APPENDIX M

Response to Peer-Review Comments on MINTEQA2 Model Results

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Peer review of the SSL MINTEQA2 model results identified several issues of concern, including

- The charge balance exceeds an acceptable margin of difference (5 percent) in most of the simulations. A variance in excess of 5 percent may indicate that the model problem is not correctly chemically poised and therefore the results may not be chemically meaningful.

- The model should not allow sulfate to adsorb to the iron oxide. Sulfate is a weakly outer-sphere adsorbing species and by including the adsorption reaction, sulfate is removed from the aqueous phase at pH values less than 7 and is prevented from participating in precipitation reaction at these pH values.

- Modeled K_d values for barium and zinc could not be reproduced for all studied conditions.

The remainder of this Appendix addresses each of these issues.

Charge balance in the MINTEQA2 model runs

Although the charge imbalances (e.g., 6.8% at pH 8.0 and 54.9% at pH 4.9) are present especially at high and low pH conditions, the conclusion that the charge imbalance makes the model results not chemically meaningful is not warranted.

MINTEQA2 uses two primary equations to solve chemical equilibrium problems: the mass action equation (also called the mass law equation) and the mass balance equation. MINTEQA2 does not use the charge balance equation to obtain the mathematical solution of the equilibrium problem. This does not mean that the charge balance equation has no meaning in MINTEQA2 calculations.

The reviewer's concern is understandable. It is logical that any chemical system whose charges are not in balance must be incomplete or have erroneous concentrations for one or more components. However, the systems being modeled here are not "real" systems in the sense that they physically exist somewhere so that measurements can be made on them. Rather, they are generic, representative systems for ground water with variable (high, medium, low) concentrations of those parameters that most significantly impact K_d.

The modeled groundwater consists of national median concentrations of those major cations and anions that are most likely to impact the chemistry of the trace metal of interest by: (1) their complexation with the trace metal, (2) their competition with the trace metal for sorption sites, and/or (3) their effect on the ionic strength of the solution and thus, the activity coefficients of all species in solution including the trace metal. The settings of the three components of this representative system that have the greatest impact on the calculated K_d for various trace metals are systematically varied. The three "master variable" components are pH, iron hydroxide sorption site concentration, and concentration of natural organic matter (particulate and dissolved).

No attempt was made to reconcile charge balances at the different settings of the three master variables. If reconciling charge balance had been attempted, it would have been accomplished by adjusting the concentrations of relatively inert anions and cations (e.g., NO_3^-, Na^+) as needed to balance the charge at equilibrium. It would be unwise to adjust the concentrations of more reactive components (e.g., CO_3^{2-}, Ca^{2+}). To do so would be inconsistent with the initial assumption that those constituents could be adequately represented by median concentrations observed in ground water and that variability in the system could be captured by varying the three master components.

Table M-1 shows the result if the concentrations of the less reactive components NO_3^- and Na^+ are adjusted in the high and low pH model runs so as to give a charge imbalance of <5% at equilibrium. The results shown pertain to the medium iron hydroxide and medium natural organic matter settings for zinc at the pH values listed. As shown in the table, the K_d values computed differ little from those presented in this report. The expected degree of error in the K_d values due to the many simplifications and assumptions involved in generic modeling must surely exceed the variance due to charge imbalance.

Table M-1. K_d values with and without counter ions (Na^+ or NO_3^-) added to balance charge.

pH	K_d[1] (L/kg) No Counter Ion Added	K_d[1] (L/kg) With Na^+ or NO_3^- Added
4.9	1.61	1.51
8.0	16,161	16,135

[1] K_d values shown correspond to the medium iron hydroxide, medium natural organic matter settings. Counter ions were added to reduce charge imbalance to <5% at equilibrium.

Sulfate adsorption in MINTEQA2 model runs

The peer reviewer states that sulfate should not be allowed to adsorb to the iron oxide. The reviewer concludes that by including the adsorption reactions "sulfate is removed from the aqueous phase at pH values less than 7 and is prevented from participating in precipitation reactions at these pH values".

The sulfate adsorption reactions on iron oxide included in the MINTEQA2 model runs were taken from a database of adsorption reactions that has been shown to give reliable results in predicting sulfate adsorption on pure phase iron oxide (Dzombak, 1986). The reviewer is correct in that free sulfate concentration is enhanced at low pH in runs without sulfate adsorption relative to runs with sulfate adsorption. However, for runs with low contaminant trace metal concentrations from which the SSL K_d's were taken, metal-sulfate precipitates do not form regardless of whether sulfate adsorption is included or not. Also, the K_d values over the entire range of trace metal concentrations modeled do not differ significantly when sulfate adsorption is included versus excluded.

Test runs were conducted on barium, zinc and cadmium at various settings of the three master variables (pH, natural organic matter (NOM) concentration, and iron oxide (FeOX) sorption site concentration). Table M-2 shows the K_d values for the lowest and highest trace metal concentration for model runs with and without sulfate adsorption. Results are shown for barium, zinc and cadmium at the indicated settings of the master variables. Where results differ for the "with" and "without" sulfate adsorption cases, it is most frequently due to the formation of aqueous complexes between the trace metal and sulfate that compete with trace metal adsorption reactions, especially at low metal concentrations.

Table M-2. K_d values calculated with and without sulfate adsorption reactions.

