July 2, 1992

SUBJECT: Draft Report for SPECIATION MODELING for the Du Pont-Newport Superfund Site

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CEAM Manager
AERL

Attached is a draft report on the speciation modeling on the above Superfund Site for your review and comment. Please let us know, at your earliest convenience, if you have comments and suggestions. Also, please give me or Bob Ambrose a call to discuss future work at this site due to a rapidly changing technical assistance situation. In August, we must bring much of our Tech Assistance to a close.

Again, please feel free to call me (706 546 3324) or our on-site contractor tasked to do Technical Assistance, Kevin J. Novogradac, Ph.D. (706 546 3476) if you have any questions.

cc: file
This report summarizes the results of the speciation modeling conducted for the DuPont-Newport Site. The contaminants of concern at this site are barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and mercury (Hg). A qualitative description of the anticipated chemistry and concerns for all of these contaminants has been provided. Barium, cadmium, copper, and zinc have been modeled more extensively.

**Barium**

The modeling of barium proved more difficult than expected due to complications arising from the precipitation of barite (BaSO₄). It is surmised that barium is probably present as both barite and BaS₂ in the waste material deposited at this site. This conclusion is arrived at by examining the processes used at the site that first converted BaSO₄ to BaS₂ (a purification process) and finally back to BaSO₄ to produce a white paint pigment. It is likely that the BaSO₄ disposed at the site is not soluble at levels exceeding the MCL in the natural waters (computations have not been conducted to confirm this). BaS₂ is relatively water soluble and does pose a threat to water quality in the area. Also note that BaSO₄ can be reduced to BaS₂ and be remobilized if sufficient organic mater is present to achieve the very reducing conditions necessary for this conversion process.

Speciation modeling of barium solubility was conducted in three separate sweep runs. Data from site AS09 was used to establish the background chemistry and the system was assumed to be in equilibrium with atmospheric CO₂.

The first run assumes that both particulate organic material (POM) and amorphous iron oxyhydroxide (FEO) are present and that they can both adsorb Ba. The concentration of FEO was taken from AS07 data and is indicative of fine grained sediments such as overbank deposits. Lower levels of FEO may be more typical in other sediments at this site (AS12 may be indicative of the lower limit). If the concentration of FEO is decreased, a lower K_d would be expected. In this sense, the modeling reported here is not necessarily conservative. The results can be scaled if the K_d can be assumed to be linear in the range being examined. This applies at the lower concentrations presented in the graphs.

The concentration of POM was estimated from a measured TOC concentration as described in the MINTEQA2 v3.11 documentation and represents a high value indicative of wetland sediments. The results of this run are shown in Figure 1. The figure demonstrates that the primary control of Ba solubility at low concentrations is POM and that amorphous iron (FEO) does not reduce the Ba concentration as significantly. Also note that BaSO₄ is predicted to form at higher Ba concentrations. This modeling run predicts that a sediment concentration of 0.001 molal (moles of barium/sediment in contact with 1.0 kg of pore water) or less should not leach Ba at a level exceeding the MCL. Note that these results are very dependent on the continued presence of POM at this site.

The second MINTEQA2 sweep does not contain the POM component, and as such, predicts a more conservative allowable soil Ba level. In this case, precipitation of barite is the dominant solubility control and FEO does not effectively control Ba solubility. Soil concentrations not exceeding 0.0003 molal are predicted to leach Ba at levels below the MCL. See Figure 2.
Figure 1. Speciation of barium with POM and FeO.
Figure 2. Speciation of barium with FeO.
The third MINTEQA2 sweep is slightly more conservative than either of the previous sweeps in that the pH is fixed at a slightly lower value (6.0). The results of this run are essentially the same as the second run. See Figure 3.

Note that there is an increased uncertainty in these results due to the fact that SO$_4^{2-}$ levels control the mobility of Ba to a large extent. Also note that current conditions at the site indicate that Ba is leaching at levels that cannot be completely controlled by SO$_4^{2-}$. A more conservative approach may be necessary, wherein barite is not allowed to be a solubility control mechanism.

