

1.1)

| Process: | DIC | pCO ₂ | ¹³ DIC |
|--------------------------|---|---|---|
| Physical: warming | no direct affect (occurs through gas ex, see below) | Warming increases pCO ₂ (thermal solubility) | No direct affect |
| Physical: mixing (vert.) | Increases | Increases | decreases |
| Physical: lateral adv. | Can't say based on data | | |
| Physical: gas ex. | Increases | Increases | No data on ¹³ CO _{2(atm)} |
| Biological: | Reduces in summer | Reduces in summer | Increases in summer |

1.2) DIC varies between 1977 and 1964 $\mu\text{mol/kg}$ between the winter and summer, for a seasonal drawdown of 13 $\mu\text{mol/kg}$. This is the total affect of all the process described above, but is primarily a biological effect.

$$\frac{13 \mu\text{mol/kg}}{1970 \mu\text{mol/kg}} = 0.66\%$$

With the given Revelle factor of 10, we know that pCO₂ must therefore be changed by biology by:

$$R \equiv \frac{\Delta 10\% \text{pCO}_2}{\Delta 1\% \text{DIC}}$$

$$0.66\% * 10 = 6.6\% \text{ drop in pCO}_2$$

$$6.6\% * 340 \mu\text{atm} = -22.4 \mu\text{atm drop in pCO}_2$$

The seasonal change in T is responsible for additional changes in the pCO₂. The ΔT is about +3 deg. C from winter to summer.

$$\Delta \text{pCO}_2 = (\text{pCO}_2) * \Delta T * \left(\frac{4\%}{K} \right)$$

$$\Delta \text{pCO}_2 = (340 \mu\text{atm})(3K) \left(\frac{0.04}{K} \right) = +41 \mu\text{atm}$$

So, just the temperature increase would increase pCO₂ by 41 μatm . Since pCO₂ actually increases by about 20 μatm from the winter to the summer, we can see that thermal solubility dominates over the biological drawdown.

Alternatively, the ¹³DIC can be used to get a handle on the biological fractionation. We can assume that the surface water is essentially a closed system and use Rayleigh fractionation where $\delta_{s,0} = {}^{13}\text{DIC initial} = 0$ and $\epsilon = 23\%$.

$$\delta_{\text{substrate}} = \delta_{s,0} - \epsilon * \ln \left(\frac{\text{substrate remaining}}{\text{initial substrate}} \right)$$

If we use the summer and winter values of DIC to calculate f, or the [DIC]₀, we can then calculate the amount of draw down only due to seasonal biological uptake.

$$\delta_{\text{DIC}} = \delta_{\text{DIC},o} - (23\text{‰}) * \ln\left(\frac{[\text{DIC}]}{[\text{DIC}]_o}\right)$$

$$1.43\text{‰} = 0\text{‰} - 23\text{‰} * \ln\left(\frac{1964 \mu\text{mol}/\text{kg}}{[\text{DIC}]_o}\right)$$

$$-0.0622 = \ln\left(\frac{1964 \mu\text{mol}/\text{kg}}{[\text{DIC}]_o}\right)$$

$$0.940 = \frac{1964 \mu\text{mol}/\text{kg}}{[\text{DIC}]_o}$$

$$[\text{DIC}]_o = 2090 \mu\text{mol}/\text{kg}$$

So, about 125 $\mu\text{mol}/\text{kg}$ of the DIC drawdown is due to biology, which equals a change of about 6%, so pCO_2 would change by 60%. This is a lot more than we observe because this is the total biological drawdown – we need to also compare it with the winter drawdown (which we think of as small, but is present).