Metal (settings)	K_d[1] (L/kg) with SO_4 adsorption	K_d[1] (L/kg) without SO_4 adsorption
Ba (MMH)	2.01 - 0.10	2.01 - 0.10
Ba (MMM)	1.37 - 0.04	1.37 - 0.04
Ba (LMM)	0.59 - 0.04	0.59 - 0.04
Ba (LLM)	0.12 - 0.01	0.12 - 0.01
Ba (LLL)	0.12 - 0.01	0.12 - 0.01
Zn (MMH)	1537 - 863	1478 - 830
Zn (LMM)	1.61 - 0.42	1.57 - 0.41
Zn (LML)	1.46 - 0.26	1.43 - 0.25
Cd (LMM)	0.94 - 0.01	0.91 - 0.01

[1] K_d range shown corresponds to the lowest and highest trace metal concentrations. Master variable settings are indicated by a three letter code for each model run: the leftmost letter indicates pH, the middle letter represents the NOM concentration, and the rightmost letter indicates the concentration of FeOX adsorption sites (eg., HLM indicates high pH, low natural organic matter, medium and iron oxide site concentration).

Reproducing RTI results for barium and zinc

The peer reviewer had difficulty reproducing the K_d values computed for barium and zinc. The reviewer included two sample input files for MINTEQA2 that had failed to produce results similar to the SSL calculations.

The SSL results can be reproduced for all metals using the current version of MINTEQA2 (v3.11) distributed by EPA. As indicated in the 1994 Technical Background Document, a modified version of this model was used to calculate SSL K_ds. The current version can be used to calculate the same results by performing the following steps:

1) Edit the v3.11 component database file COMP.DBS to insert a component to represent particulate organic matter (POM). Use the 3-digit identifying number 251, a charge of -2.8, and a molar mass of zero.
2) Edit the v3.11 file THERMO.DBS to add the metal POM reactions shown in Appendix H of the RTI draft report. The file DATABASE.DOC included with MINTEQA2 v3.11 gives detailed instructions for modifying the database file. After all reactions are added, del or rename the current THERMO.UNF and TYPE6.UNF files and execute program UNFRMT (included with v3.11) to create new *.UNF files.

3) Observe that there were two modifications to v3.11 that make calculation of K_d in L/kg easier in the version used by RTI. Since those modifications are not present in v3.11 itself, the user must take care in computing K_d. The procedure is to first obtain the calculated concentration of the metal of interest (say, barium) bound with POM from PART 3 of the output file. If you have set the solid precipitation flag to print a report each time a solid precipitates or dissolves, there will be a series of PART 3 outputs each corresponding to a precipitation or dissolution event. You must be sure that the PART 3 output from which you obtain the metal-POM concentration is the equilibrium output (i.e., it occurs prior to the PART 5 EQUILIBRATED MASS DISTRIBUTION with no intervening PROVISIONAL MASS DISTRIBUTION). After obtaining the metal-POM concentration, locate the line corresponding to the trace metal of interest, say barium in the PART 5 EQUILIBRATED MASS DISTRIBUTION section. Obtain the total sorbed concentration value and to this value add the concentration of metal-POM species. This is necessary because v3.11 recognizes only components with number 811 through 859 as sorption components. The metal-POM concentration will not have been added in the sorbed column. It will instead have been included in the dissolved column, so subtract the metal-POM concentration from the dissolved total. Finally, to compute K_d, take the ratio of sorbed over dissolved (after the adjustment for metal-POM). The resulting K_d must be divided by 3.1778 kg/L (the mass of soil that one liter of solution is equilibrated with) to express the result in L/kg.

If the above three steps are followed, the v3.11 MINTEQA2 will give the same result as in the 1994 Technical Background Document provided the data in the input file is correct. The two input files sent designed by the reviewer did not give correct results even when these steps were followed because of faulty values in the input file. The files supplied by the reviewer (SSLBA.INP and SSLZN.INP) were correct in all respects except two:

1) The site concentration for the POM component at the medium setting was entered as 1.930×10^3 mg/L. This value was evidently obtained from the table on page 33 of the EPA report (US EPA, 1992) after converting to mg/L. This is not the correct value for this the POM component. The correct value is 9.31×10^{-4} mol/l and is found in the table on page 38 of EPA report.

2) The iron oxide adsorbent is represented by two site types (components 811 and 812). The high population site has a lower affinity for the iron oxide surface for metals (expressed in a smaller log K in the adsorption reactions involving metals). For a particular metal, say, zinc, it will be noted that there are two reactions in the database of 42 iron oxide adsorption reactions (FEW-DLM.DBS). This three-digit component number associated with the reaction having the smaller log K of the two is the number to that must be used for the high population site. That is, component 812 should be entered at the higher site concentration and 811 at the lower site concentration. The set of site concentrations is given on page 44 of the EPA report. In the sample input files, component 811 was associated with the high site concentration and 812 with the lower.

After correcting these two errors and observing the special requirements of using of v3.11 as indicated above, the K_d values obtained using MINTEQA2 v3.11 with the peer reviewer's files were virtually identical to the SSL results.

References

Dzombak, D.A., 1986. Toward a Uniform Model for the Sorption of Inorganic Ions on Hydrous Oxides. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA.

US EPA (Environmental Protection Agency), 1992. Background Document for Finite Source Methodology for Wastes Containing Metals. HWEP-S0040. Office of Solid Waste, Washington, DC, 68 pages.