DMS as an Integrator of Dynamic, Chemical, and Biological Processes during VOCALS

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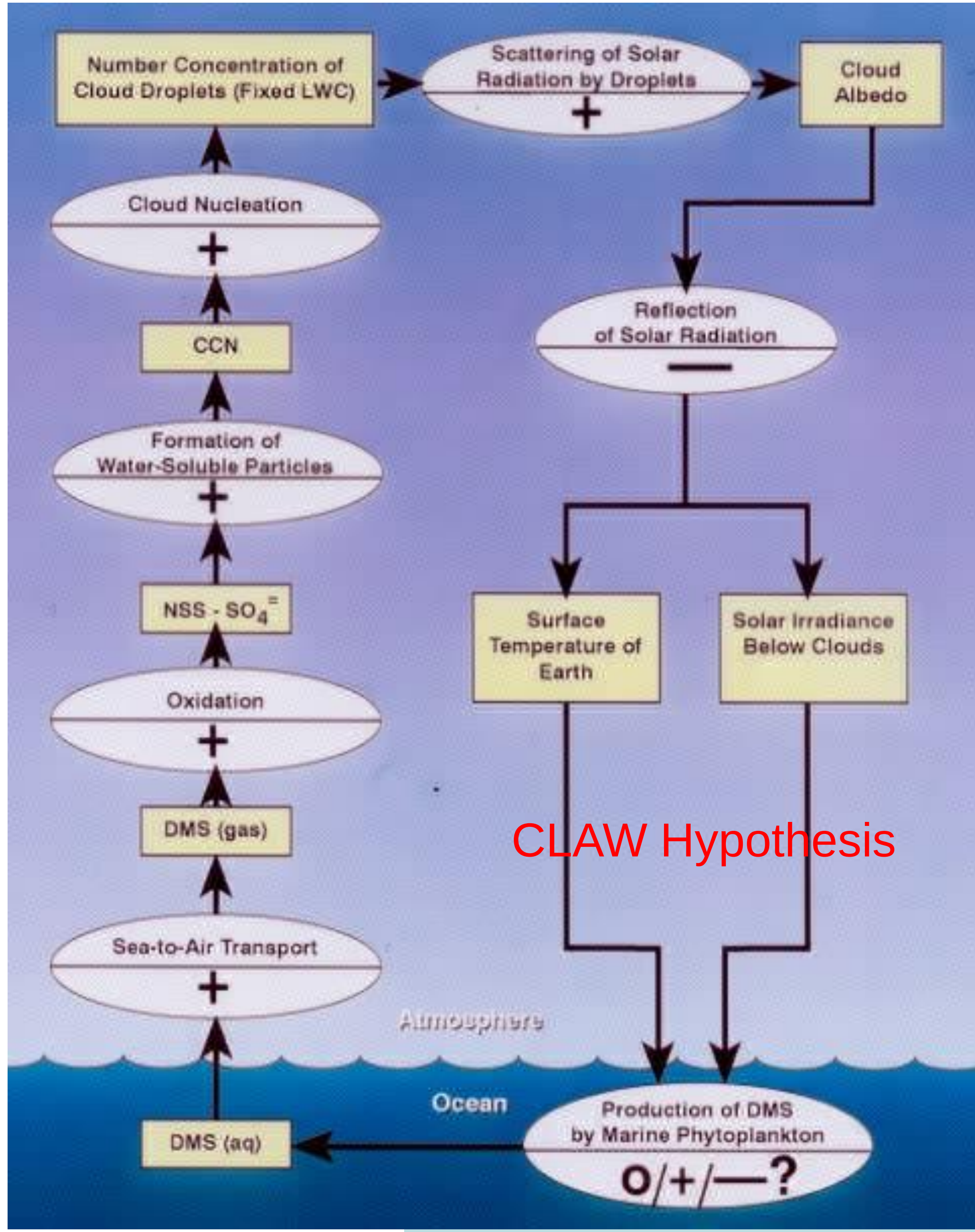


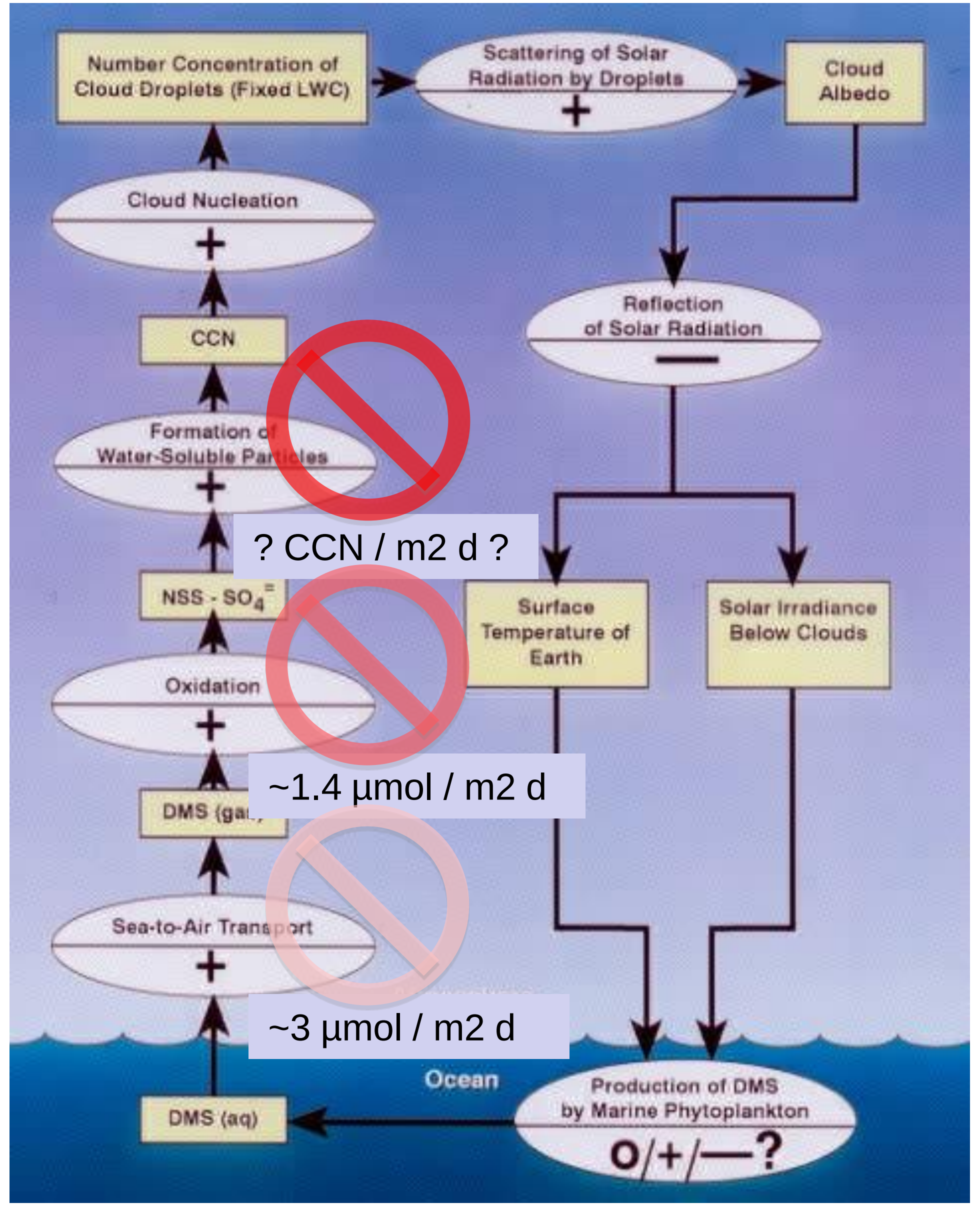
Charlson et al., *Nature*, *326*, 655-661, 1987.

