Appendix E

Review of Validation Studies Concerning the U.S. EPA Geochemical Speciation Model MINTEQA2

This page intentionally left blank.

**Review of Validation Studies Concerning
the U.S. EPA Geochemical Speciation Model
MINTEQA2**

Prepared for the
U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Ecosystems Research Division
Athens, GA

Prepared by
Allison Geoscience Consultants, Inc.
Flowery Branch, GA

August 30, 2002

This page intentionally left blank.

Table of Contents

List of Figures

List of Figures (continued)

Executive Summary

This report documents and reviews available reports, papers, and studies relating to the validation and verification of the U.S. EPA geochemical speciation model, MINTEQA2. Evidence relating to the verification of MINTEQA2 calculations, including its initial verification and verification efforts over the course of its history are reviewed. Quality assurance efforts used during modifications of the MINTEQA2 thermodynamic database are discussed. There have been hundreds of reported studies in which MINTEQA2 was applied. Only a small fraction of these qualify as validation studies, and in many of these, validation of MINTEQA2 was not the central focus of the work. Regardless of the overall focus of the reported study, the key requirement for considering a particular work as a MINTEQA2 validation study is that results calculated by MINTEQA2 are compared with some measure of reality. We have attempted to include all studies that illuminate the question of MINTEQA2 validation, regardless of whether pro or con. The table below summarizes the validation studies discussed in the text.

Study Citation	Basis of Validation	Metals
Unpublished MINTEQA2 workshop problem	Comparison of a pH curve from a leaching experiment showing leachate pH versus concentration of acetic acid in the leachant with similar curve computed by MINTEQA2.	pH
Frandsen and Gammons (2000)	Comparison of dissolved metal concentrations predicted by MINTEQA2 with measured values	Zn, Cu, Fe
Marani *et al.* (1995)	Comparison of equilibrium mineral phases predicted by MINTEQA2 with sample mineral phases identified by X-ray diffraction.	Pb
Fotovat and Naidu (1997)	Compares free Cu^{2+} and Zn^{2+} in solution as determined using ion exchange procedures versus computed by MINTEQA2	Cu, Zn
Jensen *et al.* (1998)	Compares speciation of Fe(II) and Mn(II) in solution as determined using ion exchange procedures versus computed by MINTEQA2	Fe(II), Mn(II)
Yu (1996)	Comparison of solid phases predicted to precipitate by MINTEQA2 versus solid phases identified in field samples using X-ray diffraction and other analytical methods	Fe, Al
Palmer *et al.* (1998)	Comparison of Cu^{2+} activity measured using an ion-selective electrode with Cu^{2+} activity computed by MINTEQA2	Cu
Davis *et al.* (1992)	Comparison of MINTEQA2-calculated metal solubilities with measured solubilities	As, Pb
Loux *et al.* (1989)	Comparison of fraction of metal remaining in solution in batch equilibrium experiments using aquifer materials versus fraction of metal dissolved at equilibrium as calculated by MINTEQA2 using diffuse-layer sorption model	Ba, Be, Cd, Cu, Ni, Pb, Tl, Zn
Jenne (1994)	Solid phases predicted to exist at equilibrium by MINTEQA2 were compared with solid phases identified using analytical methods	Ca, Fe, Mn, Al, Si
Stollenwerk (1994)	Comparison of dissolved concentrations of metals measured in a series of wells with solution concentrations predicted using MINTEQa2 with diffuse-layer model	Al, Fe, Mn, Ca, Cu, Co, Ni, Zn, pH, SO_4

Study Citation	Basis of Validation	Metals
Stollenwerk (1996)	Comparison of dissolved concentrations of metals measured in a column experiment effluent with dissolved concentrations predicted using MINTEQA2 with diffuse-layer model	Al, Cu, Co, Ni, Zn
Stollenwerk (1995)	Comparison of dissolved concentration of molybdate in column experiment effluent with dissolved concentration predicted using MINTEQA2 with diffuse-layer model	MoO_4
Doyle *et al.* (1994)	Comparison of dissolved concentrations of As in batch and column tests with dissolved concentrations predicted by MINTEQA2	As(V)
Saunders and Toran (1995)	Comparison of dissolved concentrations of metals at monitoring wells near a disposal pond with dissolved concentrations predicted by MINTEQA2	Co, Cd, Pb, Sr, U, and Zn
Christensen and Christensen (1999)	Concentrations of metal-DOC complexes determined in batch experiments using a resin exchange method were compared with concentrations of metal-DOC complexes computed by MINTEQA2	Cd, Ni, Zn
Christensen *et al.* (1999)	Concentrations of metal-DOC complexes determined in batch experiments using a resin exchange method were compared with concentrations of metal-DOC complexes computed by MINTEQA2	Cu, Pb
Christensen and Christensen (2000)	Concentrations of metal-DOC complexes determined in batch experiments using a resin exchange method were compared with concentrations of metal-DOC complexes computed by MINTEQA2 over a range of pH values	Cd, Ni, Zn
Khoe and Sinclair (1991)	Comparison of dissolved metal concentrations predicted by MINTEQA2 versus concentrations measured in neutralization experiments	Al, Fe, Ca, Mn, SiO_2, PO_4, Pb, U
Webster and Webster (1995)	Comparison of dissolved As concentrations measured in batch experiments with dissolved concentrations predicted by MINTEQA2 using the diffuse-layer model	As(III), As(V)
Woodfine *et al.* (2000)	Comparison of QWASI simulation results of average lake water dissolved metal concentrations with observed values when MINTEQA2-predicted partition coefficients are used	Cu, Ni
Routh and Ikramuddin (1996)	Comparison of MINTEQA2-predicted equilibrium solid phases with solid phases observed by X-ray diffraction and comparison of predicted water concentrations with observed values	Pb, Zn

E.1 Introduction and Background

The purpose of this report is to review and document available reports, papers, and studies relating to the validation and verification of the U.S. EPA geochemical speciation model, MINTEQA2. MINTEQA2 has been used to estimate metal partition coefficients in several rulemaking activities by the U.S. EPA Office of Solid Waste. Given the importance of the partition coefficient in determining the outcome of fate and transport modeling for metals, it is anticipated that those responsible for reviewing these rules and those to be regulated by them will be interested in the degree to which MINTEQA2 has or has not been validated. This report reviews studies that relate to validation of MINTEQA2 to provide an assessment of its validation status. Prior to the presentation of the validation studies, the efforts that have been made to verify MINTEQA2 calculations are documented.

E.1.1 Description of MINTEQA2

MINTEQA2 is an equilibrium geochemical speciation model maintained and distributed by the U.S. EPA. From input data consisting of total concentrations of chemical constituents, MINTEQA2 calculates the fraction of a contaminant metal that is dissolved, adsorbed, and precipitated at equilibrium (see Figure 1). As input data, the total concentrations of major and minor ions, trace metals and other chemicals are specified in terms of key species known as components. MINTEQA2 automatically includes an extensive database of solution species and solid phase species representing reaction products of two or more of these input components. The model does not automatically include sorption reactions, but these can be included in the calculations if supplied by the user. When sorption reactions are included, the dimensionless partition coefficient can be calculated from the ratio of the sorbed metal concentration to the dissolved metal concentration at equilibrium. The dimensionless partition coefficient is converted to K_d with units of liters per kilogram (L/kg) by normalizing by the mass of soil (in kilograms) with which one liter of solution is equilibrated (the phase ratio). An isotherm is generated when the equilibrium metal distribution between sorbed and dissolved fractions is estimated for a series of total metal concentrations.

