CHANGES IN THE MINTEQA2 MODELING PROCEDURE FOR ESTIMATING METAL PARTITION COEFFICIENTS IN GROUNDWATER
FOR
HWIR99

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July 1999

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ACKNOWLEDGMENTS

A number of individuals have been involved with the development of the modified modeling procedure used with MINTEQA2. Dr. Zubair A. Saleem of the U.S. EPA, Office of Solid Waste, provided overall technical coordination and review throughout this work. The revision of the thermodynamic database for the MINTEQA2 geochemical speciation model was performed by Dr. Jerry Allison of HydroGeologic, Inc. and Mr. Terry Allison of Allison Geoscience Consultants, Inc. for the U.S. EPA, Office of Research and Development, National Exposure Research Laboratory, Ecosystems Research Division under contract No. 68-C6-0020. Dr David S. Brown of the U. S. EPA served as Work Assignment Manager for the database revisions and advised on other issues concerning speciation of metals.

1.0 INTRODUCTION

The model and modeling procedure used in estimating metal partition coefficients for the groundwater pathway were similar to that used in previous modeling described in U.S. EPA (1996). The changes in the current modeling procedure relative to that described in U.S. EPA (1996) were:

- An improved thermodynamic database was used
- An expanded database of hydrous ferric oxide sorption reactions was used
- An expanded database of metal-organic matter reactions was used
- Additional metals were included in the modeling
- The hydrous ferric oxide content was adjusted
- The ionic strength was held at a constant value
- No trace metal solids were allowed to precipitate
- The concentration of leachate organic acids was held constant

Each of these changes and the resulting impact on the computed metal partition coefficients are discussed separately in the following sections.

2.0 IMPROVED THERMODYNAMIC DATABASE

The thermodynamic constants (equilibrium constants and enthalpies of reaction) for inorganic species in the MINTEQA2 database have been updated and new species have been added. The updates and additions to the database are described in the supplement to the MINTEQA2 user manual for version 4.0 (U.S. EPA,1998a). The main objectives of the revisions in the database were to insure that the most recent and accepted thermodynamic data are included and to add data for some metals for which the database was incomplete. Approximately 230 new inorganic species were added to the database. The electronic database *Critical Stability Constants of Metal Complexes Database* (versions 2.0, 3.0, and 4.0) published by the National Institute of Standards and Technology (NIST, 1998) was used as the main data source for updating thermodynamic constants and for adding new reactions.

The impact of updating the thermodynamic database on the computed partition coefficients was not significant for most metals. In the previous modeling, the partition coefficients for beryllium (Be) could not be computed using MINTEQA2 because of the inadequate thermodynamic database. The updated database has allowed Be partition coefficients to be computed. For metals that were well represented in the database prior to the update, the impact on partition coefficients arising from changing some of the equilibrium constants was generally not significant.

3.0 EXPANDED DATABASE OF HYDROUS FERRIC OXIDE SORPTION REACTIONS

The database of reactions for sorption on hydrous ferric oxide (HFO) has been expanded. Details of the additional reactions are described in U.S. EPA (1998b). Reactions were added for the metals and metalloids: arsenic (As), antimony (Sb), beryllium (Be), chromium(VI), cobalt (Co), selenium (Se), and vanadium (V). The source of these data was a consistent set of sorption reactions presented in Dzombak and Morel (1990). Techniques similar to those described in Dzombak and Morel (1990) were used to estimate reaction equilibrium constants for thallium (Tl) with HFO. In addition, the equilibrium constants for some metals that were in the MINTEQA2 HFO database already were updated with values from Dzombak and Morel (1990).

The impact of the expanded HFO database on estimated metal partition coefficients is significant only for those metals that previously could not be modeled with MINTEQA2 because the reactions were not present. Changes in equilibrium constants for metals that were represented in the HFO database already were too slight to have substantial impact.

4.0 EXPANDED DATABASE OF METAL-ORGANIC MATTER REACTIONS

MINTEQA2 represents dissolved organic matter (DOM) as a mixture of many types of metal binding sites. The probability of occurrence of a binding site with a particular log K is given by a normal probability function defined by a mean log K and standard deviation in log K. A limitation of the DOM binding calculations in MINTEQA2 and similar models is that the metal-DOM reactions necessary to obtain results are available only for a limited number of metal cations and for none of the anionic metals. For the metals Ag, Co, Hg, and Tl, it was necessary to estimate the mean log K for DOM binding for use in MINTEQA2. The mean log K values for Ag, Co, and Tl were derived from a linear free-energy relationship using the first hydrolysis constants and the binding constant for acetate. For Hg, the mean log K was estimated from binding constants for humic- and fulvic acid as given by Tipping (1994). As in previous modeling, the POM reactions were assumed to be the same as those of DOM. However, in the previous modeling the charge on all POM species was treated as zero. In the current modeling, the charge on POM is treated in the same way as that of DOM.

