PEER REVIEW OF EPA'S HAZARDOUS WASTE IDENTIFICATION RULE RISK ASSESSMENT MODEL

MINTEQA2/PRODEFA2 Version 4.0

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NOTE

This report was prepared by Eastern Research Group, Inc. (ERG), an EPA contractor, under Contract Number 68-W-99-001. The report presents comments provided by peer reviewers on the MINTEQA2/PRODEFA2 Version 4.0 model, and *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0* and *Diffuse-Layer Sorption Reactions for use in MINTEQA2 for HWIR Metals and Metalloids* supporting documents that were used in EPA's Hazardous Waste Identification Rule risk assessments.

The comments presented in this report have been compiled by topic and by individual peer reviewer. As EPA requested, this report provides the peer review comments exactly as they were submitted to ERG. Also attached are the original comments submitted by each individual reviewer.

July 21, 1999

CHARGE TO PEER REVIEWERS

Peer Review of:

MINTEQA2 / PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0

INTRODUCTION AND BACKGROUND:

The MINTEQA2 / PRODEFA2 Geochemical Assessment Model for Environmental Systems (MINTEQ) is a component part of the methodology the Office of Solid Waste (OSW) is considering for use in the Hazardous Waste Identification Rule (HWIR). MINTEQ, Version 3.0 was used to analyze solution / solid phase equilibria and sorption behaviors of metals contaminants in the previous OSW proposal known as HWIR95. During an extensive series of reviews on that proposal, the EPA Science Advisory Board (SAB) and others urged the Agency to update the primary thermodynamic databases that are internal to MINTEQ. These databases were mostly compiled some years ago, and the Agency agreed that they were in need of updating to incorporate currently available data sources. As a part of the process for developing the methodology for HWIR99, the MINTEQA2 / PRODEFA2 codes and databases have been substantially revised and updated. These changes involved the following aspects:

Database Revisions:

* Update of the main thermodynamic databases

* Development of a new database for Diffuse-Layer sorption reactions for metals and metalloids

* Addition of reference citations to the thermodynamic database

Code Modifications:

* Addition of Gaussian model for dissolved organic ligands

* Modifications to minimize violations of Gibb's Phase Rule

* Other changes, including:

    - improvements in execution speed
    - modifications to minimize non-convergence
    - modifications for modeling titrations

- modifications to facilitate specialized output
- modifications for customized database filenames
- elimination of known errors in earlier versions

The overall plan for development of the HWIR99 methodology (ORD / OSW Integrated Research and Development Plan for the Hazardous Waste Identification Rule) underwent review in Phase I of the overall peer review plan. In the present Phase II reviews, the Agency is implementing peer review of key modeling components that are anticipated for use as part of the HWIR99 methodology. The revised MINTEQ codes and databases, along with several other modules, are included in that. Each module will be independently reviewed. This particular review segment focuses on the Version 4.0 MINTEQA2 code, its associated preprocessor PRODEFA2, the internal thermodynamic databases, and the specialized database of reactions necessary to drive the internal Diffuse-Layer sorption model option that will be employed for predicting sorption behavior of metals and metalloids in the envisioned HWIR99 modeling approach.

MATERIALS OFFERED FOR REVIEW:

Two documents describing the above modifications and updates are offered for review. The first is a supplement to the Version 3.0 MINTEQA2 / PRODEFA2 user's manual describing both code modifications and revisions to the main thermodynamic databases. It is entitled, MINTEQA2 / PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0. This document includes a revised listing of the primary thermodynamic databases. The second is a description of the methods and data compiled for driving the internal Diffuse-Layer model calculations to be used in the HWIR99 methodology for estimating partitioning behavior of metals and metalloids. It is entitled, Diffuse-Layer Sorption Reactions for use in MINTEQA2 for HWIR Metals and Metalloids.

Also offered for review are the Version 4.0 executable codes. Documentation on the earlier version of MINTEQ is provided as reference material.

CHARGE TO REVIEW PANEL:

The overall goal of the HWIR99 development effort is to develop a methodology suitable for determining constituent-specific waste stream concentrations that represent a threshold below which Subtitle C disposal will not be required, and thus the waste may "exit" the hazardous waste management system. Since HWIR99 is to be a risk-based rule, the intent is to set exit levels such that no significant risk to human or ecological health shall occur as the result of implementing the new exit levels. In characterizing risks, HWIR99 will employ mathematical models to simulate the multimedia release of contaminants from land-based waste management units, their multimedia transport, and the subsequent exposure and risk to human and ecological receptors. In so doing, it is intended to address the major review comments obtained on the earlier proposal.

The HWIR99 methodology embodies six general objectives: 1) developing a revised risk-based assessment strategy, 2) developing a site-based multimedia, multi-pathway exposure

and risk model, 3) developing the required assessment databases, 4) developing a computer-based technology for implementing the strategy, 5) developing a sound science foundation for the assessment, and 6) conducting the necessary peer reviews. In addition, the methodology under development is framed by a number of assumptions that are elaborated in the overall plan. In brief, these are: 1) concentration limits to be determined are chemical-specific, 2) receptors of concern are within a 2 km radius of the site, 3) human and ecological impacts of exposure are based on near-field, long term exposure, 4) the total mass of a given chemical in the waste management unit (WMU) is finite, 5) mass balance is conserved at the source at all times, 6) calculation of measures of protection is performed at the site level and aggregated over sites to estimate National statistics, 7) waste management units are located as indicated in OSW's industrial Subtitle D database, 8) impacts on receptors are calculated from the beginning of the site operation and until a maximum time when all impacts are included, and 9) receptors will be subject to exposures from all pathways simultaneously.

The HWIR99 technical approach is based on the Agency's risk paradigm and is composed of five basic elements as follows:

* Assessment Strategy
* Assessment Data
* Assessment Model
* Science Support
* Peer Review

The HWIR research plan (reviewed earlier) provides an overview of how these elements are combined to produce the technical basis for developing the exit levels described earlier.

Since HWIR99 is a direct attempt to improve the hazardous waste management regulations by addressing important limitations identified in a previous peer review process (SAB and others of HWIR95), the most important feedback needed for this specific MINTEQ module review is an indication of the adequacy of the current MINTEQ code and database revisions for that intended purpose. Review panelists should focus their efforts on providing an informed answer to that question, as well as providing recommendations for improvements that are practical and implementable in the time frame involved, if at all possible. In so doing, it is asked that each panelist address the following component aspects of this general question:

1) Did the process for revising the main thermodynamic databases utilize the appropriate sources? What others, if any, should specifically be investigated?

2) Was the process for compiling data on reactions for implementation of the Diffuse-Layer model option appropriate? How might it have been improved?

3) Is the implementation of the Gaussian model for addressing dissolved organic ligand reactions in MINTEQ appropriate?

4) Are the modifications to address Gibb's Phase Rule violations appropriate?

5) Are the modifications to minimize non-convergence appropriate?

6) Are the other code modifications including those for 1) increased execution speed, 2) modeling titrations, 3) specialized outputs, 4) customized database filenames, and 5) correction of known errors, adequate and useful?

Reviewer Comments Summary Report for
MINTEQA2/PRODEFA2 Version 4.0

Charge 1: *Did the process for revising the main thermodynamic database utilize the appropriate sources? What others, if any, should specifically be investigated?*

Dr. Dudley

The appropriate sources were considered and the proper corrections of the equilibrium constants to standard state conditions were performed when necessary. Two other thermodynamic databases, Lindsay (1979) and Parker et al. (1995) were consulted in this review as one way of checking on missing equilibrium constants for potentially important reactions. Time restrictions for this review did not permit an exhaustive review of the database. Instead, the review focused on species where the differences would be most likely such as in components added in the revision. Although the compilation of Lindsay (1979) is older than the database used with MINTEQA2 v.3.1, it contained a number of equilibrium constants for solution and solid phases that were not in the MINTEQA2 3.1 database and was the source of a database that a large number of MINTEQA2 users preferred. The stability constants in Lindsay (1979) are, by and large, in the revised database. The thermodynamic database of Parker et al. (1995), for the model GEOCHEMPC, was developed in California for use in understanding bioavailability and solution speciation of many HWIR contaminants. Database entries of U, V, As, B, Be, Sr, and Sn were selected for a comparison of Parker and MINTEQA2 databases. The Parker database contained additional entries for UO_2Cl^+, $BeSO_4$ (aq), a number of Sr complexes and significantly more complexes of B and As. The Parker database is available on the web at http//:envisci.ucr.edu/faculty/dparker/default.htm, is reasonably well referenced, and should be consulted for additional possible entries to the MINTEQA2 database.

The only chelating agent incorporated in the MINTEQA2 database is ethylendiaminetetraacectic acid (EDTA). The lack of other chelating agents is a noticeable deficiency in the database. Chelating agents have been proposed for use in phytoremediation of metal and metalloid waste sites. Incorporation of thermodynamic constants for chelating agents such as diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), and hydroxyethylethylenediaminetriacetic acid (HEEDTA) would facilitate the use of MINTEQA2 in understanding the effects of chelate addition on bioavailability and the potential for off-site transport of chelated metals. Stability constants for reaction of HWIR metals Zn, Cu, Cd, Pb, Mg, Ni, Co, Hg, and Ag as well as important competing reactions with Ca, Mg, and Fe may be found in Lindsay (1979). Parker et al. (1995) also contains data for a number of chelating agents.

Dr. Johnson

In general I believe that the processes used to revise the main thermodynamic databases are appropriate and complete. State-of-the-art sources of thermodynamic data were used. The additions of Be(II), Co(II and III), Mo(VI) and Sn(II and IV) are essential to the use of MINTEQA2 for the HWIR99. The process of data reduction provided a consistent data set. The

quality assurance system should have practically eliminated the errors that commonly occur in large-scale data manipulation.

However, another search for aqueous species that are important in environmental behavior of metals would be worthwhile. For example, the aqueous species of molybdate paired with sodium, potassium and calcium are not in the data base. In alkaline solutions, these species have been shown to control the dissolved concentrations of molybdenum (Essington, 1990). In addition, the database does not appear to contain the methylated forms of arsenic and mercury which are known to affect the dissolved concentrations as well as toxicity, particularly under anaerobic environments.

In the discussion of data reduction in the User Manual Supplement, it is noted that for reactions in which the enthalpy is not available, zero is entered and the equilibrium constant is incorporated without correction to 25 degrees. It would be helpful if these equilibrium constants were marked so that the user could exercise caution in interpretation.

Dr. Robinson

The priority or precedence of the databases used and the methodology used to reduce and format the equilibria and thermodynamic data for the MINTEQ database files is appropriate. This reviewer could not identify any other relevant and significant "English language" databases.

Chapter 5 of the *User Manual Supplement for Version 4.0* discusses the databases used and the methodology for reducing the data into the MINTEQ database. The National Institute of Standards and Technology (NIST) *Critical Stability Constants of Metal Complexes Database* (CRITICAL) was used as the primary source of thermodynamic equilibria data. Among aquatic chemistry researchers, the NIST database appears to be the most recognized. The precedence of other databases describes, e.g., using IUPAC SC-DATABASE as the next source, appears reasonable to this reviewer. Based on an online search of Chemical Abstracts and based on a web search using multiple search engines through *Copernic*, no other significant and relevant English language databases were identified.

One issue that does warrant discussion in the manual is the uncertainty in the thermodynamic data. If MINTEQ is to be used to set environmental regulations and risk criteria, then the uncertainty in the predictions of MINTEQ must be addressed. This uncertainty begins with the uncertainty in the data. Equilibria constants are not determined with the same precision as many fundamental physical constants. Rather there is uncertainty in many of the equilibria constants that can easily approach an order of magnitude or more.

A couple of minor comments are listed below:

a) Although Chapter 5 discusses the databases used, references for these databases were not found in the bibliography.
b) Correction on page 30: The SC-Database is published by Academic Software rather than Academic Press if the reviewer is not mistaken.
c) The database identifies the source of data for each species and this will be very

valuable for the user. However, if possible, it would also be useful to have footnotes in the thermodynamic database to define the abbreviations used for the sources and the units used for delta H.

d) Some species appear to have no enthalpy values for temperature corrections. It would be valuable to have a flag in the MINTEQ output to indicate to the user when this occurs. Otherwise, the user may erroneously believe that temperature corrections were correctly made.

