12.742 - Marine Chemistry Fall 2004

Lecture 16 - DOM and Water Column

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Dissolved Organic Matter (technically TOM)

- Compared with deep water, POC < 1 μm/kg (Hansall 2002)
- Deep-water DOC ~40 micromol/kg; variations in deep-water DOC only a few micromol/kg

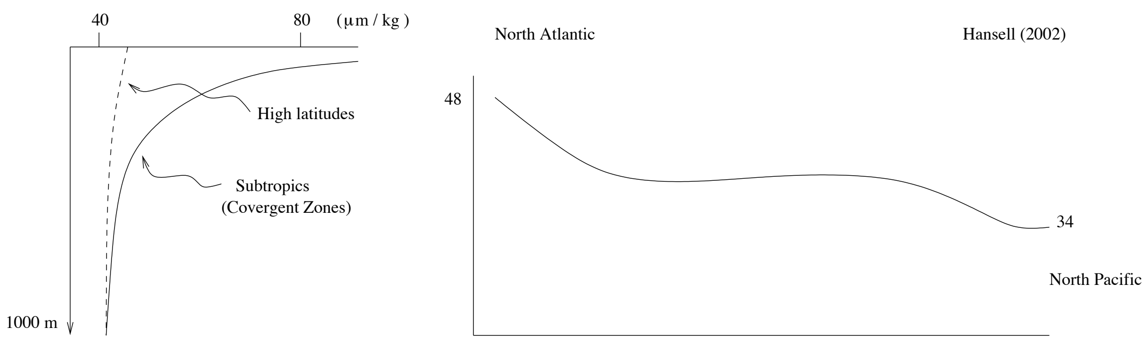


Figure 1.

- One suggestion was that deep-water DOC decreased monotonically from North Atlantic to North Pacific, but hasn't held up.
- DON 4-6 μm/kg C/N 10-145
- DOP 0.1-0.4 μm/kg C/P 200-600
- DOM - Multiple pools/time secales
- Labile - hours to days, < 5μm/kg
- Semi-labile - Days to months (transport into thermocline) 0-20 μm/kg
- refractory - 1000's of years, ~ 40μm/kg

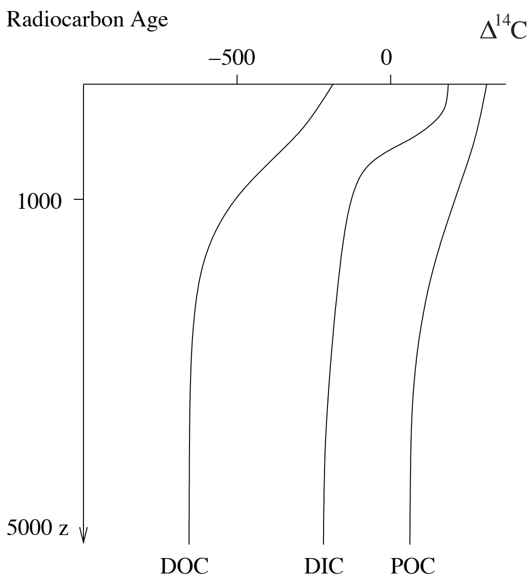


Figure 2.

- DOC deep water 4000 years deep in Atlantic, 6000 in the pacific
- Radiocarbon age of DOC much older than radiocarbon age of DIC at same depth
- Transport from slopes?
- Seasonal variation of surface DOC
- eg. Bermuda
- Export via convection and mixing

- Carbohydrates vs. protein content C/N
- Size class (ultra filtration), > 1000 Daltons, ↑ C/N carbohydrates
  - Large size class more labile?
  - Bacterial use; relative bacterial growth efficiencies low, 10-40%
  - "Microbial Loop" respired - only small fraction moves back up trophic structure
- DOM respiration account for perhaps 1/2 resp[iration in upper thermocline
- Water Column signature of remineralization can also have differential remineralization and non-Redfield production
- Respiration and inorganic remineralization in the thermocline
- Redfield elemental stoichiometry - mixing, preformed nutrients
- Rates of respiration; some form of clock, tracers

  $$C_{\text{Organic}} : N : P : O_2 = (117 \pm 14) : (16 \pm 1) : 1 : (-170 \pm 10)$$

  (add diff. remin. prod. on Redfield)
- Need to define flow path (primarily isopycnal flow in thermocline)

  $$\begin{aligned} C_{\text{obs}} &= C_{\text{preformed}} + \Delta C_{\text{Remin}} && \text{(metabolic)} \\ [\Delta O_2]_{\text{remin}} &= [O_2]_{\text{Obs}} - [O_2]_{\text{Preformed}} && \text{(results in negative)} \end{aligned}$$

  (add isopycnal analysis)
- Apparent Oxygen utilization (AOU)

  $$\begin{aligned} \text{AOU} &= [O_2]_{\text{Sat}} - [O_2]_{\text{Obs}} \\ \text{AOU} &= -[O_2]_{\text{remin}} \end{aligned}$$

  Assume surface water equilibrium (not always best)

- Map of AOU from Sarmiento and Gruber
- Circulation, age, organic matter remineralization rates
- Note how AOU is really high in equatorial thermocline; much slower circulation and longer ages

Oxygen Utilization rate (OUR)

$$\text{OUR} = \frac{d\text{AOU}}{dt} \approx \frac{\text{AOU}}{\text{age}}$$

So how do you estimate age?

