An Intro to the Oceanic Carbon Cycle

- Carbon reservoirs
- The CO₂ & 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
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
The Chemistry of CO₂ in the Ocean

Dissolution of CO₂ in seawater undergoes the following reaction:

\[ \text{CO}_2(\text{gas}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-} \]

Carbonic acid  Bicarbonate  Carbonate

The buffering capacity of seawater:
As CO₂ dissolved in seawater, only ~1% remains as CO₂ and the rest is converted to bicarbonate and carbonate.

- 90% in the form of HCO₃⁻
- 9% in the form of CO₃²⁻
- 1% in the form of dissolved CO₂
Time series of Atm $CO_2$, $pCO_2$ and pH

Doney et al. 2009

Mauna Loa $CO_2$ record

- $CO_{atm}$: $y = 1.74x - 3105.9$
  - $R^2 = 0.94$, st. err. = 0.029
- $pCO_{atm}$: $y = 1.86x - 3364$
  - $R^2 = 0.3104$, st. err. = 0.223

pH: $y = -0.0019x + 11.815$
  - $R^2 = 0.2654$, st. err. = 0.00025

Ocean $CO_2$ Surveys

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 TCO\(_2\) (μmol kg\(^{-1}\))
Differences between $pCO_2$ atm and $pCO_2$ surface water ... set the potential for air-sea $CO_2$ flux

- $pCO_2$ atm: 360 - 380 µatm
- $pCO_2$ surface water: 150 - 750 µatm

- Air-sea $CO_2$ flux is driven by variability in OCE $pCO_2$
- Global ave of $pCO_2$ 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:

Wind driven circulation

CO$_2$ escapes

Equator

CO$_2$ invades

Pole

Wind stress & Cooling

Upper ocean layer

Pycnocline

Deep Ocean layer

SINKING

Figure 5

Carlson et al 2001
Does increased delivery of nutrients from depth have a net effect on OCE uptake of atm CO$_2$?

Michaels et al. 2001
Michaels et al. 2001

Sarmiento and Gruber 2006

**Pumps maintain vertical gradient in DIC**

DIC (µmol kg\(^{-1}\))

- **"Biological pump"**
  - 80%
- **"Solubility pump"**
  - 20%
Estimations of Anthropogenic CO2 concentrations in the Atlantic, Pacific, Indian Oceans.

Sabine et al. 2004

Dissolved Organic Carbon
The other C reservoir
Soil and Detritus 1,580

Recoverable fossil fuel 10,000

Surface Ocean 1,020

Deep Ocean 38,100

Surface sediments 150

C in Earth’s crust 90,000,000

Atmosphere 750

Vegetation 610

Figure 1

Units are $10^{15}$ g C

Size spectrum of organic matter

Hedges 2002
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

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
"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

“34 separate analyses of the same sample

• order of magnitude range in values from same sample!!!

• Blanks were not properly accounted for

Seattle DOM Workshop 1991

Intercalibration results

Hedges et al. 1992

Fine tuning the instrument, column conditioning, proper blank correction, implementation of reference materials and community intercalibrations ...helped get to the bottom of it.
Use of referencing to resolve small variability

DOC (umol/L)

Sample #

0 10 20 30 40 50 60 70 80 90

Surface Reference
Deep Reference
A22 Samples

Home Made

High Temperature Combustion Systems (HTC)

Modified Shimadzu - High throughput!!
DOC and the Oceanic Carbon Cycle

Typical summer profile oceanic system

Refractory

DOC and the Oceanic Carbon Cycle

DOC [UMOL/L]

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
Relationship between the maximum depth of convective overturn and DOC export at BATS

Adapted from Hansell and Carlson 2001
Annual Carbon Budget for Upper Ocean Near Bermuda

Geochemical estimates of new Production
2.9-4.16 Jenkins and Colleagues

Particulate Export
Lohrenz et al 1992
Michaels et al 1994

DOC export
Carlson et al 1994
Hansell and Carlson 2001 *more data

Potential importance of DOM stoichiometry and the biological pump

Adapted from Hopkinson and Vallino 2005
Active vertical migration of C by phytoplankton (fixation of C by phytoplankton).

Passive sinking of POC, PIC (physical and isopycnal mixing of DOC).

Respiration, excretion, and consumption, repackaging (zooplankton).

Break up (bacteria) and (zooplankton).

Seabed Decomposition (bacteria).

Base of euphotic zone Respiration, excretion.