Charge 2: *Was the process for compiling data on reaction of implementation of the Diffuse-Layer model option appropriate? How might it have been improved?*

Dr. Dudley

MINTEQA2 contains a number of adsorption/exchange options that could be used in HWIR99 protocols. It appears that sorption reactions will be modeled using only the Diffuse-Layer model. This is a cause for some concern. In support of the approach it is noted that iron-oxides surfaces, the surface used for predicting HWIR metals and metalloids by MINTEQA2, are ubiquitous in subsurface environments. Chemical extraction studies, and more recent spectroscopic techniques, have identified iron oxides as important sorbents in virtually all geochemical environments. But, natural systems are complex and contain highly variable iron oxide surfaces and a number of other surfaces that can control fate and transport of HWIR metals and metalloids, such as aluminum oxides, phyllosilicates, manganese oxides, disordered aluminosilicates, carbonates and humic substances (Sposito 1984). The sorbent may effect both solution concentrations and exposure risk. For example, cation exchange reactions on the surface of smectite clays have been identified as important to the geochemistry of Cd and Zn and because cation exchange reactions are reversible, exchangeable cations represent a human and ecological risk. Important surfaces are missing from the HWIR99 protocol for use of MINTEQA2. Solid-phase organic matter, shown to be important in Cu, Pb and Hg sorption in soil environments. It is conceivable that the transport path of the waste stream may be through soils where solid phase organic matter is present. Carbonate surfaces are another potentially important sorbent. Carbonate surfaces have a high affinity for a number of HWIR metals and metalloids, sorbing both cations and anions. Consideration of iron-oxide surfaces limits the applicability of the model to more humid environments and calls to question its use in chemical environments such as those of arid and semi-arid regions where carbonates are often present. In its present form, MINTEQA2 is best suited to more weathered systems, low in organic matter where iron oxides are the primary reactive surface. On the positive side, omitting reactive solid phases from computations should result in under-prediction of immobilization and conservative estimates of waste-stream concentrations.

Some concerns regarding the modeling of surface reactions for HWIR99 objectives were discussed in a previous section. Those concerns need not be repeated here. The focus in this section is on the implementation and parameterization of the Diffuse-Layer model.

Use of the intrinsic constants provided for estimating surface adoption of HWIR metals and metalloids with the Diffuse-Layer model is based on two assumptions: that heterogenous

surfaces in natural systems can be adequately represented by constants determined in well-characterized laboratory iron oxides and that reasonable estimates of constants not measured can be obtained from linear relationships with measured constants. Both assumptions are untested and therefore represent potential sources of error in the application of the model to the stated purpose. Modeling of surface reaction is the weakest component of the proposed HWIR99 strategy. The literature in colloid, soil and geochemical literature should be monitored for improvements in estimates of the relevant intrinsic adsorption constants and for examples of application of the model to natural systems. For example, a cursory review of the soil science literature produced a manuscript describing the application of the Diffuse-Layer model to boron adsorption. The manuscript (*Soil Science Society of America Journal* 59:395-404) identified the borate ($B(OH)_4^-$) as the dominant specie adsorbed at pH values greater than 7.0. Borate is not included in the database.

The assumption of linear relationships among free energies of solution complexation and ion pairing reactions has been established and it is likely that the same relations hold for surface constants. However, experimental determination of selected constants would not be overly burdensome and would add significantly to confidence in the model. Experimental determination of intrinsic adsorption constants for laboratory prepared iron oxides and selected subsurface materials should be a component of the model implementation plan.

Dr. Johnson

The compilation of equilibrium constants for sorption of metals, metalloids and cyanide is certainly an important addition to MINTEQA2. The use of the linear free energy relationship to estimate constants that are not derivable from experimental data is acceptable and defensible. Although the data provided by Dzombak and Morel (1990) provide a set of internally consistent reaction equilibrium constants they have not been updated since their book was published. The recent literature should be searched and any new data that has become available since 1990 be compared to the data in MINTEQA2 (Robertson and Leckie, 1997 and Venema et al., 1996). In addition, the sorption reactions should allow competition among trace metals and organic acids for sites on hydrous ferric oxide (Ali and Dzombak, 1996 and Evanko and Dzombak, 1999).

For ease in modeling sorption reactions, modification of MINTEQA2 to automate the two-step precipitation/sorption process would be useful. The mass of precipitated hydrous ferric oxide calculated in the precipitation step of the model could be automatically entered into the adsorption step of the model. This would eliminate the need to run the model twice, first to calculate the mass of hydrous ferric oxide and then to model the adsorption that occurs on that mass of hydrous ferric oxide.

Dr. Robinson

The process for compiling data on reactions for implementation of the Diffuse-Layer model does seem appropriate for this model.

The manual on *Diffuse-Layer Sorption Reactions for use in MINTEQA2 for HWIR Metals and Metalloids* includes scant information on how the data for these reactions were compiled. The manual merely says that the data were a compilation of reactions for hydrous

ferric oxide (HFO) by Dzombak and Morel published in a monograph in 1990 title *Surface Complexation Modeling: Hydrous Ferric Oxide*. It is not possible to conclude whether the method of compilation was valid based on just this statement. No evidence is presented in the manual that the data have been peer reviewed by the profession although it does appear that the process for determining such data were described in an earlier 1987 journal paper by Dzombak and Morel. Furthermore, the reviewer was able to obtain a copy of *Surface Complexation Modeling: Hydrous Ferric Oxide* and reviewed the relevant chapters. Based on a review of the relevant chapters in *Surface Complexation Modeling: Hydrous Ferric Oxide*, the reviewer believes Dzombak and Morel went through considerable efforts to develop quality assured data for HFO sorption reactions. It is doubtful that there is a better source of compiled data for HFO sorption equilibria constants for the model used. However, there are certain assumptions quality assurance (QA) criteria that should be recognized in the manual. These assumptions ands QA criteria were discussed by Dzombak and Morel in their monograph and have to do with the HFO preparation method, types of reaction vessels, background electrolyte, sorption kinetics, solid-liquid separation method, site densities, etc. Dzombak and Morel went through a very careful process to screen the literature available in 1991 and to develop equilibria constants. It appears that most of the data in the Feo-dlm.dbs database do come from *Surface Complexation Modeling: Hydrous Ferric Oxide*. Undoubtedly, more research on HFO sorption has appeared in the last 10 years, hopefully of more uniform and better quality, and EPA should allocate resources to thoroughly update the database. Consistent with being a valuable source of data for DLM model, the 1991 monograph by Dzombak and Morel has been referenced hundreds of times according to the *Web of Science* citation index.

The characteristics of HFO are highly variable. A discussion in the manual of the uncertainty and potential ranges in sorption equilibria constants is warranted even if it is very qualitative. Certain quantitative error statistics were available in the source reference.

A couple of minor comments are listed below:

a) On page 2, last paragraph, the manual on *Diffuse-Layer...* stated that manganese is not a contaminant metal in HWIR. Interestingly, manganese is a metal of concern to DOE as the reviewer observed while on leave to DOE. This concern apparently arises out of toxicity information on manganese in the IRIS data base.

b) Much of the equilibria data used for HFO sorbent in the diffuse-layer model (DLM) are the same as those in earlier versions of MINTEQ. Additional data for several species have been added. There was some confusion to the reviewer in that the species and data listed in Appendix A of the manual on *Diffuse-Layer...* are different than in the actual Feo-dlm.dbs data files used by MINTEQ. The Actual data file in MINTEQ appears to be more extensive than in Appendix A. It would seem that Appendix A ought to be brought in line with the Feo-dlm.dbs file.

Charge 3: *Is the implementation of the Gaussian model for addressing dissolved organic ligand reactions in MINTEQ appropriate?*

Dr. Dudley

The supporting documentation indicates that the implementation of the Gaussian model for reactions with DOM was carefully considered. The review of current approaches and their relative merits is excellent. The choice of the Gaussian model is well justified and properly implemented. Review of the equations and narrative raised two relatively minor points.

Equations (16) and (17) show that an activity coefficient, computed from the Davies equation, is used to compute the activity of the ligand and metal-ligand complex. This reviewer would argue that the Davies equation is not appropriate for such a purpose because it assumes mobile charges, whereas the charges on the organic ligand are restricted in space. An alternative approach would be to use conditional constants. The conditional constants should be concentration-based for the ligand and complex and activity based for free metals and protons. Coupling the conditional constants with implicit electrostatic effects in the Gaussian distribution would result in a formulation more logically consistent with model rational.

In a discussion of the study of colloidal and molecular dissolved organic matter, page 10 of the Manual Supplement states that "no distinction will be made herein between complexation and adsorption reactions in discussion of binding with humic substances." Since there needs to be no distinction between adsorption and complexation in application of the model, the Gaussian model could be used to represent adsorption by solid organic matter. The user would simply have to convert solution concentrations to an equivalent concentration in the solid phase, if necessary, in data interpretation. It might be beneficial to users to include such a statement in the narrative.

There is a marked contrast in modeling philosophy between the treatment of dissolved organic matter and surface adsorption, discussed the previous section. In computing surface sorption reactions, a number of assumptions about the systems are made to provide the user with a pre-packaged set of intrinsic constants. In contrast, intrinsic complexation-adsorption constants and Gaussian distribution properties are user specified parameters. Treatment of sorption reactions is highly generalized whereas treatment of reactions with organic matter is condition specific.

Dr. Johnson

The addition of DOM-ligand complexation is an important contribution to the MINTEQA2 model and addresses a fundamental process that affects dissolved metals concentrations in natural water. Questions raised in my review include, 1) the appropriateness of the continuous distribution model, 2) the validity of assuming a Gaussian probability function, i.e., normal distribution, 3) the validity of assuming a Langmuir-type expression for the complexed metal, and 4) the validity of assuming that the standard deviation is the same for all cations. In addition, this review comments on the practicality of implementation of the model for environmental problems.

The literature makes a strong case for the use of a continuous distribution model. Not only does a continuous distribution allow the development of thermodynamic binding constants but allows a variety of distributions to represent the relationship between affinity, concentration

of ligands and ionic strength.

The Gaussian distribution may be an oversimplification. A Gaussian probability function only applies if the relationship between the concentration of ligands and affinity constants is normally distributed. Although many of the models used to fit experimental data assume a Gaussian distribution this assumption has not been proven. At a minimum a bimodal Gaussian distribution is necessary to describe competing metals with pH- independent binding constants (Manunza, 1995). The affinity distributions become even more complicated with multiple competing metals and protons (Rusch et al., 1997). Although MINTEQA2 allows treatment of a biomodal distribution, data to support such a distribution is not available.

The fact that the data set included with MINTEQA2 uses the standard deviation for the proton affinity distribution for all metals is likely a deficiency. A constant standard deviation requires that the shape of the affinity distribution is the same for all metals across all substrates. Research conducted in The Netherlands provides data that shows this is not the case (Benedetti et al., 1995 and Riemsdijk et al., 1996). Their data show that different metals do not experience the same apparent heterogeneity. Different heterogeneity of the substrate will produce differently shaped affinity distributions for each metal. Experimental data by Riemsdijk et al. (1996) for copper and the proton at different pH and ionic strengths did not fit the model assuming a constant standard deviation of the affinity distribution for both the proton and metals.

It has also been shown that the binding affinity of humic acid for a specific ion is affected by electrostatic potentials that are a function of the ionic strength (Milne et al., 1995 and Benedetti et al., 1996). Recent efforts by van Riemsdijk et al. (1996) and Avena et al. (1999) advocate an affinity distribution that takes into account ion-specific non-ideality and the heterogeneity characteristic of the surface including the electrostatic potential as a function of ionic strength.

Most of the modeling efforts reported in the literature rely on the Langmuir equation to describe the complexation of the metal. There are suggestions, however, that the Langmuir equation is only valid for affinity distributions that are represented by well-defined narrow peaks. A Freundlich-type binding equation is more appropriate for affinity distributions that are represented by one or more broad peaks (Wit et al., 1993 and Benedetti et al., 1995). Ligand-metal complexation is similar to adsorption processes and it is well known that the Langmuir isotherm does not apply to substrates with sites that have different energies of adsorption. Freundlich-type isotherms generally apply to substrates with heterogeneous surfaces typical of humic substances (Stumm and Morgan, 1996). It would be prudent to develop the option within MINTEQA2 for the use of different binding equations. Considering that the Freundlich isotherm is essentially a log distribution of the Langmuir equation the mathematics of this should be manageable.

In general it seems that the MINTEQA2 DOM-metal model suffers from an oversimplification of the theoretical basis and the lack of thermodynamic data. Its theoretical approach has not incorporated research characterizing the interaction of metals with humic

substances published since 1995 or 1996. The literature published since 1996, much of it coming from The Netherlands, is critical of the simplistic type model used in MINTEQA2 and advocate more complex models to handle multi-component competition. In addition, the data included in MINTEQA2 are limited to those available in 1991. Even though MINTEQA2 allows for bimodal distribution and metal-specific affinity distributions, the data are not available to support these options. Also, the data applies only to the Suwannee River humic substances.

