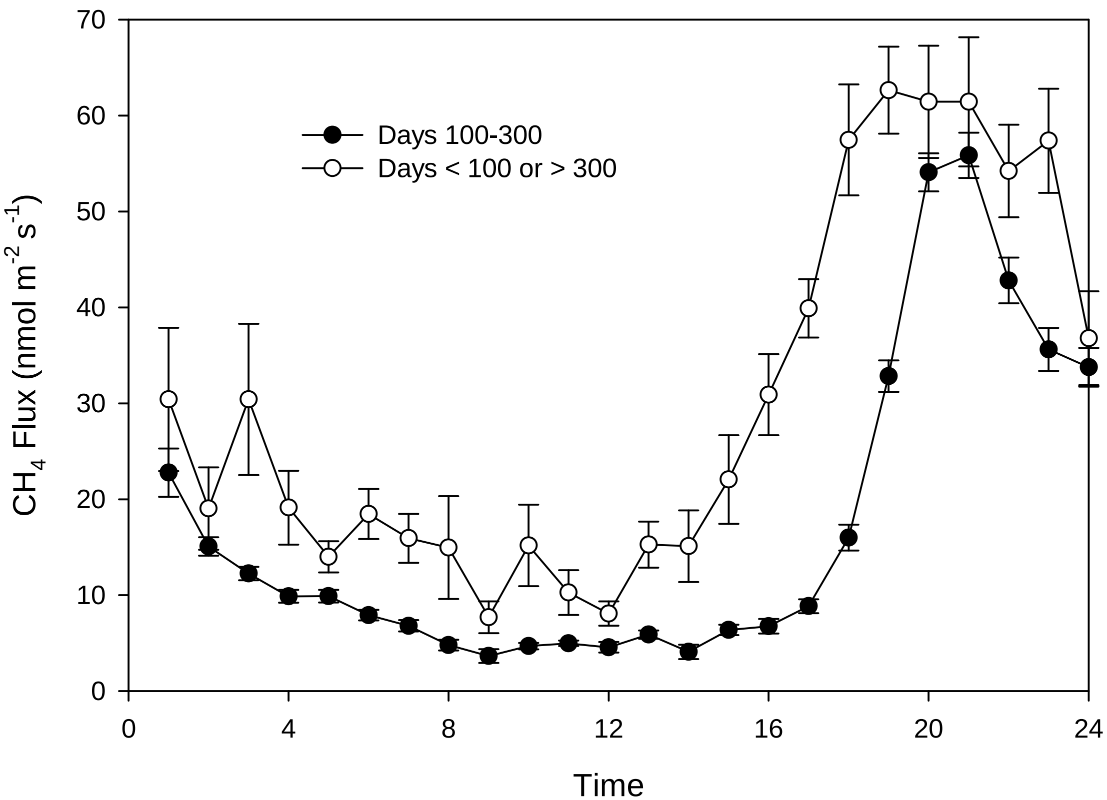


Boundary Layer Rectifier Effect ?

Baldocchi et al AgForMet, 2012

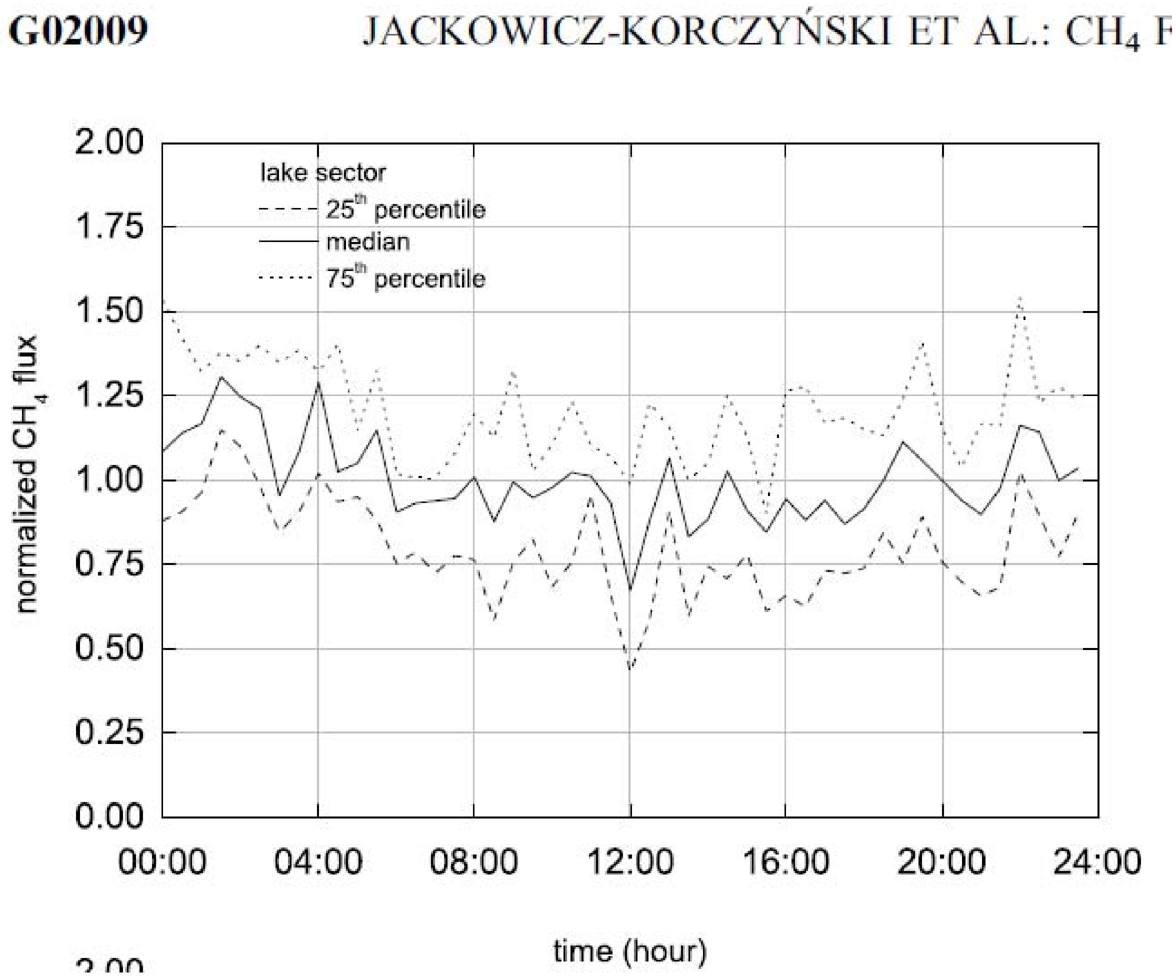
Emerging Mystery:

Strong, Unexpected Diurnal Pattern in Methane Efflux with a Nocturnal Efflux Maximum…



Baldocchi et al AgForMet, 2012

No Diurnal Trend of Methane Efflux over sub-Arctic Peatland



JGR-Biogeoscience, 2010

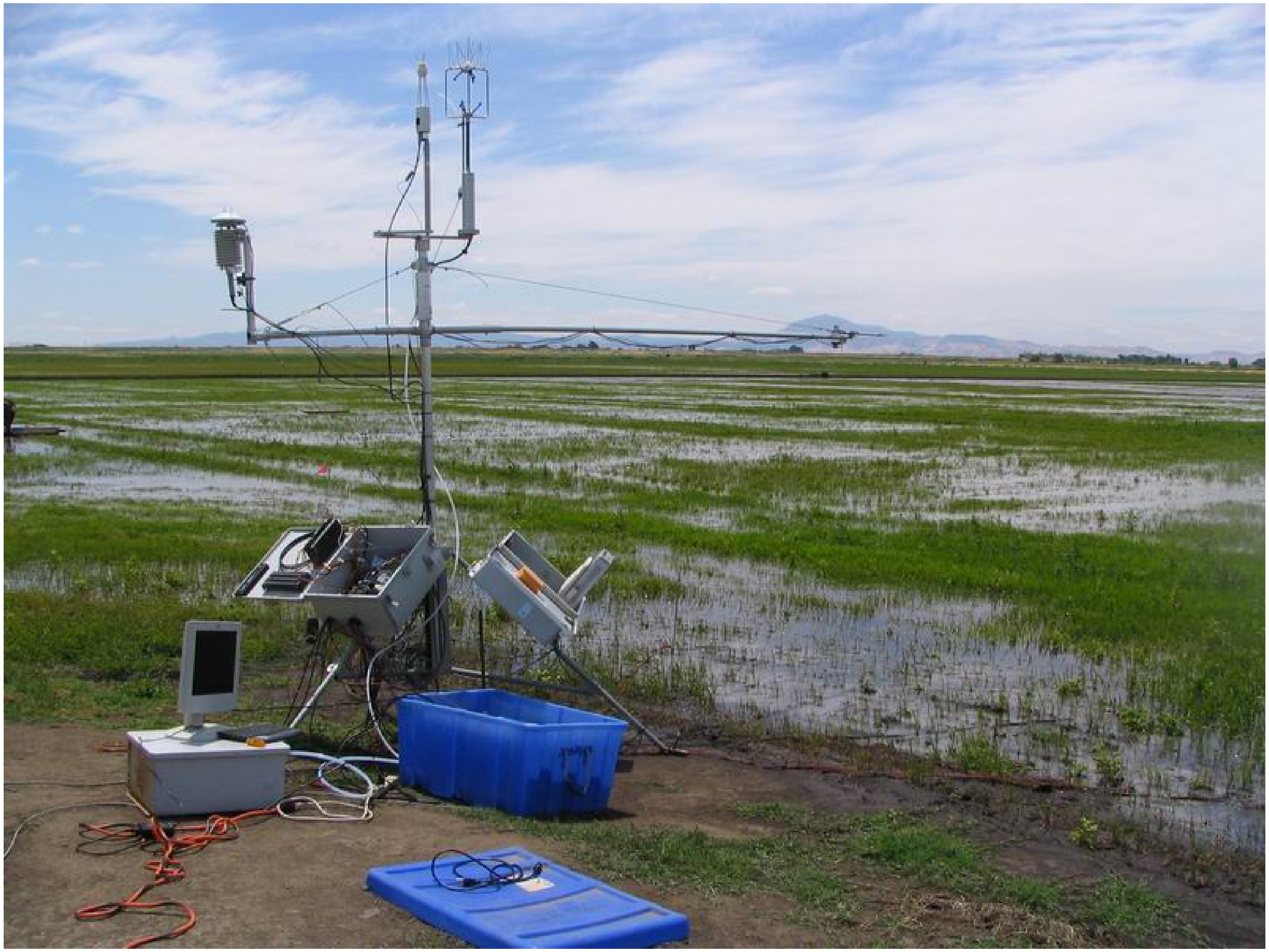
Why are Large Methane Concentrations and Fluxes Observed at Night?