The impact of including reactions for DOM and POM for Ag and Hg on the estimated partition coefficients is variable. Including DOM reactions tends to increase the equilibrium dissolved metal concentration resulting in reduced K_d values. Including POM reactions tends to increase the equilibrium sorbed concentration resulting in increased K_d values. The net impact depends upon the value of pH and the relative concentration of DOM and POM, and upon the concentrations of major ions that also bind with organic matter.

5.0 ADDITIONAL METALS

Changes in the MINTEQA2 databases discussed above made it possible to use the model for several metals not included in the previous MINTEQA2 modeling. The newly included metals were antimony, arsenic, beryllium, cobalt, chromium(VI), selenium, thallium, and vanadium.

6.0 ADJUSTMENT OF THE HYDROUS FERRIC OXIDE CONTENT

The concentration of hydrous ferric oxide sorbent included in the MINTEQA2 runs was decreased by a factor of 10. This reduction was deemed appropriate in response to a comparison of MINTEQA2 estimates of K_d versus those reported in the literature for soils (U.S. EPA, 1999). In addition, the reduction was made in recognition of the limited data available on HFO content and the uncertainty in measurements of binding capacity of HFO in soils. The reduction factor of 10 was decided upon by comparing the MINTEQA2 estimates of K_d with those obtained in a literature survey for two cationic and two anionic metals well represented in the literature (Cd and Pb, and As and Cr(VI), respectively). The HFO content was adjusted until the model response gave a range that approximated the range of observed K_d values for those metals.

The reduction in the HFO content produced the greatest effect on K_d values among all the modifications in parameters and procedure. The direction of change was unformly towards reduced K_d, but the magnitude was quite variable. Generally, metals with stronger affinity for HFO binding (e.g., Cr(III), Pb) were more affected that those with lower affinity (e.g., Ag, Cd). Likewise, the impact was generally greatest for cases where the pH favors HFO sorption (high pH for cationic metals, low pH for anionic metals) and less pronounced where sorption is not favored (low pH for cationic metals, high pH for anionic metals).

7.0 TREATMENT OF IONIC STRENGTH

The ionic strength was held constant at 0.005 M for all MINTEQA2 simulations. In previous modeling, the ionic strength was computed based on the background chemistry specified. However, as pointed out by some reviewers, the background chemistry is simplistic and probably not adequate to represent variability in the ionic strength. Use of a constant ionic strength provides a consistent basis for calculation of activity coefficients. The value of 0.005 M was selected after exercising the model at values of 0.01 and 0.001 M and observing the effect on the computed K_d values for Cd and Pb at each of the three pH values used in the modeling. The variability in K_d induced by changing the ionic strength within these bounds was deemed less than the uncertainty in K_d due to uncertainty in input parameters and unaccounted for effects.

The impact on the estimated metal partitioning coefficients is variable in direction and magnitude among the different metals and settings of pH and other variables. However, the effect is generally expected to be insignificant compared with other factors.

8.0 NO TRACE METAL SOLID PHASES

Only solid phases of major ions (e.g., Fe, Al hydroxides, calcite) were allowed to precipitate in the MINTEQA2 model runs. Solid phases involving the metals of interest were allowed to precipitate in the previous modeling, but it was observed that this had little effect on K_d. Precipitation only occurred at very high metal concentrations. The impact was to temporarily stabilize K_d until the co-precipitating major ion was exhausted.

The impact on the metal partition coefficients of allowing only the major ions to precipitate as solid phases was not quantified. However, the occurrence of metal precipitates only at very high total concentrations in the previous modeling and the degree of impact on K_d when precipitation did occur makes it improbable the impact could be significant.

9.0 CONCENTRATION OF LEACHATE ORGANIC ACIDS

Only the low setting of leachate organic acids was used in the current modeling. Previous modeling employed low, medium, and high concentrations in MINTEQA2, but the results were indexed by the setting (the leachate organic acid concentration constituted a “master variable”). Only the K_d values associated with the low setting were used in for industrial scenarios.

10.0 REFERENCES

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