I believe that the question is one of: Should the addition of DOM model to MINTEQA2 be delayed until more comprehensive equations are prepared and more data become available? or Despite its limitations, is the current version better than nothing to describe the metal complexation with DOM? With or without the benefit of additional equations and data, the accuracy of the MINTEQA2 model should be tested by comparison with the analysis and speciation of actual groundwater and surface water samples. The results of these validation tests should accompany the user manual and give the user a basis for judging the results. Also, the user manual should be improved by including a discussion on use of the model. For example, because of the strong affinity between humic substances and calcium, barium, sodium and aluminum (Moto et al., 1996) the user should be cautioned against omitting the major cations in the input data.

Dr. Robinson

The implementation of the Gaussian model is appropriate.

The Gaussian approach to organic ligand reaction seems to be one of the favored approaches based upon papers seen in the literature. The manual supplement has a very nice discussion of this theory and should allow the user to better understand and interpret the MINTEQ input and output. The reviewer did a limited number of tests with the Gaussian model to test whether the MINTEQ results make sense. In the past, the reviewer discovered errors in the old HIWAY (1974) air dispersion model and also in one group's uses of MEPAS contaminant transport and risk assessment model by simply seeing how the model responded to variations in input values, i.e., partial sensitivity analysis. The response of the Gaussian model in MINTEQ to the limited testing appeared logical to the reviewer.

A couple of minor comments are listed below:

a) There does seem to be some problems in PRODEFA2.exe. The reviewer was not able to use a seed file and then change the DOM data, e.g., concentration of DOM1, in the seed file. PRODEFA2 skipped over the screen that asks for that input. This problem also occurred when creating the original file and then trying to go back and change the DOM information. Also, the reviewer could not specify input for more than DOM1. In trying to run a test file with DOM1, DOM2, and DOM3, an execution error resulted. The acidity and site concentration were zero for both DOM2 and DOM3 and may have been the cause of the execution error. However, PRODEFA2 did not give a chance to enter any inputs for DOM2 or DOM3, and besides, the reviewer thought that these would

be set as defaults. Obviously, the reviewer does not understand something here about the input data setup for bi- or tri-modal DOM. Finally, the manual supplement was not totally clear, but the reviewer assumes that the Gaussian model can only have one DOC source but with different types of functional groups, i.e., DOM1, DOM2, and DOM3. The different DOM's are not for different DOC sources, i.e., 10 mg/L of DOM1, 20 mg/L of DOM2, etc., but rather just different functionalities on the DOM.

b) Page 1, equation 1: t would be helpful to have { } around X_j to read $\{ X_j \}$, i.e., activity of component j, consistent with $\{ S_j \}$.

c) Page 2, equations 3 and 4: the summation should terminate with "m" rather than "n" since "i" corresponds to species and "m" is the number of different species.

d) On page 10 and figures 2.1 and 2.2, shouldn't T_{Li} and the y-axis be a probability density function, rather than just ligand concentration? That is, ligand concentration density (units of ligand concentration/log K).

e) A summary list of all assumptions would be useful.

f) More properly mathematically, equation 22 should be thought of as:

$$\Delta[ML_i] + (\text{existing terms}) \cdot \Delta \log K_{MLi}$$

The above is then integrated to yield equation 23.

Charge 4: *Are the modifications to address Gibb's Phase Rule violations appropriate?*

Dr. Dudley

As described in the User Manual Supplement, the modifications to the MINTEQA2 are appropriate and should result in improved model execution and eliminate a potential source of error. However, a problem with an erroneous phase rule violation was encountered with PRODEFA2. The modifications to the code need further revision for proper implementation. The PRODEFA2 provided in the review materials did not permit introduction of a gas phase component to the data file. The error message "no degrees of freedom left" was generated each time an attempt was made to introduce a gas phase. In fact, there should be a degree of freedom in the form of an unspecified total concentration of the dissolved gas specie. Using a previous version of PRODEFA2, it was possible to create data files that included a fixed partial pressure of CO_2 and did not produce violations of the Phase Rule upon execution. It appears that the logic statements in the code are out of order so that the dissolved gas (with total dissolved concentration unspecified to prevent the Phase Rule violation) is not added before checking for Phase Rule violations. Alternatively, the logic statements have not made provision to account for the dissolved gas concentration in determining the degrees of freedom. An additional, but not serious error was discovered while working on the dissolved CO_2 problems, two choices for CO_3^{2-} were encountered in the Level II edit (CO_3^{2-} was both component 1 and 2).

Dr. Johnson

Corrections of MINTEQA2 to allow precipitated solids to re-dissolve as other solids precipitate, therefore eliminating violations of Gibb's phase rule, are long overdue. Most

important, this change allows for more accurate representation of natural systems.

Dr. Robinson

The modifications to address "Gibb's Phase Rule" violations appear to solve this problem based on results of a simple test. Thus, the modifications are appropriate.

The simple test mentioned above in the response was based on the example "phase rule" violation discussed in the Version 4 supplement manual. The example consisted of Ca^{2+} = 3.0 mM, Mg^{2+} = 1.0 mM, CO_2 = 0.003 atm, and pH = 11.5. In older versions of MINTEQ, this problem gave an error when magnesium tried to precipitate. In Version 4, no error occurred and MINTEQ appears to have executed correctly. One comment, though. The manual stated that adding an extra component such as nitrate in the older MINTEQ version, would solve the problem unless additional solids tried to precipitate in which case another additional component would be needed. Indeed, adding nitrate in the older MINTEQ version allowed magnesite to precipitate after calcite precipitated in the above problem. However, a subsequent "phase violation" error occurred when dolomite tried to precipitate. Adding chloride as an additional component did not eliminate the error as the manual implied.

Chapter 3 of the manual supplement discusses the phase rule issue. The chapter is somewhat murky and confusing. The confusion arises partly over whether there actually is or isn't a Gibb's phase rule violation in the example chemical system at equilibrium. The confusion is increased by the uncertainty in how the program handles water as a component and how it actually works with the phase rule equation. For example, consider the problem discussed in the manual. If one thinks about adding $CaCO_{3,(S)}$ and $Mg(OH)_{2,(S)}$ into H_2O under an atmosphere of $CO_{2,g}$, then following the lead of Stumm and Morgan on page 306 of Aquatic Chemistry:

C = number of components = 4 (i.e., $CaCO_{3,(S)}$, $Mg(OH)_{2,(S)}$, H_2O, $CO_{2,g}$)
P = number of phases = 4 ($CaCO_{3,(S)}$, $Mg(OH)_{2,(S)}$, aqueous phase, gas phase)

Hence, the degrees of freedom are:

$F = C - P + 2 = 4 - 4 + 2 = 2$

Thus one can set two variables, e.g., temperature and p_{co2}. If H^+ is added as a component, then F = 5 - 4 + 2 = 3 and one can set three variables, e.g., temperature, p_{co2}, and pH. Thus there is no phase rule violation. But the manual supplement is confusing about whether water is a component or not. The manual supplement says that water is understood to be a pure phase and a component and thus essentially cancels out. But there is no pure phase of water in the problems of interest. Water will of course cancel out if one considers that there is always an aqueous phase. Is this what is meant? Also, the manual refers to temperature and pressure always being set and hence using the equation F = C- P. But it is then not clear how MINTEQ might handle problems where pressure that is set is not the vapor pressure of water but the partial pressure of some other component such as CO_2. Based on Chapter 3 in the manual supplement, the reviewer is confused whether MINTEQ correctly manipulates the Gibb's phase rule equation

in all cases.

Charge 5: *Are the modifications to minimize non-convergence appropriate?*

Dr. Dudley

The two modifications to the code, temporarily fixing ionic strength and limiting changes in component concentrations to an order of magnitude, will improve speed of convergence and help to prevent non-convergence. This reviewer has employed both "tricks" and found that they work well. The reviewer has experimented with using more or less than an order of magnitude restriction on the iterate and the order of magnitude rule seems to provide the quickest convergence.

The code should be further modified to eliminate the possibility of non-convergence due to the generation of a singular matrix. Test cases requiring computations redox potential from poor estimates of the solution redox potential, resulted in a singular matrix and non-convergence. There are three potential pitfalls in obtaining a solution to the mass balance equations using Newton-Raphson (1) the method is locally convergent, (2) the Jacobian matrix may be singular, and (3) the Jacobian matrix is not singular, but finite word length in computation results in numerical singularities. Of course, Newton-Raphson will converge if and only if the iterates are at some time sufficiently close to the solution. Large, multi-component systems containing components with very small numerical values (for example, H^+, redox potential or free concentrations of highly reactive components) are particularly pathological. For these systems, the difficulty making an initial estimate sufficiently close to the solution is non-trivial and the possibility of encountering a numerically singular Jacobian matrix significant. MINTEQA2 does make some provision for overcoming the problem of making an initial estimate of pH or Eh not sufficiently close to the solution through the "sweep" option. By sweeping through a range of pH or Eh values, a value close to the solution may be encountered and the problem solved. However, this trial and error approach may still require significant time on the part of the user.

Alternatives have been suggested to overcome the problem of a numerically singular Jacobian matrix. An obvious solution is to use double precision arithmetic. However, there is no guarantee of convergence for large problems involving pH and/or Eh computations. One successful strategy has been to switch components such that Newton-Raphson solves for increments in the components present in the greatest concentration. For example, at near neutral pH the carbonate component is HCO_3^- rather than CO_3^{2-} . A second alternative is to make use of some advances in the mathematics of solving for the iterate change and employ a singular value decomposition algorithm (SVD) in place of the Gaussian elimination routine. The SVD FORTRAN code is readily available (Dalhquist and Björck 1974; ISML Library 1987) and incorporation of the code into MINTEQA2 should be straight forward.

Objections to using an iterative technique like SVD to solve for the increment in Newton-Raphson have been that it slows computation speed and, because a number of arrays are required by the algorithm, consumes memory. Those arguments were worth considering ten years ago when the subroutines were first made available in the ISML Library but increases in

computer speed and memory strengthens the case for SVD. It seems worth the effort to use SVD when one considers the time that may be required to find an initial estimate sufficiently close for multi-component problems requiring computation of pH or Eh, or both as may be necessary under HWIR99. Overall, an increase in computational time may be offset by decreasing the time required for difficult cases. Moreover, SVD will provide an unequivocal differentiation between matrices that are numerically singular and those that are truly singular, due to user created errors in the input files.

Dr. Johnson

The modifications to reduce non-convergence appear to be sensible and helpful. And because they are options that can be specified in PRODEFA2 the user controls their implementation.

Dr. Robinson

The modifications described in section 4.2 to minimize non-convergence seem appropriate.

Charge 6: *Are the other code modifications including those for 1) increased execution speed, 2) modeling titrations, 3) specialized outputs, 4) customized database filenames, and 5) correction of known errors, adequate and useful?*

Dr. Dudley

The other code modifications are adequate and useful. The spreadsheet formatted output should be expanded so that more specie concentrations can be transferred to a spreadsheet for quick incorporation into tabular form, graphical representation, further statistical analysis, etc. This feature has a great deal of potential utility and should be fully developed.

Dr. Johnson

The code modifications to 1) increase the execution speed, 2) allow any species to be added as a titrant, 3) provide more options in specialized output, 4) allow database files to be named as the user wishes, and 5) correct known errors are all useful and important to fully utilize MINTEQA2. A future modification that users will find helpful is to create additional options for specialized output, such as more than six components or species.

Dr. Robinson

All of the additions and improvements listed in question 6 are beneficial, useful, and commendable. However, the reviewer would like to see further enhancements in the titration and output capabilities. These two aspects are discussed in more detail below.

The ability to do titrations (item **6b** above) is a useful addition to the program, but the titration capability does not appear to be able to handle volumes of the sample and titrant. In other words, the program simply allows the user to vary the total concentration of species in the aqueous solution, but doesn't actually simulate a lab titration involving volumes. Such as ability would be useful for analyzing laboratory data.

The addition of the ability to produce files that are more directly importable into a spreadsheet (item **6c** above) is also very useful. A maximum of 6 species can be written to the file. A higher maximum number of species would be valuable on occasion.

