DMS Fluxes and Scales of Variability in the Marine Boundary Layer

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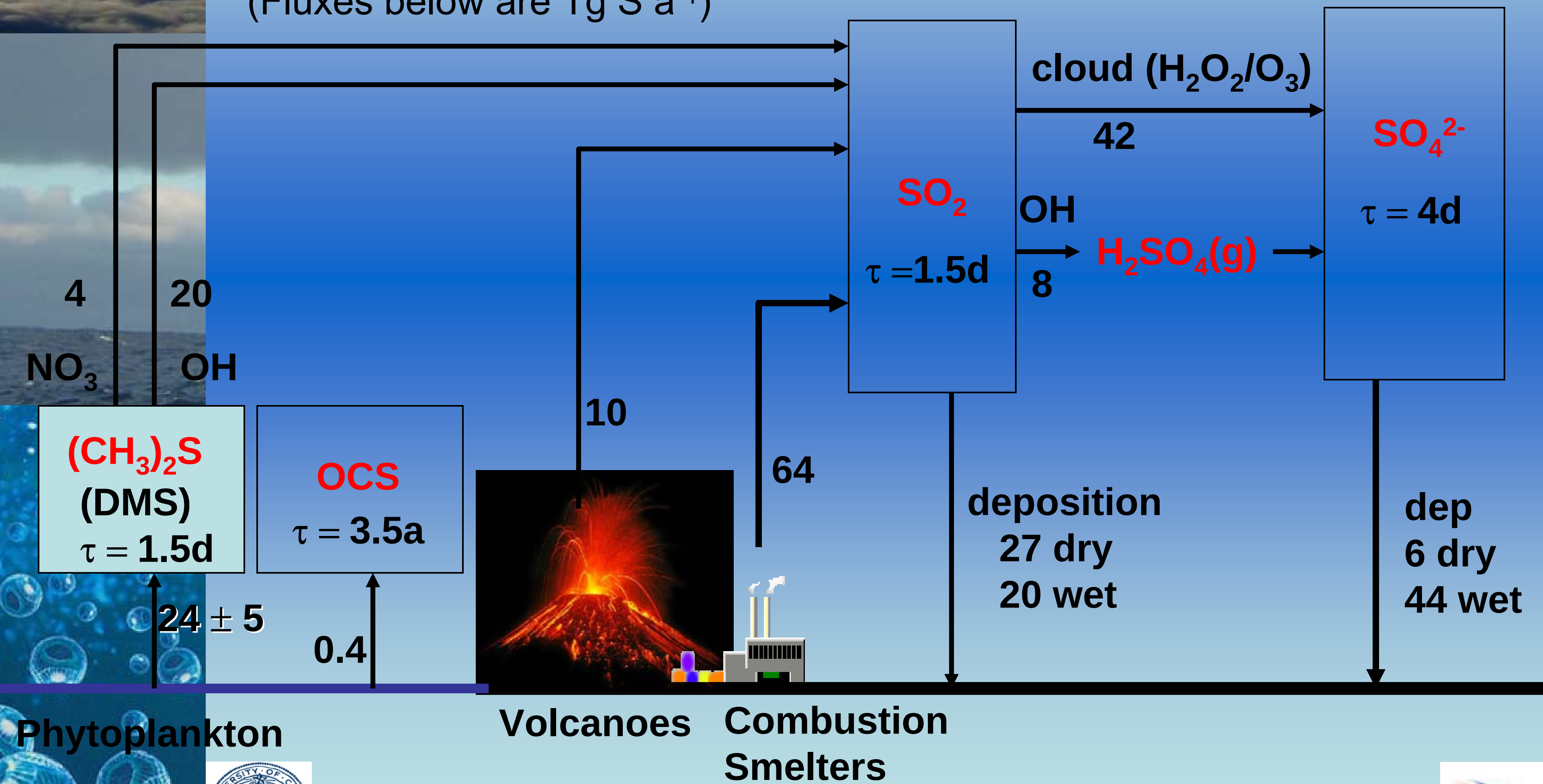
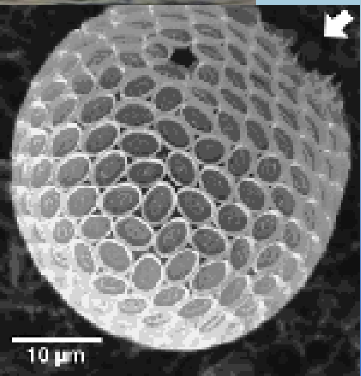
Global Sulfur Budget

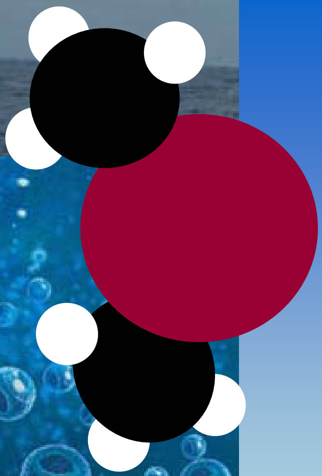
Atmospheric reservoirs:	OCS	5 Tg (0.5 ppb)	DMS	0.1 Tg
	aerosol SO_4	1.7 Tg	H_2S	0.02 Tg
	SO_2	0.3 Tg		

(Fluxes below are Tg S a^{-1})



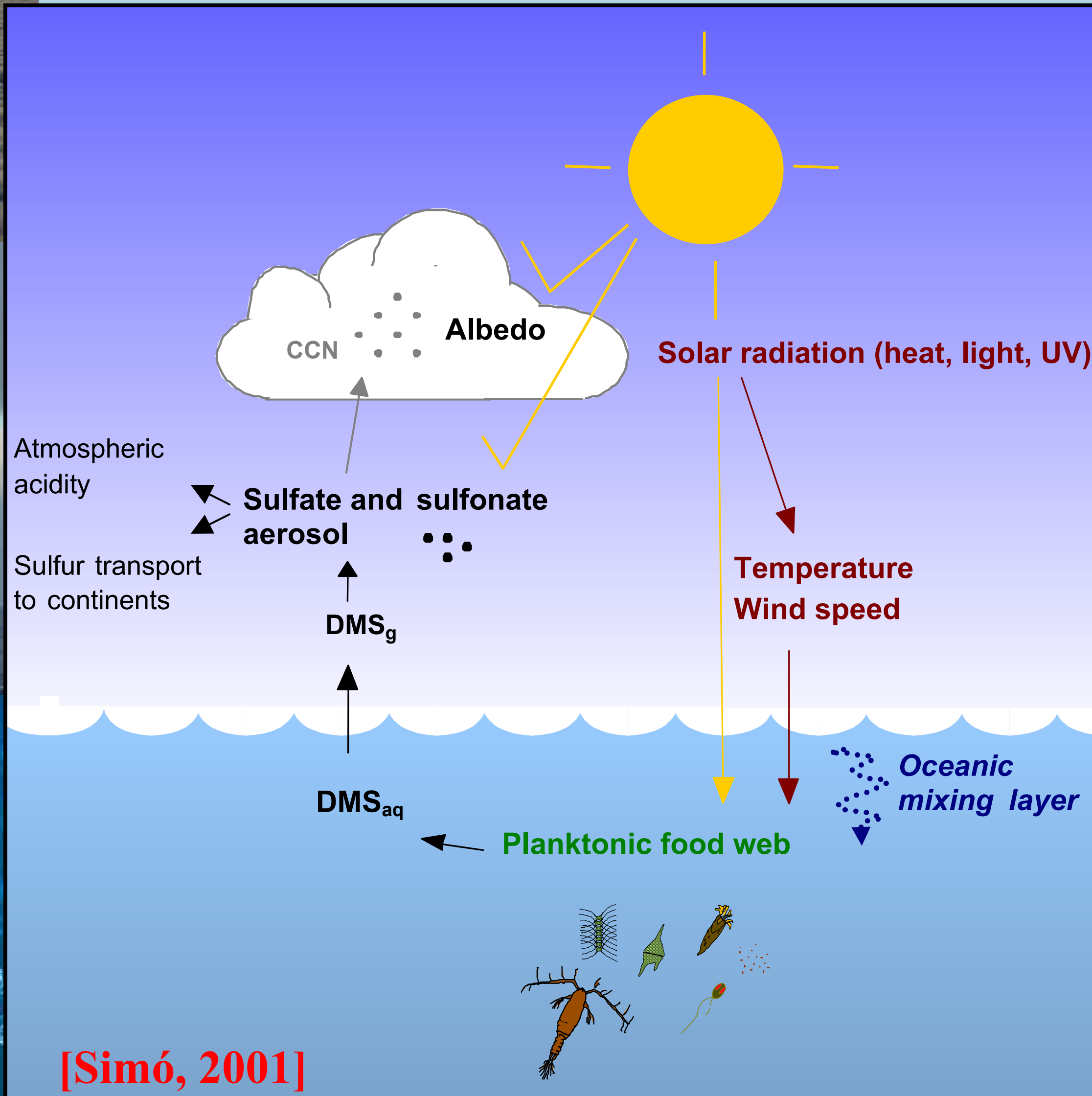
Dimethylsulfide (DMS)





- Important component of Earth’s biogeochemical sulfur cycle: major conduit of S, abundant in the ocean, to terrestrial ecosystems where it is often a limiting nutrient.
- Its metabolic precursor dimethyl sulfonium propionate (DMSP) is a Zwitterionic compound believed to be used in osmotic regulation.
- Only a small fraction of oceanic DMS is released to the atmosphere.
- The principal component of the ‘smell of the sea’, and is thought to be widely supersaturated in seawater.
- Oxidation end products H_2SO_4 & MSA serve as important CCN components ($\tau_{chem} \sim 2$ days).

