"Emerging trends in Ocean Observations and Ocean Data Analysis"

- Brief on Marine Ecosystem Observations and Data
- Bio-geochemical observations; Indian Ocean scenario

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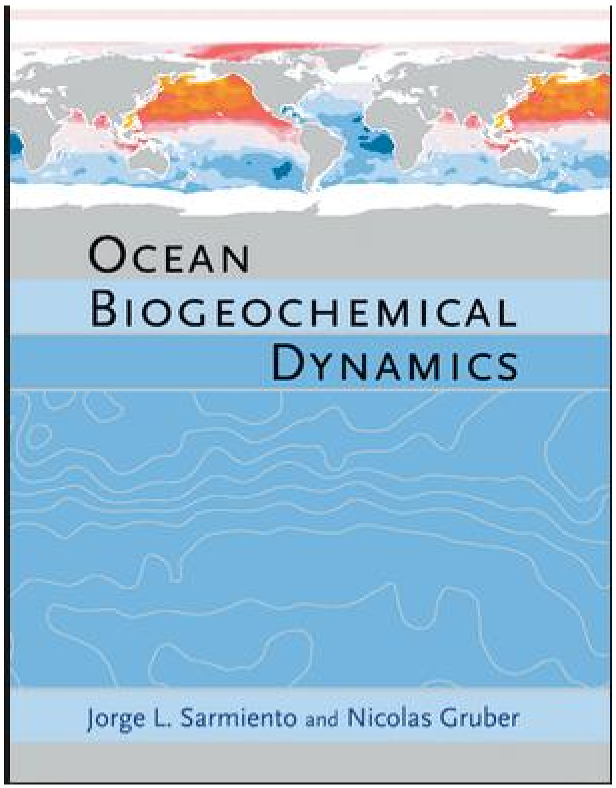
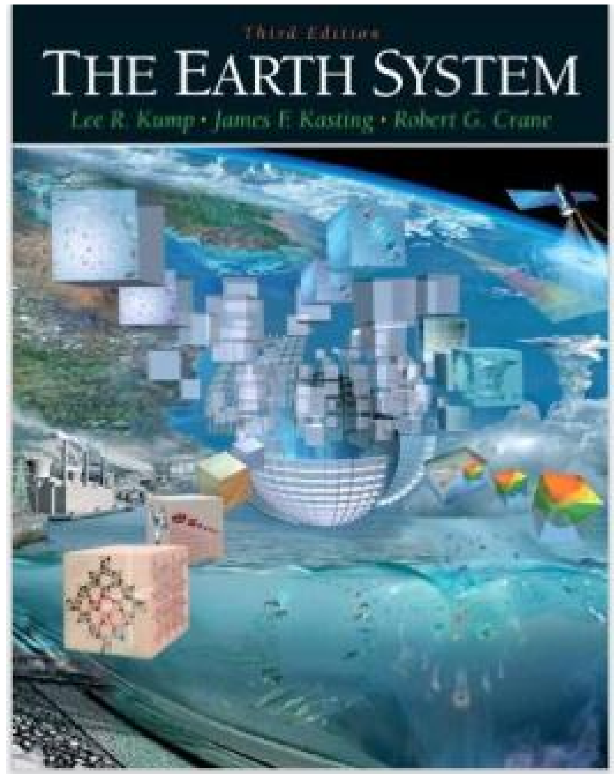
Research Interests: Ocean Biogeochemistry, Carbon Cycle, Ocean Modeling

Outline of the lecture

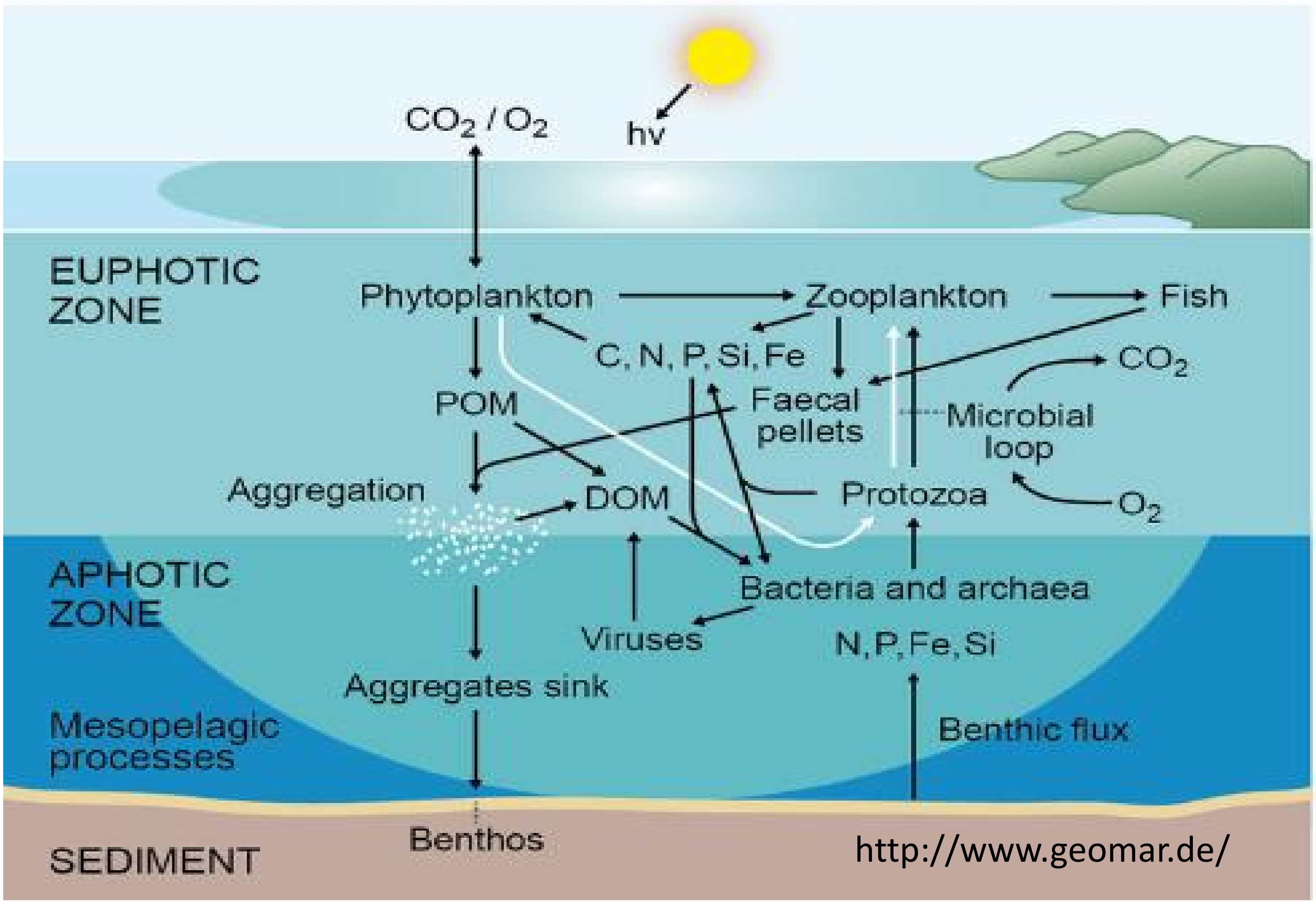
- Briefing on Marine Ecosystem Processes
- Biogeochemistry → Carbon Cycle
- Indian Ocean → observation and modeling scenario
- Data analysis of Ocean Carbon Cycle
- Practicals on pCO_2 component analysis

Books for further reading





Marine Biogeochemistry and Ecosystem processes



Ecosystem processes.

Ecosystem processes

$$\frac{\partial c}{\partial t} = -U\cdot\nabla c + \nabla\cdot(D\nabla c) + SM(c)$$

- $\frac{\partial c}{\partial t}$: Tendency
- $-U\cdot\nabla c$: Advection/transport
- $\nabla\cdot(D\nabla c)$: Diffussion/mixing
- $SM(c)$: source/sink terms

C = Nutrient (eg: NO_3, PO_4 etc.)
or
Phytoplankton, Zoo-plankton, Bacteria.

ie $SM(N) = -SM(P) - SM(Z) - SM(B)$

Instead of tracking all major nutrients, we focus on "Nitrate" as our state variable.

Why Nitrogen (Nitrate) as convenient master variable?

↳ Because of nearly constant stoichiometric ratios.

$$[C:N_2:O:P \approx 106:16:-138:1]$$

↳ Because of the evidence that whenever the micronutrient limit the growth of microorganisms, it is generally due to inadequate supply of Nitrate rather than phosphate.

$$106\,CO_2 + 16\,HNO_3 + H_3PO_4 + 78\,H_2O \rightleftharpoons C_{106}H_{175}O_{42}N_{16}P + 150\,O_2$$

Nutrient cycle:

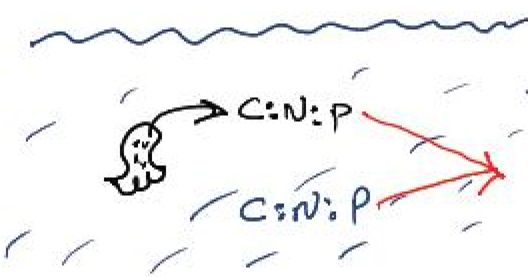
Biomass production

$$106\, CO_2 + 16\, NO_3 + HPO_4^{2-} + 78\, H_2O + 18H^+ \rightleftharpoons C_{106}H_{175}O_{42}N_{16}P + 150\, O_2$$

Redfield Ratio [Alfred C. Redfield]

"Marine phytoplankton incorporate many nutrient elements into their tissues in ratios that appear to be nearly identical in all species."

$$C:N:P = 106:16:1$$



Inside the marine species & outside in the ocean water C:N:P is nearly identical.

Nutrient limitation

Nutrient limitation

① Leibig Concept

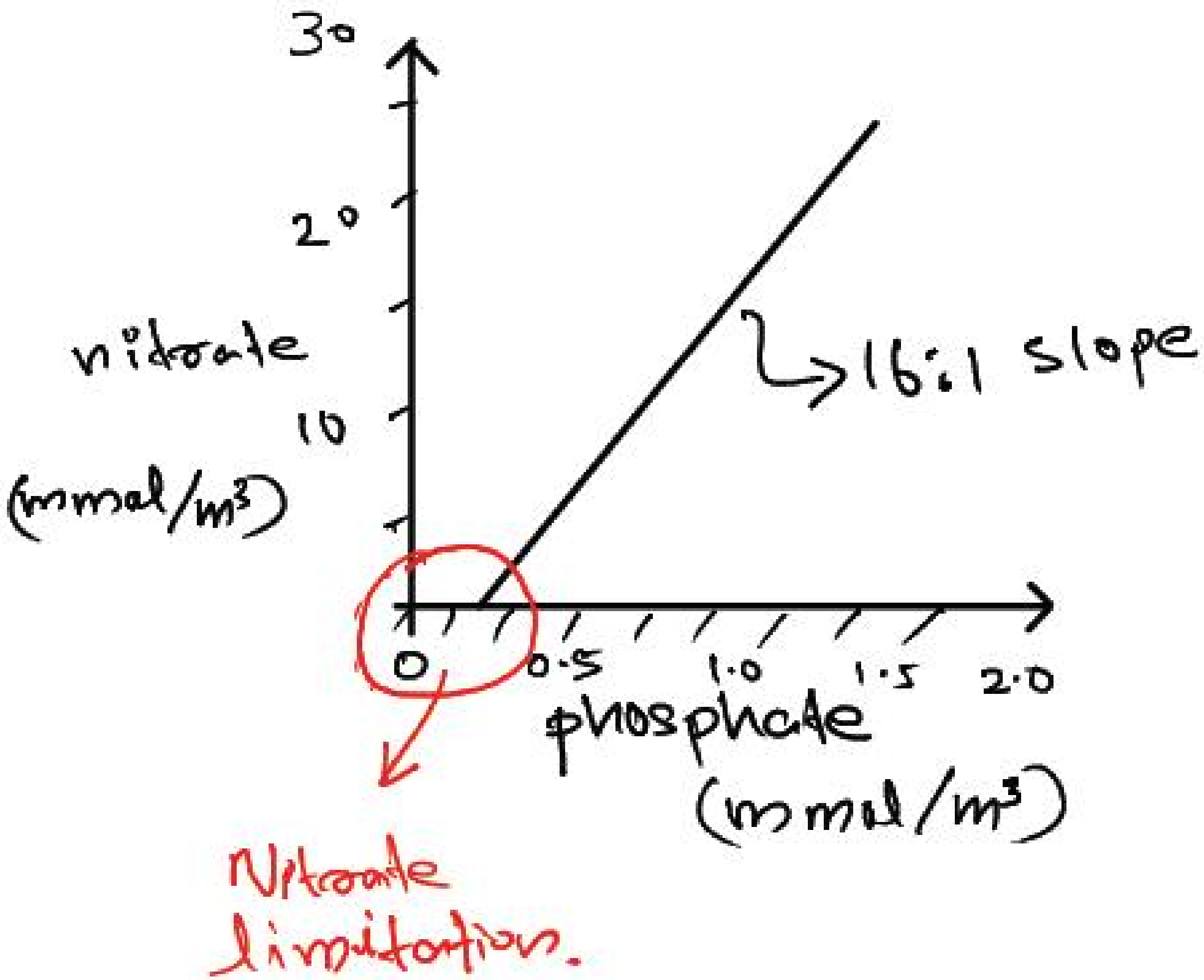
↳ The stock of phytoplankton will eventually be limited by the supply of a single cellular nutrient and growth will cease.

[Leibig, 1840]

② Monod Concept

↳ Influence of nutrient concentration on rate of photosynthesis rather than on the extend of growth.

Nitrate vs. Phosphate comparisons in the world ocean



Nitrogen fixation (Nitrogen to bio-available nitrogen)

A Natural process, either biological or abiotic, by which nitrogen (N_2) in the atmosphere is converted into ammonia (NH_3).

Microorganisms that fix nitrogen (Diazotrophs)
Cyanobacteria
Azotobacteraceae
Rhizobia
Frankia

Organisms are able to directly modify the total amount of nitrogen accessible to them for synthesis of organic mater by nitrogen fixation.

Phosphate as a limiter.

Phosphate as a limitor

↳ Because Nitrogen can be "fixed" by nitrogen fixation.

↳ Because phosphate supply is only through external sources.

↳ on "large" space & time scale nitrate is maintained as a constant mean concentration and that is determined by how much phosphate is available.

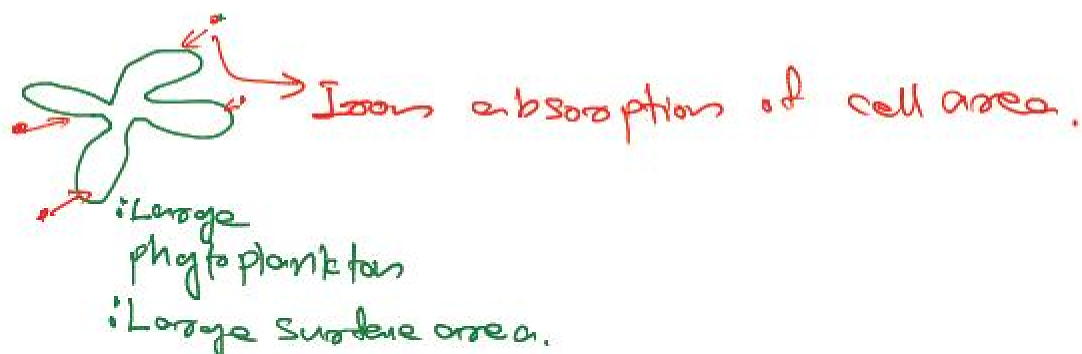
: on small space & time scale Nitrate is limitor

: on longer scale phosphate can be a limitor.

Iron as a limiter.

Iron as a nutrient limiter

- Iron is an important component of electron transport protiens involved in photosynthesis & respiration.
- Iron is a component of enzymes required to utilize nitrate & nitrite, as well as for nitrogen fixation.
- Reduced supplies of iron → reduced growth rate and reduced abundance of larger phytoplankton.



Nitrogen cycling.

Paradigm of surface ocean Nitrogen cycle

Regenerated production.

