1.018/7.30J Ecology 1: The Earth System Problem Set 1, Fall 2009

Assigned: Ses #2 Due: Ses #6 at the <u>beginning</u> of class. Please turn in your assignments (hard copy) to the TAs.

You may work individually or in groups of up to three.

1. (11 points)

a. The following is a series of coupled electron donors and electron acceptors. Using Table 1, order this series from most energy yielding to least energy yielding. Assume that the pH for all reactions is 7. H_2/Fe^{3+} H_2S/O_2 CH₃OH/NO₃ H_2/O_2 NO_2^{-}/Fe^{3+} Fe^{2+}/O_2 H₂S/NO₃⁻ 1. $H_2/O_2 (0.414 + 0.816 = 1.23 V)$ 2. H_2/Fe^{3+} (0.414 + 0.771 = 1.185 V) 3. $H_2S/O_2 (0.243 + 0.816 = 1.059 V)$ 4. H_2S/NO_3^- (0.243 + 0.421 = 0.664 V) or (0.243 + 0.36 = 0.603 V) or (0.243 + 0.75 = 0.993 V) 5. CH_3OH/NO_3^- (0.18 + 0.421 = 0.601 V) or (0.18 + 0.36 = 0.54 V) or (0.18 + 0.75 = 0.93 V) 6. NO_2^{-}/Fe^{3+} (-0.421 + 0.771 = 0.35 V) 7. $Fe^{2+}/O_2(-0.771 + 0.816 = 0.045 V)$

NOTE: "energy yielding" was a poor choice of words. What we were really looking for was "highest potential" to "least potential". Therefore, reactions ranked using G_0 are acceptable.

b. Explain how it is possible that the same substance could be either an electron donor or an electron acceptor for different microorganisms. Under what conditions might this happen? Give one example.

Some compounds that are in an intermediate redox state can serve as either electron donors or electron acceptors depending on different environmental conditions and microorganisms involved. This can happen because the thermodynamics is dependent on the redox couple of electron donor and acceptor species. One example of a compound that can serve as either an electron donor or acceptor is nitrite, NO_2^- . Some nitrifying bacteria can oxidize nitrite to nitrate to gain energy (coupling the nitrite oxidation to the reduction of oxygen, an aerobic respiration).

 $NO_2^{-} + H_2O \rightarrow NO_3^{-} + 2 H^+ + 2 e^-$

On the other hand, in the absence of oxygen as a terminal electron acceptor, some denitrifying bacteria can reduce nitrite to ammonia (using nitrite as the terminal electron acceptor, and glucose or other compounds as electron donors).

 $NO_2^- + 8 H^+ + 6 e^- \rightarrow NH_4^+ + 2 H_2O$

Other possibilities of compounds that could serve as either electron donors or acceptors from the Standard Reduction Potential table include Fe^{2+} and S:

Fe²⁺ → Fe³⁺ + e⁻ Fe²⁺ + 2 e⁻ → Fe S + 4 H₂O → SO₄²⁻ + 8 H⁺ + 6 e⁻ S + 2 H⁺ + 2 e⁻ → H₂S

c. Consider the following reaction:

 $NADH + H^+ + fumarate \Rightarrow [succinate + NAD^+]$

Using Table 1 calculate the delta E_o' of the reaction. What is the delta $G^{o'}$? Does this reaction produce or consume energy? Does this look to you like a potential reaction in a respiratory pathway? Why or why not?

NADH \rightarrow NAD⁺ + H⁺ + 2 e⁻ Fumarate + 2 H⁺ + 2 e⁻ \rightarrow Succinate

$$\begin{split} &E_{o}{}^{'}=0.320+0.031=0.351~V\\ &G_{o}{}^{'}=-2~*~23~kcal~V^{-1}~mol^{-1}~*~0.351~V=-16.146~kcal~mol^{-1}\\ &G_{o}{}^{'}=-2~*~96.5~kcal~V^{-1}~mol^{-1}~*~0.351~V=-67.743~kJ~mol^{-1} \end{split}$$

This reaction is exothermic (produces energy). This does look like a potential reaction in a respiratory pathway because it produces energy. This reaction takes place in the electron transport chain of *E. coli*.

