The Abdus Salam International Centre for Theoretical Physics

2339-10

Workshop on Atmospheric Deposition: Processesand Environmental Impacts

21 - 25 May 2012

Air Sea Interactions and Chemical Exchange

A. Pozzer

ICTP, Italy
&
Max Planck Institute for Chemistry
Germany

Air-Sea Interactions and Chemical Exchange

A. Pozzer

Int. Centre for Theoretical Physics
&
Max Planck Inst. for Chemistry

21/05/2012

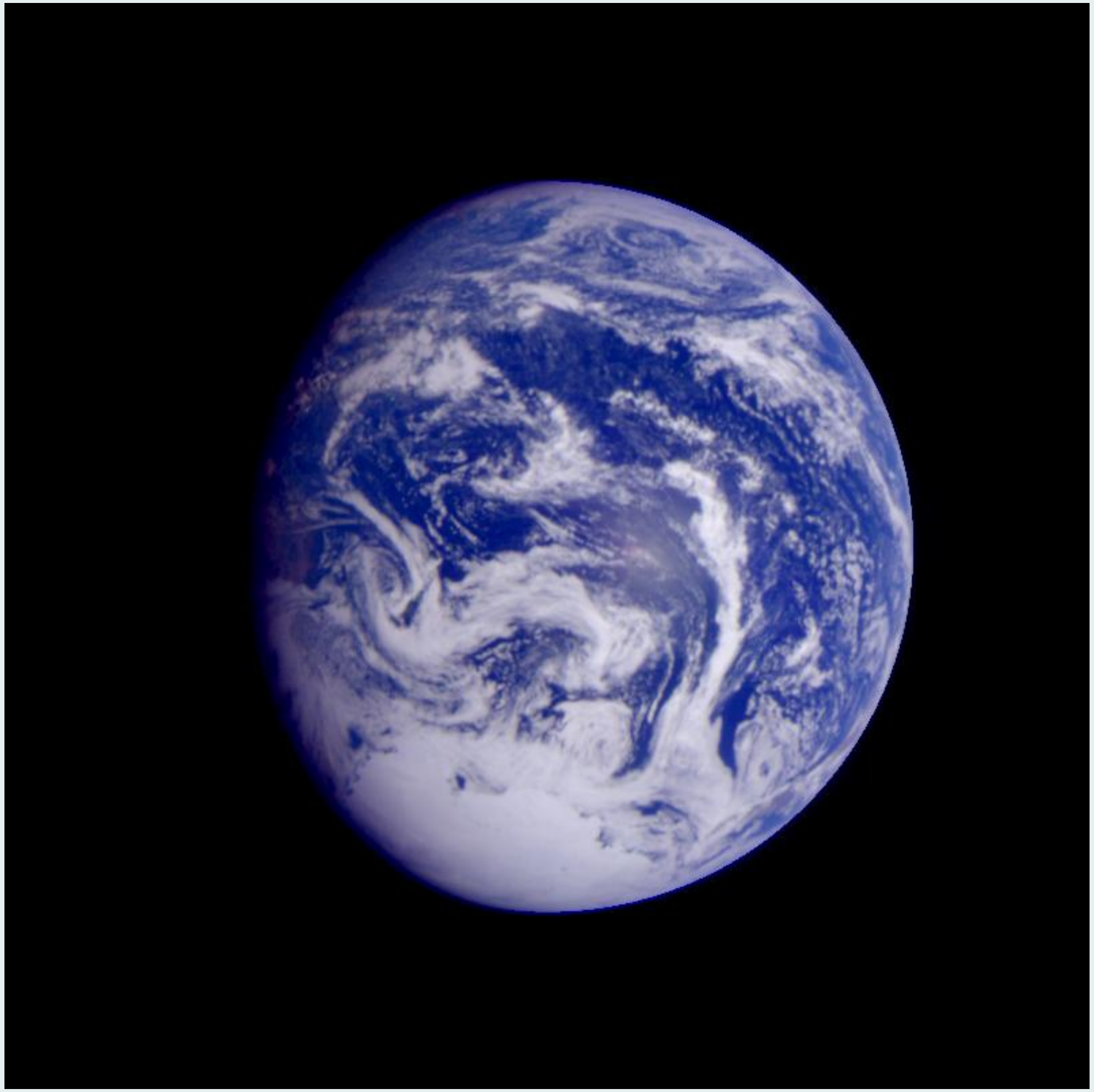
MAX-PLANCK-GESELLSCHAFT

Synopsis

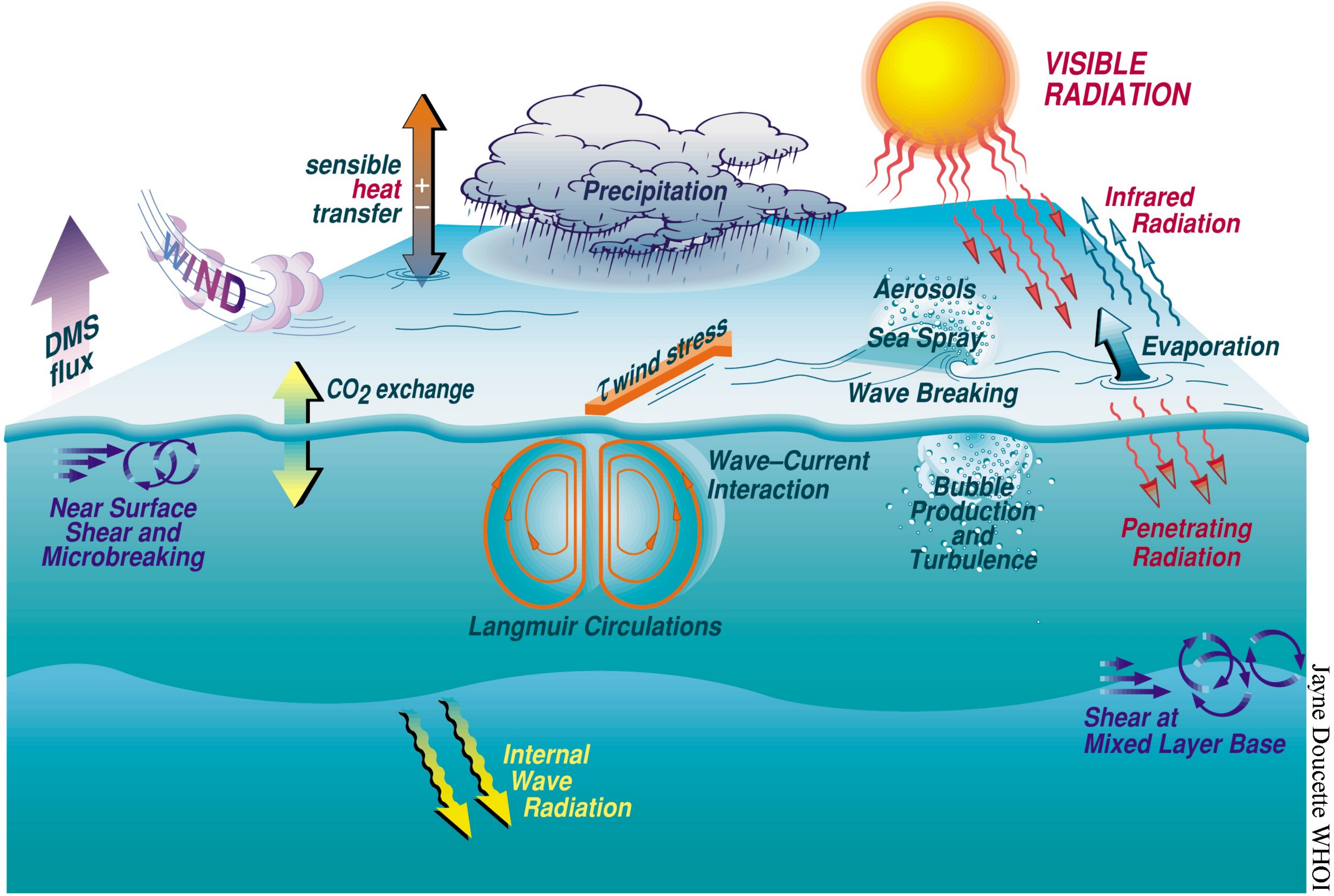
- Introduction
- Chemical air-sea exchange
