HW3

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Setup

In this assignment you will be reviewing the major ideas we have covered in class so far including: watershed hydrology, history of water quality change, pollutant flux versus concentration, nutrient cycling, redox chemistry, gibbs free energy yield, algae blooms, weathering, and water treatment approaches.

This assignment counts for double compared to all the other assignments and should be an excellent way for you to prepare for the mid-term.

Question 1)

A wetland was constructed to remove nitrogen from a small municipality that couldn't afford to install a traditional wastewater treatment plant. However, the bedrock surrounding the community is rich in Gypsum ($CaSO_4$) which enriches the water in sulfate (SO_4^{2-}). A retired biogeochemist in the community pointed out that all this excess sulfate could make denitrification less likely. She's too old to really want to work out the math, so she has asked you: **Will denitrification likely occur in these wetlands?**

Setup

We'll start with where hw3 ended and Gibbs free energy. This time instead of estimating Gibbs free energy at standard state, we will calculate energy yield based on real-world concentrations using the equation for a generic reaction

$aA + bB = cC + dD$

$\Delta G = \Delta G^o + RTln\left(\frac{([C]^c * [D]^d)}{([A]^a * [B]^b)}\right)$

Where ΔG^o is the standard free energy yield of a reaction (calculated in hw3), R is the universal gas constant $R = 0.008314\frac{kJ}{molK}$ and K is temperature in Kelvin $K = Temp^oC + 273.15$

Evaluation

We will be using a slightly simplified equation for calculating denitrification vs sulfate reduction energy potential.

$4NO_3^- + 5CH_2O + 4H^+ -> 5CO_2 + 2N_2 + 7H_2O$ ΔG^o = -113 kJ

$SO_4^{2-} + 2CH_2O + 2H^+ -> 2CO_2 + H_2S + 2H_2O$ ΔG^o = -25kJ

To see if denitrification will likely occur in this wetland we need to know the concentrations of all the constituents and compute the actual gibbs free energy of sulfate reduction versus the gibbs free energy of denitrification. If one is more efficient than the other then those microbes will be more active.

Based on your analysis is denitrification likely to be the dominant redox pathway in this environment? Please show gibbs free energy calculations for both.

Temperature in the wetland is 15 degrees C.

Answer 1)

I used the following code to answer this question

```
ch2 = 16*10^-2
hc = 10^-4
noc = 4*10^-4
soc = 300*10^-3
co2c=.1
h2oc=.1
h2sc=20*10^-5
temp=288.15
R = .008314
n2c=.001

tibble(compound = c('no3','ch2o','h+','co2','n2','h2o','so4','h2s'),
       `concentration_molar`=c(noc,ch2,hc,co2c,n2c,h2oc,soc,h2sc)) %>%
  knitr::kable()
```

compound	concentration_molar
no3	0.0004
ch2o	0.1600
h+	0.0001
co2	0.1000
n2	0.0010
h2o	0.1000
so4	0.3000
h2s	0.0002

```
sulfate_reduction = -25 + R*temp*log((co2c^2*h2sc*h2oc^2)/(ch2^2*soc*hc^2))

nitrate_reduction = -113 + R*temp*log((co2c^5*n2c^2*h2oc^7)/(hc^4*noc^4*ch2^5))
```

ΔG of denitrification = -27.1055104

ΔG of sulfate reduction = -11.6745551

Denitrification will still occur because it still yields more energy than sulfate reduction.

Question set 2 (watersheds)

1) What is a watershed? (see online notes)
2) What is a hydrograph? (see online notes)
3) The presenter at this conference talked about dilution, chemostasis, and enrichment. Could you draw these three ideas on a graph? What does each process tell us about how water pollution changes with flooding? (see online notes)
4) Can you name some elements that enrich, dilute, or are chemostatic with large changes in discharge?

Frequently soil-associated compounds can enrich during a storm as they are flushed out of soil solution and into streamwater. This applies for dissolved organic carbon and nitrate in many systems.

In snowmelt dominated systems, much of the water will not directly interact with the bedrock, leading to mostly pure water mixing directly into a stream which can dilute any weathering products like cations and anions.

Conversely in many rain-dominated systems or even in snow/rain systems weathering products are chemostatic because incoming rain reacts with bedrock to dissolve bedrock at approximately the same rate that it moves through the system. When reaction rate equals transport rate, you get a chemostatic signal, which is quite common for weathering products.