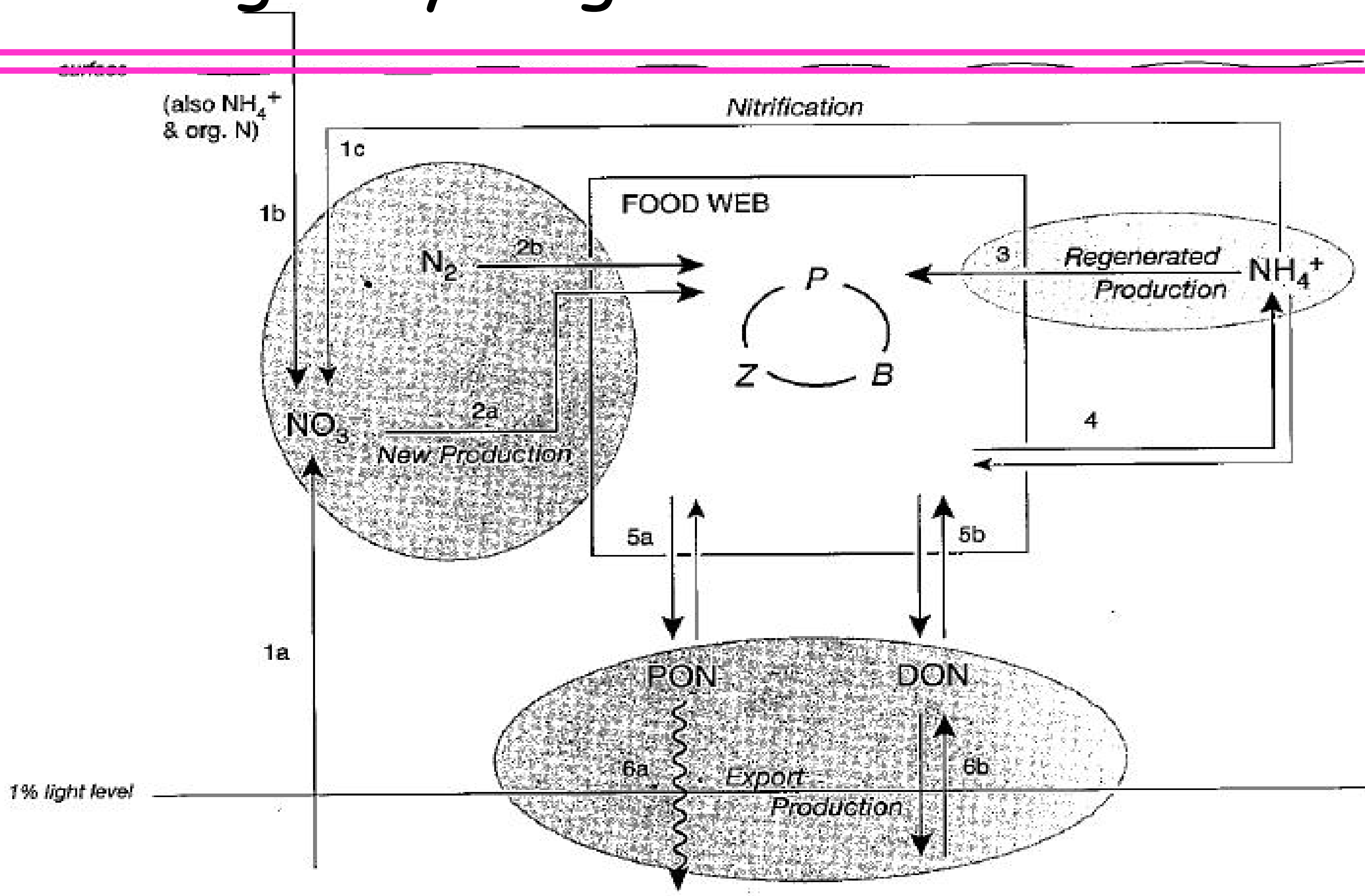
↳ Nutrients (Nitrate) that are supplied (replenished) by recycling of organic matter within the surface ocean.

New production.

Replenishing of Nitrate by external sources [ie by upwelling, upward mixing from thermocline.

On large scale, export of organic matter from the surface [ie export production] has to be equal to large scale new production.

Nitrogen cycling.



Nitrogen cycling.

The breakdown of biological production into
① New production
② regenerated production
③ Export production

leads to following useful ratios.

$$f\text{-ratio} = \frac{\text{New production}}{\text{Primary production}}$$

$$e\text{-ratio} = \frac{\text{Export production}}{\text{Primary production.}}$$

Primary Production or
Net Primary Production (NPP) = Net CO_2 uptake by phytoplankton
= Gross Prim. Prod [ie photosynth] − Respiration

or

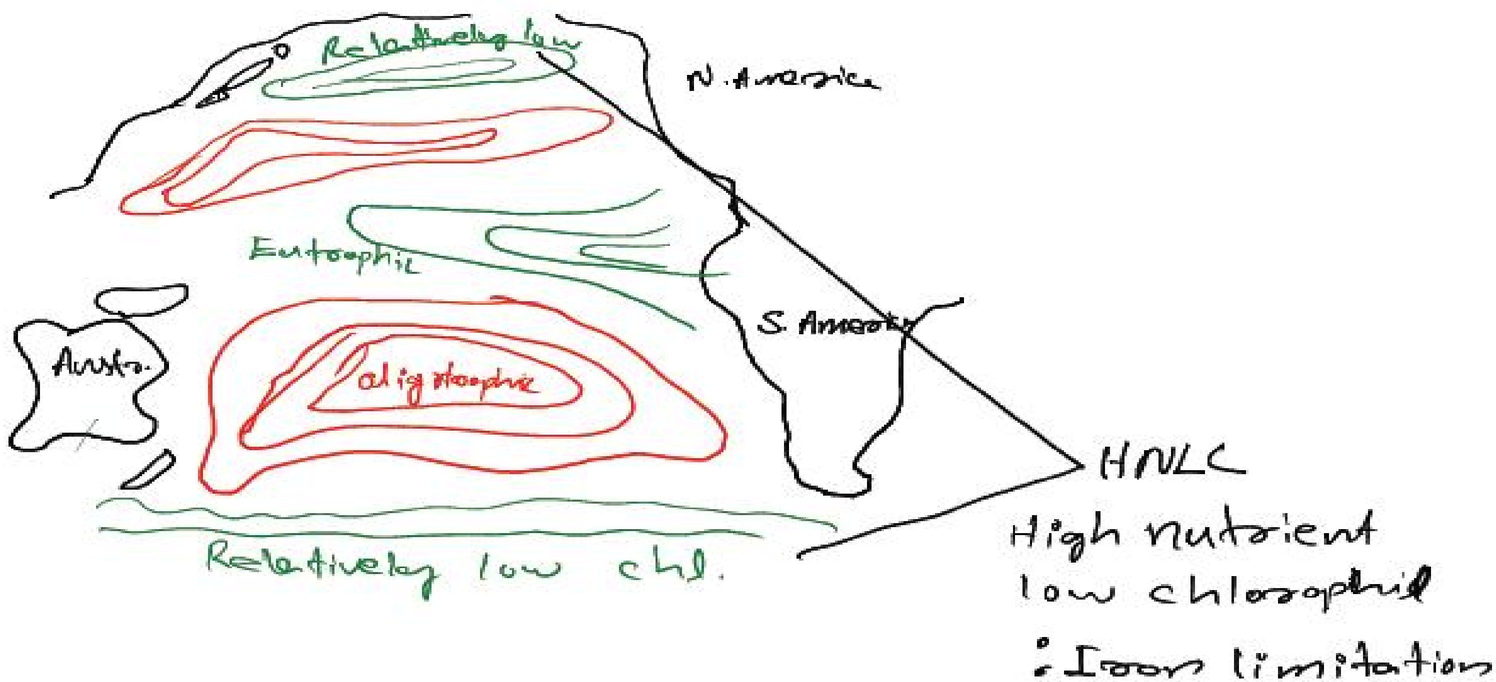
Net community Production (NCP) = PP − Respiration.

Eutrophic and Oligotrophic zones

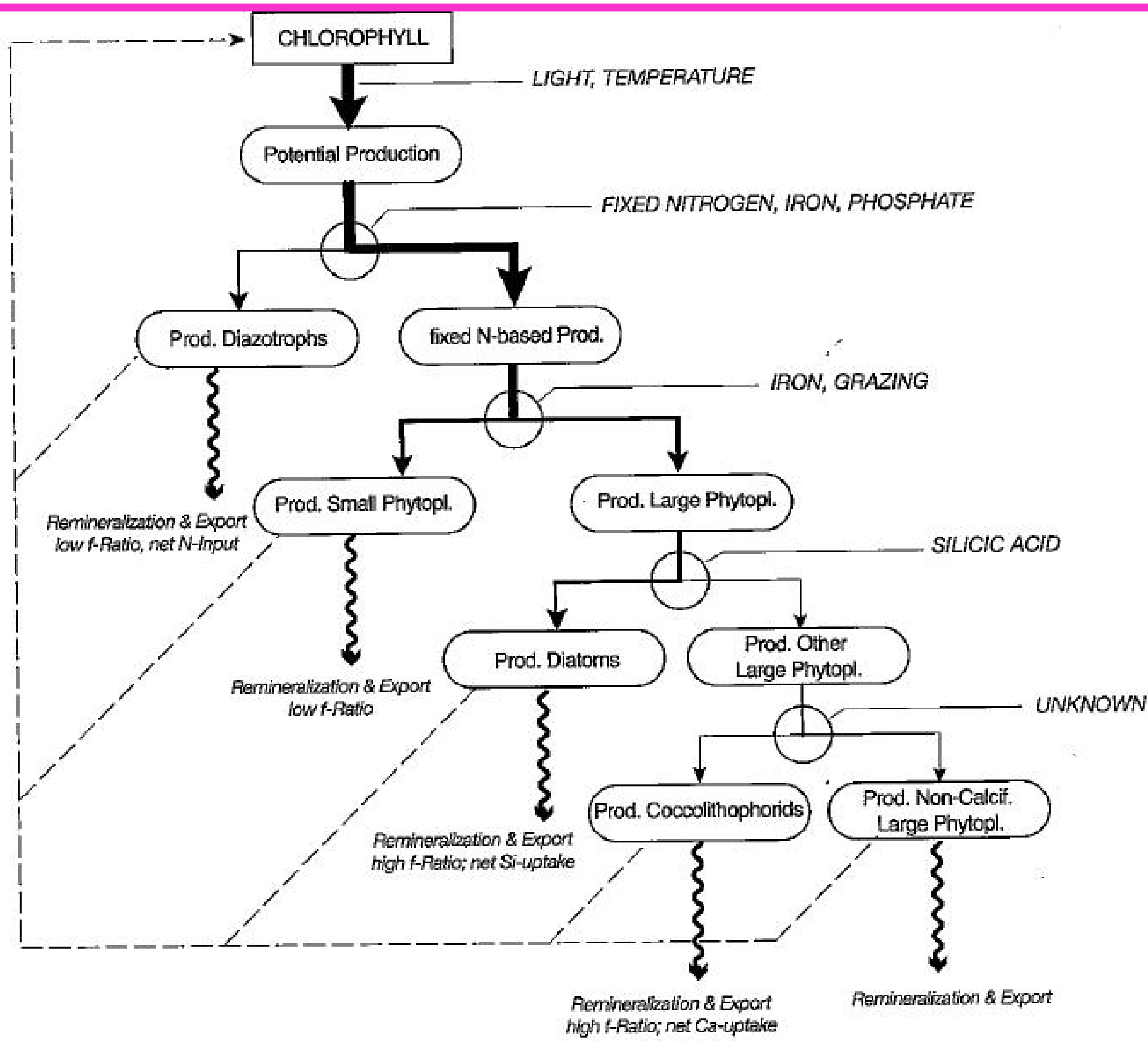
Eutrophic & Oligotrophic zons

↳ Nutrient rich regions with high productivity is called Eutrophic

↳ Nutrient low regions with low productivity is called Oligotrophic.



Allocation of Primary Production to different phytoplankton functional group.



Modeling photosynthesis.

↳ I ; irradiance W/m^2 or Einst/m^2/s

↳ N ; Nutrients mmol/m^3

↳ T ; Temperature °C.

↳ G ; zoo-plankton grazing mmol/m^3/s

↳ P ; phytoplankton mmol/m^3

$$SMS(P) = V_p(T) \cdot \mathcal{V}_p(I,N) \cdot P - G(P) - \text{sinks}$$

$V_p(T)$ ⇒ Temperature dependent maximum growth rate

⇒ $a \cdot b^{cT}$

⇒ $a = 0.6/\text{day}$

$b = 1.066$

$c = 1(°C)^{-1}$

e.g.: Eppley [1972]

Continued …

$\nu_p(I, N)$ ⇒ Light & Nutrient sensitivity function

⇒ $\nu_p(I) \cdot \nu_p(N)$

⇒ $\min[\nu_p(I), \nu_p(N)]$

$\nu_p(N)$ ⇒ Hyperbolic function

⇒ $\frac{N}{K_N + N}$ Monod et al., 1949

⇒ K_N = Monod Constant

↳ Concentration of N at which growth rate is half of its maximum value. (Half saturation Constant).

For Nitrate $K_n = 0.1\ mmol/m^3$

$\approx 3\ mmol/m^3$

Continued ...

For more than one form of nitrate
(eg: NO_3^-, NH_4^+)

$$\nu_p(N) = \frac{NO_3^-}{K_{NO_3} + NO_3^-} \cdot \exp(-\psi \cdot NH_4^+) + \frac{NH_4^+}{K_{NH_4^+} + NH_4^+}$$

eg: Wroblewski, 1977.

$$\nu_p(I) \Rightarrow \frac{I}{I_K + I}$$

$$\Rightarrow I(z) = I_0 \cdot \exp(-k \cdot z)$$

Continued ...

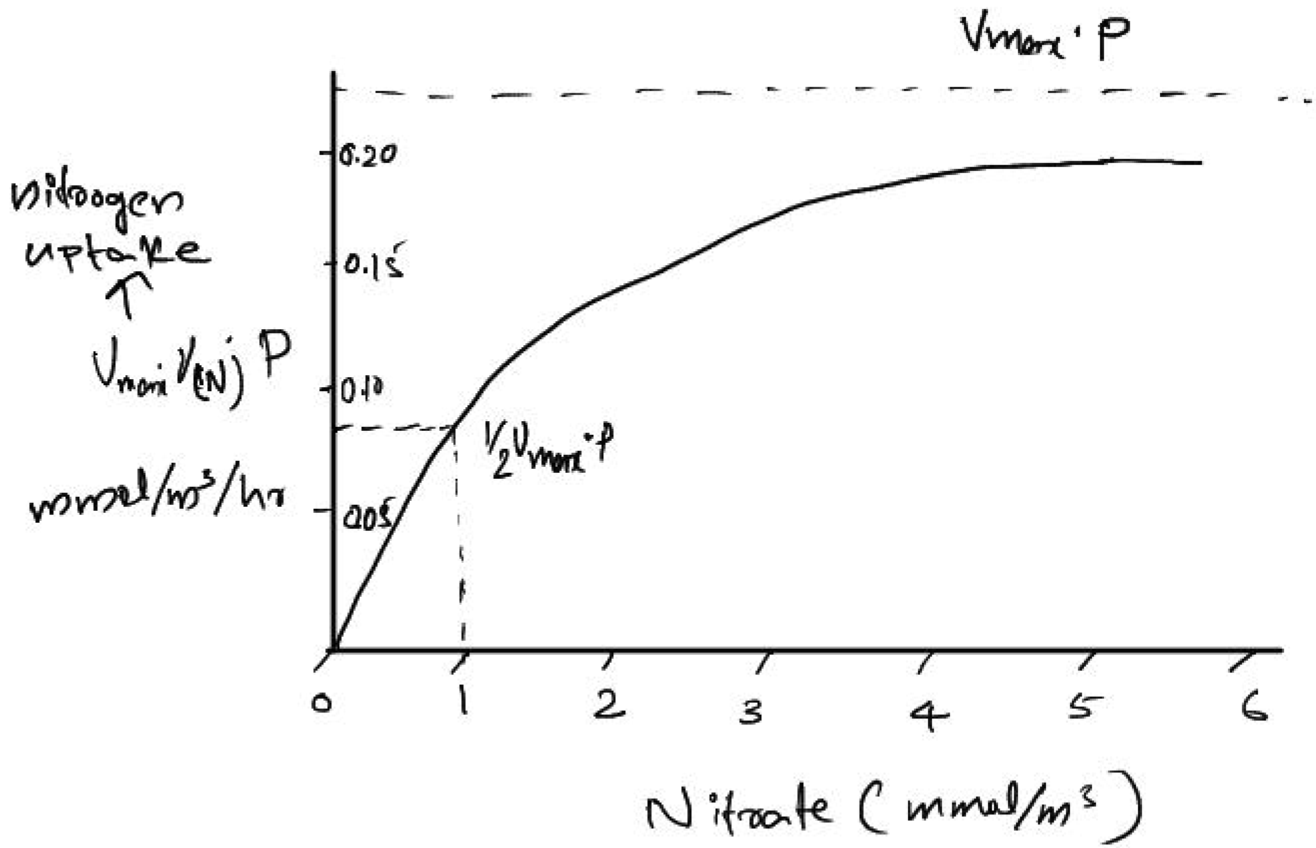
Zoo-plankton grazing

$$G(P) \Rightarrow g \cdot \frac{P}{K_p + P} \cdot Z$$

$\Rightarrow g =$ maximum grazing rate.

$$G(P) \Rightarrow g \cdot [1 - \exp(-k \cdot P)] \cdot Z.$$

Nitrogen uptake vs. Nitrate conc.



Rate of nitrate uptake Vs. Nitrate Concentration

Doring et al., 1982.

