## 1.018/7.30J Ecology 1 Quiz #1 October 8, 2009

**Please put your name on every page!** Space is provided for your answers; if you need more room, use the back of the **same** page. This exam is worth 100 points, with an additional 4 points of bonus problems. You have 80 minutes to work on it and the value of each question is roughly proportional to the amount of time you should spend answering it. The test will begin at 11:05am and promptly end at 12:25pm.

**Mean = 74.4, Standard Deviation = 10.1** 

Useful Equations and Information			
$\Delta G_{o}' = -nF(\Delta E_{o}')$	$n = # e^{-t}$ transferred per mol of reductant		
$\Delta E_{o}$ = $E_{o}$ (oxidizing agent) – $E_{o}$ (reducing agent)	F = Faraday constant (96.5 kJ V mol-)		
$\Delta G' = \Delta G_0' + RT \ln(([C]^c [D]^d) / ([A]^a [B]^b))$	T = Temperature (K)		
$aA + bB \rightarrow cC + dD$	R = gas constant (8.31 J $K^{-1}$ mol <sup>-1</sup> )		
	Standard reactants: 1 M, 1 atm, 25°C (298 K)		

Half-Reaction			E <sub>o</sub> ' (V)
$NO_2^- + 4 H^+ + 3 e^-$	$\Rightarrow$	$^{1}/_{2}$ N <sub>2</sub> + 2 H <sub>2</sub> O	+0.956
$\frac{1}{2}$ O <sub>2</sub> + 2 H <sup>+</sup> + 2 e <sup>-</sup>	$\Rightarrow$	$H_2O$	+0.816
$Fe^{3+} + e^{-}$	$\Rightarrow$	Fe <sup>2+</sup>	+0.771
$NO_3^- + 6 H^+ + 6 e^-$	$\Rightarrow$	$^{1}/_{2}$ N <sub>2</sub> + 3 H <sub>2</sub> O	+0.75
$NO_3^- + 2 H^+ + 2 e^-$	$\Rightarrow$	$NO_2 + H_2O$	+0.421
$NO_3^- + 10 H^+ + 8 e^-$	$\Rightarrow$	$\mathrm{NH_4}^+ + 3 \mathrm{H_2O}$	+0.36
$NO_2^- + 8 H^+ + 6 e^-$	$\Rightarrow$	$\mathrm{NH_4}^+ + 2~\mathrm{H_2O}$	+0.34
$CH_{3}OH + 2 H^{+} + 2 e^{-}$	$\Rightarrow$	$CH_4 + H_2O$	+0.17
fumarate + 2 $H^+$ + 2 $e^-$	⇒	succinate	+0.031
$2 H^+ + 2 e^-$	⇒	H <sub>2</sub> (pH 0)	+0.00
oxaloacetate + 2 $H^+$ + 2 $e^-$	$\Rightarrow$	malate	-0.166
$CH_2O + 2 H^+ + 2 e^-$	$\Rightarrow$	CH <sub>3</sub> OH	-0.18
pyruvate + 2 $H^+$ + 2 $e^-$	$\Rightarrow$	lactate	-0.185
acetaldehyde + 2 $H^+$ + 2 $e^-$	$\Rightarrow$	ethanol	-0.197
$SO_4^{2-} + 8 H^+ + 6 e^-$	$\Rightarrow$	$S + 4 H_2O$	-0.20
$SO_4^{2-}$ + 10 H <sup>+</sup> + 8 e <sup>-</sup>	$\Rightarrow$	$\mathrm{H_2S} + 4~\mathrm{H_2O}$	-0.21
$FAD + 2 H^{+} + 2 e^{-}$	$\Rightarrow$	FADH <sub>2</sub>	-0.219
$CO_2 + 8 H^+ + 8 e^-$	$\Rightarrow$	$CH_4 + 2 H_2O$	-0.24
$S + 2 H^{+} + 2 e^{-}$	$\Rightarrow$	$H_2S$	-0.243
$\frac{1}{2}$ N <sub>2</sub> + 4 H <sup>+</sup> + 3 e <sup>-</sup>	$\Rightarrow$	$\mathrm{NH_4}^+$	-0.28
$NAD^+ + H^+ + 2 e^-$	$\Rightarrow$	NADH	-0.320
$NADP^+ + H^+ + 2 e^-$	$\Rightarrow$	NADPH	-0.324
$2 H^+ + 2 e^-$	$\Rightarrow$	H <sub>2</sub> (pH 7)	-0.414
$CO_2 + 4 H^+ + 4 e^-$	$\Rightarrow$	1/6 glucose + H <sub>2</sub> O	-0.43
$Fe^{2+} + 2e^{-}$	$\Rightarrow$	Fe	-0.85

