Nitrogen Fixation and Carbon Sequestration

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Outline

• Carbon Storage in the Sea - Mechanisms
• Nitrogen Fixation
• Verification Issues
• Academic Conflicts of Interest
Disclosure of Relevant Commercial Associations

• Planktos (conversations only, pre-2001)
• Climos (discussions 2006-Present, no contract relationship at present)
• Proteus Environmental Research.LLC (R&D Incubator and Venture Fund, have personal equity and significant management roles)
Carbon Storage in the Sea - Biogeochemical Mechanisms

- Relative use of surface macronutrients
  - Residual Nitrate (HNLC)
  - Residual Phosphate in the absence of NO₃
- Changes in C:N:P of export
- Changes in remineralization length-scale
- Changes in PIC rain rate ratios with POC
All of these are Time-Shifting
Ocean biology maintains a vertical DIC gradient - ocean biology is limited by the supply of nutrients:

- **Nitrate+Nitrite**
- **Dissolved Inorganic Carbon**

- **Century residence times**
- **Decadal residence times**
- **Millenial residence times**

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![Graph](HOT_1-110.png)

**Dissolved Inorganic Carbon**

**Nitrate+Nitrite**

**Pressure**
Incomplete Nutrient Utilization in the Surface Waters (HNLC)
(Leaves un-used DIC in the surface and more CO2 in the atmosphere)

- Decadal residence times
- Century residence times
- Millennial residence times

Dissolved Inorganic Carbon

Nitrate+Nitrite
Changes in Total Nitrate Stock
Nitrogen Fixation - Denitrification Balance

Extra Nitrogen Fixation

Lower DIC

Higher DIC

Dissolved Inorganic Carbon

Stronger gradient, lower Surface DIC
Changes in Total Nitrate Stock
Nitrogen Fixation - Denitrification Balance

Extra Denitrification

Higher DIC

Lower DIC

Decadal residence times

Century residence times

Millenial residence times

Dissolved Inorganic Carbon

Weaker gradient, higher Surface DIC
*Trichodesmium* spp.
Best Known Planktonic Diazotroph
Trichodesmium makes enormous blooms (space shuttle picture of 10,000 km² bloom)
Changes in C-N-P stoichiometry

Increase C:N or C:P Of export

Dissolved Inorganic Carbon

Pump more carbon, lower Surface DIC
Changes in remineralization length-scales

Increase depth of remineralization

Dissolved Inorganic Carbon

Push carbon deeper, lower Surface DIC
Changes in PIC:POC rain

- Changes in carbonate fluxes impacts the alkalinity of the surface ocean
- Changes in surface alkalinity changes pCO2
- Secondary issues with other gases.
Carbon Storage in the Sea - Mechanisms
Focus on Nitrogen Fixation

• Relative use of surface macronutrients
  – Residual Nitrate (HNLC)
  – Residual Phosphate in the absence of NO₃
• Changes in C:N:P of export
• Changes in remineralization length-scale
• Changes in PIC rain rate ratios with POC
Sequestration Time-scale

• How long will this carbon stay below the surface mixed layer?
How to Understand and Measure the Effect: Create Mass Balance Model for Mixed Layer

Atmospheric CO₂

Surface

Total CO₂, pCO₂

Organic Carbon (dissolved, particulate)

100 m or 100 year

Total CO₂

Sinking Flux of C
How to Understand and Measure the Effect:
Create Mass Balance for Mixed Layer

Atmospheric N₂

Surface

N₂ → Organic Nitrogen (dissolved, particulate)

100 m or 100 year

Nitrate → Sinking Flux of N
Sequestration Time-scale

- Biological re-use should keep carbon and new nitrate below the surface for extended periods.
- Carbon storage until:
  - Upwelled in HNLC area and extra nitrate is left unused (if that happens)
  - Passes through denitrification zone, followed by upwelling to the surface without the extra nitrate
- Both of these time-scales can be centuries when the correct location is chosen.
Fe Addition and Nitrogen Fixation - Existing Data

- FeeP - Fe and SRP addition in NE Atl.
- Bottle Incubations (Fe, SRP, dust)
- Amazon Plume (High Fe, PO4)
- HOT data - recurring summer signal (Karl)
FeeP (Rees, et al., 2007)

- Added Fe and PO4 to a low Fe and P area of NE Atlantic
  - 25 km² patch of Fe only
  - 25 km² patch with Fe and P
- Followed for about 3 weeks
- Fe+P patch, *Trichodesmium* increases
- N fixation rates increased 6 fold and 4.5 fold respectively
Nitrogen Fixation

• FeeP - Fe and SRP addition in NE Atl.