  - Air-sea exchange model
  - Transfer velocities
  - Concentration differences
  - Ocean as source/sink of gases
- Conclusions and future research

Blue planet

29/01/1996, Galileo mission, Pacific Ocean view



Atmosphere-Ocean interactions



Atmosphere-Ocean interactions

The ocean is hence important for exchange of:

- Heat
- Momentum
- Mass

A. Pozzer

Exchange of mass : air sea exchange of gases

Henry's law:

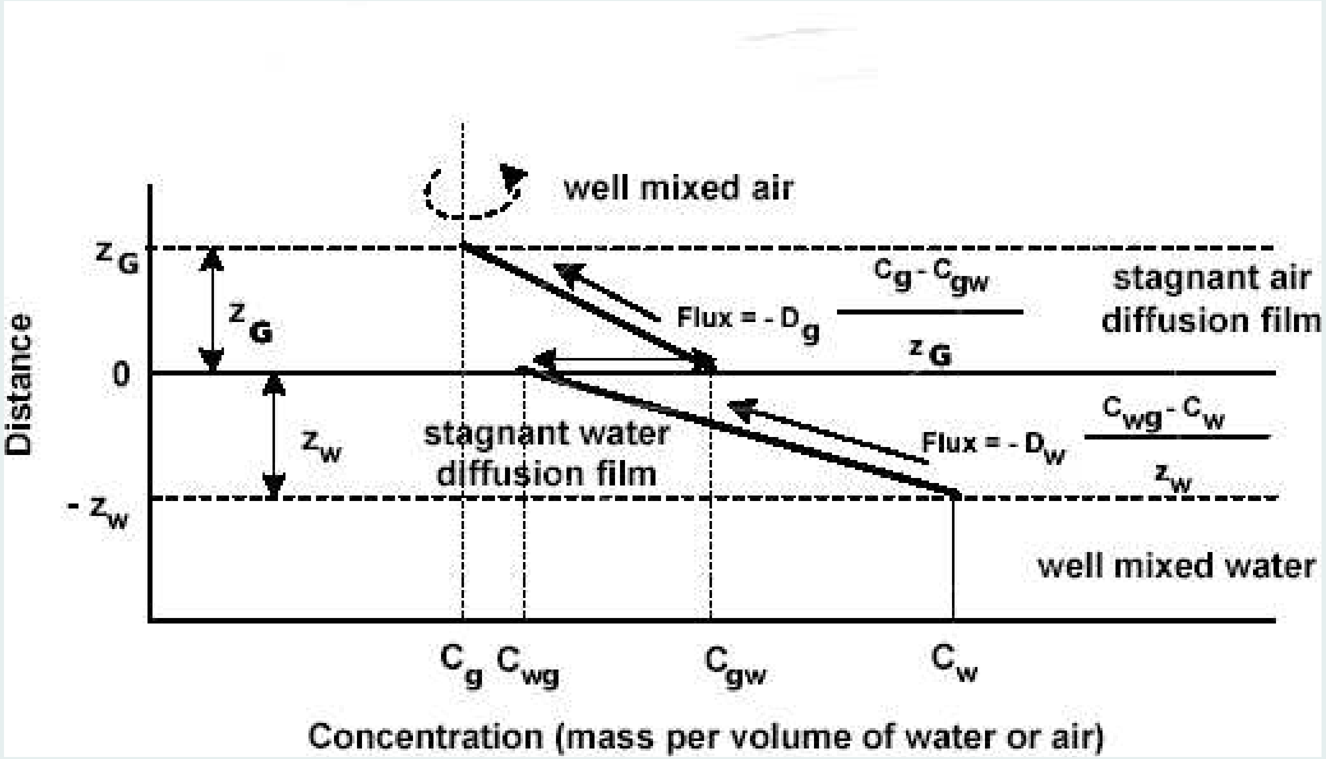
The solubility of a gas in a liquid at a particular temperature is proportional to the pressure of that gas above the liquid.

