## 12.742 - Marine Chemistry

Fall 2004

Lecture 14 - Primary Production (Continued)

Prof. Scott Doney

- Photosynthesis (continued)
- Ways of measuring primary production
  - $-\Delta O_2$
  - $-\Delta CO_2$
  - Formation of organic matter
  - Time dependent change in light consumption

Nice description in

"Phytoplankton and their role in primary, new, and export production." P. G. Falkowski, E. A. Laws, R. T. Barber, and J. W. Murray in Ocean Biogeochemistry ed. M. J. R. Fasham.

- Gran 1918 Light/dark bottle incubations of A $O_2;$  good for coastal time-scale (hours); nanoplankton; Winkler titration for  $O_2$
- Steemann Nielsen  ${}^{14}C$  carbon fixation in short-term incubations in 1952. More sensitive, less labor intensive; scintillation counter; light on deck or in-situ,  ${}^{14}C$  uptake into POC issue of  ${}^{14}C$  labelled DOC; dark/light; filtering
- Koblentz-Mishke et. al. 1970 from ~ 7000 stations of daily NPP estimated global NPP of 24 Pg C/yr. issues of whether  ${}^{14}C$  method measures GPP vs. NPP (depending on incubation length), trace metal contamination, bottle effects
- New computer controlled  $O_2$  incubations,  $TCO_2$  incubations (coulometers)  ${}^{18}O_2$  incubation  $H_2^{18}O \rightarrow {}^{18}O^{16}O$ ; measured by mass spectrometer; estimate of GPP
- P-I curves applied to field data; variable fluorescence methods satellite based and in-situ bio-optical approaches; in-situ  ${}^{14}C$  calibration, also poor spatial coverage
- pre-mid 1970's  $^{14}C$  measurements somewhat dubious/trace metal contamination

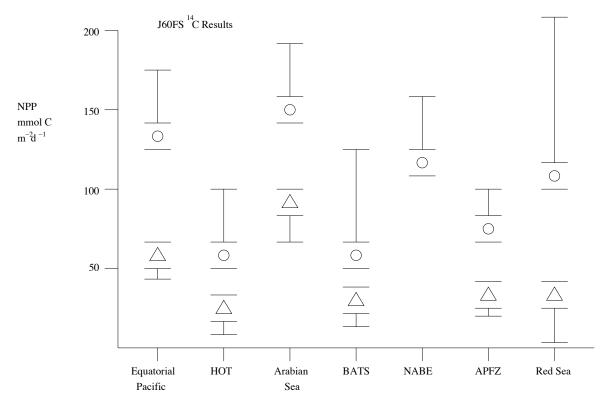
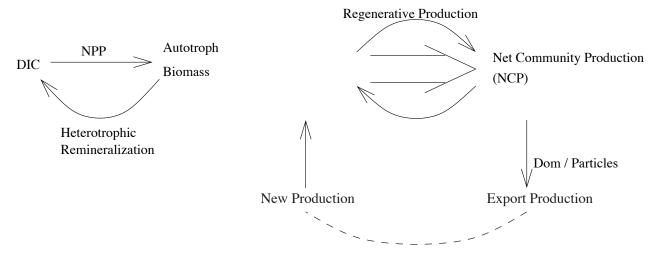


Figure 1.

- Satellite Methods- SeaWiFS, MODIS, biomass, PAR, some form of empirical temperature or nutrient curve/relationship, Current global estimates of 45 – 57 Pg C/yr (comparable to terrestrial), issues on continental margins
- Diurnal $\Delta O_2, \Delta NO_3, \Delta CO_2$
- Marine phytoplankton biomass  $< 1~{\rm Pg}$  C with turnover time ; 1 week (for comparison on land vegetation  $\sim$  500 PgC and wood/trees can have turnover times of decades to centuries)
- New production, Net community production
  - New production: production supported by external supply of nutrients (e.g. mixing or upwelling from below, atmospheric deposition)
  - Regenerated production: production supported by nutrients released by grazing and respiration in surface layer
  - NPP = new + regenerated production
  - Net community production: net difference in surface layer between primary production and respiration
  - Export production: net export of organic matter (dissolved or particulate form) from surface layer On some time and space scales mass balance requires that new, net community, and export production should be equal"

What is the fate of all this NPP?



New, NCP, and export balance on some time scale

Figure 2.