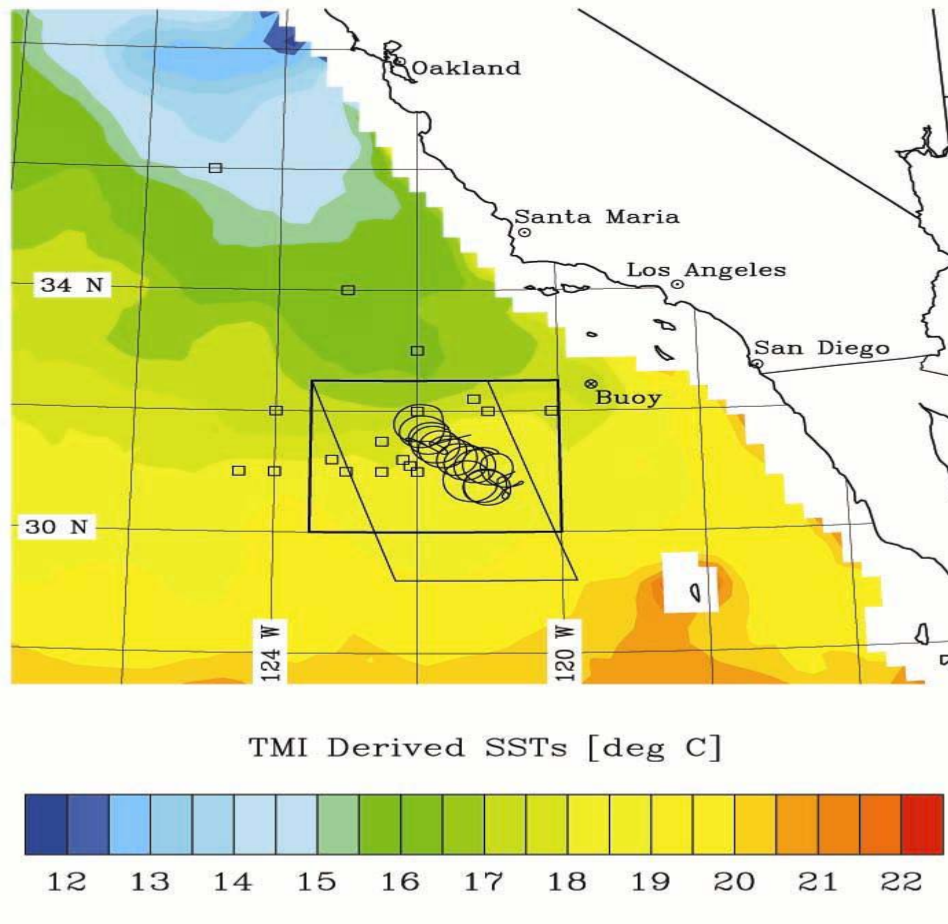
CLAW Hypothesis



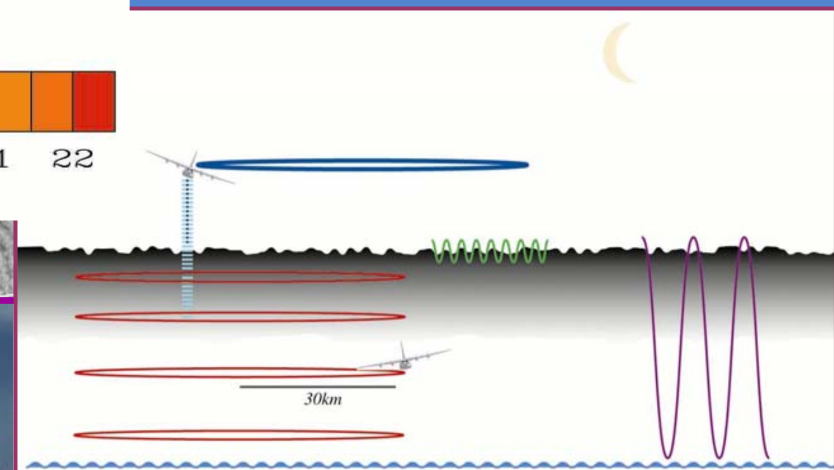
- Estimates of global source vary greatly: 15-109 Tg/yr
- Its precursor dimethyl sulfonium propionate (DMSP) is thought to be important in osmotic regulation (antioxidant).
- Senescence, viral attack, or grazing ⇒ DMSP, enzymatic cleaving ⇒ DMS ⇒ air/sea.
- Oxidation end products H_2SO_4 & MSA serve as important CCN components (τ_{chem} ~ 2 days).

DYCOMS-II

DYNAMICS AND CHEMISTRY OF MARINE STRATOCUMULUS

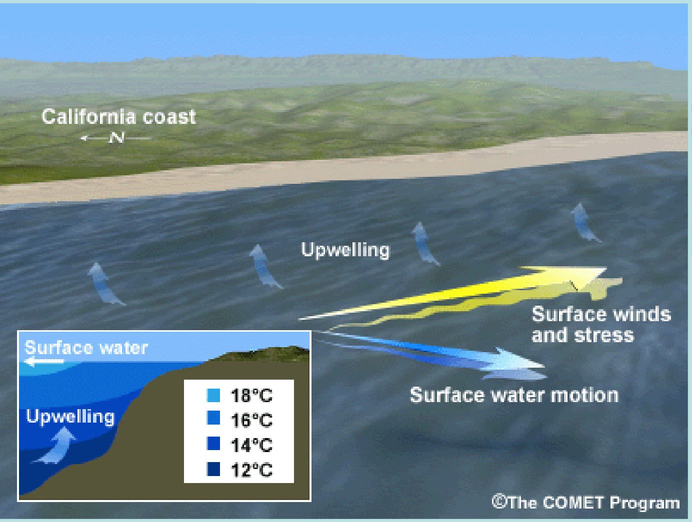


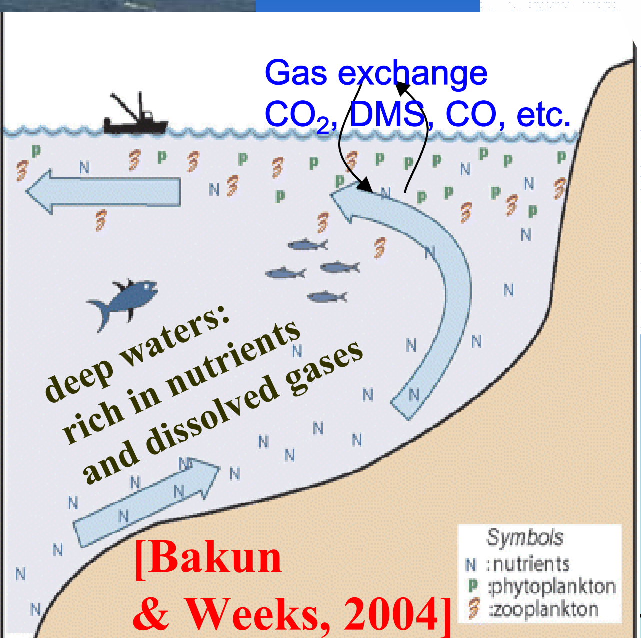
- Fast DMS instrument (Drexel) used to measure flux profiles & entrainment using eddy-covariance
- Direct EC measurements indicate modest and ‘typical’ surface fluxes (~2 μmol m^{-2} d^{-1})
- Scalar budgets of DMS are thwarted by large mesoscale variability encountered