2. (11 points)

a. In the article by Des Marais, an estimate is given for global photosynthetic productivity. Using this number and the formula for photosynthesis in the Remmert paper, estimate, in kg, the annual amount of water and CO_2 consumed by photosynthesis, as well as the amount of O_2 produced.

Global photosynthetic productivity $-9000 \times 10^{12} \text{ mol C year}^{-1}$ Formula for photosynthesis $-6 \text{ CO}_2 + 12 \text{ H}_2\text{O} + \text{Light} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2 + 6 \text{ H}_2\text{O}$

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Water = 9000 \times 10^{12} \text{ mol H}_2\text{O year}^{-1} * 0.018 \text{ kg mol}^{-1} = 162 \times 10^{12} \text{ kg H}_2\text{O year}^{-1} \text{ (net)}
Water = 18000 \times 10^{12} \text{ mol H}_2\text{O year}^{-1} * 0.018 \text{ kg mol}^{-1} = 324 \times 10^{12} \text{ kg H}_2\text{O year}^{-1} \text{ (gross)}
\text{CO}_2 = 9000 \times 10^{12} \text{ mol CO}_2 \text{ year}^{-1} * 0.044 \text{ kg mol}^{-1} = 396 \times 10^{12} \text{ kg CO}_2 \text{ year}^{-1}
\text{O}_2 = 9000 \times 10^{12} \text{ mol O}_2 \text{ year}^{-1} * 0.032 \text{ kg mol}^{-1} = 288 \times 10^{12} \text{ kg O}_2 \text{ year}^{-1}
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b. The total mass of the Earth's atmosphere is approximately 5×10^{18} kg and composed of 78% Nitrogen, 21% Oxygen, and 1% Argon. In what ways was the atmosphere of the Earth 4 billion years ago different than it is today? Since there is still disagreement about Earth's early atmosphere, be sure to note sources in your answer.

- 1. Essentially devoid of oxygen Des Marais 2005; Kump 2008
- 2. Hydrogen rich reducing environment composed of methane, ammonia, hydrogen, water Miller and Urey 1953 from Chyba 2005; Tian et al. 2005 from Chyba 2005
- 3. CO₂ rich Walker 1977 from Chyba 2005
- 4. Before core formation CH₄ and NH₃, after CO₂ Holland 1962 from Chyba 2005
- 5. CO_2 rich with 30% H₂ Tian et al. 2005 from Chyba 2005

c. Calculate how many years it took for the current levels of O_2 in the atmosphere to accumulate. Assume that the early atmosphere contained no O_2 , photosynthesis started instantaneously at today's rate, photosynthesis was constant in time, and that respiration was negligible. Is your answer reasonable? If not, explain why.

 $5 \times 10^{18} \text{ kg} * 0.21 = 1.05 \times 10^{18} \text{ kg} \text{ O}_2$

 $1.05 \times 10^{18} \text{ kg O}_2 / 288 \times 10^{12} \text{ kg O}_2 \text{ year}^{-1} = 3645.8 \text{ years}$

This answer is unreasonable, in large part because of the assumptions included in the calculation. The development of photosynthesis at today's rate occurred over billions of years. During this time, complex, respiring organisms were evolving, consuming much of the O_2 produced by photosynthesis (today O_2 levels are at an approximate steady state because of the balance of photosynthesis and respiration).

NOTE: The composition of the atmosphere is given by volume. Technically, it should be given by mass. Any answers that try to convert from percentage by volume to percentage by mass are acceptable.

d. Al Gore has hired you as a scientific consultant for his new movie, *More Inconvenient Truths*. While attending last Thursday's 1.018 lecture, Al heard Prof. Chisholm say that O₂ levels are declining, but not by much. Al wants to incorporate this idea into his movie, but doesn't want to use "scare tactics". Find the rate at which O₂ levels are declining (looking this number up is fine, but note sources) and explain to Al why this is occurring. Given your findings, should he include this as a detrimental effect of burning fossil

fuels in his new movie? If so, why? If not, describe a mechanism by which O_2 could be reduced significantly in the atmosphere. Your idea need not be likely, just possible.