The higher MCL for barium (1.0 mg/l - 10 times greater than the fresh acute criteria for zinc) would probably cause less concern about this element than for zinc. Barium is not predicted to adsorb as strongly as zinc, but it is most likely present in the wetland sediments as a very insoluble precipitate (BaSO$_4$). This is true as long as conditions are not extremely reducing. If sulfate is converted to sulfide in the natural conditions then barium may be remobilized. Since the surface water in the region has a high sulfate level (30 - 60 mg/l) it is likely that a significant quantity of dissolved barium arriving at the wetland would precipitate as BaSO$_4$ in the wetlands. The most likely exposure route may be ingestion of sediments and that exposure route may drive the cleanup levels in the wetlands.

Cadmium

The presence of Cd at the Du Pont-Newport site is not surprising considering the quantity of Zn present. The chemical behavior of Cd is very similar to Zn and Cd often occurs as an impurity in Zn ores. Note that the levels of Cd are much lower than those for Zn.

- Both FEO and POM will be important in controlling the dissolved Cd concentration although FEO dominates in this process.
- Precipitation of Cd solids will not sufficiently control dissolved Cd levels in water in contact with those solids.

The results of three MINTEQA2 sweep runs performed on the data supplied for sample station AS09 are provided below. Both particulate organic material (POM) and amorphous iron oxide (FEO) adsorption routines were employed in the first run. The concentration of FEO was taken from AS07 and is indicative of fine grained sediments deposits. It is expected that lower FEO levels would be present elsewhere and may vary with depth (perhaps AS12 is indicative of a lower limit). POM was estimated from the measured TOC concentration (as described in MINTEQA2 v3.11 documentation) and represents a high value indicative of wetland sediments. The results of this run are shown in Figure 4.
Figure 3. Speciation of barium with FeO at pH = 6.0.
Figure 4. Speciation of cadmium with POM and FeO.
The predominant controlling factors in this run were POM, FeO, pH, and Cd. Many of the other parameters were not found to be of critical importance for Cd. Only at very high levels of Cd was precipitation predicted. The precipitate that is predicted is CdCO$_3$ (otavite) and it is a reasonable natural solubility control. Cd was predominantly adsorbed to the iron oxide phase.

The model predictions suggest that the bulk of the Cd is currently bound to FEO. A horizontal line corresponding to the MCL on the y-axis is drawn to the dissolved Cd line. The intersection of these two lines yield a soil cleanup criteria based on the drinking water MCL on the x-axis. Note that animals that ingest contaminated soil may not be protected by imposing a cleanup based on a drinking water MCL. ECAO may be able to help you in resolving this exposure route. Also note that a number of factors can affect the effectiveness of the sorbents present in the system.

The second MINTEQA2 run addresses the concern that organic matter (POM) may be reduced to a low concentration. See Figure 5. In this run, POM was removed from the modeling. The result is that a slightly lower soil cleanup level would be predicted. The impact of POM is not very great (approximately a factor of 2).

The third MINTEQA2 run addresses another worst case scenario where pH, the dominant control of the effectiveness of FEO adsorption, drops to 6.0. This assumes that a pH of 6.0 represents the lowest likely pH at this site. See Figure 6. POM was not used in this case. The predicted cleanup level is much lower - approximately 4.0E-06 molal. This value is more protective of wildlife and should probably be used since pH is known to vary substantially at this site. Note that this value is probably not low enough since soil ingestion may pose the dominant risk to wetland wildlife. Others should be consulted, possibly ECAO, to investigate other exposure routes.

Copper

The chemical behavior of Cu is very similar to the three other metals modeled at this site since they are all present as divalent cations.

- Both FEO and POM will be important toward controlling the dissolved Cu concentration at the current elevated levels. FEO dominates this process at the lower concentrations while POM is more important at higher levels of contamination.

- Precipitation of Cu solids will not sufficiently control dissolved Cu levels in water in contact with those solids.

The results of three MINTEQA2 sweep runs performed on the data supplied for sample station AS09 are provided below. Both particulate organic material (POM) and amorphous iron oxide (FEO) adsorption routines were employed in the first run. The concentration of FEO was taken from AS07 and is indicative of fine grained sediments. It
Figure 5. Speciation of cadmium with FeO.
Figure 6. Speciation of cadmium with FEO at pH = 6.0.
is expected that lower FEO levels would be present elsewhere and may vary with depth (perhaps AS12 is indicative of a lower limit). POM was estimated from the measured TOC concentration (as described in MINTEQA2 v3.11 documentation) and represents a high value indicative of wetland sediments. The results of this run are shown in Figure 7.