Sinking particle flux and bacterial source sink.

$$SMS(Z) = Z \cdot \left[\nu_Z \, g \frac{P}{K_P} - \lambda_Z \right]$$

$\nu_Z = 0 \sim 1.$

λ_Z = zooplankton mortality rate.

g = specific growth rate

$$SMS(B) = V_B(T) \cdot \nu_B(DON, NH_4^+) \cdot B - (\Omega(B) - \text{sinks}).$$

(↳ Bacterial formation)

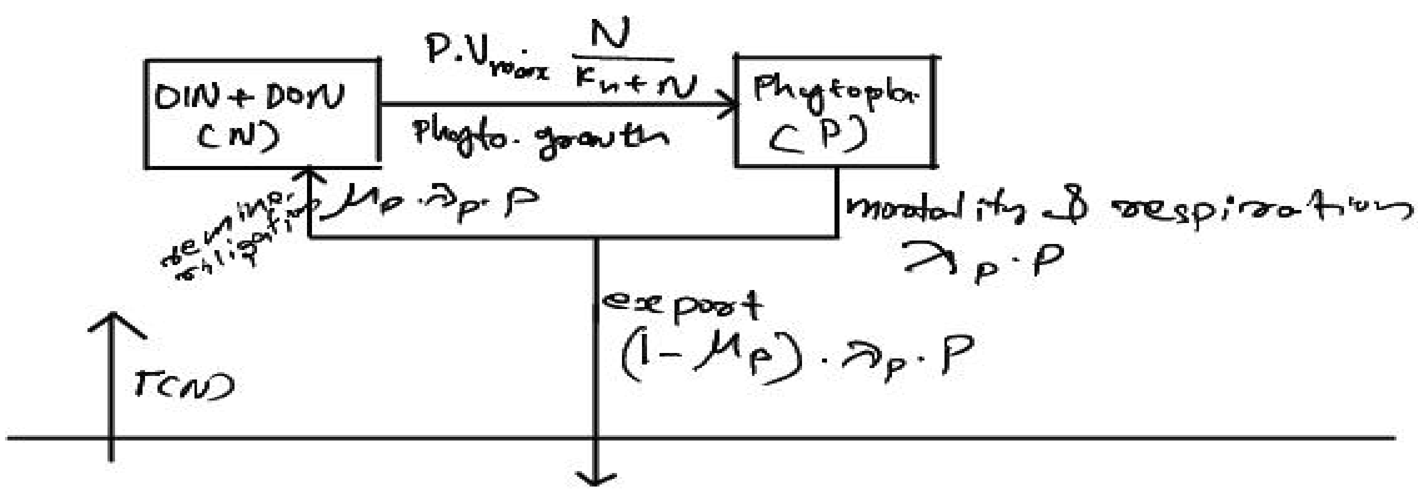
N-P Ecosystem models

Analysis of ecosystem behaviour using Eco-models

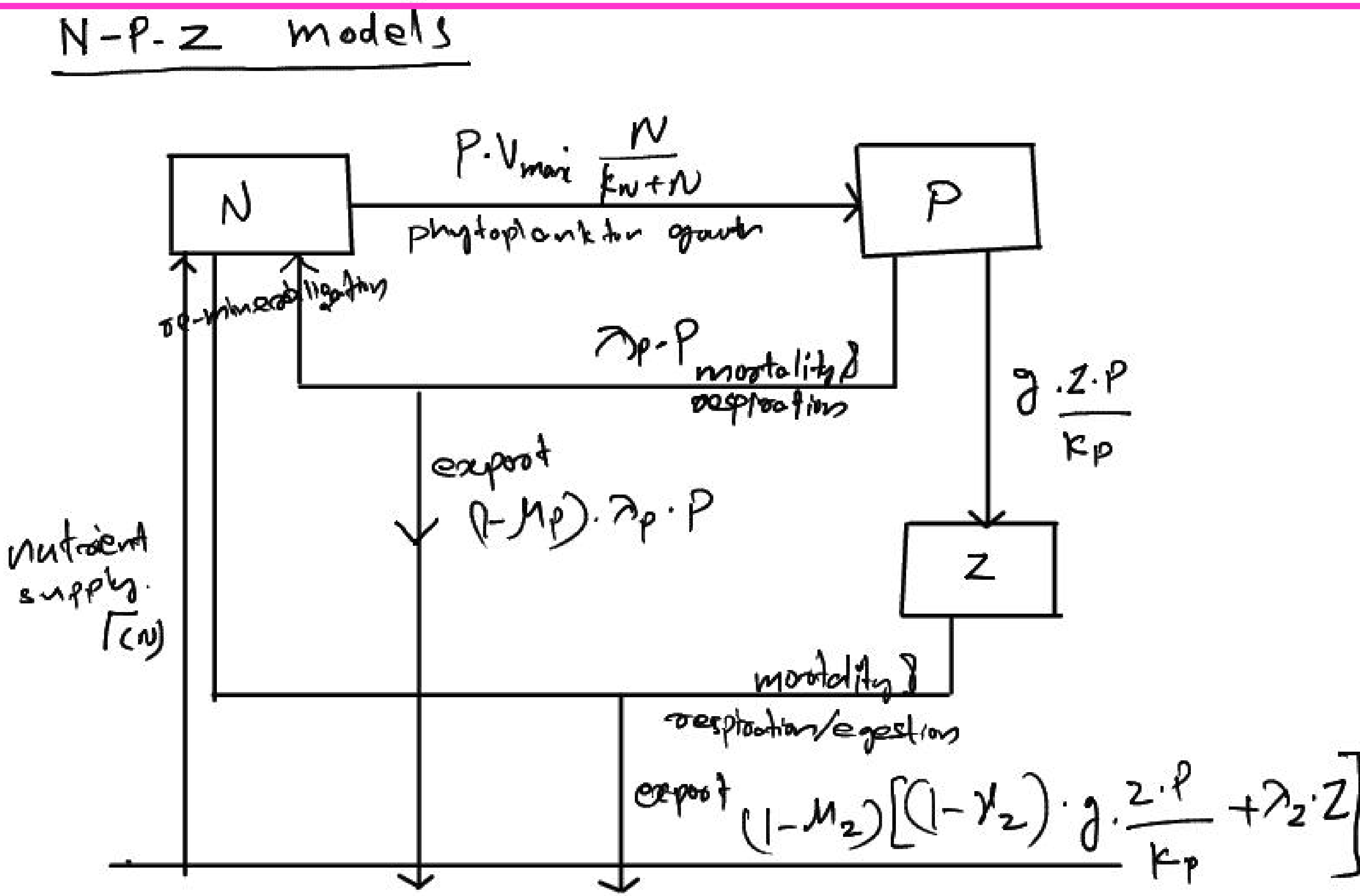
N-P models [nitrate - phytoplankton models]

N = Dissolved inorganic Nitrogen (NO_3^{2-}, NH_4^+, DON)
P = Nitrate in form of phytoplankton.

↳ Biological Production is controlled entirely by N-supply ⟹ Bottom-up limitation



N-P-Z Ecosystem models



Ecosystem models

N-P models

$$sms(N) = P \cdot \left(-V_{max} \cdot \frac{N}{K_n + N} + \mu_p \lambda_p\right)$$

$$sms(P) = P \cdot \left(V_{max} \frac{N}{K_n + N} - \lambda_p\right)$$

$$N_T = N + P$$

N-P-Z models

$$sms(P) = P \cdot \left(V_{max} \cdot \frac{N}{K_n + N} - \lambda_p - \frac{g \cdot Z}{K_p}\right)$$

$$sms(N) = P \cdot \left(-V_{max} \cdot \frac{N}{K_n + N} + \mu_p \lambda_p\right) + Z \cdot \mu_z \cdot \left[(1 - \nu_z) g \frac{P}{K_p} + \lambda_z\right]$$

$$sms(Z) = Z \cdot \left[\nu_z \cdot g \frac{P}{K_p} - \lambda_z\right]$$

$$N_T = N + P + Z$$

Nemuro model

15-component BGC-Model. Yamanaka et al., 2004,

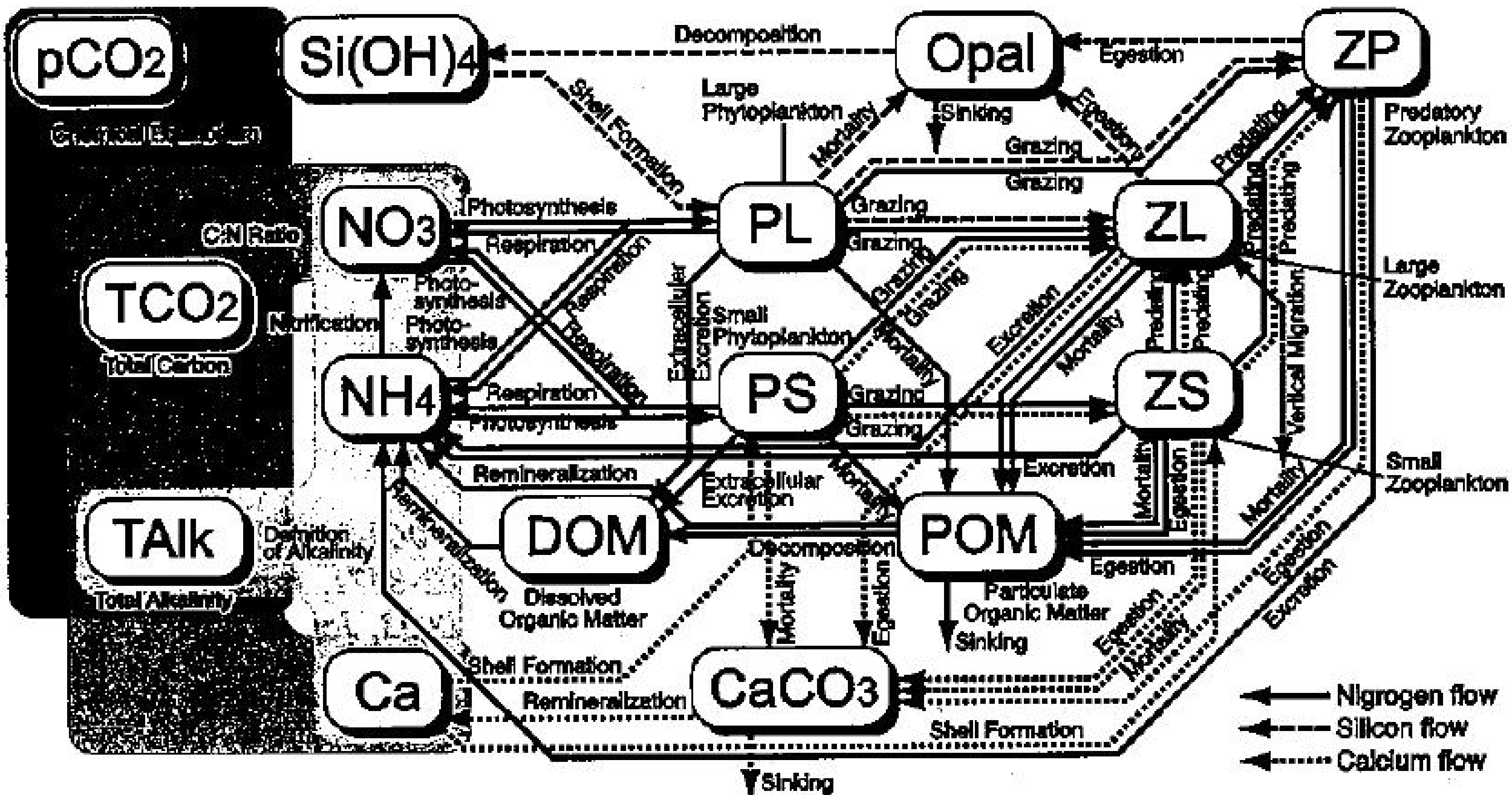


Fig. 1. Schematic view of interactions among the fifteen model compartments.

Nemuro model

$$\frac{\partial[PS]}{\partial t} = (\text{PS Photosynthesis}) - (\text{PS Respiration}) - (\text{PS Extracellular Excretion}) - (\text{PS Mortality}) - (\text{PS Grazing by ZS}) - (\text{PS Grazing by ZL}) + \text{Adv}(PS) + \text{Diff}(PS), \quad (A1)$$

$$\frac{\partial[PL]}{\partial t} = (\text{PL Photosynthesis}) - (\text{PL Respiration}) - (\text{PL Extracellular Excretion}) - (\text{PL Mortality}) - (\text{PL Grazing by ZL}) - (\text{PL Grazing by ZP}) + \text{Adv}(PL) + \text{Diff}(PL), \quad (A2)$$

$$\frac{\partial[ZS]}{\partial t} = (\text{PS Grazing by ZS}) - (\text{ZS Excretion}) - (\text{ZS Egestion}) - (\text{ZS Mortality}) - (\text{ZS Predating by ZL}) - (\text{ZS Predating by ZP}) + \text{Adv}(ZS) + \text{Diff}(ZS), \quad (A3)$$

$$\frac{\partial[ZL]}{\partial t} = (\text{PS Grazing by ZL}) + (\text{PL Grazing by ZL}) + (\text{ZS Predating by ZL}) - (\text{ZL Excretion}) - (\text{ZL Egestion}) - (\text{ZL Mortality}) - (\text{ZL Predating by ZP}) + (\text{Ontogenetic Migration}) + \text{Adv}(ZL) + \text{Diff}(ZL), \quad (A4)$$

$$\frac{\partial[ZP]}{\partial t} = (\text{PL Grazing by ZP}) + (\text{ZS Predating by ZP}) + (\text{ZL Predating by ZP}) - (\text{ZP Excretion}) - (\text{ZP Egestion}) - (\text{ZP Mortality}) + \text{Adv}(ZP) + \text{Diff}(ZP), \quad (A5)$$

$$\frac{\partial[NO_3]}{\partial t} = (\text{Nitrification}) - \{(\text{PS Photosynthesis}) - (\text{PS Respiration})\} \times R_{newS} - \{(\text{PL Photosynthesis}) - (\text{PL Respiration})\} \times R_{newL} + \text{Adv}(NO_3) + \text{Diff}(NO_3), \quad (A6)$$

$$\frac{\partial[NH_4]}{\partial t} = (\text{ZS Excretion}) + (\text{ZL Excretion}) + (\text{ZP Excretion}) + (\text{DOM Remineralization}) + (\text{POM Remineralization}) - (\text{Nitrification}) - \{(\text{PS Photosynthesis}) - (\text{PS Respiration})\} \times (1 - R_{newS}) - \{(\text{PL Photosynthesis}) - (\text{PL Respiration})\} \times (1 - R_{newL}) + \text{Adv}(NH_4) + \text{Diff}(NH_4), \quad (A7)$$

$$\frac{\partial[POM]}{\partial t} = (\text{PS Mortality}) + (\text{PL Mortality}) + (\text{ZS Mortality}) + (\text{ZL Mortality}) + (\text{ZP Mortality}) + (\text{ZS Egestion}) + (\text{ZL Egestion}) + (\text{ZP Egestion}) - (\text{POM Remineralization}) - (\text{POM Decomposition to DOM}) + \text{Sinking}(POM) + \text{Adv}(POM) + \text{Diff}(POM), \quad (A8)$$

$$\frac{\partial[DOM]}{\partial t} = (\text{PS Extracellular Excretion}) + (\text{PL Extracellular Excretion}) + (\text{POM Decomposition to DOM}) - (\text{DOM Remineralization}) + \text{Adv}(DOM) + \text{Diff}(DOM), \quad (A9)$$

$$\frac{\partial[Si(OH)_4]}{\partial t} = (\text{Opal Decomposition}) - (\text{Si\_PL Shell Formation}) + \text{Adv}(Si(OH)_4) + \text{Diff}(Si(OH)_4), \quad (A10)$$

$$\frac{\partial[Opal]}{\partial t} = (\text{Si\_ZL Egestion}) + (\text{Si\_ZP Egestion}) + (\text{Si\_PL Mortality}) - (\text{Opal Decomposition}) + \text{Sinking}(Opal) + \text{Adv}(Opal) + \text{Diff}(Opal), \quad (A11)$$

$$\frac{\partial[Ca]}{\partial t} = (CaCO_3\ \text{Decomposition}) - (\text{Ca\_PS Shell Formation}) - (\text{Ca\_ZS Shell Formation}) + \text{Adv}(Ca) + \text{Diff}(Ca), \quad (A12)$$

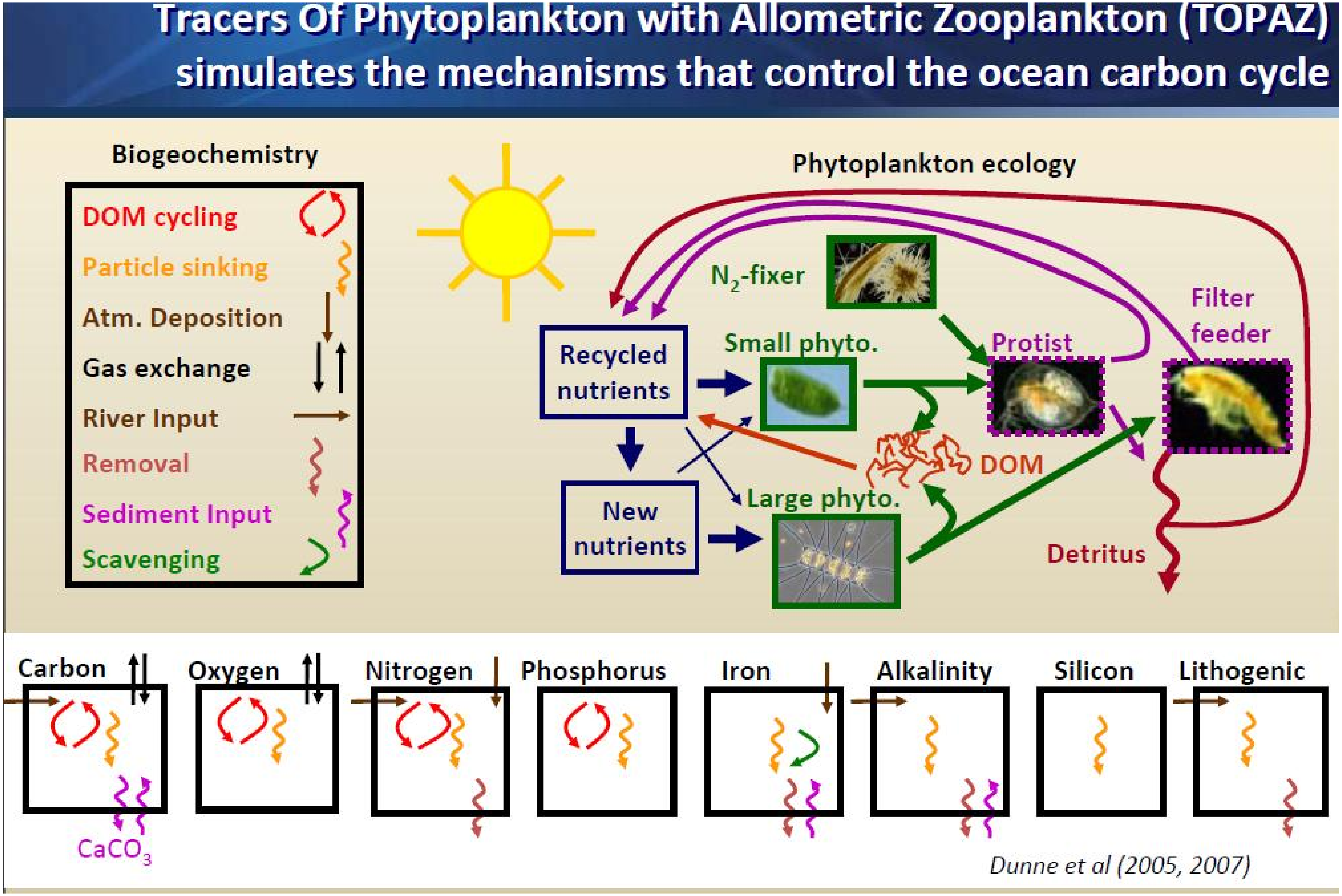
$$\frac{\partial[CaCO_3]}{\partial t} = (\text{Ca\_ZS Egestion}) + (\text{Ca\_ZL Egestion}) + (\text{Ca\_ZP Egestion}) + (\text{Ca\_PS Mortality}) + (\text{Ca\_ZS Mortality}) - (CaCO_3\ \text{Decomposition}) + \text{Sinking}(CaCO_3) + \text{Adv}(CaCO_3) + \text{Diff}(CaCO_3), \quad (A13)$$

$$\frac{\partial[TCO_2]}{\partial t} = -\left[\left(\frac{\partial[NO_3]}{\partial t}\right)_{\text{biological}} + \left(\frac{\partial[NH_4]}{\partial t}\right)_{\text{biological}}\right] \times R_{CN} + \left(\frac{\partial[Ca]}{\partial t}\right)_{\text{biological}} + (CO_2\ \text{Air-Sea Gas Exchange}) + \text{Adv}(TCO_2) + \text{Diff}(TCO_2), \quad (A14)$$