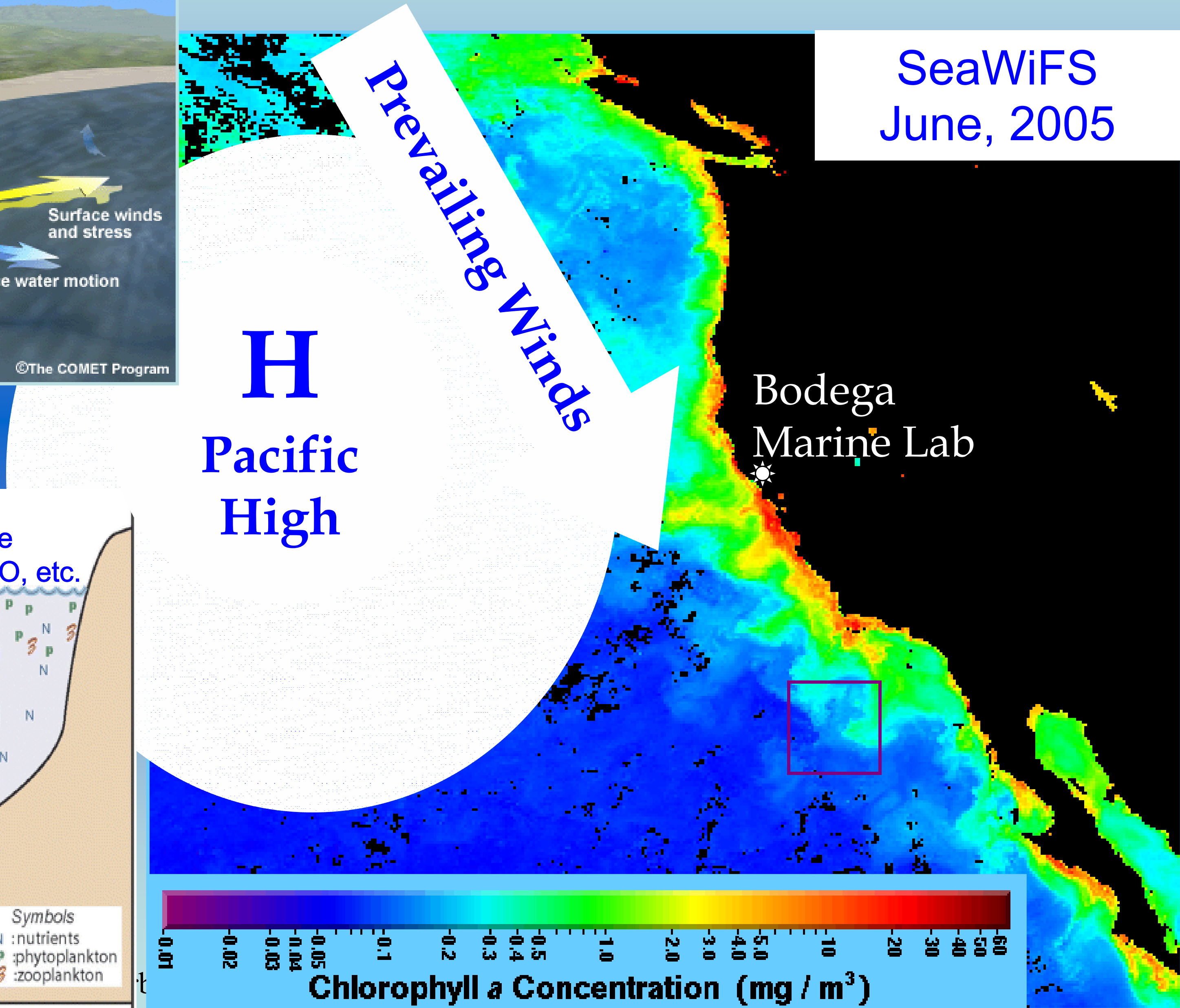


Stevens et al., *BAMS*, **84** (2003)