Can We Integrate Up The CLAW Hypothesis?

Not Even Close!!

So why even try to quantify fluxes and conversion rates?

It is of great value to know the direction and magnitude of process changes in a different climate



Charlson et al., *Nature*, 326, 655-661, 1987.

solas surface.ocean lower.atmosphere.study

1. Atmospheric Chemistry: Reaction Rates, Branching Ratios

Average Effective [OH] was Derived from DMS Fluxes during VOCALS

$$\cancel{\frac{\partial \bar{S}}{\partial t}} + \bar{u}\cancel{\frac{\partial \bar{S}}{\partial x}} + \frac{\partial \overline{S'w'}}{\partial z} = \cancel{P} - L$$

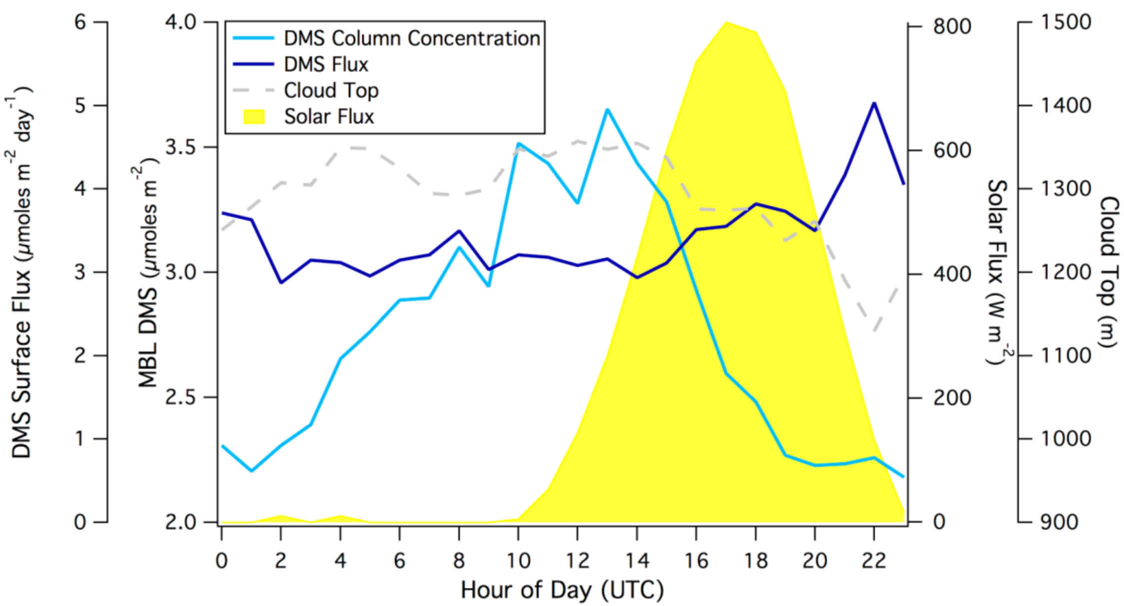
Continuity Equation

$$F_0(DMS) - F_{zi}(DMS) = L(DMS) = k_{DMS}[OH]$$

$$[OH] = \frac{F_0 - \omega_e(1-\alpha)[DMS_0]}{\langle \overline{DMS} \rangle k_{OH}}$$

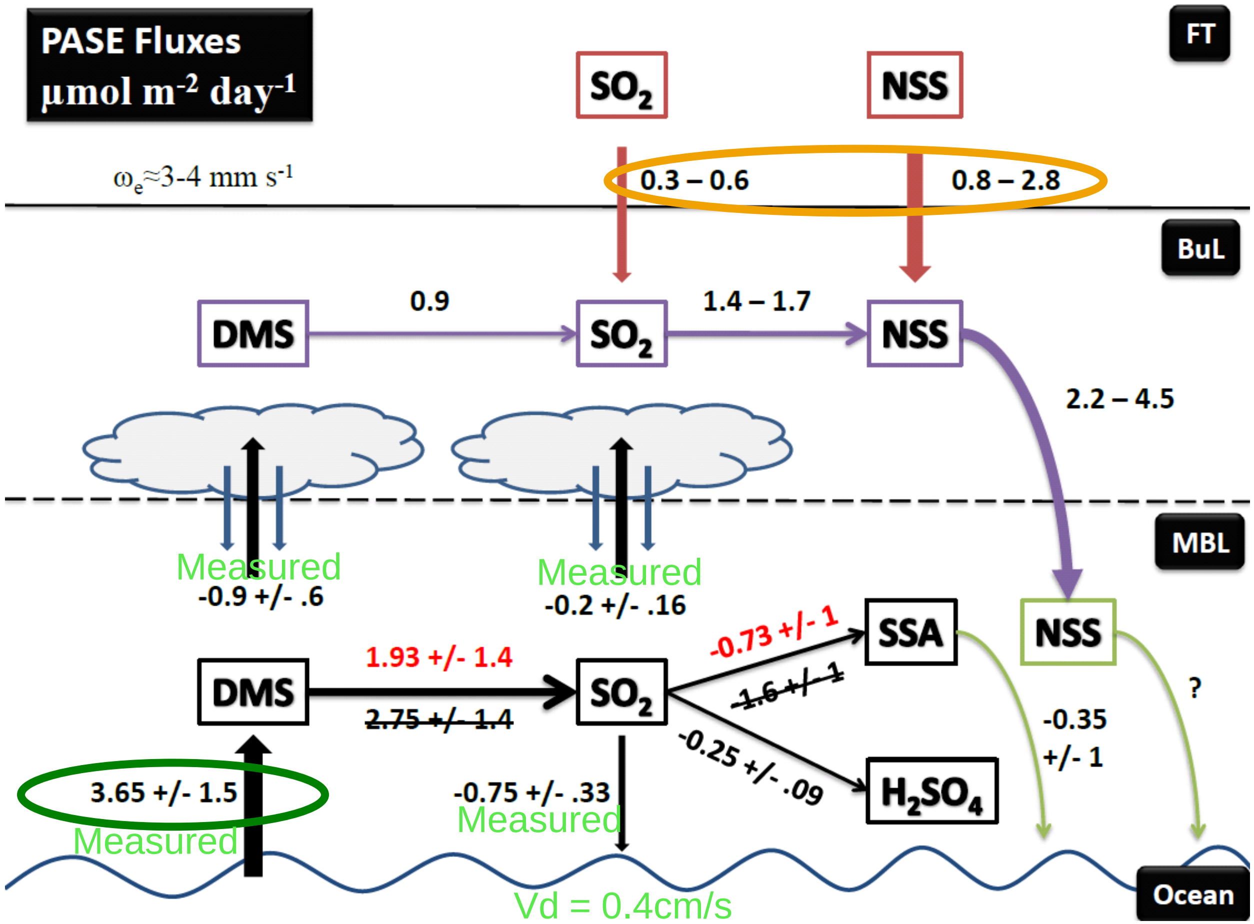
Oct/Nov Average:
$[OH] = 1.5 \times 10^{-6}\ cm^{-3}$

Noontime Peak:
$[OH] = 5 \times 10^{-6}\ cm^{-3}$



Yang, Blomquist, Huebert (2009), *Atmos. Chem. Phys., 9, 9225-9236.*

2. Natural vs LRT Sulfur Fluxes to Remote Regions – Sulfur Budget From PASE – Pollution vs Natural Sulfur?



PASE Average:

Poll'n S ≅ DMS S

Intermittent ≅ Continuous

What about VOCALS?