Dimensionless Henry's law number

- C_w = concentration in water phase.
- C_g = concentration in gas phase.
- At equilibrium : $H = C_w/C_g$.

Chemical air-sea exchange model

Two layer model



Fick's law

The transfer flux across each film is :

$$F = -D \times \frac{\partial C}{\partial z}$$

Chemical air-sea exchange model

Adding the hypothesys of:

- Steady state (fluxes are the same in gaseous an liquid phase)
- No strong chemical reactions between the layers

and using:

- Henry's law : $HC_g = C_w$
- a bit of math

Chemical air-sea exchange model

We end up with:

$$F = \frac{1}{\frac{z_w}{D_w} + \frac{Hz_g}{D_g}} \times (C_w - HC_g)$$

where:

- gas phase trasfer velocity $K_g = \frac{D_g}{z_g}$
- water phase trasfer velocity $K_w = \frac{D_w}{z_w}$
- total transfer velocity $K_{tot} = \frac{1}{\left(\frac{z_w}{D_w} + \frac{Hz_g}{D_g}\right)}$
- or better $K_{tot} = \frac{1}{\left(\frac{1}{\alpha K_w} + \frac{H}{K_g}\right)}$

Chemical air-sea exchange model

Two layer model

- Flux in mol/m^2s
- Transfer velocity in m/s : $K_{tot} = \left(\frac{1}{\alpha K_w} + \frac{H}{K_g}\right)^{-1}$
- Concentration difference in mol/m^3

$$F = K_{tot} \times (C_w - HC_g)$$

Basic modeling equation !

Trasfer velocities

Transfer velocity in m/s : $K_{tot} = \left(\frac{1}{\alpha K_w} + \frac{H}{K_g}\right)^{-1}$

- $K_w << K_g/H$: the flux is controlled by the water film transfer
- $K_w >> K_g/H$: the flux is controlled by the gas film transfer

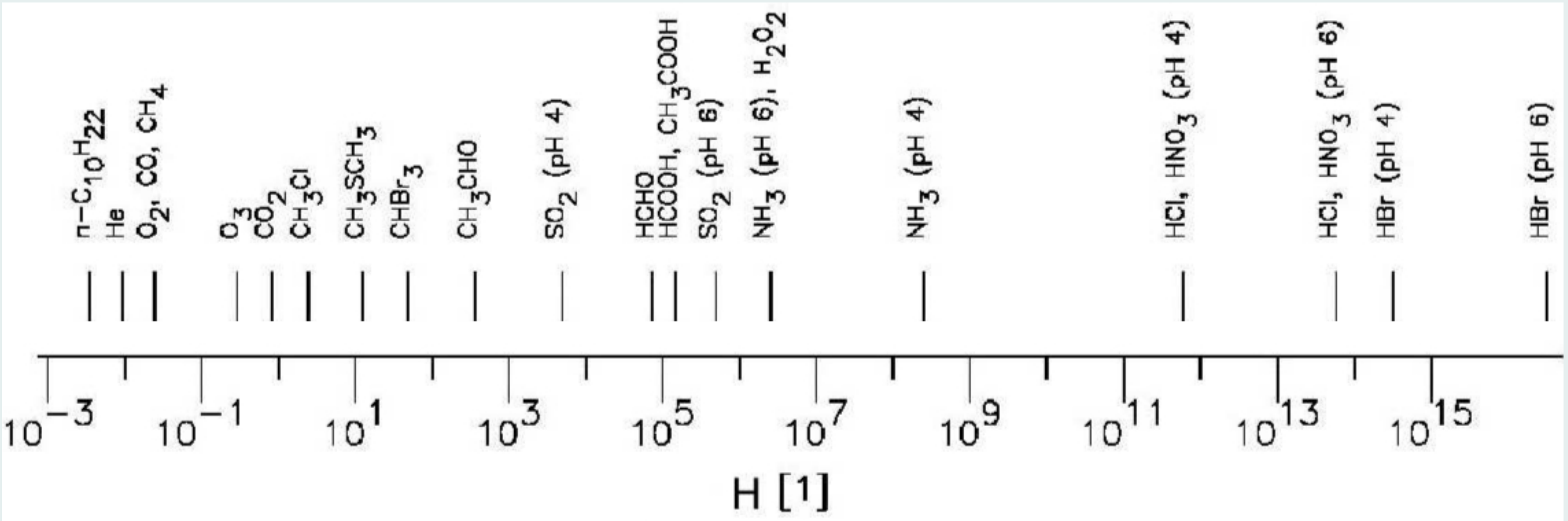
The water side transfer velocity (K_w) is generally three orders of magnitude lower than the air side transfer velocity (K_g).

Trasfer velocities

However :

having H as dimensionless Henry's law coefficient

- H $> 10^5$ (soluble gases): K_{tot} is dominated by K_g.
- $10 <$ H $< 10^5$: $K_g \simeq K_w$ *both* have to be considered in the calculations.
- H < 10 (non soluble gases) : K_{tot} is dominated by K_w.



