12.741 Marine Bioinorganic Chemistry

Problem Set 2

Exercise #1: Examining the influence of parameters on profile structure

This problem set allows you to experiment with a modified version of Johnson et al.'s 1996 and 1997 Mn and Fe models at three locations in the North Pacific. Place file Hybrid_12741.m and supporting oxygen data files into the "work" subdirectory in your Matlab directory (c:/Matlab/R2007b/work, or whatever the exact path is, you can also create your own path, write me if you have problems here). Start Matlab you will see and ">>" command prompt. Type Hybrid_12741 and hit enter to run the model in its current format. Under the file tab use "open" to open Hybrid_12741.m script within Matlab's editor. Notice that near the top of the script there is a section entitled "Set Metal Constants and Boundary conditions". These are the constants that you will be modifying in this problem set. Whenever you make changes, save the file before running it (control-S or save under the file tab), then return to the >> command line and retype Hybrid_12741 to run the new version. Stations 5 and 9 are from the equatorial pacific, station T5 is a Vertex station with a broad low oxygen region (see figure 2 for O2 distributions for each station). The 10 lines shown in each figure are representative of F100 flux values between 1 and 10 (low to high export fluxes). (Note that this model simplifies the oxygen effect on scavenging replacing the O_2 and pH dependent kinetic term in Johnson et al., 1996 with a simpler Michaelis- Menten O_2 expression). I have purposefully not included oxygen values in the table below so that you can play with these. Below are vertical profiles for these elements at the two Equatorial Pacific stations near Hawaii (from Saito et al., unpublished).

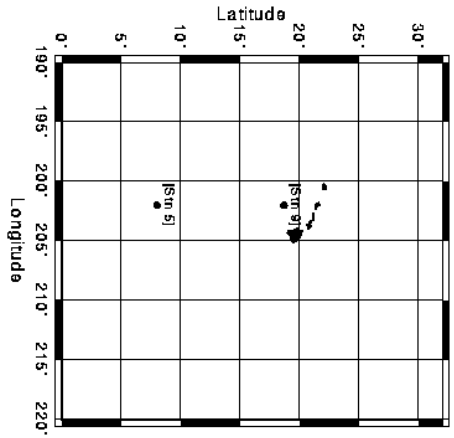
The parameters below can be used to reproduce the vertical structure for Co, Mn and Fe. Enter these values and examine how the profiles change. Then play around with modifying the specific parameters to answer the questions below.