General Comments:

Dr. Dudley

Version 4.0 and its accompanying database contain a number of key elements necessary to provide reasonable estimates of waste-stream HWIR metal and metalloid concentrations. The important elements are as follows: a number of poorly crystalline solid phases have been added to the database (addition of these solid phases is important to achieving the HWIR99 objectives because even though these solids are not the thermodynamically favored phase, they may be kinetically favored and therefore control concentrations within the time frames of interest); metals and metalloids have been added to the database as well as a number of important solution complexes; a subroutine for organic complexation in the solution phase has been added as well as a database for predicting adsorption by iron-oxide surfaces; the model makes provision for systems in which redox reactions may occur. Though the model contains elements necessary for accomplishing HWIR99 objectives, there are at least two critical factors that may result in erroneous or misleading model output. In order to achieve HWIR99 objectives the model user must have sufficient knowledge of the system to make site specific selections of model inputs such as appropriate solid phases, sorbent characteristics, DOM parameters, etc. The six objectives of HWIR99 appear to contain the necessary modeling, science and peer review elements to minimize the risk of user generated problems, but the narrative is non-specific. It seems prudent to state what may be an obvious caution. EPA should develop some protocol for model use, that may include practices such as peer review of modeling approaches, in order to minimize the risk of inappropriate description of site geochemistry. The second factor involves potentially important sorbants not included in the HWIR Diffuse-Layer adsorption model and database.

MINTEQA2/PRODEFA2 should be a useful tool for estimating waste-stream concentrations of HWIR metals and metalloids. Meaningful results can be obtained with an "expert" user, i.e., one who has knowledge of the geochemical environment. The following recommendations are made with respect to application and further revision of MINTEQA2/PRODEFA2.

1) Proper protocol must be established for MINTEQA2/PRODEFA2 use that should include provisions for expert users and peer review of geochemical characterization of the systems in question and interpretation of model results.
2) Application of the model using only the Diffuse-layer sorption module should be limited to systems in which the dominant reactive surface is an iron oxide, i.e. well-weathered systems that are low in organic matter.
3) The literature should be searched for the intrinsic constants used in the Diffuse-layer model. Selected constants that have been estimated by linear extrapolation should be experimentally determined.

4) The thermodynamic database has been improved, and for HWIR purposes, no serious deficiencies in the database were found. The method of selecting constants and, when necessary, correcting the values to standard state conditions were appropriate. It is recommended that the database of Parker et al. (1995) be consulted for additional thermodynamic data. Incorporation of additional constants for chelation reactions would be of benefit to individuals involved in waste remediation.

5) The User Manual Supplement should be revised to indicate that the Gaussian DOM module could be used to estimate adsorption by solid organic matter.

6) The version of PRODEFA2 included in the review materials contained an error that would not permit introduction of a gas phase to the data file. The module produced a phase violation error message where one should not have occurred and further revision of the model will be required to resolve the problem. Otherwise, modifications to the model to prevent Gibb's phase rule violations should be an aid to model users and to HWIR99.

7) Modifications to prevent non-convergence and to speed convergence were appropriate. Use of an iterative method to find the increment in Newton-Raphson is recommended. An iterative method avoids problems associated with numerical singularity in the Jacobian, a problem that may occur in multi-component problems and problems in which the pH and/or Eh is to be calculated.

8) The number of species that can be output in a format compatible with a spreadsheet should be increased.

Dr. Johnson

The additions to MINTEQA2 improve its adequacy to support the HWIR99. The Gaussian DOM model is the only questionable addition to MINTEQA2. Although the ability to model the interaction among humic substances and metals is very important for the HWIR99, incorporation of the DOM model in MINTEQA2 may be premature. Its simplicity does not represent advancements, since 1996 in describing complexation among competitive ions and the effects of ionic strength, nor is a comprehensive thermodynamic data set available. However, regardless if the advancements are incorporated in the DOM model, before release for use it should be validated against equilibrium concentrations and species of actual contaminated groundwater and surface water. The results of the validation exercise should be described in the user manual to give a basis for the user for interpretation. Also, a section should be added to the user manual to assist the user in setting up a problem to get the most accurate results.

Also, the beta version of Version 4 did not initially run on my computer with a 32-bit compiler running Windows95. The error message received was:

Error TNT.20056: Can't read 386|VMM file: vmm.exp.
Seek in file returned DOS error. DOS error code is: invalid file handle.

I contacted Jerry Allison and the problem was corrected when he sent me the file VMM.EXP, a virtual memory manager, and I included it in the MINTEQ directory.

Dr. Robinson

MINTEQ is one of the most widely used and accepted geochemical equilibria programs. Its database's robustness, its flexibility, and the diversity of problems that it can address are some of its assets. Because MINTEQ is free, it has also proven to be a very useful educational tool.

The reviewer has been using MINTEQ in research and instruction for roughly 15 years and has been very satisfied with MINTEQ in the past. However, this reviewer is disappointed in the apparent lack of resources that have been devoted by EPA in the last several years to keep this highly valuable program up-to-date. Although MINTEQ's chemical computational abilities are among the best if not the best of any of the several geochemical equilibria programs available, MINTEQ's interface is woefully antiquated. No doubt the improvements to MINTEQ for Version 4 were the highest priority, but additional resources need to be invested to make MINTEQ Windows compatible, to greatly improve its input and output interfaces, and generally to make it much more user friendly.

The reviewer's impression is that MINTEQ will be used in the HWIR rule making process to set EPA criteria. The reviewer expects that MINTEQ will be used by environmental scientists and engineers well versed in aqueous chemistry. MINTEQ is primarily a tool for this type of user. MINTEQ is not a tool that can be recommended by the reviewer for users who are not expert in aqueous chemistry, because MINTEQ has a few idiosyncracies and is not especially user friendly. The user must be able to understand what MINTEQ is doing and to be able to interpret and judge the MINTEQ output.

i) Input and output names are restricted to 8 characters plus a 3 character extension. This makes it very awkward to create a long sequence of similar input files and to have meaningful names still make sense in several months. If there are any versions of Fortran that allow longer file names, this would be very useful.

ii) It has always seemed to the reviewer that very low concentrations of species predicted by MINTEQ might be unreliable, because those species might not have converged before MINTEQ met its overall convergence criteria. If this is indeed possible, then MINTEQ should have a flag as to which species might not have converged.

iii) Instruction about MINTEQ appear now in several different reports and manuals. It would be very helpful to integrate (with emphasis on integrate) these several manuals into one manual.

iv) The manner in which MINTEQ handles hydroxide is certainly legitimate (i.e., it is not a component whose concentration can be entered as input), but it is awkward and confusing to the uninitiated. It would be useful to allow the user to add hydroxide as a species and let MINTEQ convert it into negative proton internally

Typographical and editorial comments:

Dr. Dudley
User Manual Supplement

Pg. 27. The option for selection of the use of the non-convergence option was not provided in the Level I edit.

Pg. 28. Second to the last line. A "less than" symbol is missing.

Pg. 29. Awkward sentence in the middle of the page. Editorial note left in the narrative about halfway down the page.

Pg. 31. μ is used for ionic strength and the mean of the association constant for metal-DOM reaction. "I" could be used to denote ionic strength.

Pg. 31. There is an error in notation on the free energy and enthalpy of formation. It should be ΔG_f^0 and ΔH_f^0.

Pg. 34. There is an error in notation on the free energy and enthalpy of formation. It should be ΔG_f^0 and ΔH_f^0.

Pg. 37. The sentence should read. <u>The</u> log K values in the MINTEQA2 database are ~~should~~ be referenced to the standard state (zero ionic strength).

Pg. 37. Typo at the bottom of the page "knpwn".

Diffuse-Later Sorption Reactions

Pg. 4. Even though the asterisk is denoting LFER derived constants is mentioned in the text, the definition should be repeated at the bottom of the page.

Dr. Johnson

The User Manual Supplement needs thorough editing. In addition to correcting typographical errors the references must be checked. There are several references that are named in the text that are not in the reference list (for example, Serkiz et al., 1996) and there are errors in the reference listings (for example, the page numbers are interchanged between the two Cabaniss references).

Dr. Robinson
Manual Supplement for version 4.0

i) Page 14, second full paragraph: this seems redundant with earlier material.
ii) Page 29, 3rd paragraph, 2nd to the last sentence: "Add something here..." appears to be a

note to manual author.

iii) Page 31, 1st paragraph in section 5.2, line 5: "values or..." should be "values of..."

iv) Page 31, 1st paragraph in section 5.2, line 9: should it read "not already corrected..."?

v) A global search should be done to catch the several instances of "data was" rather than "data were"

vi) Page 37, 6th line from bottom: "known" rather than "knpwn"

Diffuse-Layer Sorption Reactions for Use in MINTEQA2 for HWIR Metals and Metalloids

i) Page 2, 7th from bottom: insert "to" to read "belongs to the alkaline..."

ii) Page 2, 5th line from the bottom: increase clarity by changing "Its" to Beryllium's behavior..."

iii) A global search should be done to catch the several instances of "data was" rather than "data were"

References:

Dr. Dudley

Dalhquist, G. ; and Björck, Å. *Numerical Methods*; Prentice-Hall: Englewood Cliffs, NJ, 1974.

IMSL Library; Ed. 10 Subroutine LSVRR, DLSVRR; IMSL Inc., 1987.

Lindsay, W.L. *Chemical Equilibria in Soils*; John Wiley & Sons, Inc., 1979.

Parker, D.R.; Norvell, W.A.; Chaney, R.L., GEOCHEM-PC —A chemical speciation program for IBM and compatible personal computers, Leoppert, R.H.; Schwab, P.A.; Goldberg, S. *Chemical Equilibrium and Reaction Models*, Soil Sci. Soc. Am., Madison, WI, 1995.

Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press, NY, 1984.

Dr. Johnson

Ali, Muhammad A. and David A. Dzombak. 1996. Interactions of Copper, Organic Acids, and Sulfate in Goethite Suspension. *Geochimica et Cosmochimica Acta*, Vol. 60, No. 24, pp. 5045-5053.

Avena, Marcelo, Luuk K. Koopal and Willem, H. Van Riemsdijk. 1999. Proton Binding to Humic Acids: Electrostatic and Intrinsic Interactions. *Journal of Colloid and Interface Science*, Vol. 217, pp. 37-48.

Benedetti, Marc. F., Chris J. Milne, David Kinniburgh, Willem, H. Van Riemsdijk and Luuk K. Koopal. 1995. Metal Ion Binding to Humic Substances: Application of the non-Ideal Competitive Adsorption Model. *Environmental Science & Technology*, Vol. 29, No. 2, pp. 446-457.

Benedetti, Marc. F., Willem, H. Van Riemsdijk and Luuk K. Koopal. 1996. Humic Substances Considered as a Heterogeneous Donnan Gel Phase. *Environmental Science & Technology*, Vol. 30, No. 6, pp. 1805-1813.

de Wit, Johannes C.M., Willem H. van Riemsdijk and Luuk K. Koopal. 1993. Proton Binding to Humic Substances. 2. Chemical Heterogeneity and Adsorption Models. *Environmental Science and Technology*, Vol. 27, No. 10, pp. 2015-2022.

Dzombak, David A. and Francois M.M. Morel. 1990. *Surface Complexation Modeling*. Wiley-Interscience. 393 pp.

Essington, Michael E. 1990. Calcium Molybdate Solubility in Spent Oil Shale and a Preliminary Evaluation of the Associated Constants for the Formation of $CaMoO_4^o$(aq), $KMoO_4^-$(aq) and $NaMoO_4^-$(aq). *Environmental Science & Technology*, Vol. 24, No. 2, pp. 214-220.

Evanko Cynthia and David A. Dzombak. 1999. Surface Complexation Modeling of Organic Acid Sorption to Goethite. *Journal of Colloid and Interface Science*, Vol. 214, pp. 189-206.

Manunza, Bruno, Salvatore Deiana, Vittoria Maddau, Carlo Gessa and Renato Seeber. 1995. Stability Constants of Metal-Humate Complexes: Titration Data Analyzed by Bimodal Gaussian Distribution. *Soil Science Society of American Journal*, Vol. 59, pp. 1570-1574.

Milne, C.J., D.C. Kinniburgh, J.C.M. de Wit, W.H. van Riemsdijk and L.K. Koopal. 1995. Analysis of Proton Binding by a Peat Humic Acid Using a Simple Electrostatic Model. *Geochimica et Cosmochimica Acta*, Vol. 59, No. 6, pp. 1101-1112.

Moto, A.M., A. Rato, C. Brazia and M.L. Simoes Goncalves. 1996. Competition of Al^{3+} in Complexation of Humic Matter with Pb^{2+}: A Comparative Study with Other Ions. *Environmental Science and Technology*, Vol. 30, No. 6, pp. 1970-1974.

