Exercise 5. Chemistry of a Toxic Metal in an Estuary

This exercise concerns a problem on the Squeamish River and its estuary. To make it realistic, I am giving you a lot of verbiage and info in the problem, but the calculations themselves are quite straightforward.

The Squeamish River is in a rural part of the Pacific Northwest. The largest employer in that region is a cadmium plating plant that belongs to Cadmax, Inc. Cadmax supplies cadmium-plated parts to the electronics industry as well as to Boeing for use in aircraft. Cadmax has a permit, granted in 1983, to discharge waste water with an average total Cd conc. of about 1,100 mg/L (coming out of the pipe). For the past 20 years the state DEQ has ignored this remote operation, but now it must pay more attention. In the late summer of 2003, the "Friends of the Squeamish" filed a lawsuit in Federal District Court claiming the Squeamish is a "noncomplying waterway" with respect to Cd, under the Federal Clean Water Act as amended since the original permit of 1983. The relief sought in the suit is to enjoin the DEQ to establish a new Total Maximum Daily Load (TMDL) for Cd in the Squeamish, and set discharge limits on the Cadmax plant that will bring total Cd impacts back within current guidelines. (The DEQ has "primacy" in this state, which means that this state agency has the right and the responsibility to enforce federal regulations).

The case is slowly working its way through the legal system and the first hearings are scheduled for later in the spring. Cadmax has hired your consulting firm to do some studies of Cd chemistry in the estuary so the lawyers can best shape their case. Cadmax is notoriously cheap, however, and has given you only a very small contract for services.

The plant discharges a near-neutral-pH waste that is very dilute in all constituents except Cd. The Cd enters the river from a pipe near midstream and mixes with river water, forming a plume approximately 0.5 km long. This plume region is formally defined in the regulations as a "mixing zone" in which the regulations do not need to be met (i.e., dilution is allowed to occur). Downstream of the mixing zone, the plume is fully dispersed in the water and there follows a region in which the total Cd conc. is uniform everywhere. The river channel in this region has a nearly constant width and depth, so you can easily compute the Cd conc. immediately after the mixing zone as $Cd_T = 10^{-6}$ M

After the "uniform Cd zone", the river enters the estuary and begins mixing with seawater which, away from the estuary, contains only negligible Cd ($<10^{-9}$ M). Salinity data allow you to infer the composition of the water mixture throughout the estuary.

Your ultimate goal is to deploy an automated water sampler on a tethered buoy at three locations in a transect down the mainstem of the estuary at mean salinities of $S = 0, 10,$ and $30$ part per thousand (w/w; i.e, g/kg). The autosampler will collect hourly samples throughout a 24-h cycle of tides and aggregate them to create a single, tidal-cycle-averaged sample for each site.

Unfortunately, Cadmax wants to see some preliminary assessments from available data before they will pay the expense of field sampling. Fortunately for your budget, calculations are cheap.

Prepare a brief report for submission to the environmental compliance manager at Cadmax (Ms.
1. Assume the whole estuary and river is in equilibrium with atmospheric CO2.

2. Assume the clean river has negligible alkalinity and negligible major cations (is pure H2O)

3. Assume the ocean, for simplicity is a 30 parts per thousand (w/w) NaCl solution (ignore other seawater ions). The seawater has the typical seawater alkalinity of 1 meq/L.

4. The ocean dilutes the waste but increases the concentration of Cl-. Ignore any ion pairs that Na+ forms.

5. To keep things simple assume the CdCO3 solid otavite does not precipitate even if it is oversaturated.

6. Find the alkalinity and pH of the estuary water at 0, 10, 20, and 30 ppt salinity.

7. Determine the Cd speciation (species and their concentrations) at those 4 salinities. Plot data as suggested below.

8. The chief engineer at Cadmax is considering a new process in which the finished Cd-plated parts are washed in a solution of the organic chelating agent nitrilotriacetic acid (NTA). The solution is actually made up from the Na salt Na3NTA (sodium nitrilotriacetate, sold commercially as Trilon A™). The Trilon A wash solution is adjusted with HCl to pH 5-6 and used at a concentration of about 10 times the amount of Cd in the waste. Recalculate the speciation of Cd at the sampling points in the estuary if NTA is added to the discharge. Discuss the impact of the NTA on Cd speciation in the river water and in the estuary. Discuss the relative importance of NTA to Cd speciation in various parts of the system.

