Anammox is one of the new and exciting areas of biogeochemical oceanography. The half reactions for the reduction of NO$_3^-$ to N$_2$ and reduction of N$_2$ to NH$_4^+$ are given below. Let's assume that anammox uses nitrate (NO$_3^-$) even though we really know that it uses nitrite (NO$_2^-$).

a) Write a balanced reaction of NO$_3^-$ plus NH$_4^+$ to produce N$_2$ and give the equilibrium constant. (10 pts)

\[
\begin{align*}
\frac{1}{5} \text{NO}_3^- + \frac{6}{5} \text{H}^+ + e^- &= \frac{1}{10} \text{N}_2(g) + \frac{3}{5} \text{H}_2\text{O} & \log K = +21.05 \\
\frac{1}{6} \text{N}_2(g) + \frac{4}{3} \text{H}^+ + e^- &= \frac{1}{3} \text{NH}_4^+ & \log K = +4.68 \\
\end{align*}
\]

multiply both half reactions by 30x, and reverse the second reaction, then add:

\[
\begin{align*}
6 \text{NO}_3^- + 36 \text{H}^+ + 30 e^- &= 3 \text{N}_2 + 18 \text{H}_2\text{O} & \log K = 631.5 \\
10 \text{NH}_4^+ &= 30 e^- + 40 \text{H}^+ + 5 \text{N}_2 & \log K = -140.4 \\
\end{align*}
\]

b) Will anammox proceed if the concentrations of NO$_3^-$ = 10$^{-6}$, NH$_4^+$ = 10$^{-6}$ and P$_{N_2}$ = 0.8 atm? Use pH = 8.0 (10 pts)

\[
Q = \frac{[\text{H}^+]^2[\text{N}_2]^4[\text{H}_2\text{O}]^6}{[\text{NO}_3^-]^5[\text{NH}_4^+]^3} = \frac{[10^{-8}]^2[0.8]^4}{[10^{-6}]^5[10^{-6}]^3} = 4.09 \times 10^{31} = 10^{31.6}
\]

\[
Q/K = 10^{31.6} / 10^{245.55} << 1 \quad \text{Therefore the reaction will proceed to the right as written. Anammox will occur!}
\]
2) **What controls atmospheric CO\textsubscript{2}**.
As water upwells ($V_{\text{mix}}$) from the deep ocean to the surface, it equilibrates with the atmosphere. Biological activity in the surface ocean affects the oceanic carbonate system and the resulting pCO\textsubscript{2} in the atmosphere. For this problem, please calculate atmospheric pCO\textsubscript{2}, deep water O\textsubscript{2}, and AOU for the following four cases:

a.) an abiotic ocean (10 pts)
b.) a productive ocean with preformed phosphate $[\text{PO}_4]^o = 0.90$ µmol / kg (10 pts)
c.) a productive ocean with no surface PO\textsubscript{4} (10 pts)
d.) a productive ocean with $[\text{PO}_4]^o = 0.90$ µmol / kg that is dominated by siliceous organisms (there are no CaCO\textsubscript{3} shells, and hence alkalinity is not affected by particle flux) (10 pts)

Information you’ll need:

$[\text{DIC}_d] = 2250$ µmol / kg

$[\text{PO}_4 \text{deep}] = 2.2$ µmol / kg

$K_H'(\text{CO}_2) = 10^{-1.5}$ mol / kg atm

$pO_2 = 0.2095$ atm

$K_2' = 10^{-9}$ mol / kg

$[\text{Alk}_d] = 2365$ µeq / kg

$V_{\text{mix}} = 300$ cm / yr (note units!)

$K_H'(\text{O}_2) = 10^{-2.77}$ mol / kg atm

$K_1' = 10^{-6}$ mol / kg

Assume 1 kg = 1 L

Assume the ocean is in steady state. What this implies is that river input is equal to permanent particle burial, so for this problem do not include rivers or sedimentation since they will cancel and have a net zero influence on the system. You’ll want to start by making a PO\textsubscript{4} balance for the surface box, and then use Redfield ratios to figure out surface DIC and alkalinity (see hints below). Assume that the pO\textsubscript{2}, the partial pressure of oxygen in the surface ocean, stays constant and in equilibrium with the atmosphere throughout all four cases.