Robertson, A.P. and J.O. Leckie. 1997. Cation Binding Predictions of Surface Complexation Models: Effects of pH, Ionic Strength, Cation Loading, Surface Complex and Model Fit. *Journal of Colloid and Interface Science*, Vol. 188, pp. 444-472.

Rusch, Ursula, Michael Borkovec, John Daicic and Willem H. van Riemsdijk. 1997. Interpretation of Competitive Adsorption Isotherms in Terms of Affinity Distributions. *Journal of Colloid and Interface Science*, Vol. 191, pp. 247-255.

Stumm, Werner and James J. Morgan. 1996. *Aquatic Chemistry*. Wiley-Interscience. 1022 pp.

van Riemsdijk, Willem H., Johnannes C.M. de Wit, Sipko L.J. Mous, Luuk K. Koopal and David G. Kinniburgh. 1996. An Analytical Isotherm Equation (CONICA) for Nonideal Mono- and Bidentate Competitive Ion Adsorption to Heterogeneous Surfaces. *Journal of Colloid and Interface Science*, Vol. 183, pp. 35-50

Venema, Peter, Tjisse Hiemstra, and Willem H. van Riemsdijk. 1996. Comparison of Different Site Binding Models for Cation Sorption: Description of pH Dependency, Salt Dependency and Cation-Proton Exchange. *Journal of Colloid and Interface Science*, Vol. 181, pp. 45-59.

ATTACHMENT A

Peer Review of MINTEQA2/PRODEFA2 Version 4.0 by:

Lynn M. Dudley
Utah State University

Peer Review Report
MINTEQA2/PRODEFA2
Version 4.0

Prepared for
Eastern Research Group
Lexington, MA

by
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Logan, Utah

September 13, 1999

Table of Contents

Introduction

The instructions direct panelists to address the question, is MINTEQA2 scientifically adequate for use in estimating release and fate HWIR metals and metalloids from land-based waste management units? Panelists were to answer six sub-questions relating to the adequacy of the thermodynamic database, the parameterization and implementation of the thermodynamic database, the appropriateness of the Gaussian model for dissolved organic matter (DOM), appropriateness of the modifications to the code to prevent violation of Gibb's Phase Rule, appropriateness of the modification to improve convergence, and the appropriateness of other code modifications in the process of answering the larger question. This report is organized into six subsections that address each of the questions above.

The procedure for this review was to critically read the supporting documentation, review the thermodynamic database, execute the test cases provided on the diskette (to assure proper installation), and execute the model using data files designed to test the model under a variety of geochemical scenarios. Generally, the supporting documents were well written and useful in understanding and executing MINTEQA2/PRODEFA2. A list of typographical errors, errors in notation, suggested changes in wording and notation, etc. are provided in an appendix to this report, along with edited pages from the manual. Some problems encountered in executing both MINTEQA2 and PRODEFA2. Problems encountered in executing MINTEQA2 involved the generation of singular matrices. A description of the problems and a possible remedy are discussed below. The changes to PRODEFA2, designed to prevent violations of the Gibb's Phase Rule, need revision since they prevented the addition of a gas phase to a data file when the addition did not constitute a violation of the rule. This problem is also discussed in a subsequent section and will have to be remedied before release of version 4.0.

Review of Model Function and Conclusions

Use of MINTEQA2 for Estimating Waste Stream Concentrations

Version 4.0 and its accompanying database contain a number of key elements necessary to provide reasonable estimates of waste-stream HWIR metal and metalloid concentrations. The important elements are as follows: a number of poorly crystalline solid phases have been added

to the database (addition of these solid phases is important to achieving the HWIR99 objectives because even though these solids are not the thermodynamically favored phase, they may be kinetically favored and therefore control concentrations within the time frames of interest); metals and metalloids have been added to the database as well as a number of important solution complexes; a subroutine for organic complexation in the solution phase has been added as well as a database for predicting adsorption by iron-oxide surfaces; the model makes provision for systems in which redox reactions may occur. Though the model contains elements necessary for accomplishing HWIR99 objectives, there are at least two critical factors that may result in erroneous or misleading model output. In order to achieve HWIR99 objectives the model user must have sufficient knowledge of the system to make site specific selections of model inputs such as appropriate solid phases, sorbent characteristics, DOM parameters, etc. The six objectives of HWIR99 appear to contain the necessary modeling, science and peer review elements to minimize the risk of user generated problems, but the narrative is non-specific. It seems prudent to state what may be an obvious caution. EPA should develop some protocol for model use, that may include practices such as peer review of modeling approaches, in order to minimize the risk of inappropriate description of site geochemistry. The second factor involves potentially important sorbants not included in the HWIR Diffuse-Layer adsorption model and database.

MINTEQA2 contains a number of adsorption/exchange options that could be used in HWIR99 protocols. It appears that sorption reactions will be modeled using only the Diffuse-Layer model. This is a cause for some concern. In support of the approach it is noted that iron-oxides surfaces, the surface used for predicting HWIR metals and metalloids by MINTEQA2, are ubiquitous in subsurface environments. Chemical extraction studies, and more recent spectroscopic techniques, have identified iron oxides as important sorbents in virtually all geochemical environments. But, natural systems are complex and contain highly variable iron oxide surfaces and a number of other surfaces that can control fate and transport of HWIR metals and metalloids, such as aluminum oxides, phyllosilicates, manganese oxides, disordered aluminosilicates, carbonates and humic substances (Sposito 1984). The sorbent may effect both solution concentrations and exposure risk. For example, cation exchange reactions on the surface of smectite clays have been identified as important to the geochemistry of Cd and Zn and

because cation exchange reactions are reversible, exchangeable cations represent a human and ecological risk. Important surfaces are missing from the HWIR99 protocol for use of MINTEQA2. Solid-phase organic matter, shown to be important in Cu, Pb and Hg sorption in soil environments. It is conceivable that the transport path of the waste stream may be through soils where solid phase organic matter is present. Carbonate surfaces are another potentially important sorbent. Carbonate surfaces have a high affinity for a number of HWIR metals and metalloids, sorbing both cations and anions. Consideration of iron-oxide surfaces limits the applicability of the model to more humid environments and calls to question its use in chemical environments such as those of arid and semi-arid regions where carbonates are often present. In its present form, MINTEQA2 is best suited to more weathered systems, low in organic matter where iron oxides are the primary reactive surface. On the positive side, omitting reactive solid phases from computations should result in under-prediction of immobilization and conservative estimates of waste-stream concentrations.

The Thermodynamic Database

1) Did the process for revising the main thermodynamic database utilize the appropriate sources? What others, if any, should specifically be investigated?

The appropriate sources were considered and the proper corrections of the equilibrium constants to standard state conditions were performed when necessary. Two other thermodynamic databases, Lindsay (1979) and Parker et al. (1995) were consulted in this review as one way of checking on missing equilibrium constants for potentially important reactions. Time restrictions for this review did not permit an exhaustive review of the database. Instead, the review focused on species where the differences would be most likely such as in components added in the revision. Although the compilation of Lindsay (1979) is older than the database used with MINTEQA2 v.3.1, it contained a number of equilibrium constants for solution and solid phases that were not in the MINTEQA2 3.1 database and was the source of a database that a large number of MINTEQA2 users preferred. The stability constants in Lindsay (1979) are, by and large, in the revised database. The thermodynamic database of Parker et al. (1995), for the model GEOCHEMPC, was developed in California for use in understanding bioavailability and solution speciation of many HWIR contaminants. Database entries of U, V, As, B, Be, Sr, and

Sn were selected for a comparison of Parker and MINTEQA2 databases. The Parker database contained additional entries for UO_2Cl^+, $BeSO_4$ (aq), a number of Sr complexes and significantly more complexes of B and As. The Parker database is available on the web at http//:envisci.ucr.edu/faculty/dparker/default.htm, is reasonably well referenced, and should be consulted for additional possible entries to the MINTEQA2 database.

The only chelating agent incorporated in the MINTEQA2 database is ethylendiaminetetraacectic acid (EDTA). The lack of other chelating agents is a noticeable deficiency in the database. Chelating agents have been proposed for use in phytoremediation of metal and metalloid waste sites. Incorporation of thermodynamic constants for chelating agents such as diethylenetriaminepentaacetic acid (DTPA), ethylenediaminetetraacetic acid (EDTA), and hydroxyethylethylenediaminetriacetic acid (HEEDTA) would facilitate the use of MINTEQA2 in understanding the effects of chelate addition on bioavailability and the potential for off-site transport of chelated metals. Stability constants for reaction of HWIR metals Zn, Cu, Cd, Pb, Mg, Ni, Co, Hg, and Ag as well as important competing reactions with Ca, Mg, and Fe may be found in Lindsay (1979). Parker et al. (1995) also contains data for a number of chelating agents.

Implementation of the Diffuse-Layer Model

2) Was the process for compiling data on reaction of implementation of the Diffuse-Layer model option appropriate? How might it have been improved?

Some concerns regarding the modeling of surface reactions for HWIR99 objectives were discussed in a previous section. Those concerns need not be repeated here. The focus in this section is on the implementation and parameterization of the Diffuse-Layer model.

Use of the intrinsic constants provided for estimating surface adoption of HWIR metals and metalloids with the Diffuse-Layer model is based on two assumptions: that heterogenous surfaces in natural systems can be adequately represented by constants determined in well-characterized laboratory iron oxides and that reasonable estimates of constants not measured can be obtained from linear relationships with measured constants. Both assumptions are untested and therefore represent potential sources of error in the application of the model to the stated purpose. Modeling of surface reaction is the weakest component of the proposed HWIR99

strategy. The literature in colloid, soil and geochemical literature should be monitored for improvements in estimates of the relevant intrinsic adsorption constants and for examples of application of the model to natural systems. For example, a cursory review of the soil science literature produced a manuscript describing the application of the Diffuse-Layer model to boron adsorption. The manuscript (*Soil Science Society of America Journal* 59:395-404) identified the borate ($B(OH)_4^-$) as the dominant specie adsorbed at pH values greater than 7.0. Borate is not included in the database.

The assumption of linear relationships among free energies of solution complexation and ion pairing reactions has been established and it is likely that the same relations hold for surface constants. However, experimental determination of selected constants would not be overly burdensome and would add significantly to confidence in the model. Experimental determination of intrinsic adsorption constants for laboratory prepared iron oxides and selected subsurface materials should be a component of the model implementation plan.

Gaussian Model For Reactions with Dissolved Organic Matter

3) Is the implementation of the Gaussian model for addressing dissolved organic ligand reactions in MINTEQ appropriate?

The supporting documentation indicates that the implementation of the Gaussian model for reactions with DOM was carefully considered. The review of current approaches and their relative merits is excellent. The choice of the Gaussian model is well justified and properly implemented. Review of the equations and narrative raised two relatively minor points.

Equations (16) and (17) show that an activity coefficient, computed from the Davies equation, is used to compute the activity of the ligand and metal-ligand complex. This reviewer would argue that the Davies equation is not appropriate for such a purpose because it assumes mobile charges, whereas the charges on the organic ligand are restricted in space. An alternative approach would be to use conditional constants. The conditional constants should be concentration-based for the ligand and complex and activity based for free metals and protons. Coupling the conditional constants with implicit electrostatic effects in the Gaussian distribution would result in a formulation more logically consistent with model rational.

In a discussion of the study of colloidal and molecular dissolved organic matter, page 10

of the Manual Supplement states that "no distinction will be made herein between complexation and adsorption reactions in discussion of binding with humic substances." Since there needs to be no distinction between adsorption and complexation in application of the model, the Gaussian model could be used to represent adsorption by solid organic matter. The user would simply have to convert solution concentrations to an equivalent concentration in the solid phase, if necessary, in data interpretation. It might be beneficial to users to include such a statement in the narrative.

There is a marked contrast in modeling philosophy between the treatment of dissolved organic matter and surface adsorption, discussed the previous section. In computing surface sorption reactions, a number of assumptions about the systems are made to provide the user with a pre-packaged set of intrinsic constants. In contrast, intrinsic complexation-adsorption constants and Gaussian distribution properties are user specified parameters. Treatment of sorption reactions is highly generalized whereas treatment of reactions with organic matter is condition specific.

Modifications to Address Gibb's Phase Rule Violations

4) Are the modifications to address Gibb's Phase Rule violations appropriate?