Progress in accounting for sorption in equilibrium calculations over the past decade has resulted in the development of coherent databases of sorption reactions for particular sorbents. These databases include acid-base sorption reactions and reactions for major ions in aquatic systems (Ca, Mg, SO_4, etc.). Including such reactions along with those representing sorption of trace metals makes it possible to estimate sorption in systems of varying pH and composition. Examples of coherent databases of sorption reactions include that for the hydrous ferric oxide surface presented by Dzombak and Morel (1990) and a similar database for goethite presented by Mathur (1995).
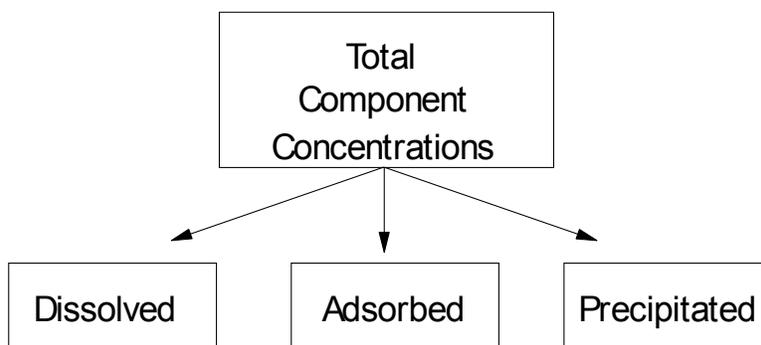
**Figure E-1. MINTEQA2 Computes the Equilibrium
Distribution of Metal**

E.1.2 History of MINTEQA2

The original version of this model (called MINTEQ) was developed in the early 1980's at Battelle Pacific Northwest Laboratory by Felmy and coworkers (Felmy *et al.*, 1984) as a cooperative effort funded by the U.S. Department of Energy and the U.S. EPA. The MINTEQ package was delivered to the U.S. EPA Environmental Research Laboratory at Athens, Georgia (AERL) in 1985.[1] The model was renamed MINTEQA1 to designate this Athens version which was anticipated to diverge from the original as it was adapted to the special needs of the U.S. EPA.   The model was first distributed with this name from the Athens lab in 1986, but there were very few differences between this MINTEQA1 and the original MINTEQ. The distribution package, available for DOS-based PC's or for Digital Equipment Corporation VAX machines, included a preprocessor program PRODEFA1 for the preparation of MINTEQA1 input files. After more significant revisions were made in the late 1980's, the name was changed to MINTEQA2. With further development, version numbers were used to indicate new versions, and the model's formal name was left as MINTEQA2.

E.1.2.1   Code Modifications

The original MINTEQ developed by Felmy and coworkers was produced by combining the mathematical structure of MINEQL (Westall *et al.*, 1976), with the thermodynamic database of the WATEQ3 model developed by the U.S. Geological Survey (Ball *et al.*, 1981). The mathematical formulation which MINEQL embodies was also used in MINTEQ. Many of the Fortran subroutines in MINEQL were used directly or with little modification in MINTEQ, which was also written in Fortran. After MINTEQ was delivered to the U.S. EPA, it underwent continuous testing and development by an on-site computer specialist and geologist staff person assigned for that purpose through 1992. Development slowed after 1992, with further modifications occurring in response to specific U.S. EPA needs. Important revisions to the code since its initial delivery in 1986 include:

---

[1] This lab is now known as the National Exposure Research Laboratory, Ecosystems Research Division.

- Addition of the diffuse-layer adsorption model (also known as the MIT two-layer model) with a database for sorption onto hydrous ferric oxide (HFO) as compiled by David Dzombak (Dzombak, 1986; later modified in Dzombak and Morel, 1990)

- Addition of the Gaussian distribution model for dissolved organic matter (DOM) with an associated database of reactions (Dobbs *et al.*, 1989; Susyeto *et al.*, 1991; Allison, 1997)

- Alteration of the code to include sparse-matrix techniques to increase execution speed (Allison, 1997)

- Addition of an automated procedure for producing successive model executions as one parameter (e.g., pH, pe, total concentration of a species) is varied

- Addition of a procedure to write key equilibrium results to a file for input to a spreadsheet program and subsequent plotting

- Provision to display the source of thermodynamic data for each species listed in the output file. The source of the thermodynamic data was added to the database as described in the section on database quality

- Continual improvements in convergence methods and correction of minor errors encountered and reported by users worldwide

- Continual improvement in the PRODEFA1 (later, PRODEFA2) preprocessor program.

The version of the model distributed publicly by the U.S. EPA Center for Exposure Assessment Modeling (CEAM) was periodically updated as these improvements were implemented. The succession of model names and versions numbers was: MINTEQA1 (no version numbers); MINTEQA2, versions 2.0, 2.01, 3.0, 3.10, 3.11, 4.0, 4.01, 4.02 (current version; released 1999).

Since the delivery of MINTEQ by Battelle, the U.S. EPA has maintained and distributed the model through the Center for Exposure Assessment Modeling (CEAM) at the EPA Environmental Research Laboratory (Athens). CEAM has provided an orderly procedure for maintaining and distributing MINTEQA2 and other computer codes. Users who obtain MINTEQA2 through CEAM are provided with a contact to report errors or suspected errors in the model or its results. Also, prior to releasing any new version of MINTEQA2, the revised code is subjected to verification tests by CEAM to ensure that the modifications work as intended and produce the desired results. These tests include compiling on multiple compilers and test executions of a battery of equilibrium problems with known solutions. The tests were designed to exercise all important algorithms in the code. Each successive version of the model has been required to pass these tests before release.

E.1.2.2   **Database Modifications**

The thermodynamic database contained in WATEQ3 was selected for use in the original MINTEQ because it was felt to be among the best such databases available in the 1980's. The log equilibrium constants for the reactions it contained had been tested for consistency (Nordstrom and Muñoz, 1986). The main shortcoming of its implementation in MINTEQ was that the source of the thermodynamic constants (log equilibrium constants and enthalpies of reaction) were not documented. The MINTEQA2 thermodynamic database has been updated occasionally throughout the model's history to add new component species or to update the thermodynamic constants of existing reaction species. MINTEQ thermodynamic data for species involving the trace metals chromium (+2, +3, and +6 oxidation states), mercury (+1 and +2 oxidation states) , selenium (+4 and +6 oxidation states), and thallium (+1 and +3 oxidation states) were updated in an EPA-funded project shortly after the model was developed (Deutsch and Krupka, 1985). Components and reaction products with accompanying thermodynamic data were added in 1989 for antimony (+3 and +5 oxidation states) and cyanide (Sehmel, 1989). The thermodynamic database released with version 2.0 in 1988 included the addition of 22 organic ligands and several hundred reaction products between those ligands and trace metals. The metal-organic complexes were added through an EPA-funded research project at Colorado School of Mines in which carboxylic and dicarboxylic acids and other organic substances associated with landfill leachate were identified. Nine more organic ligands and associated reactions were added in version 2.01 (1989). An article appearing in *Water Research* in 1996 pointed out several errors in the formulation of these metal-organic complexes as entered in the MINTEQA2 database (Serkiz *et al.*, 1996). Those database entries were reviewed and corrected and a revised database was prepared in 1996 (Allison, 1996). The database was modified again in 1999 for version 4.0 to add species for beryllium (Be), cobalt (Co), molybdenum (Mo), and tin (Sn); to update the equilibrium constants for other inorganic species; and to add the source of the reaction thermodynamic constants (log K and enthalpy of reaction) for all species for which these could be determined (USEPA, 1998). These last two modifications to the thermodynamic database utilized the electronic databases CRITICAL (NIST, 1997) and SC-DATABASE (IUPAC, 1998) as primary data sources. The former represents the continued development of the compilation of critically reviewed metal stability constants by Smith and Martell published in book format in the 1970's and 80's. The sources of thermodynamic data are important in considering the validity of the modeling results; these sources are discussed more fully in Section 2.2 below.

E.2 Verification and Validation

In the background material above, custom has been followed in that MINTEQA2 has been referred to as a "model." In a sense, this is incorrect. MINTEQA2 should rather be thought of as a convenient framework that within which a particular geochemical model may be implemented. That MINTEQA2 includes its own database of thermodynamic reactions may obscure the fact that a geochemical model does not exist until the user specifies certain MINTEQA2 input parameters that define the system. Defining the system includes specifying components to represent total concentrations of major and trace ions and imposing equilibrium conditions such a pH, E_h, solid phases present at equilibrium, equilibrium gas partial pressures, etc. The point that MINTEQA2 is a modeling framework rather than a model is important when one considers its validation status. To help clarify this point, the term *partial validation* has sometimes been used to indicate the validation of a particular geochemical model posed within the MINTEQA2 framework or that of another speciation "model" (Krupka *et al.*, 1983; Jenne and Krupka, 1985; Zachara *et al.*, 1987; Jenne, 1994).