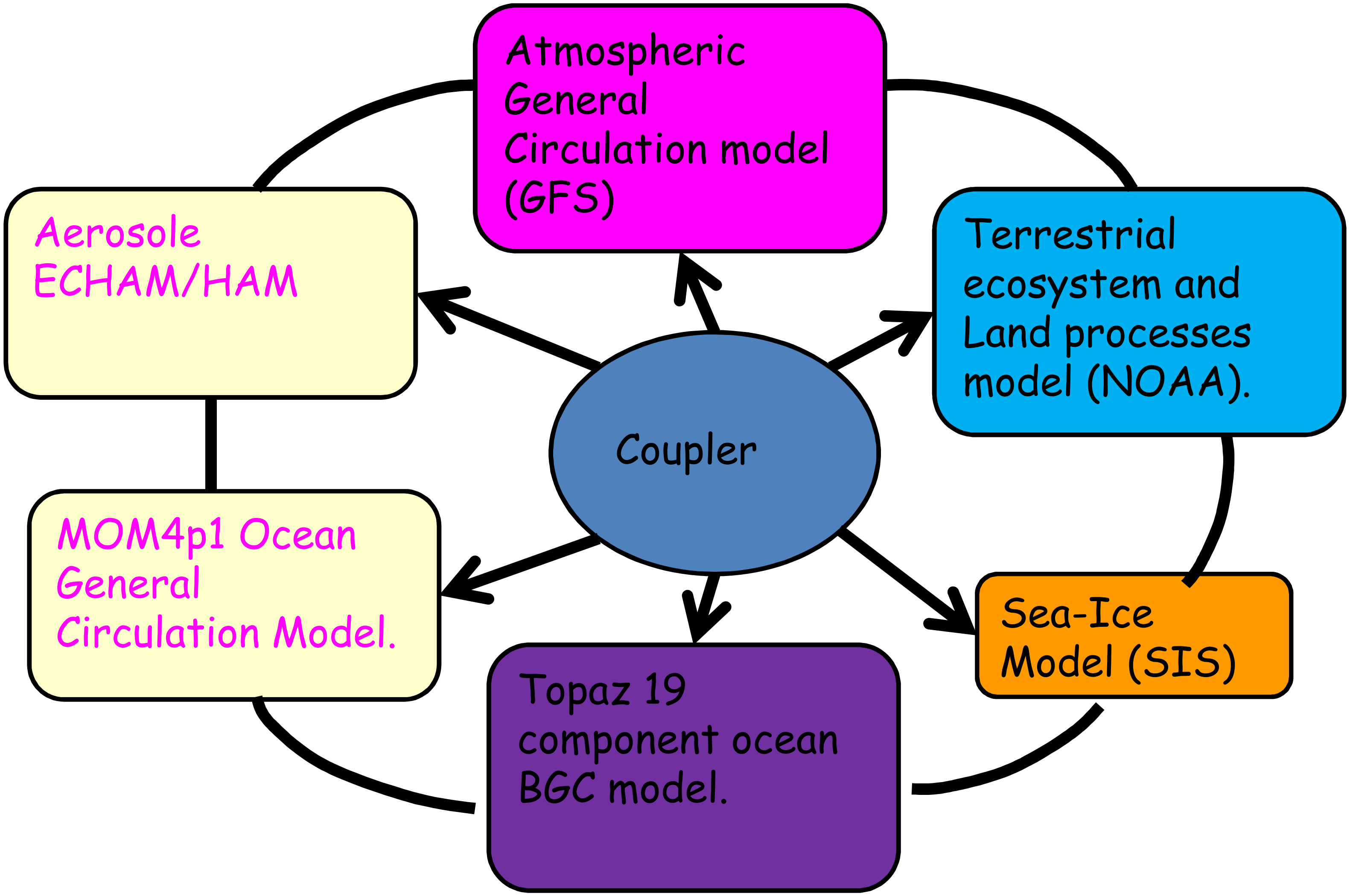
$$\frac{\partial[TALK]}{\partial t} = 2.0\left(\frac{\partial[Ca]}{\partial t}\right)_{\text{biological}} - \left(\frac{\partial[NO_3]}{\partial t}\right)_{\text{biological}} + \left(\frac{\partial[NH_4]}{\partial t}\right)_{\text{biological}} + \text{Adv}(TALK) + \text{Diff}(TALK), \quad (A15)$$

Yamanaka et al., 2004, J. Oceanography, Vol. 60, 227-241

Topaz- 19 component BGC.



Earth-System-Model @ CCCR, IITM



Marine Organic/Inorganic Carbon Cycle

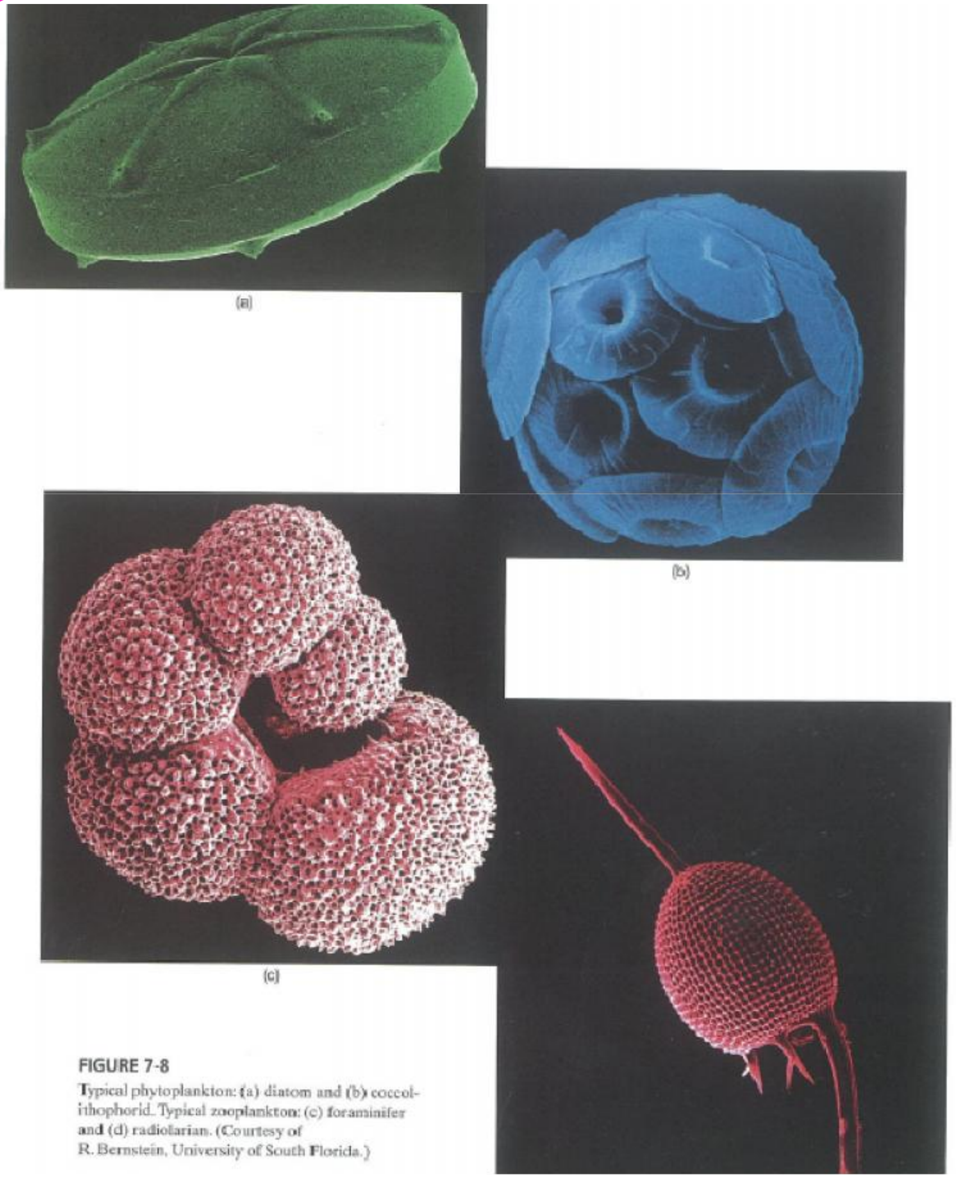


FIGURE 7-8
Typical phytoplankton: (a) diatom and (b) coccolithophorid. Typical zooplankton: (c) foraminifer and (d) radiolarian. (Courtesy of R. Bernstein, University of South Florida.)

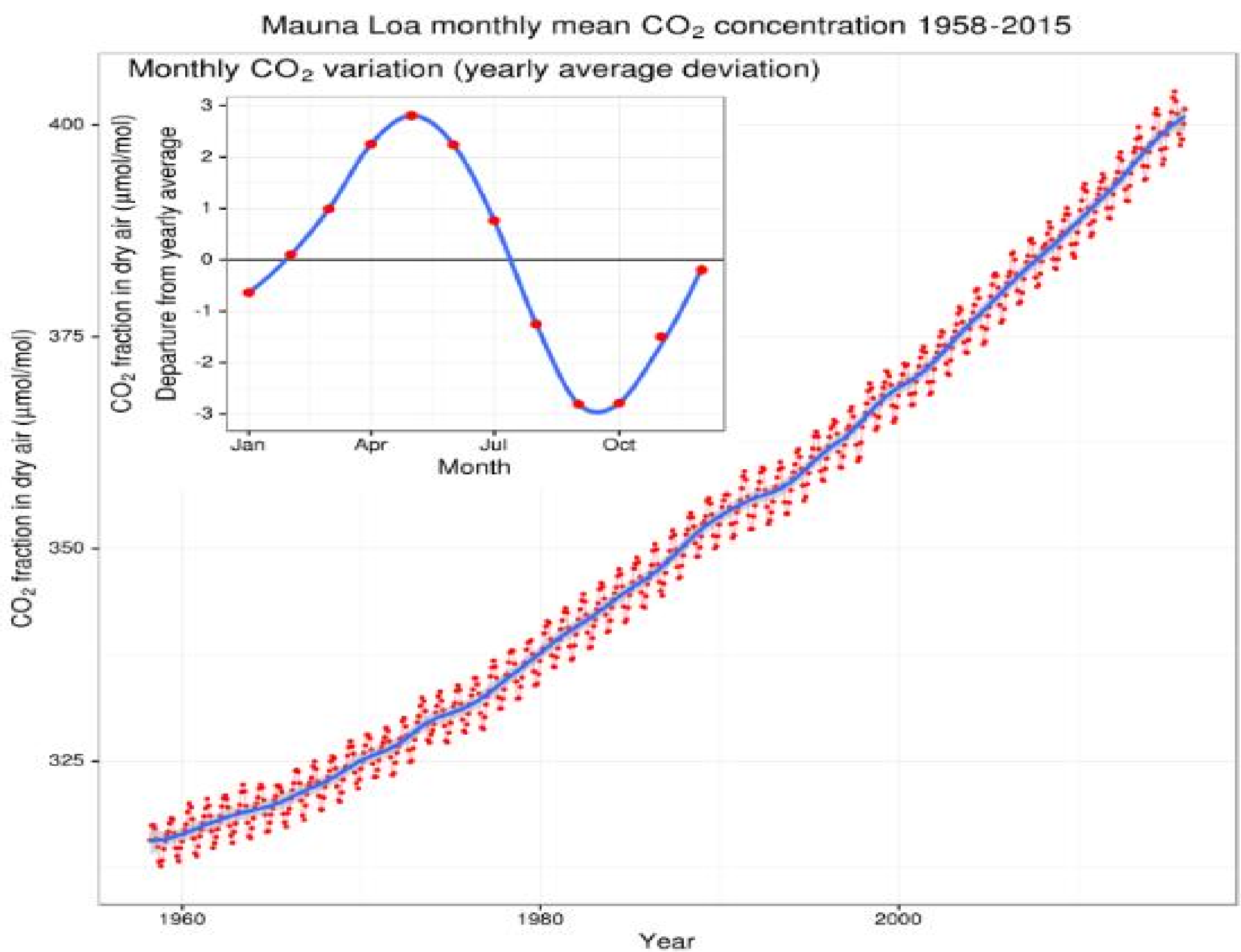
Phytoplankton

(a) Diatom
(b) Coccolithophorid

Zoo-plankton

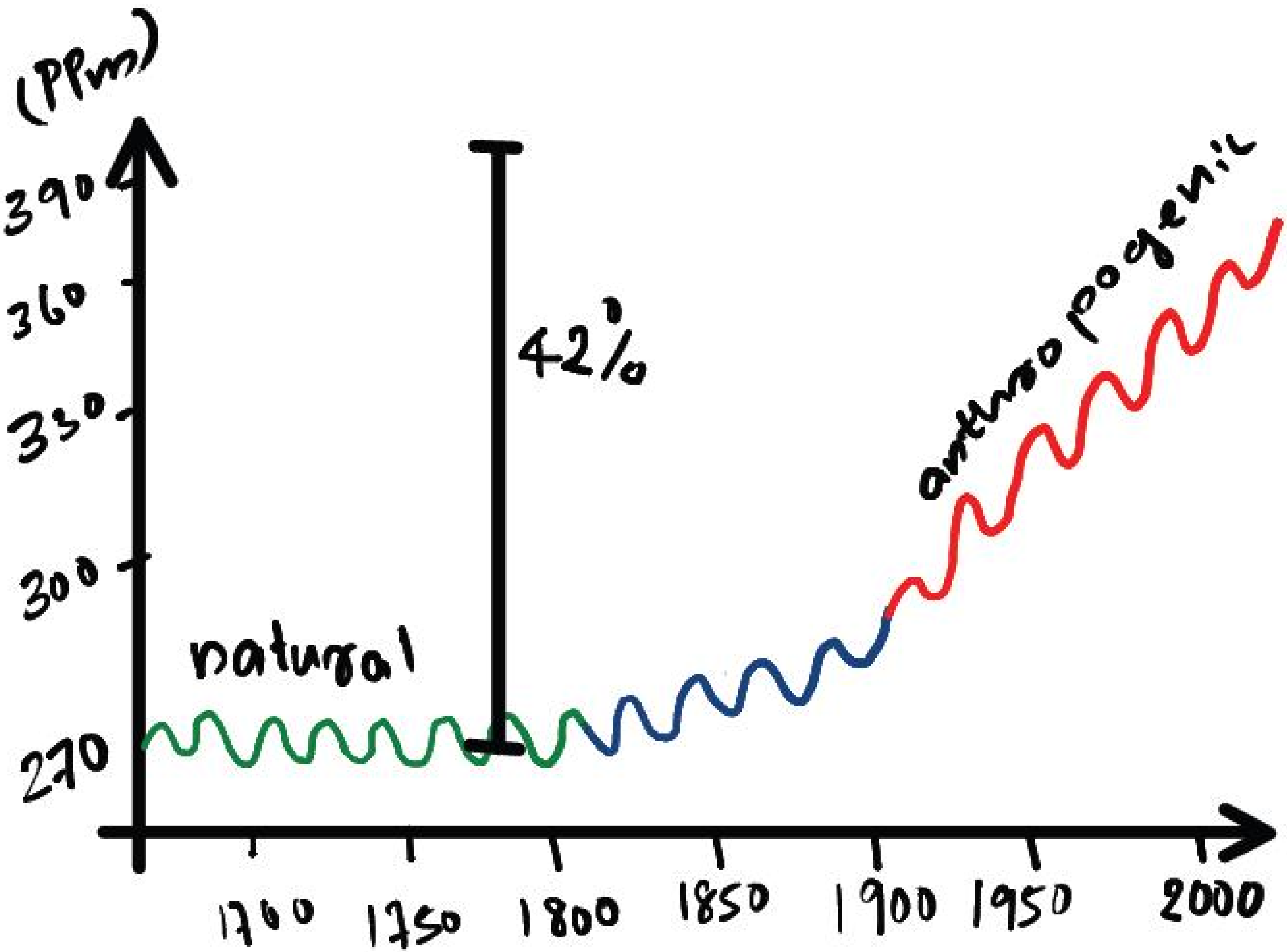
(a) Foraminifer
(b) Radiolarian

Present day CO_2; Keeling curve.