To calculate DIC from the phosphate balance, use the composite Redfield ratio determined by Broecker and Peng, which takes into account both “soft” and “hard” parts, $\text{P:N:C:Ca} = 1:15:131:26$. Assume all the Ca in the B flux is due to CaCO\textsubscript{3}, so you can use the ratio of P:Ca:CO\textsubscript{3}:Alk to find B\textsubscript{Alk}. In part (d), since no CaCO\textsubscript{3} shells are forming, you should use the Redfield ratio, 1 P:106 C.

We highly recommend that you do your calculations in a spreadsheet after drawing your box model diagram and writing out your equations. You won’t be graded based on the equations in the spreadsheet.

Here is a basic outline and some hints so that you can stay on track!

--Figure out $B_{\text{PO}_4}$ first. The concept of “preformed” nutrients, like phosphate, is described in the Power Point Lecture (it might help to think of it as excess or unutilized nutrient).
--You can use elemental ratios (use the composite Redfield ratio determined by Broecker and Peng, which takes into account both “soft” and “hard” parts, P:N:C:Ca = 1:15:131:26) to then figure out BC and BCa. Since we assume the whole Ca flux is due to CaCO3, you can also get BAlk by using the ratio of P:Ca:CO3²⁻:Alk. Hint: each CO3²⁻ contributes two units of alkalinity!

--Do a mass balance for the surface box to figure out DICs.

--Do the same to get Alks.

--When you have DIC and Alk, you’ll need to do some algebra (what equations to use?) to get the (surface ocean) pH. Hint: consider using α values.

--When you have pH (and you already know DIC), you can figure out the pCO2 in the atmosphere. pCO2 is entirely dependent on the ocean.

--For O2: the atmospheric O2 is fixed, so you can calculate the amount of O2 in the surface ocean using KH for O2 (given).

--Calculating O2_deep can be done exactly as we did in a previous problem set using the C:O2 ratio of 106:154. sources = sinks...(we can assume all of the B flux is consumed in the deep ocean, since we are neglecting burial, and thus all of the particulate carbon flux will contribute oxygen utilization in the deep ocean).

--Once you have that, AOU should be a cinch.

Random items:
--Check your units! You will need to do conversions. Assume 1 kg = 1 L.
--The quadratic equation. If:

\[ ax^2 + bx + c = 0 \]

where a, b, and c are constants, then

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

Note that your a, b, and c might not necessarily be easy numbers, so it can help to calculate these first, and then try and solve the part you actually want. If you’re doing a spreadsheet, I recommend having columns or rows for a, b, and c.
a.) an abiotic ocean

In an abiotic ocean, there is no production, no organic matter being made or remineralized, and a negligible particle flux. There is only mixing, so concentrations will be the same everywhere since

\[ V_{mix} \times [Conc]_s = V_{mix} \times [Conc]_d. \]

Therefore:

\[ [PO_4 \_d] = [PO_4 \_s] = 2.2 \ \mu\text{mol} / \text{kg} \]
\[ [DIC\_d] = [DIC\_s] = 2250 \ \mu\text{mol} / \text{kg} \]
\[ [Alk\_d] = [Alk\_s] = 2365 \ \mu\text{eq} / \text{kg} \]

Great. So how do we figure out atmospheric pCO₂? We should be able to solve the carbonate system if we have 2 out of the following 4 variables: pCO₂, Alk, DIC, and pH. Since we have DIC and Alk, this is solvable! Use the expression for Alk:

\[ \text{Alk} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- \cdot \text{H}^+ \]

(We assume that H and OH are much smaller than the carbon species.)

\[ \text{Alk} = \text{HCO}_3^- + 2\text{CO}_3^{2-} \]

Then, the total carbon is the DIC and the fraction of one carbonate species is “\( \alpha \)”: \[ \text{Alk} = \frac{\text{DIC} \times (\text{H}^+ \ K_{i'} + 2 \ K_i \ K_{i'2})}{(\text{H}^+ \ K_{i'} + 2 \ K_i \ K_{i'2})} \]