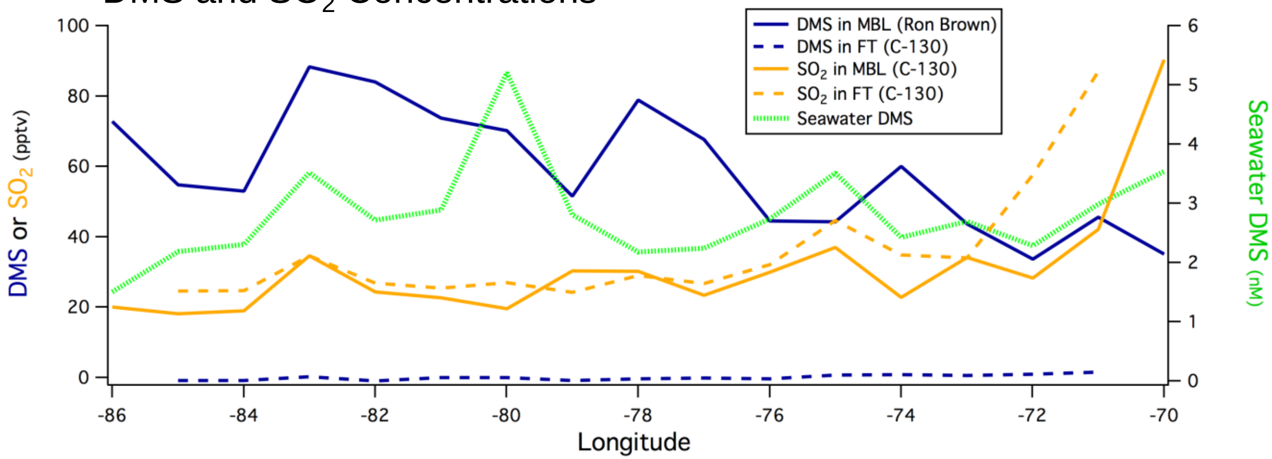
R. Simpson MS Thesis, UH, 2010.

2. Natural vs LRT Sulfur Fluxes to Remote Regions

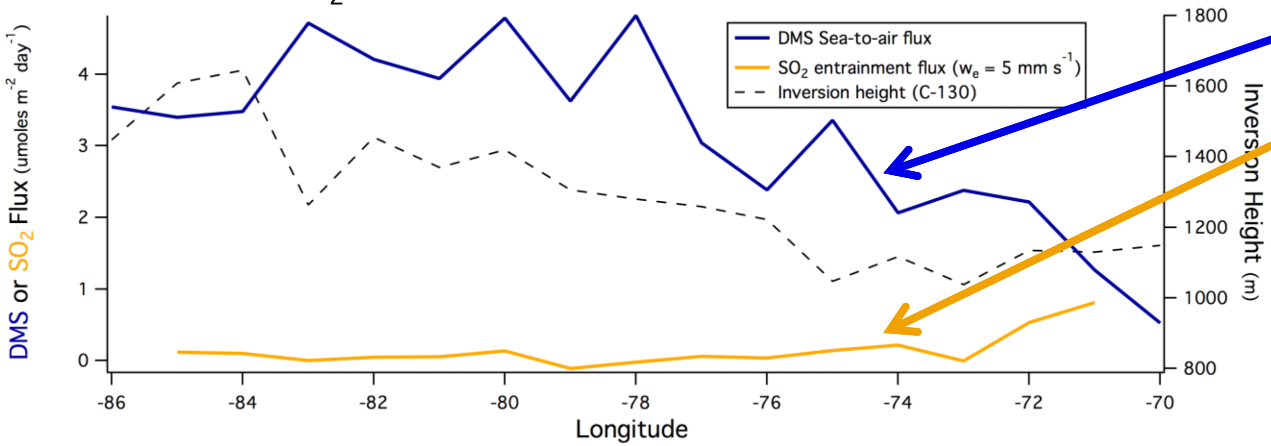
What was the Main Sulfur Source for nss-Aerosols during VOCALS?

Zonal Averages along 20° S (except RF-14 from the C-130)

DMS and SO_2 Concentrations



DMS and SO_2 Fluxes



Away from the coast,

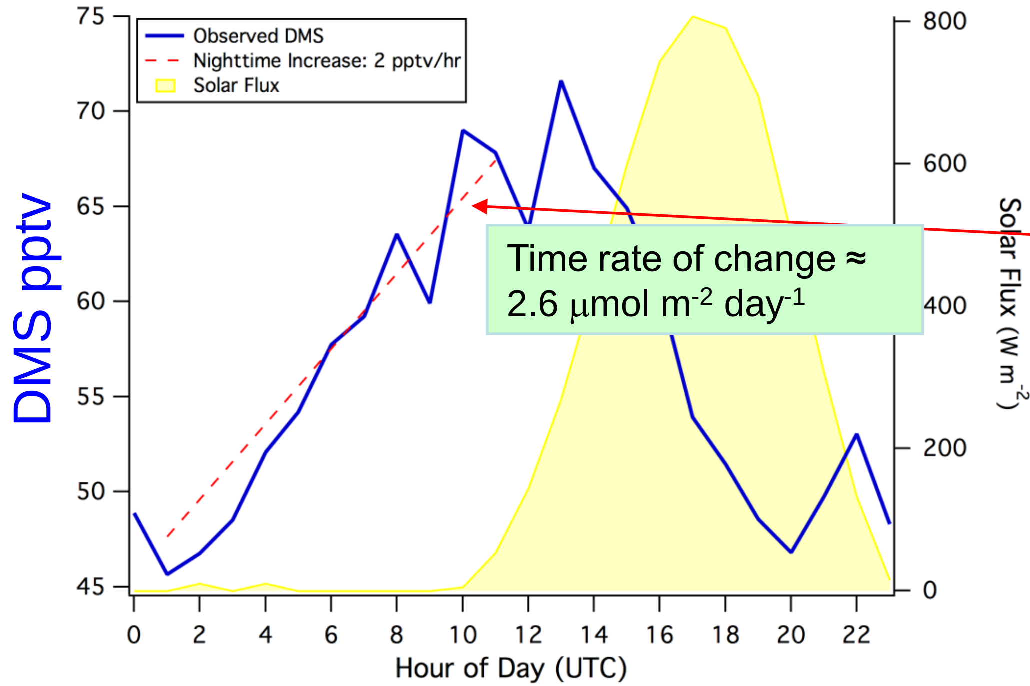
DMS Sea-to-air flux
>>
SO_2 entrainment flux

On average anthropogenic SO_2 had virtually no impact on off-shore MBL Sulfur

Yang, MX, PhD Dissertation, Dept Oceanography, UHawaii, 2010.