• Bottle Incubations (Fe, SRP, dust)
  – Lots of experiments with variable results
  – Often both addition of Fe and Dust stimulate nitrogen fixation
  – Always questions about how to extrapolate to nature
Fe and Dust Addition Experiments in Pacific (Sohm data)

Figure 3 Acetylene reduction rates with nutrient additions to culture and field samples of *Trichodesmium*.  

a) Phosphate additions of 20 and 45 µM phosphate to culture grown on 5 µM phosphate (10 times less than in standard YBCII media).  
b) and c) 10 nM Fe and 100 nM PO₄³⁻ additions to colonies picked from net tows in the North Pacific Subtropical Gyre.  
D) Incubation of colonies from the North Pacific Subtropical Gyre and incubated for 0, 24 and 48 hours before initiation of acetylene reduction assay.
Nitrogen Fixation

• FeeP - Fe and SRP addition in NE Atl.
• Bottle Incubations (Fe, SRP, dust)
• Amazon Plume (High Fe, PO4)
  – Mimics Fe patch after the nitrate and ammonia have been used up - Amazon plume is still Fe, PO4 and Silica rich water diluted into open ocean seawater.
Amazon Plume Data (Cooley et al)

N-fixation blooms in Amazon plume

Highest carbon Drawdown in center Of N-fixation blooms
Figure 6. Community impact on DIC (ΔDIC_Bio), calculated with the mixing model, plotted against salinity. The 95% confidence interval error bars are within the size of the marker. Station numbers are shown for summer samples. Endmembers used to calculate ΔDIC_Bio included: A_s = 2359.4 ± 5.9, S_s = 36.07 ± 0.10, DIC_s = 2024.5 ± 6.8, S_t = 0 ± 0. The shaded region above salinity 35 indicates data outside the influence of the plume. Markers indicate the prevailing macroscopic nitrogen-fixing organisms observed at a station: square, none; circle, Richelia; asterisk, Trichodesmium; circle and star superimposed, Richelia and Trichodesmium together.
Nitrogen Fixation

• FeeP - Fe and SRP addition in NE Atl.
• Bottle Incubations (Fe, SRP, dust)
• Amazon Plume (High Fe, PO4)
• HOT data - recurring summer signal (Karl)
  – Indicate recurring blooms of diazotrophs every summer in N. Pacific Gyre, lead to high export to depth, strong delN15 signal
Conclusions From Previous Research

- Reasonable likelihood that nitrogen fixation is influenced by availability of Fe in the North Pacific and that addition of Fe will stimulate growth of diazotrophs (variable N:P)
- Growth of diazotrophs can lead to DIC drawdown
- Increases in total reactive nitrogen (ultimately nitrate) could impact air sea partitioning of CO2 until those waters experience denitrification (100s to 1000 years).
Site Selection

- Nitrate near detection
- Phosphate measurable
- Fe low
- Diazotrophs present, but not growing because of Fe stress
- Shallow Mixed Layers and Warm Waters
- Subsurface conditions conducive to sequestration and minimal negative environmental impacts
Most of the ocean shows near-complete nutrient utilization

Surface Nitrate (µmoles/kg)
Look for areas of low but positive nitrogen fixation

Moore et al., 2004
Find areas where diazotrophs limited by Fe

Moore et al., 2004
Pick areas with “extra” phosphate
Compelling Logic?

- The best place for nitrogen fixation is where there is excess phosphate - usually derived from the upwelling of waters that recently experienced denitrification, but that have not yet experienced N fixation.
Environmental Impact Issues

- Other Trace Greenhouse Gases
  - \( \text{N}_2\text{O} \), methane, DMS
- Harmful algae or other ecosystem distortions
- Oxygen anomalies
- Acidification Issues
  - Reduce surface acidification
  - Increase deep-sea acidification
  - Volumes different - impact should be less
Back to Conflict of Interest

• Academic role is analogous to university-run trials of new drugs or biomedical devices
• Commercial linkages are inherent
• Disclosure of potential conflicts and formal management are critical
• Appearance is as important as reality
• Learn from the other fields

We have to do this well!
Disclose and Manage

• Assume outsiders will think the worst
• Hidden ties, no matter how innocent can look bad (particularly when coupled to non-disclosure agreements)
• Over-disclosure is fine - fine line between internal disclosures and public knowledge
• External reviews and layers of checks and balances provide real protection
• Guard academic freedom (particularly for graduate students and Assistant Professors)
Some of Our Plans

- Independent data analysis of 5-10% of samples - hired by university
- Independent assessment of process and methods - hired by company
- Use full assets of university contract and IP offices
- Independent faculty and university oversight of contract research when faculty have equity stake in the company (esp. for verification projects)
- Independent co-advising for graduate students funded under contracts (use techs!)
Familiarize Yourself with Your Institutional Policy

• Conflict of Interest Policy
• Conflict of Commitment Policy
• IP Licensing Policy and Process
  – Protectable IP
  – Know-how
• Rules and Traditions for Commercial Activities within Academia
  – Medical School
  – School of Engineering
Thank you

Questions?