- Microbial Mechanism: ??
  - Temperature is cooler at night
  - Not observed in Literature, Nor at the Rice site
- Tides Modulate Wetlands and Water table: ??
  - Not always at night
  - Tidal Marsh too far upwind ??
  - Peatland is drained & water table fluctuations are weak
- Advection: ??
  - Collapse of the Convective Boundary Layer can increase [CH_4]
  - Wetlands are upwind and Maybe huge Sources of Methane ??
  - Elongation of Flux and Concentration Footprint can occur at Night under Stable Stratification
- Cows:??
  - 100 cows over 38 ha
  - Strong source of methane

What to Do?; What to Believe?

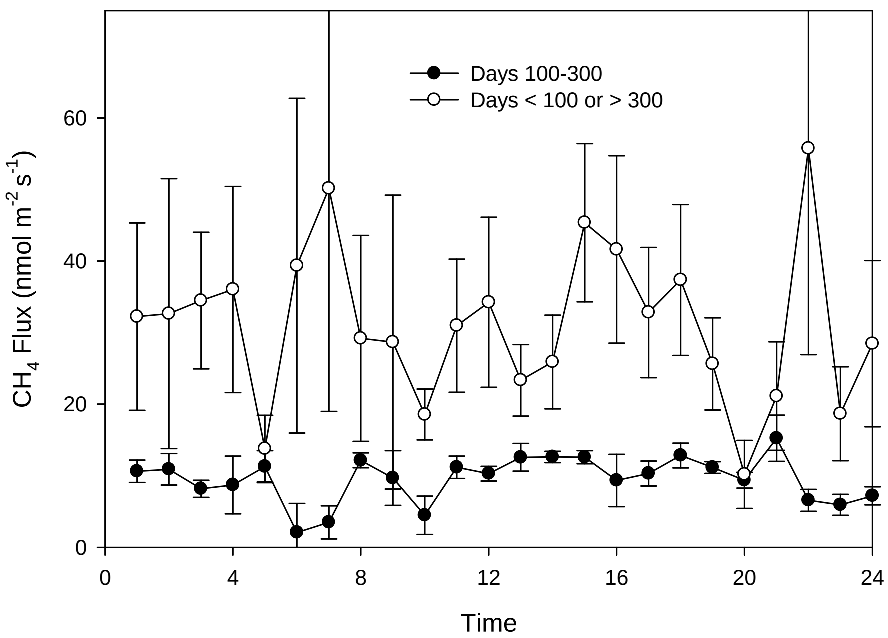
- Measure Methane Flux over Rice, a known, uniform methane source, downwind 10 km
- Bound Problem and Check Advection with
  - PBL Box Model and Flux Footprint Model
  - Flux Divergence Studies
- Commando Field Campaigns to Measure Methane Effluxes from the Marshlands upwind of the Site
- Measure Methane Fluxes of Tidal Marshland Upwind on the Levee
  - Site not secure, power limited, 2nd methane sensor not available
- Use Web Cam and Watch and Count Cows

Eddy Flux System at Rice

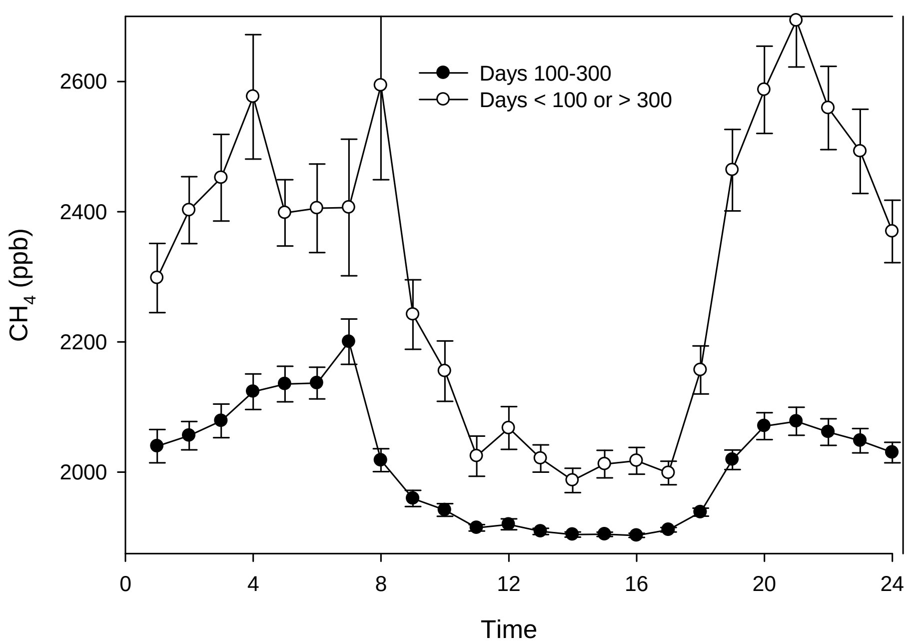


Companion Study over Rice on Twitchell Island, 2009

Twitchell Island, Rice, 2009-2010, Westerly Winds



Rice Does Not Exhibit Diurnal Pattern in Methane Efflux;
Fetch is Uniform and Extensive



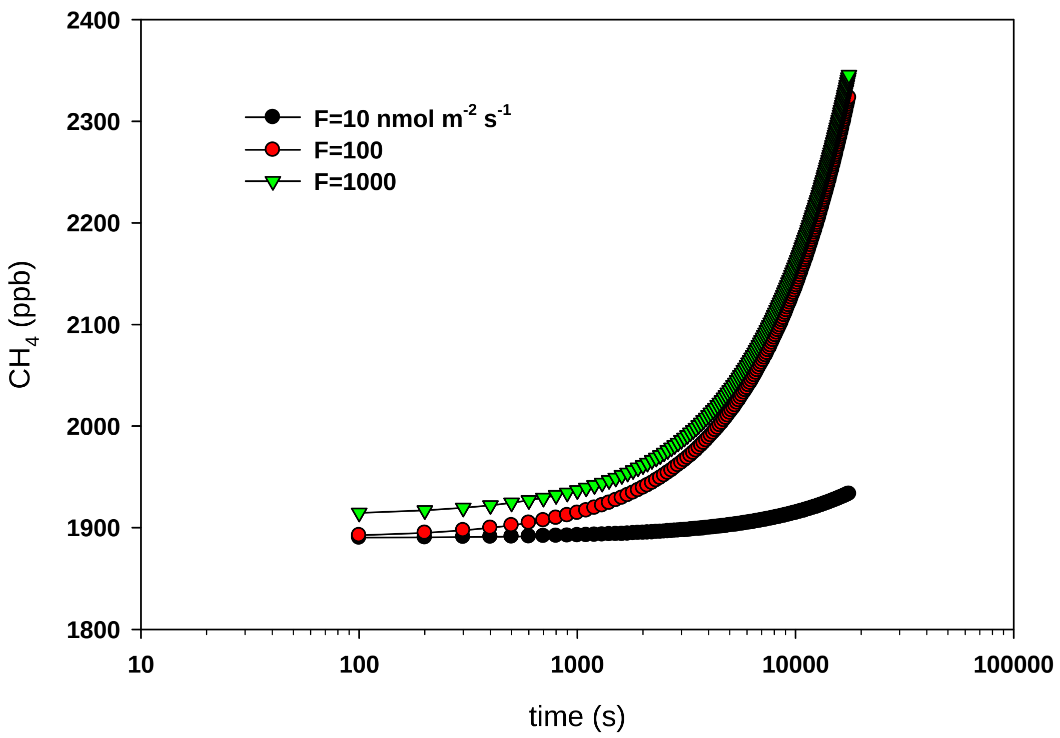
Rice Experiences Strong diurnal Pattern in Methane Concentration