K_g : air side transfer velocity

Thanks to tracer deposition studies we have that:

$$K_g = \frac{1}{R_a + R_{qbr}}$$

where :

- R_a (in s/m) the aerodynamic resistance
- R_{qbr} (in s/m) the quasi-laminar boundary layer resistance

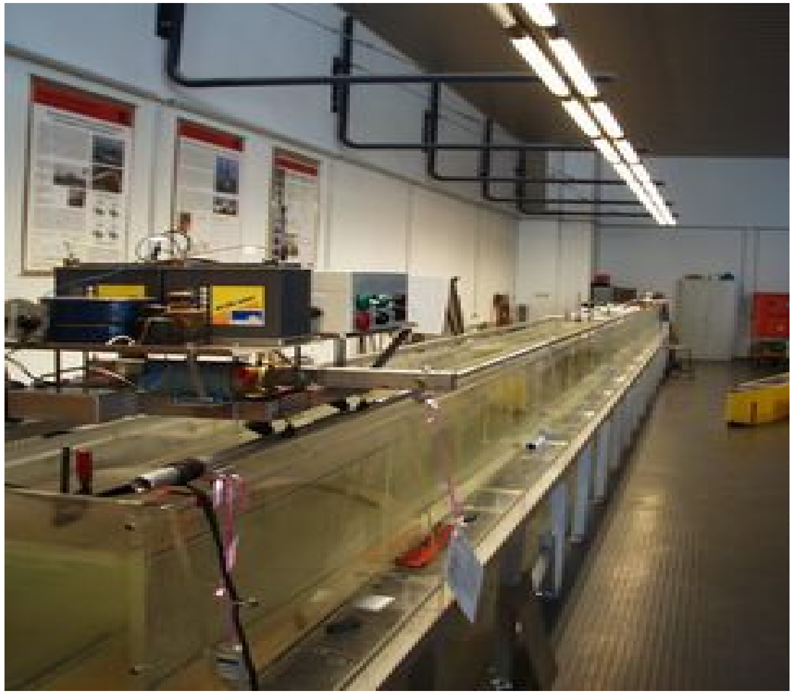
in addition:

- R_a is a function of the physical state of the atmosphere.
- $R_{qbr}(X)$ is controlled by molecular diffusion.

K_w : water side transfer velocity

K_w is the most important for many gases of environmental interest.

K_w : water side transfer velocity



Wave simulator at FUB

K_w : water side transfer velocity

Following laboratories studies, it has been show that K_w can be influenced by:

- wind
- bubbles
- surfactants
- rain
- temperature/humidity (skin effect)

However

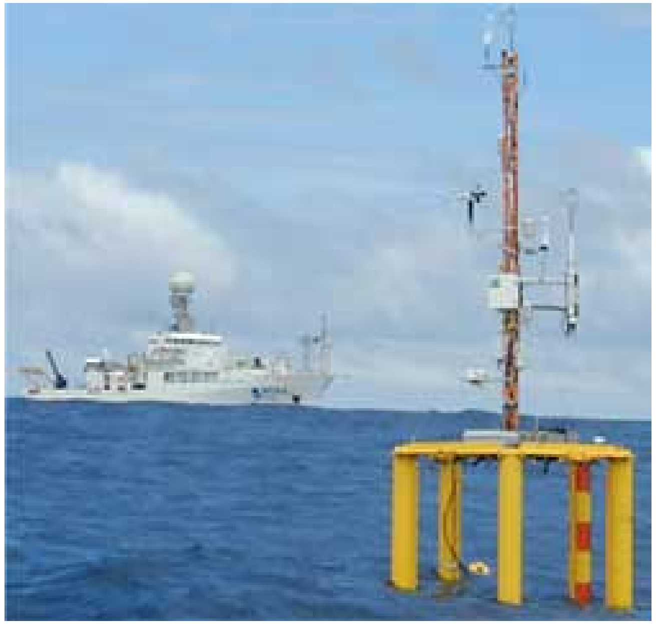
It is extremely difficult to use these data to extrapolate results to coastal seas and oceans, due to more complex mechanism (missing direct/immediate wave-wind connection).

K_w : water side transfer velocity

Where is the thin diffusion layer ?

K_w : water side transfer velocity

Despite the importance, measuring air-sea tracer exchange in situ is extremely difficult.....



NOAA/Equatorial air-sea exchange experiment

K_w : water side transfer velocity

Despite the importance, measuring air-sea tracer exchange in situ is extremely difficult.....
Methodologies used:

Large scale techniques

- Radiocarbon ($^{14}CO_2$)
- Oxygen/Nitrogen ratios

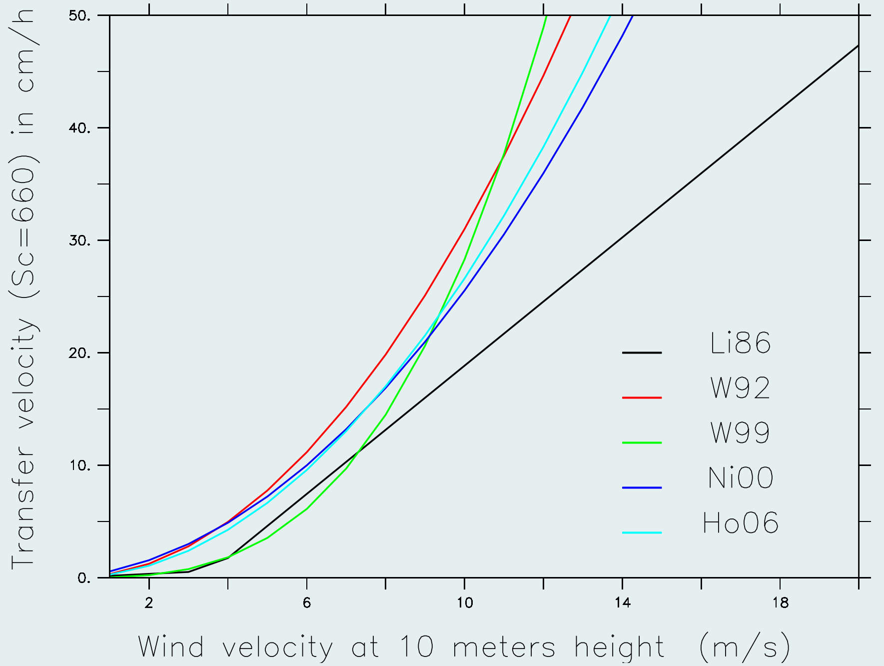
Local scale techniques

- Mass balance
- Radon
- Deliberate tracers experiment (e.g. SF_6)
- Eddy correlation technique
- Relaxed eddy accumulation
- Atmospheric profiles

K_w : water side transfer velocity

K_w parametrisations

Reference	relationship
	$0.17U_{10}$ $(U_{10} < 3.6m/s)$
Liss and Merlivat 1986	$2.85U_{10} - 9.65$ $(3.6 < U_{10} < 13m/s)$
	$5.9U_{10} - 49.3$ $(13m/s < U_{10})$
Wanninkhof 1992	$0.31(U_{10})^2$
Wanninkhof-Mc-Gills 1999	$0.0283(U_{10})^3$
Nightingale 2000	$0.333(U_{10}) + 0.222(U_{10})^2$
Ho 2006	$0.266(U_{10})^2$



Uncertainties of more than a factor of 2!