3. Atmospheric Dynamics / Entrainment Velocities

DMS showed a Clear Diurnal Cycle
- allowing us to estimate entrainment velocity (ω_e)



VOCALS-average DMS shows a clear diurnal cycle, with maximum just after sunrise (built up from air-sea exchange) and minimum just before sunset (OH oxidation)

Horizontal advection small

No chemical production

Nighttime oxidation small

$$\frac{\partial\langle\bar{S}\rangle}{\partial t} + \langle\bar{u}\rangle\frac{\partial\langle\bar{S}\rangle}{\partial x} - F_0 + F_{z_i} = \langle P\rangle - \langle L\rangle$$

Sea-to-air flux measured by EC ≈ 3.3 μmol m^{-2} day^{-1}

Entrainment flux ≈ (3.3 - 2.6) = 0.7 μmol m^{-2} day^{-1}

No DMS above the inversion

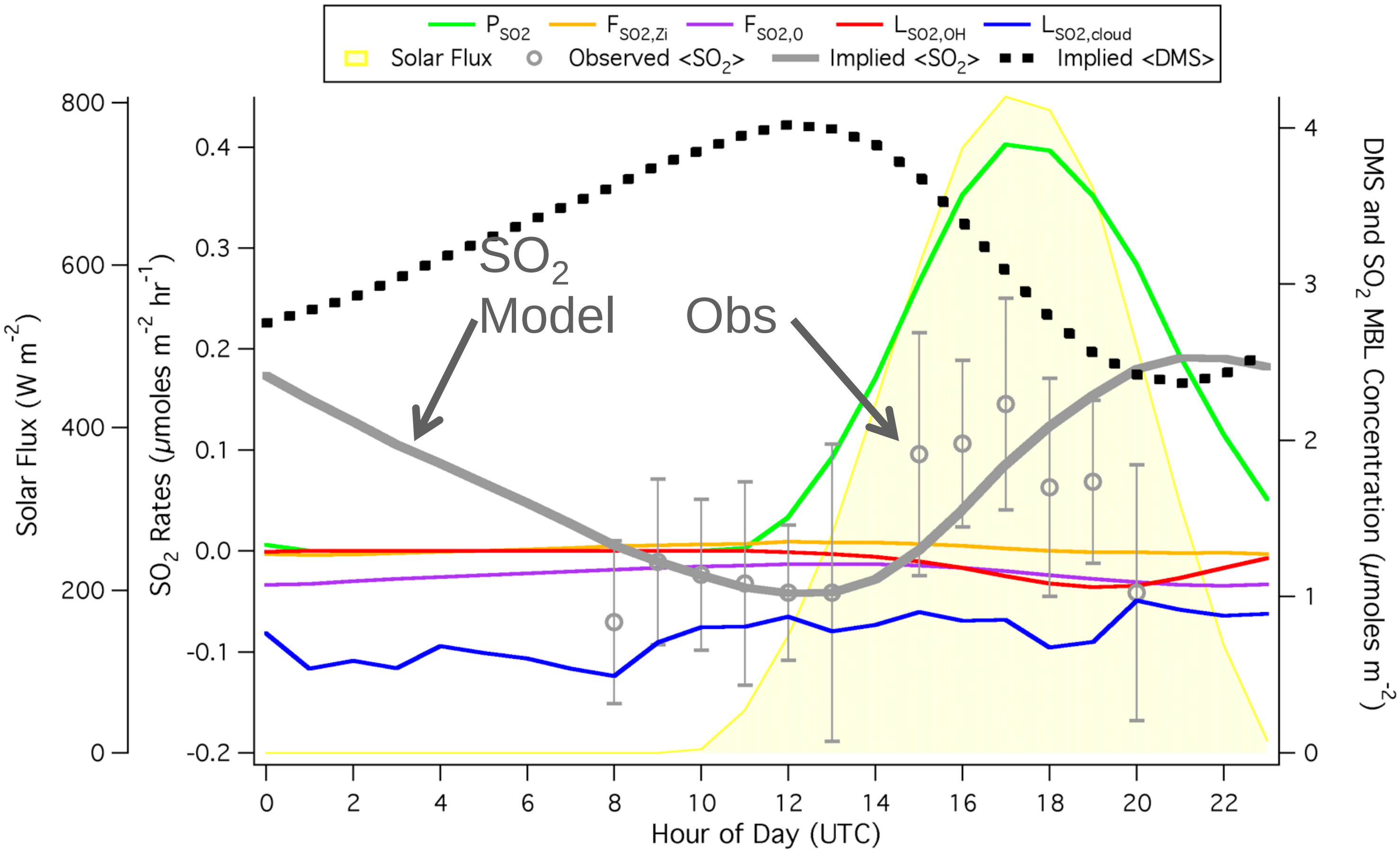
$$F_{z_i} = \omega_e\{[DMS_{z_i^-}] - [DMS_{z_i^+}]\}$$

ω_e ≈ 5 mm sec^{-1}

(agrees well with Wood and Bretherton 2004; Caldwell et al. 2005)

Yang, Blomquist, Huebert (2009), *Atmos. Chem. Phys., 9, 9225-9236.*

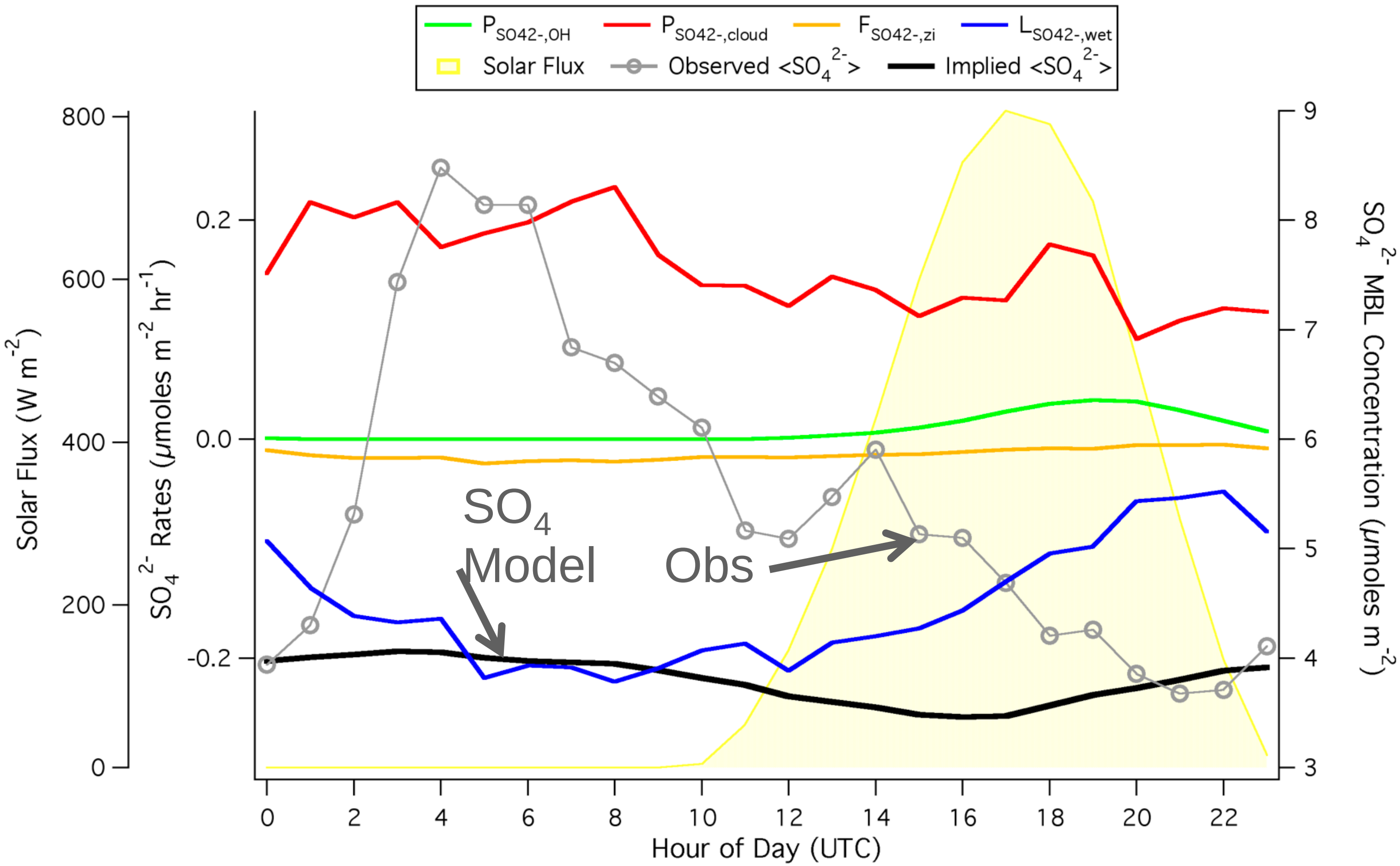
Atmospheric Chemistry helps Constrain Dynamics