Export production drives biogeochemistry in the deep ocean

("balanced" state versus "perturbed" state; paradigm (move to later) )

• elemental ratios/stiochiometry - Redfield 1934

$$[106(CH_2O)16NH_3PO_4^{3-}] + 138O_2 \rightarrow 106CO_2 + 122H_2O + 16NO_3^{-} + PO_4^{2-}]$$

More recent estimates suggest  $\sim 154O_2$ 

Note reduction of  $NO_3 \rightarrow NH_4$ 

Dugdale + Goering (1967) "new" versus "regenerated" production "here" new-N to euphotic zones; upwelled  $NO_3$ , atmospheric  $N, N_2$  fixation exogenous inputs

Eppley and Peterson (1979)

$$\text{f-ratio} = \frac{\text{new}}{\text{new} + \text{regenerated}} \approx \frac{NO_3^- \text{ uptake}}{NO_3^- + NH_4^+ + NO_2^- + DON \text{ uptake}}$$

New Production, NCP, Export

Export production

- Particle sinking
- Lateral/horizontal advection of DOM and suspended particles
- Zooplankton migration

 $e-ratio = \frac{export production}{primary production}$ 

NCP - build up in biomass, detrital matter, DOM

- export, new, NCP measured by different techniques
- time-scales different
- local imbalance (time-space integration)
- Measuring new production

f-ratio  $\approx \frac{{}^{15}NO_3^- \text{ uptake}}{{}^{14}CO_2 \text{ uptake}} \qquad {}^{15}NO_3^- \text{ incubations} \Rightarrow PO^{15}N$ 

Complications :  $DO15^N$  release, low ambient  $NO_3^-$  of only a few nM in oligotrophic gyres

- Measureing net community production
  - $O_2$  incubation, issues: length of integration, including enough of community, exclusion of grazers; episodic events (whole net autotrophy, heterotrophy controversy), duration versus precision,  $0.1 - 0.2\mu$ mol  $O_2/L$  per approximately 24 hours
  - Seasonal build-up in  $O_2$  (Jenkins and Goldman, 1985) Properly account for mixing, air-sea gas-exchange Upper ocean supersaturated for  $O_2$
  - Seasonal drawdown in  $NO_3$ ,  $TCO_2$

Air-sea mixing, lateral advection

 $\Delta^{13}C$  very useful for estimating biological from physical changes

mirrored in subsurface ocean, apparent oxygen utilization (AOU), oxygen utilization rate (OUR), Riley 1951, Jenkins 1982)

- Measuring export
  - Upper ocean (floating) sediment traps
  - Traps are poisoned (in some cases)
    biases, swimmers, hydrodynamic over/under sampling
  - "Lagrangian" floating traps; rotating ball traps
  - Short duration (a few days)
  - <sup>234</sup>*Th* method

Th particle reactive "scavenging"

24.1 day half-life $^{238}U \rightarrow^{234} Th$ 

U well-mixed  $(200 - 400 \cdot 10^6 \text{ year residence time})$  predict from salinity

Th is "particle sticky" For secular equilibrium  $A^{238}U = A^{234}Th \ (dpm/m^3)$ 

$$\frac{d^{234}Th}{dt} = {}^{238U} \lambda^{238} U - {}^{234}Th \lambda^{234} Th - \gamma_{\rm scav} {}^{234}Th + V_{Th}$$

 $V_{Th}$  is Thorium advection term  $\gamma_{\rm scav} \left(\frac{1}{time}\right)$  has first order loss

At steady state,  $\gamma_{\rm scav}^{234} Th = ^{238U} A - ^{234\text{Th}} A$ 

$$\gamma_{\rm scav} = \frac{234Th\lambda \left(238UA - 234ThA\right)}{234ThA}$$

but what if the time-scale for Th loss is different (on particles) than carbon (eg. if Th preferentially stuck to small suspended particles)?

Step 1: Integrate activity deficit w/depth (or alternatively integrate particle loss/scavenging)

$$\int_{0}^{z} \underbrace{dx}_{m} \underbrace{\gamma_{\text{scav}}}_{\text{time}} \underbrace{\frac{234}{\text{th}}Th}_{\text{time}} = \underbrace{F_{\text{th}}}_{\frac{\text{atoms}}{\text{time} \text{m}^{2}}} \\ = \left(2^{38U}A - 2^{34Th}A\right)z \\ \underbrace{F_{C}}_{\frac{\text{mol }C}{\text{time }\text{m}^{2}}} = \underbrace{\left(\frac{C}{Th}\right)_{\text{particles}}}_{\text{mol/atoms}} \cdot F_{Th} = \left(\frac{C}{234ThA}\right)_{\text{particles}} \cdot F_{Th} \cdot 2^{34Th}\lambda$$

Caught in sediment traps:

$$\left(\frac{C}{Th}\right)_{\text{particles}} \cdot \int_0^z dx \, \left(\frac{238U}{A} - \frac{234Th}{A}\right) z = \left(\frac{C}{234ThA}\right)_{\text{particles}} \lambda^{234Th} \int_0^z dx \, \left(\frac{238U}{A} - \frac{234Th}{A}\right)$$