Concentration difference

Basic modeling equation :

$$F = K_{tot} \times (C_w - HC_g)$$

$$\Delta C = (C_w - HC_g)$$

ΔC defines the flux direction

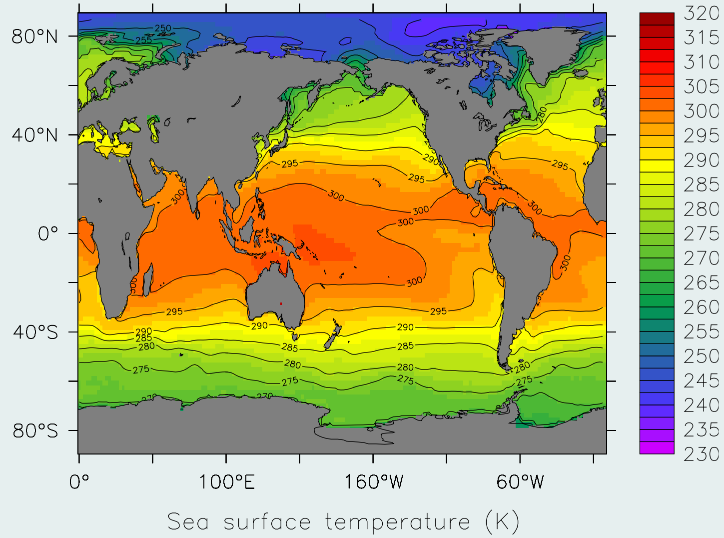
- $C_w > HC_g$: water is supersaturated.
- $C_w < HC_g$: water is undersaturated.

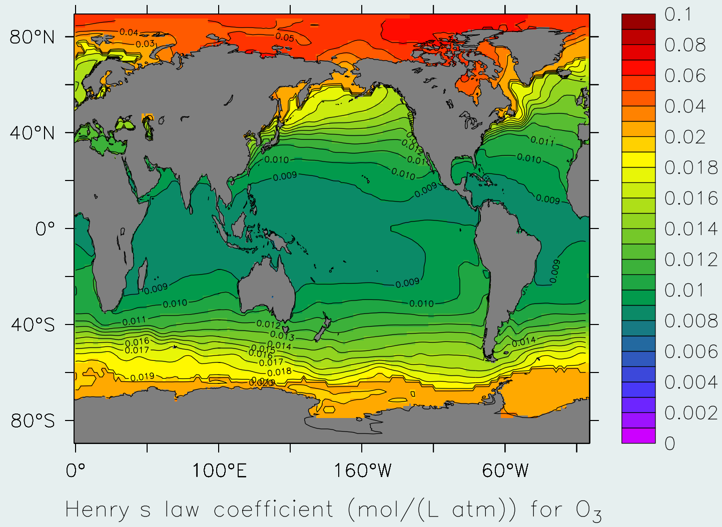
Henry's law number

H can be influenced by:

- salinity (higher salinity ⇒ higher solubility)
- temperature (higher temperature ⇒ lower solubility)