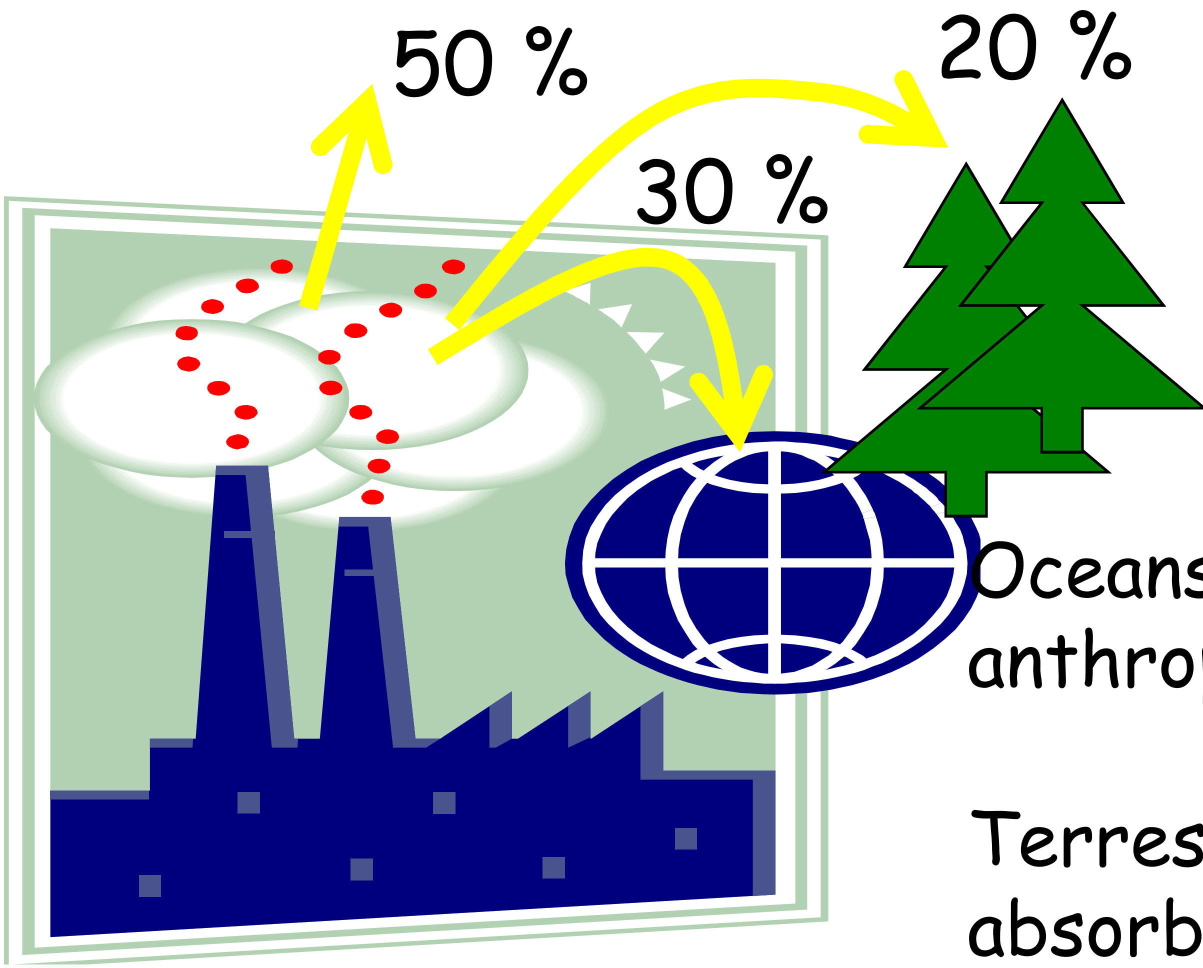


© http://en.wikipedia.org/wiki/File:Mauna_Loa_Carbon_Dioxide-en.svg

Atmospheric CO2 from 1700 to 2010



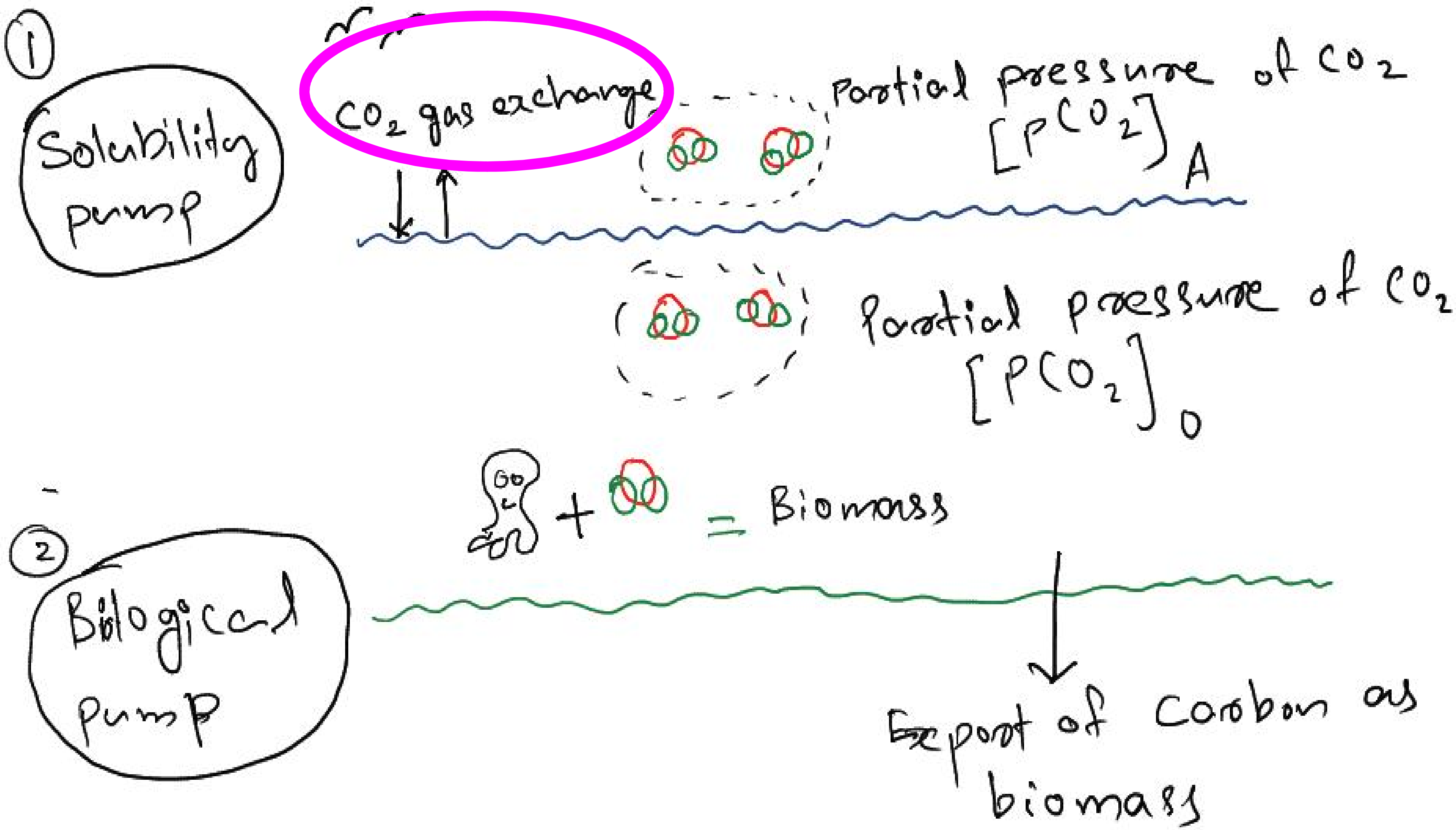
But ~50% of man-made CO2 is absorbed by oceans and land.



Oceans sink ~30% of anthropogenic CO2

Terrestrial ecosystem absorbs ~ 20% of anthropogenic CO2.

Carbon pumps in the ocean



Exchange of CO2 with atmosphere.

CO$_2$- exchange Between ocean & atmosphere.

$$\phi_{CO_2} = K_w \left[pCO_{2_{ocean}} - pCO_{2_{atmosphere}} \right]$$

$$= K_w \cdot \Delta pCO_2 \Big|_{oc.}^{At.}$$

K_w = piston velocity.

$$K_w = a \cdot u^2 \cdot \left(\frac{Sc}{660} \right)^{-1/2}$$

a = coefficient

Sc = schmidt Number

Solubility pump: Carbonate Chemistry

Equilibrium constants,

$$K_0 = \frac{[H_2CO_3^*]}{pCO_2}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{H_2CO_3^*}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{HCO_3^-}$$

There are total 5 unknowns

pCO_2, $H_2CO_3^*$, HCO_3^-, CO_3^{2-} and H^+

and 3 equations.

Solubility pump: Carbonate Chemistry

$$CO_{2(g)} + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

Therefore CO_2 in the ocean exists as three derivatives $CO_{2(g)}$, HCO_3^-, CO_3^{2-}.

↓

Dissolved Inorganic Carbon [DIC]

DIC is a conserved quantity. (mole/m^3)

Solubility pump: Carbonate Chemistry

Therefore we assume the combinations of $H_2CO_3^*$, HCO_3^-, CO_3^{2-} as one conserved tracer "DIC"

i.e. $DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$

DIC is Dissolved Inorganic Carbon

Also,

$$ALK = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [B(OH)_4^-]$$

+ minor bases.

ALK is total Alkalinity.

Both DIC & ALK are conservative tracers.

Solubility pump: Carbonate Chemistry

Alkalinity

↳ Alk is a measure of the excess of bases (proton acceptors) over acids (proton donors).

↳ Alk has alternate definition as,

$$Alk = [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + \text{minor cations}$$
$$- [Cl^-] - 2[SO_4^{2-}] - [Br^-] - [NO_3^-] - \text{minor anions}$$

Total carbonate chemistry Equations

$$K_0 = \frac{H_2CO_3^-}{pCO_2} \quad \text{--- (1)}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \quad \text{--- (2)}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad \text{--- (3)}$$

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad \text{--- (4)}$$

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [B(OH_4)^-] + \text{minor bases} \quad \text{--- (5)}$$

$$K_w = [H^+][OH^-] \quad \text{--- (6)}$$

$$K_B = \frac{[H^+][B(OH_4^-)]}{[H_3BO_3]} \quad \text{--- (7)}$$

$$[B(OH_4^-)] + H_3BO_3 = C \cdot \text{Salinity} \quad \text{--- (8)}$$

$$= T_B$$

Unknowns

$H_2CO_3^*$, HCO_3^-, CO_3^{2-}, H^+, OH^-, $B(OH)_4^-$, H_3BO_3, DIC, Alk.

Total = 10

8-equations and 10-unknowns.

↳ Therefore, specify any two variables.

Solution

- Specify DIC and Alk. as "state variables"
- Re-write Alk in terms of DIC, T_B and solve for H^+!
- $$DIC = \frac{[H^+]^2[CO_3^{2-}]}{K_1 K_2} + \frac{[H^+][CO_3^{2-}]}{K_2} + [CO_3^{2-}]$$

The pH of the water is $-\log_{10}[H^+]$ is found iteratively.

- $$pCO_2 = \frac{DIC}{K_0} \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2}$$

Simplified carbonate chemistry.

DIC & Alk approximations

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

$CO_2 + H_2O \rightleftharpoons H_2CO_3^*$

0.5% 88.6% 10.9%

$$Alk = [HCO_3^-] + [2CO_3^-] + [OH^-] - [H^+] + [B(OH)_4^-]$$

$$= 76.8\% \quad 18.8\% \quad 0.2\% \quad 4.2\%$$

Therefore,

$$DIC \approx [HCO_3^-] + [CO_3^{2-}] \quad \text{—— (1)}$$

$$Alk \approx [HCO_3^-] + [2CO_3^{2-}] \quad \text{—— (2)}$$

carbonate Alkalinity.

Solving —(1) & (2)

$$[HCO_3^-] \approx 2 \cdot DIC - Alk$$

$$[CO_3^{2-}] \approx Alk - DIC$$

∴ with < 10% error.

Carbonate alkalinity

Simplified carbonate chemistry.

Surface ocean pCO_2

$$K_0 = \frac{[H_2CO_3^*]}{pCO_2} \quad \text{— (1)}$$

$$K_1 = [H^+][HCO_3^-] \quad \text{— (2)}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad \text{— (3)}$$

$$[HCO_3^-] \approx 2 \cdot DIC - Alk \quad \text{— (4)}$$

$$[CO_3^{2-}] \approx Alk - DIC \quad \text{— (5)}$$

$$\therefore pCO_2 \approx \frac{K_2}{K_0 \cdot K_1} \frac{(2 \cdot DIC - Alk)^2}{[Alk - DIC]}$$

TABLE 8.2.2

Equations used to calculate seawater equilibrium constants

T: Temperatures in [K], S: Salinity on the practical salinity scale.

Equation		Source
Solubility of CO_2 (mol kg^{-1} atm^{-1}):		
$\ln K_0 = -60.2409 + 93.4517\left(\frac{100}{T}\right) + 23.3585 \ln\left(\frac{T}{100}\right) + S\left(0.023517 - 0.023656\left(\frac{T}{100}\right) + 0.0047036\left(\frac{T}{100}\right)^2\right)$	(20)	[*Weiss*, 1974]
Dissociation constants of CO_2† (mol kg^{-1}):		
$-\log K_1 = -62.008 + \frac{3670.7}{T} + 9.7944 \ln(T) - 0.0118\, S + 0.000116\, S^2$	(21)	[*Mehrbach et al.*, 1973] as refitted by *Dickson and Millero* [1987]
$-\log K_2 = +4.777 + \frac{1394.7}{T} - 0.0184\, S + 0.000118\, S^2$	(22)	[*Mehrbach et al.*, 1973] as refitted by *Dickson and Millero* [1987]
Dissociation constants of other species† (mol kg^{-1}) for K_w and [(mol kg^{-1})^2] for K_b:		
$-\ln K_w = 148.96502 + \frac{-13847.26}{T} - 23.6521 \ln(T) + S^{\frac{1}{2}}\left(-5.977 + \frac{118.67}{T} + 1.0495 \ln(T)\right) - 0.01615\, S$	(23)	[*Millero*, 1995]
$-\ln K_b = \frac{1}{T}(-8966.9 - 2890.53\, S^{0.5} - 77.942\, S + 1.728\, S^{1.5} - 0.0996\, S^2) \times 148.0248 + 137.1942\, S^{0.5} + 1.62142\, S + 0.053105\, S^{0.5}\, T + \ln(T)\,(-24.4344 - 25.085\, S^{0.5} - 0.2474\, S)$	(24)	[*Dickson*, 1990]
Total boron equation (µmol kg^{-1}):		
$TB = 1.185 \cdot S$	(25)	[*Uppström*, 1974]

† All dissociation constants are given with respect to the seawater pH scale [*Dickson*, 1993].

K_0, K_1 and K_2 is a function of Temperature.

pCO2 as a function of Temperature and Salinity

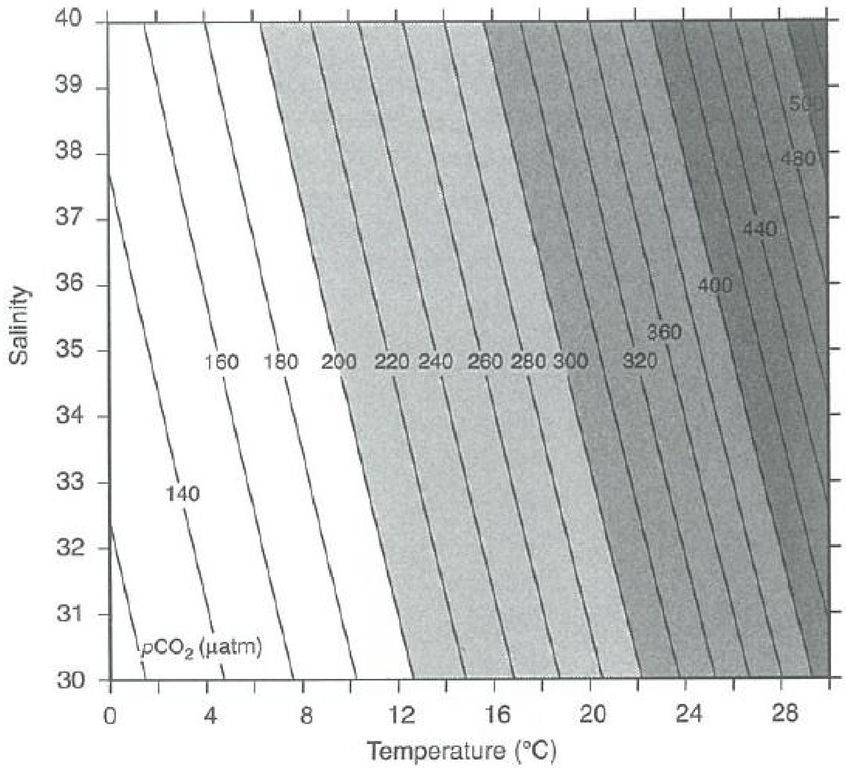


FIGURE 8.3.1: Plot of the partial pressure of CO_2 (pCO_2) as a function of temperature and salinity for constant *DIC* and *Alk*. Shown are the results for a typical surface water sample with an alkalinity of 2322 μmol kg^{-1} and a *DIC* content of 2012 μmol kg^{-1}.

K_0, K_1 and K_2 as a function of temperature.