In every application of a speciation model, it is incumbent upon the user to apply geochemical wisdom in reviewing the completeness and quality of the thermodynamic database and to make necessary additions or changes. The completion of the database review step is another requirement necessary to develop a true geochemical model within the MINTEQA2 modeling framework. This requirement is especially important in selection of solid phases that are to be allowed to precipitate. For example, a user designing a model to represent a laboratory system must consider precipitation kinetics (or dissolution kinetics) in deciding which phases MINTEQA2 should consider. A particular solid may indeed be the equilibrium phase if the system is to be allowed years to equilibrate, but not if the equilibration period is one day. Sorption modeling imposes another critical chore of database management on the user. Sorption reactions and their associated equilibrium constants are specific to the particular sorbent type: aluminum oxide, amorphous hydrous ferric oxide, various crystalline oxides, etc. One cannot directly use reactions describing trace metal sorption onto hydrous ferric oxide to represent reactions onto an aluminum oxide surface. Interchangeability of reactions is even less likely for clay surfaces and more complicated natural sorbents such as organic matter. Another complicating factor in including sorption reactions is that the available reactions are specific to the sorption model within which they were derived. MINTEQA2 includes seven sorption models. A uniform database containing acid-base, major ion, and trace metal reactions is included for only one sorbent: hydrous ferric oxide (Dzombak and Morel, 1990). This database is designed for use in the diffuse-layer sorption model and cannot be used directly for any other. Thus, the geochemical model actually consists of the combination of the user's input parameters that describe and constrain the system, the user-approved or user-modified thermodynamic database, and the computer code that implements equilibrium in the system.

Verification refers to tests and studies that, by design or otherwise, show that the computations performed by the computer code representing a model are true to the intent of the conceptual model. Verification tests determine whether the computer code, compiled into an executable program, arrives at the intended and expected answer for a given set of input values. Here, "input values" include total concentrations of components, the set of equilibrium reactions and their thermodynamic constants, perhaps one or more imposed equilibrium conditions, and the settings of various program flags and options such as ionic strength, method of estimating activity coefficients, and system temperature. The "answer" obtained from the computer code consists of all computed quantities including the equilibrium concentrations of all solution species and the amounts of solid phases that have dissolved from an initially present solid or precipitated from the solution. The computed answer also may include the ionic strength and activity coefficients of solution species. Verification can be achieved for individual algorithms that make up the entire computer program. For MINTEQA2, it is impossible to test all program options and features in one program execution. The basis of judging a computer code as verified rests on comparison of the computed answer with a standard. The standard may be the result of a hand calculation or the result from a similar computer code that has itself been verified In either case, it is necessary to use the same reactions and thermodynamic data when calculating the results from the code to be verified as was used in calculating the results for the standard of comparison.

Validation refers to tests and studies that show that the geochemical model that is implemented by the combination of the user's input parameters, the thermodynamic database, and the computer code provides an acceptable representation of reality or that it produces an outcome that is an acceptable representation of reality. This definition presupposes that there exists a measurement or group of measurements that may be taken as reality and that can be used as the standard to which the model result is compared. For geochemical models, validation is significantly more complicated and uncertain than verification.

There are difficulties in validating geochemical models regardless of whether the model outcome is compared with measurements on natural field systems or lab systems that mimic the natural environment. Natural systems are replete with complicating factors that result in imprecise or uncertain measurements and conditions that fail to correspond to the primary tenet of MINTEQA2-based geochemical models: that the system reflects equilibrium conditions. Problems and issues in measuring (analytical methods, sample handling, determining redox status), problems in incomplete knowledge of the natural environment (true nature of sorption reactions, partial pressures of gases, rates of reaction, degree of mediation by biota), and the high degree of variability in important chemical characteristics of natural systems all serve to complicate comparisons of model systems with their real counterparts. In consideration of the challenges of validating geochemical models, the U.S. EPA convened a meeting of geochemists, soil scientists, and other groundwater professionals at the Athens, Georgia, Environmental Research Lab in 1989. Opinions were varied among those present as to what might constitute a validation of the model (Dr. Dave Brown, pers. comm., 2002). Those professionals who specialized in laboratory analysis felt that comparisons of MINTEQA2 predictions with measurements made on closely controlled laboratory systems would provide the most relevant validations. Those who were more field-oriented felt that laboratory systems could not faithfully represent the real systems that are of interest; they preferred a validation exercise closely tied to field sampling of an appropriate system. The statisticians pointed out that the natural variability

in many important MINTEQA2 input parameters would required that the model be validated at a host of diverse sites. All of these viewpoints have merit. This diversity of opinions on how to validate MINTEQA2 is a reflection of the difficulty of the undertaking. However, in the fourteen years since that workshop, numerous and varied studies have been performed that, directly or indirectly, relate to the validation of MINTEQA2. These are discussed individually in Section 3.0.

E.2.1 Verification of MINTEQA2 Calculations

This section documents evidence relating to the verification of MINTEQA2. As mentioned above, it is not possible to verify all parts of the MINTEQA2 computer code in a single model execution. In part, this is due to the mutually exclusive nature of some program options. All parts of the MINTEQA2 code have been verified. Those sections that existed at the beginning of the model's lifetime were verified by comparison of results with those of similar (verified) models. As a quality assurance measure, CEAM policy has required that all code modifications and additions to MINTEQA2 be tested by a combination of compiler tests and model execution tests before final adoption. The compiler tests required that the model be compiled using Fortran compilers from multiple vendors and that the effect of various compiler options on execution time and computed results be examined and accounted for. The execution tests for MINTEQA2 consisted of a series of equilibrium problems for which the answer was known or could be computed by hand calculations. This quality assurance requirement is a primary basis that supports the assertion that MINTEQA2 calculations have been verified.

E.2.1.1   Initial Comparison with Other Computer Models

In a 1988 report discussing the feasibility of validating MINTEQ, Zachara and coworkers at the Battelle PNL where MINTEQ was developed stated that all major code algorithms including calculation of mass balance, activity coefficients, and equilibrium speciation were verified by comparison with hand calculations during the model's initial development (Zachara *et al*., 1988). Speciation results from test executions, some involving adsorption reactions, also were found to agree with identical test calculations using WATEQ3 and MINEQL. In a study comparing the results of several equilibrium speciation models including MINTEQ, Morrey *et al.* (1985) verified that results from these models are the same when identical thermodynamic data and program options are used.

E.2.1.2   Later Verification Efforts

As mentioned above, after its delivery to the U.S. EPA, MINTEQ was developed further (under the names MINTEQA1 and finally MINTEQA2). Development of the code was performed under the auspices of a centralized modeling group, the Center for Exposure Assessment Modeling (CEAM) at the US. EPA lab at Athens, Georgia. The CEAM group administered the development, public distribution, and user-assistance for MINTEQA2 and other useful water quality models. CEAM established guidelines that required modifications to model codes be tested by comparison of before and after results and by compiling the modified code using multiple compilers. A standard battery of test problems was used in these comparison tests.

Additional verification tests were performed when new algorithms were added to give MINTEQA2 capabilities. For example, the diffuse-layer (Generalized Two-Layer) sorption model was added in 1989. This sorption model had previously been added to MICROQL (Westall, 1979) and MINEQL by David Dzombak (Dzombak, 1986). Test problems were presented in Dzombak (1987) along with their computer solutions (using MICROQL) and hand calculated solutions. These formed the basis of comparison to verify the correct implementation of the diffuse-layer model in MINTEQA2. In similar manner, the Gaussian distribution model for computing the complexation of metals with organic matter was verified by hand calculation when it was added to MINTEQA2 version 3.11 and further developed in version 4.0 (Allison, 1997). The correct implementation of the Gaussian DOM model was also verified by a procedure described in (Fish *et al.*, 1986) in which the Gaussian distribution of ligand concentration and log K is approximated by a small set of ligands whose concentrations and reaction log K values are scaled to conform to the Gaussian distribution. This method can be implemented in MINTEQA2 without recourse to the formally introduced Gaussian model option. Results from the formally implemented Gaussian DOM model were found to agreed with the "manually implemented" Gaussian results, excepting a margin of error in the latter inversely proportional to the number of ligands used to implement it (Allison and Perdue, 1994).

The organized public distribution of MINTEQA2 under CEAM provided a useful clearinghouse chore for reporting suspected errors in the code or in the thermodynamic database. Especially during the early years of its distribution, many errors (especially in the pre-processor PRODEFA2) were discovered and corrected. The confidence that can be placed in MINTEQA2 has been enhanced by its use by the public and their feedback in reporting errors. Modifications made to correct errors as well as to enhanced the model were alike subject to verification tests prior to release in new versions.