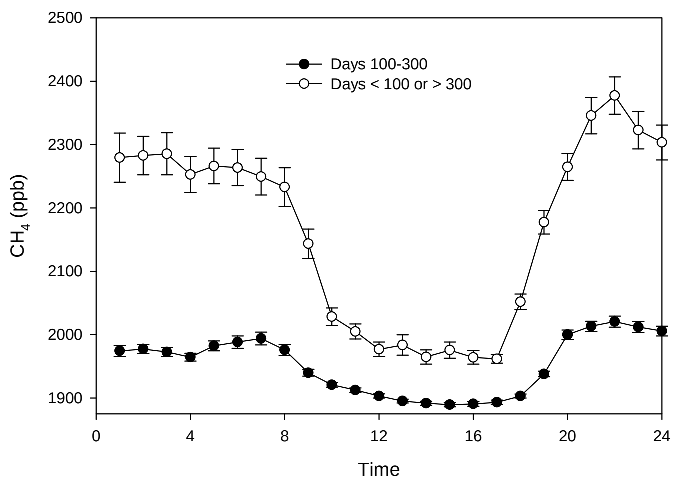
Baldocchi et al AgForMet, in press

Is the Tule Wetland, Upwind of Sherman Island, a Large CH_4 source?

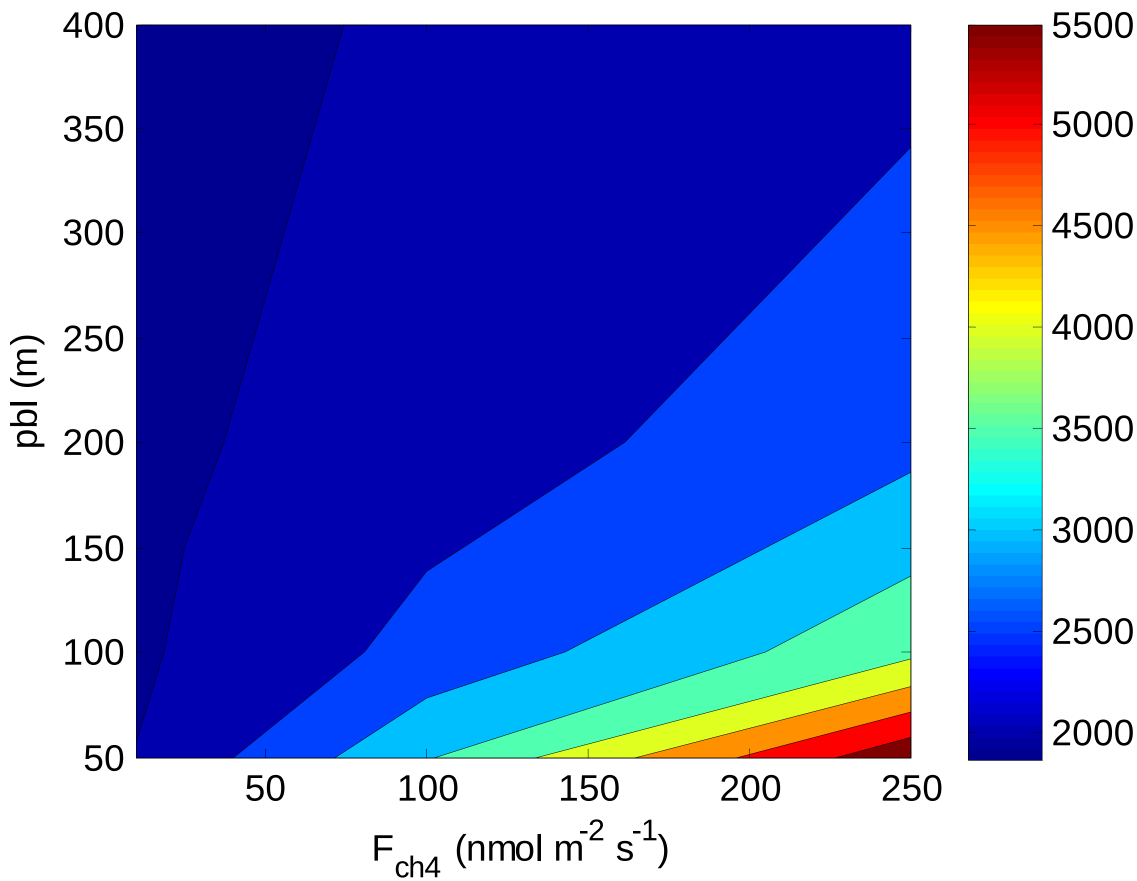
Observed increase in [CH4] after Sunset is too Fast to be Explained by the PBL Box, which infers a complex source due to wetlands, wet fields and ditches

pbl height = 100 m





Elevated [CH4] (> 2500 ppb) corresponds with Low Boundary Layers (< 200 m) and High Effluxes (50 to 250 nmol m-2 s-1)



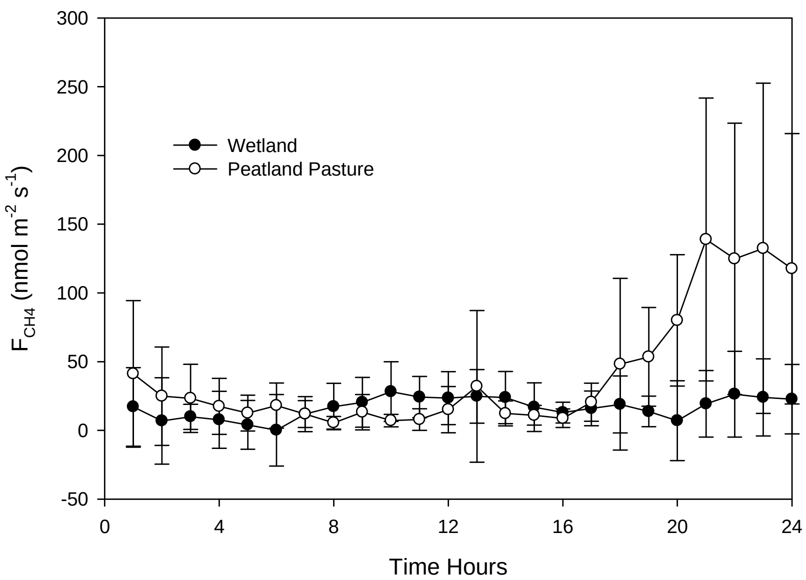
$$\rho_a \frac{\Delta c}{\Delta t} = -\frac{F_0}{z_i}$$

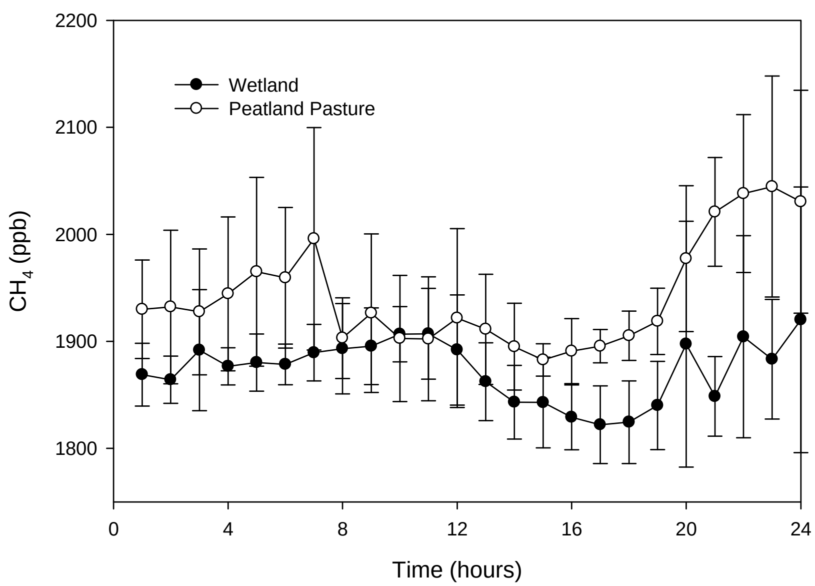
$$c(t) = c(t_0) + \frac{F_0}{\rho_a z_i}(t - t_0)$$

Figure 5 Computation of CH_4 concentrations using a one-dimensional box model for a stable and steady nocturnal boundary layer. The figure is plotted as a function of flux density (F_{CH4}, nmol m^{-2} s^{-1}) and height of the planetary boundary layer. The color contours represent methane concentration. These computations were derived after a time integral of 10 hours.