$$\delta_{\text{DIC}} = \delta_{\text{DIC},o} - (23\text{‰}) * \ln\left(\frac{[\text{DIC}]}{[\text{DIC}]_o}\right)$$

$$1.35\text{‰} = 0\text{‰} - 23\text{‰} * \ln\left(\frac{1977 \mu\text{mol}/\text{kg}}{[\text{DIC}]_o}\right)$$

$$-0.0587 = \ln\left(\frac{1977 \mu\text{mol}/\text{kg}}{[\text{DIC}]_o}\right)$$

$$0.943 = \frac{1977 \mu\text{mol}/\text{kg}}{[\text{DIC}]_o}$$

$$[\text{DIC}]_o = 2096 \mu\text{mol}/\text{kg}$$

You can see that our two values for $[\text{DIC}]_o$ come out very close. In the winter the drawdown is about 119 $\mu\text{mol}/\text{kg}$. Therefore the seasonal drawdown in DIC is equal to about 6 $\mu\text{mol}/\text{kg}$. From here we proceed as above, using the Revelle factor, to get a seasonal drawdown in pCO_2 of:

$$\Delta \text{DIC} = \frac{\text{DIC change}}{\text{average DIC}} = \frac{6 \frac{\mu\text{mol}}{\text{kg}}}{2030 \frac{\mu\text{mol}}{\text{kg}}} = 0.30\%$$

$$R \equiv \frac{\Delta 10\% \text{pCO}_2}{\Delta 1\% \text{DIC}}$$

$$0.30\% * 10 = 3.0\% \text{ drop in pCO}_2$$

$$3.0\% * 340 \mu\text{atm} = -10.2 \mu\text{atm drop in pCO}_2$$

Although the number is slightly different from that calculated above the effect is the same, and thermal solubility of CO₂ clearly dominates the system.

1.3) For this part of the question we are using what we know about the radiotracers ²²²Rn and ²²⁶Ra to get a handle on the piston velocity at this time and location, then we can use the piston velocity to estimate gas exchange for CO₂. ²²⁶Ra is conservative in seawater (it is quite soluble) and decays to ²²²Rn, which is a gas, and therefore undergoes gas exchange. The difference between the activity of ²²⁶Ra and ²²²Rn is therefore equal the amount of ²²²Rn that has already been removed to the atmosphere, if we assume that the activity of ²²²Rn is not changing with time (steady state).

$$\frac{d^{222}\text{Rn}}{dt} = {}^{226}\text{A}_{\text{Ra}} - {}^{226}\text{A}_{\text{Rn}} - \left(\frac{k_{\text{gas ex.}}}{Z_{\text{mixed layer}}} \right) [^{222}\text{Rn}]$$

Luckily, we were given the Rn piston velocity ($k_{\text{gas ex}}$) as 3.4 m/d, knowing this and the Schmidt numbers for both Rn and CO₂ we can calculate k for CO₂, then use it to calculate the gas exchange of CO₂.

$$k_{\text{CO}_2} = k_{\text{Rn}} \left(\frac{Sc_{\text{CO}_2}}{Sc_{\text{Rn}}} \right)^{-0.67}$$

$$k_{\text{CO}_2} = \left(3.4 \text{ m/d} \right) \left(\frac{660}{2000} \right)^{-0.67} = 7.15 \text{ m/d}$$

If you used an n of 0.5 the answer would be 5.9 m/d. Both answers are fine.

The ΔCO_2 varies considerably between winter and summer. I can see three reasonable values to use, the summer, winter and average values. Converting between μatm and $\mu\text{mol/kg}$ is accomplished with the bunsen solubility coefficient or Henry's law constant:

$$\ln K_{\text{H}} = -3.56 \text{ (at 25 deg. C)}$$

$$K_{\text{H}} = 0.028 \frac{\mu\text{mol}}{\mu\text{atm kg}}$$

$$\Delta[\text{CO}_2] = \Delta\text{pCO}_2 * 0.028 \frac{\mu\text{mol}}{\mu\text{atm kg}}$$

