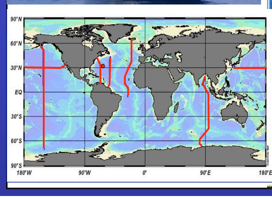
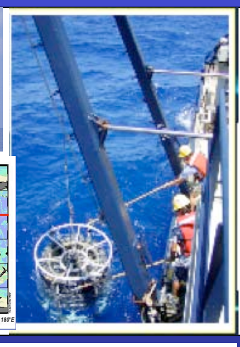
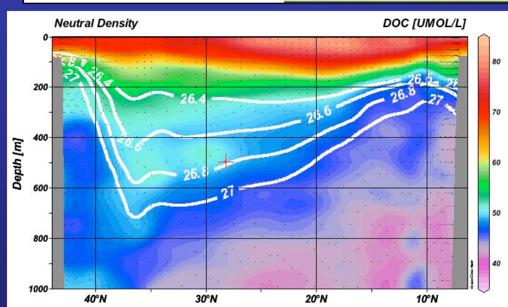
An Intro to the Oceanic Carbon Cycle





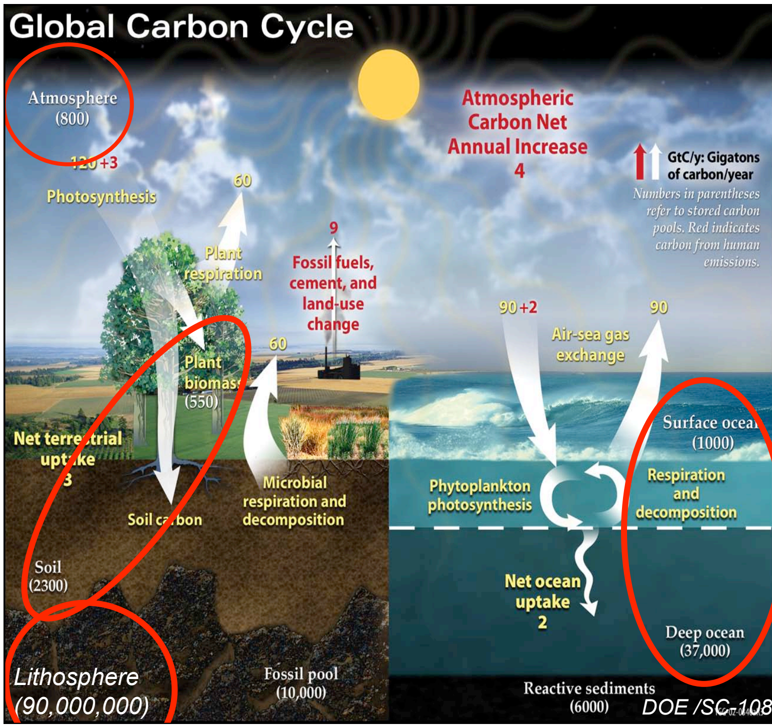


- Carbon reservoirs
- The CO_2 & carbonate system
- The carbon pumps – their contributions and limitations
- Intro to DOC –history and controversy
- DOC contribution to Ocean biogeochemistry

Oceanic Carbon Cycle

Why is C an important element?

- Cellular level – essential for macromolecular synthesis
- Trophodynamics- important in energy flow between trophic levels.
- biogeochemistry – stoichiometry demands ties C to other
  - important nutrient cycles
  - green house properties

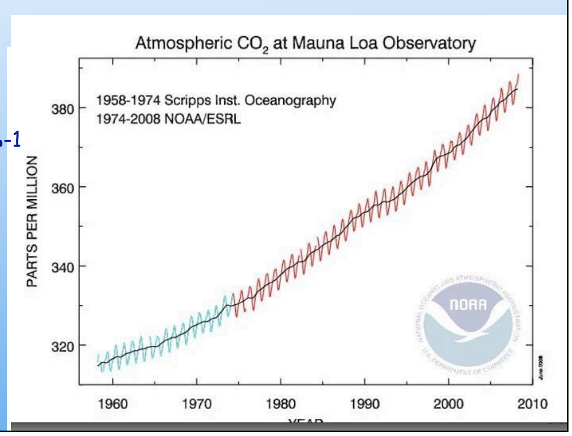


Four reservoirs

- Lithosphere
- Atmosphere
- Terrestrial biosphere
- Ocean

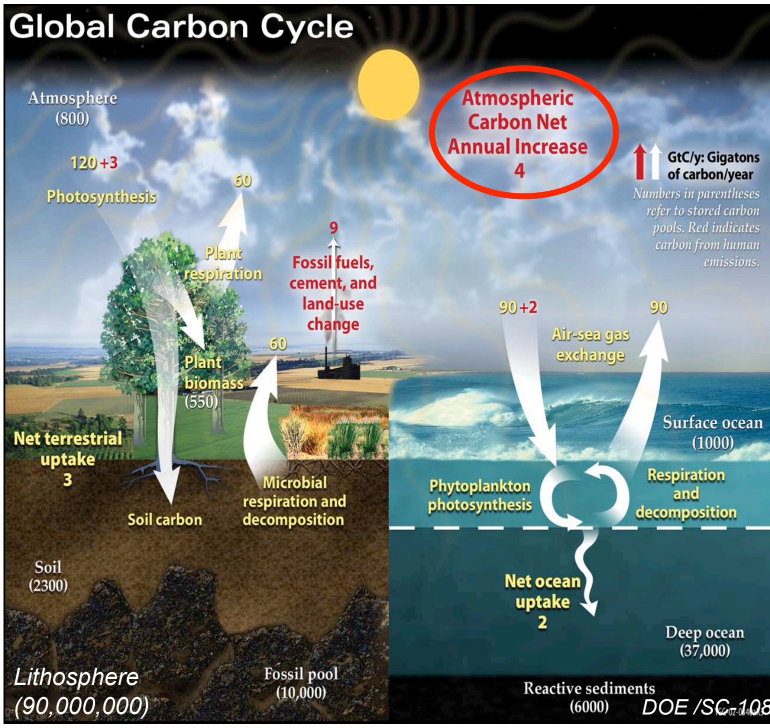
Anthropogenic rise in CO2

- pCO_2 has increase from 280 ppm to 384 ppm (2007)
- Increase of 40% over past 250 yrs



Anthropogenic input is ~9 Pg C yr^{-1}

- Fossil fuel burning
- Cement manufacturing
- deforestation



~ 4 Pg remains in the Atm

Rests is removed by OCN and TB

~ 93% of C in active reservoirs is contained in the ocean

The Chemistry of CO_2 in the Ocean

Dissolution of CO_2 in seawater undergoes the following reaction:

$$CO_2(gas) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

Carbonic acid — Bicarbonate — Carbonate

The buffering capacity of seawater:

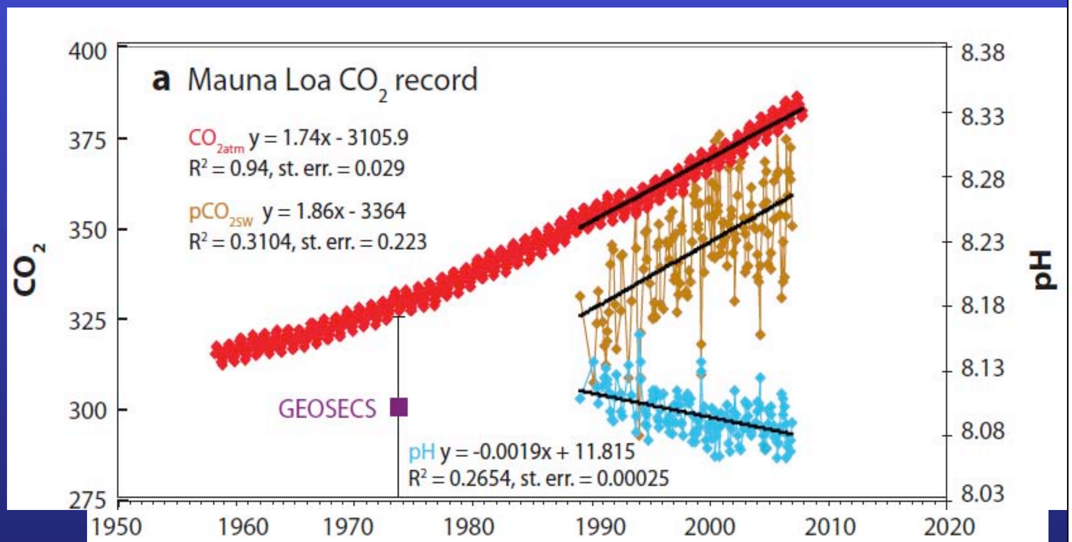
As is CO_2 dissolved in seawater, only ~1% remains as CO_2 and the rest is converted to bicarbonate and carbonate.