Sniff Methane from the Levee, Upwind from Cows, Downwind from the Wetland

Sherman Island, D 98-124, 2010





Natural Tule Wetland, upwind of Paddock, Does NOT experience diurnal pattern in methane Efflux

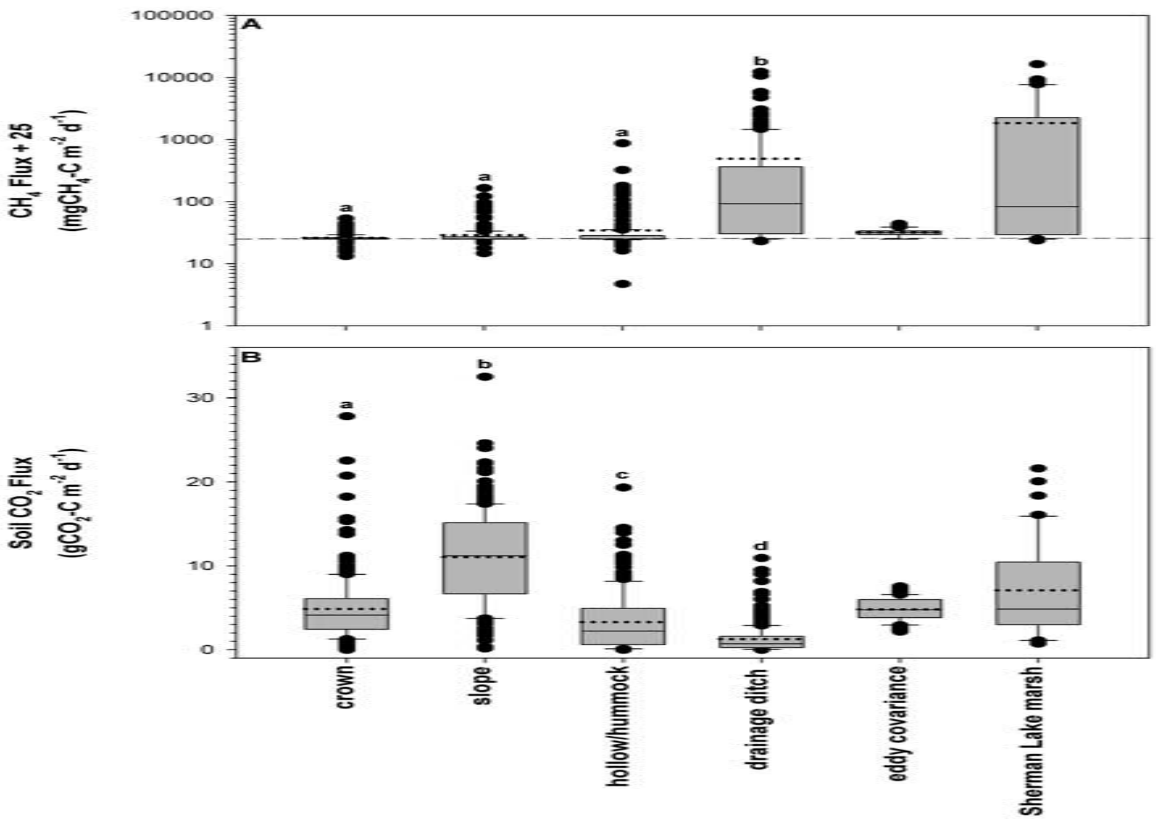
Natural Tule Wetland, upwind of Paddock, Experiences lower methane concentrations than grazed paddock, downwind, and No Diurnal Variation

Baldocchi et al AgForMet, 2012

Chamber Fluxes Across Landscape Features

Ditches, upland hummocks, wet areas

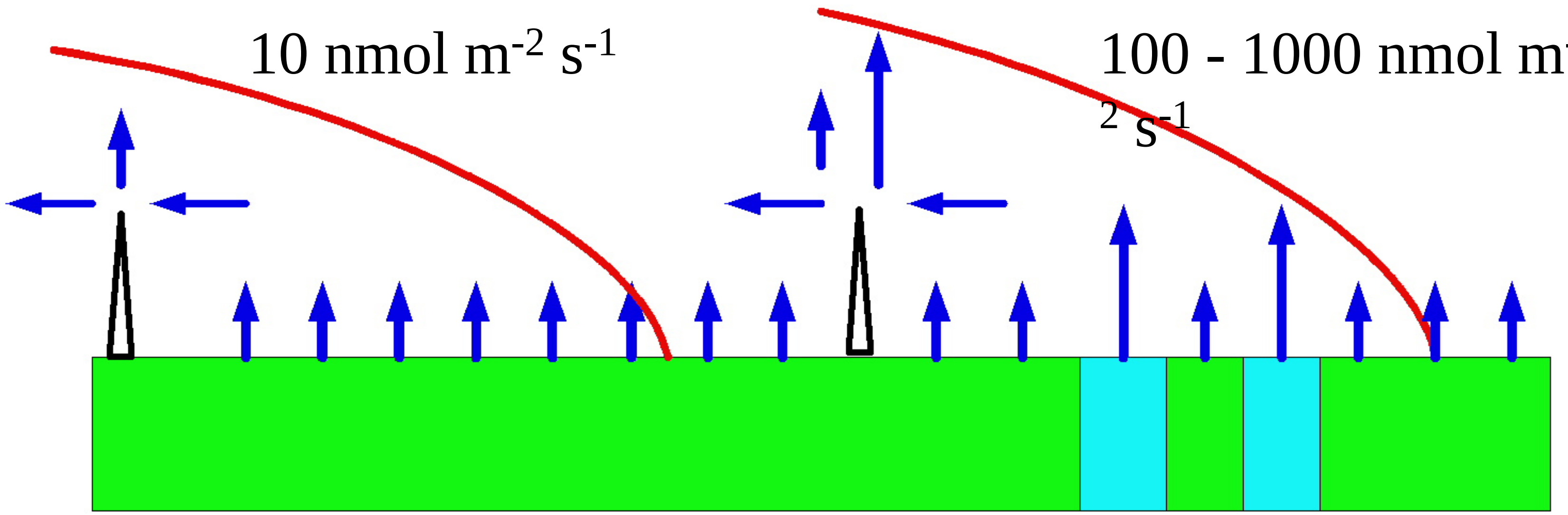
Chamber Fluxes by Land Form
Mean Methane Fluxes vary by 2 orders of Magnitude, Extremes by 3 orders of Magnitude



Teh et al, Ecosystems, 2011

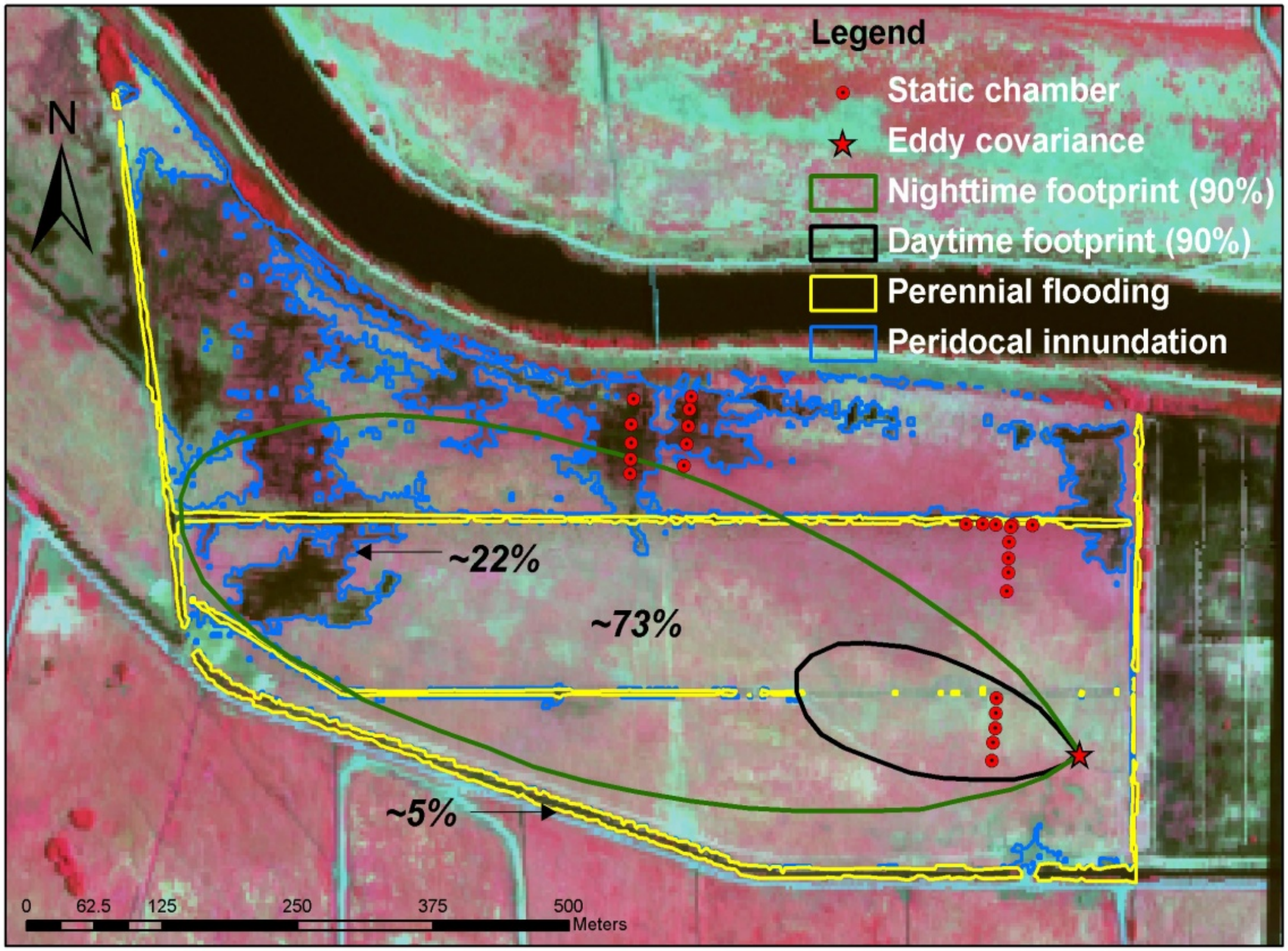
Even Over Perfect Flat Sites with Extensive Fetch
Advection can/does Occur with Methane:

Source Strength of Hot spots and Cold Spots can Differ by 1 to 2 orders of Magnitude (10x to 100x)



Such Advection is Less Pronounced for Water Vapor and CO_2 Fluxes Because Flux Differences Emanating from the Different LandForms are Smaller

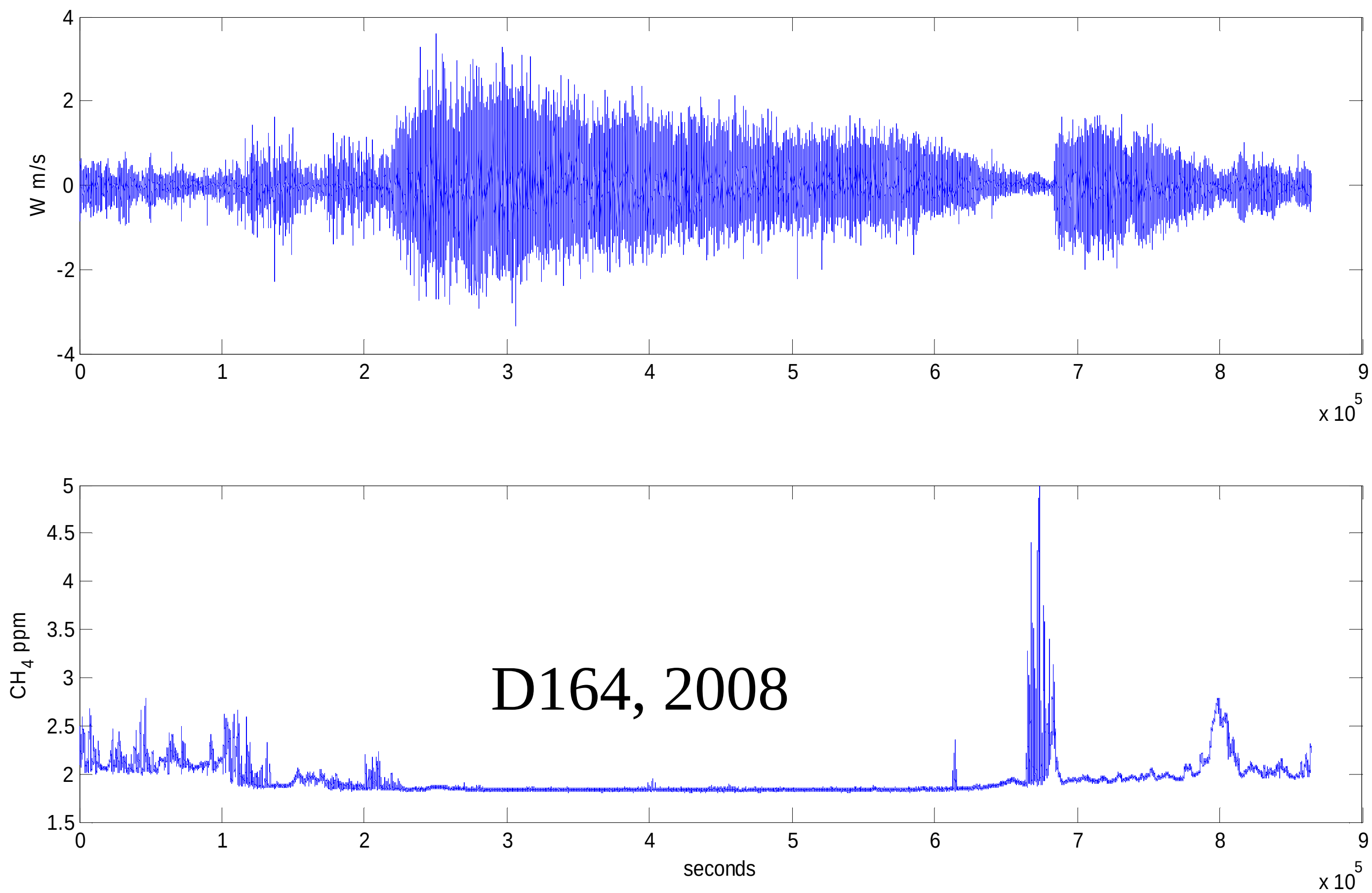
Methane Flux Footprint of a Peatland Pasture



Detto et al. 2011 AgForMet

Are Pheasants and Cows Releasing Methane in the Near Field?

24 Hour Time Series of 10 Hz Data, Vertical Velocity (w) and Methane (CH_4) Concentration



Sherman Island, CA: data of Detto and Baldocchi

Cow efflux calculations!!