The predominant controlling factors in this run were POM, FeO, pH, and Cu. The other parameters were not found to be of critical importance for Cu. Only at very high levels of Cu was any precipitation predicted. A number of potential precipitates are predicted including malachite and cupric ferrite. Cu was predominantly adsorbed to the iron oxide at levels where the marine chronic criteria is not exceeded.

The model predictions suggest that the bulk of the Cu is currently bound to FEO. A horizontal line corresponding to the fresh acute criteria on the y-axis is drawn to the dissolved copper line. The intersection of these two lines yield a soil cleanup criteria based on the fresh acute criteria. Note that animals that ingest contaminated dirt may not be protected by imposing a cleanup based on an acute or chronic criteria for water. ECAO may be able to help you in resolving this exposure route. Also note that a number of factors can affect the effectiveness of the sorbents present in the system.

The second MINTEQA2 run addresses the concern that organic matter (POM) may be reduced to a low concentration. See Figure 8. In this run, POM was removed from the modeling. The result is that a slightly lower soil cleanup criteria would be predicted. The impact of POM is not very great (approximately a factor of 3).

The third MINTEQA2 run addresses another worst case scenario where pH, the dominant control of the effectiveness of FEO adsorption, drops to 6.0. See Figure 9. POM was not used in this case. The predicted cleanup criteria is much lower - approximately 5.0E-04 molal. This value is much more protective of wildlife and should probably be used since pH is known to vary substantially at this site. This assumes that a pH of 6.0 represents the lowest likely pH at this site. Note that this value is probably not low enough since soil ingestion may pose the dominant risk to wetland wildlife. Others should be consulted, possibly ECAO, to resolve this matter.

Chromium

Speciation modeling was not performed for this element. It is likely that any Cr present at this site, particularly in the wetlands, is present as Cr(III). If Cr(III) is the only form present, then it is not expected to be present in a soluble form. A common precipitate of Cr(III) is Cr(OH)₃ and it does not dissolve in exceedance of the MCL at a pH of 6.0 or above unless there are very unusual circumstances. It is possible that complexation by dissolved organic material could enhance the mobility of Cr(III) in the wetlands.
Figure 7. Speciation of copper with POM and FeO.
Figure 8. Speciation of copper with FeO.
Figure 9. Speciation of copper with FeO at pH = 6.0.
Lead

Speciation modeling has not been conducted on Pb; however, previous applications of MINTEQA2 to Pb have shown that Pb has a high affinity for FEO and is typically not very mobile. Any Pb present at the site is probably sorbed to the FEO surface and may reduce the availability of binding sites for the other metals.

Mercury

The speciation of mercury is quite complex and a number of concerns arise concerning mercury. Hg is potentially present in a number of different oxidation states ranging from (0) to (+2). The inorganic forms of mercury are considered much less toxic than the organometallic forms. The reason for the increased toxicity of the methylated forms lies in the fact that they are more readily absorbed and stored in fatty tissue. In fact, the methylated forms can be biomagnified much like pesticides. Speciation modeling does not address the issue of methylation in a satisfactory manner since the process is controlled by kinetics and is biologically mediated.

Zinc

The speciation of zinc in the wetlands at the Du Pont-Newport site was modeled using MINTEQA2 for a few different scenarios. The modeling indicates the following conclusions are valid:

- A reduction in the concentration of zinc in the sediments will be required to achieve dissolved zinc levels below the fresh acute criteria.
- Both iron oxides and solid natural organic material will be important toward controlling the dissolved zinc concentration at the current elevated levels.
- Iron oxide will be the dominant sorbent if the zinc levels in sediments are dropped below the level where an exceedance of the fresh acute criteria occurs.
- Precipitation of zinc solids will not sufficiently control dissolved zinc levels in water in contact with those solids.
- MINTEQA2 with iron oxide and POM adsorption modeling appears to reasonably quantify dissolved levels of zinc.