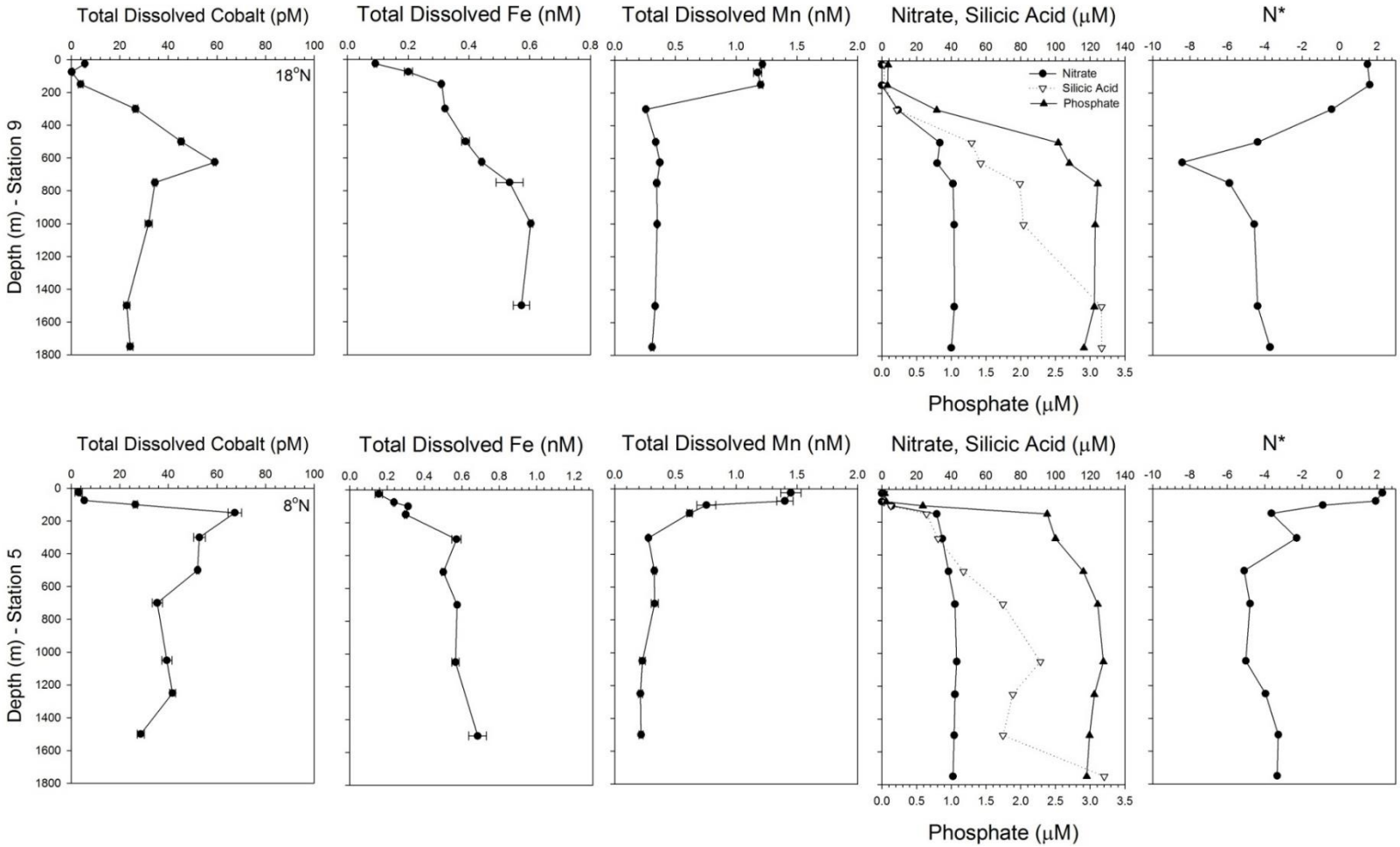
Questions: answer in a paragraph each, with sketches if useful:

1. Describe what effect increasing the Metal-carbon ratio has on vertical structure? Why do different elements have different M:C ratios? Looking at Sunda and Huntsman's papers, how great is the variability in M:C ratios for different phytoplankton for Fe and Co? (see their two 1995 papers)?
2. What effect does changing the ligand concentration have? There is recent speculation that there may be Mn(III) ligands, what is the effect of going from zero Mn ligands to some non-zero value?
3. Varying the oxygen parameter can you create a secondary maximum of Mn? What is causing this to be created in this model? Make the O_2 Figure 2 the same size as Figure 1 to allow comparison of depths.

Table 2. Parameters for Hybrid Type Metal Model (*data from Sunda and Huntsman 1995)

Parameter	Units	Co	Mn	Fe
Metal-Carbon Ratio in POC	(μM:M)	0.3(*)	44	5
Ligand Concentration	(nM)	0.025	0.3	0.6
Scavenging rate constant	(yr^{-1})	0.052	2	.005
O_2 Half Saturation Constant	(μM)	tbd	tbd	0
Initial Condition	(nM)	0.01	0.4	0.05
Lower Boundary Concentration	(nM)	0.06	0.3	0.6


Latitude
0°
5°
10°
15°
20°
25°
30°
190°
195°
200°
205°
210°
215°
220°
Longitude
[Stn 5]
[Stn 9]


Total Dissolved Cobalt (pM)
Total Dissolved Fe (nM)
Total Dissolved Mn (nM)
Nitrate, Silicic Acid (μM)
N*
18°N
Depth (m) - Station 9
Nitrate
Silicic Acid
Phosphate
