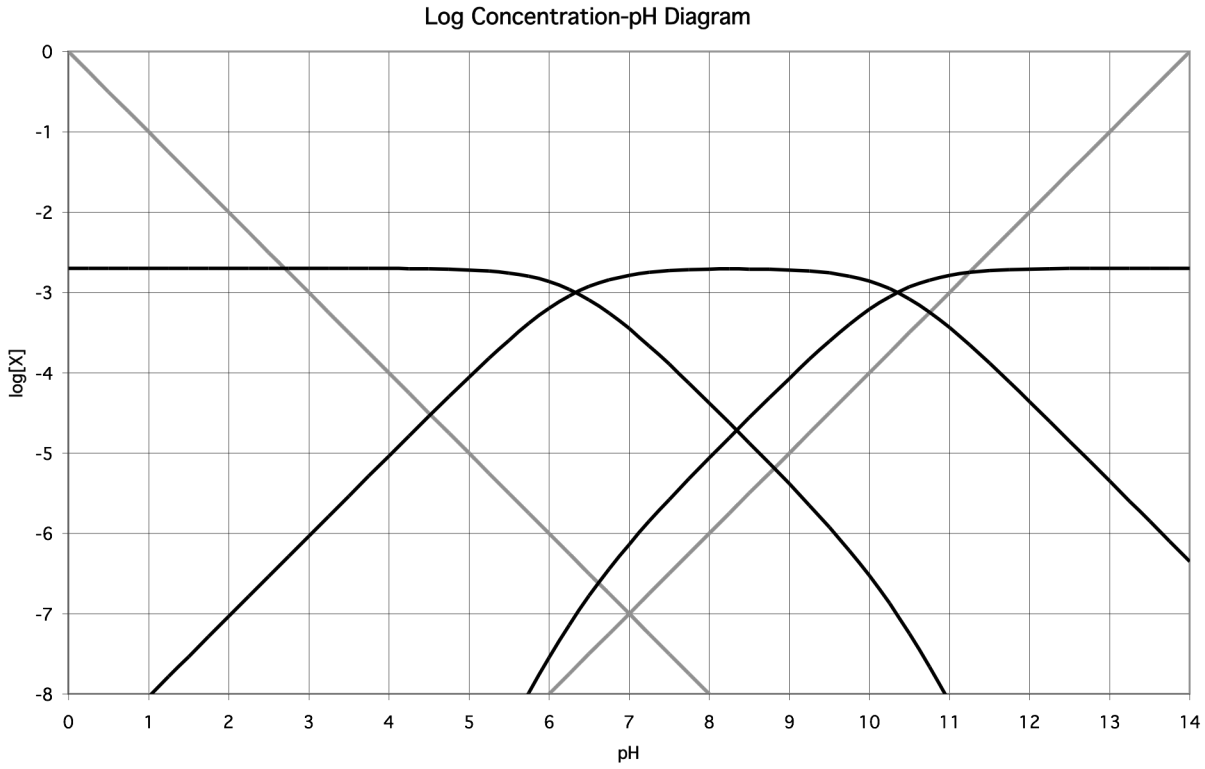
Evidence for Anthropogenic Inorganic Carbon and Water Export

Raymond, P. A., N.-H. Oh, et al. (2008). "Anthropogenically enhanced fluxes of water and carbon from the Mississippi River." *Nature* **451**(7177): 449-452.

1. The authors' state: "the water and dissolved inorganic carbon (DIC) exported by rivers are important net fluxes that connect terrestrial and oceanic water and carbon reservoirs." List the four components of dissolved inorganic carbon (we often refer to these as C_T).

2. Alkalinity is defined by the USGS as "the capacity of solutes in an aqueous system to neutralize acid." Assuming that alkalinity comes only from the dissolution of carbonate, what chemical species are used to define alkalinity? Another way to define alkalinity is "what is the proton balance for H_2CO_3? Why are these equivalent definitions?

3. Label all the lines on the log concentration (in M units) vs. pH diagram for a 2 mM solution on the figure below. What are the values of pK_{a1} and pK_{a2}?



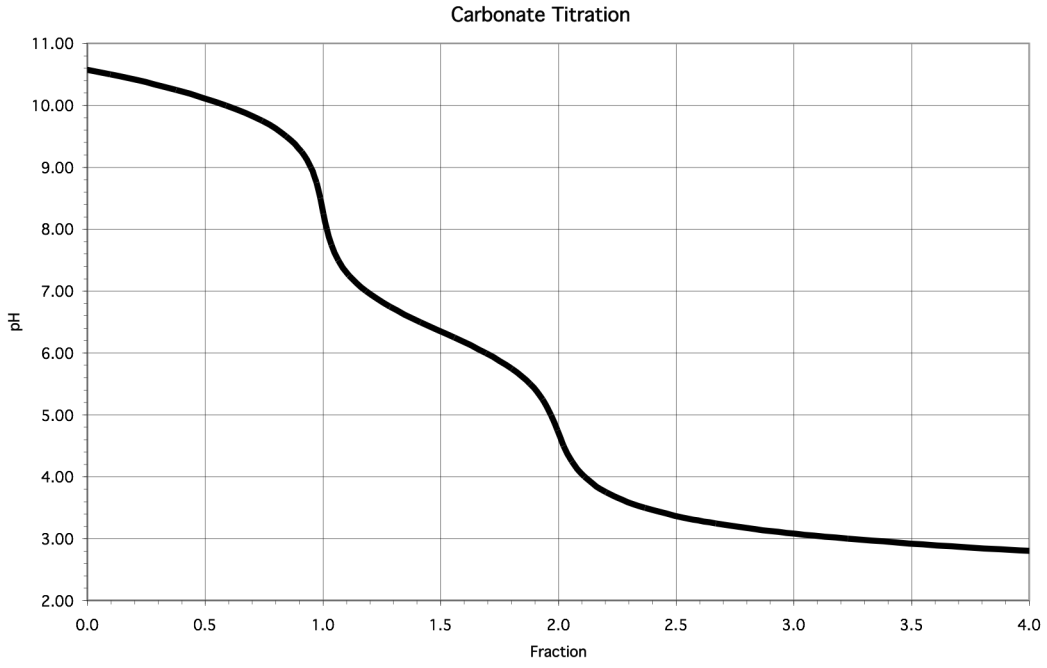
4. Alpha equations for a diprotic acid are a bit more complicated than for a monoprotic acid. What is the meaning of K_1 and K_2 in the equations?