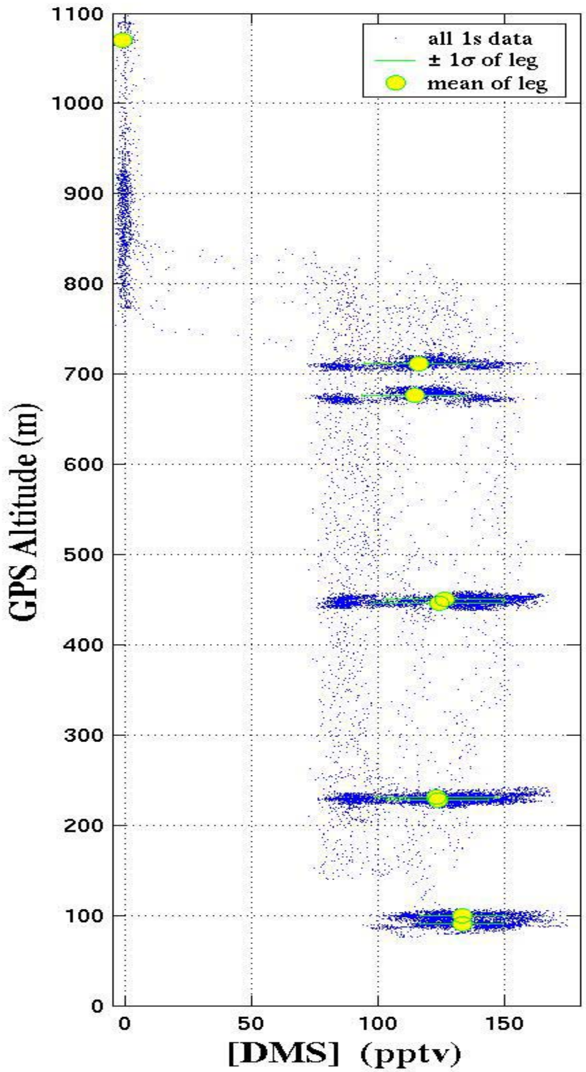
Coastal Biometeorology



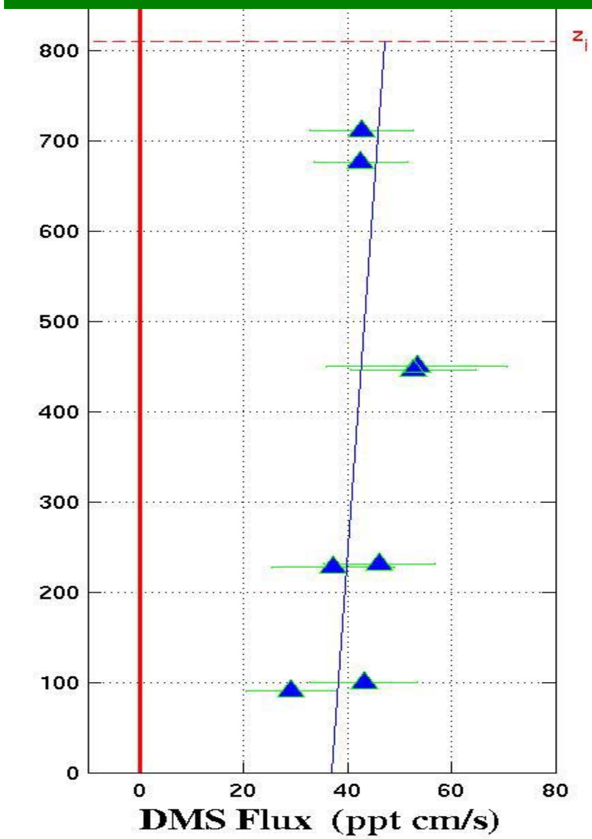




DMS Profiles RF03



$$w_e = \frac{\overline{-w'[DMS]'_{z_i}}}{\Delta^{FT}_{MBL}[DMS]}$$



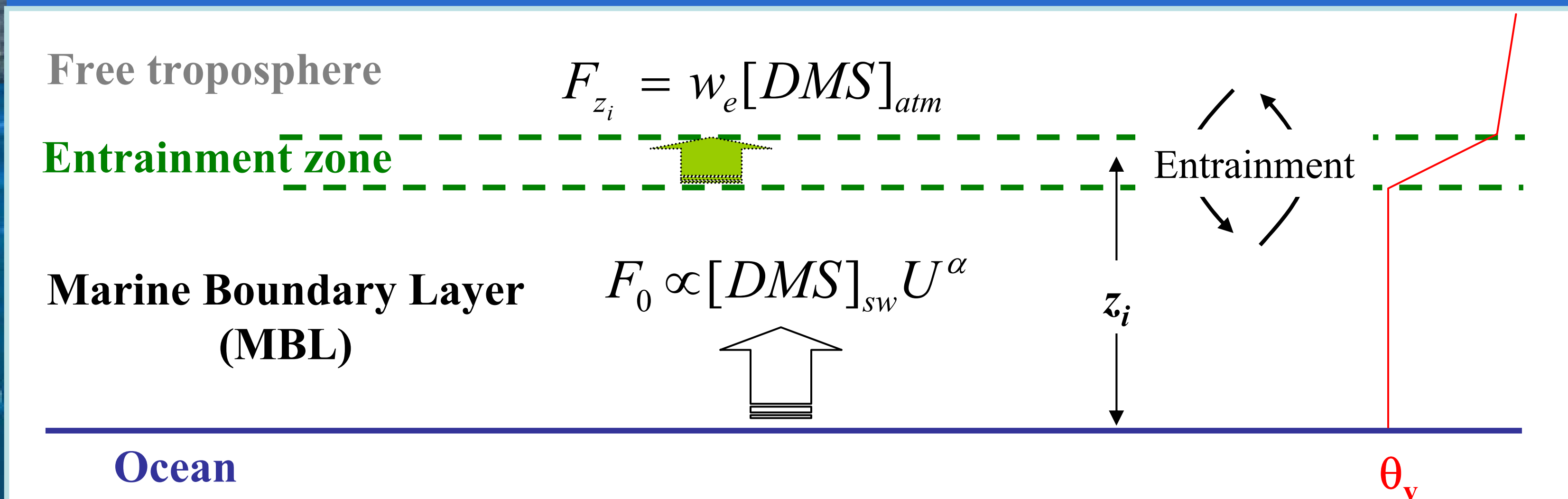
Equilibrium MBL Model

Within a couple of days an equilibrium is expected between a constant surface flux, entrainment dilution, and photochemical destruction:

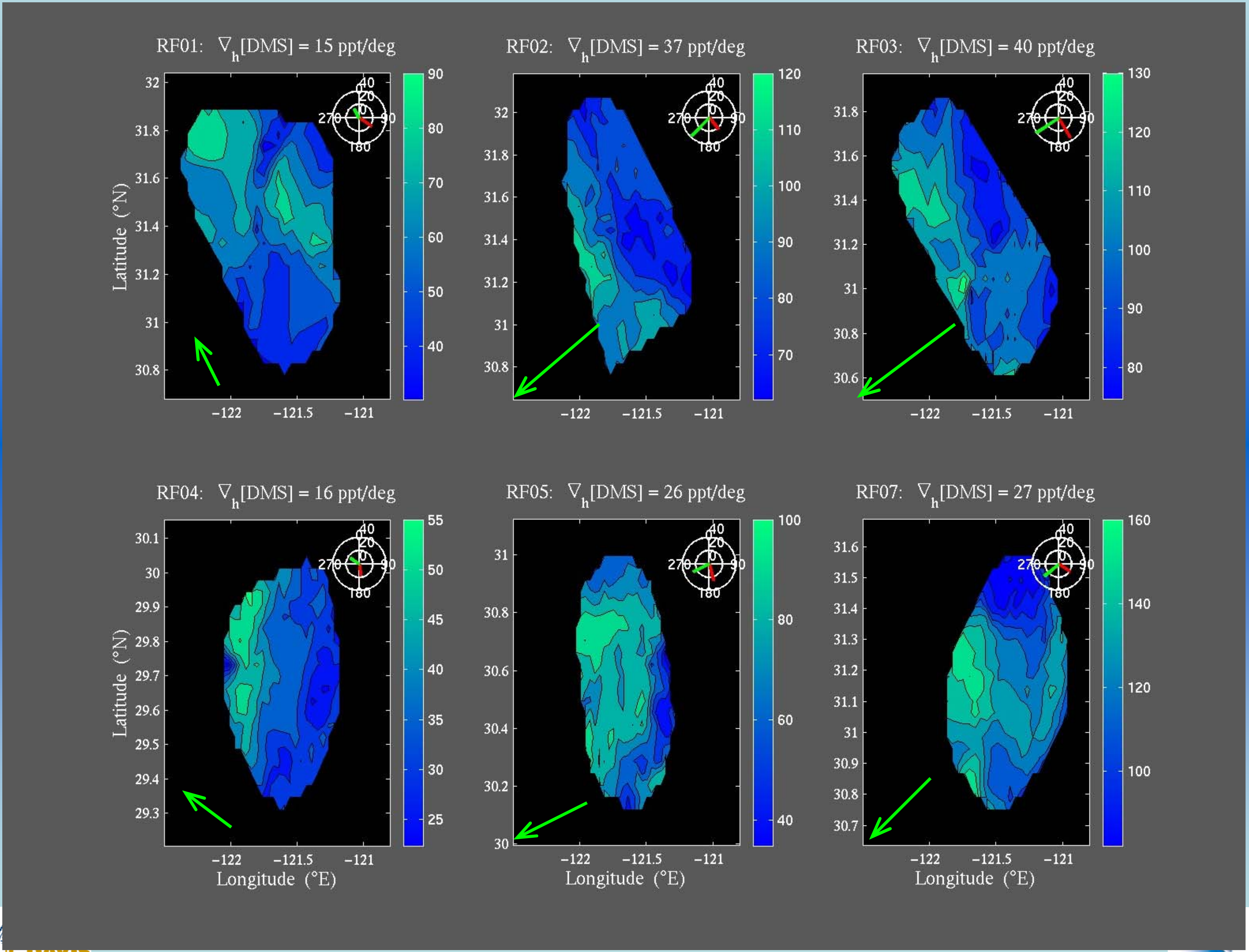
$$\frac{d[DMS]}{dt} = \frac{F_0 - w_e[DMS]_{eq}}{z_i} - \frac{[DMS]_{eq}}{\tau_{chem}} \cong 0$$

$$[DMS]_{eq} = \frac{F_0}{w_e + z_i / \tau_{chem}}$$

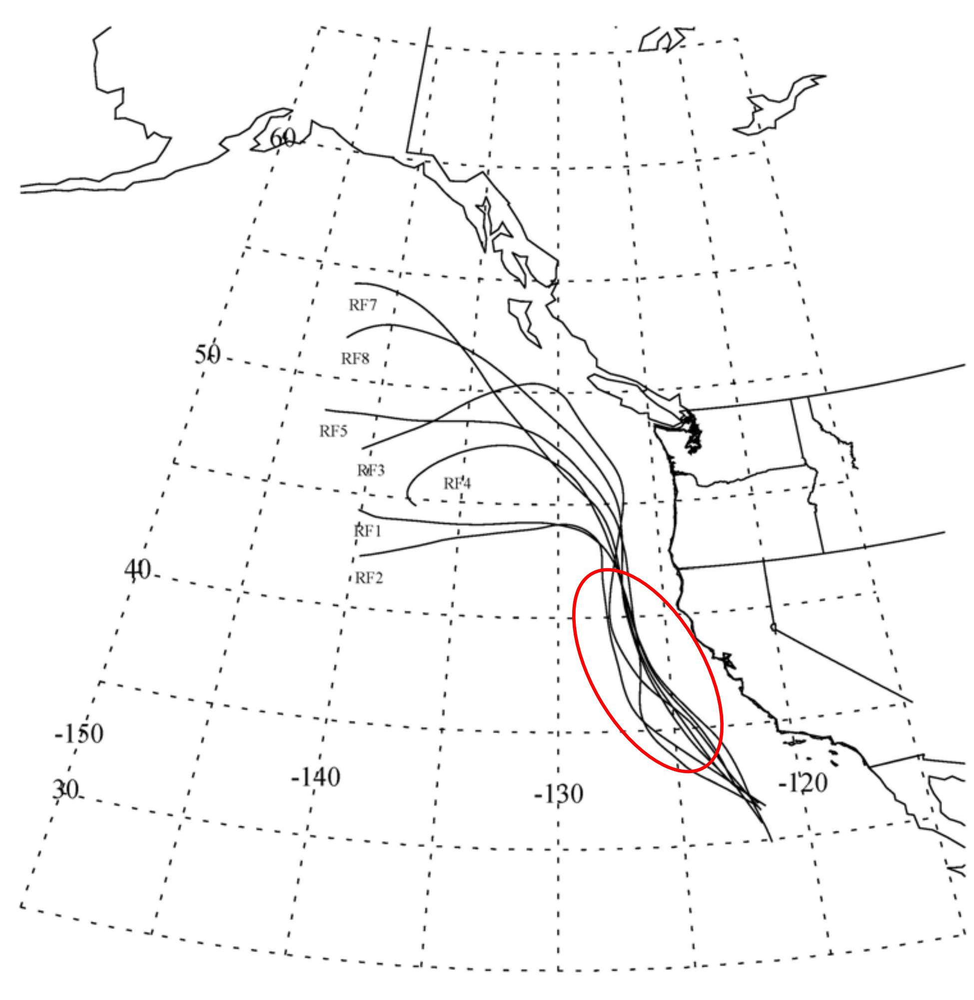
$F_0 = 2\ \mu mol\ m^{-2}\ d^{-1}$, $w_e = .005\ m\ s^{-1}$,
$z_i = 750\ m$, $\tau_{chem} = 40\ hr$ $\Rightarrow$ $[DMS]_{eq} \cong 50\ ppt$