1. (25 points) You are hired to develop and operate a wastewater treatment plant for a fertilizer company that produces an effluent high in ammonium. You are given two choices for breaking down ammonium:

 $NH_4^+ + O_2 \rightarrow NO_2^-$  (1)  $NH_4^+ + NO_2^- \rightarrow N_2 + 2 H_2O$  (2)

a. Write the four half-reactions associated with processes (1) and (2).

 ${}^{1}\!\!\!/_{2} O_{2} + 2 H^{+} + 2 e^{-} \rightarrow H_{2}O$ NH<sub>4</sub><sup>+</sup> + 2 H<sub>2</sub>O  $\rightarrow$  NO<sub>2</sub><sup>-</sup> + 8 H<sup>+</sup> + 6 e<sup>-</sup>

 $\begin{array}{c} NO_{2}^{-} + 4 H^{+} + 3 e^{-} \rightarrow \frac{1}{2} N_{2} + 2 H_{2}O \\ NH_{4}^{+} \rightarrow \frac{1}{2} N_{2} + 4 H^{+} + 3 e^{-} \end{array}$ 

b. Identify the reducing agent in process (1) and the substance that is being reduced in (2).

## $\mathrm{NH_4}^+, \mathrm{NO_2}^-$

c. Assume that you can extract all of the free energy produced by these reactions and you want to maximize your energy yield (under standard conditions). Which process would you choose? Show your work.

${}^{1/2}O_{2} + 2 H^{+} + 2 e^{-} \rightarrow H_{2}O$ $NH_{4}^{+} + 2 H_{2}O \rightarrow NO_{2}^{-} + 8 H^{+} + 6 e^{-}$	$\Delta E_{o}' = +0.816 \text{ V} - 0.340 \text{ V} = 0.476 \text{ V}$ $\Delta G_{o}' = -6 * 96.5 \text{ kJ V}^{-1} \text{ mol}^{-1} * 0.476 \text{ V} = -275.6 \text{ kJ mol}^{-1}$
$NO_{2}^{-} + 4 H^{+} + 3 e^{-} \rightarrow \frac{1}{2} N_{2} + 2 H_{2}O$	$\Delta E_{o}' = +0.956 \text{ V} + 0.280 \text{ V} = 1.236 \text{ V}$
$NH_{4}^{+} \rightarrow \frac{1}{2} N_{2} + 4 H^{+} + 3 e^{-}$	$\Delta G_{o}' = -3 * 96.5 \text{ kJ V}^{-1} \text{ mol}^{-1} * 1.236 \text{ V} = -357.8 \text{ kJ mol}^{-1}$

d. After you turn on your wastewater treatment plant, you find that you're not getting as much energy as you thought you would. Recall that your above calculations are based on standard conditions of 1 M for solutes and 1 atm for gases. You measure the  $NH_4^+$  concentration and find that it is only 0.01 M. Using your selected process, what would you expect your energy yield (1 atm, 298 K) to be?

 $\Delta G_{o}' = -357.8 \text{ kJ mol}^{-1} + 0.00831 \text{ kJ K}^{-1} \text{ mol}^{-1} * 298 \text{ K} * \ln(([1]^{1} * [1]^{2}) / ([0.01]^{1} * [1]^{1})) = -346.4 \text{ kJ mol}^{-1}$ 

BONUS (2 points): Identify the common names of processes (1) and (2)

Nitrification, Anaerobic Ammonium Oxidation (Anammox) or Denitrification

2. (25 points) Jonathan and Skylar are trying to recreate the Early Earth experiment of Miller and Urey. They decide to use some air from outside Building 48, put it in a reaction chamber and apply sparks. To Jonathan and Skylar's surprise, their results don't match up with those of Miller and Urey.

a. Describe what the air that Jonathan and Skylar added to their tank was composed of (rough proportions of major gases).

78% nitrogen, 21% oxygen, trace amounts of other gases.

b. Describe which gases Miller and Urey used (i.e. the gases of the early atmosphere) and explain what the Miller-Urey experiment found.