90% in the form of HCO_3^-

9% in the form of CO_3^{2-}

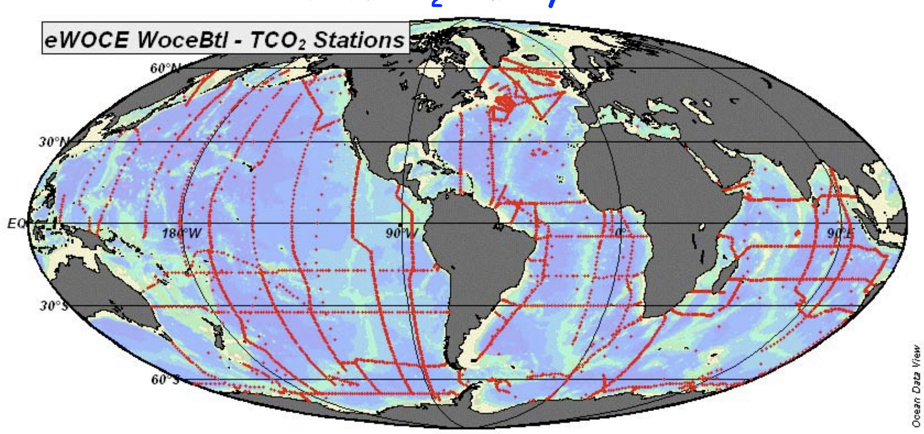
1% in the form of dissolved CO_2

Time series of Atm CO_2, pCO_2 and pH



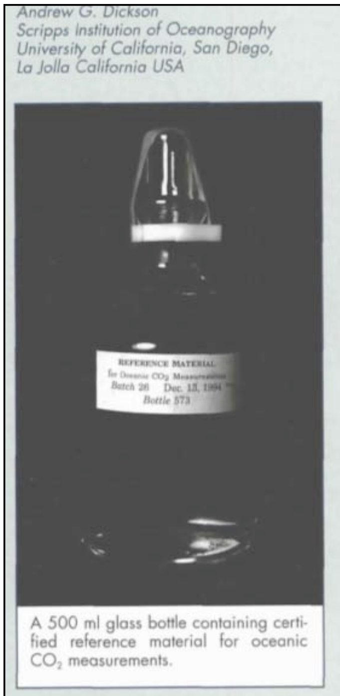
Doney et al. 2009

Ocean CO_2 Surveys



Early Ocean CO_2 surveys:

GEOSECS (1973- 1979)
TTO (1981- 1983)
WOCE (1990's)
CLIVAR (2003 – present)



Early programs did not have CRM's

- variability btw analytical group ±30 µmol kg^{-1}

- >1% of total signal i.e. larger than anthropogenic signal

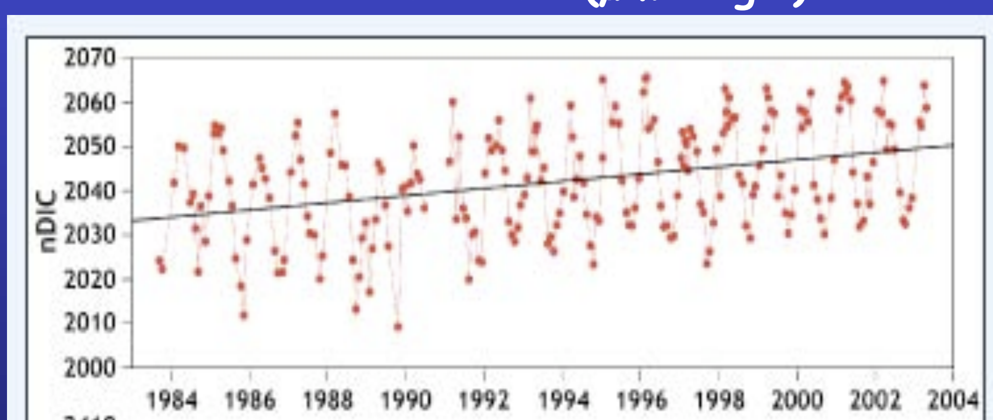
Andrew Dickson supported by NSF and DOE

- CRM for DIC and total Alkalinity

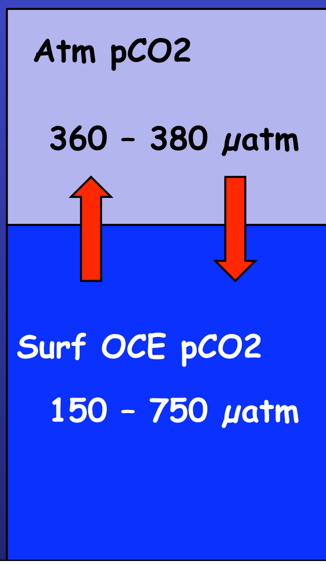
- reduced variability to ±3 µmol kg^{-1}

Can resolve increase in TCO_2 in Surface waters

BATS TCO2 (µmol kg^{-1})

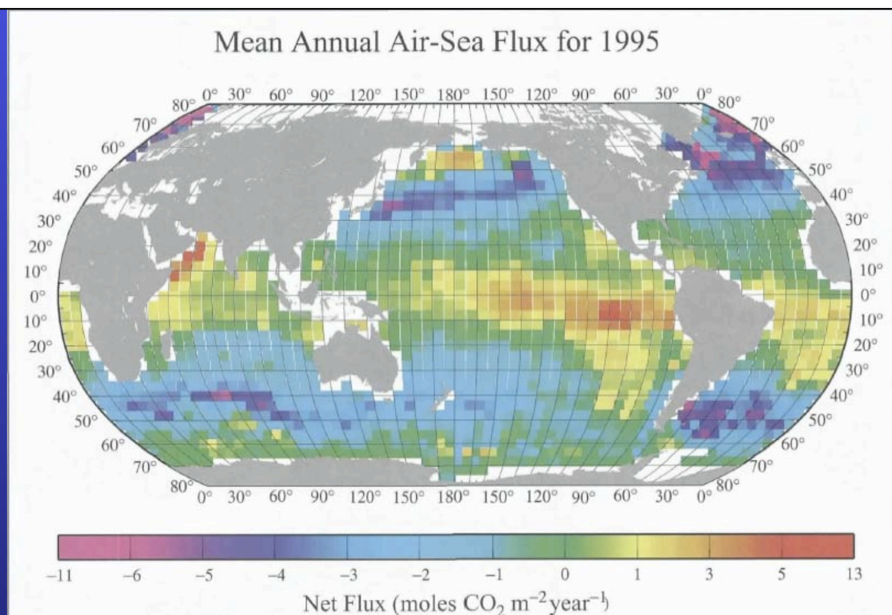


Differences between pCO_2 atm and pCO_2 surface water ….set the potential for air- sea CO_2 flux



- air sea CO_2 flux is driven by variability in OCE pCO2
- global ave of pCO2 in Surf OCE is ~ 7 µatm less than atm

Feely et al. 2001

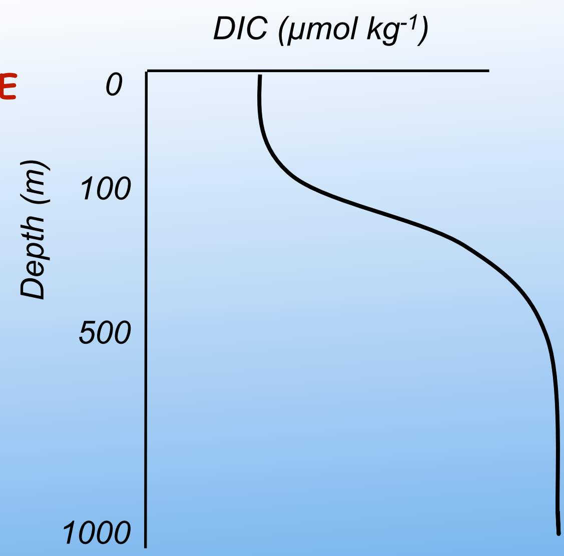


- OCE uptake of ~ 2.2 Pg C y^{-1}

Gradients and distribution of CO_2 (DIC) over depth controls the role the ocean plays as a CO_2 sink