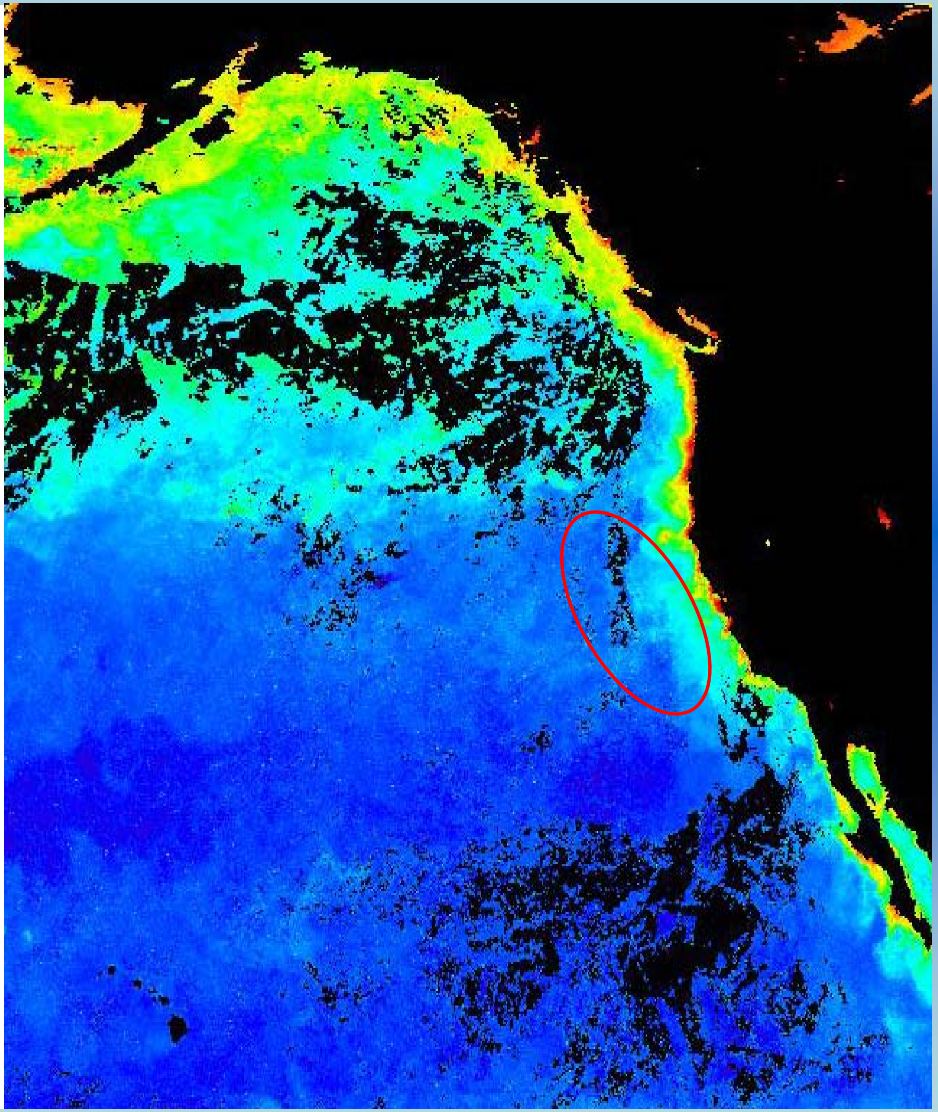
DMS Gradients



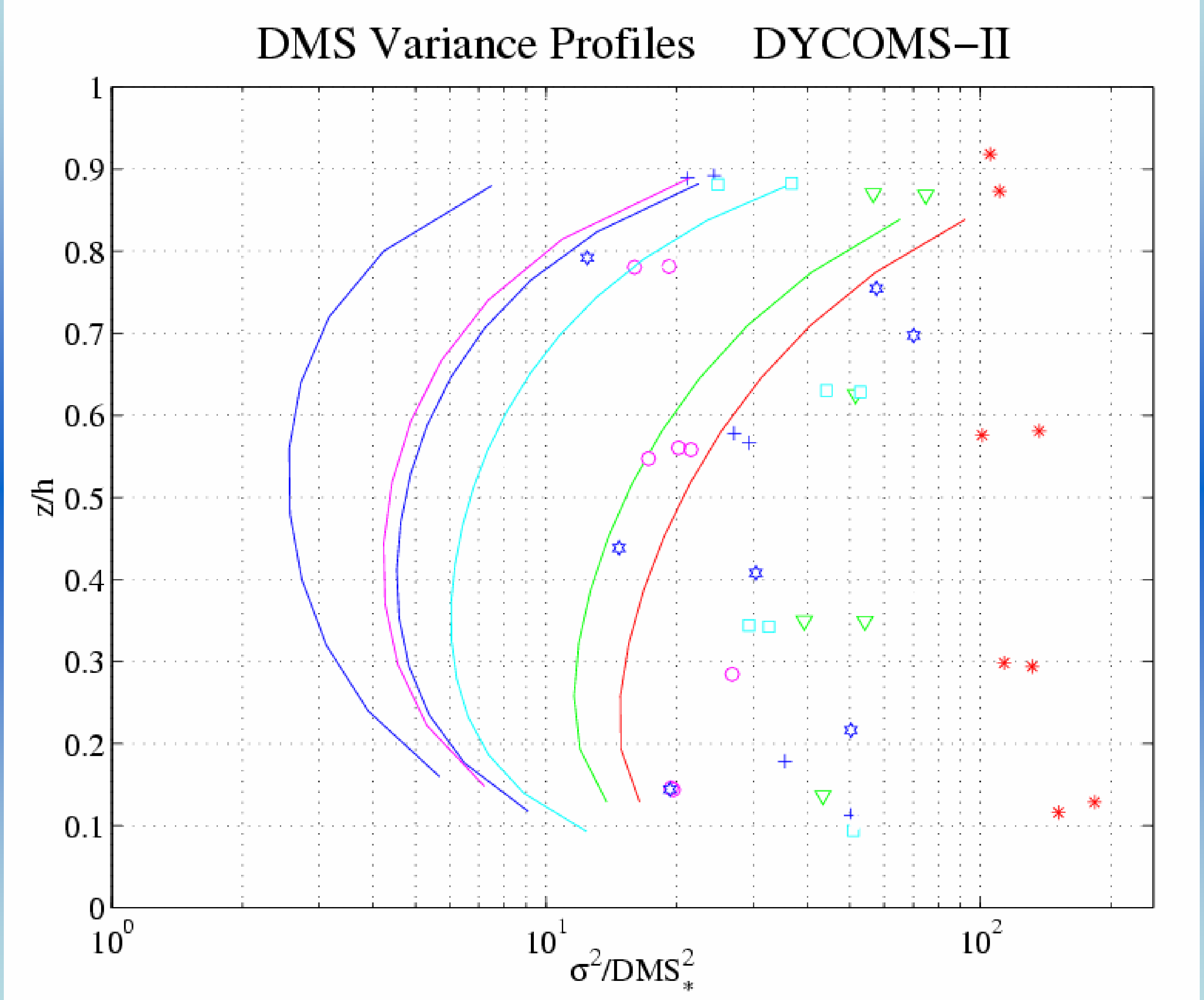
Upstream Source



HYSPLIT4 3D backtrajectories



Extra PBL Variance



Importance/Evidence of Extra Variance

'Variance technique' for estimating surface fluxes (from observed σ^2, a surface flux can be inferred from universal similarity relationships)