Temperature effect



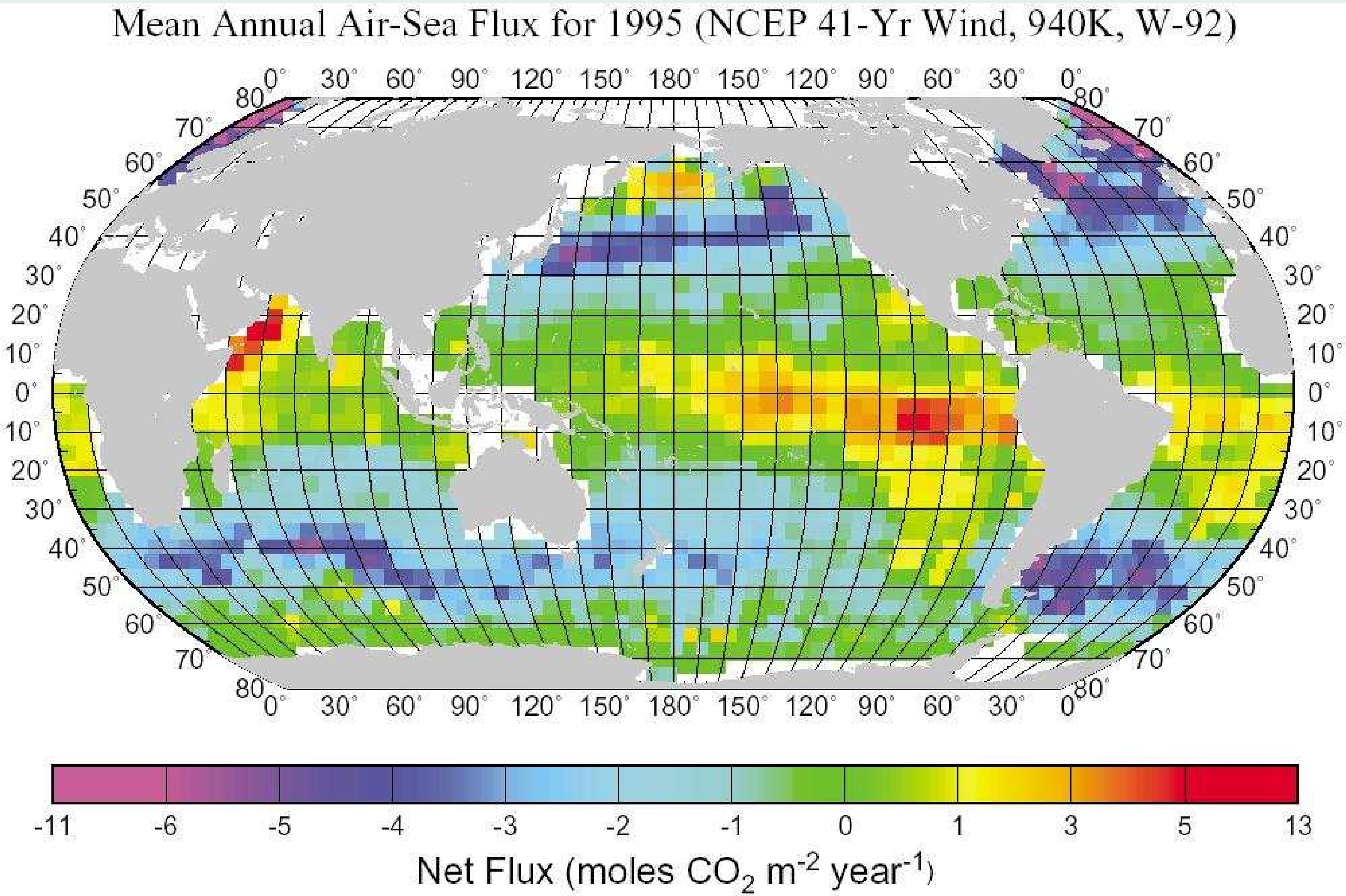


Origin of the solubility pump.

$$\Delta C = (C_w - HC_g)$$

Solubility pump

Takahashi et al. (2002)



C_w: how can it be estimated?

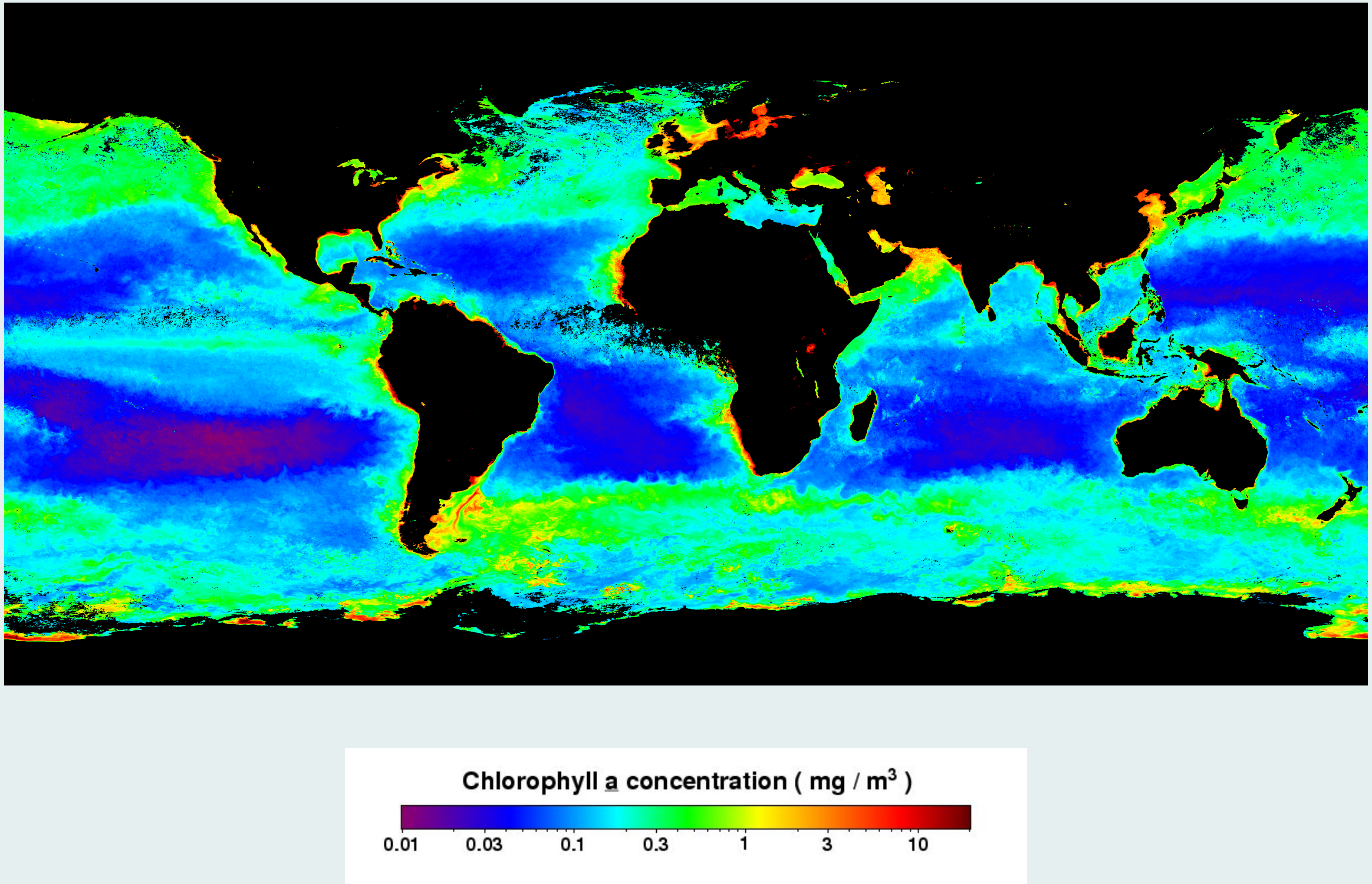
Mechanism of formation of tracer in seawater

- Phytoplankton (*DMS*)
- Photochemistry/Photodissociation (*NMHC*)
- Bacterial (CH_4) / Microbial (N_2O)

In addition: tracers are transported in the ocean...