Combine the numerators:

\[ \text{Alk} \times (\text{H}^+ \ K_{i'} + 2 \ K_i \ K_{i'2}) = \text{DIC} \times (\text{H}^+ \ K_{i'} + 2 \ K_i \ K_{i'2}) \]

Now move the denominator to the other side:

\[ \text{Alk} \times (\text{H}^+ \ K_i \ K_{i'} + 2 \ K_i \ K_{i'2}) = \text{DIC} \times (\text{H}^+ \ K_{i'} + 2 \ K_i \ K_{i'2}) \]

Subtract to set the equation equal to zero:

\[ \text{Alk} \times (\text{H}^+ \ K_{i'} + 2 \ K_i \ K_{i'2}) - \text{DIC} \times (\text{H}^+ \ K_{i'} + 2 \ K_i \ K_{i'2}) = 0 \]
\[ \text{Alk} \times (\text{H}^+ \ K_{i'} + 2 \ K_i \ K_{i'2}) - \text{DIC} \times (\text{H}^+ \ K_{i'} + 2 \ K_i \ K_{i'2}) = 0 \]

Look familiar? This is a quadratic equation, which we can solve with

\[ \text{H}^+ = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

Plugging in the numbers,

\[ \text{H}^+ = 1.43 \times 10^{-8} \text{mol} / \text{kg}; \text{the pH is then 7.8}. \]

We can now calculate atmospheric pCO₂; all we need is the concentration of carbonic acid and the Henry’s Law constant for CO₂.

\[ [\text{H}_2\text{CO}_3] = \text{DIC} \alpha_0 \]
\[ [\text{H}_2\text{CO}_3] = \text{DIC} \times (\text{H}^+)^2 / ((\text{H}^+)^2 + \text{H}^+ \ K_1 + K_1 \ K_2) \]
\[ [\text{H}_2\text{CO}_3] = 2.98 \times 10^{-5} \text{mol} / \text{kg} \]

\[ [\text{H}_2\text{CO}_3] = K_{H} \times \text{pCO}_2 \]
\[ \text{pCO}_2 = [\text{H}_2\text{CO}_3] / K_{H} \]
\[ pCO_2 = 1.01 \times 10^{-3} \text{ atm or 1008 ppm} \]

That seems really high, doesn’t it? But it makes sense; if the ocean was dead, there would be no marine biological pump removing CO\(_2\) from the air, and so atmospheric CO\(_2\) would increase (sources vs. sinks).

Finally, we need deep water O\(_2\) and AOU. This is straightforward for an abiotic ocean; if there is no life then there is no consumption of O\(_2\), and deep O\(_2\) will equal the surface value. What is the surface value? Since we know the atmospheric concentration of oxygen, we can just use Henry’s Law again. Notice I’m using the value of KH for seawater at 0°C. This is probably a bit high, but because of high nutrient utilization in part c, it provides a more realistic value for deep water oxygen for all scenarios.

\[
[O_2\text{ (aq)}] = K_H \times pO_2
\]

\[
1.69 \times 10^{-3} \text{ (mol / kg atm)} \times 0.2095 \text{ (atm)} = 3.56 \times 10^{-4} \text{ mol / kg}
\]

Since there is no biology, there is no O\(_2\) consumption. \([O_2]_a = 3.56 \times 10^{-4} \text{ mol / kg}\)

The AOU (\( [O_2\text{ (aq, sat)}] - [O_2\text{ (aq, measured)}] \)) = 0.

b.) productive ocean with preformed phosphate \([PO_4^\circ] = 0.90 \text{ µmol / kg}\)

This is in essence the same problem, but we must calculate the particle flux to get the DIC and Alk at the surface. Balance the surface phosphate:

\[
\text{sources} = \text{sinks} \\
V_{\text{mix}} \times [PO_4\text{deep}] = V_{\text{mix}} \times [PO_4\text{surf}] + B_P
\]

\[
B_P = V_{\text{mix}} \times [PO_4\text{deep}] - V_{\text{mix}} \times [PO_4\text{surf}]
\]

\[
B_P = (3 \text{ m / yr}) \times (2.2 \text{ µmol / kg} - 0.90 \text{ µmol / kg})
\]

\[
B_P = 3.9 \text{ m} \times \text{µmol} \times \text{kg}^{-1} \times \text{yr}^{-1}
\]