To calculate the gas exchange we use the following equation:

$$F_{\text{gas ex.}} \left(\frac{\text{mol}}{\text{m}^2 \cdot \text{y}} \right) = k \Delta [\text{CO}_2] \left(\frac{1025 \text{ kg}}{\text{m}^3} \right) \left(\frac{365 \text{ d}}{\text{year}} \right) \left(\frac{1 \text{ mol}}{10^6 \mu\text{mol}} \right)$$

| | Summer | Winter | Average |
|--|--------|--------|---------|
| $\Delta p\text{CO}_2$ (μatm) | 3 | 30 | 15 |
| $\Delta[\text{CO}_2]$ ($\mu\text{mol}/\text{kg}$) | 0.08 | 0.8 | 0.4 |
| $F_{\text{gas ex.}}$ ($\text{mol m}^{-2} \text{y}^{-1}$) | 0.214 | 2.14 | 1.07 |

1.4) To calculate the Net Community Production in this part we need to consider seasonal DIC drawdown and the effect of gas exchange – we are ignoring lateral and vertical mixing for the moment. If the seasonal DIC draw down is $13 \mu\text{mol}/\text{kg}$, and gas exchange supplies:

$$\left(\frac{1.07 \text{ mol CO}_2}{\text{m}^2 \text{y}} \right) \times \left(\frac{1}{75 \text{ m}} \right) \times \left(\frac{10^6 \mu\text{mol}}{\text{mol}} \right) \times \left(\frac{1 \text{ m}^3}{1025 \text{ kg}} \right) \times \left(\frac{\text{year}}{2} \right) = 7 \mu\text{mol}/\text{kg}$$

Remember, DIC is equal to the sum of CO_2 , HCO_3^- and CO_3^{2-} , so a $7 \mu\text{mol}/\text{kg}$ seasonal increase in CO_2 is equal to a $7 \mu\text{mol}/\text{kg}$ seasonal increase in DIC. Biological uptake must therefore include both the drawdown and the DIC supplied by gas exchange:

$$\text{biological rate} = \left(13 \mu\text{mol}/\text{kg} + 7 \mu\text{mol}/\text{kg} \right) \times \left(\frac{1}{0.5 \text{ year}} \right) = 40 \mu\text{mol}/\text{kg} \cdot \text{y}$$

1.5) We could use our knowledge of the $\delta^{13}\text{C}$ DIC to improve our estimates because we know the biological fractionation (23‰) and we are given the initial DIC $\delta^{13}\text{C}$. If there are no lateral gradients in ^{13}C DIC, then we can assume that biological uptake is the same over the entire transect. The lateral gradients in DIC then must be due to lateral advection of DIC-rich water. Using kinetic isotope fractionation along with our knowledge of the system, allows us to separate these two variables.

2.a) We are back to our old friend ‘Production = Loss’, for this system:

$$\frac{d^{234}\text{Th}}{dt} = 0 = H * {}^{238}\text{A}_U - H * {}^{234}\text{A}_{Th} - H * k_{\text{scav.}} [{}^{222}\text{Th}]$$

$$H * {}^{238}\text{A}_U = H * {}^{234}\text{A}_{Th} + H * k_{\text{scav.}} [{}^{234}\text{Th}]$$

$$H * {}^{238}\text{A}_U * \lambda_{234} = H * {}^{234}\text{A}_{Th} * \lambda_{234} + H * k_{\text{scav.}} * {}^{234}\text{A}_{Th}$$

$$k_{\text{scav.}} = \lambda_{234} * \frac{{}^{238}\text{A}_U - {}^{234}\text{A}_{Th}}{{}^{234}\text{A}_{Th}}$$

$$k_{\text{scav.}} = 0.029 \text{ d}^{-1} * \left(\frac{2480 - 1800}{1800} \right) = 0.011 \text{ d}^{-1}$$

$$\tau_{\text{export}} = \frac{1}{k_{\text{scav.}}} = \frac{1}{0.011 \text{ d}^{-1}} \approx 91 \text{ days}$$

b) If we know the ratio of C to Th in the trap we can then calculate the carbon export flux. There are two ways to do this

$$F_{Th\ scav.} = H * k_{scav.} * {}^{234}A_{Th}$$

$$F_{Th\ scav.} = 100\ m * 0.011\ d^{-1} * 1800\ \frac{dpm}{m^3} = 1980\ \frac{dpm}{m^2 \cdot d}$$

or...