As described in the User Manual Supplement, the modifications to the MINTEQA2 are appropriate and should result in improved model execution and eliminate a potential source of error. However, a problem with an erroneous phase rule violation was encountered with PRODEFA2. The modifications to the code need further revision for proper implementation. The PRODEFA2 provided in the review materials did not permit introduction of a gas phase component to the data file. The error message "no degrees of freedom left" was generated each time an attempt was made to introduce a gas phase. In fact, there should be a degree of freedom in the form of an unspecified total concentration of the dissolved gas specie. Using a previous version of PRODEFA2, it was possible to create data files that included a fixed partial pressure of CO_2 and did not produce violations of the Phase Rule upon execution. It appears that the logic statements in the code are out of order so that the dissolved gas (with total dissolved concentration unspecified to prevent the Phase Rule violation) is not added before checking for

Phase Rule violations. Alternatively, the logic statements have not made provision to account for the dissolved gas concentration in determining the degrees of freedom. An additional, but not serious error was discovered while working on the dissolved CO_2 problems, two choices for CO_3^{2-} were encountered in the Level II edit (CO_3^{2-} was both component 1 and 2).

Modifications to Minimize Non-Convergence

5) Are the modifications to minimize non-convergence appropriate?

The two modifications to the code, temporarily fixing ionic strength and limiting changes in component concentrations to an order of magnitude, will improve speed of convergence and help to prevent non-convergence. This reviewer has employed both "tricks" and found that they work well. The reviewer has experimented with using more or less than an order of magnitude restriction on the iterate and the order of magnitude rule seems to provide the quickest convergence.

The code should be further modified to eliminate the possibility of non-convergence due to the generation of a singular matrix. Test cases requiring computations redox potential from poor estimates of the solution redox potential, resulted in a singular matrix and non-convergence. There are three potential pitfalls in obtaining a solution to the mass balance equations using Newton-Raphson (1) the method is locally convergent, (2) the Jacobian matrix may be singular, and (3) the Jacobian matrix is not singular, but finite word length in computation results in numerical singularities. Of course, Newton-Raphson will converge if and only if the iterates are at some time sufficiently close to the solution. Large, multi-component systems containing components with very small numerical values (for example, H^+, redox potential or free concentrations of highly reactive components) are particularly pathological. For these systems, the difficulty making an initial estimate sufficiently close to the solution is non-trivial and the possibility of encountering a numerically singular Jacobian matrix significant. MINTEQA2 does make some provision for overcoming the problem of making an initial estimate of pH or Eh not sufficiently close to the solution through the "sweep" option. By sweeping through a range of pH or Eh values, a value close to the solution may be encountered and the problem solved. However, this trial and error approach may still require significant time on the part of the user.

Alternatives have been suggested to overcome the problem of a numerically singular

Jacobian matrix. An obvious solution is to use double precision arithmetic. However, there is no guarantee of convergence for large problems involving pH and/or Eh computations. One successful strategy has been to switch components such that Newton-Raphson solves for increments in the components present in the greatest concentration. For example, at near neutral pH the carbonate component is HCO_3^- rather than CO_3^{2-} . A second alternative is to make use of some advances in the mathematics of solving for the iterate change and employ a singular value decomposition algorithm (SVD) in place of the Gaussian elimination routine. The SVD FORTRAN code is readily available (Dalhquist and Björck 1974; ISML Library 1987) and incorporation of the code into MINTEQA2 should be straight forward.

Objections to using an iterative technique like SVD to solve for the increment in Newton-Raphson have been that it slows computation speed and, because a number of arrays are required by the algorithm, consumes memory. Those arguments were worth considering ten years ago when the subroutines were first made available in the ISML Library but increases in computer speed and memory strengthens the case for SVD. It seems worth the effort to use SVD when one considers the time that may be required to find an initial estimate sufficiently close for multi-component problems requiring computation of pH or Eh, or both as may be necessary under HWIR99. Overall, an increase in computational time may be offset by decreasing the time required for difficult cases. Moreover, SVD will provide an unequivocal differentiation between matrices that are numerically singular and those that are truly singular, due to user created errors in the input files.

Other Code Modifications

6) Are the other code modifications including those for 1) increased execution speed, 2) modeling titrations, 3) specialized outputs, 4) customized database filenames, and 5) correction of known errors, adequate and useful?

The other code modifications are adequate and useful. The spreadsheet formatted output should be expanded so that more specie concentrations can be transferred to a spreadsheet for quick incorporation into tabular form, graphical representation, further statistical analysis, etc. This feature has a great deal of potential utility and should be fully developed.

Summary

MINTEQA2/PRODEFA2 should be a useful tool for estimating waste-stream concentrations of HWIR metals and metalloids. Meaningful results can be obtained with an "expert" user, i.e., one who has knowledge of the geochemical environment. The following recommendations are made with respect to application and further revision of MINTEQA2/PRODEFA2.

1) Proper protocol must be established for MINTEQA2/PRODEFA2 use that should include provisions for expert users and peer review of geochemical characterization of the systems in question and interpretation of model results.

2) Application of the model using only the Diffuse-layer sorption module should be limited to systems in which the dominant reactive surface is an iron oxide, i.e. well-weathered systems that are low in organic matter.

3) The literature should be searched for the intrinsic constants used in the Diffuse-layer model. Selected constants that have been estimated by linear extrapolation should be experimentally determined.

4) The thermodynamic database has been improved, and for HWIR purposes, no serious deficiencies in the database were found. The method of selecting constants and, when necessary, correcting the values to standard state conditions were appropriate. It is recommended that the database of Parker et al. (1995) be consulted for additional thermodynamic data. Incorporation of additional constants for chelation reactions would be of benefit to individuals involved in waste remediation.

5) The User Manual Supplement should be revised to indicate that the Gaussian DOM module could be used to estimate adsorption by solid organic matter.

6) The version of PRODEFA2 included in the review materials contained an error that would not permit introduction of a gas phase to the data file. The module produced a phase violation error message where one should not have occurred and further revision of the model will be required to resolve the problem. Otherwise, modifications to the model to prevent Gibb's phase rule violations should be an aid to model users and to HWIR99.

7) Modifications to prevent non-convergence and to speed convergence were appropriate. Use of an iterative method to find the increment in Newton-Raphson is recommended. An iterative method avoids problems associated with numerical singularity in the Jacobian, a problem that may occur in multi-component problems and problems in which

the pH and/or Eh is to be calculated.

8) The number of species that can be output in a format compatible with a spreadsheet should be increased.

Literature Cited

Dalhquist, G. ; and Björck, Å. *Numerical Methods*; Prentice-Hall: Englewood Cliffs, NJ, 1974.

IMSL Library; Ed. 10 Subroutine LSVRR, DLSVRR; IMSL Inc., 1987.

Lindsay, W.L. *Chemical Equilibria in Soils*; John Wiley & Sons, Inc., 1979.

Parker, D.R.; Norvell, W.A.; Chaney, R.L., GEOCHEM-PC —A chemical speciation program for IBM and compatible personal computers, Leoppert, R.H.; Schwab, P.A.; Goldberg, S. *Chemical Equilibrium and Reaction Models*, Soil Sci. Soc. Am., Madison, WI, 1995.

Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press, NY, 1984.

Appendix - Typographic Errors and Editorial Comments

User Manual Supplement

Pg. 27. The option for selection of the use of the non-convergence option was not provided in the Level I edit.

Pg. 28. Second to the last line. A “less than” symbol is missing.

Pg. 29. Awkward sentence in the middle of the page. Editorial note left in the narrative about halfway down the page.

Pg. 31. μ is used for ionic strength and the mean of the association constant for metal-DOM reaction. “I” could be used to denote ionic strength.

Pg. 31. There is an error in notation on the free energy and enthalpy of formation. It should be ΔG_f^0 and ΔH_f^0.

Pg. 34. There is an error in notation on the free energy and enthalpy of formation. It should be ΔG_f^0 and ΔH_f^0.

Pg. 37. The sentence should read. <u>The</u> log K values in the MINTEQA2 database are ~~should~~ be referenced to the standard state (zero ionic strength).

Pg. 37. Typo at the bottom of the page “knpwn”.

Diffuse-Later Sorption Reactions

Pg. 4. Even though the asterisk is denoting LFER derived constants is mentioned in the text, the definition should be repeated at the bottom of the page.

ATTACHMENT B

Peer Review of MINTEQA2/PRODEFA2 Version 4.0 by:

Kathryn Johnson
Johnson Environmental Concepts

Peer Review of:

MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Use Manual Supplement for Version 4.0

By:

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Prepared for:
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September 1999

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1. Introduction

Per the charge to peer reviewers, this review addresses the adequacy and appropriateness of the revisions to MINTEQA2/PRODEFA2 Version 4.0 that have been made in support of the Hazardous Waste Identification Rule (HWIR99). The intent of the HWIR99 is to use MINTEQA2/PRODEFA2 to model waste stream concentrations released from land-based waste management units and multimedia transport pathways so that exposure and risk to human and ecological receptors can be evaluated.

The review addresses the modifications and revisions of the:

- Thermodynamic databases,
- Diffuse-layer adsorption model,
- Gaussian model for reactions between dissolved organic matter and metals,
- Gibb's Phase Rule violations,
- Non-convergence problems, and
- Other code modifications.

Additional findings of my review are also described.

2. Summary

The additions to MINTEQA2 improve its adequacy to support the HWIR99. The Gaussian DOM model is the only questionable addition to MINTEQA2. Although the ability to model the interaction among humic substances and metals is very important for the HWIR99, incorporation of the DOM model in MINTEQA2 may be premature. Its simplicity does not represent advancements, since 1996 in describing complexation among competitive ions and the effects of ionic strength, nor is a comprehensive thermodynamic data set available. However, regardless if

the advancements are incorporated in the DOM model, before release for use it should be validated against equilibrium concentrations and species of actual contaminated groundwater and surface water. The results of the validation exercise should be described in the user manual to give a basis for the user for interpretation. Also, a section should be added to the user manual to assist the user in setting up a problem to get the most accurate results.

3. Review

3.1 Modifications to the Thermodynamic Database

In general I believe that the processes used to revise the main thermodynamic databases are appropriate and complete. State-of-the-art sources of thermodynamic data were used. The additions of Be(II), Co(II and III), Mo(VI) and Sn(II and IV) are essential to the use of MINTEQA2 for the HWIR99. The process of data reduction provided a consistent data set. The quality assurance system should have practically eliminated the errors that commonly occur in large-scale data manipulation.

However, another search for aqueous species that are important in environmental behavior of metals would be worthwhile. For example, the aqueous species of molybdate paired with sodium, potassium and calcium are not in the data base. In alkaline solutions, these species have been shown to control the dissolved concentrations of molybdenum (Essington, 1990). In addition, the database does not appear to contain the methylated forms of arsenic and mercury which are known to affect the dissolved concentrations as well as toxicity, particularly under anaerobic environments.

In the discussion of data reduction in the User Manual Supplement, it is noted that for reactions in which the enthalpy is not available, zero is entered and the equilibrium constant is incorporated without correction to 25 degrees. It would be helpful if these equilibrium constants were marked so that the user could exercise caution in interpretation.

3.2 Diffuse-Layer Adsorption Model

The compilation of equilibrium constants for sorption of metals, metalloids and cyanide is certainly an important addition to MINTEQA2. The use of the linear free energy relationship to estimate constants that are not derivable from experimental data is acceptable and defensible. Although the data provided by Dzombak and Morel (1990) provide a set of internally consistent reaction equilibrium constants they have not been updated since their book was published. The recent literature should be searched and any new data that has become available since 1990 be compared to the data in MINTEQA2 (Robertson and Leckie, 1997 and Venema et al., 1996). In addition, the sorption reactions should allow competition among trace metals and organic acids for sites on hydrous ferric oxide (Ali and Dzombak, 1996 and Evanko and Dzombak, 1999).

For ease in modeling sorption reactions, modification of MINTEQA2 to automate the two-step precipitation/sorption process would be useful. The mass of precipitated hydrous ferric oxide calculated in the precipitation step of the model could be automatically entered into the

adsorption step of the model. This would eliminate the need to run the model twice, first to calculate the mass of hydrous ferric oxide and then to model the adsorption that occurs on that mass of hydrous ferric oxide.

3.3 Gaussian Model of Dissolved Organic Matter (DOM) and Metal Reactions

The addition of DOM-ligand complexation is an important contribution to the MINTEQA2 model and addresses a fundamental process that affects dissolved metals concentrations in natural water. Questions raised in my review include, 1) the appropriateness of the continuous distribution model, 2) the validity of assuming a Gaussian probability function, i.e., normal distribution, 3) the validity of assuming a Langmuir-type expression for the complexed metal, and 4) the validity of assuming that the standard deviation is the same for all cations. In addition, this review comments on the practicality of implementation of the model for environmental problems.