Funny units, huh? Well, we know that—since it’s a flux—years and moles should be in there, but the m/kg thing is annoying. Let’s fix that by relating m and kg using density.

\[
(3.9 \times \text{µmol} \times \text{kg}^{-1} \times \text{yr}^{-1}) \times (1000 \text{ kg/m}^3)
\]

\[
B_P = 3900 \text{ µmol} \times \text{yr}^{-1} \times \text{m}^{-2}
\]

“Moles per year per square meter” is just the flux relative to the surface area; it is how much particle forms and sinks for any given square meter of ocean.

Now that we have \(B_P\), we can calculate \(B_C\) and \(B_{Alk}\). To get those, we just multiply \(B_P\) by the appropriate ratio. For C, the classic Redfield ratio is 106:1, but remember, our particles aren’t just made up of “algal protoplasm”, but their shells as well. Therefore we use the “composite” value, given in the notes: it’s the sum of the soft parts and the hard parts, for a total of 131 C : 1 P. Therefore,

\[
B_C = 131 \times B_P = 51 \text{ mol} \times \text{yr}^{-1} \times \text{m}^{-2}
\]
As for BAlk, 1 P = 26 Ca → 26 CO₃ (remember, the Ca is in CaCO₃, so 1 Ca = 1 CO₃). Since CO₃ counts for 2 alkalinity, 1 P = 52 Alk.

\[ B_{\text{Alk}} = 52 \times B_P = .20 \text{ mol} \times \text{yr}^{-1} \times \text{m}^2 \]

Now we can calculate the surface values of DIC and Alk, which, as we've already seen, gives us the pH and atmospheric pCO₂.

**DIC:**

sources = sinks

\[ \text{mixing up} = \text{mixing down} + \text{B} \]

\[ V_{\text{mix}} \times [\text{DIC}_{\text{deep}}] = V_{\text{mix}} \times [\text{DIC}_{\text{surf}}] + B_C \]

\[ [\text{DIC}_{\text{surf}}] = \frac{V_{\text{mix}} \times [\text{DIC}_{\text{deep}}] - B_C}{V_{\text{mix}}} \]

\[ [\text{DIC}_{\text{surf}}] = \frac{3 \text{ m} / \text{yr} \times 2.250 \times 10^{-3} \text{ mol} / \text{kg} \times 1000 \text{ kg} / \text{m}^3 - .51 \text{ mol} \times \text{yr}^{-1} \times \text{m}^2}{3 \text{ m} / \text{yr}} \]

\[ [\text{DIC}_{\text{surf}}] = 2.08 \text{ mol} / \text{m}^3 = 2.08 \times 10^{-3} \text{ mol} / \text{kg} \]

Similarly, for Alk:

\[ [\text{Alk}_{\text{surf}}] = \frac{V_{\text{mix}} \times [\text{Alk}_{\text{deep}}] - B_{\text{Alk}}}{V_{\text{mix}}} \]

\[ [\text{Alk}_{\text{surf}}] = \frac{3 \text{ m} / \text{yr} \times 2.365 \times 10^{-3} \text{ mol} / \text{kg} \times 1000 \text{ kg} / \text{m}^3 - .20 \text{ mol} \times \text{yr}^{-1} \times \text{m}^2}{3 \text{ m} / \text{yr}} \]

\[ [\text{Alk}_{\text{surf}}] = 2.30 \text{ eq} / \text{m}^3 = 2.30 \times 10^{-3} \text{ eq} / \text{kg} \]

Now that we've got that, we use our expression relating \( H, K_1, K_2, \text{Alk}, \) and DIC, and after another bout with the quadratic equation we get the answer.

\[ [H^+] = 7.9 \times 10^{-9}; \text{pH} = 8.1 \]