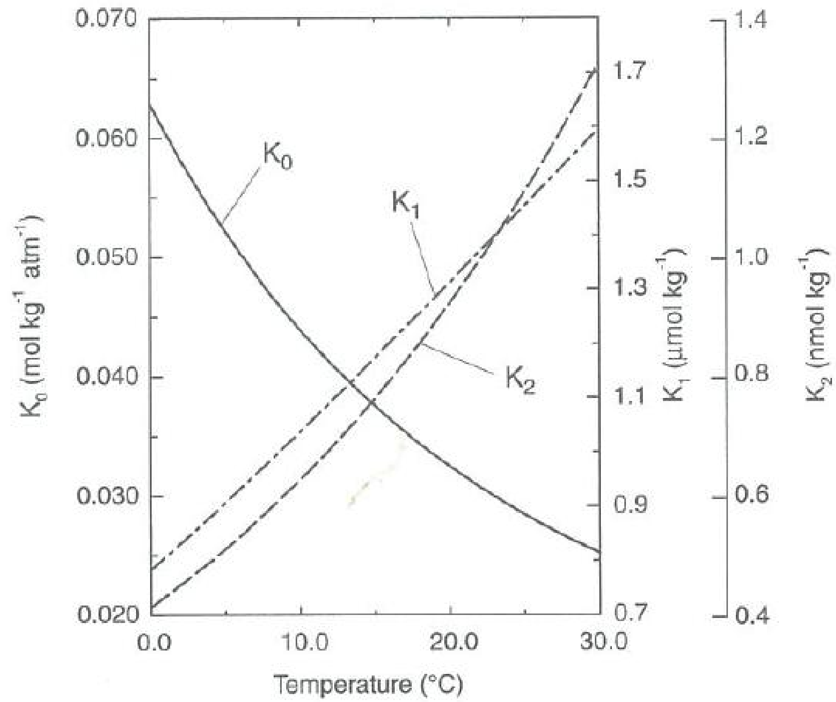


FIGURE 8.3.2: Plot of the CO_2 solubility (K_0), and of the first and second dissociation constants of carbonic acid (K_1 and K_2) as a function of temperature.

Dependency of pCO_2 on

(i) $\frac{K_2}{K_0 \cdot K_1}$

(ii) DIC } Interrelated.

(iii) Alk.

✓ DIC changes by ocean-atmosphere CO_2 exchange & Biology.

✓ Alk changes by Biology.

Sensitivity of pCO_2 on T, S.

↳ pCO_2 is weakly sensitive to salinity

$$\therefore \quad \frac{1}{pCO_2}\frac{\partial pCO_2}{\partial T} \approx 0.0423\,°C^{-1}$$

[Takahashi, 1999]

$$\gamma_s = \frac{S}{pCO_2}\frac{\partial pCO_2}{\partial S} = \frac{\partial \ln pCO_2}{\partial \ln S} \approx 1$$

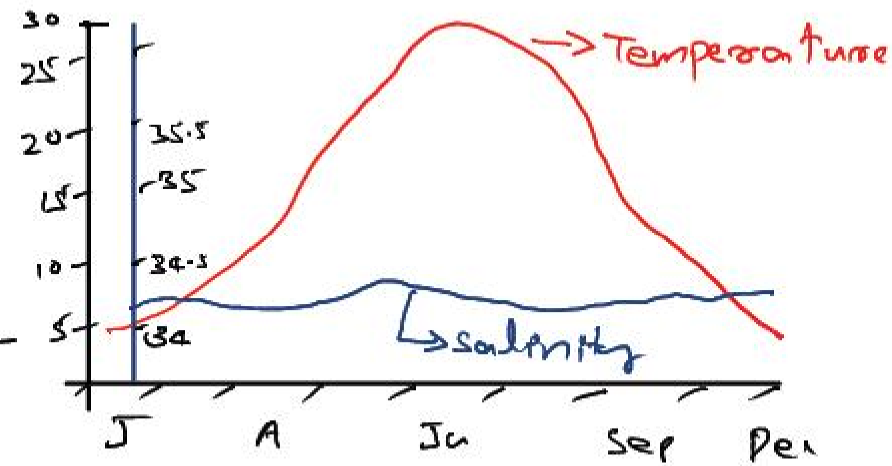
Seasonal dependency of pCO2 on T, S.

pCO_2 sensitivity to T, S.

pCO_2	T	S
300 (ppm)	20°C	35

ΔpCO_2	ΔT	ΔS
13 (ppm)	1°C	

9 ppm 1 psu



Temperature variation is larger than Salinity variations

$\therefore \Delta pCO_2 \approx f(\Delta T, S)$

Effect of rainfall on surface ocean carbonate chemistry.

Effect of fresh water on DIC & Alk

↳ DIC & Alk dilutes by freshwater addition.

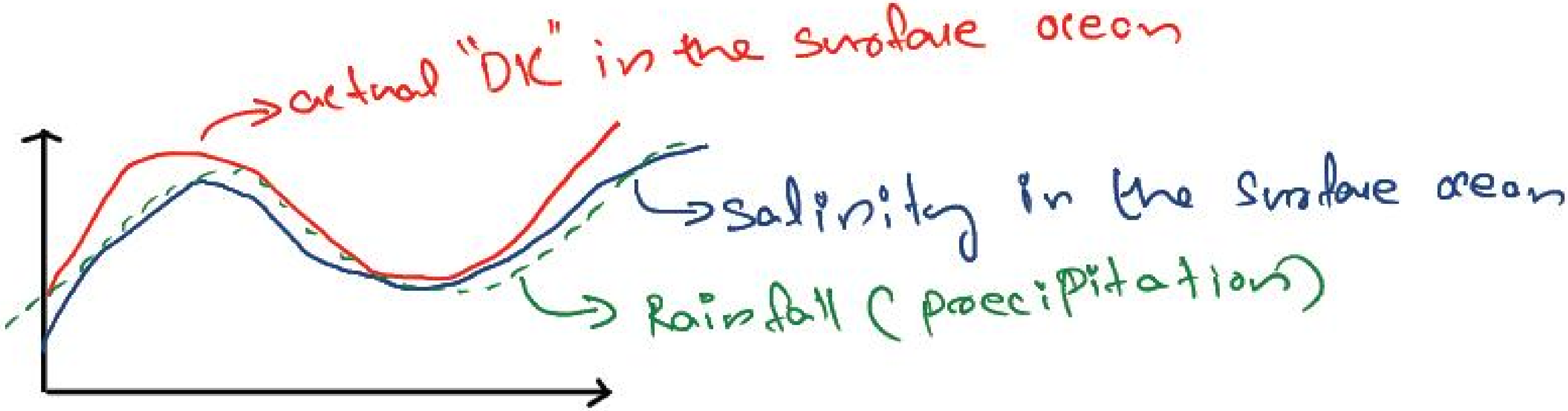
↳ chemical & biological changes of DIC & Alk are often "smaller" than freshwater induced changes.

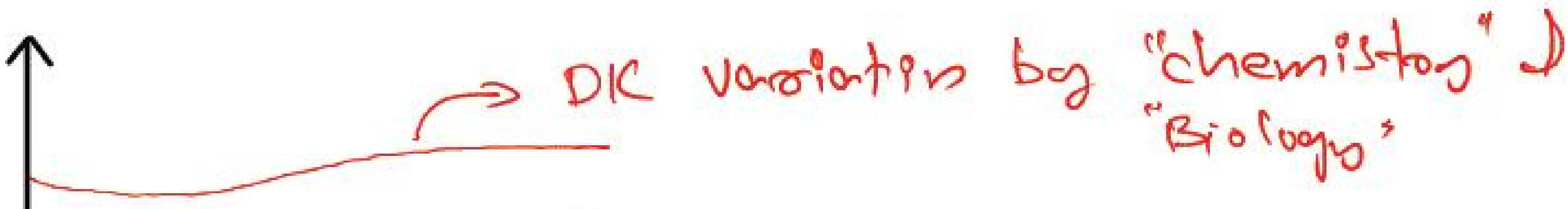
↳ Therefore we recomend a "normalized DIC" and "normalized Alkalinity";

$$sDIC = \frac{DIC}{S} \times S_g \Rightarrow S_g = \text{global mean salinity}$$

$$sAlk = \frac{Alk}{S} \times S_g \Rightarrow S_g = \text{global mean salinity.}$$

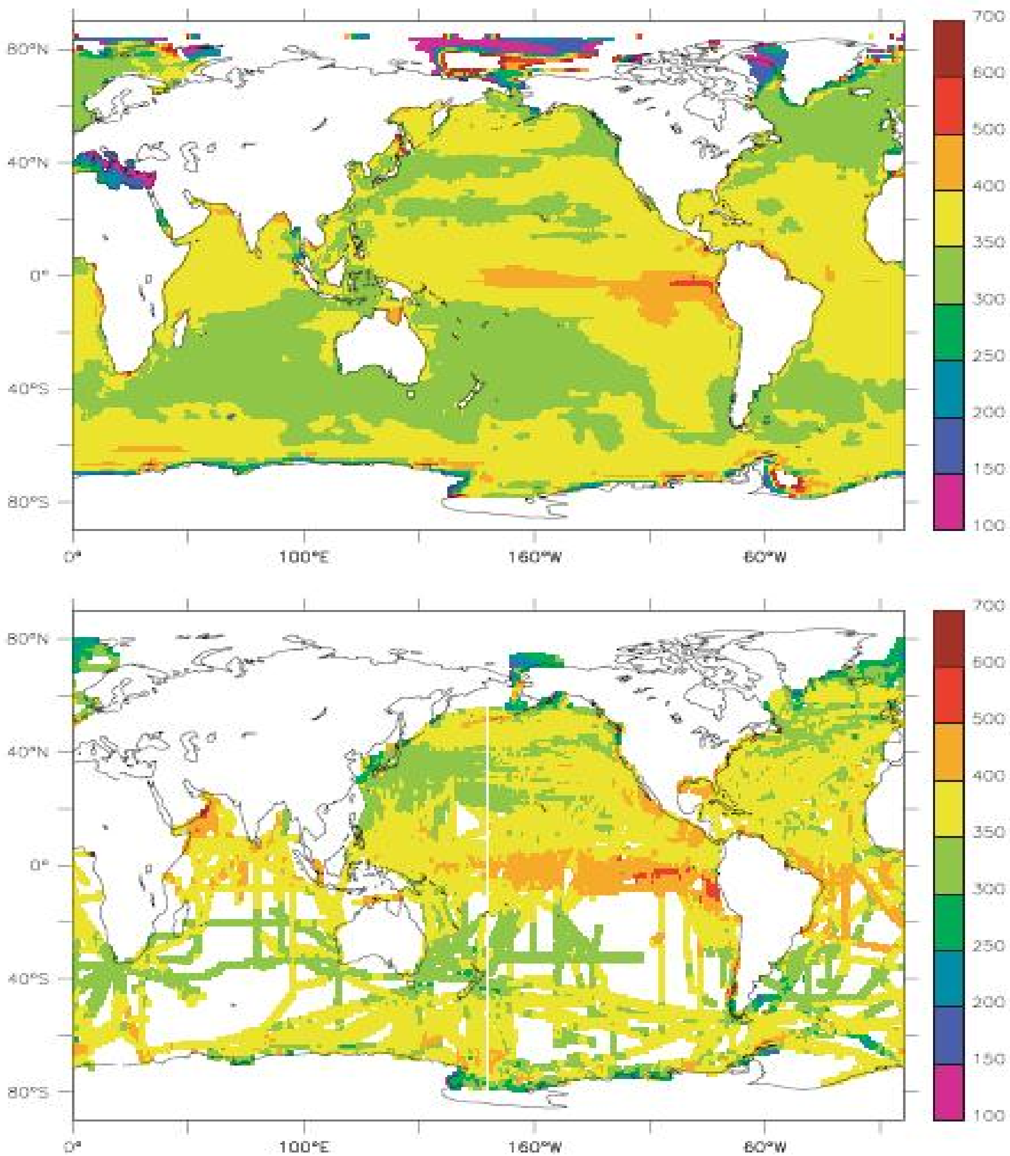
Normalized DIC and Alk.



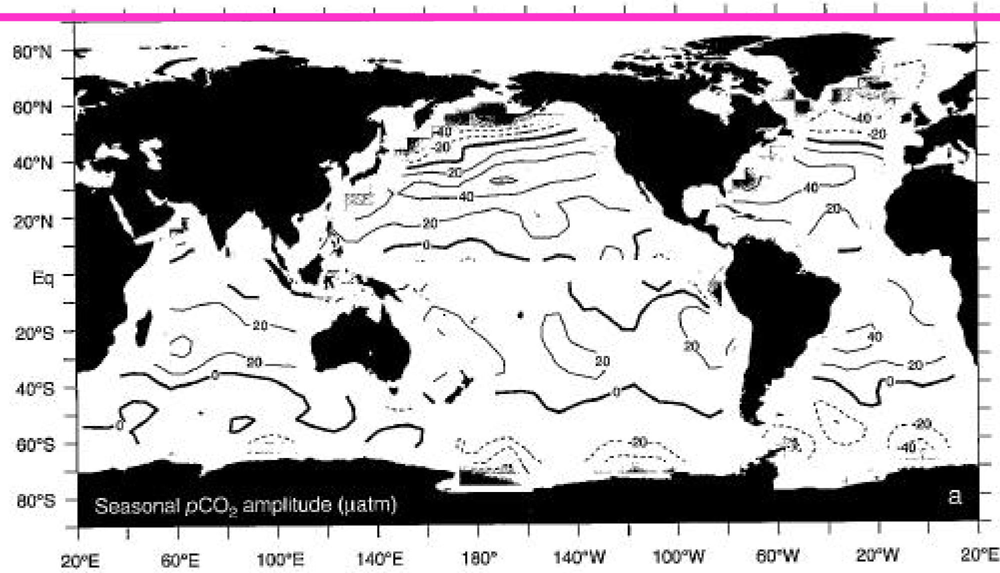


$$sDIC = \frac{DIC}{S} \times S_g.$$

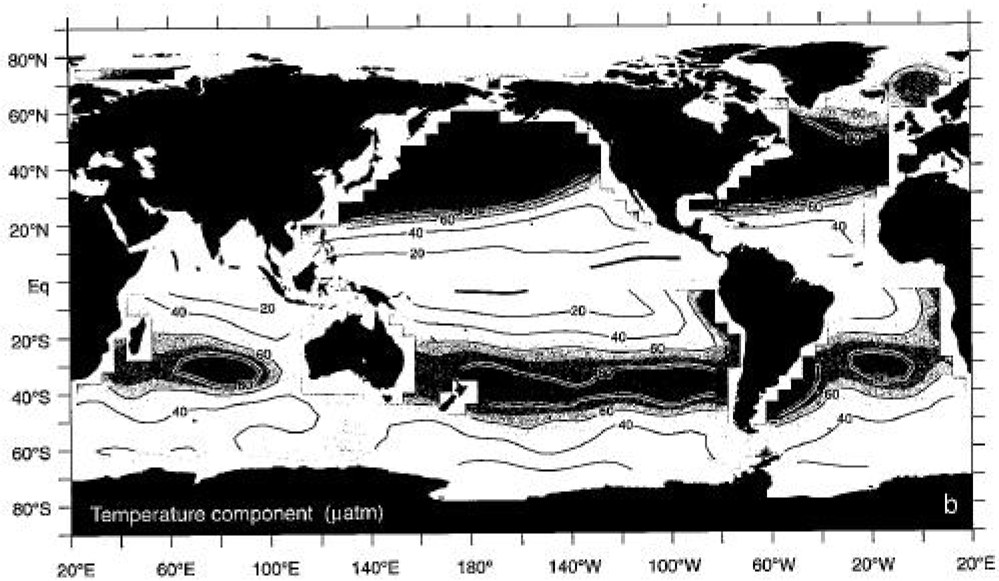
Surface ocean pCO2.



Units: ppm
(top) model
(bottom) ship-survey

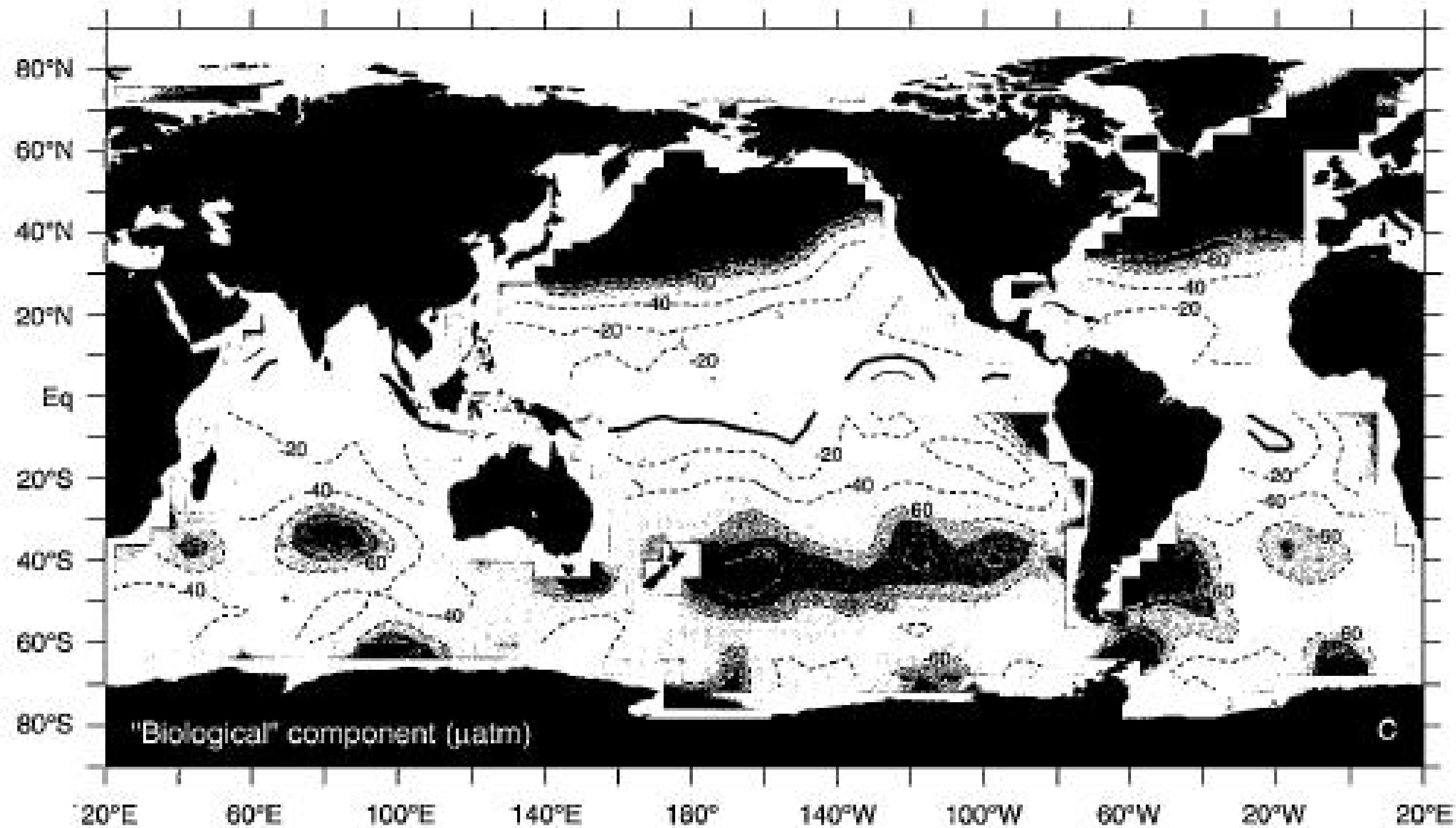


Seasonal pCO2 amplitude (uatm).