The literature makes a strong case for the use of a continuous distribution model. Not only does a continuous distribution allow the development of thermodynamic binding constants but allows a variety of distributions to represent the relationship between affinity, concentration of ligands and ionic strength.

The Gaussian distribution may be an oversimplification. A Gaussian probability function only applies if the relationship between the concentration of ligands and affinity constants is normally distributed. Although many of the models used to fit experimental data assume a Gaussian distribution this assumption has not been proven. At a minimum a bimodal Gaussian distribution is necessary to describe competing metals with pH- independent binding constants (Manunza, 1995). The affinity distributions become even more complicated with multiple competing metals and protons (Rusch et al., 1997). Although MINTEQA2 allows treatment of a biomodal distribution, data to support such a distribution is not available.

The fact that the data set included with MINTEQA2 uses the standard deviation for the proton affinity distribution for all metals is likely a deficiency. A constant standard deviation requires that the shape of the affinity distribution is the same for all metals across all substrates. Research conducted in The Netherlands provides data that shows this is not the case (Benedetti et al., 1995 and Riemsdijk et al., 1996). Their data show that different metals do not experience the same apparent heterogeneity. Different heterogeneity of the substrate will produce differently shaped affinity distributions for each metal. Experimental data by Riemsdijk et al. (1996) for copper and the proton at different pH and ionic strengths did not fit the model assuming a constant standard deviation of the affinity distribution for both the proton and metals.

It has also been shown that the binding affinity of humic acid for a specific ion is affected by electrostatic potentials that are a function of the ionic strength (Milne et al., 1995 and Benedetti et al., 1996). Recent efforts by van Riemsdijk et al. (1996) and Avena et al. (1999) advocate an affinity distribution that takes into account ion-specific non-ideality and the heterogeneity characteristic of the surface including the electrostatic potential as a function of ionic strength.

Most of the modeling efforts reported in the literature rely on the Langmuir equation to describe the complexation of the metal. There are suggestions, however, that the Langmuir equation is only valid for affinity distributions that are represented by well-defined narrow peaks. A Freundlich-type binding equation is more appropriate for affinity distributions that are represented by one or more broad peaks (Wit et al., 1993 and Benedetti et al., 1995). Ligand-metal complexation is similar to adsorption processes and it is well known that the Langmuir isotherm does not apply to substrates with sites that have different energies of adsorption. Freundlich-type isotherms generally apply to substrates with heterogeneous surfaces typical of humic substances (Stumm and Morgan, 1996). It would be prudent to develop the option within MINTEQA2 for the use of different binding equations. Considering that the Freundlich isotherm is essentially a log distribution of the Langmuir equation the mathematics of this should be manageable.

In general it seems that the MINTEQA2 DOM-metal model suffers from an oversimplification of the theoretical basis and the lack of thermodynamic data. Its theoretical approach has not incorporated research characterizing the interaction of metals with humic substances published since 1995 or 1996. The literature published since 1996, much of it coming from The Netherlands, is critical of the simplistic type model used in MINTEQA2 and advocate more complex models to handle multi-component competition. In addition, the data included in MINTEQA2 are limited to those available in 1991. Even though MINTEQA2 allows for bimodal distribution and metal-specific affinity distributions, the data are not available to support these options. Also, the data applies only to the Suwannee River humic substances.

I believe that the question is one of: Should the addition of DOM model to MINTEQA2 be delayed until more comprehensive equations are prepared and more data become available? or Despite its limitations, is the current version better than nothing to describe the metal complexation with DOM? With or without the benefit of additional equations and data, the accuracy of the MINTEQA2 model should be tested by comparison with the analysis and speciation of actual groundwater and surface water samples. The results of these validation tests should accompany the user manual and give the user a basis for judging the results. Also, the user manual should be improved by including a discussion on use of the model. For example, because of the strong affinity between humic substances and calcium, barium, sodium and aluminum (Moto et al., 1996) the user should be cautioned against omitting the major cations in the input data.

3.4 Gibb's Phase Rule Violations

Corrections of MINTEQA2 to allow precipitated solids to re-dissolve as other solids precipitate, therefore eliminating violations of Gibb's phase rule, are long overdue. Most important, this change allows for more accurate representation of natural systems.

3.5 Non-Convergence Problems

The modifications to reduce non-convergence appear to be sensible and helpful. And because they are options that can be specified in PRODEFA2 the user controls their implementation.

3.6 Other Code Modifications

The code modifications to 1) increase the execution speed, 2) allow any species to be added as a titrant, 3) provide more options in specialized output, 4) allow database files to be named as the user wishes, and 5) correct known errors are all useful and important to fully utilize MINTEQA2. A future modification that users will find helpful is to create additional options for specialized output, such as more than six components or species.

3.7 Additional Findings of the Review

The User Manual Supplement needs thorough editing. In addition to correcting typographical errors the references must be checked. There are several references that are named in the text that are not in the reference list (for example, Serkiz et al., 1996) and there are errors in the reference listings (for example, the page numbers are interchanged between the two Cabaniss references).

Also, the beta version of Version 4 did not initially run on my computer with a 32-bit compiler running Windows95. The error message received was:

> Error TNT.20056: Can't read 386|VMM file: vmm.exp.
> Seek in file returned DOS error. DOS error code is: invalid file handle.

I contacted Jerry Allison and the problem was corrected when he sent me the file VMM.EXP, a virtual memory manager, and I included it in the MINTEQ directory.

4 References

Ali, Muhammad A. and David A. Dzombak. 1996. Interactions of Copper, Organic Acids, and Sulfate in Goethite Suspension. *Geochimica et Cosmochimica Acta*, Vol. 60, No. 24, pp. 5045-5053.

Avena, Marcelo, Luuk K. Koopal and Willem, H. Van Riemsdijk. 1999. Proton Binding to Humic Acids: Electrostatic and Intrinsic Interactions. *Journal of Colloid and Interface Science*, Vol. 217, pp. 37-48.

Benedetti, Marc. F., Chris J. Milne, David Kinniburgh, Willem, H. Van Riemsdijk and Luuk K. Koopal. 1995. Metal Ion Binding to Humic Substances: Application of the non-Ideal Competitive Adsorption Model. *Environmental Science & Technology*, Vol. 29, No. 2, pp. 446-457.

Benedetti, Marc. F., Willem, H. Van Riemsdijk and Luuk K. Koopal. 1996. Humic Substances Considered as a Heterogeneous Donnan Gel Phase. *Environmental Science & Technology*, Vol. 30, No. 6, pp. 1805-1813.

de Wit, Johannes C.M., Willem H. van Riemsdijk and Luuk K. Koopal. 1993. Proton Binding to Humic Substances. 2. Chemical Heterogeneity and Adsorption Models. *Environmental Science and Technology*, Vol. 27, No. 10, pp. 2015-2022.

Dzombak, David A. and Francois M.M. Morel. 1990. *Surface Complexation Modeling*. Wiley-Interscience. 393 pp.

Essington, Michael E. 1990. Calcium Molybdate Solubility in Spent Oil Shale and a Preliminary Evaluation of the Associated Constants for the Formation of $CaMoO_4^o$(aq), $KMoO_4^-$(aq) and $NaMoO_4^-$(aq). *Environmental Science & Technology*, Vol. 24, No. 2, pp. 214-220.

Evanko Cynthia and David A. Dzombak. 1999. Surface Complexation Modeling of Organic Acid Sorption to Goethite. *Journal of Colloid and Interface Science*, Vol. 214, pp. 189-206.

Manunza, Bruno, Salvatore Deiana, Vittoria Maddau, Carlo Gessa and Renato Seeber. 1995. Stability Constants of Metal-Humate Complexes: Titration Data Analyzed by Bimodal Gaussian Distribution. *Soil Science Society of American Journal*, Vol. 59, pp. 1570-1574.

Milne, C.J., D.C. Kinniburgh, J.C.M. de Wit, W.H. van Riemsdijk and L.K. Koopal. 1995. Analysis of Proton Binding by a Peat Humic Acid Using a Simple Electrostatic Model. *Geochimica et Cosmochimica Acta*, Vol. 59, No. 6, pp. 1101-1112.

Moto, A.M., A. Rato, C. Brazia and M.L. Simoes Goncalves. 1996. Competition of Al^{3+} in Complexation of Humic Matter with Pb^{2+}: A Comparative Study with Other Ions. *Environmental Science and Technology*, Vol. 30, No. 6, pp. 1970-1974.

Robertson, A.P. and J.O. Leckie. 1997. Cation Binding Predictions of Surface Complexation Models: Effects of pH, Ionic Strength, Cation Loading, Surface Complex and Model Fit. *Journal of Colloid and Interface Science*, Vol. 188, pp. 444-472.

Rusch, Ursula, Michael Borkovec, John Daicic and Willem H. van Riemsdijk. 1997. Interpretation of Competitive Adsorption Isotherms in Terms of Affinity Distributions. *Journal of Colloid and Interface Science*, Vol. 191, pp. 247-255.

Stumm, Werner and James J. Morgan. 1996. *Aquatic Chemistry*. Wiley-Interscience. 1022 pp.

van Riemsdijk, Willem H., Johnannes C.M. de Wit, Sipko L.J. Mous, Luuk K. Koopal and David G. Kinniburgh. 1996. An Analytical Isotherm Equation (CONICA) for Nonideal Mono- and Bidentate Competitive Ion Adsorption to Heterogeneous Surfaces. *Journal of Colloid and Interface Science*, Vol. 183, pp. 35-50

Venema, Peter, Tjisse Hiemstra, and Willem H. van Riemsdijk. 1996. Comparison of Different Site Binding Models for Cation Sorption: Description of pH Dependency, Salt Dependency and Cation-Proton Exchange. *Journal of Colloid and Interface Science*, Vol. 181, pp. 45-59.

ATTACHMENT C

Peer Review of MINTEQA2/PRODEFA2 Version 4.0 by:

Bruce Robinson
University of Tennessee - Knoxville

Review of MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0

MINTEQ is one of the most widely used and accepted geochemical equilibria programs. Its database's robustness, its flexibility, and the diversity of problems that it can address are some of its assets. Because MINTEQ is free, it has also proven to be a very useful educational tool.

Prefatory comments: The reviewer has been using MINTEQ in research and instruction for roughly 15 years and has been very satisfied with MINTEQ in the past. However, this reviewer is disappointed in the apparent lack of resources that have been devoted by EPA in the last several years to keep this highly valuable program up-to-date. Although MINTEQ's chemical computational abilities are among the best if not the best of any of the several geochemical equilibria programs available, MINTEQ's interface is woefully antiquated. No doubt the improvements to MINTEQ for Version 4 were the highest priority, but additional resources need to be invested to make MINTEQ Windows compatible, to greatly improve its input and output interfaces, and generally to make it much more user friendly.

The reviewer's impression is that MINTEQ will be used in the HWIR rule making process to set EPA criteria. The reviewer expects that MINTEQ will be used by environmental scientists and engineers well versed in aqueous chemistry. MINTEQ is primarily a tool for this type of user. MINTEQ is not a tool that can be recommended by the reviewer for users who are not expert in aqueous chemistry, because MINTEQ has a few idiosyncracies and is not especially user friendly. The user must be able to understand what MINTEQ is doing and to be able to interpret and judge the MINTEQ output.

The peer reviewers were asked to address 6 specific questions. These questions are used to frame the review below.

1). Did the process for revising the main thermodynamic database utilize the appropriate sources? What others, if any, should specifically be investigated?

Response: The priority or precedence of the databases used and the methodology used to reduce and format the equilibria and thermodynamic data for the MINTEQ database files is appropriate. This reviewer could not identify any other relevant and significant "English language" databases.

Elaboration: Chapter 5 of the *User Manual Supplement for Version 4.0* discusses the databases used and the methodology for reducing the data into the MINTEQ database. The National Institute of Standards and Technology (NIST) *Critical Stability Constants of Metal Complexes Database* (CRITICAL) was used as the primary source of thermodynamic equilibria data. Among aquatic chemistry researchers, the NIST database appears to be the most recognized. The precedence of other databases describes, e.g., using IUPAC SC-DATABASE as the next source, appears reasonable to this reviewer. Based on an online search of Chemical Abstracts and based on a web search using multiple search engines through *Copernic*, no other significant

and relevant English language databases were identified.