Cows and Methane emissions

10 to 30 mol/cow/day is reasonable bound for a number of studies

100 cows over 0.38 km2 and 24*3600 s

Bounded flux density averaged over landscape

10 * 100/(380000*24 *60*60) = 30

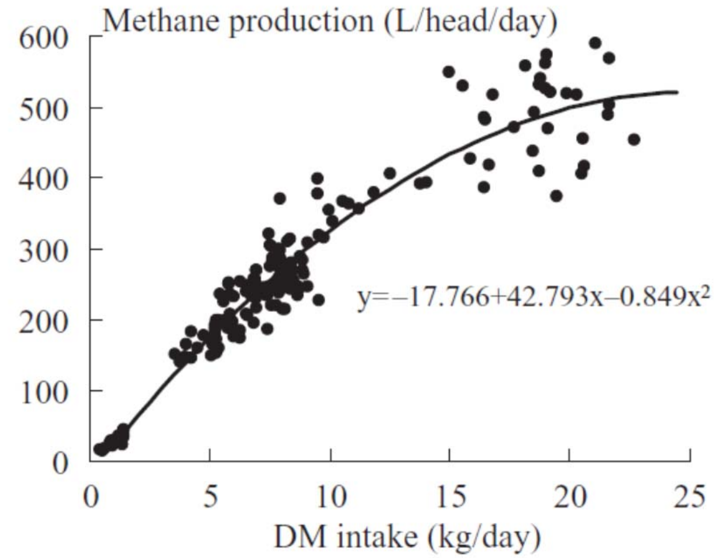
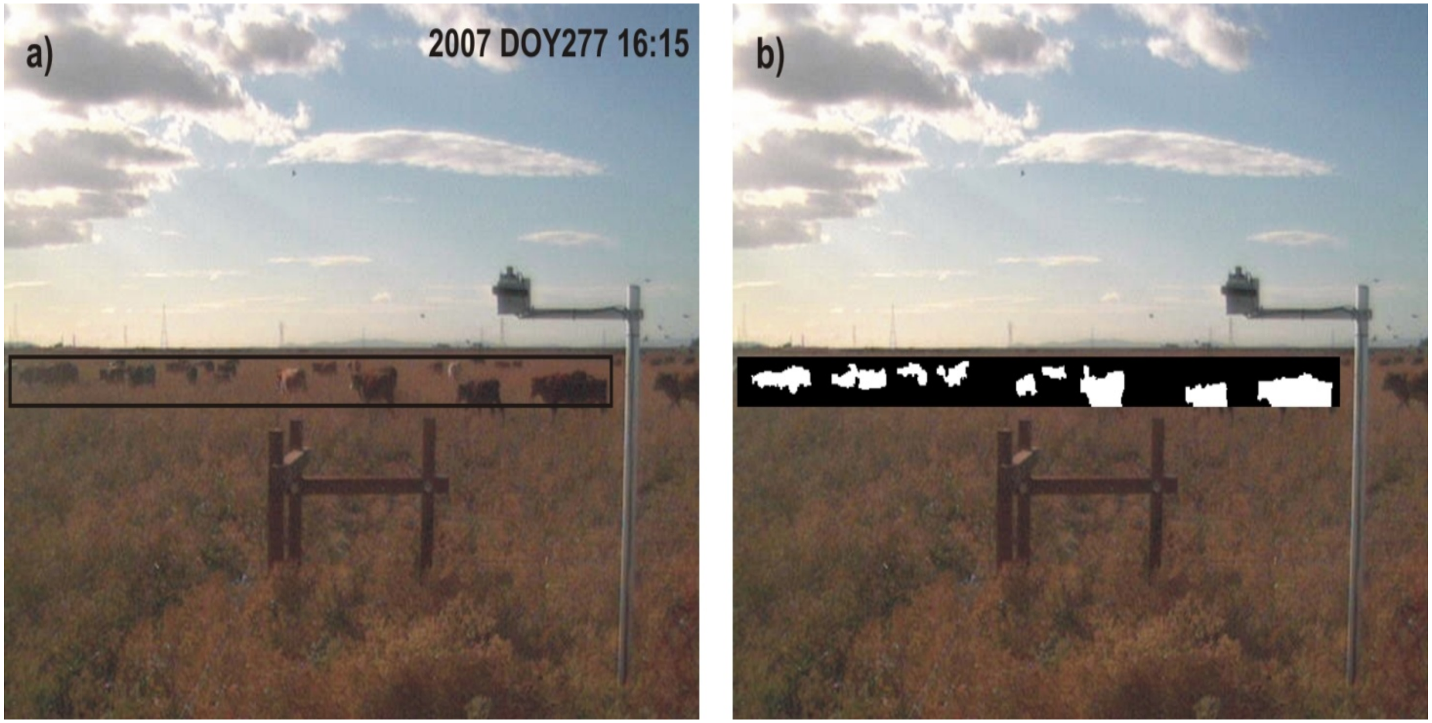


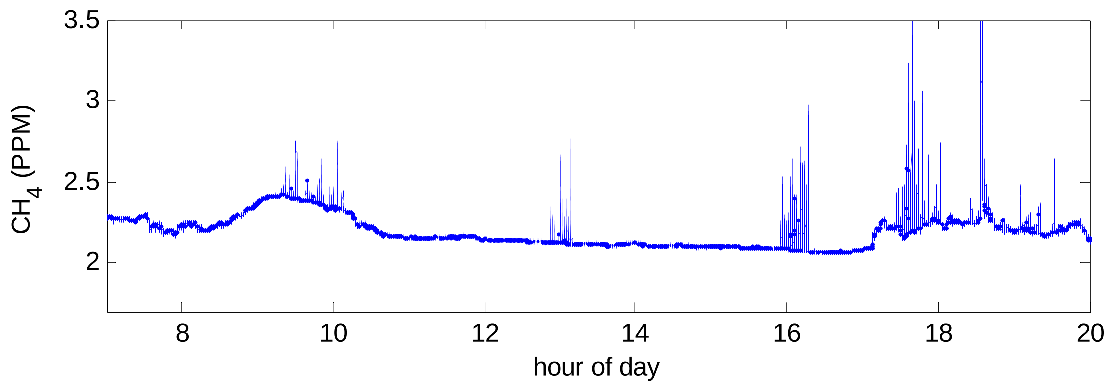
Figure 1 Relationship between dry matter (DM) intake (kg/day) and methane production (L/head/day). Data from Shibata *et al.* (1993).

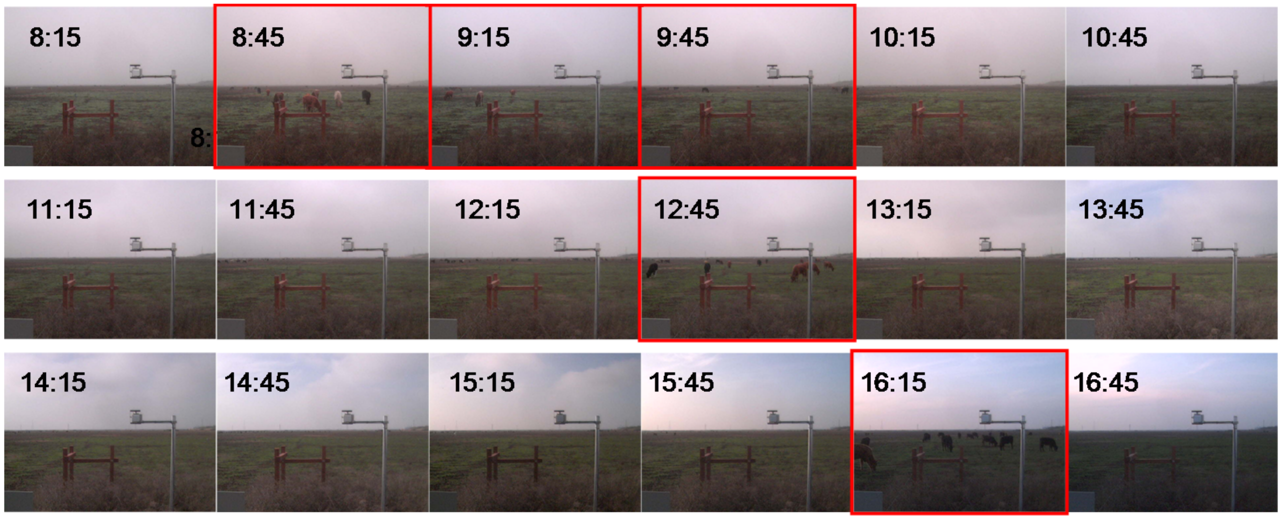
Cow Cam



Oliver Sonnentag, analyst

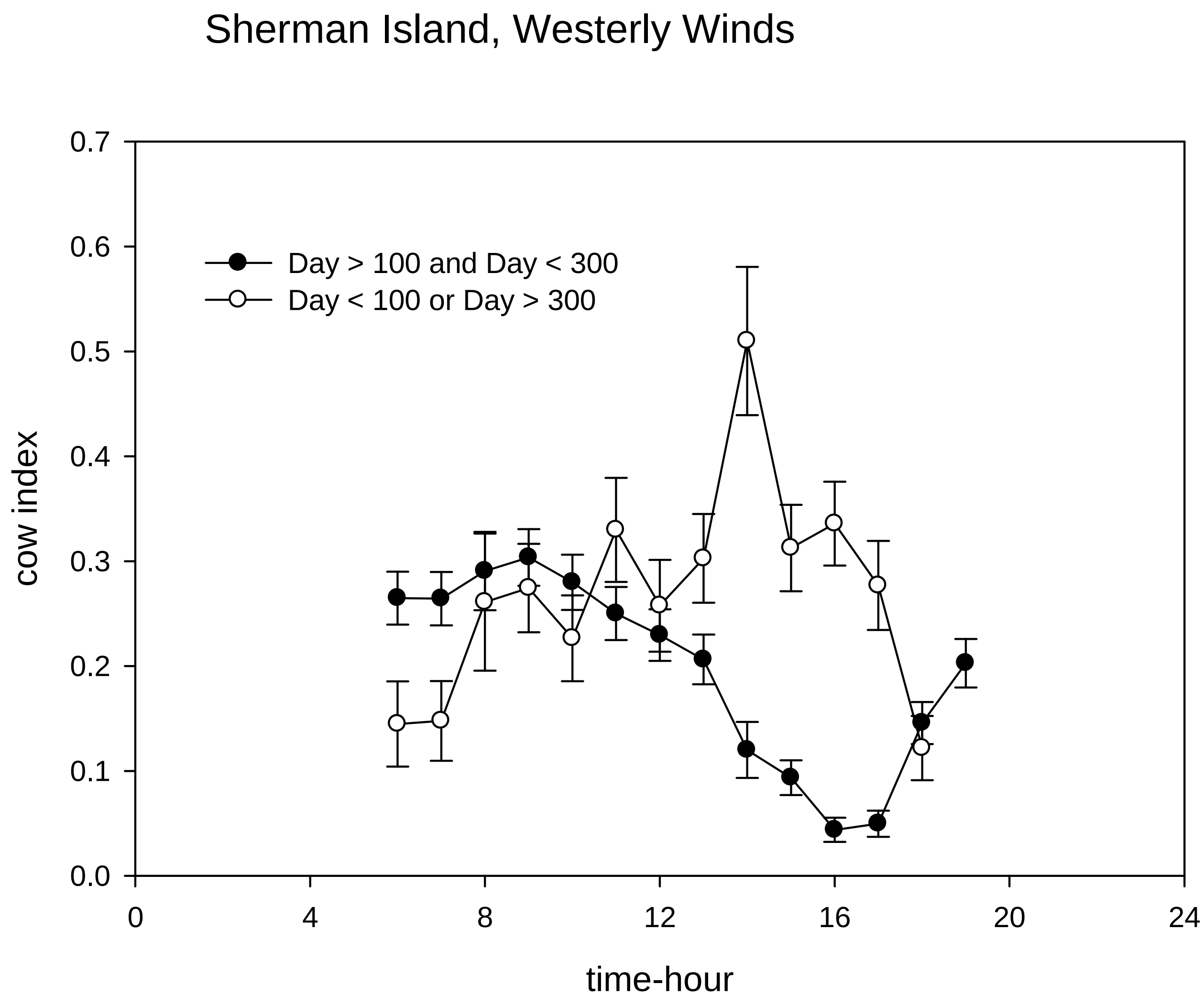
The Wonders of MatLab and Inspecting Raw Data
Cows, Near-Field Diffusion and CH_4 Spikes