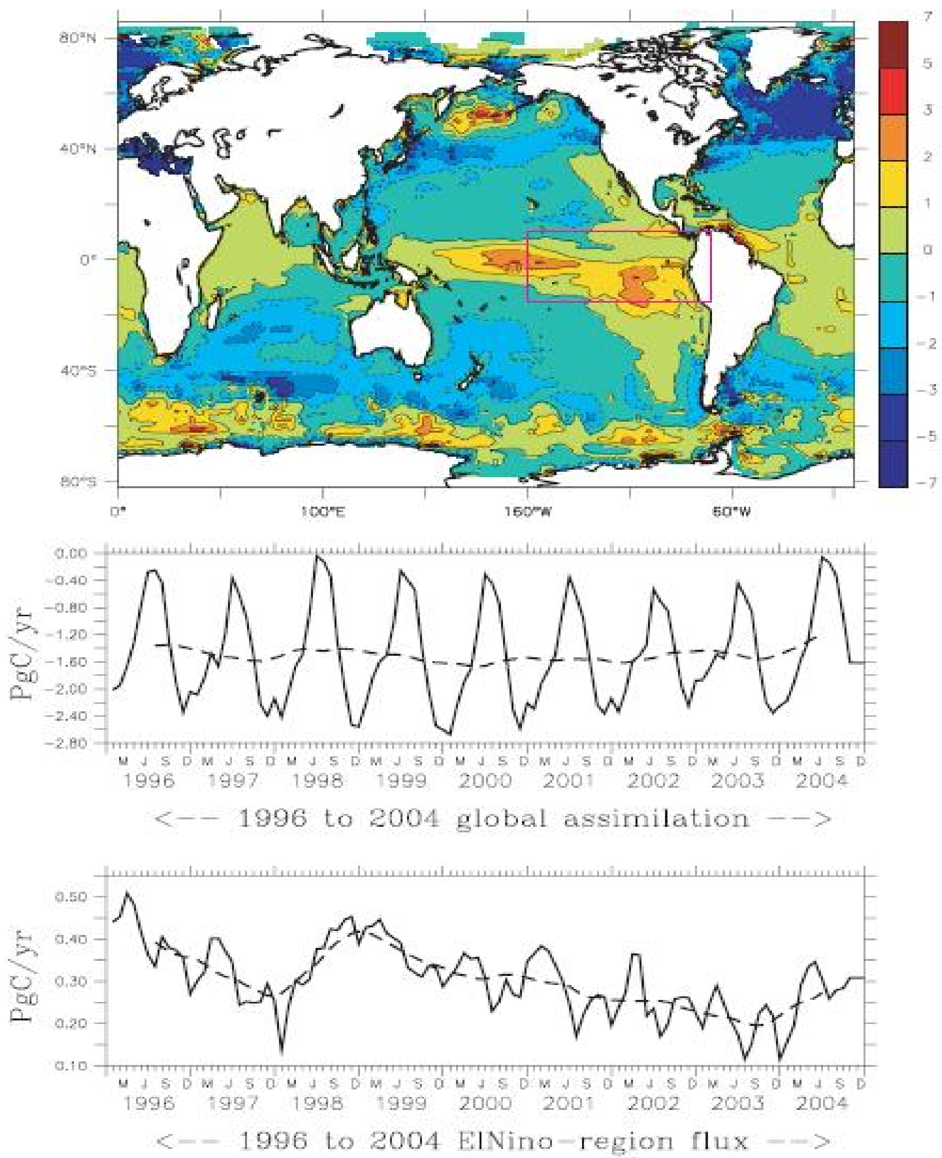


Temperature effect of surface ocean pCO2.

Biological effect on pCO2
= Seasonal pCO2 - Temperature effect

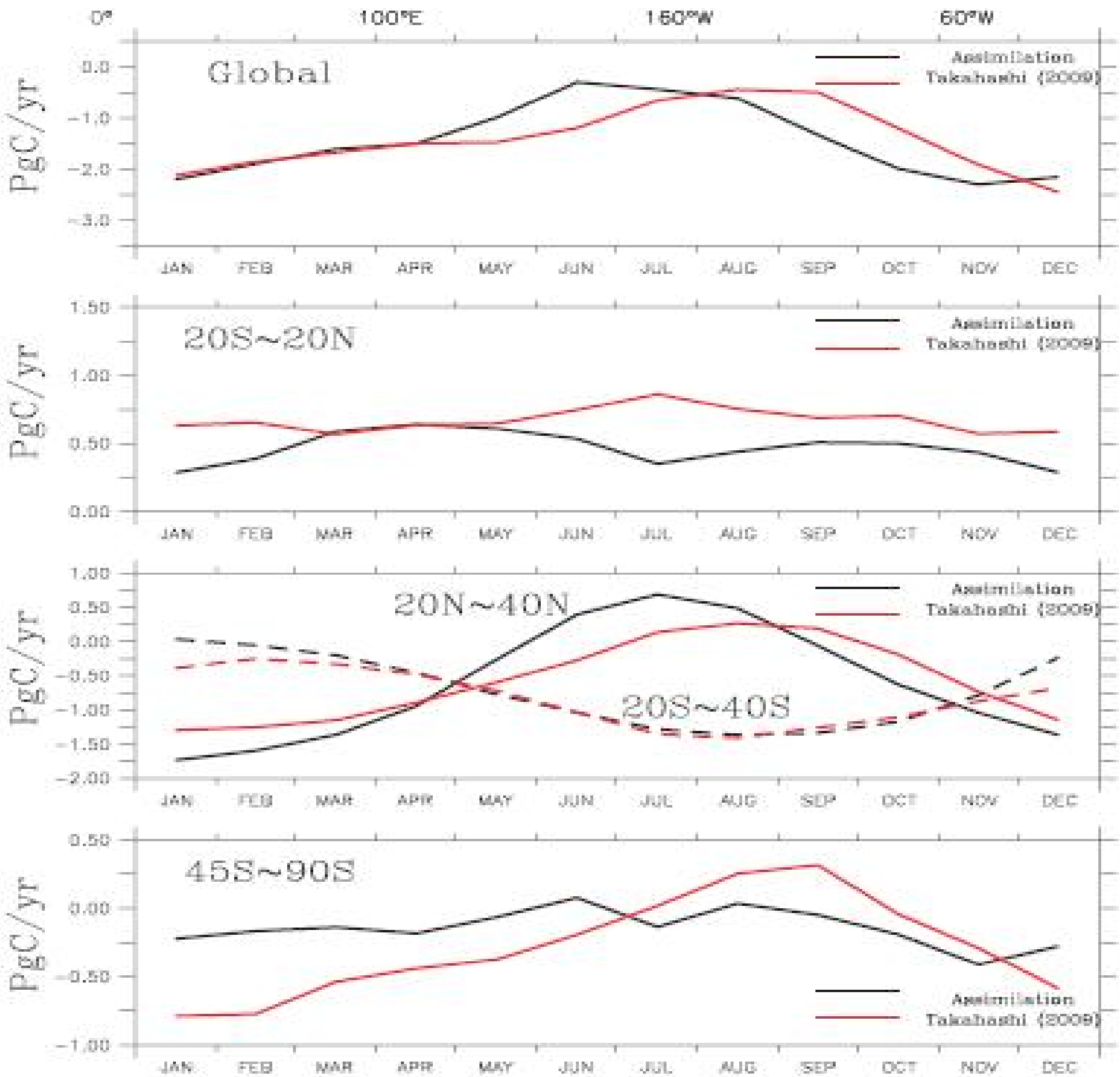


Air-sea fluxes of CO2.



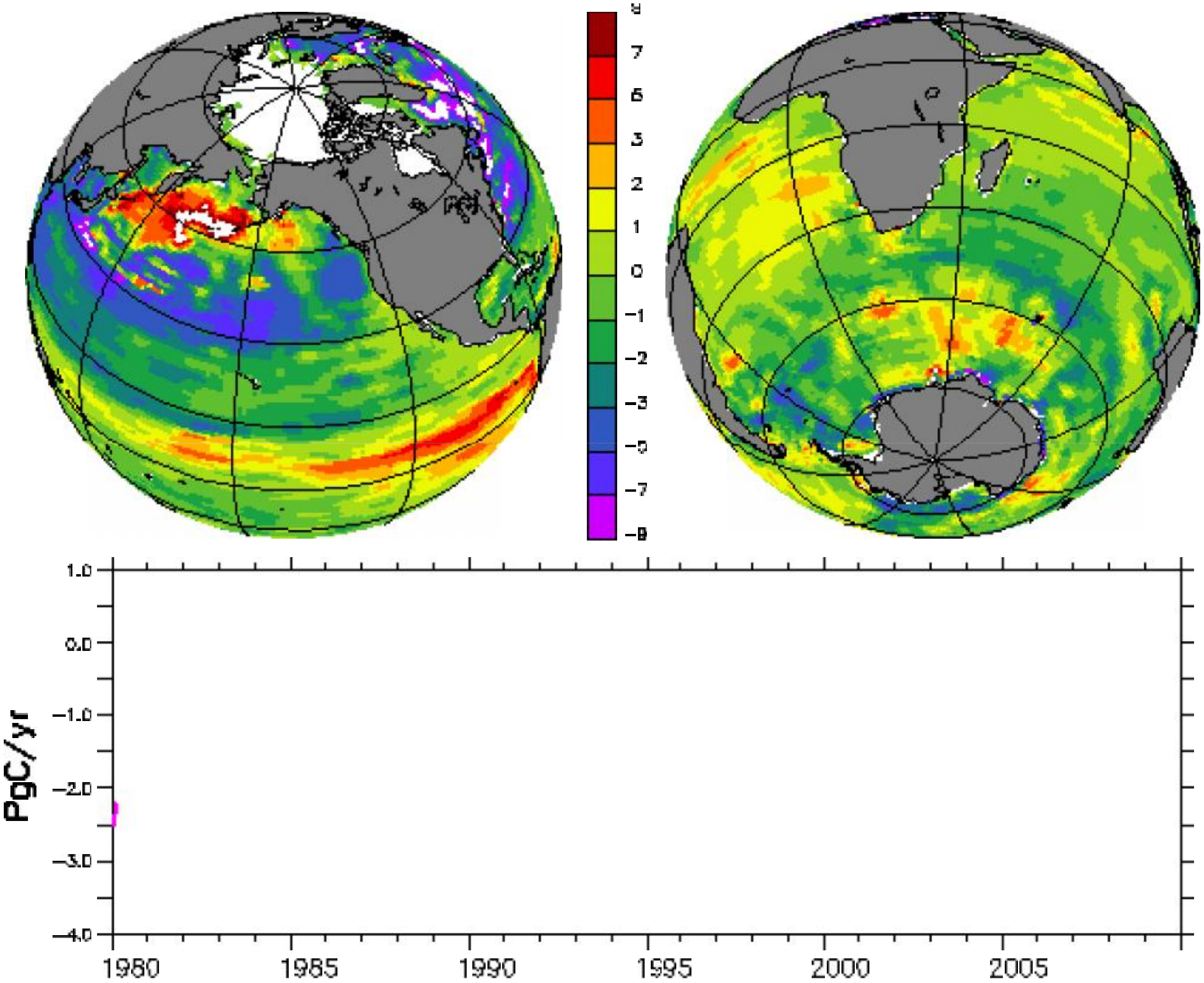
Units: mole/m2/year
(top) model
(middle) global integral.
(bottom) Eastern Pacific

Seasonal cycle of air-sea CO2 flux.



Unit = PgC/yr.

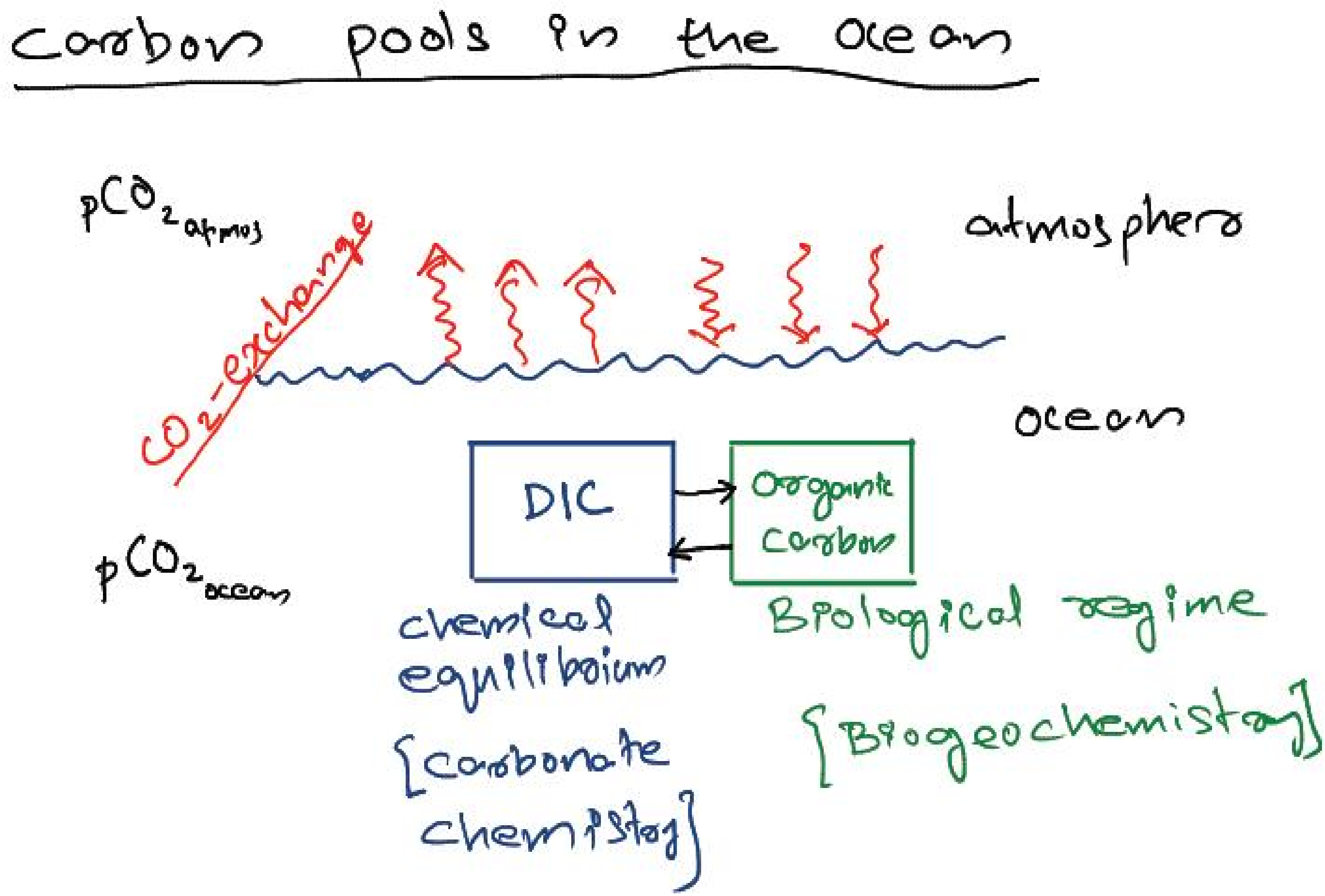
Air-sea fluxes of CO2.



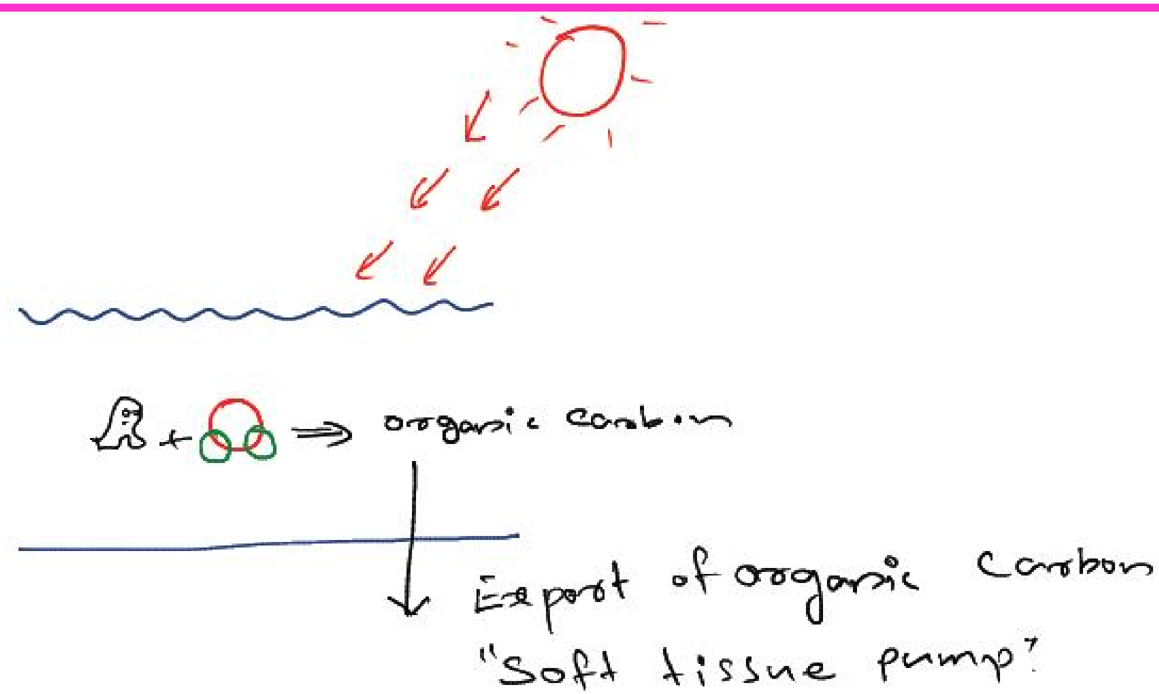
10^{15} Gram Carbon/year

1980 1990 2000 2010

Carbon pools in the ocean.



