OCN400-Problem Set #5 **Jim Murray**
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1. Box Models: Atmospheric CO_2 and the Biological Pump
As water upwells from the deep ocean to the surface water, it equilibrates with the atmosphere. Biological activity in the surface ocean effects the oceanic carbonate system and the resulting P_{CO2} in the atmosphere.

Calculate atmospheric P_{CO2}, deep water O_2 and AOU for the following four cases.

a) an abiogenic ocean
b) a productive ocean with preformed phosphate $[PO_4]°$ = 0.90 μmol kg^{-1}.
c) a productive ocean with no surface PO_4.
d) a productive ocean with preformed phosphate $[PO_4]°$ = 0.90 μmol kg^{-1} if all biological production is in the form of siliceous organisms (e.g. no $CaCO_3$ shells or alkalinity change)

Useful info:

DIC_d = 2250 μmol kg^{-1}	Alk_d = 2365 μeq kg^{-1}
K_1' = $10^{-6.0}$	K_2' = $10^{-9.1}$
K_H' (CO_2) = $10^{-1.53}$ mol kg^{-1} atm^{-1}	V_{mix} = 300 cm y^{-1}
PO_{4deep} = 2.2 μmol kg-1	P_{O2} = 0.2095 atm

(hints: First set up a PO_4 balance for the surface. Use the RKR ratios to calculate the surface DIC and Alk. Calculate the alkalinity flux based on the Ca/P ratio in the lecture notes. Calculate P_{CO2} from DIC and Alk using the equations in the OCN421 notes. Derive or find the equation to calculate P_{CO2} from DIC and Alk and then do these calculations in an Excel spreadsheet.)

2. Box Models: ^{234}Th as a Tracer for Particulate Export Flux
The surface ocean almost invariably shows a radioactive disequilibrium of ^{234}Th from ^{238}U due to the export of particulate material from the surface ocean to which ^{234}Th is adsorbed. This is one approach for estimating the flux of carbon from the euphotic zone.

Consider the 2-box model: By knowing the activity of ^{238}U, we know the source of ^{234}Th into the surface box. By knowing the activity of ^{234}Th, we know the particulate flux out of the surface box for a steady state ocean.

a) If the total activity of ^{234}Th in the surface box is 1.8 dpm l^{-1} and ^{238}U is 2.4 dpm l^{-1}, what is the magnitude of the export flux of ^{234}Th (in moles m^{-2} y^{-1}). The decay constant for ^{234}Th is $\lambda = 0.0288$ d^{-1}.

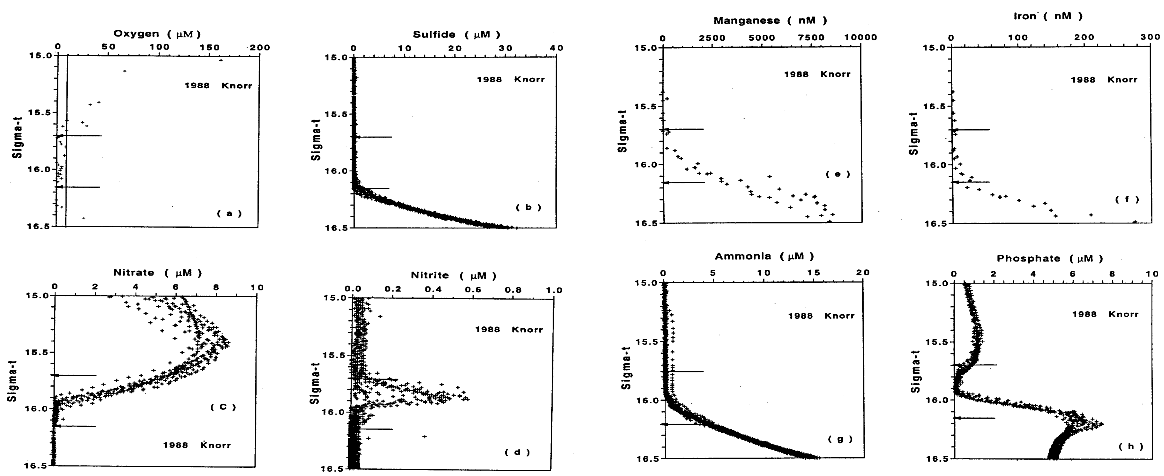
b) How does this flux compare with the flux due to mixing? Is vertical mixing important for ^{234}Th cycling?

c) If the global average sinking material has an average value of 0.20 dpm ^{234}Th per μmol organic carbon, what is global new production?

d) How does this value compare with global values of primary production given in Lecture? Calculate the global average ratio of export flux to primary production. Is this a reasonable value? Explain.

3. Oxidation-Reduction reactions

The Black Sea is the world's largest permanently anoxic water body. It is a semi-enclosed marginal sea with a physical and chemical structure that is determined by its hydrological balance. Seawater flows in through the Bosporus to the deep layer of the basin. Freshwater inflow from European rivers keeps the salinity low in the surface layer. As a result the water column is strongly stratified with respect to density. A consequence is that the surface layer (about 0 to 50m) is well oxygenated while the deep layer (100m to 2000m) has no oxygen and high sulfide concentration. At the boundary between the oxic surface and anoxic deep layers there is a suboxic zone (from approximately 50m to 100m depth) where O_2 and HS^- are essentially both absent. The distributions of nutrients (e.g. NO_3^-, NH_4^+ , PO_4) and metals (e.g. Mn, Fe) and the absence of O_2 and HS^- suggest the occurrence of unique or unusual metabolic processes within the suboxic zone (e.g., anaerobic Mn(II), Fe(II), NH_4^+, HS^-, and S(0) oxidation and the possibility for unusual photosynthetic reactions).



Thor has proposed that nitrate reacts with ammonia to produce N_2 (g). Using the half-reactions in Table 15-1 of the Chapter 15 notes do the following:

a) Write a balanced reaction for NO_3 + NH_4^+ to produce N_2 (g)

b) What is the equilibrium constant for this reaction?

c) How much free energy would be available from this reaction given the following concentrations at the point of reaction at $\sigma_t = 15.90$?

N_2 (g) = 0.80 atm
pH = 7.5
NO_3^- = 0.1 µM
NH_4^+ = 0.1 µM