$$\alpha_{H_2A} = \frac{[H_3O^+]^2}{[H_3O^+]^2 + K_1[H_3O^+] + K_1K_2}$$

$$\alpha_{HA^-} = \frac{K_1[H_3O^+]}{[H_3O^+]^2 + K_1[H_3O^+] + K_1K_2}$$

$$\alpha_{A^{2-}} = \frac{K_1K_2}{[H_3O^+]^2 + K_1[H_3O^+] + K_1K_2}$$

5. In the Raymond paper supplement, the authors' claim that DIC concentrations in the paper are calculated using data from alkalinity titrations. They state "alkalinity is generally from bicarbonate, with little contribution from carbonate in well-buffered rivers like the Mississippi." Using U.S. Geological Survey (USGS) temperature and pH measurements they estimate that on average ~93% of total dissolved inorganic carbon is in the form of HCO_3^-, with the remaining 7% being mostly $CO_{2(aq)}$. Assuming the equilibrium concentrations were calculated at 25°C, estimate (within 0.5 pH units) the average pH the authors assumed to get these numbers for the distribution of carbon? Explain.



6. The supplement implies that two acid-base indicators have been used historically for alkalinity determination, methyl orange and erythrosine. Methyl orange changes from red (base) to yellow (acid) with a $pK_a = 3.7$ and erythrosine changes from green fluorescence (base) to non-fluorescent (acid) with a pK_a of 4.1. Bromcresol green (BCG, the indicator we used) has $pK_a = 4.8$. According to the alpha and titration diagrams for Mississippi water, which indicator should give the best result? Explain. A proton balance may help. Was our choice of BCG for determining alkalinities of ~ 1 mM bicarbonate a good one? Explain briefly.

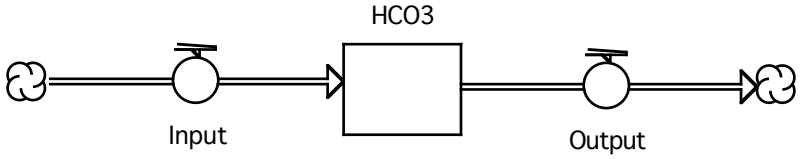
7. Chemical reactions, such as those written below, describe chemical weathering processes referenced in the paper. Where does the H_2CO_3 and $CO_2(aq)$ come from in soils for these weathering reactions? According to LeChatellier's Principle, does increased CO_2 in the soil promote or diminish chemical weathering?

$$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightleftharpoons 2Mg^{2+} + 4HCO_3^- + H_4SiO_4$$

$$2KAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightleftharpoons Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2K^+ + 2HCO_3^-$$

$$CaCO_3(s) + H_2CO_3(aq) \Leftrightarrow Ca^{2+}(aq) + HCO_3^-(aq)$$

8. The authors claim that the lower values in Figure 2 indicate transport limitation. Using the STELLA diagram below as a guide, briefly describe the input and output processes and how they describe a transport-limited situation. Why does transport limitation occur mostly in streams with low annual precipitation? How does transport limitation relate to weathering?



9. The authors rely on FaveD for many arguments in the paper. What is FaveD and why is it used?

10. The authors normalize all discharges to get FaveD in Figure 1, but it is a bit unclear from the text which number they use to normalize the flux data. Taking the point on the lower left of the graph from 1900 (460 km^3/year; 20 mgC/L), determine whether they used 494 km^3/year, 578 km^3/year or some other value for normalization by comparing your calculation to the data in the figure. Does it appear that they used the same number for all normalization calculations or a different number for different groups of years?

11. What is the best inference that can be made by FaveD increasing with greater precipitation as shown in Fig. 2? Explain.

12. Figure 3 shows the difference between agricultural areas (3b, 3d) and all areas (3a, 3c) where the slopes indicate $\frac{d(\Delta Q)}{d(\Delta P)}$ and $\frac{d(\Delta Q)}{d(\Delta Q)_{P_{average}}}$ where Q represents discharge and P represents precipitation. What inferences can best be made from the diagrams?

13. Explain briefly and clearly how the authors use the slope and y-intercept data from these graphs to determine which mechanism below is most likely to increase bicarbonate and water.

> Mechanism 1: Increases in water discharge increase total amounts of bicarbonate export, but imply no change in bicarbonate concentration.
>
> Mechanism 2: Increases in bicarbonate flux at equivalent discharge values represent net increases in mean bicarbonate concentration.

14. List three mechanisms that can explain why the slope in Figure 4 seems to increase as %cropland increases (at more than 60%). For each mechanism listed, briefly describe the physical basis for why it changes as it does.