Chlorophyll-a, a proxy for Phytoplankton

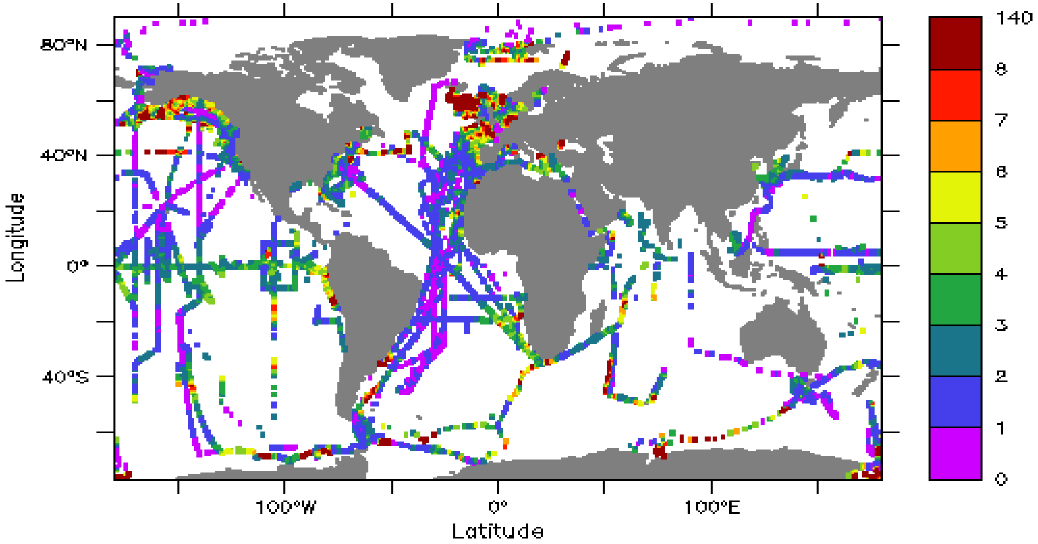
Winter 2006/2007, Acqua MODIS Level 3 data.



How to model the concentration difference?

- Interpolated global map of observations
- Satellite observation of proxies
- Model simulation

Kettle et al. (1999)

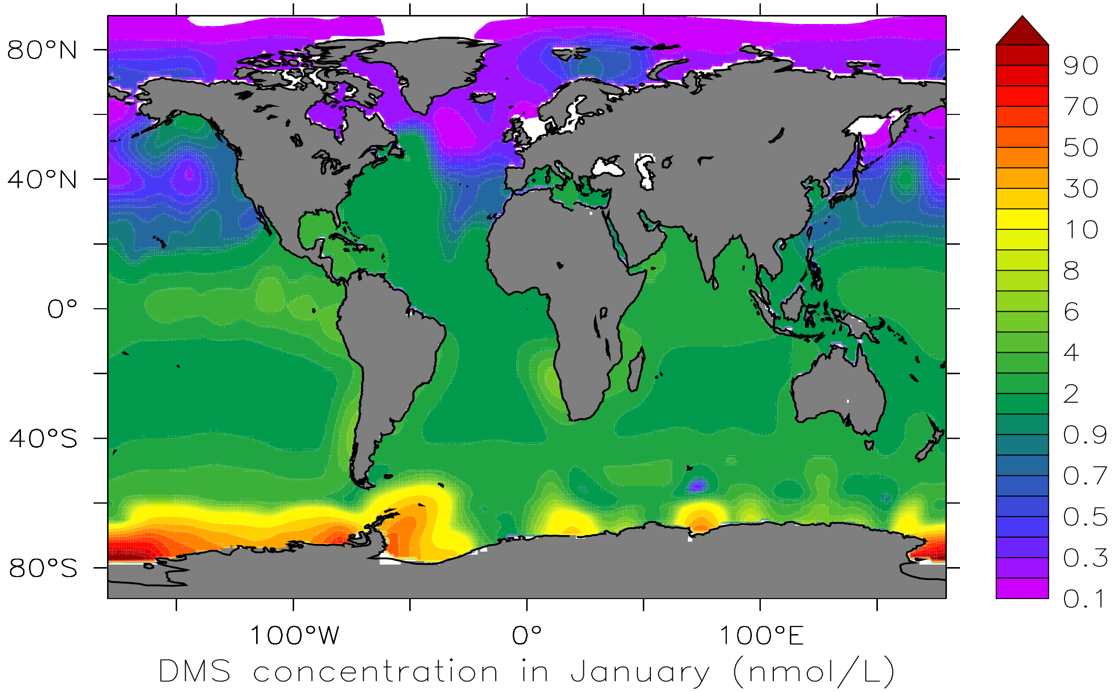


DMS obsrvations

How to model the concentration difference?

- Interpolated global map of observations
- Satellite observation of proxies
- Model simulation

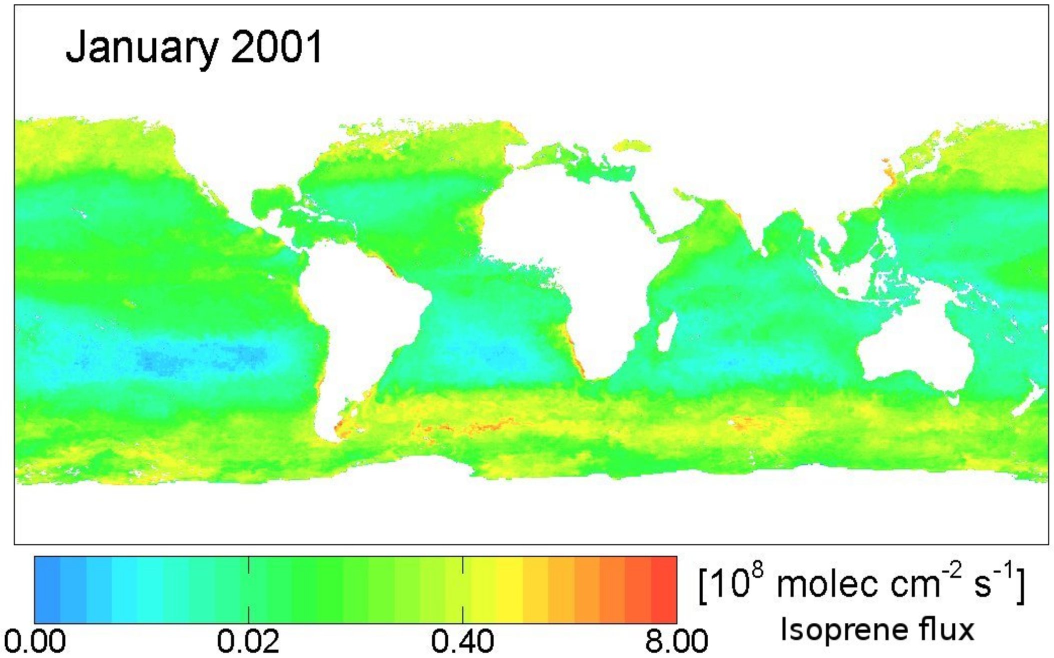
Kettle et al. (1999)