Phosphate (μM)
8°N
Depth (m) - Station 5

Exercise #2: Calculate Monod parameters

Download the m-files: ps_monod.m, monod.m, dfdp.m, and nlleasqr.m from the class website. The first two are custom files written to solve for the Km and umax paramters in the Monod (or Michaelis-Menten) equation. The last two files are needed for a non-linear fit solver. Open ps_monod.m in the editor as you did in the previous problem, this version was written to calculate values for *Phaeocystis antarctica* (Saito and Goepfert 2008), and can be run with the test data by typing ps_monod.m at the >> prompt. You can calculate the Km and umax values for new datasets by replacing the data within the Zndata=[ ] and Codata= [ ] sections of the ps_monod.m file. Using Table 1 from Sunda and Huntsman 1995 (pasted below), calculate the Km and umax for *Thalassiosira oceanica* and *Thalassiosira pseudonana* for Co and Zn, *when each other metal is at its lowest concentration* (the edges of the 3D plot). Also calculate Km and umax for *Synechococcus bacillaris* for Co (there is no Zn data) and make a table of the results and take screenshots of the plots. For reference the radii of *Synechococcus* is 0.6, and those for *Thalassiosira* are in the notes. What are the major differences in the two parameters across the 3 species/strains? Why might these differences exist? Which species will do best when Zn is lowest? When Co is lowest (and no Zn)?