- Riley (1951) - geostrophic velocity, oxygen divergence rates
- Jenkins (1980) - tritium - ^{3}He, from weapons testing

$$\begin{aligned} {}^3\text{H} &\xrightarrow{12.45} {}^3\text{He (gas)} \\ \frac{\partial {}^3\text{He}_{\text{ex}}}{\partial t} &= +\lambda {}^3\text{H} + \text{etc.} \\ \frac{\partial {}^3\text{H}}{\partial t} &= -\lambda {}^3\text{H} \end{aligned}$$

sum of $^3\text{He}_{ex}$ and ^{3}H is 'conservative':

$$\frac{{}^3\text{H}}{{}^3\text{H} + {}^3\text{He}} = \frac{A}{A_0} = e^{-\lambda t}$$

$$\begin{aligned} e^{-\lambda t} &= \frac{{}^3\text{H}}{{}^3\text{H} + {}^3\text{He}} \\ -\lambda t &= \log\left(\frac{{}^3\text{H}}{{}^3\text{H} + {}^3\text{He}}\right) \\ t &= \frac{1}{\lambda}\ln\left(1 + \frac{{}^3\text{He}}{{}^3\text{H}}\right) \end{aligned}$$

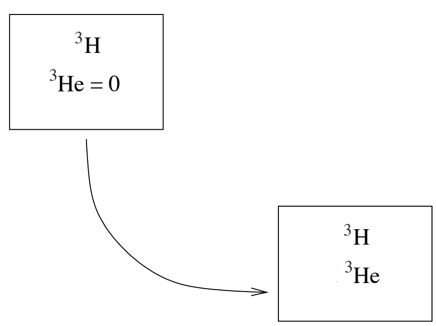


Figure 3.

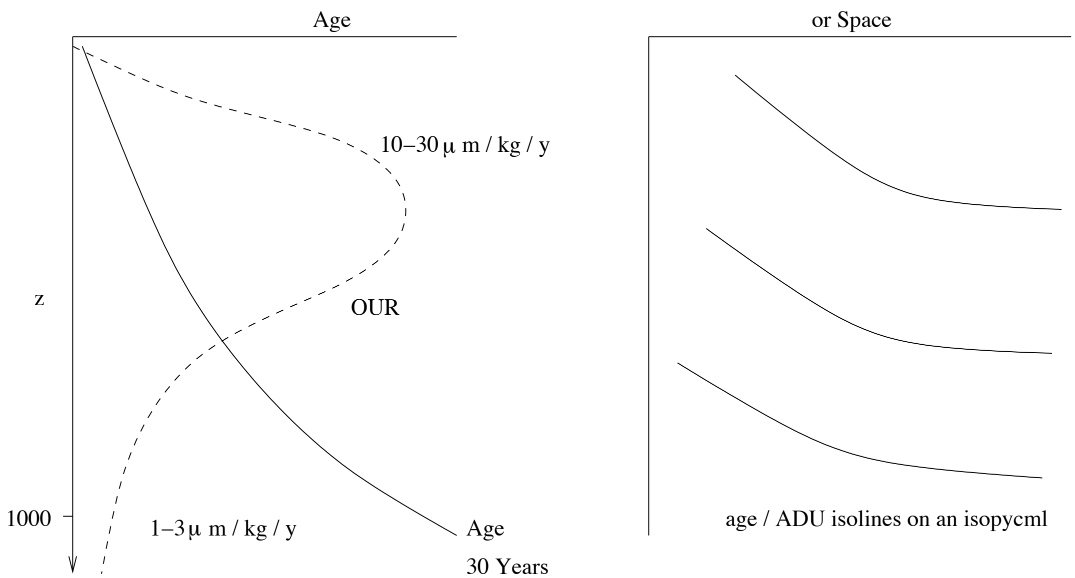


Figure 4.

- Age of thermocline a few years to decades
- Integrate OUR with depth to get water column remineralization
- Only ∼ 10% of export production reaches 1000 m
- Geochemical techniques - average over ∼ 1 decade and large region
- Rate of say a 3-6 mol $O_2/m^2/yr$
- Reconcile with export flux, traps etc.