Methane (CH<sub>4</sub>), ammonia (NH<sub>3</sub>), molecular hydrogen (H<sub>2</sub>), and water (H<sub>2</sub>O). By adding a spark (to simulate lightning), Miller and Urey created amino acids from simple organic molecules formed in the gas mixture (e.g. hydrogen cyanide and formaldehyde).

c. Why was the early atmosphere more conducive to the success of this experiment? Hint: you should mention the properties of the gases in parts (a) and (b).

The early atmosphere, whether that described by Miller and Urey or in different proportions, did not have oxygen. This lack of oxygen in the Earth's early atmosphere prohibited the formation of complex molecules. The Miller-Urey model is of a "reducing" atmosphere.

d. The "Great Oxygenation Event" is one of the most important, yet poorly understood, events in the Earth's history. Scientists use various indicators in the geologic record to determine when and why this occurred. Please check the boxes beside the factors that may be helpful in determining when the oxygenation of Earth's atmosphere occurred.

- Charcoal record to indicate large fires
- □ Nitrogen concentrations derived from ice cores
- Deep ocean crust patterns
- Record of fossilized phytoplankton
- Mass-independent fractionation (MIF) of sulfur isotopes
- **Red** banding in sedimentary geologic formations
- □ Fossil record of early eukaryotes

e. Emily and Kate were studying for 1.018 on flashcards, but they left the window open and the cards became disordered. Please number the following events in the order that they occurred.

Macroscopic Eukaryotes	4	Cyanobacteria	3	Algal Kingdoms	5	Vascular Plants	7
Phototrophic Bacteria	2	Life	1	Mammals	8	Shelled Invertebrates	6

3. (25 points) In the aquatic ecosystem pictured below: (A) is the amount of  $CO_2$  reduced to organic carbon by phytoplankton; (B) is the amount of  $CO_2$  reduced to organic carbon by rooted aquatic plants; (C) is the amount of organic carbon respired by phytoplankton; (D) is the amount of organic carbon respired by rooted aquatic plants; (E) is the respiration of the zooplankton, bacteria, and fish in the water; and (F) is the respiration of the mud-dwelling organisms and bacteria.



a. For the whole ecosystem, write the equations (using the letters describe above) for:

Gross Primary Production	Net Primary Production	Net Community Production
A + B	A + B - C - D	A + B - C - D - E - F

b. A = 200,000 g C year<sup>-1</sup>; B = 20,000 g C year<sup>-1</sup>; C = 50,000 g C year<sup>-1</sup>; D = 50,000 g C year<sup>-1</sup>; Net Community Production = 2000 g C year<sup>-1</sup>; and Mean Residence Time = 0.15 years. Find the total biomass of the ecosystem. Show your work and state any assumptions made.

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MRT = Biomass/NPP
NPP = 200,000 g C + 20,000 g C - 50,000 g C - 50,000 g C = 120,000 g C
Biomass = MRT * NPP
Biomass = 0.15 year * 120,000 g C year<sup>-1</sup> = 18,000 g C
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c. You want to measure the productivity of a sample of surface water from the Charles River. At 9 am you collect two 500 mL bottles of water, one completely opaque and one clear, measure their  $O_2$  content, seal them, and leave them in the river. 8 hours later you retrieve your samples and measure their  $O_2$  content (total amount of  $O_2$  in the 500 mL sample). Calculate the GPP in g C hour<sup>-1</sup> of your water sample. The molecular weight of C is 12 g mol<sup>-1</sup> and  $O_2$  is 32 g mol<sup>-1</sup>.

Time	Opaque	Clear
9am	1.0 mol O <sub>2</sub>	1.0 mol O <sub>2</sub>
5pm	0.37 mol O <sub>2</sub>	1.23 mol O <sub>2</sub>

Gross O<sub>2</sub> produced =  $|\text{clear } \Delta O_2|$  + opaque  $\Delta O_2$ 6 CO<sub>2</sub> + 12 H<sub>2</sub>O + Light  $\rightarrow$  C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> + 6 O<sub>2</sub> + 6 H<sub>2</sub>O For every 1 mole of O<sub>2</sub> produced 1 mole of C is fixed. GPP = (0.23 mol O<sub>2</sub> + 0.63 mol O<sub>2</sub>) \* 1 mol C / 1 mol O<sub>2</sub> \*12 g mol<sup>-1</sup> / 8 hours = 1.29 g C hour<sup>-1</sup>

d. You now want to measure the productivity of the open ocean. Would you use the same method? If not, briefly describe the technique you would use.