SO_2: Model and Obs fit pretty well.

Implied SO_2 diel cycle, with oxidation from DMS being the principal source and in-cloud oxidation as the main sink. The implied cycle agrees well with observations until 1500 UTC, with measurements in the subsequent hours likely subject to greater spatial bias.

Atmospheric Chemistry helps Constrain Dynamics



Sulfate: Not so good

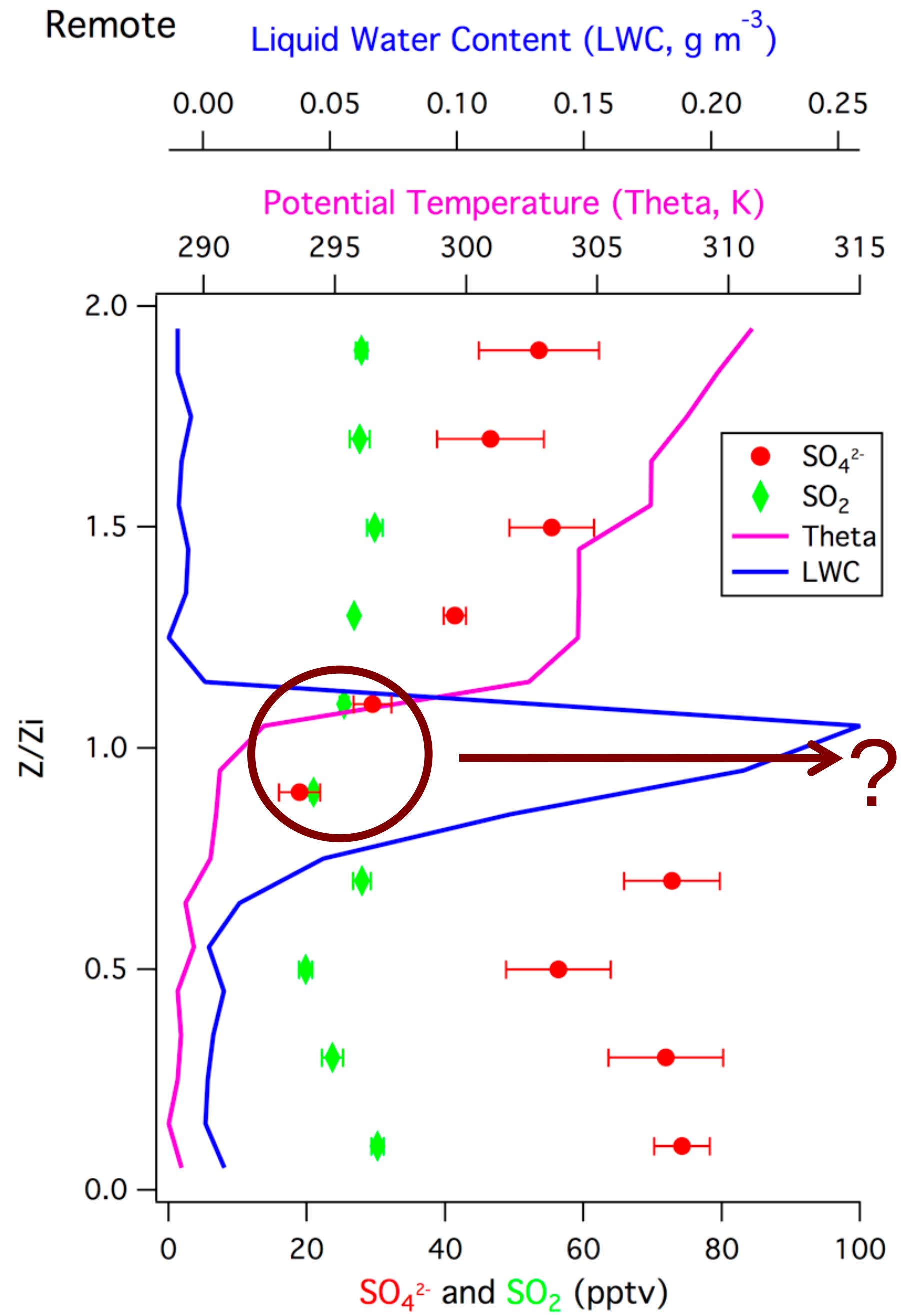
Implied SO_4^{2-} cycle assuming a well-mixed MBL.

The observed diel cycle in SO_4^{2-} is not captured by this calculation.

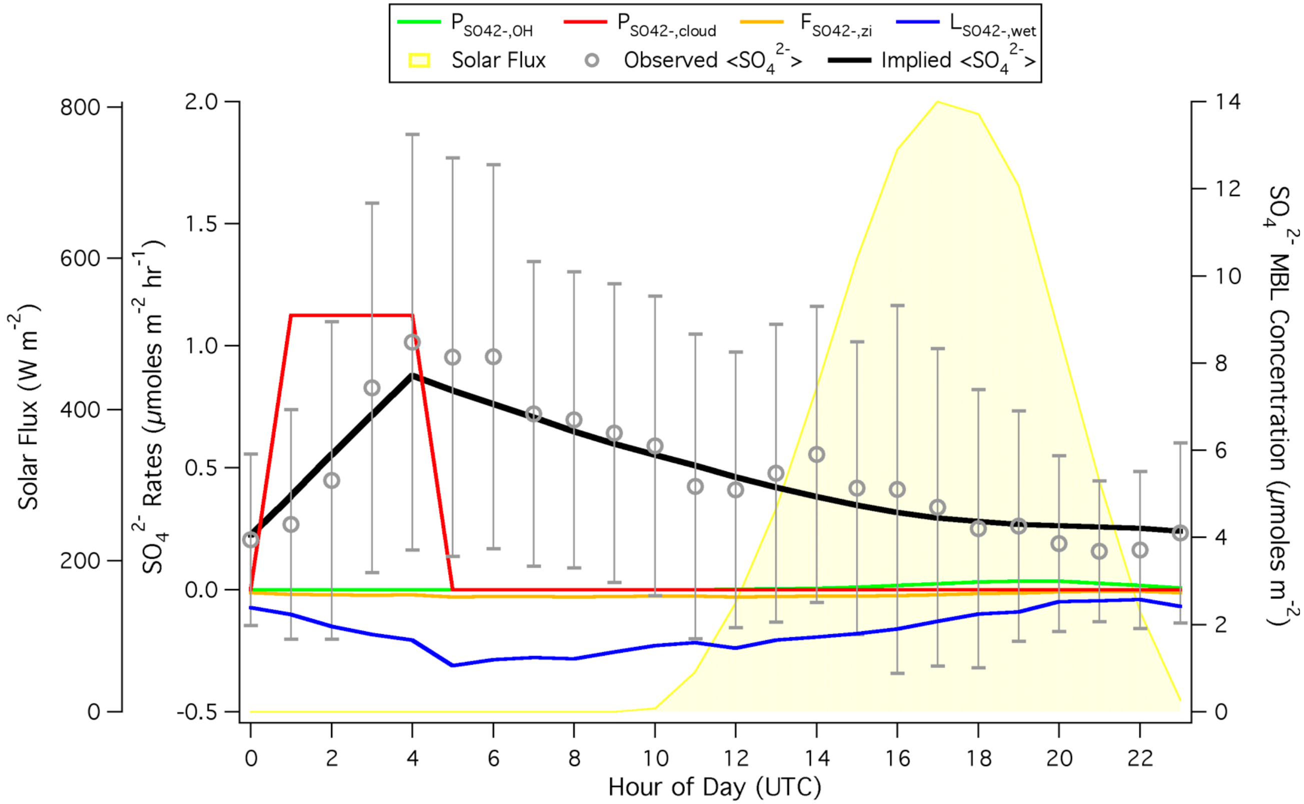
There is virtually no vertical gradient of SO_2, so entrainment won't change its concentration.