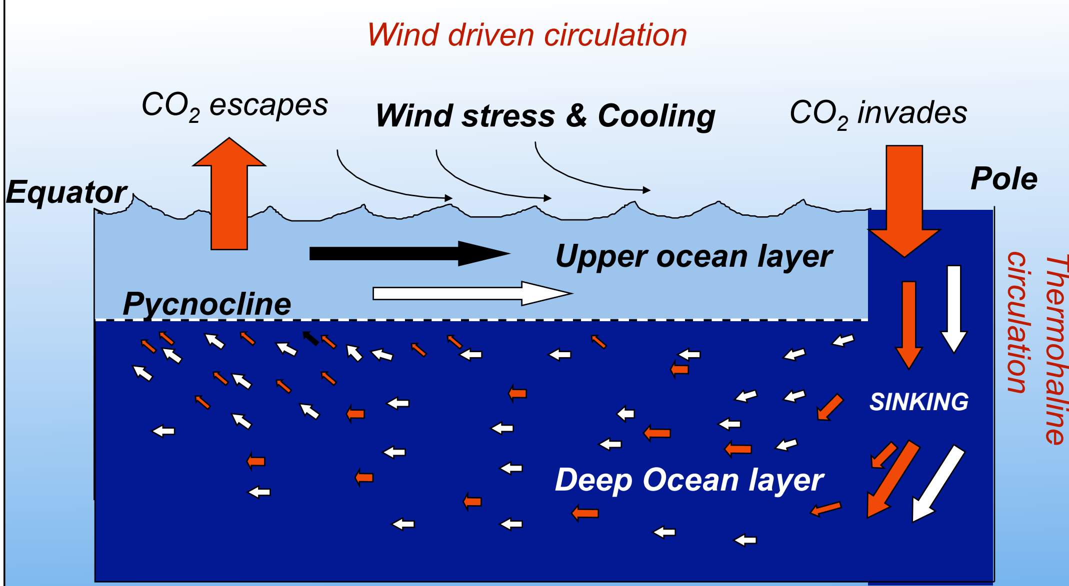
Distribution of DIC in the OCE is controlled by 2 mechanisms:

- Solubility Pump- solubility of CO_2
- Biological Pump- photosynthesis & respiration

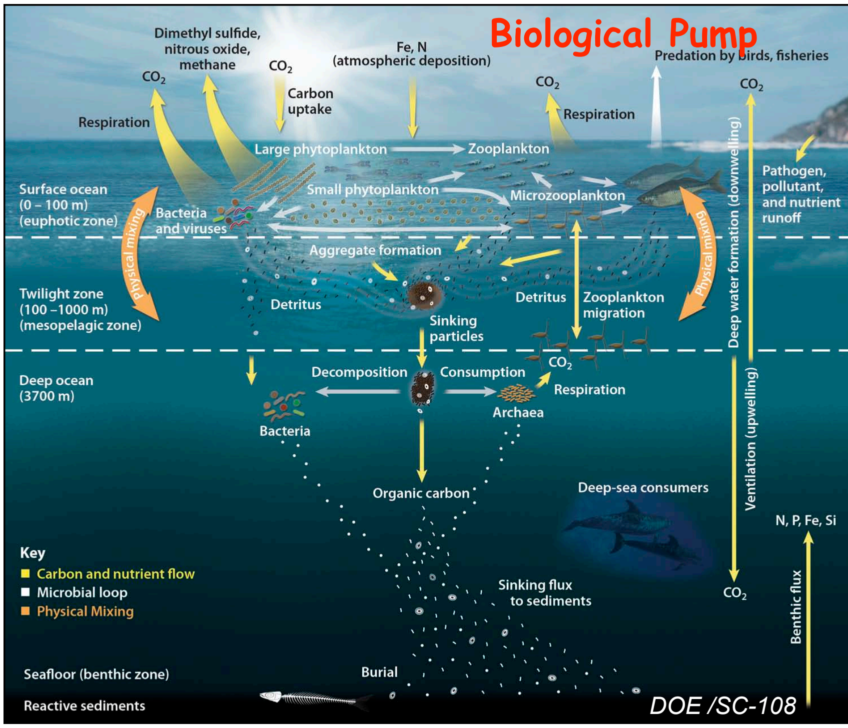


Solubility Pump:

Figure 5



Carlson et al 2001



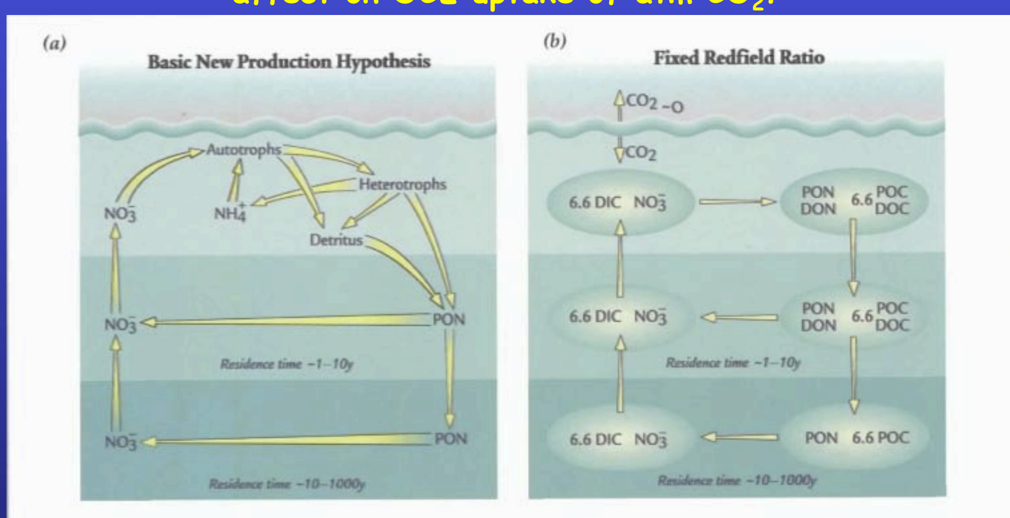
Primary particles

- living organisms
- TEP
- fecal pellets

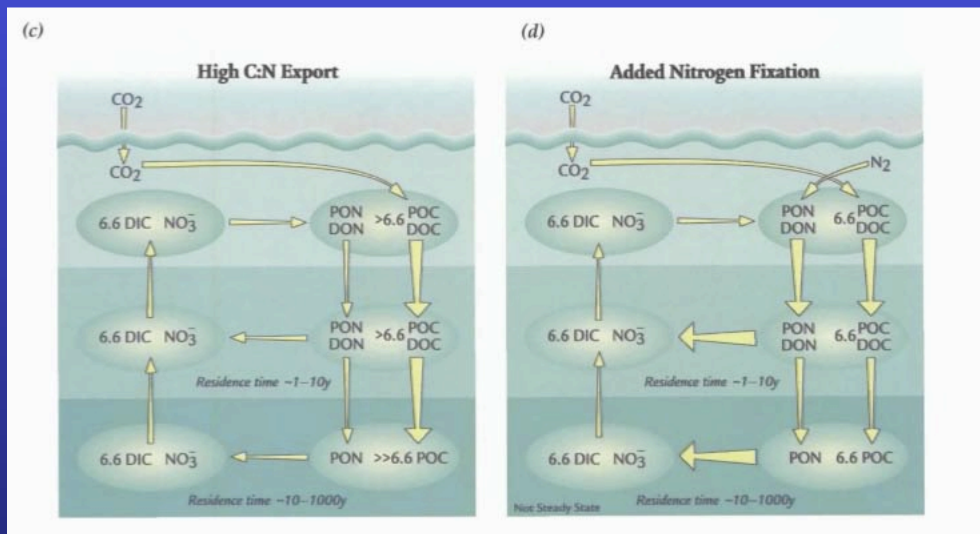
Aggregate particles

- molts
- marine snow

Does increased delivery of nutrients from depth have a net affect on OCE uptake of atm CO_2?