Other age models (CFCs, Radium 228)

- Caveats, mixing tends to distort tracer ages - biases
- Deep water can use AOU andΔ ^{14}C

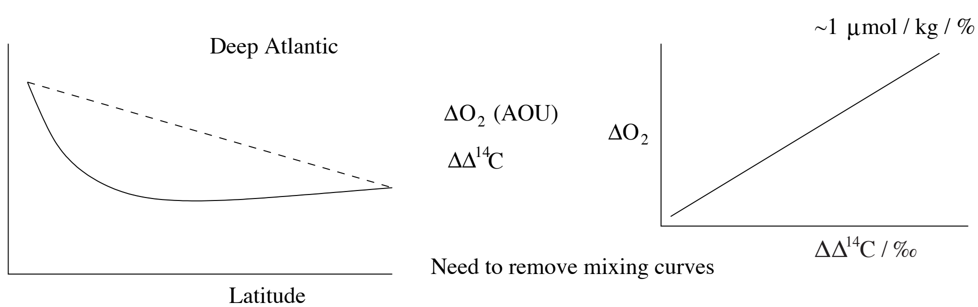


Figure 5.

Deep Atlantic and Pacific: 10-15 μmol/kg-century is two orders of magnitude slower than surface OUR

Preformed Nutrients and Remieralization Stoichiometries

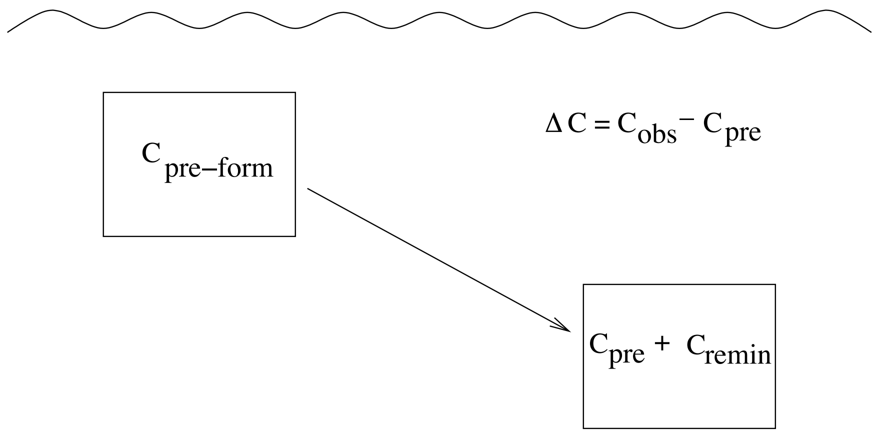


Figure 6.

For preformed nutrients, O_2, DIC, Alk, surface measurements need winter values at isopycnal outcrops (deep winter mixing) often lack of data, seasonal cycle

- Glover and Brewer 1988

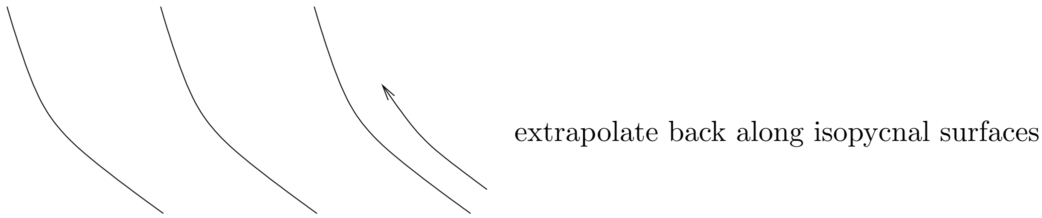
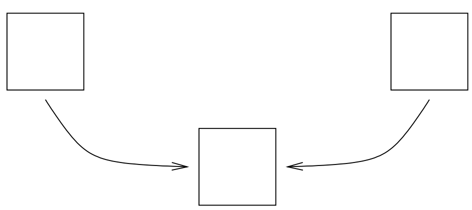


Figure 7.

- Mixing (2, 3 endmember mixing)
- multiple linear regression



- Use temperature and salt
- "Things that people think are conservative"
- Need surface endmembers
- Mixing ratios

Figure 8.

- Elemental ratios may not be as "fixed as one would like to think
- Takahashi et al. 1985 (TTO data and GEOSECS data)

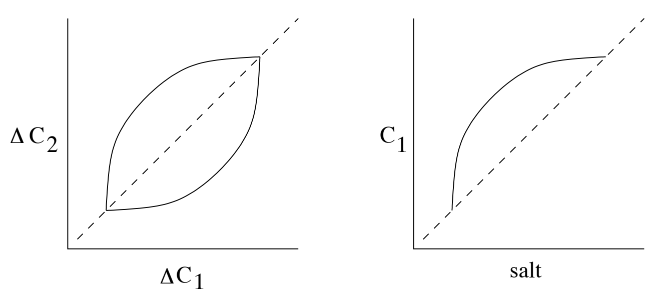


Figure 9.

