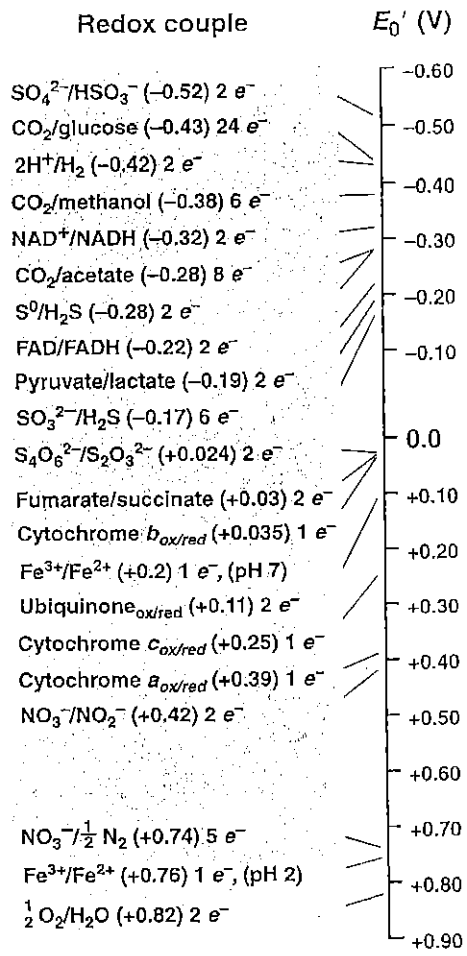
1. The groundwater in Oak Ridge, TN has been contaminated and characterized with extremely low pH (about 3) and elevated levels of nitrate and hexavalent uranium (i.e., U^{6+}). Environmental engineers decided to take bio-remedial action at this site by neutralizing the groundwater first and then adding electron donors (e.g., sugars) into injection wells, trying to stimulate indigenous subsurface microbes to grow and immobilize uranium (by reducing U^{6+} to U^{4+}). It turned out that this strategy worked very well, as data of monitoring wells indicated that nitrate and uranium disappeared within 30 and 90 days, respectively. It is also noted that by the time uranium was not detected, 1000 ppm of dissolved ferrous-iron (i.e., Fe^{2+}) were measured.

   Using the concept of cell energetics and the electron tower that is given below, show the "concentrations vs. time" figure of nitrate (initially 3000 ppm) and ferrous-iron would look like, and label the (two) primary microbial populations involved in the entire bioremediation process. Explain your results. (Hints: iron is abundant in subsurface environments) **[10 points]**



(Figure source: Brock Biology of Microorganisms)

2. A 10 g (dry weight) mouse is accidentally drowned in a 25 L bottle of non-sterile spring water that initially contains 10 mg/L oxygen. Assume that 70% of the mouse's dry weight is CH_2O.
   (1) Write the relevant reaction for respiration of the mouse with oxygen. **[10 points]**
   (2) Does the jug become anaerobic? **[10 points]**
   (3) If 2 ppm NO_3^- and 15 ppm SO_4^{2-} are in the spring water, how much of each will be left when the jug reaches equilibrium? Write relevant reactions. **[10 points]**
   (4) How much of the mouse will be left, assuming no organism capable of fermentation are present? **[10 points]**

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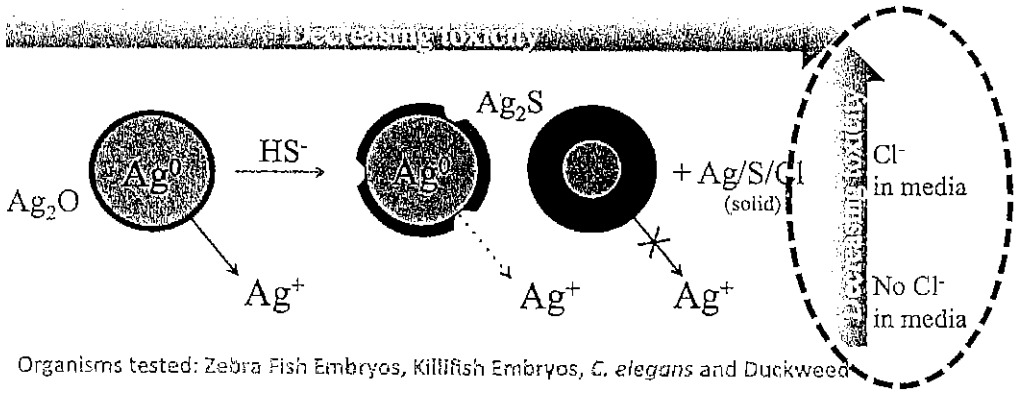
3. Methylmercury is the most toxic form of mercury and is intra-cellularly (means inside the cell) produced by some bacteria. Because mercury has no known biological roles in cells, uptake of inorganic mercury has been hypothesized through passive diffusion of small-sized, uncharged, lipophilic mercury species. Indeed, $HgCl_2^0{}_{(aq)}$ is considered and proved to be the most "bioavailable" Hg-chloro complex.

(1) If a solution has the total mercury concentration [Hg(+II)$_T$] fixed at 200 ppb (the atomic weight of mercury is 200) and pH fixed at 7, show the predominance of each mercury species (i.e., % of the total concentration) when the free chloride concentration [Cl^-] is at the level of 1, 10, 100, and 1000 mM, respectively. Consider no precipitation occurs. **[40 points]**

$\mathbf{Hg^{2+}} + Cl^- = HgCl^+$	$K_1 = 10^7$
$\mathbf{HgCl^+} + Cl^- = HgCl_2^0{}_{(aq)}$	$K_2 = 10^7$
$\mathbf{HgCl_2^0{}_{(aq)}} + Cl^- = HgCl_3^-$	$K_3 = 10^1$
$\mathbf{HgCl_3^-} + Cl^- = HgCl_4^{2-}$	$K_4 = 10^1$
$Hg^{2+} + OH^- + Cl^- = \mathbf{HgOHCl}$	$K_5 = 10^{18}$

(2) It is known that the chloride concentration of freshwater and seawater is 17 and 340 mM, respectively. According to your calculation results above, which water body under circumneutral pH conditions would be prone to have a methylmercury problem? Explain your answer. **[5 points]**

(3) It is also known that microbial toxicity of silver nano-particles (AgNP) is primarily resulted from the formation of dissolved Ag(+I) species in aqueous phase. Using the "bioavailability" concept, explain why Cl^- in media would decrease AgNP toxicity as shown in the dashed circle of the cartoon given below. **[5 points]**



(Figure source: Levard et al. *Environ. Sci. Technol.* 2013)

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