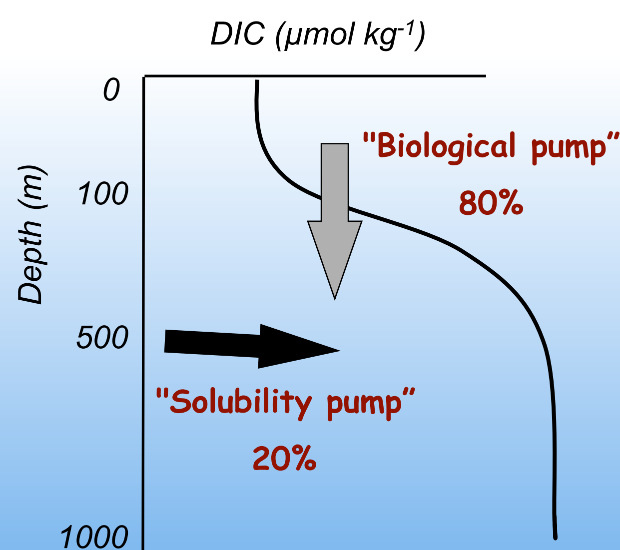


Michaels et al. 2001

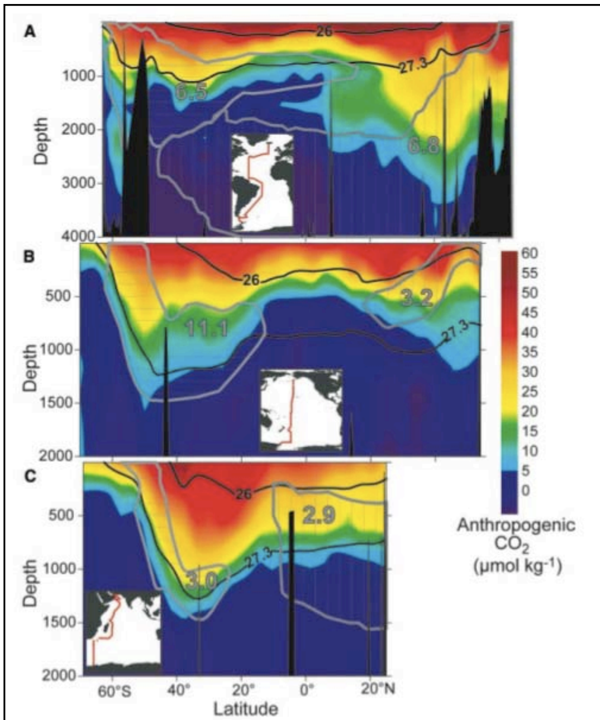


Michaels et al. 2001

Pumps maintain vertical gradient in DIC



Sarmiento and Gruber 2006



Estimations of Anthropogenic CO2 concentrations in the

Atlantic,

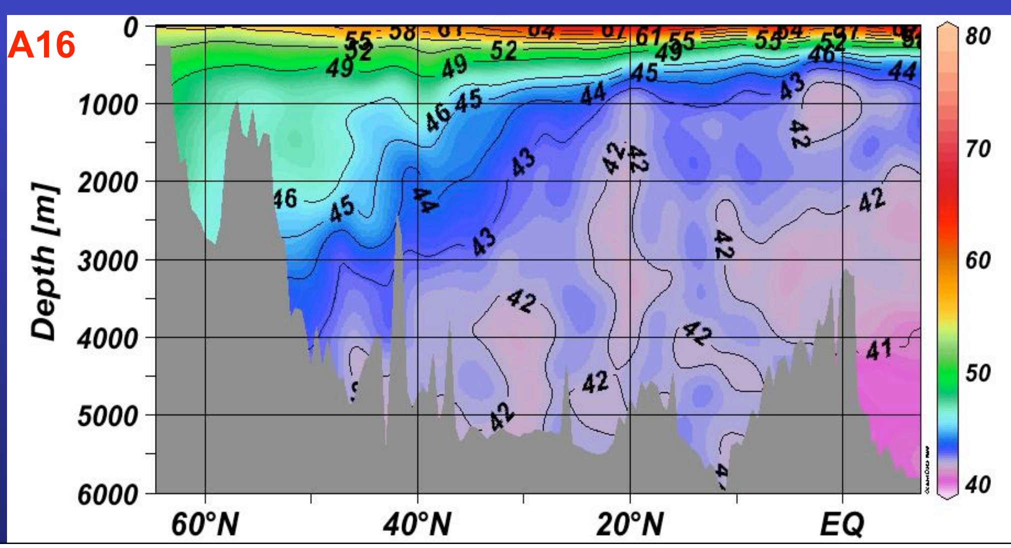
Pacific

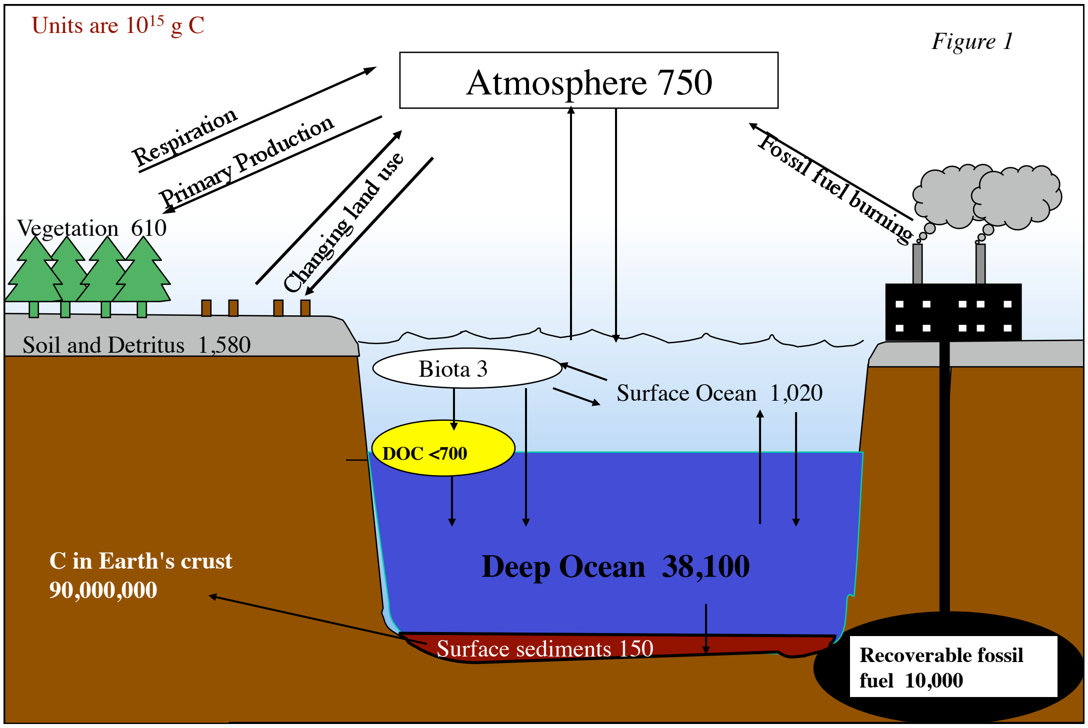
Indian Oceans.