Because the productivity of a sample taken from the open ocean is so low, you could not use the  $\Delta O_2$  technique. Even after days of incubation, there would be no discernable change in  $O_2$ . Instead, you would use the <sup>14</sup>C technique. This method uses radiolabeled CO<sub>2</sub> to track the uptake of CO<sub>2</sub> into organisms. By measuring the amount of <sup>14</sup>CO<sub>2</sub> reduced to <sup>14</sup>C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> and <sup>12</sup>CO<sub>2</sub> available, as well as knowing the amount of <sup>14</sup>CO<sub>2</sub> added, the total amount of <sup>12</sup>CO<sub>2</sub> reduced to C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> can be determined.

e. The figure below describes the change in above-ground net primary production with age for a stand of white spruce (Ryan et al. 1997). Explain how GPP and  $R_A$  change over time by sketching them on the graph. Explain the trends below.



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**GPP** – Gross primary productivity increases until about year 70, and then levels off or decreases. At this point the forest has fully matured and photosynthesis is limited (or reduced) by some factor (e.g. nutrients, light, water).

 $\mathbf{R}_{A} - \mathbf{R}_{A}$  shadows GPP as increasing photosynthesis requires more autotrophs, thus autotroph respiration also increases until year 70. However, after year 70  $\mathbf{R}_{A}$  levels off or decreases with decreasing photosynthesis. Answers that describe  $\mathbf{R}_{A}$  as increasing after year 70 because carbon stored in roots and stems require greater maintenance respiration are acceptable.

f. Describe how Net Community Production would change and why.

NCP – Net community production will increase until year 70, and then decline to approximately zero as photosynthesis (GPP) equilibrates with respiration ( $R_A + R_H$ ).

BONUS (2 points): According to Remmert, why is ecological theory crucial to our continued existence?

"We can live on earth under the conditions now prevailing, and under no others. As a pure science, ecology is concerned with understanding the balance and turnover of matter and energy in nature. In its applied form, ecology faces the problem of discovering how the conditions essential for present-day life can be maintained."

4. (10 points) Write in a metabolic process that is likely to take place in each environment listed in the table below. A list of metabolic processes is provided. Some processes may be used more than once or not at all.

Environment	Metabolic Process
Deep-sea hydrothermal vents	Sulfur/Sulfide Oxidation (CO Oxidation,
	Methanogenesis, Iron Oxidation, H <sub>2</sub> Oxidation)
An aquarium filled with well-fed fish	Ammonia Oxidation (Photosynthesis)
Termite guts	Methanogenesis
The surface of living stromatolites	Photosynthesis
Iron oxide particles in anoxic sediments	Iron Reduction

**Metabolic Processes:** H<sub>2</sub> Oxidation, Ammonia Oxidation, CO Oxidation, Methanogenesis, Iron Oxidation, Sulfur/Sulfide Oxidation, Photosynthesis, Iron Reduction

5. (15 points) Your TAs have decided to take you to the Harvard Forest instead of Plum Island for the class field trip. The diagram below indicates the general nitrogen cycle in this particular ecosystem.



a. Label what form of nitrogen or what process is occurring at:

А	В	С
Dead Organic N	NH4 <sup>+</sup> (Ammonium)	Denitrification

b. On your field trip, the TAs take you to a part of the forest where a clear-cutting experiment is being conducted. One of the TAs notes that the soil is losing nitrogen to surface and groundwater runoff. Explain why.

Internal cycling of nitrogen is an important component of the terrestrial nitrogen budget. Plants are vital to this internal cycling, as they both assimilate dead organic nitrogen that has been mineralized to ammonium and nitrate that has been produced from nitrite by nitrifying bacteria. If plants are not present to uptake and store nitrate and ammonium, they are leached from the soil.

c. In what major ways does the nitrogen cycle differ from the phosphorous cycle? Specifically, compare and contrast the flow of nitrogen and phosphorous through Earth's biosphere.

Nitrogen is plentiful and cycles readily throughout the biosphere. Humans can create ammonium from nitrogen gas using the Haber-Bosch process, and thus have an incredibly large influence on the nitrogen cycle. Phosphorous, in contrast, is scarce and travels on a "one-way street" from soils and rocks to the ocean. Humans also have a large impact on the phosphorous cycle. Phosphorous is mined to use in fertilizers, and while some phosphorous taken up by plants, much of it runs off to oceans where it is stored in relatively inaccessible marine sediments.

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