NOTE: NTA is a triprotic acid but if you look at the pKa values, it’s obvious that only ONE species is important over the whole pH range found in the estuary. However, the binding to Cd is via NTA3− which does vary with pH. So, easiest thing is to assume the total NTA is just given by dilution, but then define a pH-conditional K value (we’ll discuss this in class) at each location and use that to compute the Cd-NTA complexes. It’s really pretty simple when you see it (and you will in class).

Tips for Effective Report Data: Take a few minutes to think about what you would want to read if someone handed you the report you are creating. Step back and think about what is the most important finding of a particular run. The think about what is either equally important, or the second most important. Iterate a few times and you will soon find the level at which the information is no longer important enough to worry about. Remember: Information is a difference that makes a difference.

Cd is the obvious item of greatest interest; see next section for some ideas about this component. But besides Cd, what is the one chemical species that someone most want to see from your output. The choice is yours, but I’d probably pick the pH. It would be interesting and informative to know how the pH varies from the river to the sea, so I would plot pH as a function of salinity. Because we want to depict a causal relationship between two variables, make a scatter graph that plots pH on the
vertical axis against salinity on the horizontal. Because we assume there is a continuous connection among these data points in the real system, it is appropriate to connect the points with lines.

The next most interesting thing to a water chemist might be the alkalinity, which rises from river to sea. A really nice graphic would be to take the line/scatter graph of pH vs. salinity and then add a series of vertical bars along the x-axis depicting the alkalinity at each point. The left hand axis would show the pH scale and the right hand axis the scale for the alkalinity bars. At a glance, a reader would get both the pH and the alkalinity on the same graph for easy comparison, but they would also be clearly distinguished. Unfortunately, that sort of compound plot is beyond Excel's capabilities, but many graphics packages could produce such a plot, and I include the idea to stimulate your thinking. Here, you might just settle for two separate plots, placed next to each other for comparison.

**Ideas for the Cd and NTA Parts of the Problem.** Clearly, the total Cd in the system is of interest. In this case it depends only on dilution by seawater, but it is important to know how it varies so plot it vs. salinity. Also, the concentration of the "free" Cd\(^{2+}\) ion is important. A useful graph would be a scatter plot (connected with lines) of both data series (i.e., Cd\(_T\) and [Cd\(^{2+}\)]. That is a sort of "bottom line" plot for giving to the regulators to show the possible mitigating effects of natural and synthetic ligands (i.e., the ions that bind to the Cd like Cl\(^-\) and NTA).

Would also be worth showing stacked bar graphs depicting the various Cd species. Use vertical bars along a horizontal axis to give a general sense of the spatial relationship among the sampling sites. The height of bar will correspond to Cd\(_T\) and the stack will show the various species.

Although NTA is a weak triprotic acid the distribution of NTA among its acid species is less interesting than its associations with Cd\(^{2+}\).

It is also interesting to look at a "titration" plot: show \(-\log[\text{Cd}^{2+}]\) vs. \(-\log\text{Cd}_T\) (scatter plot, with lines). Plot both curves (with and without NTA) on the same graph for comparison. Note that a diagonal line across the graph corresponding to [Cd\(^{2+}\)] = Cd\(_T\) indicates the condition when there in NO binding of Cd at all, so you should sketch it in to give a useful reference line for the viewer. Be sure to explain this line in the caption.

**Tips for Effective Graphs:** Make sure you label all information clearly, either in text on the graphs or in separate captions. The rule is that a reader should be able to basically figure out the meaning of a graph from the caption and graph alone, without having to resort to the text. This is especially important if the report is going to a managerial type who will have no time to read the whole report but who will be drawn to your figures.

And, practice making clean and attractive graphs. Some Excel defaults add unnecessary clutter. Omit grid lines. Use a minimum of tickmarks on the axes. Do not use 3D bars or drop-shadows.