One issue that does warrant discussion in the manual is the uncertainty in the thermodynamic data. If MINTEQ is to be used to set environmental regulations and risk criteria, then the uncertainty in the predictions of MINTEQ must be addressed. This uncertainty begins with the uncertainty in the data. Equilibria constants are not determined with the same precision as many fundamental physical constants. Rather there is uncertainty in many of the equilibria constants that can easily approach an order of magnitude or more.

A couple of minor comments are listed below:

a) Although Chapter 5 discusses the databases used, references for these databases were not found in the bibliography.
b) Correction on page 30: The SC-Database is published by Academic Software rather than Academic Press if the reviewer is not mistaken.
c) The database identifies the source of data for each species and this will be very valuable for the user. However, if possible, it would also be useful to have footnotes in the thermodynamic database to define the abbreviations used for the sources and the units used for delta H.
d) Some species appear to have no enthalpy values for temperature corrections. It would be valuable to have a flag in the MINTEQ output to indicate to the user when this occurs. Otherwise, the user may erroneously believe that temperature corrections were correctly made.

2) Was the process for compiling data on reactions for implementation of the Diffuse-Layer model option appropriate? How might it have been improved?

Response: The process for compiling data on reactions for implementation of the Diffuse-Layer model does seem appropriate for this model.

Elaboration: The manual on *Diffuse-Layer Sorption Reactions for use in MINTEQA2 for HWIR Metals and Metalloids* includes scant information on how the data for these reactions were compiled. The manual merely says that the data were a compilation of reactions for hydrous ferric oxide (HFO) by Dzombak and Morel published in a monograph in 1990 title *Surface Complexation Modeling: Hydrous Ferric Oxide*. It is not possible to conclude whether the method of compilation was valid based on just this statement. No evidence is presented in the manual that the data have been peer reviewed by the profession although it does appear that the process for determining such data were described in an earlier 1987 journal paper by Dzombak and Morel. Furthermore, the reviewer was able to obtain a copy of *Surface Complexation Modeling: Hydrous Ferric Oxide* and reviewed the relevant chapters. Based on a review of the relevant chapters in *Surface Complexation Modeling: Hydrous Ferric Oxide*, the reviewer believes Dzombak and Morel went through considerable efforts to develop quality assured data for HFO sorption reactions. It is doubtful that there is a better source of compiled data for HFO sorption equilibria constants for the model used. However, there are certain assumptions quality assurance (QA) criteria that should be recognized in the manual. These assumptions ands QA

criteria were discussed by Dzombak and Morel in their monograph and have to do with the HFO preparation method, types of reaction vessels, background electrolyte, sorption kinetics, solid-liquid separation method, site densities, etc. Dzombak and Morel went through a very careful process to screen the literature available in 1991 and to develop equilibria constants. It appears that most of the data in the Feo-dlm.dbs database do come from *Surface Complexation Modeling: Hydrous Ferric Oxide*. Undoubtedly, more research on HFO sorption has appeared in the last 10 years, hopefully of more uniform and better quality, and EPA should allocate resources to thoroughly update the database. Consistent with being a valuable source of data for DLM model, the 1991 monograph by Dzombak and Morel has been referenced hundreds of times according to the *Web of Science* citation index.

The characteristics of HFO are highly variable. A discussion in the manual of the uncertainty and potential ranges in sorption equilibria constants is warranted even if it is very qualitative. Certain quantitative error statistics were available in the source reference.

A couple of minor comments are listed below:

a) On page 2, last paragraph, the manual on *Diffuse-Layer...* stated that manganese is not a contaminant metal in HWIR. Interestingly, manganese is a metal of concern to DOE as the reviewer observed while on leave to DOE. This concern apparently arises out of toxicity information on manganese in the IRIS data base.

b) Much of the equilibria data used for HFO sorbent in the diffuse-layer model (DLM) are the same as those in earlier versions of MINTEQ. Additional data for several species have been added. There was some confusion to the reviewer in that the species and data listed in Appendix A of the manual on *Diffuse-Layer...* are different than in the actual Feo-dlm.dbs data files used by MINTEQ. The Actual data file in MINTEQ appears to be more extensive than in Appendix A. It would seem that Appendix A ought to be brought in line with the Feo-dlm.dbs file.

3) Is the implementation of the Gaussian model for addressing dissolved organic ligand reactions appropriates?

Response: The implementation of the Gaussian model is appropriate.

Elaboration: The Gaussian approach to organic ligand reaction seems to be one of the favored approaches based upon papers seen in the literature. The manual supplement has a very nice discussion of this theory and should allow the user to better understand and interpret the MINTEQ input and output. The reviewer did a limited number of tests with the Gaussian model to test whether the MINTEQ results make sense. In the past, the reviewer discovered errors in the old HIWAY (1974) air dispersion model and also in one group's uses of MEPAS contaminant transport and risk assessment model by simply seeing how the model responded to variations in input values, i.e., partial sensitivity analysis. The response of the Gaussian model in MINTEQ to the limited testing appeared logical to the reviewer.

A couple of minor comments are listed below:

a) There does seem to be some problems in PRODEFA2.exe. The reviewer was not able to use a seed file and then change the DOM data, e.g., concentration of DOM1, in the seed file. PRODEFA2 skipped over the screen that asks for that input. This problem also occurred when creating the original file and then trying to go back and change the DOM information. Also, the reviewer could not specify input for more than DOM1. In trying to run a test file with DOM1, DOM2, and DOM3, an execution error resulted. The acidity and site concentration were zero for both DOM2 and DOM3 and may have been the cause of the execution error. However, PRODEFA2 did not give a chance to enter any inputs for DOM2 or DOM3, and besides, the reviewer thought that these would be set as defaults. Obviously, the reviewer does not understand something here about the input data setup for bi- or tri-modal DOM. Finally, the manual supplement was not totally clear, but the reviewer assumes that the Gaussian model can only have one DOC source but with different types of functional groups, i.e., DOM1, DOM2, and DOM3. The different DOM's are not for different DOC sources, i.e., 10 mg/L of DOM1, 20 mg/L of DOM2, etc., but rather just different functionalities on the DOM.

b) Page 1, equation 1: t would be helpful to have { } around X_j to read $\{X_j\}$, i.e., activity of component j, consistent with $\{S_j\}$.

c) Page 2, equations 3 and 4: the summation should terminate with "m" rather than "n" since "i" corresponds to species and "m" is the number of different species.

d) On page 10 and figures 2.1 and 2.2, shouldn't T_{Li} and the y-axis be a probability density function, rather than just ligand concentration? That is, ligand concentration density (units of ligand concentration/log K).

e) A summary list of all assumptions would be useful.

f) More properly mathematically, equation 22 should be thought of as:

$$\Delta[ML_i] + (\text{existing terms}) \cdot \Delta \log K_{MLi}$$

The above is then integrated to yield equation 23.

4) Are the modifications to address Gibb's Phase Rule violations appropriate?

Response: The modifications to address "Gibb's Phase Rule" violations appear to solve this problem based on results of a simple test. Thus, the modifications are appropriate.

Elaboration: The simple test mentioned above in the response was based on the example "phase rule" violation discussed in the Version 4 supplement manual. The example consisted of Ca^{2+} = 3.0 mM, Mg^{2+} = 1.0 mM, CO_2 = 0.003 atm, and pH = 11.5. In older versions of MINTEQ, this problem gave an error when magnesium tried to precipitate. In Version 4, no error occurred and MINTEQ appears to have executed correctly. One comment, though. The manual stated that adding an extra component such as nitrate in the older MINTEQ version, would solve the problem unless additional solids tried to precipitate in which case another additional component would be needed. Indeed, adding nitrate in the older MINTEQ version allowed magnesite to precipitate after calcite precipitated in the above problem. However, a subsequent "phase violation" error occurred when dolomite tried to precipitate. Adding chloride as an additional component did not eliminate the error as the manual implied.

Chapter 3 of the manual supplement discusses the phase rule issue. The chapter is somewhat murky and confusing. The confusion arises partly over whether there actually is or isn't a Gibb's phase rule violation in the example chemical system at equilibrium. The confusion is increased by the uncertainty in how the program handles water as a component and how it actually works with the phase rule equation. For example, consider the problem discussed in the manual. If one thinks about adding $CaCO_{3,(S)}$ and $Mg(OH)_{2,(S)}$ into H_2O under an atmosphere of $CO_{2,g}$, then following the lead of Stumm and Morgan on page 306 of Aquatic Chemistry:

C = number of components = 4 (i.e., $CaCO_{3,(S)}$, $Mg(OH)_{2,(S)}$, H_2O, $CO_{2,g}$)
P = number of phases = 4 ($CaCO_{3,(S)}$, $Mg(OH)_{2,(S)}$, aqueous phase, gas phase)

Hence, the degrees of freedom are:

$$F = C - P + 2 = 4 - 4 + 2 = 2$$

Thus one can set two variables, e.g., temperature and p_{co2}. If H^+ is added as a component, then F = 5 - 4 + 2 = 3 and one can set three variables, e.g., temperature, p_{co2}, and pH. Thus there is no phase rule violation. But the manual supplement is confusing about whether water is a component or not. The manual supplement says that water is understood to be a pure phase and a component and thus essentially cancels out. But there is no pure phase of water in the problems of interest. Water will of course cancel out if one considers that there is always an aqueous phase. Is this what is meant? Also, the manual refers to temperature and pressure always being set and hence using the equation F = C- P. But it is then not clear how MINTEQ might handle problems where pressure that is set is not the vapor pressure of water but the partial pressure of some other component such as CO_2. Based on Chapter 3 in the manual supplement, the reviewer is confused whether MINTEQ correctly manipulates the Gibb's phase rule equation in all cases.

5) Are the modifications to minimize non-convergence appropriate?

Response: The modifications described in section 4.2 to minimize non-convergence seem appropriate.

6) Are the other code modifications including those for a) increased execution speed, b) modeling titrations, c) specialized outputs, d) customized database filenames, and e) correction of known errors, adequate and useful?

Response: All of the additions and improvements listed in question 6 are beneficial, useful, and commendable. However, the reviewer would like to see further enhancements in the titration and output capabilities. These two aspects are discussed in more detail below.

Elaboration: The ability to do titrations (item **6b** above) is a useful addition to the program, but the titration capability does not appear to be able to handle volumes of the sample and titrant. In other words, the program simply allows the user to vary the total concentration of species in the aqueous solution, but doesn't actually simulate a lab titration involving volumes. Such as ability

would be useful for analyzing laboratory data.

The addition of the ability to produce files that are more directly importable into a spreadsheet (item **6c** above) is also very useful. A maximum of 6 species can be written to the file. A higher maximum number of species would be valuable on occasion.

Other comments of the reviewer

i) Input and output names are restricted to 8 characters plus a 3 character extension. This makes it very awkward to create a long sequence of similar input files and to have meaningful names still make sense in several months. If there are any versions of Fortran that allow longer file names, this would be very useful.

ii) It has always seemed to the reviewer that very low concentrations of species predicted by MINTEQ might be unreliable, because those species might not have converged before MINTEQ met its overall convergence criteria. If this is indeed possible, then MINTEQ should have a flag as to which species might not have converged.

iii) Instruction about MINTEQ appear now in several different reports and manuals. It would be very helpful to integrate (with emphasis on integrate) these several manuals into one manual.

iv) The manner in which MINTEQ handles hydroxide is certainly legitimate (i.e., it is not a component whose concentration can be entered as input), but it is awkward and confusing to the uninitiated. It would be useful to allow the user to add hydroxide as a species and let MINTEQ convert it into negative proton internally

Errata in Manuals
Manual Supplement for version 4.0

i) Page 14, second full paragraph: this seems redundant with earlier material.
ii) Page 29, 3rd paragraph, 2nd to the last sentence: "Add something here..." appears to be a note to manual author.
iii) Page 31, 1st paragraph in section 5.2, line 5: "values or..." should be "values of..."
iv) Page 31, 1st paragraph in section 5.2, line 9: should it read "<u>not</u> already corrected..."?
v) A global search should be done to catch the several instances of "data was" rather than "data were"
vi) Page 37, 6th line from bottom: "known" rather than "knpwn"

Diffuse-Layer Sorption Reactions for Use in MINTEQA2 for HWIR Metals and Metalloids
i) Page 2, 7th from bottom: insert "to" to read "belongs <u>to</u> the alkaline..."
ii) Page 2, 5th line from the bottom: increase clarity by changing "Its" to <u>Beryllium's</u> behavior..."
iii) A global search should be done to catch the several instances of "data was" rather than "data were"