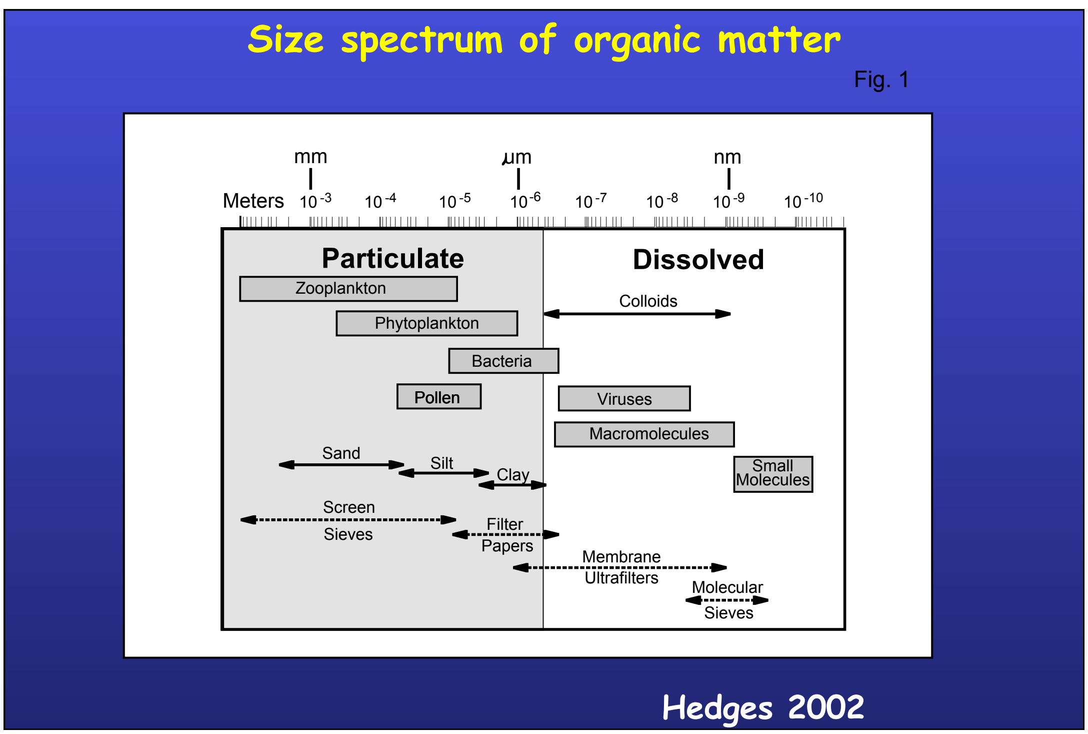
Sabine et al. 2004

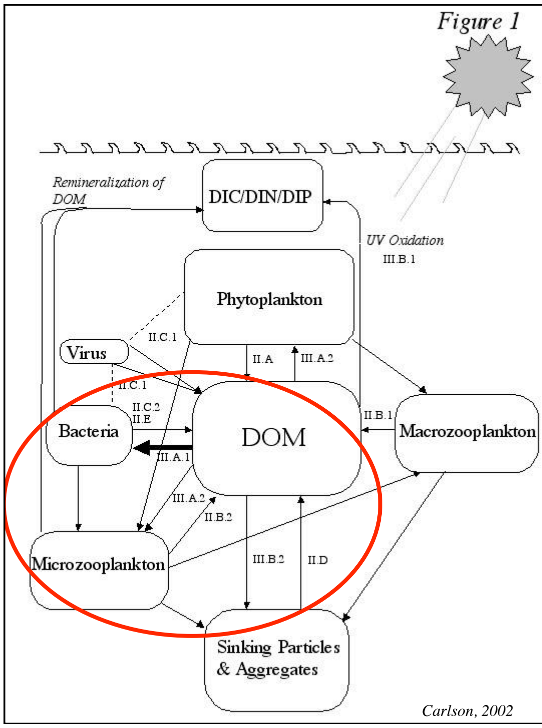
Dissolved Organic Carbon

The other C reservoir




Units are 10^{15} g C
Figure 1
Atmosphere 750
Respiration
Primary Production
Changing land use
Fossil fuel burning
Vegetation 610
Soil and Detritus 1,580
Biota 3
Surface Ocean 1,020
DOC <700
Deep Ocean 38,100
C in Earth's crust
90,000,000
Surface sediments 150
Recoverable fossil fuel 10,000


Size spectrum of organic matter
Fig. 1
mm
µm
nm
Meters 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} 10^{-10}
Particulate
Dissolved
Zooplankton
Phytoplankton
Bacteria
Pollen
Colloids
Viruses
Macromolecules
Small Molecules
Sand
Silt
Clay
Screen Sieves
Filter Papers
Membrane Ultrafilters
Molecular Sieves
Hedges 2002



DOM production and removal mechanisms

In the open ocean…..DOM production is ultimately constrained by the level of Primary production w/in a system.

Brief History and the Controversy of DOC measurements

1909 Pütter - developed first wet chemical combustion technique with chromic acid …problems with chlorine interference

1934 Krogh and Keys- removed chlorine …first reliable estimates of DOC

1950s- Soviets started trying high temperature combustion

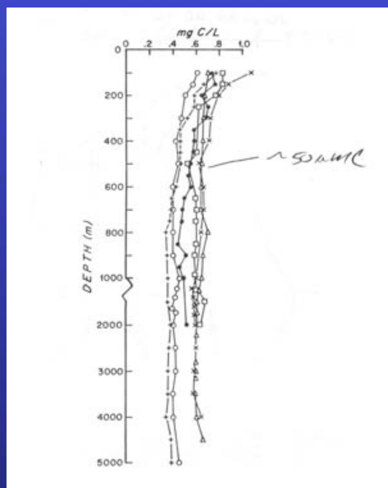
1961- Duursma - wet oxidation and coulometric titration

1964- Menzel and Vaccaro - wet persulfate oxidation

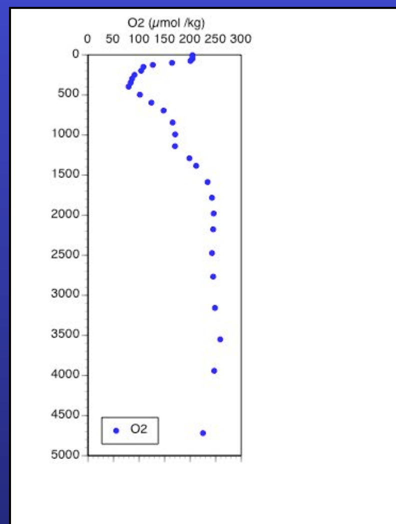
1966 - Armstrong - UV oxidation

1970's - Sharp revisited the HTC method

Historical view of oceanic DOC - relatively unvarying pool of recalcitrant organic matter



6. The average vertical distribution of dissolved organic carbon (mg C/liter) within Areas A (○), B (□), C (x), D (+) indicated on Fig. 1, and at 7°S, 4°W (•) and 24°S, 12°E (△).



Menzel and Ryther 1970

DOC: The controversy… new high concentrations

Sugimura and Suzuki 1988…used new Pt/ alumina catalyst 50- 400% higher than previous estimates

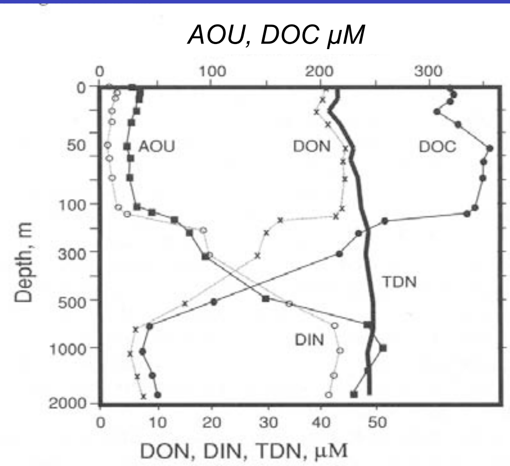
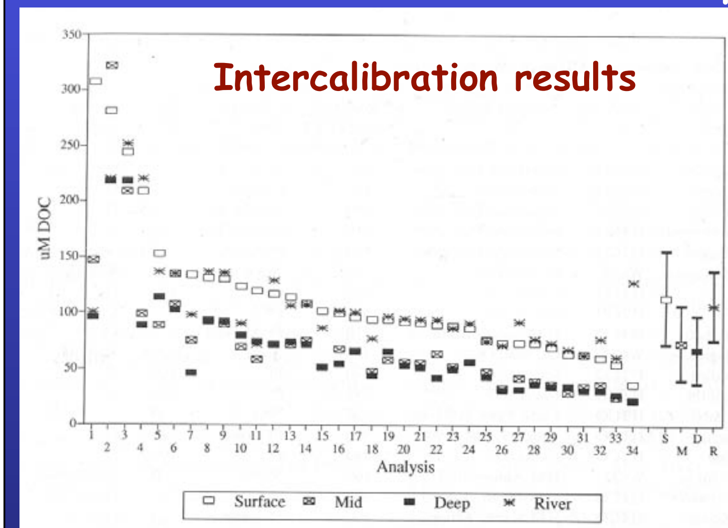


Figure 9 DON, DOC, DIN, and AOU depth profiles in the western Pacific Ocean at 19°01′ N, 134°00′ E (after Fig. 11a of Sugimura and Suzuki (1988), with TDN determined graphically as DIN + DON).

Seattle DOM Workshop 1991

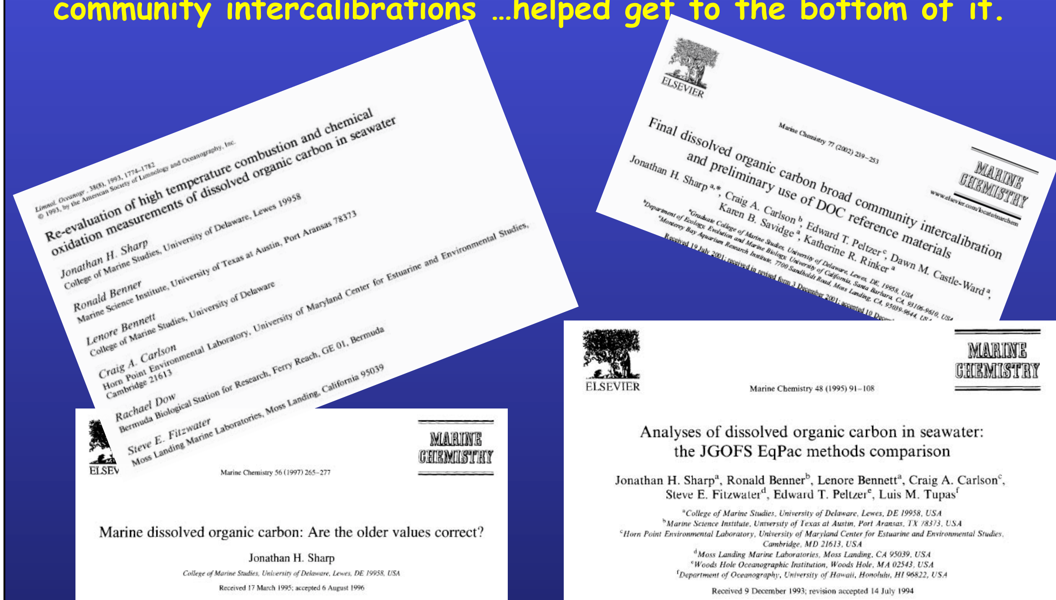


- 34 separate analyses of the same sample
- order of magnitude range in values from same sample!!!
- Blanks were not properly accounted for

Hedges et al. 1992

"We have initiated over a decade long program in ocean carbon and we have no reliable estimate for DOM….you guys have to figure this out!!!" -Neil Anderson NSF Chem OCE

Fine tuning the instrument, column conditioning, proper blank correction, implementation of reference materials and community intercalibrations …helped get to the bottom of it.