Question set 3 (watershed ecosystem)

1) What is the watershed ecosystem concept? (see online notes)
2) What decade was this idea implemented? (see online notes)
3) What is one major result from the Hubbard Brook watershed experiments?

Go to the website http://hbef.streampulse.org/

Question set 4 (nutrients)

1) What is Liebig's law of the minimum? (see online notes)
2) What is the Haber-Bosch process? (see online videos)
3) What is the Redfield ratio? What does it tell us about nutrient cycling? (see online notes)
4) How is phosphorus supplied to agricultural systems?

Mostly through apatite mining, but also guano and human biosolid applications.

Question set 5 (concentration vs flux and algae)

1) A river has relatively high mean nitrate concentrations downstream of an ag field but the units are in molar and the river watch group usually reports concentrations in mg/L. What is the concentration of NO_3^- in mg/L of a 0.0004 molar (moles/liter) average NO_3^- concentration river?

```
no3_mol = 62.0049 #g/mol
conc_molar = 0.0004 #mol/liter
no3_g_l = conc_molar*no3_mol #gram/liter
no3_mg_l = no3_g_l *1000 #mg/L
```

The concentration in mg/L is 24.80196.

2) A shrimp farming group that lives on the same river, just downstream is worried not about the concentration of NO_3^- but about the flux. What is the average daily flux of NO_3^- from the river if the average flow is 10 cubic feet per second. Flux should be reported in kg/day.

```
lps = 10*28.3168 # convert to liters per second
gps = no3_g_l*lps # grams of nitrate per second
gpd = gps*24*60*60 #60 seconds per minute #60 minutes per hour 24 hours in a day
kg_pd = gpd/1000
kg_py = kg_pd*365
```

There is 606.7976898 kg/day of nitrate moving downstream

3) What is the annual flux?

The annual flux is: 221,481.2 kg/year (in a non leap year)

4) Why might the farmers be concerned about flux more than concentration?

For shrimp farmers, presumably farming shrimp in an estuary, the build-up of nutrients over time can be a bigger problem than instantaneous concentration issues, because even with low concentration, high flux of nutrients will eventually cause problems.

5) What are the consequences of excess nutrients in lakes or the ocean?

Algal blooms, eutrophication, potentially toxic cyanobacterial blooms.

6) How does eutrophication happen? (see online notes)

7) What are two differences between algae and cyanobacteria?

Cyanobacteria can fix nitrogen from the atmosphere, and they produce a variety of toxins that depends on the species.

Question set 6 (weathering and mining)

1) What is chemical weathering? (online notes)
2) What conditions lead to high rates of chemical weathering? (online notes)
3) How does the carbon cycle interact with weathering? (online notes)
4) What is a "buffered" system? (online notes)
5) How does mining alter weathering (give at least 2 examples) (online notes)

Question set 7 (water treatment)

1) What is coagulation?

The binding of dissolved ions (usually negatively charged) with at least doubly charged cations. Binding these dissovled ions can form solid particles.

2) What is sorption?

The binding of dissolved ions onto a mineral surface.

3) What is floculation?

The bundling of many smaller suspended particles into a single larger particle, which will have increased mass and fall to the bottom of the water column.

4) How does a water treatment plant use these processes to improve water quality (either drinking or wastewater treatment).

The combination of these processes (in the order of coagulation, floculation, sorption) helps remove dissolved particles like DOC that can interfere with disinfectants, removes suspended particles that would discolor drinking water, and also removes larger parasites from solution.

5) Name two other ways we can treat water to improve it's quality (remove nutrients, get rid of disease, etc. . .)

We can use anoxic chambers to promote denitrification (nutrient removal) and also use disinfectants like bleach to kill any microscopic organisms that aren't removed by previous steps.

Question set 8 (general)

1) What is point-source pollution?

Pollution that comes from a single known source like a factory, a pipe, stormwater drainages, and other sources that have a discrete discharge point.

2) What is non-point source pollution?

Diffuse and landscape level pollution tha thas no single discharge like agriculture surface mining, and urbanization.

3) Which is easier to control? Why?

Because point source pollution has a known provenance, it is far easier to control

4) How does the Clean Air Act impact modern day water quality? (That's not a typo, if you've come to class we talk a lot about how the Clean Air Act has modern day impacts on water quality.)

No answer to this one on purpose.