$SO_4^=$, however, is being produced in cloud. It does not show up as aerosol in this profile because nearly all the BuL sulfate is tied up in cloud droplets.

Does that BuL/cloud sulfate mix downward continuously?



Atmospheric Chemistry helps Constrain Dynamics

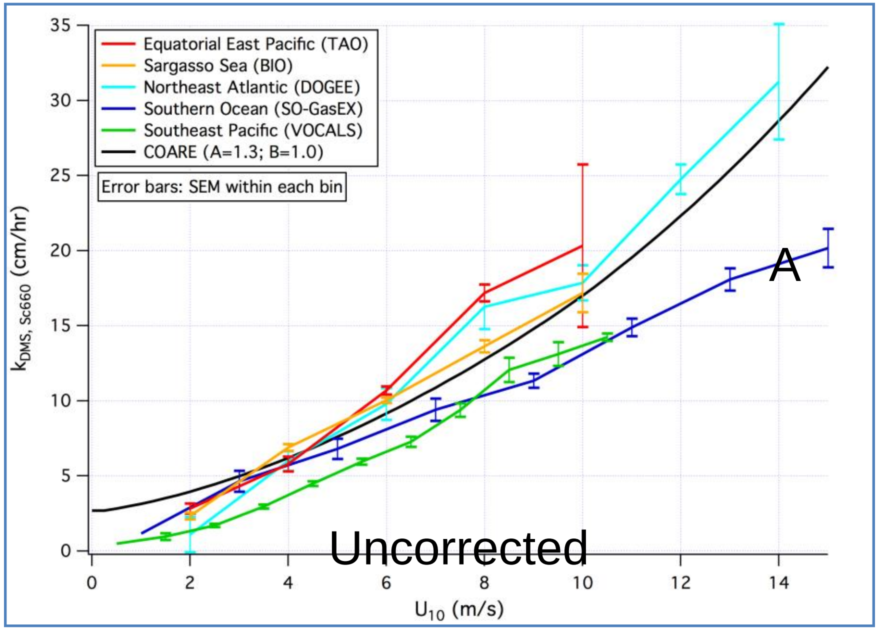


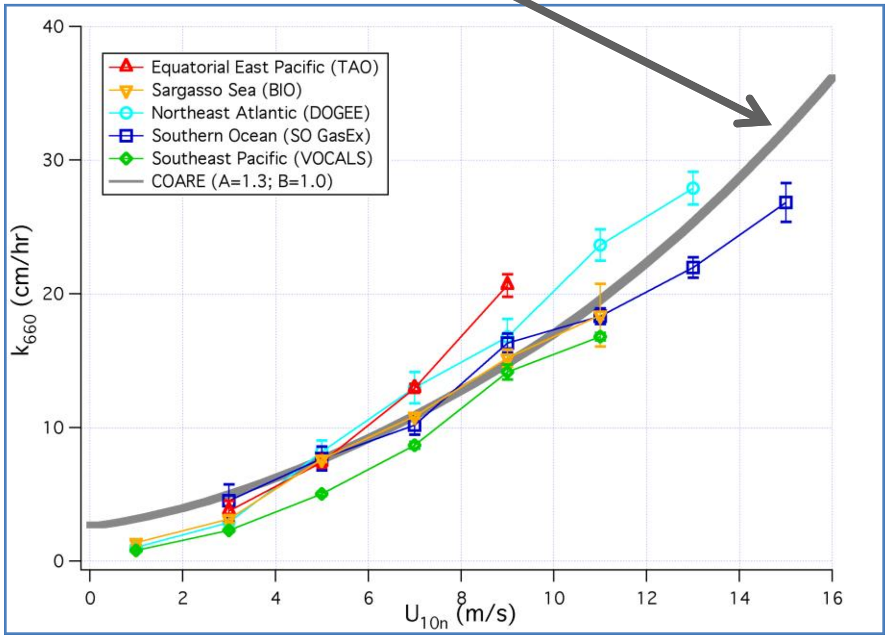
Sulfate with Post-sunset Re-coupling: Not bad

Implied SO_4^{2-} cycle assuming a well-mixed MBL at night and decoupled MBL during the day. SO_4^{2-} produced in-cloud is summed over the entire day and only added to the MBL budget over the first four hours after sunset as the MBL re-couples. The implied cycle qualitatively agrees with shipboard.

4. Physics of Air-Sea Gas Exchange – DMS Observations

Our five k_{DMS} data sets (VOCALS is Green) lie very close to the NOAA-COARE Model Line





k_{660} tends to increase with SST as noted by Marandino et al. (2008)

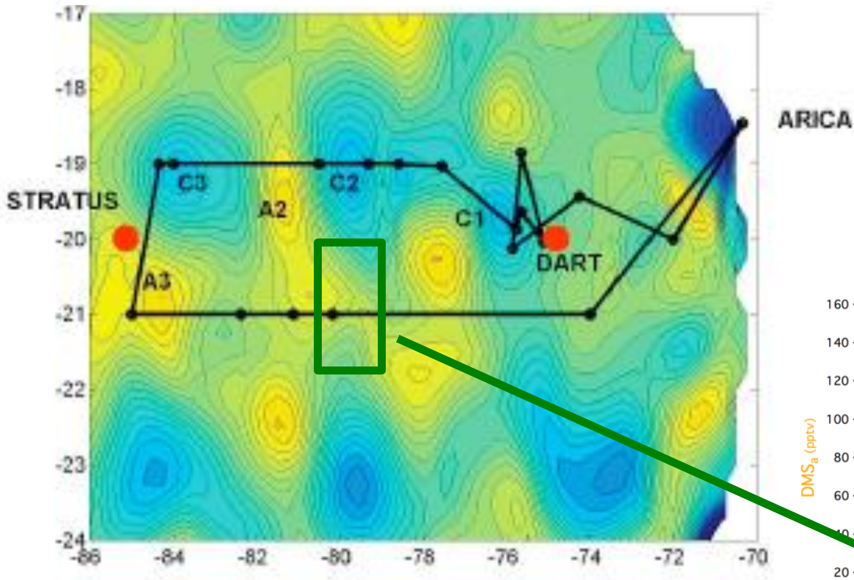
Corrected for:

Atmos Stability, Sc(T),
Solubility(T), Relative wind dir,
DMS_w variation

Yang, et al. (2010), Air-sea Exchange of Dimethylsulfide (DMS) in the Southern Ocean – Measurements from SO GasEx Compared to Temperate and Tropical Regions, SO GasEx Issue, *J. Geophys Res., in revision.*

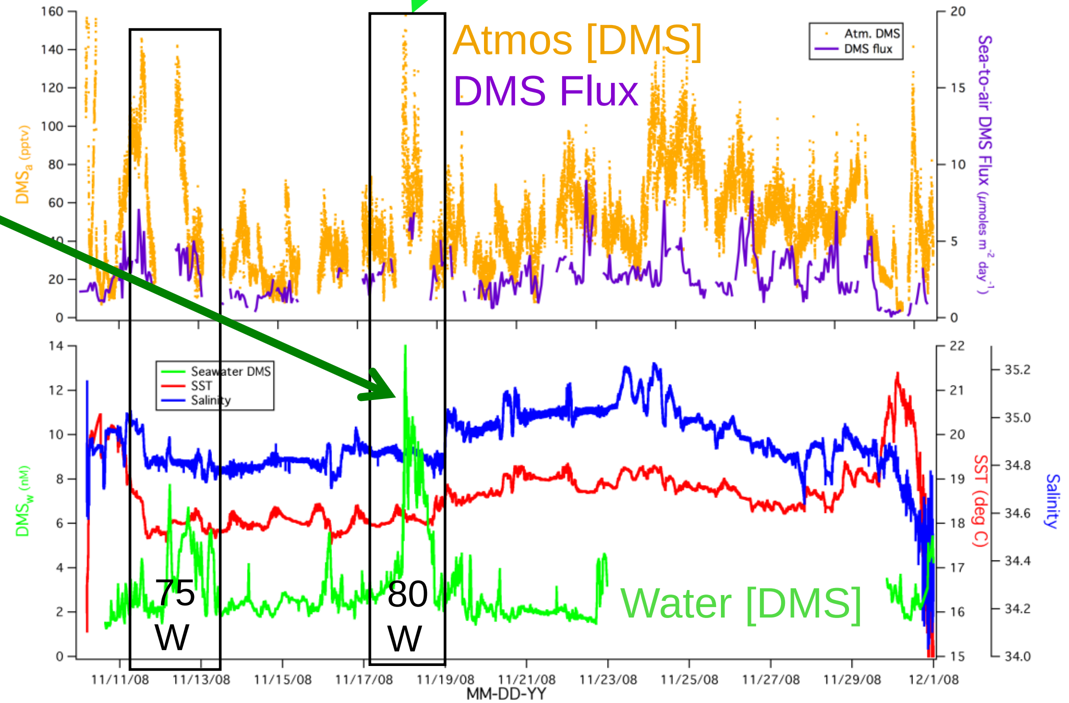
5. Marine Biogeochemistry & the Natural Sulfur Source

Eddies during VOCALS



6-7x spikes in [DMSw]
5-6x spikes in DMS flux
6-7x spikes in [DMSa]

Surprisingly coherent atmospheric variability
[DMSa] not smeared out



Dynamics drive
Bio-Variability which drives
Atmos-Variability –
All on the same scales!

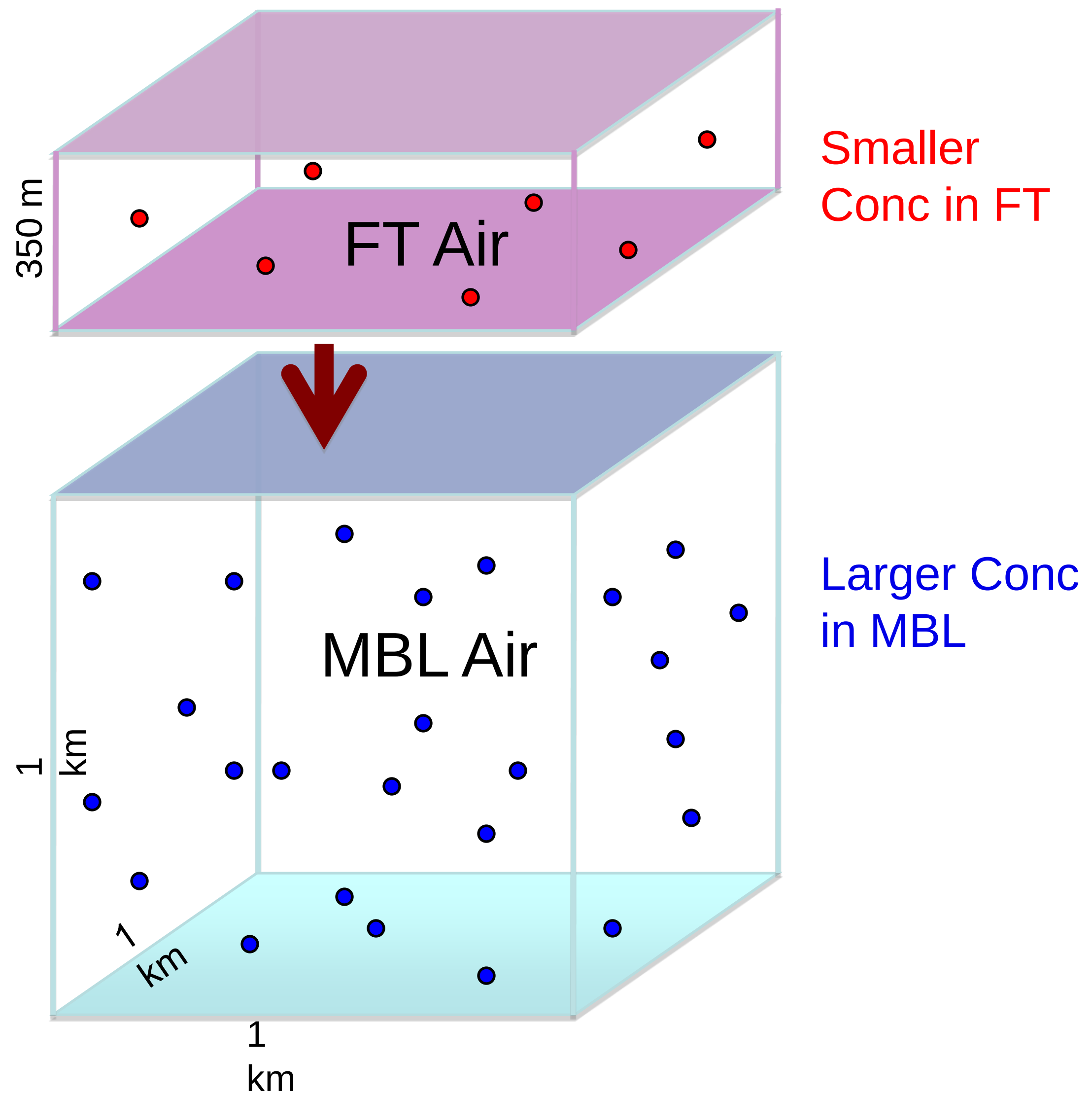
Yang, MX, PhD Dissertation, Dept Oceanography, UHawaii, 2010.