Re-evaluation of high temperature combustion and chemical oxidation measurements of dissolved organic carbon in seawater

Jonathan H. Sharp, College of Marine Studies, University of Delaware, Lewes 19958
Ronald Benner, Marine Science Institute, University of Texas at Austin, Port Aransas 78373
Lenore Bennett, College of Marine Studies, University of Delaware
Craig A. Carlson, Bermuda Biological Station for Research, Ferry Reach, GE 01, Bermuda
Rachael Dow, Horn Point Environmental Laboratory, University of Maryland Center for Estuarine and Environmental Studies, Cambridge 21613
Steve E. Fitzwater, Moss Landing Marine Laboratories, Moss Landing, California 95039

Final dissolved organic carbon broad community intercalibration and preliminary use of DOC reference materials

Jonathan H. Sharp, Craig A. Carlson, Edward T. Peltzer, Dawn M. Castle-Ward, Karen B. Savidge, Katherine R. Rinker

Marine Chemistry 56 (1997) 265–277

Marine dissolved organic carbon: Are the older values correct?

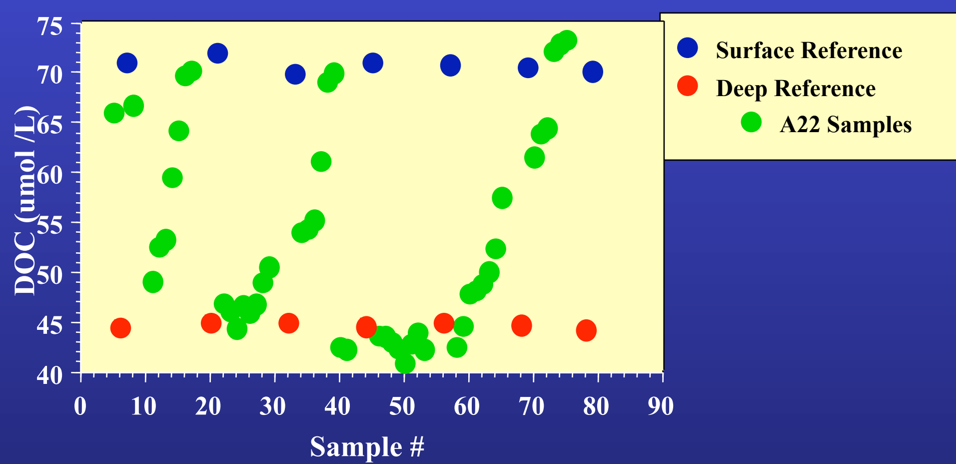
Jonathan H. Sharp

Marine Chemistry 48 (1995) 91–108

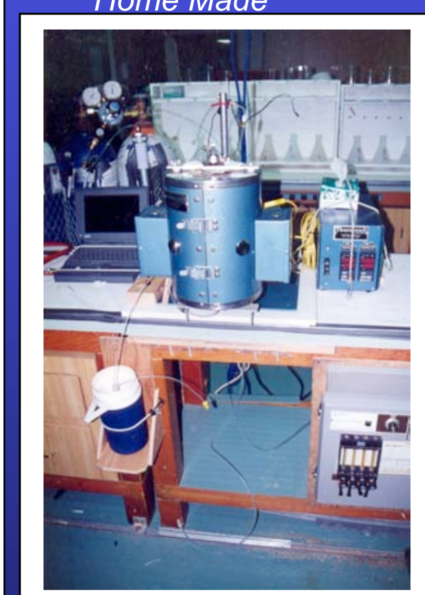
Analyses of dissolved organic carbon in seawater: the JGOFS EqPac methods comparison

Jonathan H. Sharp, Ronald Benner, Lenore Bennett, Craig A. Carlson, Steve E. Fitzwater, Edward T. Peltzer, Luis M. Tupas