Table 1. Effect of variations in $[Zn^{2+}]$ and $[Co^{2+}]$ on cellular Zn : C and Co : C ratios (μmol mol C^{-1}), Chl *a* (mmol mol C^{-1}), mean cell volume (μm^3), specific growth rate (μ, d^{-1}), steady state cellular Zn and Co uptake rates [V_{Zn} and V_{Co}, μmol (mol C)$^{-1}$ d^{-1}], and ratios of cellular uptake rate to the maximum diffusion rate (V/ρ).

Exp.	log $[Zn^{2+}]$	log $[Co^{2+}]$	Zn : C	Co : C	Chl *a*	Cell vol.	μ	V_{Zn}	V/ρ^*	V_{Co}	V/ρ^*
					Emiliania huxleyi						
129a	−12.85	−13.6	0.83		0.052	42.7	0.15	†			
	−12.57	−13.6	1.67		0.098	33.6	0.31	0.52	0.49		
	−12.25	−13.6	2.98		0.100	29.8	0.56	1.66	0.70		
	−11.84	−13.6	4.81		0.193	29.0	0.73	3.50	0.56		
	−11.36	−13.6	12.0		0.196	29.2	0.87	10.5	0.56		
129b	−12.85	−11.03	0.33		0.192	21.7	1.10	0.368	0.50		
	−12.57	−11.03	0.54		0.211	20.4	1.16	0.629	0.43		
	−12.25	−11.03	1.43		0.198	21.2	1.13	1.62	0.55		
	−11.85	−11.03	3.62		0.200	19.6	1.17	4.23	0.53		
	−11.36	−11.03	9.12		0.207	19.9	1.17	10.7	0.44		
133	−13.0	−12.00		1.61	0.117	27.6	0.82			1.33	
	−12.85	−12.00	0.55	1.42	0.150	26.7	0.83	0.462	0.71	1.18	0.28
	−12.40	−12.00	1.35	1.44	0.179	23.7	0.92	1.25	0.63	1.33	0.29
	−11.95	−12.00	3.37	1.02	0.189	22.2	1.01	3.38	0.59	1.02	0.21
	−11.50	−12.00	8.43	0.97	0.238	21.8	1.03	8.70	0.53	0.999	0.20
	−10.98	−12.00	12.5	0.64	0.217	23.3	1.02	20.8	0.40	0.650	0.139
	−10.51	−12.00	38.4	0.38	0.182	24.4	0.98	37.2	0.25	0.363	0.082
	−9.99	−12.00	62.5	0.151	0.154	30.6	0.94	59.0	0.14	0.143	0.037
	−9.51	−12.00	73.7	0.062	0.176	37.2	0.85	63.0	0.056	0.0528	0.0154
	−9.99	−10.00	37.5	3.64	0.179	23.4	1.03	38.6	0.074	3.75	0.0080
167	−9.20	−12.00	100	0.0412	0.286	29.6	0.92	91.7	0.034	0.0378	0.0094
	−8.70	−12.00	217	0.0151	0.256	46.2	0.49	105.9	0.0167	0.00735	0.0025
	−8.20	−12.00	279	0.0100	0.207	86.8	0.06	†		†	
	−10.70	−11.03	19.4	2.22	0.208	22.1	1.07	20.7	0.20	2.37	0.052
	−9.20	−11.03	77.8	0.173	0.264	22.8	1.02	78.2	0.024	0.176	0.0040
	−8.70	−11.03	185	0.0600	0.227	33.3	0.91	168.0	0.021	0.0546	0.00158
	−8.20	−11.03	243	0.0190	0.178	79.0	0.33	79.8	0.0057	0.00621	0.00032
132a	−13.0	−13.6					0				
	−13.0	−12.86		0.722	0.066	35.4	0.10			†	
	−13.0	−12.49		0.941	0.055	35.3	0.20			†	
	−13.0	−12.01		1.52	0.141	31.3	0.61			0.925	0.244
	−13.0	−11.54		2.49	0.201	24.1	1.05			2.59	0.197
	−13.0	−11.03		4.38	0.205	21.3	1.12			4.89	0.104
	−13.0	−10.55		8.71	0.205	20.6	1.17			10.2	0.071
	−13.0	−10.03		25.6	0.205	20.7	1.17			30.1	0.063
132b	−10.39	−13.37	37.3	0.017	0.134	41.1	0.75	28.1	0.20	0.013	0.093
	−10.39	−12.86	44.6	0.064	0.194	29.5	0.99	44.4	0.25	0.064	0.116
	−10.39	−12.49	42.2	0.123	0.197	26.9	1.07	45.1	0.24	0.131	0.094
	−10.39	−12.01	46.5	0.386	0.206	23.6	1.08	50.5	0.25	0.418	0.092
	−10.39	−11.54	44.3	0.776	0.199	22.4	1.11	49.3	0.23	0.863	0.063
	−10.39	−11.03	41.5	1.86	0.196	22.9	1.15	47.7	0.23	2.14	0.048
	−10.39	−10.55	38.6	3.95	0.206	21.3	1.14	44.0	0.20	4.49	0.032
	−10.39	−10.03	25.9	7.44	0.200	21.1	1.16	30.2	0.139	8.67	0.0184
173	−12.00	−13.52		0.073	0.166	32.2	0.61				
	−12.00	−13.00		0.257	0.271	26.9	0.93			0.238	0.56
	−12.00	−12.50		0.739	0.324	26.5	1.06			0.780	0.57
	−12.00	−11.00		4.35	0.305	25.1	1.20			5.20	0.112
					Thalassiosira oceanica						
141	−13.0	−13.6			0.148	82.5	0.83				
	−12.72	−13.6	0.38		0.208	87.8	0.95	0.360	0.63		
	−12.40	−13.6	0.59		0.201	84.5	1.19	0.708	0.58		
	−11.95	−13.6	1.50		0.242	84.1	1.29	1.93	0.56		
	−11.50	−13.6	4.14		0.244	84.2	1.22	5.06	0.52		
	−10.98	−13.6	8.59		0.170	86.8	1.21	10.4	0.33		
165	−13.0	−13.6	0.18		0.209	102	0.78	0.138	0.50		
	−12.70	−13.6	0.37		0.207	122	0.78	0.292	0.61		