Finally, verification of the MINTEQA2 code has been assured through the use of the model in solving elementary speciation problems for use in teaching geochemistry. Several universities have used MINTEQA2 in their courses. Dr. Willard Lindsay has discussed the use of MINTEQA2 in teaching soil chemistry (Lindsay and Ajwa, 1995). Classroom problems typically are made amenable to hand calculations so that the student may better appreciate the nuances of how the problem is solved. Dr. James Drever also used MINTEQA2 to illustrate the solution of problems in groundwater chemistry in his book *The Geochemistry of Natural Waters* (Drever, 1997). Simple problems with answers easily calculated by hand were also used in MINTEQA2 workshops sponsored by the U.S. EPA in the late 1980's and early 90's. Typically, a simple system involving $CaCO_3$ in water is solved in a series of successively more complicated problems (solution equilibria only, solution equilibria with constrained pH, with constrained CO_2 partial pressure, with solid phases). Classroom exercises illustrating correct answers using redox and sorption reactions were also performed. Wrong answers for such exercises would quickly become apparent as the results are used to explain the chemistry in intuitive terms in the classroom. Also, before MINTEQA2 was used in the first such workshop, its answers were compared with those of MINEQL for the same set of ten simple problems and were found to agree.

E.2.2 Quality of the MINTEQA2 Thermodynamic Database

As discussed in Section 1.2.2, the thermodynamic database used by MINTEQA2 has been revised repeatedly to correct and update thermodynamic constants and to add new species. Any assessment of the validity of MINTEQA2 applications must consider the quality of the thermodynamic database that it uses. The following paragraphs describe the data sources that have been used to update and add to the MINTEQA2 database in recent years. Steps taken to reduce unintended errors during the process of updating the database are also described. For the 1996 and 1999 modifications, several recognized compilations of thermodynamic constants were used as data sources. Data for reactions were also obtained from journal articles. The sources were accorded priority according to their order in the list below. If data were not found, the next source in the list was consulted, etc.

1. *Critical Stability Constants of Metal Complexes Database* (CRITICAL) published by the National Institute of Standards and Technology (NIST Standard Reference Database 46). Multiple versions of this database were used beginning with NIST version 2.0 (released in late 1995), and ending with NIST version 4.0 (released in late 1997). The correction and update of the MINTEQA2 v3.11 metal-organic reactions was completed first (see database history in Section 1.2.2). This update employed version 2.0 of the NIST CRITICAL database. The update of the general inorganic species began while version 3.0 of CRITICAL was the current NIST product. Version 4.0 of CRITICAL was released during the course of updating the inorganic species and was used to finish the project. In the final MINTEQA2 version 4.0 database, a data source reference code was added for each species. Those updated using the CRITICAL database were indicated with the code "NIST46.2," "NIST46.3," or "NIST46.4" for CRITICAL versions 2.0, 3.0, or 4.0).

2. *Stability Constants Database* (SC-DATABASE) published by the International Union of Pure and Applied Chemistry (IUPAC) and Academic Press. Two different versions of this database were used. In the correction of thermodynamic constants for metal-organic complexes in 1996, version 2.62 (released in 1996) was used. In the database review for inorganic species in 1999, version 3.02 (released in early 1998) was used. In the final MINTEQA2 version 4.0 database, the source reference code for each species updated with SC-DATABASE indicates the version from which the data were obtained ("SCD2.62" and "SCD3.02," respectively for versions 2.62 and 3.02). The reference cited in the actual MINTEQA2 database indicates the journal article reference within SC-DATABASE for version 3.02 citations.

3. Nordstrom *et al.*(1990) presented data intended to update and document data appearing in the U.S. Geological Survey equilibrium model WATEQ. Many of the reactions updated in that model also appear in the MINTEQA2 database, so those updates were incorporated. Data from this source are indicated in the final MINTEQA2 version 4.0 database with the source reference code "Nord90."

4. Relevant data from journal articles and other compilations. Use of data from journal articles is indicated by a code with the year followed by the first two author's initials (surnames) and a suffixed letter to insure uniqueness (e.g., 1993 DKa). The complete

reference is given in a bibliographic entry in a user manual supplement accompanying MINTEQA2 version 4.0 and later versions.

5. Gibbs free energy of formation ($\Delta_f G^o$) and enthalpy of formation ($\Delta_f H^o$) values from four different sources were used to compute the Gibbs free energy of reaction and enthalpy of reaction. The former was used to compute the log K for the reaction. The four data sources (in the preferred priority) were: 1) *CODATA Key Values for Thermodynamics* published by the Committee on Data for Science and Technology (CODATA) in 1989; 2) NIST *JANAF Thermochemical Tables 1985*, Standard Reference Database 13, version 1.0. Released in electronic format in 1993, the last update of the actual data in this database was 1985; 3) The NIST *Chemical Thermodynamics Database*, Standard Reference Database 2, version 1.1. This is the electronic form of the older National Bureau of Standards thermodynamic database. Version 1.1 was released in 1992, but the latest revisions to the data are from 1989; and 4) Standard Potentials in Aqueous Solution (Bard *et al*., 1985). Data obtained from these four sources are denoted by the codes "CODATA89," "NIST13.1," "NIST2.1.1," and "Bard85," respectively, in the source indication in the final MINTEQA2 database.

Apart from the accuracy of information recorded and presented in CRITICAL, SC-DATABASE, and other data sources, the process of querying a data compilation, recording the retrieved information, reducing the data in some fashion, entering the result in the MINTEQA2 database requires attention to details and repeated checking for accuracy to insure a final product that is free of secondary errors. The following steps were taken to minimize errors in the final MINTEQA2 thermodynamic database:

■   Data obtained from the CRITICAL and SC-DATABASE compilations of log K and enthalpy were recorded on data entry sheets with the exact reaction as given in the source and the pertinent ionic strength and temperature. The information recorded on each data entry sheet was double-checked, then entered in a data storage and manipulation program, MINCHEK, via on-screen prompts having the same format as the data entry sheet. After entering, the displayed data was compared against the data entry sheet for accuracy.

■   The $\Delta_f G^o$ and $\Delta_f H^o$ values from the JANAF and the NIST Reference Database 2 electronic databases were read directly into the MINCHEK program without intermediate transcription.

■   After all data was collected and entered, the data reduction module in MINCHEK was used to correct the log K values for ionic strength, temperature corrections were computed and applied, and the data were reformulated such that all reactions were expressed in terms of MINTEQA2 components. The latter step was accomplished by adding reactions and their log K and ΔH_R values as required. All data reduction steps were computed and applied internally by MINCHEK. Gram-formula weights and species charge were computed automatically by MINCHEK for each species from the stoichiometry, gram-formula weight (or atomic weight), and charge of each reactant (component).

- After log K and ΔH_R values were selected in MINCHEK for each species, the new MINTEQA2 database was automatically written in the required format, including reference citations for the data source.

- A table showing "old" and updated values of log K and ΔH_R side-by-side for each species was examined to find instances of large disparity. These were individually examined to be sure the updated data were correct.

In spite of the care taken to ensure the quality of the thermodynamic database, it must be recognized that it is still the responsibility of the MINTEQA2 user to review and edit the log K and enthalpy values for all important reactions for the system of interest.

This page intentionally left blank.

US EPA ARCHIVE DOCUMENT

E.3 MINTEQA2 Validation Studies

The consensus at the workshop on feasibility of MINTEQA2 validation was that a single study could not be regarded as validating MINTEQA2 regardless of its outcome. The natural environment is too varied and complex and the sources of uncertainty and error are too great to allow much confidence in the results of one study. Rather, it was felt that the most convincing validation would be the accumulated weight of many varied studies that each tend to provide some measure of confidence in the model's predictions. This section presents studies that show instances where MINTEQA2 model predictions have (and have not) been borne out by measurements of the corresponding real systems. These validation studies have been assembled from those known personally to the author and from other studies discovered in a literature search. The literature search employed the keyword "MINTEQA2" as the search term. There have been hundreds of reported studies in which MINTEQA2 was applied. Only a small fraction of these qualify as validation studies, and in many of these, validation of MINTEQA2 was not the central focus of the work. Many of the studies cited below were not undertaken specifically to provide validation support for MINTEQA2. Regardless of the overall focus of the reported study, the key requirement for considering a particular work as a MINTEQA2 validation study is that results calculated by MINTEQA2 are compared with some measure of reality.

We have attempted to include all studies that illuminate the question of MINTEQA2 validation, regardless of whether pro or con. However, researchers are more apt to report their successes than their failures. Although there is little reason for most researchers to personalize the failure of a MINTEQA2 application, researchers who find that the model result does not agree with their experimental work may be reluctant to mention this unless they are confident that they have used the model properly. This is especially true if the comparison is not the raison d'être of their work. These considerations may result in more reported studies that document the success of MINTEQA2 application than failure.

It is convenient to group the validation studies into those that involve simple solution chemistry or simple solid phases and those that involve sorption and/or natural organic matter. In the presentation below of published model validation studies, information identifying the study is followed by a brief statement of the standard of comparison or basis of the validation that entitles the study to be regarded as bearing on validation of MINTEQA2. A list or relevant trace metals involved in the validation and a brief description of the work are also included. Graphical results that show the match between MINTEQA2 calculations and the standard of comparison are presented where practical. Concerning graphical results, the plots presented were scanned from the originals because it was impossible to obtain the original data. Thus, all plots should be regarded as the work of the authors listed with the study.