Entrainment of FT Tracers into the MBL

Assume a box of MBL air:
1 km deep and 1 km sides

Assume an entrainment velocity of 4 mm/s

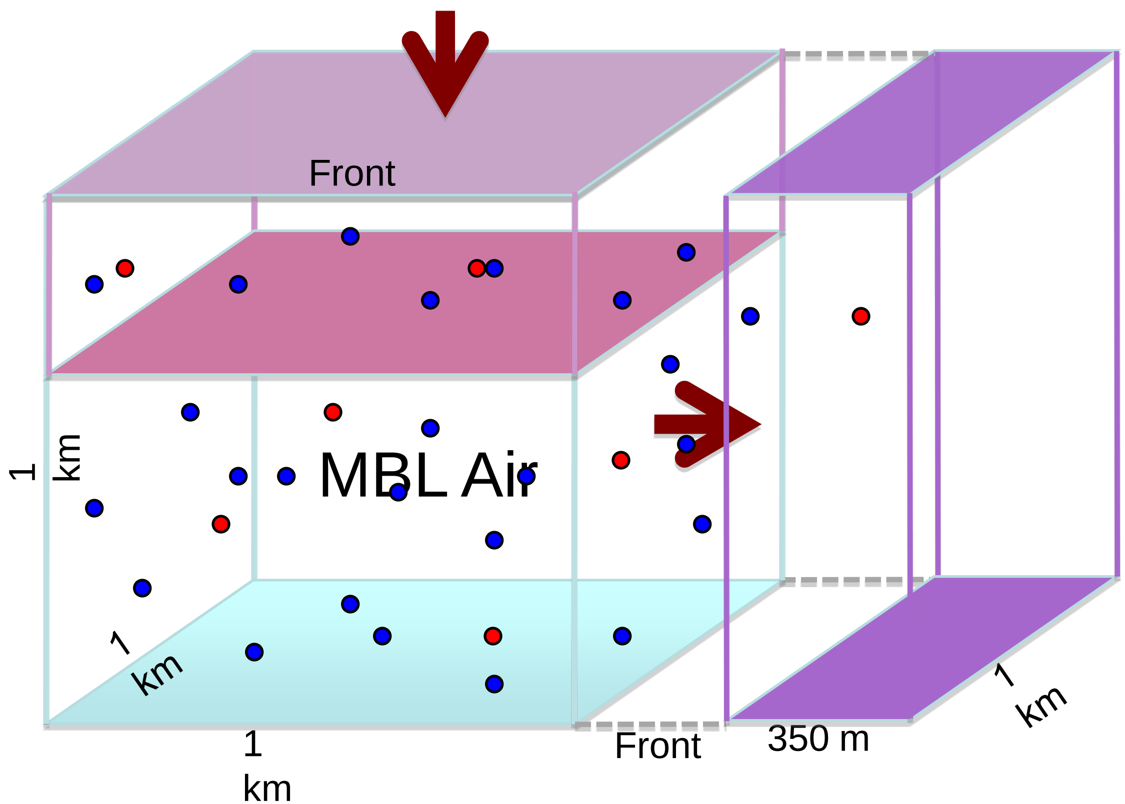
In one day, a 350 m deep layer of FT air will descend into the MBL



Entrainment of FT Air into the MBL

In one day, a 350 m deep layer of FT air will descend into the MBL

That layer of FT air will bring with it all the tracer molecules it contains.
This is a downward flux, independent of the MBL concentration of the tracer.



Entrainment of FT Air and Tracers into the MBL

Trace materials move with the air.

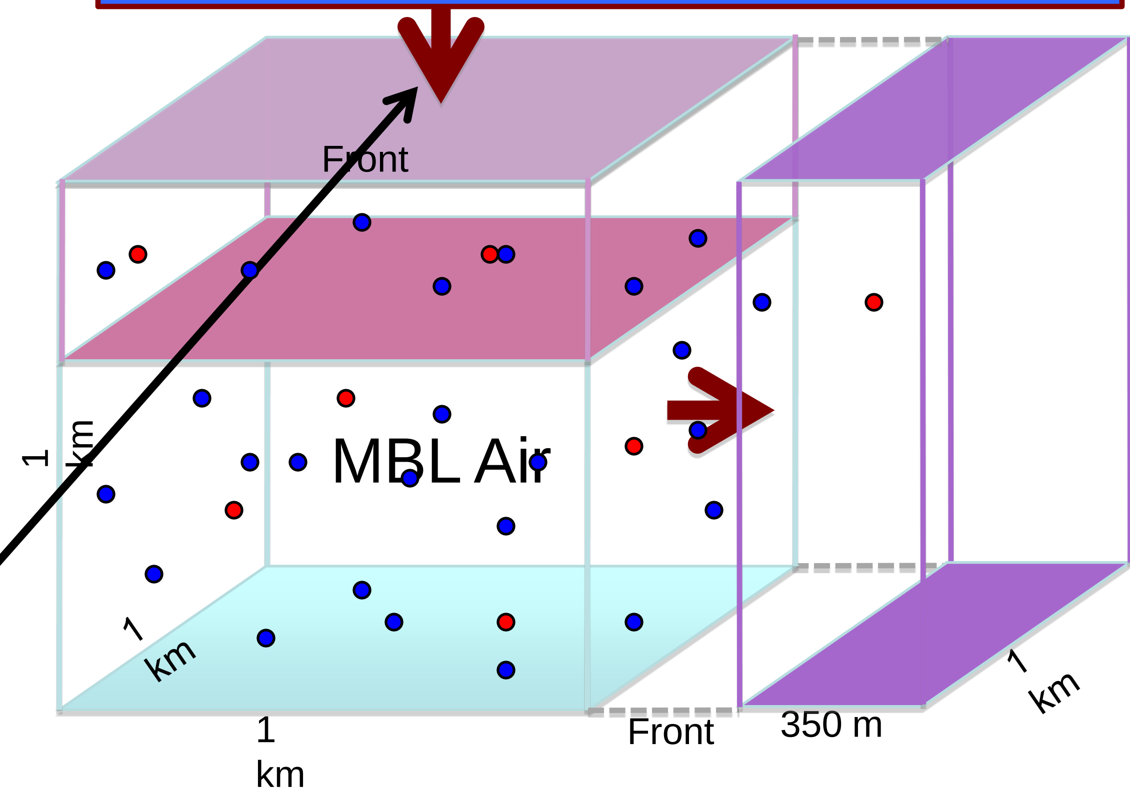
The entrainment tracer flux equals the volume of air times its FT concentration:

$F = V_{Entr}$ [tracer/volume]

The MBL tracer concentration does NOT affect this flux

The Entrainment *Flux* depends only on S_+

Its impact on MBL *Concentrations* depends on (S_+ - S_-)



Summary – EC-Measured Fluxes Clarify:

Atmos Chem Budgets and Ambient Reaction Rates

Natural Sources vs LRT/Pollution Sources

Atmospheric Dynamics & Entrainment Velocities

The Physics of Air-Sea Gas Exchange

Biogeochemical Processes

And

Knowing the functional form (physics) of each process gives us a basis for computing *sensitivities* to each controlling environmental variable.

Thanks to NSF Atmospheric Chemistry for supporting the shipboard flux measurements.