$$F_{Th\ scav.} = H * \lambda_{234} * ({}^{238}A_U - {}^{234}A_{Th})$$

$$F_{Th\ scav.} = 100\ m * 0.029\ d^{-1} * \left(2480\ \frac{dpm}{m^3} - 1800\ \frac{dpm}{m^3} \right) = 1972\ \frac{dpm}{m^2 \cdot d}$$

Now we can use the ratio of C_{org} to ${}^{234}Th$ to calculate the amount of C_{org} export:

$$F_{Th\ scav.} = 1980\ \frac{dpm}{m^2 \cdot d}$$

$$C_{org} = \left(4\ \frac{\mu mol\ C}{dpm} \right) {}^{234}Th = \left(4\ \frac{\mu mol\ C}{dpm} \right) * 1980\ \frac{dpm}{m^2 \cdot d}$$

$$C_{org} = 7.92\ \frac{mmol\ C}{m^2 \cdot d}$$

c) If we compare this calculate C export to the incubation experiments described we can see that:

$$0.3\ \frac{mmol\ N}{m^2 \cdot d} * \left(\frac{106\ C_{org}}{16\ NO_3^-} \right) = 1.99\ \frac{mmol\ C}{m^2 \cdot d}$$

Which is about 1/4 of the export flux that we calculated. Since export flux should equal new production, and the nitrate incubations should measure new production these results are not consistent. There are a variety of reasons for this disconnect. First, bottle incubations can be problematic – even if the metal issues have been carefully dealt with, scooping up a few liters of water and putting it in a container inevitably perturbs the system. Also, bottle incubations can only measure a short window of time and space, and primary production has been proven to be very episodic. Therefore, the trap, which integrates temporally and spatially, may be catching production events that the bottle is missing. And a huge amount of new production can be fueled by N_2 fixation if diazotrophs are present and there is enough P and Fe, this new production would not be measured by ${}^{15}N$ - NO_3^- incubations. These are probably the most important reasons for the disconnect between the trap and incubation.

3.a) This question is basically asking you to calculate the concentration of cells in the surface water. This can be accomplished knowing that the vertical flux is equal to the concentration of particles multiplied by the sinking rate:

$$\text{Flux (g m}^{-2}\text{y}^{-1}) = [\text{cells}] (\text{g m}^{-3}) * \text{sinking rate (m y}^{-1})$$

Since we know that we collected 91.25 g of material in our trap in one year, which has an aperture of $0.5\ m^2$, and assuming no trap artifacts (swimmers, etc.):

$$\text{Flux} = \frac{91.25\ \frac{g}{y}}{0.5\ m^2} = 182.5\ \frac{g}{m^2 \cdot y}$$

We can then calculate the sinking rate of the particles using the given Stoke's Law, given densities and a cell radius of 2 μm :

$$\omega = \sqrt{\frac{16rg(\rho_s - \rho_w)}{3 * \rho_w}}$$

$$\omega = \sqrt{\frac{16 * 2 \times 10^{-6} \text{m} * 9.81 \text{m/s}^2 (2 \text{g/cm}^3 - 1 \text{g/cm}^3)}{3 \text{g/cm}^3}}$$

$$\omega = 0.0102 \text{m/s} \left(31536000 \frac{\text{s}}{\text{y}} \right) = 323000 \text{m/y}$$

And now we can calculate the concentration of particles in the euphotic zone:

$$\text{Flux} = [\text{cells}] * \omega$$

$$[\text{cells}] = \frac{\text{Flux}}{\omega}$$

$$[\text{cells}] = \frac{182.5 \frac{\text{g}}{\text{m}^2 \cdot \text{y}}}{323000 \text{m/y}} = 5.65 \times 10^{-4} \frac{\text{g}}{\text{m}^3}$$