E.3.1 Validation in Simple Systems (No Sorption, No Doc Complexation)

Title: unpublished problem submitted for MINTEQA2 workshop
Date: 1990
Metals: pH only
Basis of validation:
Comparison of a pH curve from a leaching experiment showing leachate pH versus concentration of acetic acid in the leachant with similar curve computed by MINTEQA2.
Description:
MINTEQA2 was used to model the behavior of a cement solidification medium for hazardous wastes under the conditions of an acid neutralization test. This study problem was submitted for discussion at a U.S. EPA sponsored MINTEQA2 workshop in 1990. The cement used for solidification of hazardous waste was a dolomitic lime consisting of $Ca(OH)_2$(s, portlandite) and MgO(s, brucite) in 1:1 Ca to Mg molar ratio. One gram of solid was leached with 20 grams of aqueous acid solution. The acid solution was acetic acid in water. The experiment was repeated with successively more concentrated solutions; the acid concentration varied from 0 to 40 equivalents of acid per kg solid. MINTEQA2 was used to predict the result of the leaching experiment. The comparison of the MINTEQA2-generated equilibrium pH curve with the experimental data is shown in Figure 2. As seen in the figure, MINTEQA2 predicts more a bit more buffering that was observed in the experiment. Discussion with those who performed the experiment revealed that the cement mixture was commercial construction grade material expected to include some inert impurities. Figure 3 shows the MINTEQA2 pH response curve when a reasonable value of 5.7 weight% inert solids in the cement was assumed. The MINTEQA2 pH response is almost identical with the observed response. The reader will observe that this result tends to validate MINTEQA2, but only for the dolomitic lime system under discussion.
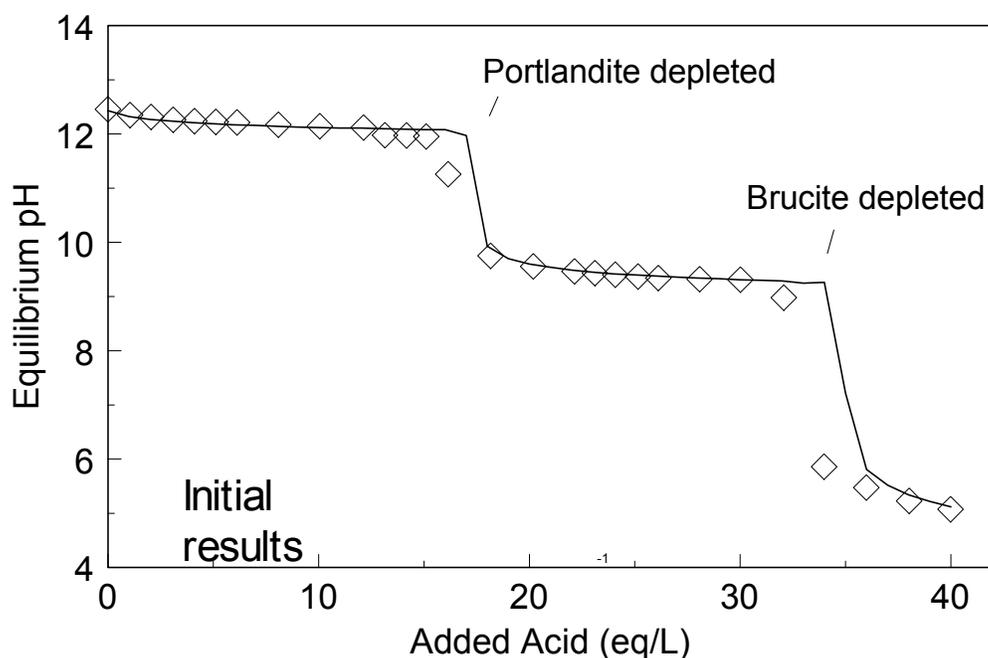

**Figure E-2. MINTEQA2 calculated pH (line) versus measured pH (diamonds)
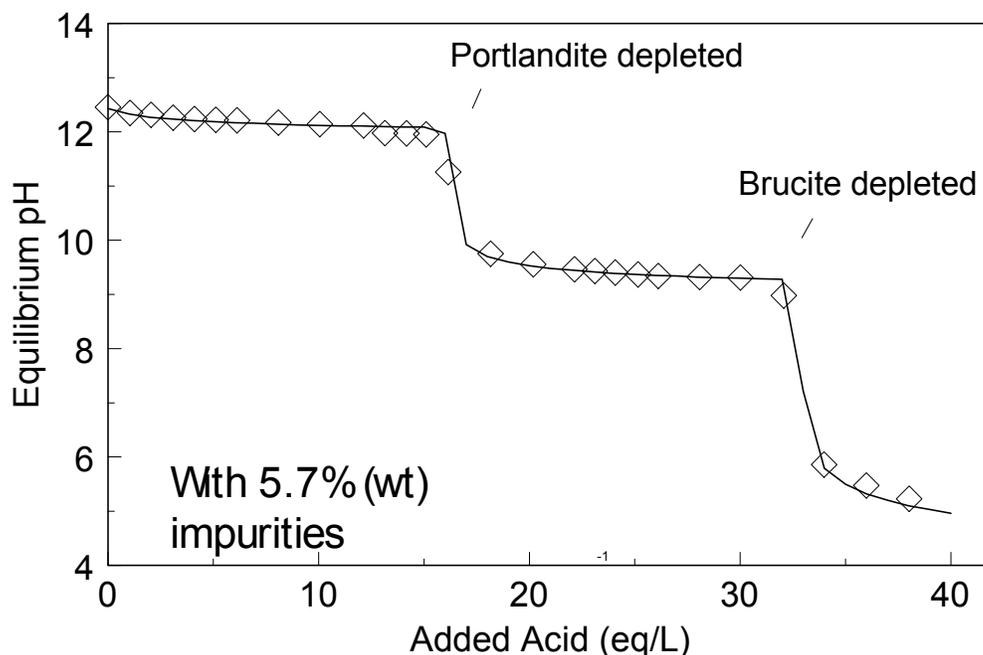for initial results cement leachate.**

**Figure E-3. MINTEQA2 calculated pH (line) versus measured pH (diamonds)
with added impurities in cement.**

Title: Heavy Metal Complexation with Aqueous Sulfide in an Anaerobic Treatment
           Wetland
Authors: Frandsen, A. K., and C. H. Gammons
Source: *Wetlands and Remediation: An International Conference*, Battelle Press, Columbus,
           OH, pp. 423-430.
Date: 2000
Metals: Zn, Cu, Fe
Basis of validation:
Comparison of dissolved total soluble metal concentrations predicted by MINTEQA2 with
measured total metal concentrations
Description:
This study compared the dissolved concentrations of Zn, Cu, and Fe measured in filtered water
samples collected from an anaerobic treatment wetland with corresponding soluble
concentrations predicted by MINTEQA2. Experimental results gave higher dissolved metal
concentrations than predicted, a circumstance which the authors attributed to the absence of
quality solution metal-sulfide complexes in the MINTEQA2 database and the consequent
prediction of precipitation of metal sulfides.

Title: Lead Precipitation in the Presence of Sulphate and Carbonate: Testing of
           Thermodynamic Predictions
Authors: Marani, D., G. Macchi, and M. Pagano
Source: *Water Research*, 29(4): 1085-1092
Date: 1995
Metals: Pb

Basis of validation:
Comparison of equilibrium solid mineral phases predicted by MINTEQA2 with solid mineral phases identified by X-ray powder diffraction (XRD).

Description:
The stated objective of this study was to evaluate the capability of MINTEQA2 for predicting realistic residual lead concentrations in aqueous solutions following an alkaline wastewater treatment procedure. Test solutions with pH range 4 to 11 were prepared with 10 mM sulfate concentration and variable carbonate concentration to simulate the alkaline treatment of battery acid wastewaters. Solutions were aged for several months, then the Pb concentration in solution was measured and precipitates were identified using XRD. Solution lead concentrations predicted by MINTEQA2 were in reasonable agreement with measured values for pH < 7. In the alkaline range, the MINTEQA2-predicted concentrations were significantly less than observed (a discrepancy of two to three orders of magnitude, depending on pH). The equilibrium solid phase predicted by MINTEQA2 in the alkaline range was $Pb(OH)_2(s)$. However, XRD analyses showed that the actual precipitates were anglesite ($PbSO_4$), cerrusite ($PbCO_3$), and hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$). It was found that if $Pb(OH)_2(s)$ is prohibited from precipitating in the MINTEQA2 model runs, one or more of anglesite, cerrusite, and hydrocerrusite precipitate depending on pH and carbonate concentration and the Pb in solution is in keeping with observations. The authors reasoned that $Pb(OH)_2(s)$ is kinetically limited and apparently forms upon extensive aging rather than as a direct precipitate.