· Non-steady state terms (time-scale of  $\sim 1$  month from Th decay) not too significant

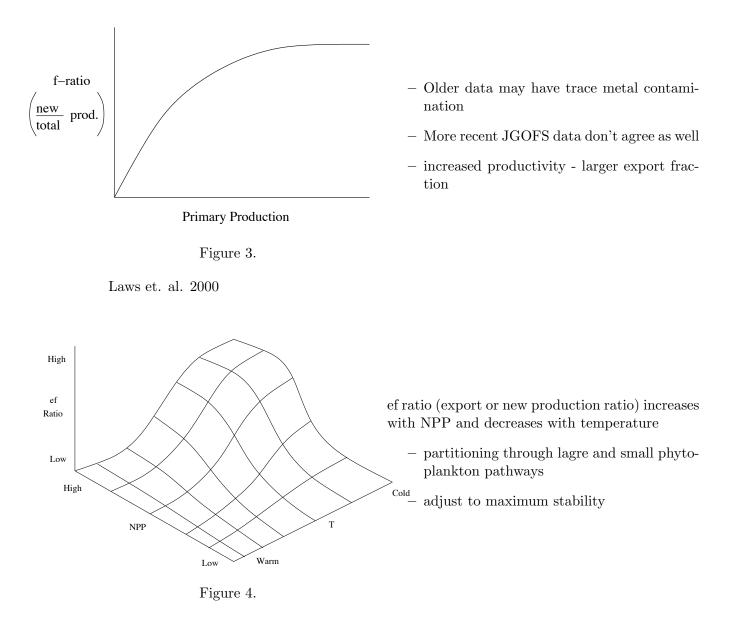
· Lateral advection (e.g. equatorial Pacific)

use Th to correct traps (collection biases)

Est. POC Flux = Trap POC Flux 
$$\cdot \frac{\text{estimated }^{234}Th \text{ flux}}{\text{trap }^{234}Th \text{ flux}}$$

- $\cdot\,$  DOM export seasonal build-up over summer at BATS then downward mixing
- $\cdot$  zooplankton
- $\cdot$  depth integration issues (1% light?<br/> 0.1% light?); traps at some fixed depth (e.g. 150m)

Export synthesis - start w/Eppley and Peterson (1979)



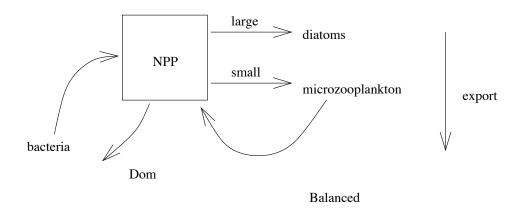
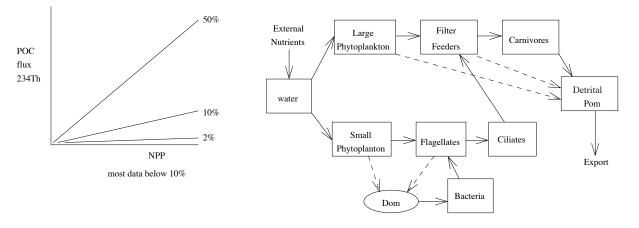


Figure 5.

Global export estimates  $\sim 5$  to 12 Pg C/yr (averaged over NPP weighted average f-ratio of 10-20%)





Balanced versus imbalanced growth (episodic, disturbance)

(Picoplankton versus diatoms)

Diatoms more efficient at rapidly acquiring nutrients under highly physically dynamic conditions (vacuoles) strategy  $(NO_3 \text{ but not } NH_4)$ 

elemental stoichiometry - "Redfield ratios" Redfield (1934)

marine phytoplankton have relatively uniform composition of various elements - we already taked about  $C:{\cal O}_2$ 

 $N: P \sim 16: 1$  (exceptions - regions of N redox, N-fixation, denitrification, ...)

 $C:N\sim 6.6$  (exceptions - nutrient stress conditions, some picoplankton, DOM (C/N) production)

 $C: P \sim 106$  (balanced versus imbalanced growth?)

Fe: C much more variable; adaptation to different Fe conditions, plasticity replacing Fe in enzyme systems; luxury uptake

Other biolimiting elements

Si - diatoms, radiolarians, some sponges

 $CaCO_3$  - coccolithophores, for aminefira

 $CaCO_3$  export ~ 0.7 Pg C/yr (Milliman et. al. 1999)

 $CaCO_3$ /POC ratio ~ 0.06 globally > 0.08 near equator, less at mid-high latitude (Sarmiento et. al. 2002)

Biogenic silicon production - 200–280 Tmol Si/yr, export ~ 50%, 100–140 Tmol/yr - Nelson et. al. 1995; Increased export in equator, coastal, subpolar, Southern Ocean