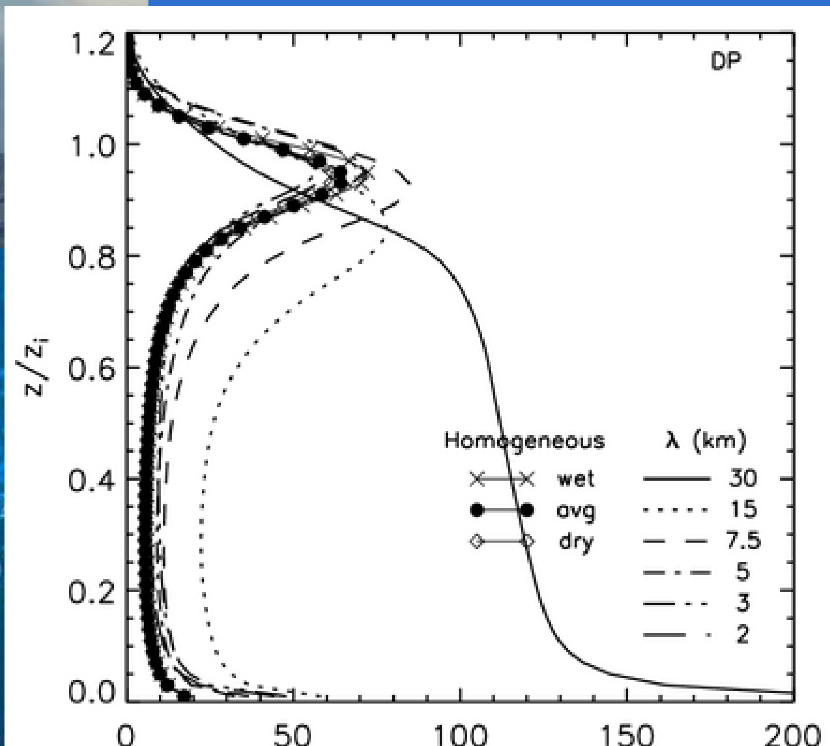
Instrumentalists may mistake atmospheric 'noise' for internal 'noise'.

Relationship (Junge) between trace gas relative variance and atmospheric lifetime.

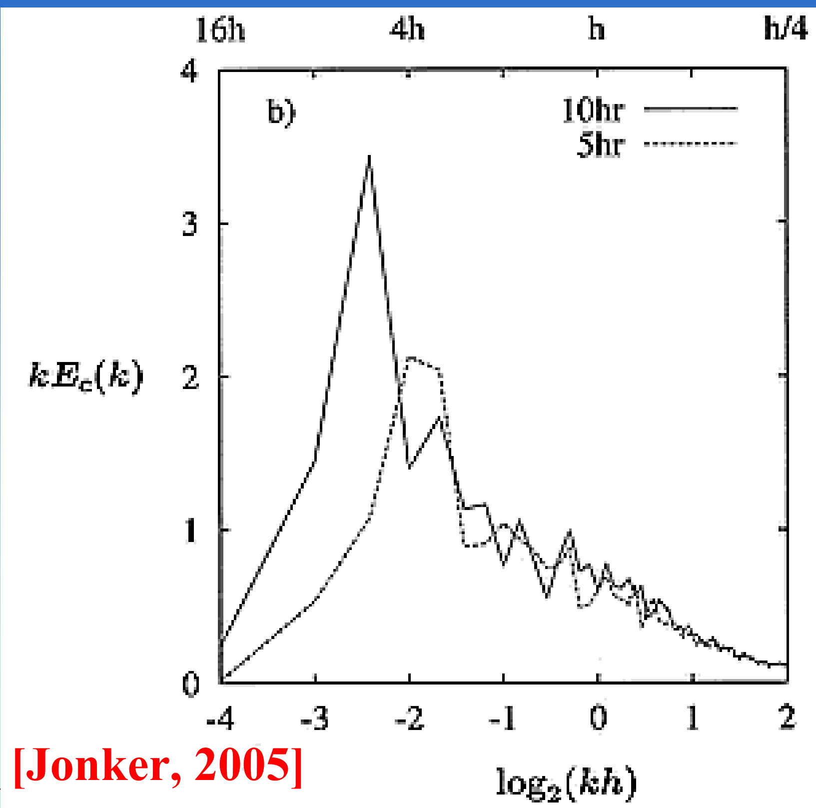
- *Jodwalis & Benner* [JGR, 1996] report DMS fluxes of 21-28 μmol m^{-2} d^{-1} using a variance technique, as opposed to 1-13 μmol m^{-2} d^{-1} [Blomquist et al., 1996] estimated from $[DMS]_{sw}$
- *Lenschow et al.* [JGR, 1999] compared 3 different flux estimation techniques and found the variance to yield the largest
- *Lewis et al.* [ACP, 2005] noted that DMS relative deviations lie well above the Junge curve of other species measured simultaneously.

Source of Variability

- ❖ Variable entrainment
- ❖ Heterogeneous surface sources
- ❖ Internal sources of variance generation (Jonker et al., 2005)



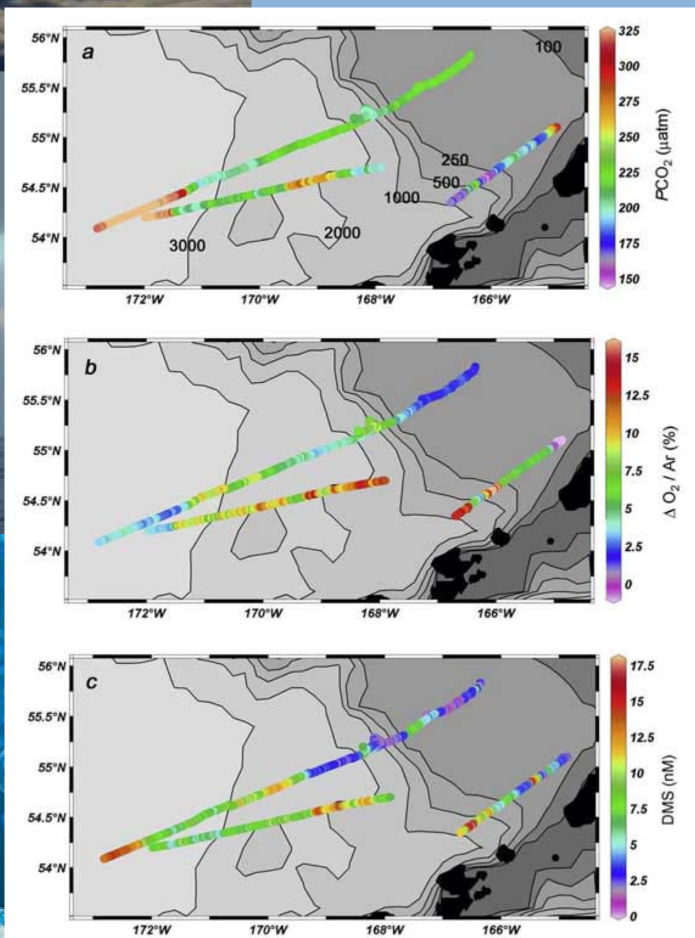
[Patton, 2005]