Title: Ion Exchange Resin and MINTEQA2 Speciation of Zn and Cu in Alkaline Sodic and Acid Soil Extracts

Authors: Fotovat, A. and R. Naidu

Source: *Australian Journal of Soil Research*, 35: 711-726

Date: 1997

Metals: Cu, Zn

Basis of validation:
Compares speciation of Cu and Zn in solution as determined from ion exchange procedures with speciation computed using MINTEQA2

Description:
Analytical speciation results obtained using the cation exchange resin Amberlite were determined for copper (Cu) and zinc (Zn) in soil water for eleven soils of varied chemical composition. The soil pH values ranged from 5.3 to 9.1. Batch experiments were conducted at various pH and major ion concentration levels to study the procedural steps to accurately measure free Zn^{2+} and Cu^{2+} at various total Zn and Cu concentrations. After adding stability constants obtained from the literature (Stevenson and Fitch, 1986) for metal-DOC complexes, the metal and ligand species in the soil extracts were calculated using MINTEQA2. The average of the absolute differences between free Zn and Cu concentrations obtained using the exchange resin and calculated using MINTEQA2 was 4.3 percent. The comparison of Zn^{2+} from the two methods is shown in Figure 4. The authors observed that Zn was often present as free hydrated Zn^{2+} in these soil extracts, with the proportion dependent primarily on pH. In contrast, Cu occurred primarily in complexed forms in all soils. For both metals they concluded that speciation determined by the ion exchange method and by MINTEQA2 were in close agreement.
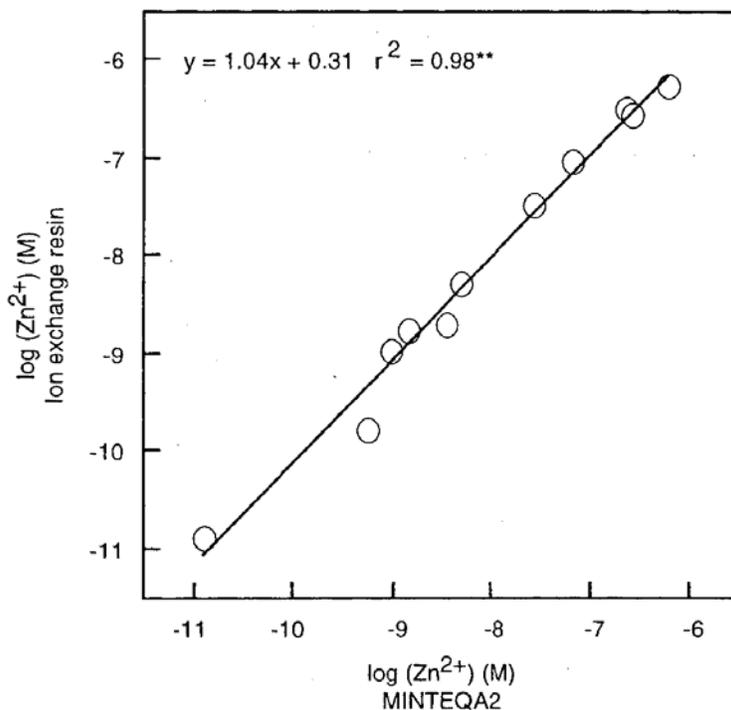
**Figure E-4. Comparison of Zn^{2+} determined by ion exchange
speciation (circles) and calculated by MINTEQA2 (line).
(After Fotovat and Naidu, 1997)**

Title: Speciation of Dissolved Iron(II) and Manganese(II) in a Groundwater Pollution
Plume
Authors: Jensen, D.L., J.K. Boddum, S. Redemann, and T.H. Christensen
Source: *Environmental Science & Technology*, 32(18): 2657-2664
Date: 1998
Metals: Fe(II), Mn(II)
Basis of validation:
Compares speciation of Fe(II) and Mn(II) in solution as determined from ion exchange
procedures versus speciation computed using MINTEQA2
Description:
Analytical speciation results obtained using the cation exchange resin Amberlite were
determined for Fe(II) and Mn(II) in groundwater having high concentrations of these
constituents from an anaerobic pollution plume down-gradient from a landfill. The groundwater
sample pH ranged from 5.2 to 7.1. Batch experiments on the samples and on a reference
solution were conducted such that the experiments differed only with respect to the possible
presence of complexing ligands in the actual samples (but not in the reference). The reference
experiment provided the required information about the distribution of free Fe^{2+} and Mn^{2+}
between the resin and the solution under conditions comparable to those of the sample. The free
Fe^{2+} and Mn^{2+} concentrations calculated for the samples was compared with that obtained using
MINTEQA2. The original database of MINTEQA2 was changed to include the stability
constants of Fe(II) and Mn(II) carbonate and bicarbonate complexes as given by Nordstrom *et
al.*, 1990. MINTEQA2 predicted about 20 percent less free divalent Fe and Mn than calculated
from ion exchange measurements. The authors speculated that this difference might be due to

uncertainty in the equilibrium constants of Fe(II) and Mn(II) carbonate and bicarbonate complexes. They observed that the constants adopted from Nordstrom *et al*. (1990) are at the high end of a range reported in the literature. Upon adjusting the equilibrium constants for $FeHCO_3^+$ and $MnHCO_3^+$ to lower values within their reported ranges, MINTEQA2 predicted the same fraction of free divalent Fe and Mn as was obtained from the ion exchange experiments. They noted that MINTEQA2 indicated negligible complexation of Mn(II) with dissolved organic matter (DOM) and that this was consistent with their interpretation of the ion exchange results. There was no complexation reaction for Fe(II) with DOM in the MINTEQA2 database, but the ion exchange results indicated that this also was negligible.

Title: Precipitation of Fe and Al Compounds from the Acid Mine Waters in Dogyae Area, Korea: A Qualitative Measure of Equilibrium Modeling Applicability and Neutralization Capacity?

Authors: Yu, J.Y.

Source: *Aquatic Geochemistry*, 2: 81-105

Date: 1996

Metals: Fe, Al

Basis of validation:

Comparison of the solid mineral phases that were predicted to precipitate by MINTEQA2 with the solid phases observed in field samples using X-ray diffraction (XRD), infared (IR), thermal and chemical analyses.

Description:

MINTEQA2 was use to predict the assemblage of Fe and Al solid mineral phases at equilibrium with acid mine waters mixed with stream water. Stream water contaminated with acid mine drainage water was collected along with associate streambed precipitates. The major ion concentration and pH of the water was characterized and used as input values for MINTEQA2. The precipitates in the collected samples were analyzed by XRD, IR, thermal, and chemical methods to identify the solid phases. The MINTEQA2 equilibrium calculations indicated that ferihydrite, $FeOHSO_4$, gibbsite, and $AlOHSO_4$ are at equilibrium with the samples. However, only ferrihydrite and $Al_4(OH)_{10}SO_4$ were identified in the experimental analyses of streambed samples. The authors suggested that $FeOHSO_4$ and $AlOHSO_4$ are kinetically inhibited and the metastable ferrihydrite and $Al_4(OH)_{10}SO_4$ appear instead.

Title: Toxicity to Embryo and Adult Zebrafish of Copper Complexes with Two Malonic Acids as Models for Dissolved Organic Matter

Authors: Palmer, F.B, C.A. Butler, M. H. Timperley, and C. W. Evans

Source: *Environmental Toxicology and Chemistry*, 17(8):1538-1545

Date: 1998

Metals: Cu(II)

Basis of validation:

Comparison of Cu^{2+} activity calculated by MINTEQA2 with Cu^{2+} activity measured by an ion-selective electrode.

Description:

Copper complexes with benzylmalonic acid and *n*–hexadecylmalonic acid were added to the MINTEQA2 database and the model was used to calculate copper speciation in test solutions used in toxicity studies. The calculated free Cu^{2+} concentration was compared with Cu^{2+} measured by ion selective electrodes. Good agreement was obtained for all test solutions. In

addition, the Cu^{2+} concentration calculated by MINTEQA2 was found to correlate with the median hatching times for zebrafish embryos in the test solutions.