- Oxygen minimum zones (denitrification)

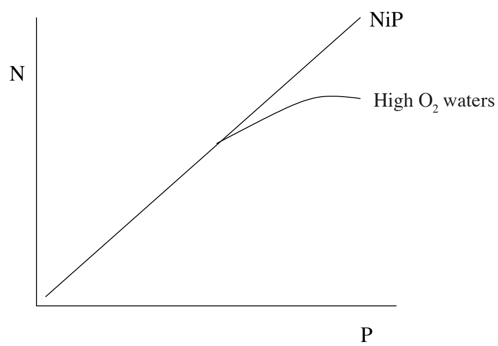


Figure 10.

- Arabian Sea, Eastern Tropical Pacific, some isolated basins

Opal production and dissolution

About ∼1/2 dissolves in euphotic zone, not so much in the deep water

$$
\begin{array}{lcl}
SiO_2{\cdot}nH_2O + H_2O \rightleftharpoons & H_4SiO_4\ (aq) & \\
\text{hydrated Silica} & \uparrow\downarrow & K_1 = 10^{-9.46} \\
 & H_3SiO_4^- + H^+ & \\
 & \uparrow\downarrow & K_2 = 10^{-12.56} \\
 & H_2SiO_4^- + 2H^+ &
\end{array}
$$

$$\uparrow \text{pH} \implies \downarrow H_4SiO_4 \implies \uparrow \text{solubility}$$

$$
\begin{aligned}
K_1 &= \frac{[H^+][H_3SiO_4^-]}{[H_4SiO_4]} \\
\frac{[H_4SiO_4]}{[H_3SiO_4^-]} &= \frac{[H^+]}{K_1} = \frac{10^{-8.2}}{10^{-9.46}} \approx 18
\end{aligned}
$$

- Most of Silicic acid already protonated
- Solubility of diatoms - $K_{sp} \sim 1000\mu$m/kg at 3°C
- Looks like amorphous Silica
- (Much higher than say quartz or other crystalline materials
- Do see Δ Alk signature in thermocline - shallow dissolution of aragonitic organisms

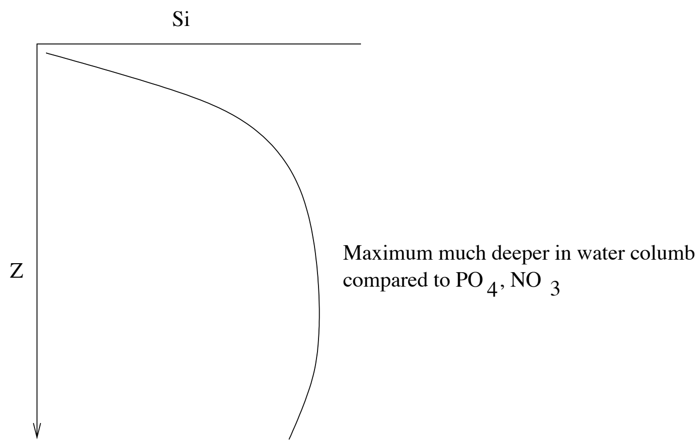


Figure 11.

- Larger spatial gradients in deep water (North Atlantic, North Pacific)
- Contrast of Si vs. $CaCO_3$ water column dissolution

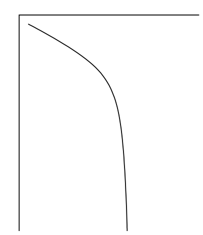


Figure 12.

- Many other species end up in biological cycling
- E.g. Acantharians produce skeletons made of $SrSO_4$ (celestite)

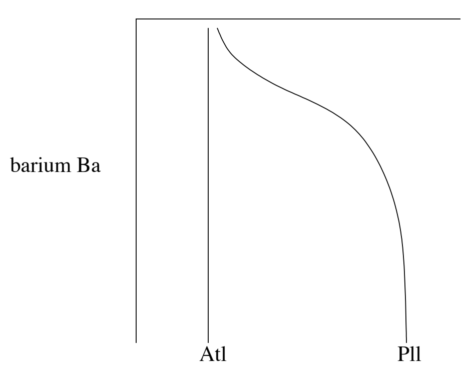


Figure 13.

- Barite formation, particle export from surface layer - Barite Supersaturation
  - S regeneration from org. S
  - S regeneration from $SrSO_4$
  - Ba release from phytoplankton