Biological Pump: Effects on Carbon cycle.
Soft tissue pump



$$106CO_2 + 16NO_3 + HPO_4^{2-} + 78H_2O + 18H^+ \rightleftharpoons C_{106}H_{175}O_{42}N_{16}P + 150O_2$$

($18H^+$ →) Reduces pH.

Organic carbon production increases the Alkalinity.

" " " reduces the DIC

Biological Pump: Effects on Carbon cycle. Carbonate pump

Biogenic formation of calcites

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3 .$$

↓

Mineral calcium carbonate shells

- ↳ coccolithophorids
- ↳ foraminifera
- ↳ pteropods.

→ Carbonate pump.

Influence of Biological pumps on carbon cycle.

Influence of "Biological Pumps" on carbon cycle.

- Soft tissue pump
  - DIC decrease
  - Alk increase
- Carbonate pump
  - DIC decrease
  - Alk decrease

Sensitivity of pCO_2 on "Biological Pump"

$$\gamma_{DIC} = \frac{DIC}{pCO_2}\frac{\partial pCO_2}{\partial DIC}$$ Revelle factor

$$\gamma_{Alk} = \frac{Alk}{pCO_2}\frac{\partial pCO_2}{\partial Alk}$$

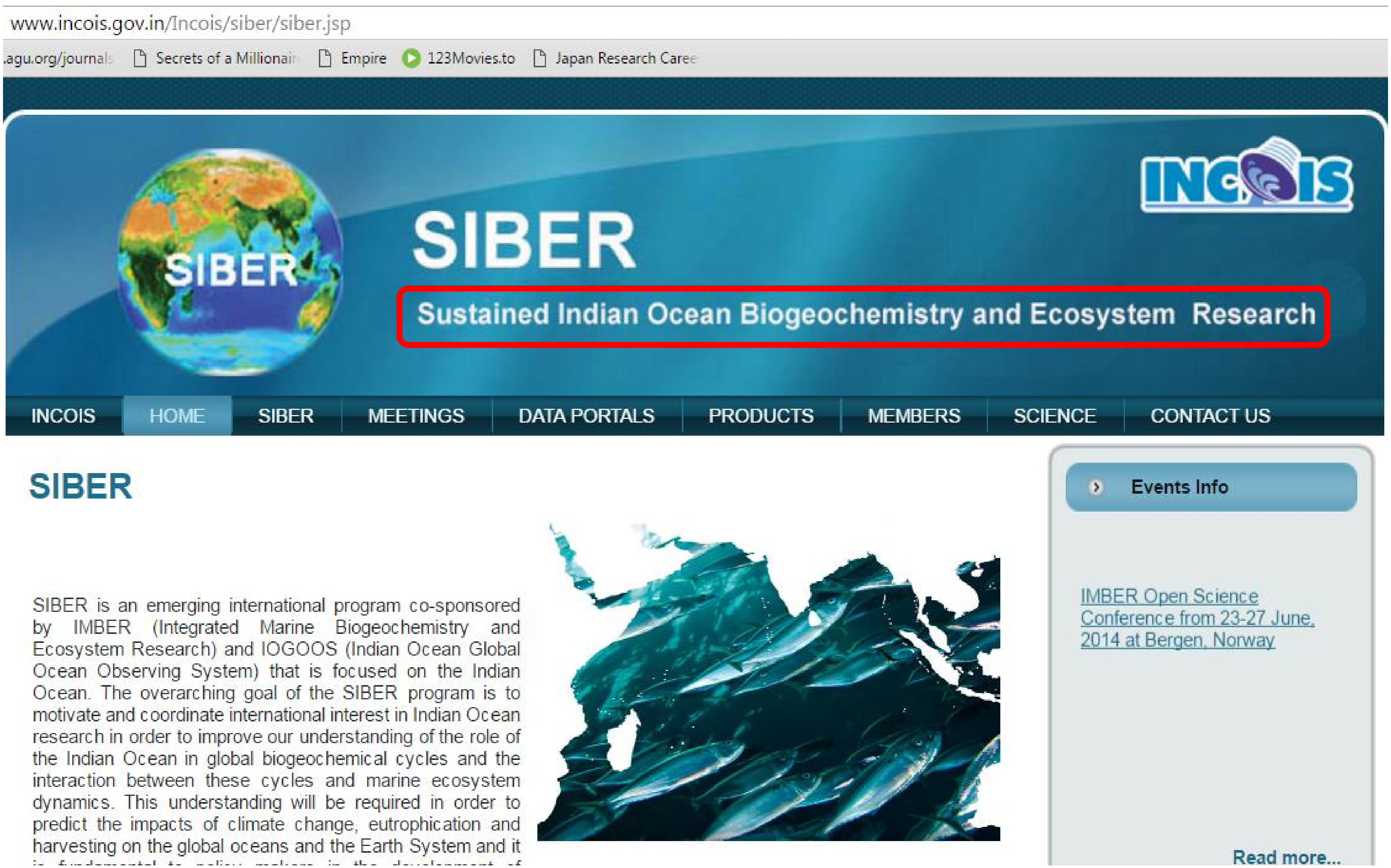
$$\gamma_{DIC} = \frac{3 \cdot Alk \cdot DIC - 2\, DIC^2}{(2 \cdot DIC - Alk)(Alk - DIC)}$$

$$\gamma_{ALK} = \frac{Alk^2}{(2 \cdot DIC - Alk)(Alk - DIC)}$$

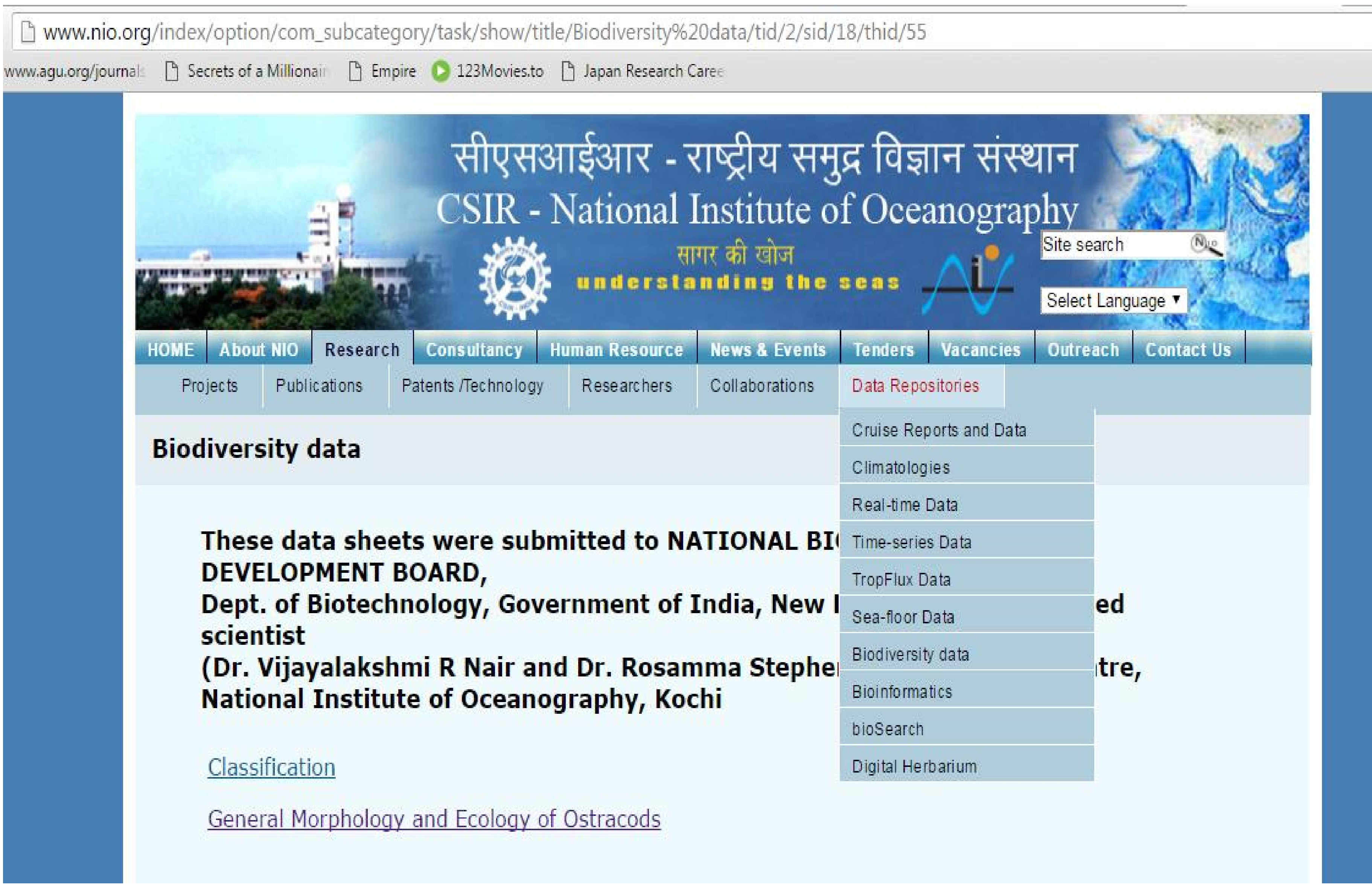
pCO_2 increases by 10%, when DIC increased by 1%

pCO_2 decreases by 9%, when Alk increases by 1%

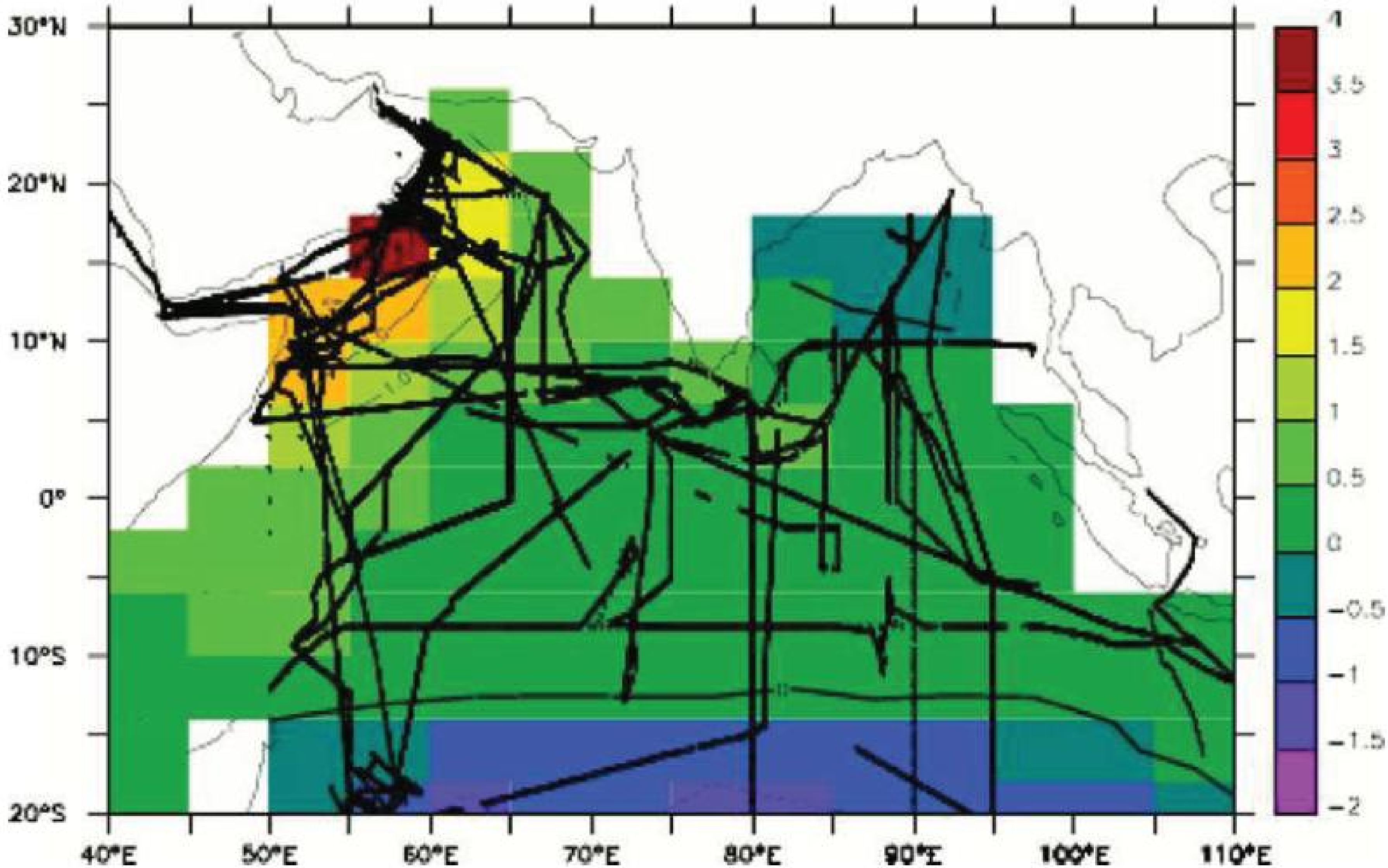
Indian Ocean → observation and scenario



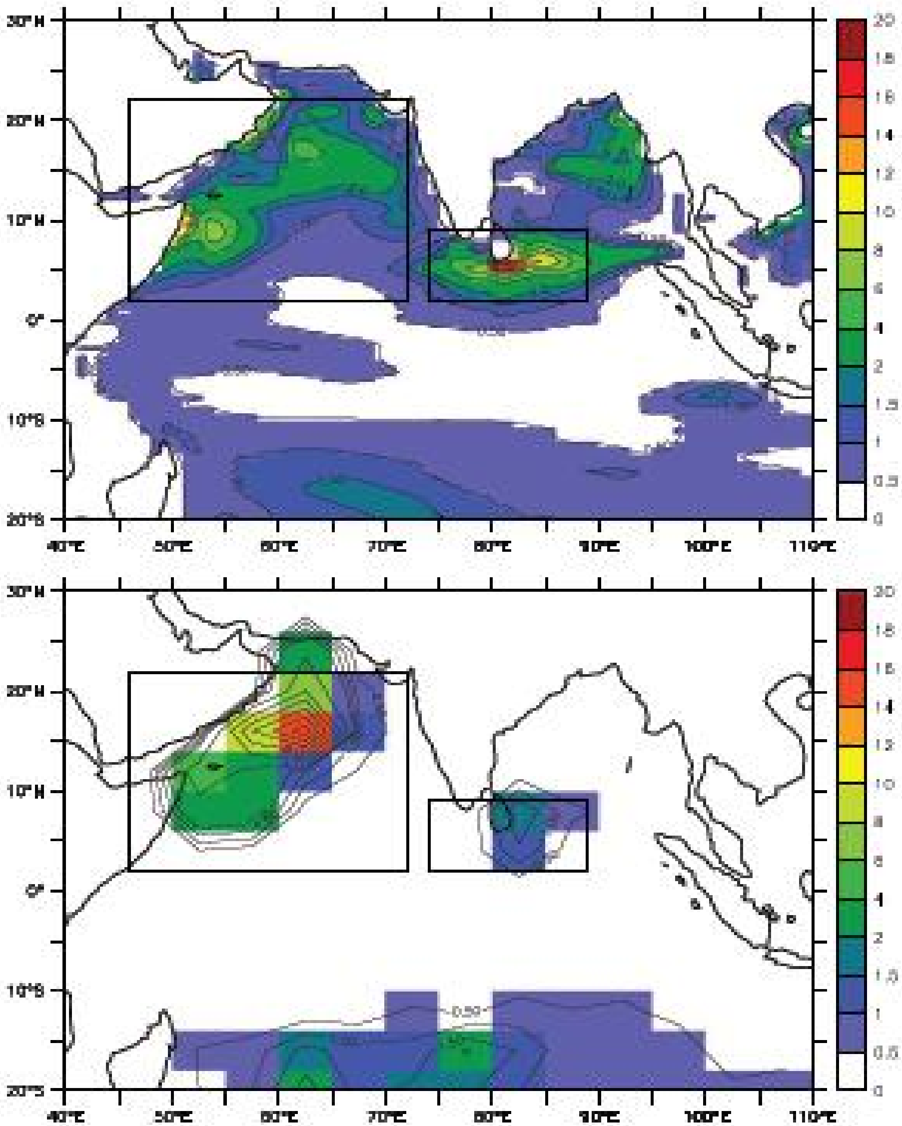
Indian Ocean → observation and scenario



Indian Ocean → observations of pCO2



Indian Ocean → observations of pCO2



Practical Sessions

- Component form of pCO2 variability in ocean → Practical session

$$\frac{dpCO_2}{dt} = \left(\frac{\partial pCO_2}{\partial \mathrm{DIC}}\frac{d\mathrm{DIC}}{dt}\right) + \left(\frac{\partial pCO_2}{\partial T}\frac{dT}{dt}\right) + \left(\frac{\partial pCO_2}{\partial \mathrm{ALK}}\frac{d\mathrm{ALK}}{dt}\right) + \left(\frac{\partial pCO_2}{\partial S}\frac{dS}{dt}\right)$$

- Air-sea CO2 fluxes of Indian Ocean; seasonal cycle, interannual variability.