Title: Bioavailability of Arsenic and Lead in Soils from the Butte, Montana, Mining District
Authors: Davis, A., M. V. Ruby, and P. D. Bergstrom
Source: *Environmental Science & Technology*, 26(3):461-468
Date: 1992
Metals: As, Pb
Basis of validation:
Comparison of MINTEQA2 calculated metal solubilities with measured metal solubilities in an experimental solution.
Description:
After determining that enargite (Cu_3AsS_4) and anglesite ($PbSO_4$) were the likely controls on arsenic and lead solubility in a test soil, the ability of MINTEQA2 to simulate the solution concentration of these solids in the human GI tract was compared with experimental results. The MINTEQA2-simulated solubility of anglesite compared well with measured solubilities: 37 mg/L simulated versus 35 mg/L measured in water at pH 7; 45 mg/L simulated versus 38 mg/L measured in a 1 mM acetate solution. Simulation of enargite solubility at conditions of the GI tract (pH 2, Eh +200 mv) showed virtually limitless solubility, as expected. The authors concluded that MINTEQA2 can predict the equilibrium solubility of these minerals, but that bioavailability of As and Pb from ingested soils would likely depend on dissolution kinetics and soil resident time in the gastric system.

E.3.2 Validation in Complicated Systems (With Sorption or Complexation by Doc)

The first three studies listed in this section were part of an organized effort by workers at the U.S. EPA and the U.S. Geological Survey (USGS) to validate MINTEQA2. The interest of the former in validating MINTEQA2 resulted from plans to possibly use the model in development of Office of Solid Waste (OSW) regulations for the disposal of metal-bearing wastes. One conclusion from the 1988 workshop discussing the feasibility of validating MINTEQA2 was that efforts should be made to conduct a field test in which MINTEQA2 model predictions could be compared with field measurements (Zachara *et al.*, 1988). It was conceded that successful application at one or two sites could not constitute a full and complete validation of MINTEQA2 because the range of geochemical conditions involved in the test (pH, E_h, nature of sorbents, solid phases, metals present, etc.) would necessarily be limited. However, one or more partial validations were viewed as important in lending credibility to the U.S. EPA's planned application of MINTEQA2 in modeling the movement of metal pollutants from landfill sites.

Title: Chemical Speciation and Competitive Cationic Partitioning on a Sandy Aquifer
              Material
Authors: Loux, N. T., D. S. Brown, C. R. Chafin, J. D. Allison, and S. M. Hassan
Source: *Chemical Speciation and Bioavailability*, 1(3):111-125
Date: 1989
Metals: Ba, Be, Cd, Cu, Ni, Pb, Tl, Zn

Basis of validation:

Comparison of percent of metal remaining in solution in batch equilibrium experiments using aquifer materials versus percent of metal dissolved at equilibrium as calculated in MINTEQA2 simulations in which sorption and precipitation were operative.

Description:

This study was conducted specifically to test the ability of MINTEQA2 to account for metal attenuation processes in a sandy aquifer material in an oxidized environment. The aquifer material and associated groundwater were obtained from a Wisconsin aquifer having a high sand content. Batch partitioning experiments on paired aquifer/groundwater samples were conducted by spiking the samples with a solution containing Ba, Be, Cd, Cu, Ni, Pb, Tl, Zn at approximate concentrations of 3 mg/L. Partitioning experiments were conducted over a pH range of 4 to 9. At the conclusion of each 48 hour equilibration period, supernatant was removed and analyzed by Inductively Coupled Plasma spectroscopy (ICP). The percent of the originally spiked metal that remained in solution was plotted versus pH. MINTEQA2 was used to simulate the partitioning experiments. Both precipitation and sorption were operative in the modeling. Sorption was included in the modeling by invoking the diffuse-layer (MIT Two-Layer) model with the database of sorption reactions for amorphous iron oxyhydroxide as given by Dzombak (1986). The amorphous iron content used in the MINTEQA2 model runs was as measured in the aquifer samples by the extraction method of Jenne and Crecilius (1988). Iron oxide sorbent site densities for two site types and specific surfaces area were as recommended by Dzombak (1986; 0.2 and 0.005 moles of sites per mole Fe and 600 m^2/g). A key point in this modeling was that the database of sorption reactions and related parameters for the amorphous ferric oxyhydroxide sorbent was used as given by Dzombak without alteration or adjustment. The sorption modeling parameters were not fitted to the specific systems modeled. The simulated percent of metal remaining in solution at equilibrium was compared with the measured value at each pH. Results were presented graphically (see Figures 5-11 below). In interpreting the model results, Loux and coworkers noted that sorption played a more important role in describing the pH-dependent behavior of Ni, Pb, and Zn than for other metals; the equilibrium solution concentration of Cd was better described by precipitation as a cadmium carbonate phase; pH-dependent behavior of Ba, Be, and Cu were poorly described by the model. The authors speculated that complexation of Cu with carbonato or organic complexes not represented in the model simulations may explain the poor match between model and experimental result for this metal. They suggested that Ba results could be explained by including non-specific adsorption terms or by invoking a pH-sensitive solid- solution solubility control. Other key conclusions by the authors were that "the agreement between model and experimental results was sufficient (for a number of elements) to move the concept of partitioning behavior in complex environmental systems from the realm of purely sediment-specific fitting to a more fundamental modeling basis," that the database of thermodynamic constants for Be should be reviewed for completeness and accuracy, and that removal of Tl from solution is relatively pH insensitive.
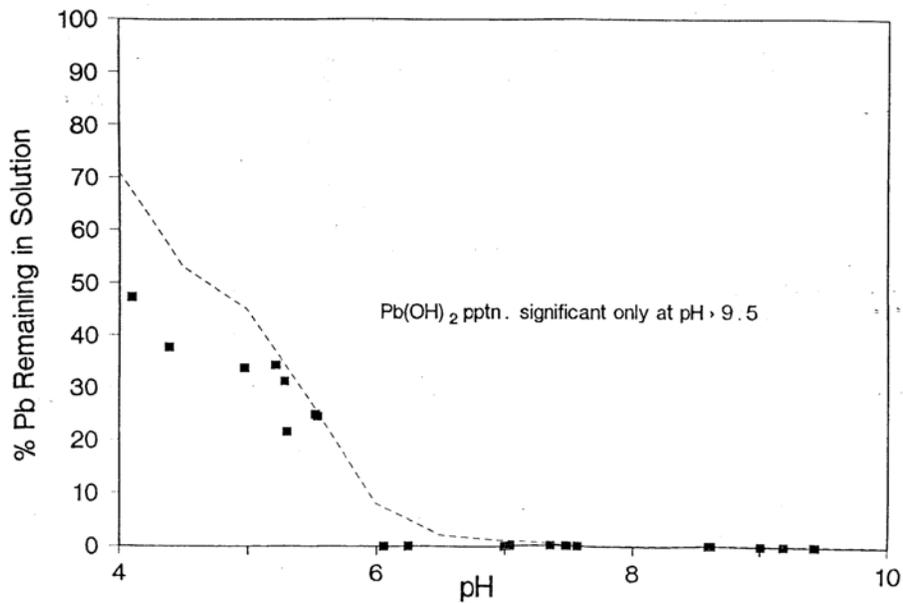
Figure E-5. MINTEQA2 predicted Pb in solution (line) versus experimentally observed values (squares). (After Loux *et al*., 1989)
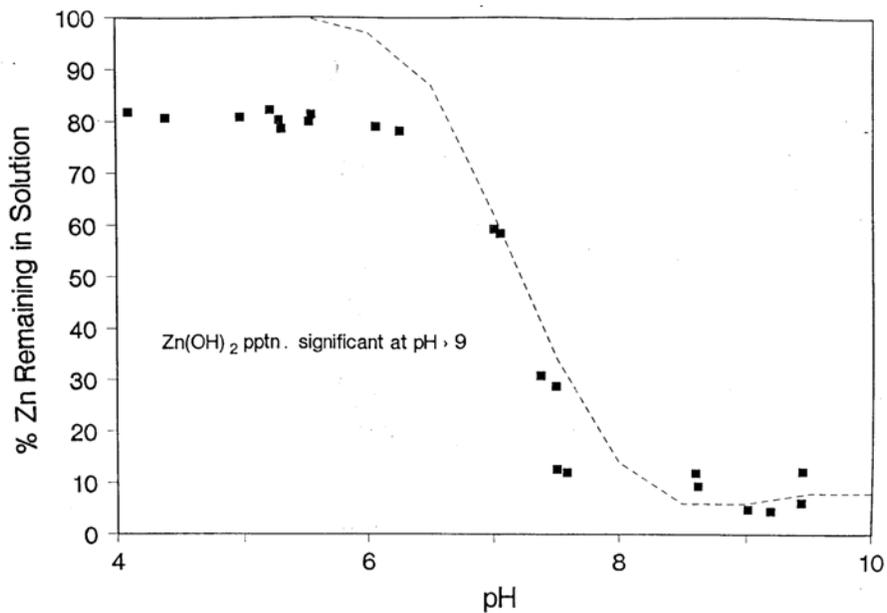