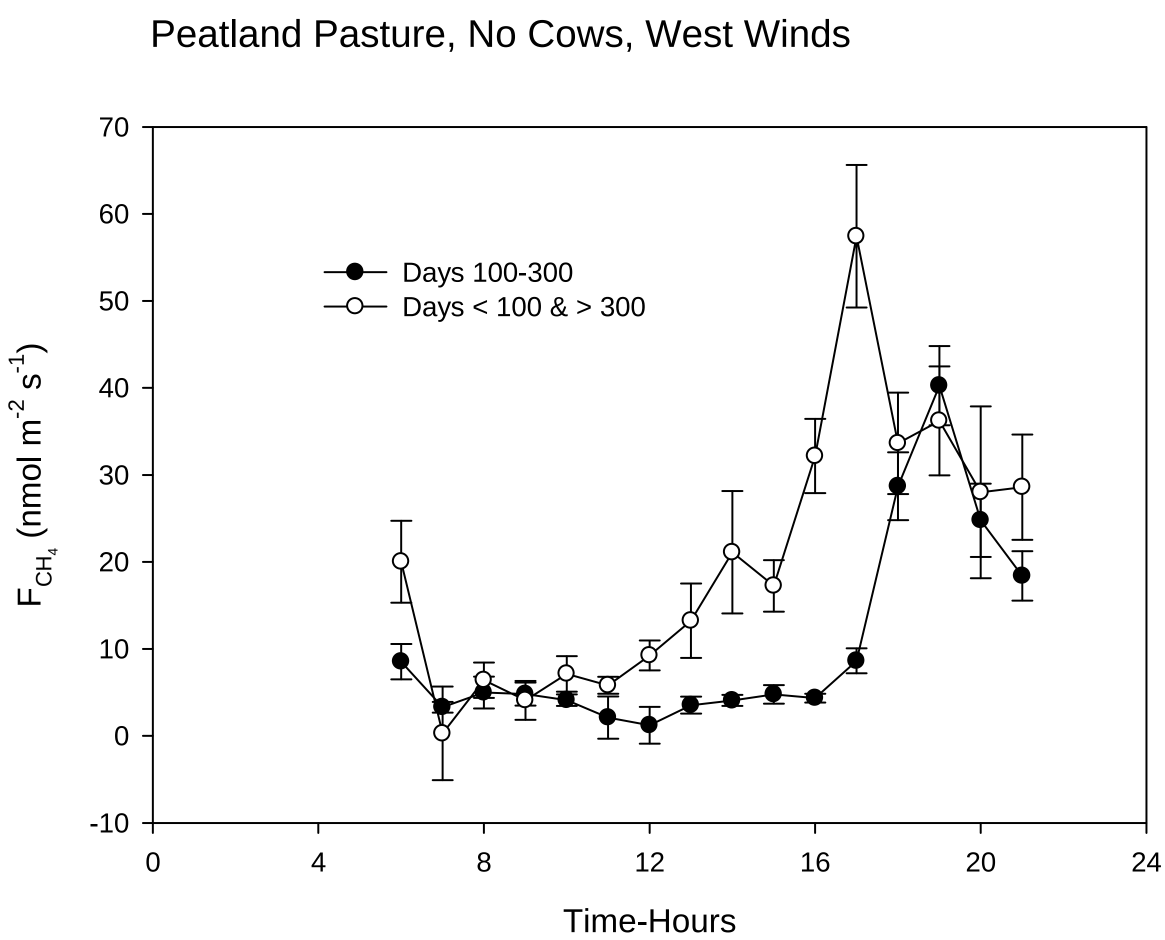
Detto et al 2011 AgForMet

Diurnal Variation in Cow-Cam Index



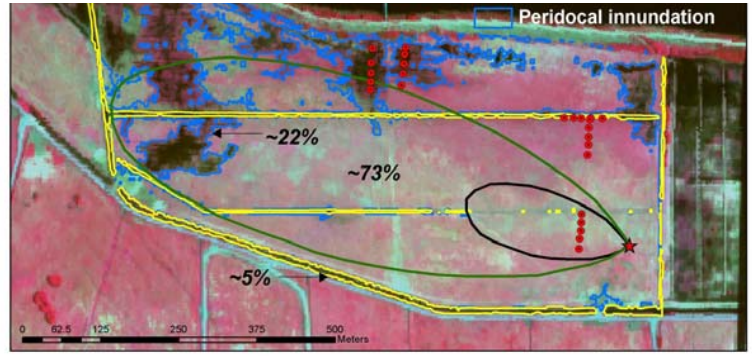
Baldocchi et al 2012 AgForMet

Night-time Maximum in CH4 Flux Persists with No Cows in l



Baldocchi et al 2012 AgForMet

Annual Budgets of Methane Efflux



	Variable footprint	Small footprint	Large footprint	Large-small footprint: flooded-portion of the field	Small footprint: Dry portion of the field
	Day and Night, with cows	Day only, with cows	Night only, with cows	Night-Day, with cows	Day only, without cows
gC m^{-2} y^{-1}	8.66+/- 6.65	4.2 +/- 1.93	13.1 +/- 6.67	8.77	2.68 +/- 1.42
mol m^{-2} y^{-1}	0.721 +/- 0.554	0.353 +/- 0.161	1.08 +/- 0.556	0.73	0.223 +/- 0.119

New Studies, Off the Grid!

Restored Wetland, Mayberry Ranch on Sherman Island

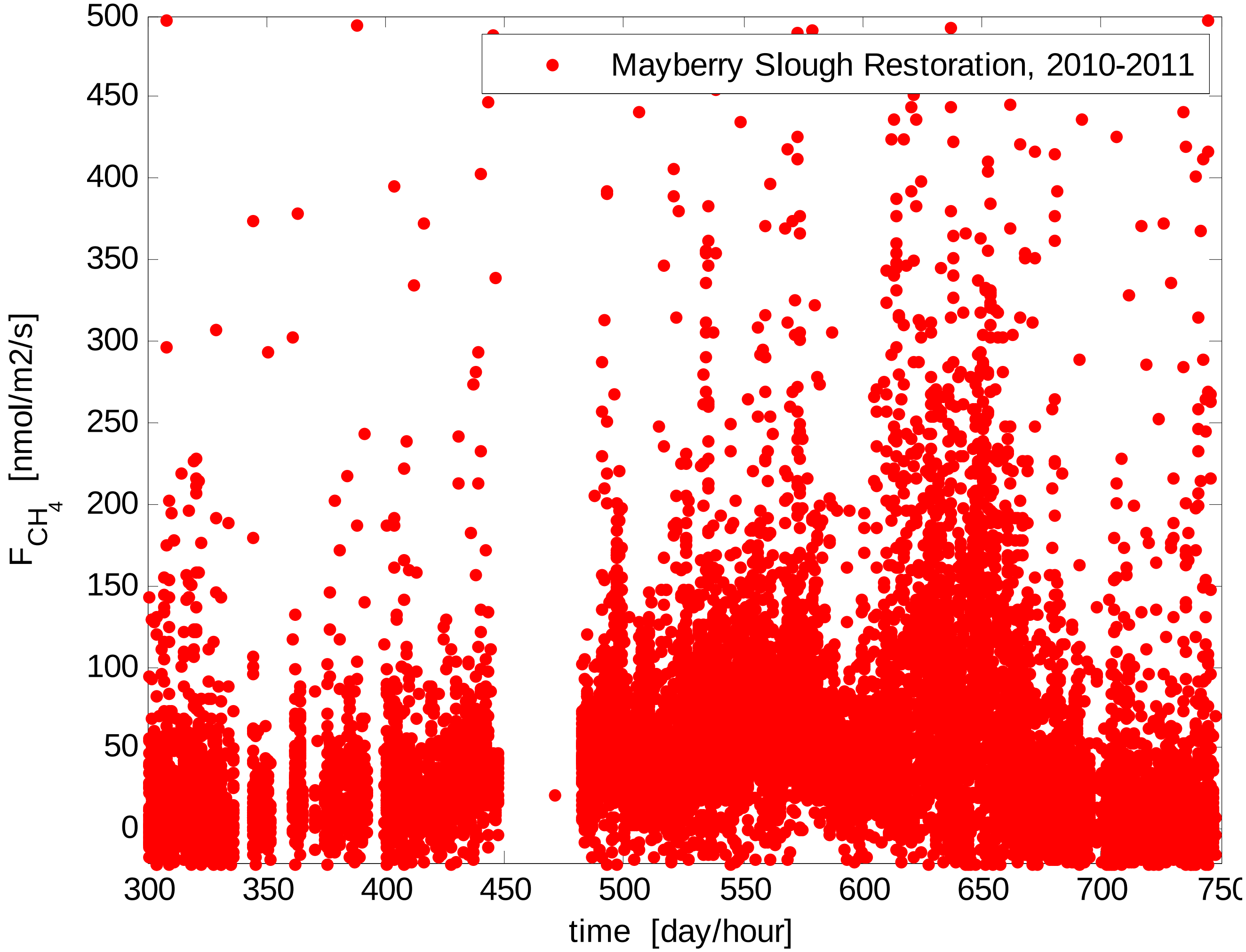
Wetland Restoration Project, Mayberry Slough