The results of three MINTEQA2 sweep runs performed on the data supplied for sample station AS09 are provided below. Both particulate organic material (POM) and amorphous iron oxide (FEO) adsorption routines were employed in the first run. The
concentration of FEO was taken from AS07 and is indicative of fine grained sediments. It is expected that lower FEO levels would be present elsewhere and may vary with depth (perhaps AS12 is indicative of a lower limit). POM was estimated from the measured TOC concentration (as described in MINTEQA2 v3.11 documentation) and represents a high value indicative of wetland sediments. The results of this run are shown in Figure 10.

The predominant controlling factors in this run were POM, FeO, pH, and Zn. Many of the other parameters were not found to be of critical importance for zinc. Only at very high levels of zinc was precipitation predicted (near conditions currently found at AS09). The precipitate that is predicted is ZnCO₃ (smithsonite). This is a reasonable natural solubility control. At intermediate levels the iron oxide sites became saturated and POM became the most important control of the dissolved zinc levels. At low concentrations, zinc was predominantly adsorbed to the iron oxide phase.

Note that when the zinc concentration in the filtered water sample is plotted against the sediment concentration the agreement with the model predictions is quite good (within an order of magnitude). This point is the hand drawn x on the plot. The site data suggests a slightly lower dissolved concentration than the model would predict. This is expected and can be explained in a number of ways 1) mixing of pore water with surface water, 2) lower levels of zinc in the sediments directly in contact with the water than indicated by the 0-6" sample, 3) an estimated FEO concentration. The MINTEQA2 results are indicative of the current pore water conditions (not measured at the site) and equilibrium conditions between overlying water and underlying sediments are not expected.

The model predictions suggest that the bulk of the zinc is currently bound to POM and will leach at levels well above the fresh acute criteria. A horizontal line (hand drawn) corresponding to the fresh acute criteria on the y-axis is drawn to the dissolved zinc line. The intersection of these two lines yield a soil cleanup criteria based on the fresh acute criteria (hand drawn vertical line). Note that animals that ingest contaminated dirt may not be protected by imposing a cleanup based on an acute or chronic criteria for water. ECAO may be able to help you in resolving this exposure route. Also note that a number of factors can affect the effectiveness of the sorbents present in the system.

The second MINTEQA2 run addresses the concern that organic matter (POM) may be reduced to a low concentration. See Figure 11. In this run, POM was removed from the modeling. The result is that a slightly lower soil cleanup criteria would be predicted. The impact of POM, even at these very high levels, is not very great (approximately a factor of 3).

The third MINTEQA2 run addresses another worst case scenario where pH, the dominant control of the effectiveness of FEO adsorption, drops to 6.0. See Figure 12. POM was not used in this case. The predicted cleanup criteria is much lower - approximately 3 m molar or 7.5 m moles/kg of sediment. This value is much more protective of wildlife and should probably be used since pH is known to vary substantially...
Figure 10. Speciation of zinc with POM and FeO.
Figure 11. Speciation of zinc with FeO.
Figure 12. Speciation of zinc with FeO and pH = 6.0.
at this site. This assumes that a pH of 6.0 represents the lowest likely pH at this site. Note that this value is probably not low enough since soil ingestion may pose the dominant risk to wetland wildlife. Others should be consulted, possibly ECAO, to resolve this matter.

Summary

A number of figures have been provided that show the absolute proportions of contaminant present in a dissolved, adsorbed, and precipitated form compared to the total amount of contaminant in a total sediment sample (includes pore water). In order to find a soil cleanup level based on a water quality criteria use the dissolved water line on the graph. Find the appropriate water concentration on the y-axis and read the corresponding total concentration from the dissolved line off the x-axis. Similarly, a water concentration can be predicted from a soil level by reversing the process.

The $K_d$ can be calculated by dividing the concentration of contaminant present in the adsorbed phases by the dissolved concentration. These values can be read off the y-axis from the corresponding lines in the chart for any total concentration. The $K_d$ calculated from the charted concentrations will be unitless and may need to be converted to the units L/kg using density and pore volume values.

Should the concentration of FEO or other adsorbents be considered to be too high, the $K_d$ can be converted. Note that this is only true in the linear $K_d$ range and each sorbent needs to be considered separately. This approximation should be valid for any of the contaminants at or near the quoted water quality criteria.
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