Looking for Nitrogen Fixation and Denitrification in All of the Right Places

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(With thanks to a host of colleagues and the meeting organizers)
Nomenclature & Background

Canonical Denitrification: \[ \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \]

Denitrification: the ensemble of biological processes that convert fixed-N to \( \text{N}_2 \)

This nomenclatural detour is made necessary because of the recent explosion of knowledge \textit{vis a vis} biological pathways that produce \( \text{N}_2 \).

Denitrification dominates when oxygen is depleted (suboxia), but can occur in the presence of oxygen. \( \text{NO}_3^- \) is the dominant suboxic electron acceptor, but the suite of suboxic/oxygen deficient electron acceptors includes \( \text{NO}_3^- \), \( \text{NO}_2^- \), \( \text{NO} \), \( \text{N}_2\text{O} \), \( \text{IO}_3^- \), Mn (III & IV), Fe (III), etc.
Themes and Quotes

“There are more things on heaven and earth than are dreamt of in our philosophy” (The Bard)

“The More We Look the More We Find” (A. Devol)

“We have looked for denitrification in less than 0.5% of the oceanic volume and in a miniscule portion of oceanic sediments, and for nitrogen fixation in less than ~ 3% of the oceanic volume, and not at all in deep and cold sediments” (Me)
My Major Thesis is that Exploration & Discovery Science and Better Methods Are Urgently Needed!

Many aspects of these systems are still poorly defined (e.g. volume and variability of suboxic waters).

Major Biological Pathways still debated.

Not all potential sites have been investigated even in a cursory way.

Anammox vs Denitrification.

Add your favorite topic!
Puzzles

Sedimentary $^{15}$N data, the atmospheric carbon dioxide record, and the oceanic nitrate/phosphate scatter diagram suggest an oceanic fixed-N budget that changes over glacial-interglacial cycles, but is more or less in balance (homeostatic) over the Holocene. Yet, recent data suggest oceanic denitrification rates that produce a budget that is significantly out of balance. How can we reconcile these results?

Do these strange results arise from undersampling, or is the ocean changing during the Holocene/Anthropocene transition?
The Holocene is Sooo Over!  Welcome to the Anthropocene!

Historic population growth

Population (millions)

Years BC / AD
The Holocene is Sooo Over! Welcome to the Anthropocene!

From < 1 billion to > 6 billion in a Few Hundred Years: 2050 UN Projections 8-10 billion

10-20% increase in the flux of nitrogen to estuaries by 2030

25% of global continental shelf swept by bottom trawls every year, etc.
Departure Points that We Agree On?

- The oceanic fixed-N budget is dominated by internal biological processes (nitrogen fixation source, denitrification sink).
- There has been a recent revolution in our understanding of the biological pathways that can convert fixed-N to N₂.
- We have found that the suite of important nitrogen-fixers in the ocean is larger and more complex than thought not so long ago.
- Some of the terms in the oceanic N regime are much larger than thought just few years ago leading to a turnover time of only ~ 1500 yrs.
- Recent advances in understanding can help with restoration/remediation.
Multiple Pathways to $N_2$

Nitrifying Bacteria

$NH_4^+$ and Organic Matter Oxidation
Using $IO_3^-$, $NO_3^-$, Mn (III & IV)
and Fe (III)

Denitrifiers & Dissimil.
Nitrate Reducers

Oxidation State

-III -II -I 0 +I +II +III +IV +V
Multiple Pathways to N₂

What happens to NH₄⁺ flux from sediments to suboxic water?

--- Nitrifying Bacteria ---

NH₄⁺

NH₄⁺ Anammox

NH₄⁺ and R-NH₂

NH₄⁺ and Organic Matter Oxidation Using IO₃⁻, NO₃⁻, Mn (III & IV) and Fe (III)

Denitrifiers & Dissimil. Nitrate Reducers

Oxidation State

-III -II -I 0 +I +II +III +IV +V
Incubation experiments suggest a dominance of anammox in suboxic oceanic water columns, but the nitrous oxide distributions (including isotopic composition of nitrous oxide) suggest otherwise. There is also the issue of how to produce enough ammonium to allow anammox to dominate at least when there is no significant sedimentary ammonium flux (i.e. Deep Arabian Sea, Deep ETNP, Deep ETSP).

How does the isotopic signal for Anammox differ from canonical denitrification?
Multiple Pathways to $N_2$

Incubation experiments suggest a dominance of anammox in suboxic oceanic water columns, but the nitrous oxide distributions (including isotopic composition of nitrous oxide) suggest otherwise. This new knowledge also provides potential opportunities for mitigation.

Enough ammonium to allow anammox to dominate at least when there is no significant sedimentary ammonium flux (i.e. Deep Arabian Sea, Deep ETNP, Deep ETSP).

How does the isotopic signal for Anammox differ from canonical denitrification?
Bacteria that Oxidize Sulfide With Nitrate

$O_2 \sim 0 \mu M; \quad NO_3^- \sim 30 \mu M$

Beggiatoa, Thioploca, Thiomargarita

$= N_2 & NH_4^+ + energy$

HS$^-$
Bacteria that Oxidize Sulfide With Nitrate

O$_2$ $\sim$ 0 µM; NO$_3^-$ $\sim$ 30 µM

Beggiatoa, Thioploca, Thiomargarita

Schulz & Schulz (2005) *Science*: These Bacteria May Also Sequester Large Amounts of P and Enhance CFA Formation.
Bacteria that Oxidize Sulfide With Nitrate

“The More We Look, The More We Find!!!