Moving on to calculate \( \text{H}_2\text{CO}_3 \) and pCO₂:

\[ [\text{H}_2\text{CO}_3] = \text{DIC}_0 \]

\[ [\text{H}_2\text{CO}_3] = \text{DIC} \times (H^+)^2 / \{(H^+)^2 + H^+K_1 + K_1K_2\} \]

\[ [\text{H}_2\text{CO}_3] = 1.45 \times 10^{-5} \text{ mol} / \text{kg} \]

\[ \text{pCO}_2 = \frac{[\text{H}_2\text{CO}_3]}{K_H} = 4.90 \times 10^{-4} \text{ atm} = 490 \text{ ppm} \]

That makes more sense, doesn't it? We switched on production, running at a significant enough rate to draw down a lot of surface PO₄, and consequently atmospheric CO₂ drops!

What about \( O_2 \) in the deep? You guessed it… sources = sinks

\[ \text{mixing down} = \text{mixing up} + \text{respiration} \]

\[ V_{\text{mix}} \times [O_2_{\text{surf}}] = V_{\text{mix}} \times [O_2_{\text{deep}}] + 154 \times B_P \]

\[ [O_2_{\text{deep}}] = \frac{V_{\text{mix}} \times [O_2_{\text{surf}}] - 154 \times B_P}{V_{\text{mix}}} \]

\[ [O_2_{\text{deep}}] = \frac{3 \text{ m} / \text{yr} \times 3.54 \times 10^{-4} \text{ mol} / \text{kg} \times 1000 \text{ kg} / \text{m}^3 - 154 \times 3.9 \times 10^{-3} \text{ mol} \times \text{yr}^{-1} \times \text{m}^2}{3 \text{ m} / \text{yr}} \]

\[ [O_2_{\text{deep}}] = .156 \text{ mol} / \text{m}^3 = 1.56 \times 10^{-4} \text{ mol} / \text{kg} \]

Not surprisingly, the oxygen in the deep ocean is depleted when compared to the abiotic ocean.

Last part: AOU.

\[ \text{AOU} = [O_2_{\text{(aq, sat)}}] - [O_2_{\text{(aq, measured)}}] \]

\[ \text{AOU} = 356 \mu\text{mol} / \text{kg} - 156 \mu\text{mol} / \text{kg} = 200 \mu\text{mol} / \text{kg} \]

That’s pretty high- you would see values like that in Arabian Sea, or the N. Pacific.
c.) productive ocean with no surface PO$_4$

The calculations for this are the same as part b. The only difference is that we use a [PO$_{4\text{surf}}$] = 0.

Results summary:

- $B_P = 6.6 \times 10^{-3} \text{ mol } \times \text{ yr}^{-1} \times \text{ m}^{-2}$
- $B_C = 0.86 \text{ mol } \times \text{ yr}^{-1} \times \text{ m}^{-2}$
- $B_{Alk} = 0.34 \text{ mol } \times \text{ yr}^{-1} \times \text{ m}^{-2}$
- $[\text{DIC}_{\text{surf}}] = 1.96 \text{ mol } / \text{ m}^3 = 1.96 \times 10^{-3} \text{ mol } / \text{ kg}$
- $[\text{Alk}_{\text{surf}}] = 2.25 \text{ eq } / \text{ m}^3 = 2.25 \times 10^{-3} \text{ eq } / \text{ kg}$
- $[H^+] = 5.55 \times 10^{-6}; \text{ pH} = 8.3$
- $[\text{H}_2\text{CO}_3] = 9.19 \times 10^{-6} \text{ mol } / \text{ kg}$
- $\text{pCO}_2 = 3.11 \times 10^{-4} \text{ atm} = 311 \text{ ppm}$

As you might expect, PO$_4$ is zero in surface because of intense production and lots of particle export; therefore the biological pump is running like mad, and atmospheric pCO$_2$ is really low.