How to model the concentration difference?

- Interpolated global map of observations
- Satellite observation of proxies
- Model simulation

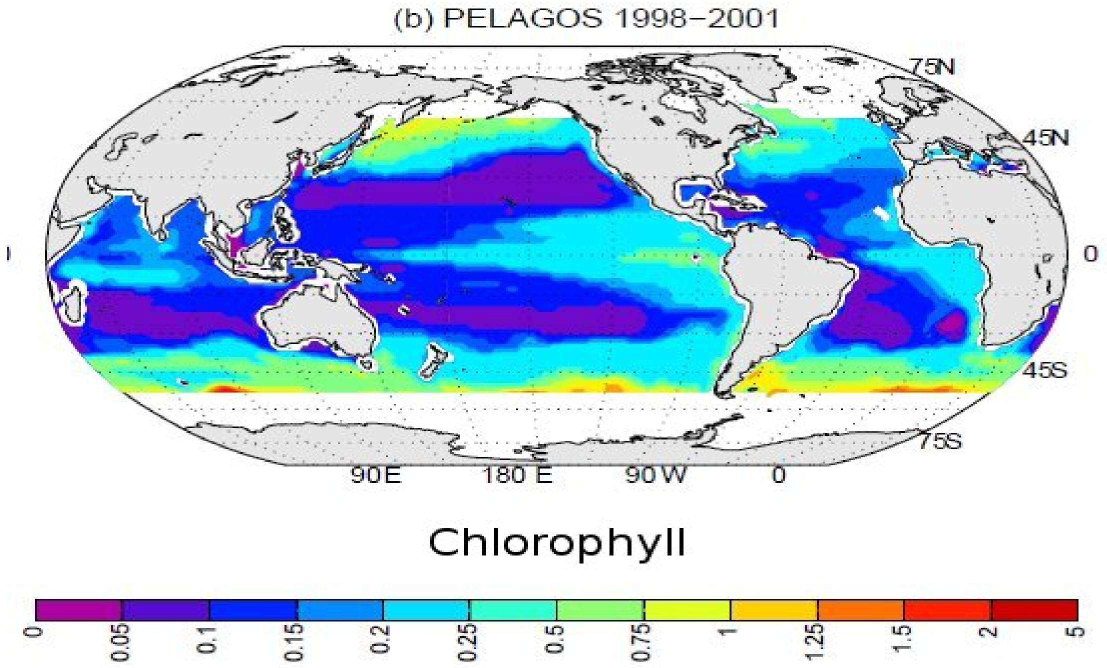
Palmer and Shaw (2005)



How to model the concentration difference?

- Interpolated global map of observations
- Satellite observation of proxies
- Model simulation

Vichi and Masina (2009)



Tracer in seawater and their atmosphere-ocean flux

Gas	Atmospheric role	Main production mechanism	Net annual flux to the atmospehre	% of atmopsheric source/sink
DMS	CCN + acidity	Phytoplankton	15-22 TgS	80
COS	CCN + acidity	Photochemistry	-0.1-0.3 Tg	40
CH_3I	Oxydation capacity	Phytoplankton	0.13-0.36 Tg	10(?)
CH_3Cl	Ozone depletion	?	0.2-0.4 Tg	7-14
N_2O	GHG, ozone depl.	(De)nitrification	11-17 Tg N	60-90
CH_4	GHG, oxydation	Bacteria	15-24 Tg	3-5
CO_2	GHG	Respiration	-1.7±0.5 PgC	-30
O_3	GHG, oxydation	-	-300 Tg	-30
CFCs	GHG, ozone depl.	-	?	?
CO	Oxydation capacity	Photochemistry	10-650 TgC	3-20
NMHC	Oxydation capacity	Photochemistry	2-3 Tg	1
OVOC	Oxydation capacity	Photochemistry	?	?

Final considerations

The key assumption for the thin-film layer model are

- The main bodies of air and water are well mixed.
- Production or removal processes in the thin film are slow compared to the transport itself.

The direction of the air-sea exchange

- depends on atmospheric and oceanic concentrations at the interface.

WARNING: each tracer is different!

The Ocean:

- covers 3/4 of our globe.
- is essential for our climate.
- has strong impact on the atmospheric composition.

The air sea transfer

- Requires expertises from different fields:
  - Micrometeorology (Ocean and Atmosphere).
  - Large scale meteorology (Ocean and Atmosphere).
  - Biology.
- Present many uncertainties.
- Rely strongly on parametrisation.
- Is it still a “terra incognita”.

Future study direction

Parametrisation (from laboratory studies) of tracer concentrations via "easy to measure" proxies.
Large observational dataset of gases concentration in the water is missing! These large scale observations requires international collaboration. Hence growth of many international projects:

- JGOFD, Joint Global Ocean Flux Study.
- SOLAS, SURface Ocean Lower Atmosphere Study.

Thank you!