Bacteria, such as Beggiatoa, Thioploca, and Thiomargarita, may also sequester large amounts of P and enhance CFA formation.
Importance

Changes/Imbalances in the oceanic fixed-N budget/inventory can impact ocean productivity and storage of carbon dioxide.

Subtle changes in nitrogen respiration can have massive impacts on the atmospheric nitrous oxide budget with knock-on effects on the planetary radiative balance and ozone distribution. (e.g. W. Indian shelf, “stop&go” denitrification results of Naqvi et al.)
Some Ramblings on the Need to Determine Excess N$_2$ Directly
Black Sea Lessons
Black Sea Lessons

$O_2 \sim 0$
With respect to sedimentary P deposition or loss, I think that there is a major difference between suboxic and anoxic conditions.
Some Nitrous Oxide Profiles

basinwide + mesoscale forcing
Some Nitrous Oxide Profiles

Some “back of the envelope calculations suggest that about 5 – 30% of the oceanic nitrous oxide production might occur in the low oxygen/high nitrous oxide waters found at the boundaries of the suboxic water masses. The volume of these waters is only ~ 0.5% of the total oceanic volume.

Some values over the W. Indian Shelf exceed 500 nM during “stop and go” denitrification (Naqvi et al., 2000).
Naqvi et al., 2000
Naqvi et al., 2000
405nM

Naqvi et al., 2000
Shaded regions = DO concentrations $<\sim 20\mu$M (from Deuser). Suboxic regions (DO $< 3 \mu$M) within the shaded areas are major denitrification sites even though only $\sim 0.1\%$ of the oceanic volume.
Naturally enough, we initially focused on regions where signals were impressive (e.g. suboxic nitrite maximum zones first pointed out in ~1959)
Since suboxic conditions apply in only ~0.1–0.2 % of the oceanic water column’s volume, minor changes in the ocean can cause large % changes in the suboxic volume.

It is important to realize that we are under-sampling a time variable system and that different types of estimates have different time scales!!!!
It would seem to be that recent anthropogenic impacts on the Ocean Ecosystem go way beyond minor!
Another Reason Why Denitrification in These Small Volumes Is Sensitive to Change

A C/N ratio “amplifier”:
During Primary Production, C/N uptake ratio is:
\[ \sim 7:1 \text{ [by atoms]} \]

During Denitrification the C oxidation to N\(_2\) production rate is:
\[ < 1 \text{ [by atoms]} \]

So, once suboxia commences, you don’t have to move much C around to make big changes in N\(_2\) production.
Most Sedimentary Denitrification Studies Have Been Conducted in Shallow/Shelf Sediments
But What About Abyssal Sediments?

On average, abyssal sediments should have 0 denitrification, but the ocean ecosystem does not survive on averages. On average, there is not enough food for critical larval stages, etc.
Oxygen Consumption in Deeper Sediments

Sedimentary Denitrification in Bering Sea Basin = 1-3 Tg N a^{-1}

benthic O_2 Flux [mol O_2 m^{-2} yr^{-1}]
Transient suboxia [W. Indian Shelf]
1. Denitrification deep within sediments at sediment base-rock boundaries.
2. Denitrification in oxygenated water.
3. Shallow sandy/silty sediments & adjacent aquifers
5. Brine pockets in Ice
6. Ice gouges/Arctic River Mouths
7. Gut Flora N-fixers
8. Vents, seeps, & brines, MOR flanks
Potential Denitrification & Nitrogen Fixation Sites that Have Received Relatively Little Attention

Transient suboxia [W. Indian Shelf]
1. Denitrification deep within sediments at sediment base-rock boundaries.
2. Denitrification in oxygenated near-sediment water.
5. Brine pockets in ice.
6. Ice gouges/Arctic River Mouths.
8. Vents, seeps, & brines, MOR flanks.

“The More We Look, The More We Find.”
Some Recent Oceanic Fixed-N Budgets (10^{12} g/yr)

Table 1. Some recent oceanic fixed-N budgets\(^1\)

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<thead>
<tr>
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<tbody>
<tr>
<td><strong>Sources</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Nitrogen Fixation</td>
<td>132±41</td>
<td>135±51</td>
<td>135+++</td>
</tr>
<tr>
<td>Riverine Inputs</td>
<td>76±14</td>
<td>80±14</td>
<td>80±14</td>
</tr>
<tr>
<td>Atmospheric Inputs</td>
<td>30±5</td>
<td>50±20</td>
<td>30??</td>
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<td>Total Sources</td>
<td>238±44</td>
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<td>(N_2O) Loss to Atmos.</td>
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<td>6+</td>
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<td>Organic N Export</td>
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<tr>
<td>Total Sinks</td>
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<td>Net Values</td>
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\(^1\)G&S = Gruber & Sarmiento (2002), G = Gruber (2004), C = Codispoti (2006 and in press) whose budget includes “+” signs to suggest the probability of increases in selected values.
Because of the uncertainty vis a vis pathways, we must put more emphasis on determination of changes in free nitrogen instead of N-star and nitrate deficits.

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Some Concluding Remarks

1. Find more nitrogen fixation.
2. Take into account changing ratios.
3. Learn more about the complexity of the sedimentary $^{15}$N signals. [effects of nitrogen fixation above, suboxic waters, & anammox for example].
4. Take a closer look at the oceanic P budget.
5. Realize that as anthropogenic impingement increases, the relative influence of orbital forcing on climate may decrease such that Holocene records may be of limited applicability in predicting the now and future ocean.
Cautionary Riddles

- If you want to make the ocean more Fe limited, add Fe in the wrong place.

- If you want to make the ocean more N limited add fixed N in the wrong place.

- If you want to increase greenhouse forcing try to decrease it by adding Fe to the ocean in the wrong place.