From 1991 – 2005, O₂ levels have dropped 0.00248%

http://www.mlo.noaa.gov/programs/coop/scripps/o2/o2.html

 $0.00248\% / 15 = 1.65 \times 10^{-4} \% \text{ year}^{-1}$

 $1.65 \times 10^{-6} * 0.21 * 5 \times 10^{18} \text{ kg} = 1.735 \times 10^{12} \text{ kg O}_2 \text{ year}^{-1}$

Assuming that the present rate of O_2 depletion continues into the future, it will be ~600,000 years before we run out of O_2 . Keeling calculates 50,000 years before we run out of O_2 , but regardless, we will use all of our fossil fuel resources long before we significantly deplete the O_2 levels of the atmosphere.

The reduction in O_2 is primarily occurring because of the combustion of fossil fuels, which requires O_2 . This effect is somewhat offset by an apparent imbalance between photosynthesis and respiration. Based on the above calculations, this should not be included as a detrimental effect of burning fossil fuels.

 O_2 could be reduced significantly in the atmosphere if the major plant communities in the world collapsed. A widespread die-off of vegetation resulting from anthropogenic activities could significantly decrease the rate of photosynthesis in the world, causing a shortage of O_2 for the remaining respiring organisms.

NOTE: The composition of the atmosphere is given by volume. Technically, it should be given by mass. Any answers that try to convert from percentage by volume to percentage by mass are acceptable.

3. (11 points)

a. You have decided to follow in your TA's footsteps and pursue a career in oceanography. Because you were so inspired by 1.018, you are especially interested in the productivity of oceans due to their importance on a global scale. You break the news to a fellow classmate who says, "But don't oceans have the same productivity as deserts? How could they possibly be important on a global scale?" Explain how you are both right.

While it is true that open oceans have low productivity on a per area basis, because they occupy such a large percentage ($\sim 2/3$) of the Earth's surface, they contribute nearly half of global NPP.

b. Your discussion about oceans and aquatic ecosystems gets you thinking about how they compare with terrestrial systems. You remember from class that five of the major environmental determinants of productivity are light, nutrients, temperature, CO_2 , and H_2O . Your classmate creates the table below and asks you to fill in the factors that are most likely and least likely to limit primary production in the following ecosystems:

	<u>Most Likely</u>	Least Likely
Boreal Forest	Light, Temperature, Nutrients	CO_2
Sewage Pond	Light, Temperature	H ₂ O, Nutrients
Tropical Rainforest	Nutrients, Light	H_2O, CO_2
North Atlantic Ocean	Nutrients, Light	H_2O, CO_2

c. For each ecosystem give a one or two sentence explanation for why you chose which factors would be most likely and least likely to limit primary production. State any assumptions you make about the ecosystems while assessing the importance of each factor.

Boreal Forest – Boreal forests have light, temperature, and nutrients as their most limiting factors. Water is also a limiting factor in some boreal forests, as plants have very little access to water in its liquid state. CO_2 is plentiful.

Sewage Pond – In sewage ponds there is an excess of nutrients (N and P due to sewage, runoff) in water. However, the large amount of nutrients creates dense and dark water making light a limiting factor. Temperature is also a limiting factor in some cases, as biological oxidation processes are sensitive to extreme hot or cold. Note that O_2 would likely be the key limiting factor in a sewage pond.

Tropical Rainforest – In this case nutrients would be more important than light because there is so much productivity that nutrients are taken out of the soil very quickly. Light would also be a limiting factor because of the dense canopies. There is plenty of water and CO_2 around from the rain and respiration of the forest.

North Atlantic Ocean – Nutrients and light are the two most limiting factors in this system. If one looks at the surface of the North Atlantic, light is not a limiting factor, but nutrients are (shoreline or shallower areas are an exception as they have more nutrients and thus higher productivity). The deep North Atlantic has next to no light reaching it and thus light would be a limiting factor in that case.

d. As you are a studious MIT student, your discussion with your classmate evolves into a conversation about the mean residence time (MRT) of carbon. Your classmate creates a table of various ecosystems and asks you to rank them in order of MRT (1-4, with 1 being the longest and 4 being the shortest). Briefly explain your methodology.

<u>Ecosystem</u>	Area	NPP	Biomass	<u>Rank</u>
	$(10^6 \mathrm{km}^2)$	$(g m^{-2} y^{-1})$	(kg m^{-2})	
Young Temperate forest	5	1300	30	1
Ocean plankton	332	125	0.003	4
Tropical Rain Forest	17	2200	45	2
Savanna	15	900	4	3

Residence Time = Biomass / Flux

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