Use of referencing to resolve small variability

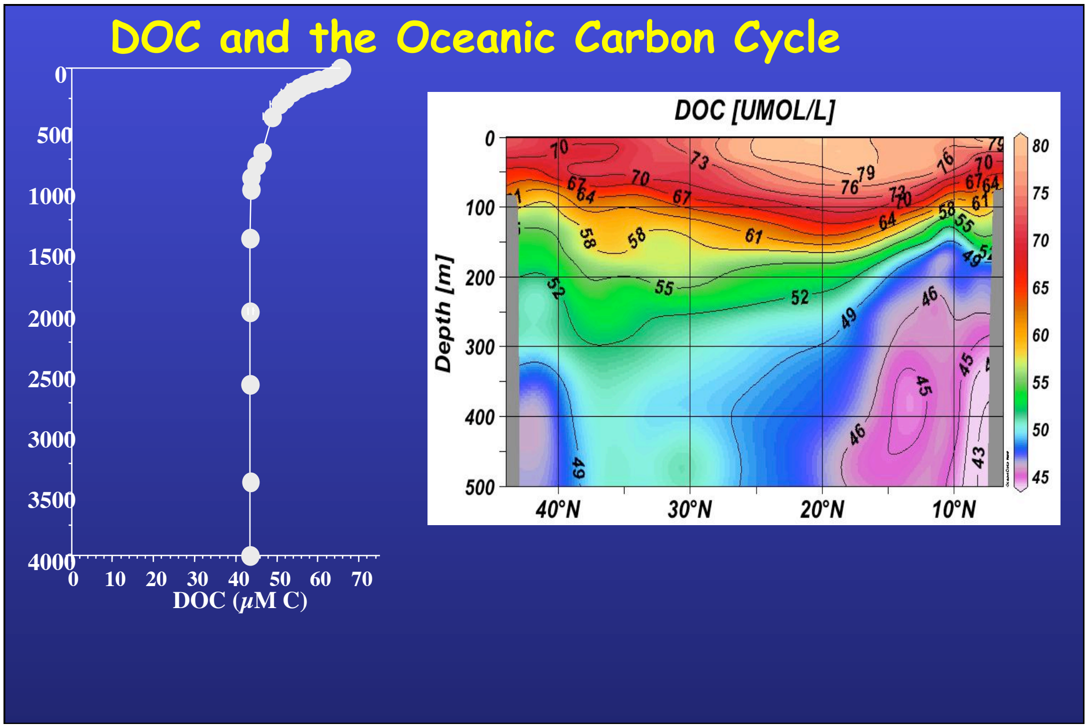


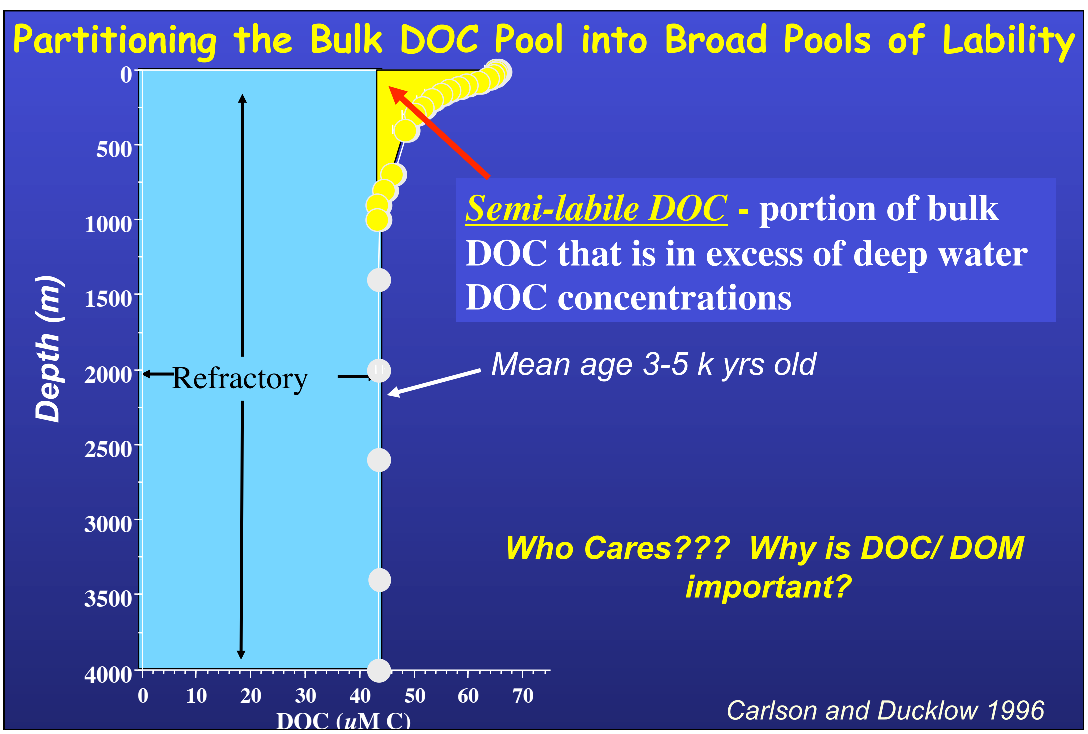
Home Made



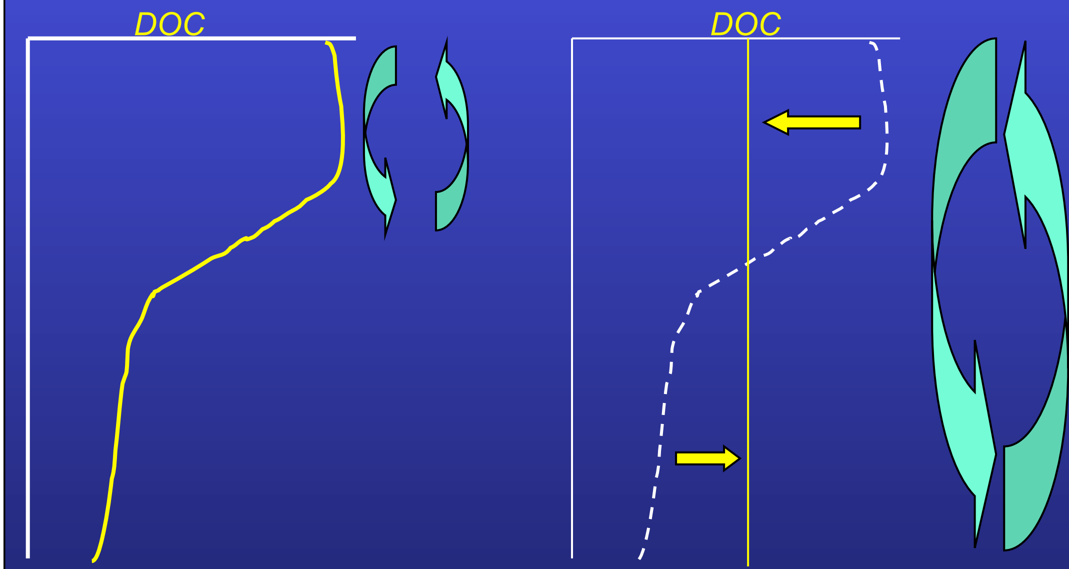
High Temperature Combustion Systems (HTC)

Modified Shimadzu - High throughput!!

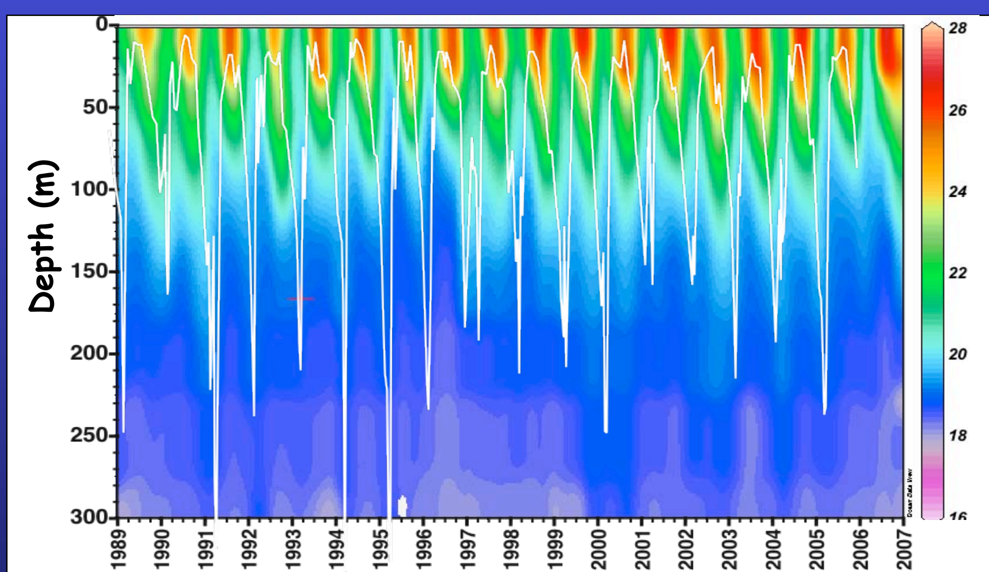

DOC and the Oceanic Carbon Cycle
0
500
1000
1500
2000
2500
3000
3500
4000
0 10 20 30 40 50 60 70
DOC (µM C)
DOC [UMOL/L]
Depth [m]
0
100
200
300
400
500
40°N 30°N 20°N 10°N
80
75
70
65
60
55
50
45


Partitioning the Bulk DOC Pool into Broad Pools of Lability
Depth (m)
0
500
1000
1500
2000
2500
3000
3500
4000
0 10 20 30 40 50 60 70
DOC (µM C)
Refractory
Semi-labile DOC - portion of bulk DOC that is in excess of deep water DOC concentrations
Mean age 3-5 k yrs old
Who Cares??? Why is DOC/ DOM important?
Carlson and Ducklow 1996