Therefore, in 1 m^3 of seawater there would be 5.65×10^{-4} g of material.

b) To calculate the number of cells we need to use the density and volume of the cells:

$$\text{Mass}_{\text{cell}} = \frac{4}{3} \pi \cdot r^3 \cdot \rho_{\text{cell}}$$

$$\text{Mass}_{\text{cell}} = \frac{4}{3} \pi \cdot (2 \times 10^{-4} \text{cm})^3 \cdot 2 \frac{\text{g}}{\text{cm}^3}$$

$$\text{Mass}_{\text{cell}} = 6.7 \times 10^{-11} \text{g}$$

Therefore, in 1 m^3 of seawater there are ~8430000 cells.

c) Now, assume that we collected the same amount of material, so the total flux is the same ($182.5 \text{g/m}^2\text{y}$), but that 95% of the particles have aggregated to colonies with an $r = 50 \mu\text{m}$. Remember, we only know what is in the trap – so 95% of the trapped particles have a radius of 50 μm . We can't solve this problem assuming that 95% of the concentration in the euphotic zone aggregated, because then we would have three unknowns: total concentration in euphotic zone, vert flux of colonies and cells.

To start, the sinking rate of colonies changes:

$$\omega = \sqrt{\frac{16rg(\rho_s - \rho_w)}{3 * \rho_w}}$$

$$\omega = \sqrt{\frac{16 * 50 \times 10^{-6} \text{ m} * 9.81 \text{ m/s}^2 (2 \text{ g/cm}^3 - 1 \text{ g/cm}^3)}{3 \text{ g/cm}^3}}$$

$$\omega = 0.0511 \text{ m/s} \left(31536000 \text{ s/y} \right) = 1610000 \text{ m/y}$$

And so the particle concentration is also changed:

$$[\text{particles}] = [\text{cells}] + [\text{colonies}] = \frac{0.95 * \text{Flux}}{\omega_{\text{colonies}}} + \frac{0.05 * \text{Flux}}{\omega_{\text{cells}}}$$

$$[\text{particles}] = \frac{0.95 * 182.5 \text{ g/m}^2 \cdot \text{y}}{1610000 \text{ m/y}} + \frac{0.05 * 182.5 \text{ g/m}^2 \cdot \text{y}}{323000 \text{ m/y}} = 1.36 \times 10^{-4} \text{ g/m}^3$$

Which is equal to a decrease of $(5.65 - 1.36 \times 10^{-4} \text{ g m}^{-3} \Rightarrow) 4.29 \times 10^{-4} \text{ g m}^{-3}$.

d) The number of cells and colonies in 1 m^3 of water thus changes as follows:

$$\text{Mass}_{\text{colony}} = \frac{4}{3} \pi \cdot r^3 \cdot \rho_{\text{cell}}$$

$$\text{Mass}_{\text{colony}} = \frac{4}{3} \pi \cdot (50 \times 10^{-4} \text{ cm})^3 \cdot 2 \text{ g/cm}^3$$

$$\text{Mass}_{\text{colony}} = 1.05 \times 10^{-6} \text{ g}$$

$$[\text{particles}] = \frac{0.95 * 182.5 \text{ g/m}^2 \cdot \text{y}}{1610000 \text{ m/y} * 1.05 \times 10^{-6} \text{ g/colony}} + \frac{0.05 * 182.5 \text{ g/m}^2 \cdot \text{y}}{323000 \text{ m/y} * 6.7 \times 10^{-11} \text{ g/cells}}$$

$$[\text{particles}] = 103 \text{ colonies/m}^3 + 422000 \text{ cells/m}^3 \approx 422000 \text{ particles/m}^3$$

By aggregating into colonies, the particle concentration in the euphotic zone has decreased by 95%.