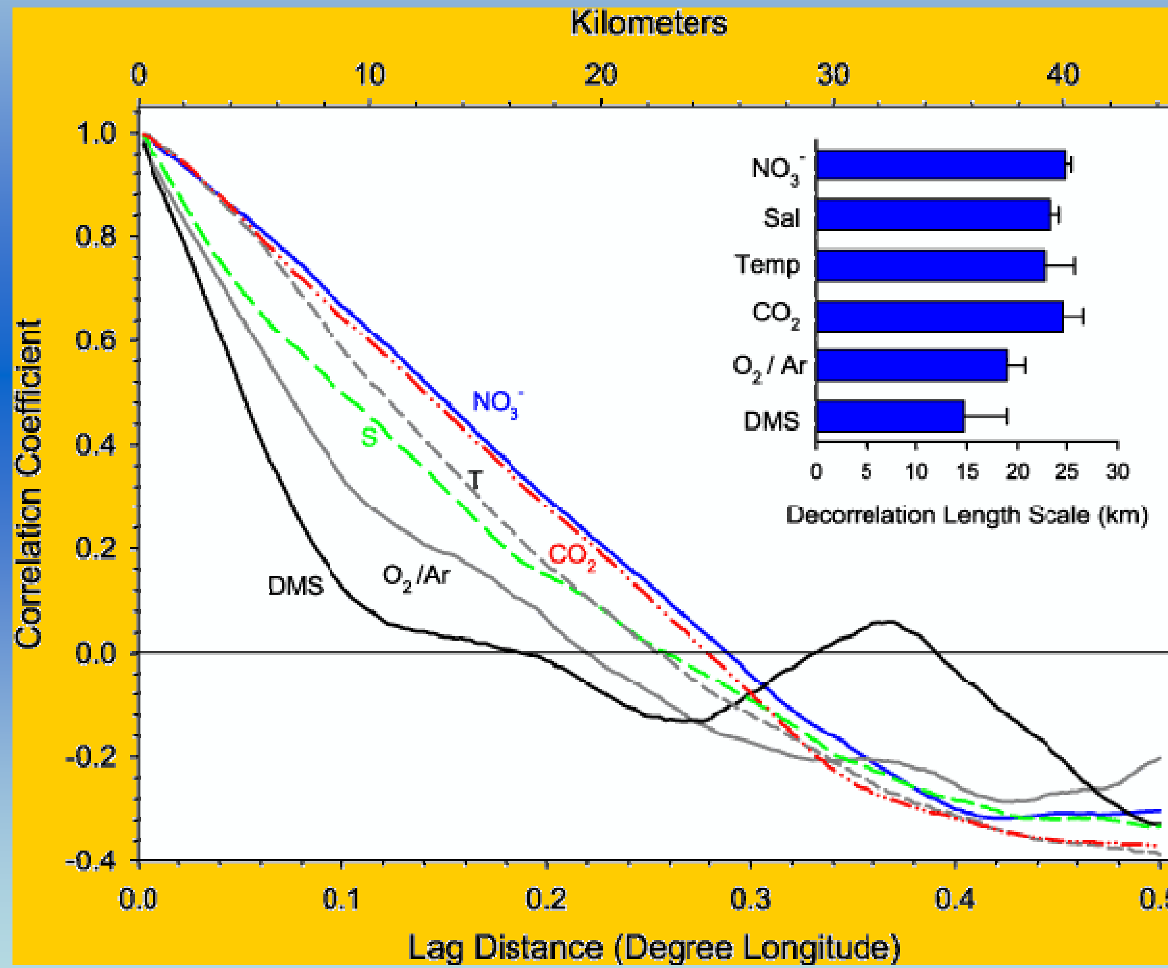


[Jonker, 2005]

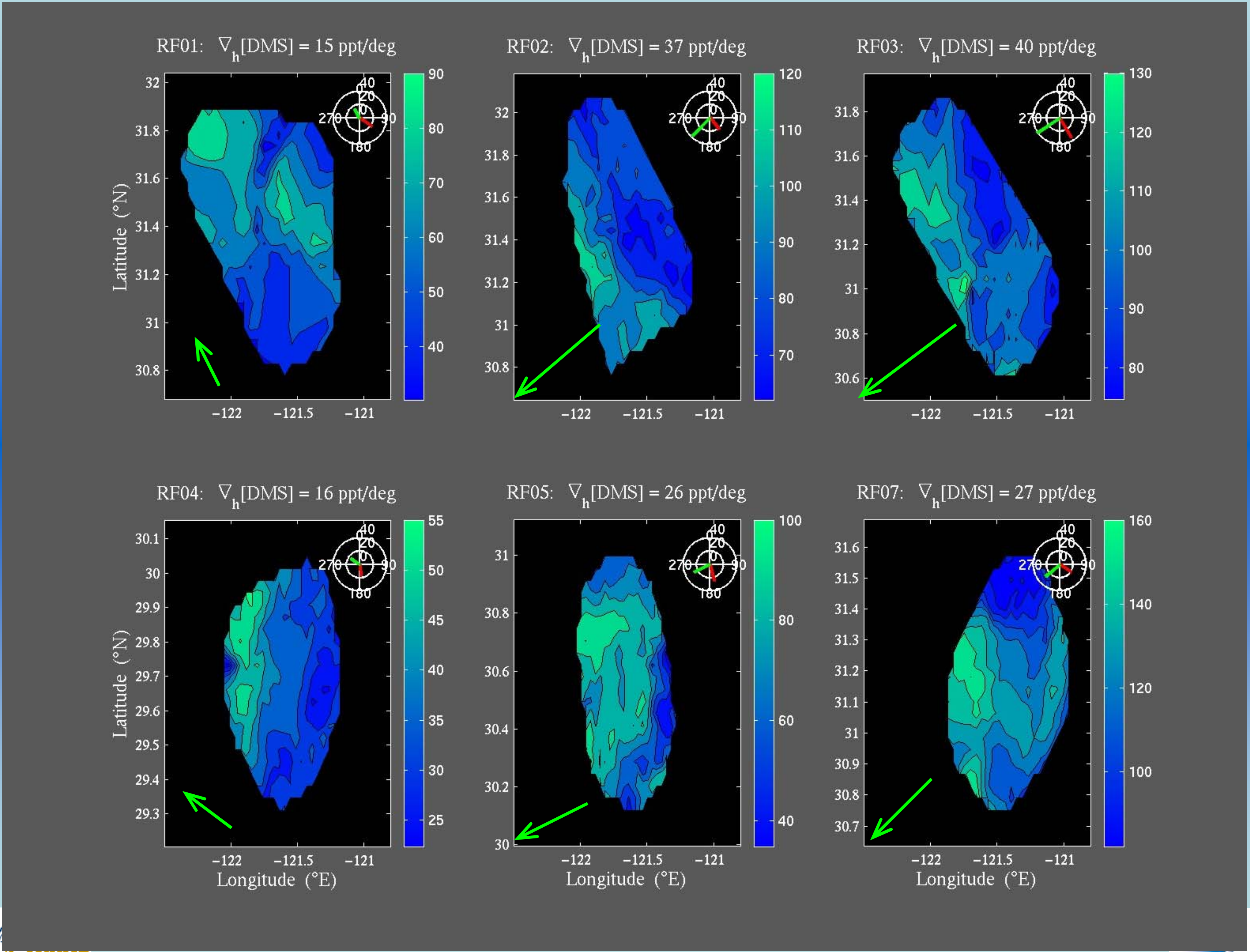
DMS Variability in ocean surface

Tortell [2005] using a MIMS method measured variability of DMS in seawater in the Bering Sea.