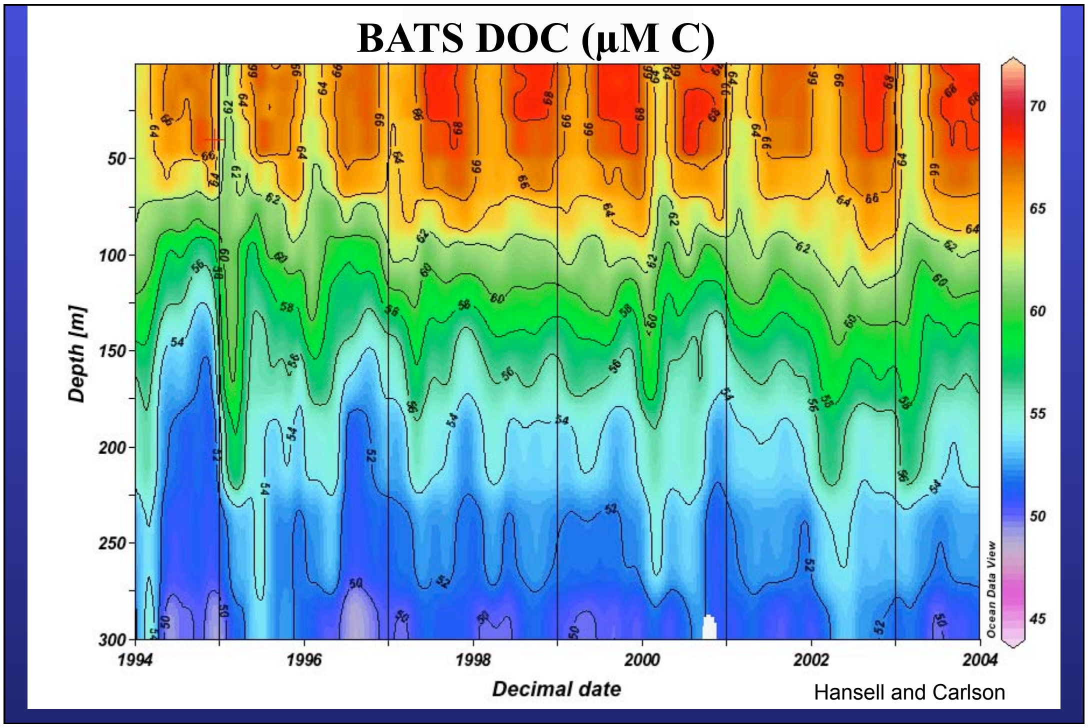
Role of mixing and DOC export

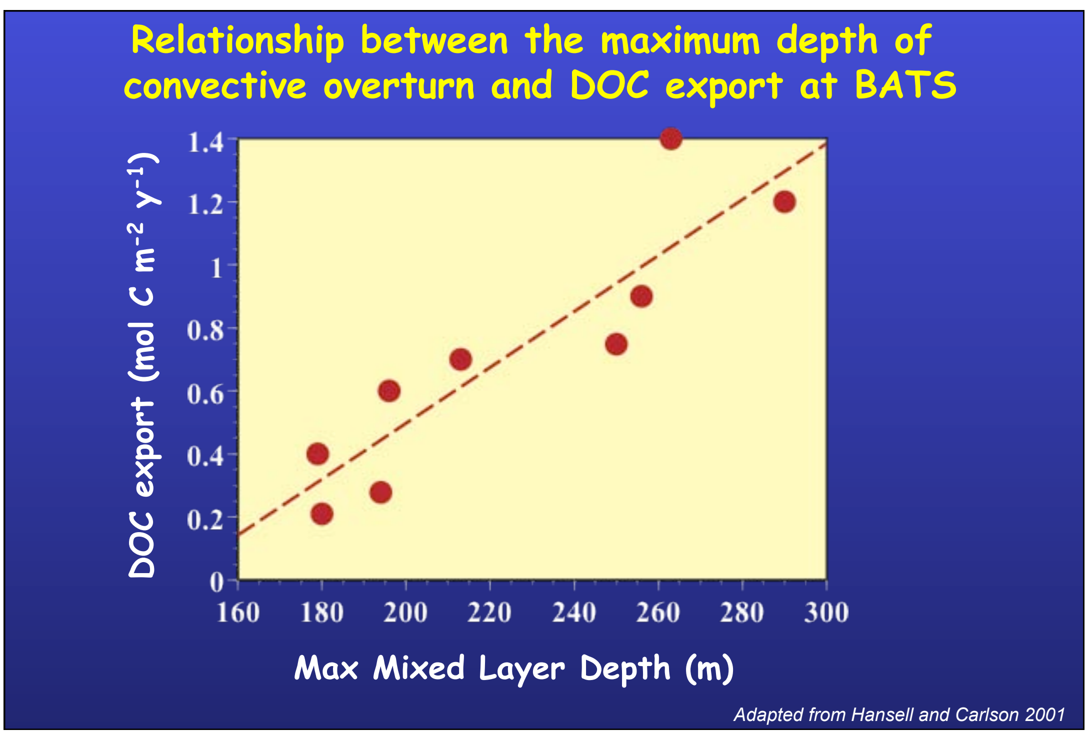


Temperature (°C) and Mixed Layer Depth at BATS



BATS core data

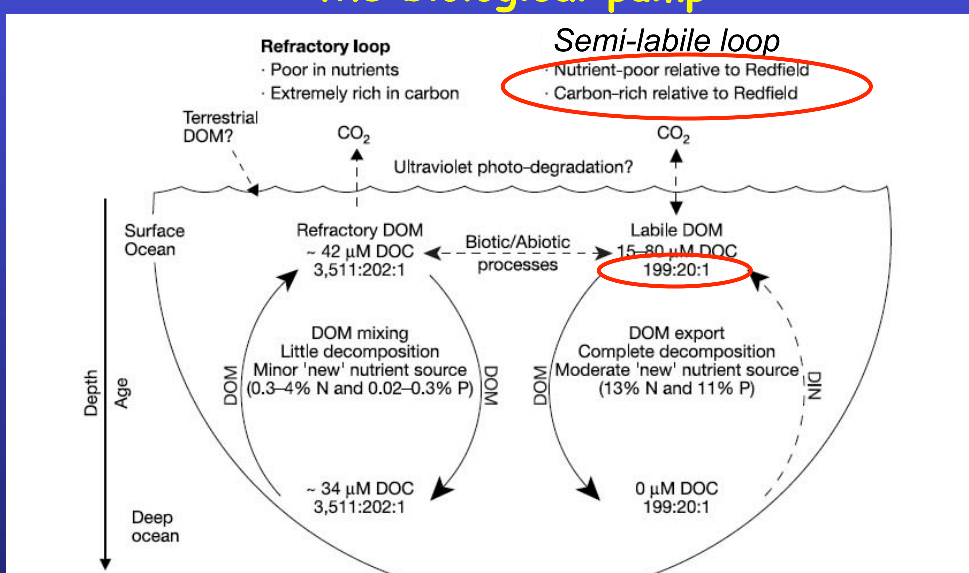

BATS DOC (µM C)
Depth [m]
Decimal date
Hansell and Carlson
Ocean Data View


Relationship between the maximum depth of convective overturn and DOC export at BATS
DOC export (mol C m-2 y-1)
Max Mixed Layer Depth (m)
Adapted from Hansell and Carlson 2001

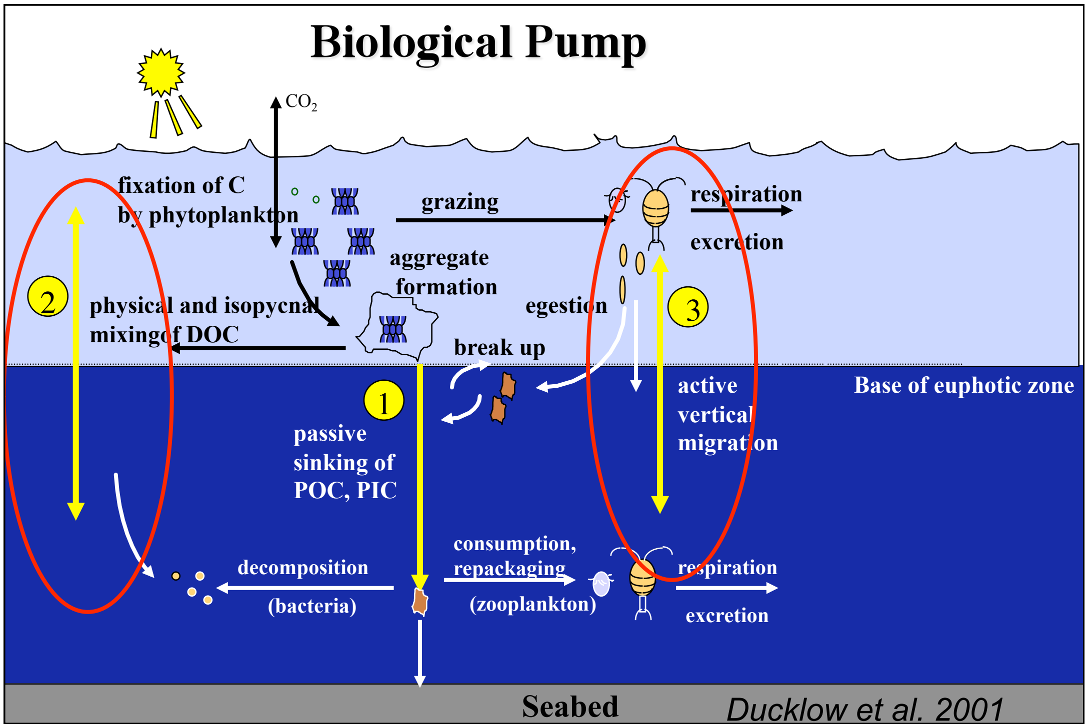
Annual Carbon Budget for Upper Ocean Near Bermuda

	mol C m^{-2} y^{-1}
Geochemical estimates of new Production	
2.9-4.16 Jenkins and Colleagues	
Particulate Export	0.7 -0.8
Lohrenz et al 1992	
Michaels et al 1994	
DOC export	
Carlson et al 1994	1.0 – 1.2
Hansell and Carlson 2001 + more data	0.3 – 1.4

Potential importance of DOM stoichiometry and the biological pump



Adapted from Hopkinson and Vallino 2005


Biological Pump
CO2
fixation of C by phytoplankton
grazing
respiration
excretion
aggregate formation
egestion
2
physical and isopycnal mixing of DOC
3
break up
1
active vertical migration
Base of euphotic zone
passive sinking of POC, PIC
consumption, repackaging
decomposition
(bacteria)
(zooplankton)
respiration
excretion
Seabed
Ducklow et al. 2001