- $[O_2_{\text{deep}}] = 0.017 \text{ mol } / \text{ m}^3 = 17 \mu\text{mol} / \text{ kg}$
- $\text{AOU} = 339 \mu\text{mol} / \text{ kg}$

This sort of AOU is very high, and not commonly found in the oceans. This tells us that the sort of particle flux we calculated is not very widespread.

d.) a productive ocean with [PO$_4$]$^\circ = 0.90 \mu\text{mol} / \text{ kg}$ that is dominated by siliceous organisms

We can start by using some of the same values that we calculated in part b.

- $B_P = 3.9 \times 10^{-3} \text{ mol } \times \text{ yr}^{-1} \times \text{ m}^{-2}$

However, $B_C$ might not be exactly the same. Before, we used a ratio of 131 C : 1 P. This was because we counted “hard parts”, i.e. CaCO$_3$, as part of the flux. Now, we just have “soft” carbon, so the ratio is 106 C : 1 P.

- $B_C = 0.41 \text{ mol } \times \text{ yr}^{-1} \times \text{ m}^{-2}$

However, $B_{Alk}$ must equal 0, since nobody is making CaCO$_3$ shells.

Let’s see… does this change $[\text{DIC}_{\text{surf}}]$?

$[\text{DIC}_{\text{surf}}] = \{ V_{\text{mix}} \times [\text{DIC}_{\text{deep}}] - B_C \} / V_{\text{mix}}$

$B_C$ has changed, so we have to redo this calculation.

$[\text{DIC}_{\text{surf}}] = 2.11 \times 10^{-3} \text{ mol } / \text{ kg}$

Surface alkalinity will return to the case a, abiotic ocean state.

- $[\text{Alk}_{\text{surf}}] = \{ V_{\text{mix}} \times [\text{Alk}_{\text{deep}}] - B_{Alk} \} / V_{\text{mix}}$
- $[\text{Alk}_{\text{surf}}] = \{ V_{\text{mix}} \times [\text{Alk}_{\text{deep}}] \} / V_{\text{mix}}$
- $[\text{Alk}_{\text{surf}}] = [\text{Alk}_{\text{deep}}]$
- $[\text{Alk}_{\text{surf}}] = 2.365 \times 10^{-3} \text{ eq } / \text{ kg}$

This, in turn, will affect the quadratic equation we used to get $[H^+]$:

- $[H^+] = 6.91 \times 10^{-6}; \text{ pH} = 8.2$

$[\text{H}_2\text{CO}_3] = \text{DIC}_{0} = \text{DIC} \times (H^+)^2 / ((H^+)^2 + H^+K_1 + K_1K_2)$

$[\text{H}_2\text{CO}_3] = 1.27 \times 10^{-5} \text{ mol } / \text{ kg}$
\[ pCO_2 = 4.29 \times 10^{-4} \text{ atm} = 429 \text{ ppm} \]

You’d think, without CaCO₃ shells being made and exported to the deep, that atmospheric CO₂ would be higher. What we’re seeing is a pH effect: because of the way the Alk and DIC balance worked out, the surface ocean pH is slightly higher. Why? When you make carbonate shells, you use up CO₃²⁻, which is then replaced by the bicarbonate and carbonic acid shifting over to take up the slack. Remember the carbonate system:

\[
H_2CO_3 = HCO_3^- + H^+ = CO_3^{2-} + 2H^+
\]

Thus the consumption of CO₃²⁻ in making shells produces acidity (2H⁺) as the system re-equilibrates! Without carbonate consumption, we have a higher pH. (We’d also have had a rather different intellectual history-- no carbonate shell formation means no chalk; no chalkboards, no easy way to practice writing and math, no hopscotch…) A higher pH means less H₂CO₃, which means less atmospheric CO₂.

This scenario is what may happen is ocean acidification ends up killing all carbonate producing organisms. It would have the effect as a positive feedback on atmospheric CO₂.

Moving on to O₂… would anything be different? Mixing is still the same, of course, and we’re respiring only “soft” organic material, which doesn’t change. The decay and decomposition of CaCO₃ shells presumably never consumes or produces oxygen. From part b:

\[
[O_2 \text{ deep}] = 156 \mu\text{mol} / \text{kg} \\
\text{AOU} = 200 \mu\text{mol} / \text{kg}
\]