Fall 2010, Wetland just Restored and is being Flooded

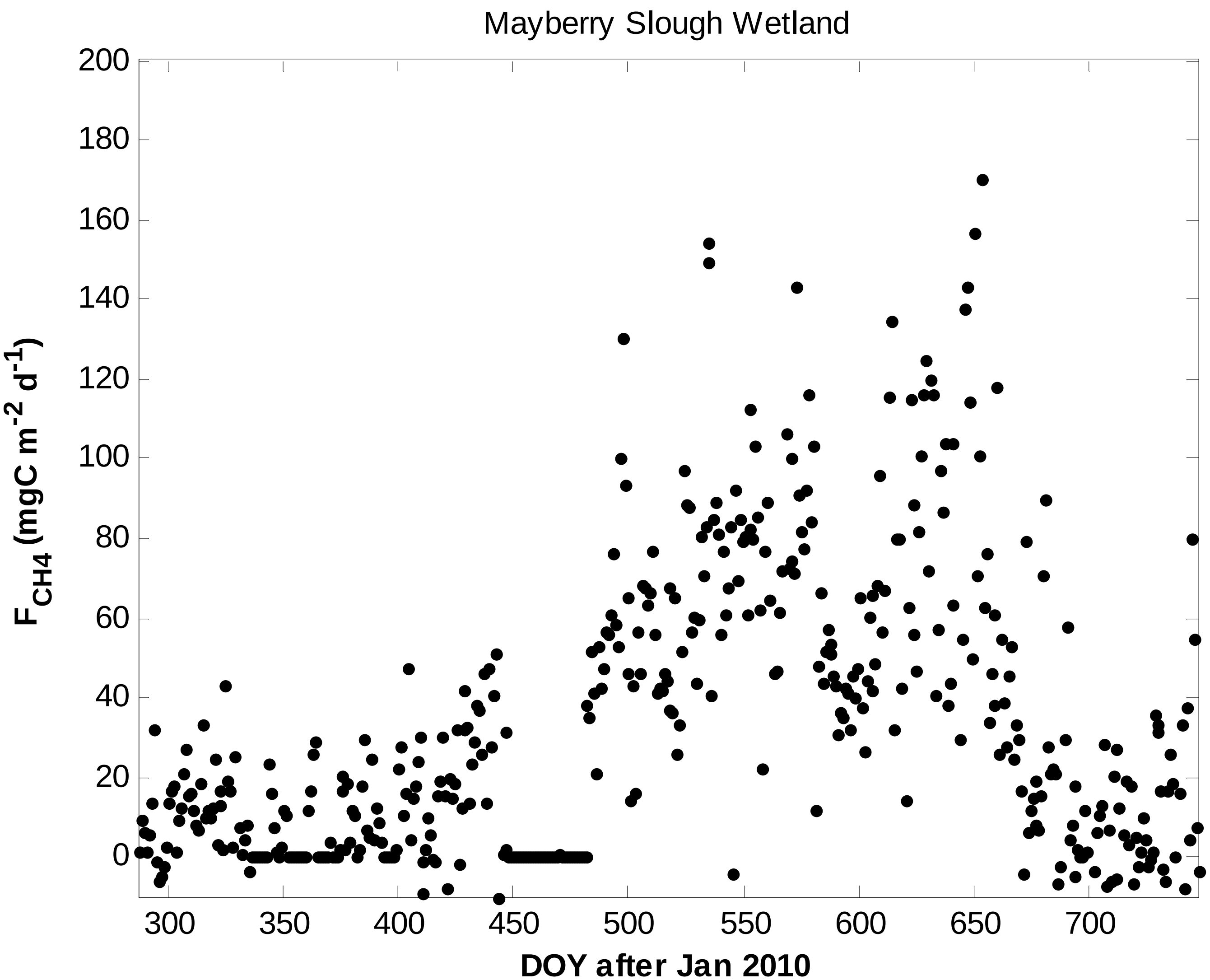
Autumn 2011, End of First full Growing Season and in fi

New Low Power Methane and CO2/H2O Flux System

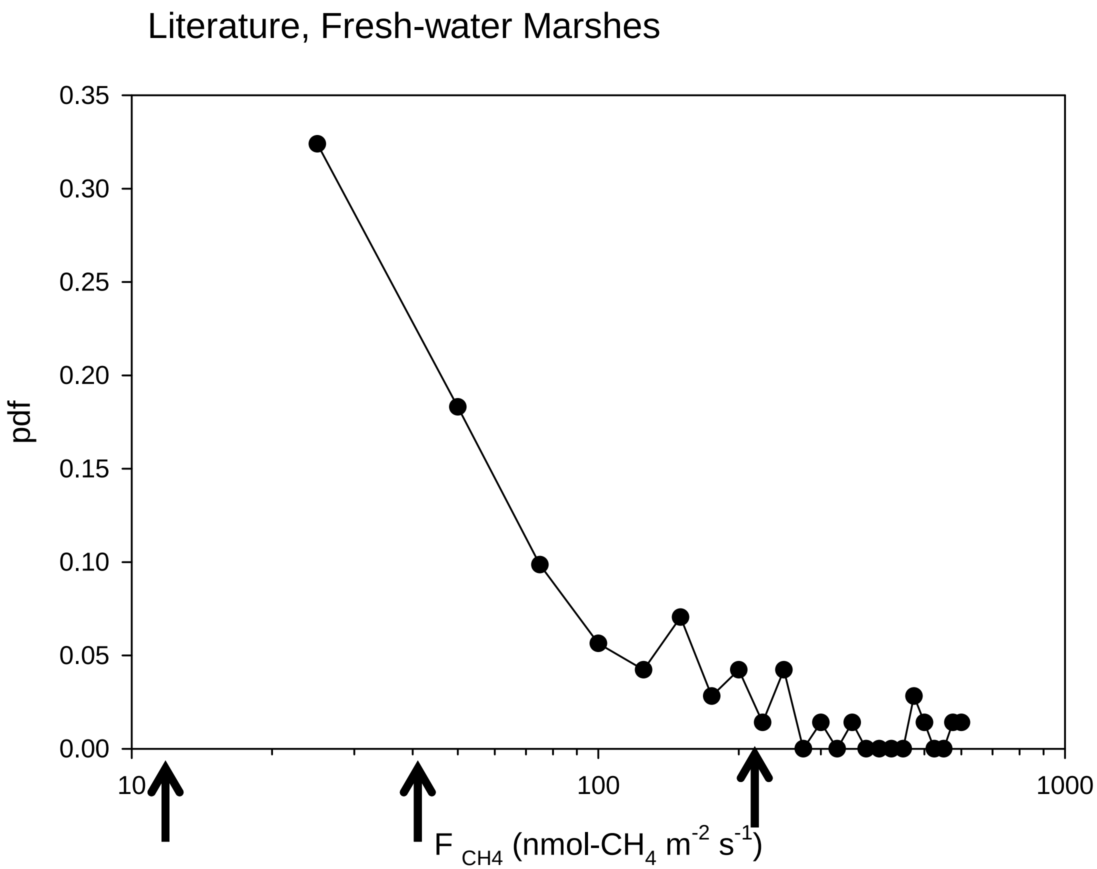
1^{st} Year of Methane Fluxes over New Wetland, hourly data



1st Year of Methane Fluxes over New Wetland, daily Integrals



Comparison with Peak and Typical Delta Methane Fluxes and the Published Literature



Drained Peatland

Rice

Restored Wetland