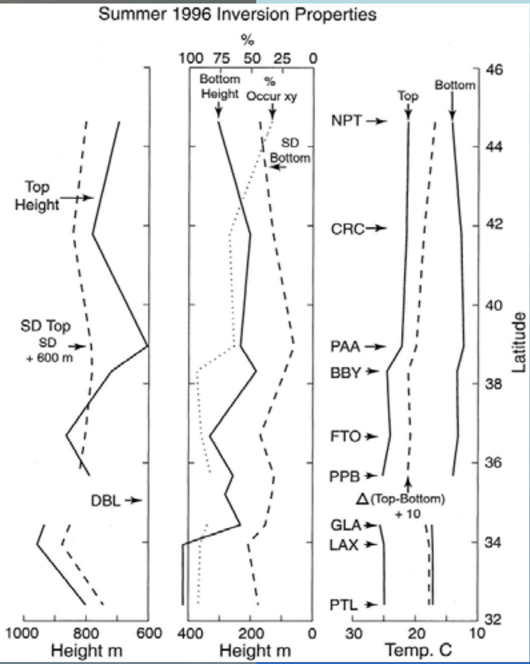




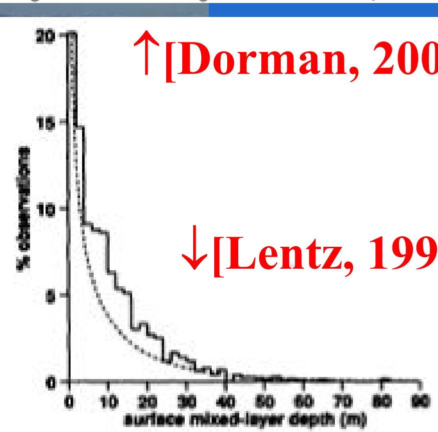
DMS Gradients



Strongly-Coupled Shallow PBLs

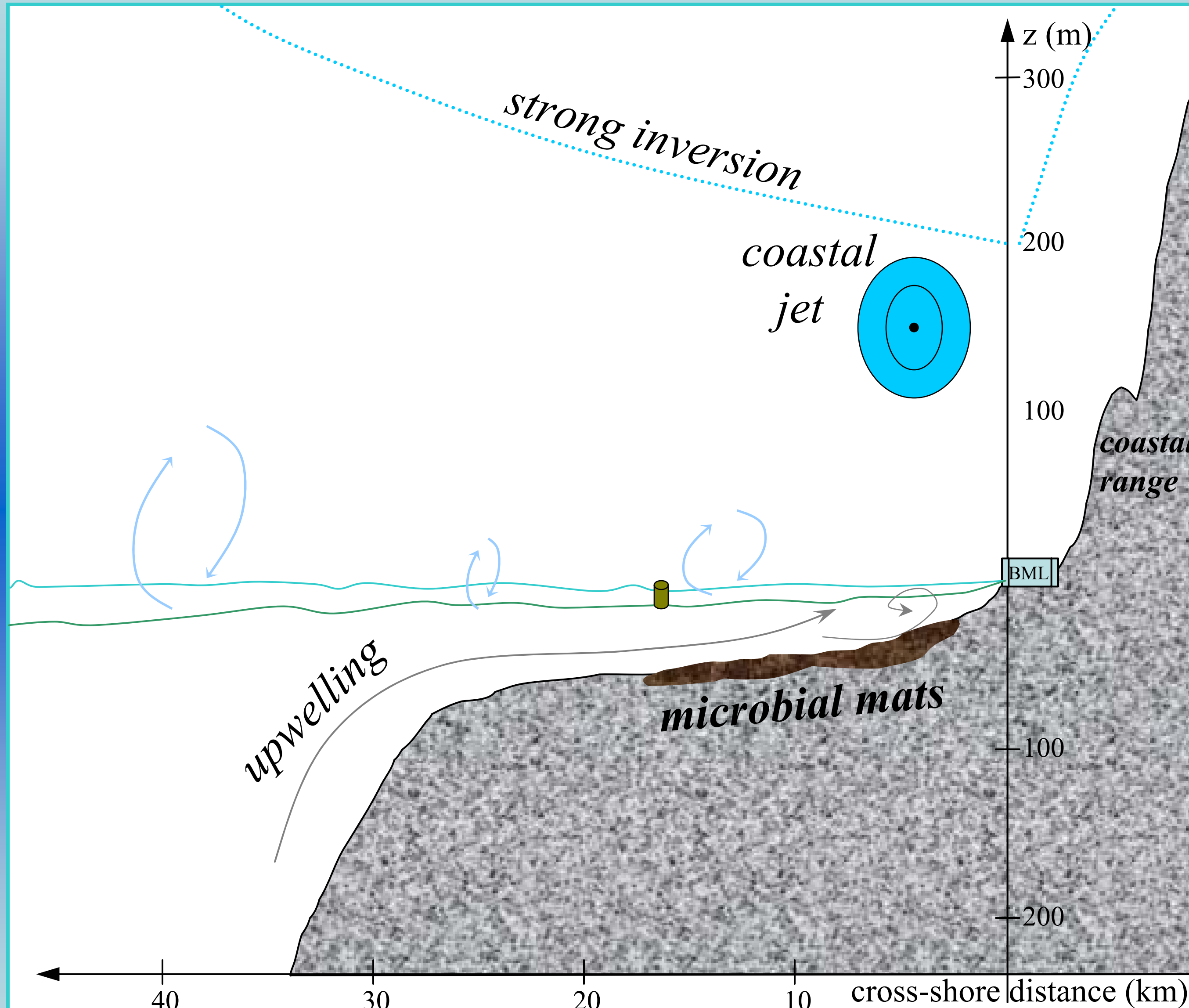


↑[Dorman, 2000]



↓[Lentz, 1992]

FIG. 5. Histogram of surface mixed-layer depth estimates from 1253 CTD profiles taken over the northern California shelf during 1981 and 1982. The mean is 10 m, and the standard deviation is 11 m. The dashed line is the theoretical chi-square (one degree of freedom) distribution with the same mean.



Conclusions

- DMS fluxes have been measured directly by eddy covariance on the NCAR C-130.
- The concentration gradients observed indicated strong DMS sources offshore of the California Current (in ecosystems well aged from their upwelled origins.)
- 'Extra' variance has been documented in DMS measurements from DYCOMS-II, which is most likely related to the spatial scales of sea water DMS variability.
- Careful Lagrangian airborne measurements can be used to better quantify the exchange between MBL and free troposphere, and surface air-sea exchange as well.
- Aircraft have the ability to cover much more area in

Geologic Ramifications

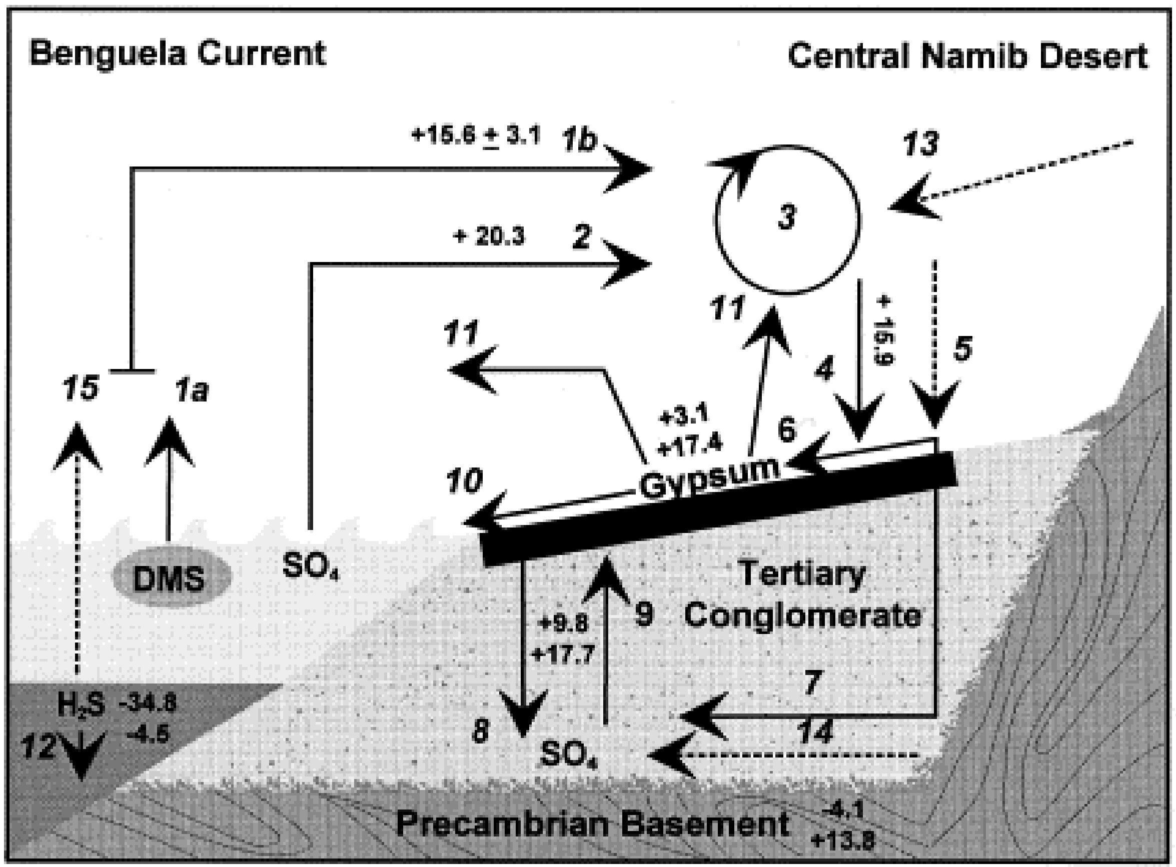


Fig. 7. Schematic representation sulphur cycle at Namib Desert/Atlantic interface.

Proposed sulphur pathways (solid arrows)
Potential sulphur pathways (dashed arrows).
Small numbers indicate range of $\delta^{34}S$
1a = DMS release from phytoplankton;
1b = NSS sulphur (Calhoun et al., 1991);
2 = SO_4 release in sea spray;
3 = mixing of aerosols in the atmosphere;
4 = dry aerosol deposition;
5 = wet aerosol deposition;
6 = runoff and gypsum formation;
7 = infiltration and groundwater flow;
8 = capillary rise and gypsum precipitation;
9 = gypsum dissolution and infiltration;
10 = gypsum dissolution and runoff;
11 = aeolian gypsum dust dispersal;
12 = in sediment sulphide/sulphate formation;
13 = subcontinental dust input;
14 = sulphide oxidation by groundwater;
15 = H_2S release to atmosphere.

[*Eckardt & Spiro*, 1999]

Sea Water Variability