Table 1. Continued.

Exp.	log $[Zn^{2+}]$	log $[Co^{2+}]$	Zn : C	Co : C	Chl *a*	Cell vol.	μ	V_{Zn}	V/ρ^*	V_{Co}	V/ρ^*
	−12.51	−13.6	0.49		0.204	87.7	0.89	0.439	0.47		
	−11.96	−13.6	1.50		0.258	81.3	1.22	1.83	0.53		
	−11.51	−13.6	4.57		0.247	81.9	1.31	6.00	0.62		
	−10.98	−13.6	8.78		0.225	84.2	1.34	11.8	0.36		
149	−13.0	−12.00		1.44	0.177	94.5	1.15			1.65	
	−12.85	−12.00	0.15	1.26	0.210	93.4	1.15	0.175	0.43	1.46	0.53
	−12.30	−12.00	0.70	1.66	0.216	93.1	1.19	0.837	0.59	1.97	0.73
	−11.91	−11.99	1.33	1.12	0.210	97.4	1.18	1.58	0.45	1.328	0.48
	−11.49	−11.99	3.34	0.656	0.217	89.4	1.24	4.15	0.46	0.816	0.30
	−10.98	−11.99	7.06	0.0454	0.194	93.1	1.27	8.98	0.29	0.0578	0.020
	−10.51	−11.98	11.5	0.00892	0.222	90.9	1.29	14.8	0.166	0.0115	0.0040
	−9.99	−12.00	13.5	0.00262	0.210	88.4	1.28	17.3	0.058	0.00335	0.00121
	−9.51	−12.00	21.3	0.00208	0.216	91.9	1.31	27.9	0.030	0.00272	0.00097
	−8.99	−12.00	42.3	0.00197	0.205	91.9	1.31	55.5	0.019	0.00258	0.00094
150a‡	−13.0	−13.6			0.144	102	0.75				
	−12.71	−13.6	0.38		0.155	100	0.90	0.345	0.65		
	−12.36	−13.6	0.80		0.180	97.3	0.90	0.654	0.58		
	−11.97	−13.6	1.72		0.178	96.9	1.03	1.77	0.59		
	−11.51	−13.6	4.41		0.175	101	1.05	4.65	0.55		
	−10.98	−13.6	8.23		0.176	101	1.05	8.63	0.30		
	−10.51	−13.6	10.6		0.181	101	1.09	11.5	0.136		
150b‡	−13.0	−12.58		0.396	0.183	93.8	0.84			0.333	0.47
	−13.0	−12.14		0.889	0.143	95.4	0.89			0.795	0.41
	−13.0	−11.62		2.20	0.163	91.8	0.99			2.18	0.33
	−13.0	−11.15		4.48	0.167	91.4	0.99			4.45	0.23
	−13.0	−10.63		9.33	0.163	94.2	0.92			8.63	0.136
	−13.0	−10.15		12.4	0.195	87.5	0.99			12.3	0.062
					Thalassiosira pseudonana						
144	−13.0	−13.49					0				
	−12.70	−13.52					0				
	−12.39	−13.52	1.90	0.0811	0.170	31.9	0.33	0.635	0.33	0.0272	0.21
	−12.39	−13.52	1.25	0.0646		41.2	0.21	†		†	
	−11.94	−13.52	2.19	0.0363	0.168	42.4	0.83	1.82	0.41	0.0302	0.28
	−11.94	−13.52	1.89	0.0359	0.150	33.9	0.97	1.85	0.36	0.0350	0.28
	−11.94	−13.6				43.2	0.87				
	−11.49	−13.49	3.40	0.0107	0.184	49.3	1.27	4.32	0.39	0.0136	0.129
	−10.99	−13.49	6.86	0.00101	0.195	55.5	1.43	9.84	0.30	0.00145	0.0149
	−9.99	−13.49	8.12	0.00047	0.197	56.0	1.43	11.6	0.035	0.00067	0.006
145	−12.99	−13.35					0				
	−12.99	−12.55					0				
	−12.99	−12.13					0				
	−12.99	−11.63	0.29	2.68	1.28	41.9	0.48	0.141	0.36	1.28	0.149
	−12.99	−11.15	0.28	5.04	2.51	48.6	0.50	0.138	0.38	2.51	0.108
	−12.99	−10.63	0.22	9.07	6.95	48.8	0.77	0.171	0.48	6.95	0.090
	−12.99	−10.16	0.23	15.8	11.8	54.6	0.75	0.173	0.52	11.8	0.056
	−12.99	−9.63	0.19	20.0	17.0	48.0	0.85	0.158	0.44	17.0	0.022
					Synechococcus bacillaris						
152‡	−13.0	−13.6					0				
	−13.0	−13.15		0.080	0.228		0.30			0.0241	
	−13.0	−12.63		0.124	0.134		0.53			0.0700	
	−13.0	−12.15		0.219	0.129		0.50			0.109	
	−13.0	−11.63		0.475	0.132		0.47			0.224	
	−13.0	−11.15		0.578	0.154		0.51			0.293	
	−13.0	−10.63		1.43	0.132		0.49			0.699	
	−10.98	−13.6					0				

* V/ρ gives the ratio of steady state Zn or Co uptake to the maximum diffusion rate of kinetically labile inorganic species (free ions plus inorganic complexes) to the cell surface. This ratio was computed by multiplying the steady state uptake rate per cell volume

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Table 1. Footnote continued.

by the mean volume per cell to give the uptake rate per cell. This value was then divided by the maximum diffusion rate per cell (ρ), computed from the equation $\rho = 4\pi rD[M']$ by assuming that the cells are approximately spherical (Hudson and Morel 1990). The cell radius, r, was computed from the mean cell volume by using the relation between the radius of a sphere and its volume. D is the diffusion rate constant for inorganic species at 20°C (6.1 and 6.4×10^{-6} cm^2 s^{-1} for Co and Zn, Li and Gregory 1974), and $[M']$ is the concentration of dissolved inorganic species computed by dividing the free ion concentration, $[M^{2+}]$, by values for $[M^{2+}]/[M']$ (0.67 for Co and 0.66 for Zn, Byrne et al. 1988).

† Insufficient cell divisions at constant growth rate for steady state to be established.

‡ No vitamin B_{12} added in this experiment.