Figure E-6. MINTEQA2 predicted Zn in solution (line) versus experimentally observed values (squares). (After Loux *et al*., 1989)
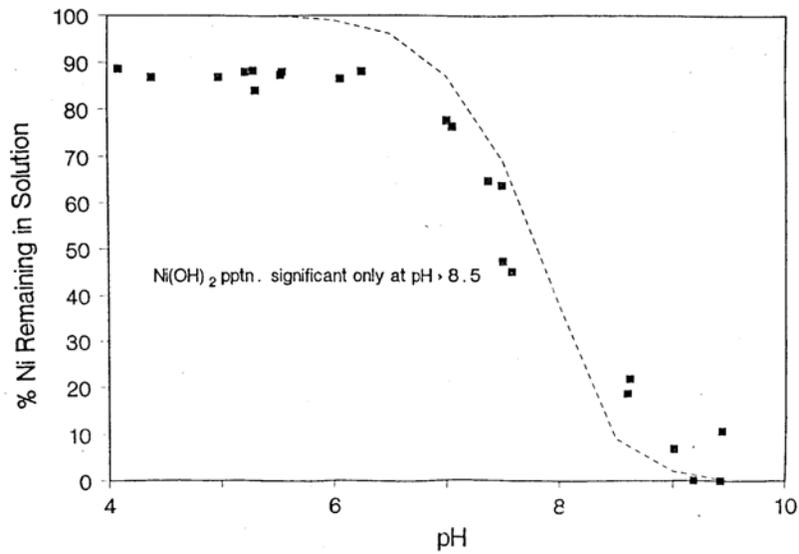
**Figure E-7. MINTEQA2 predicted Ni in solution (line) versus experimentally
observed values (squares).
(After Loux *et al.*, 1989)**

**Figure E-8. MINTEQA2 predicted Cd in solution (line) versus experimentally
observed values (squares).
(After Loux *et al.*, 1989)**

Figure E-9. MINTEQA2 predicted Cu in solution (line) versus experimentally observed values (squares).
(After Loux *et al.*, 1989)

Figure E-10. MINTEQA2 predicted Ba in solution (line) versus experimentally observed values (squares).
(After Loux *et al.*, 1989)

**Figure E-11. MINTEQA2 predicted Be in solution (line) versus experimentally
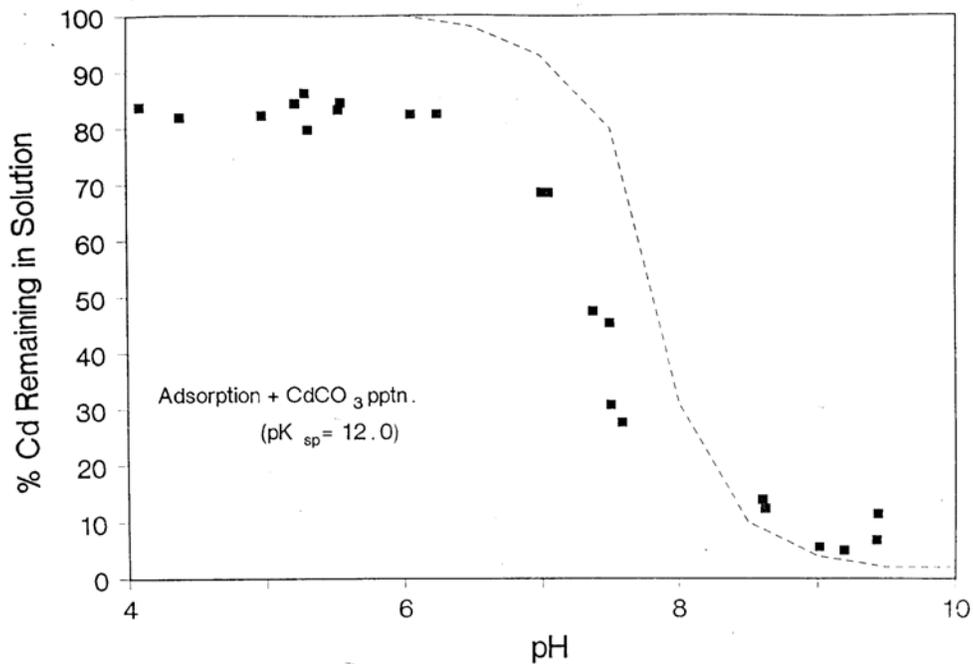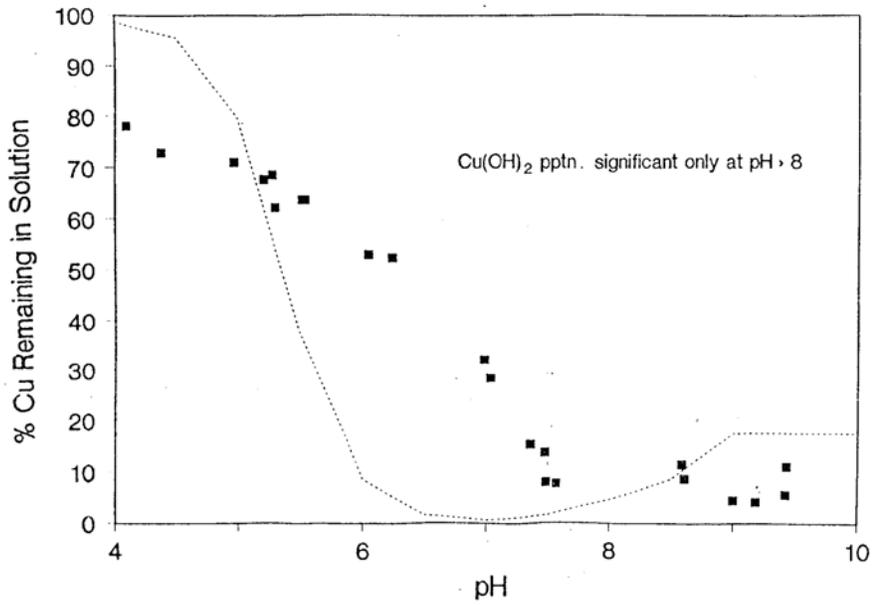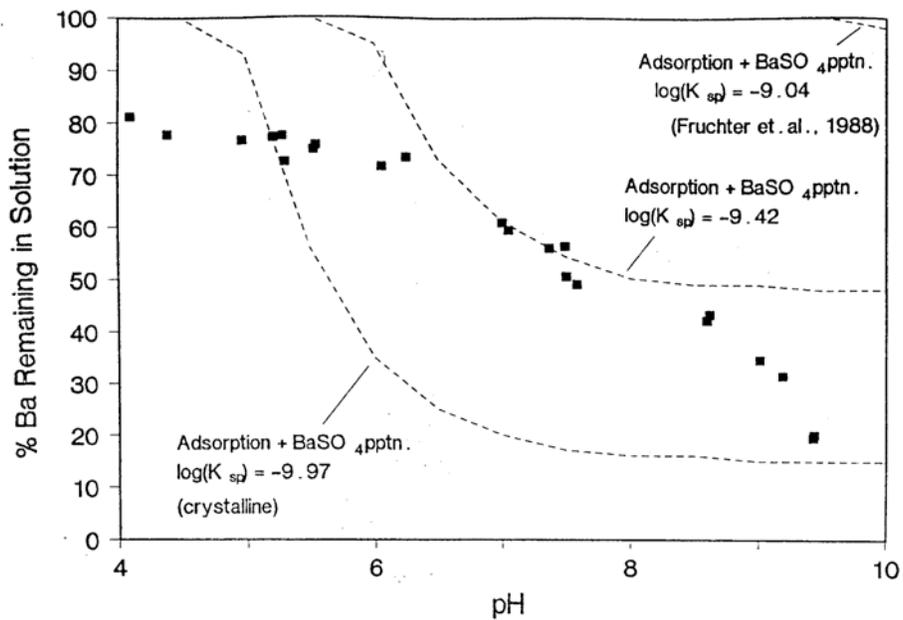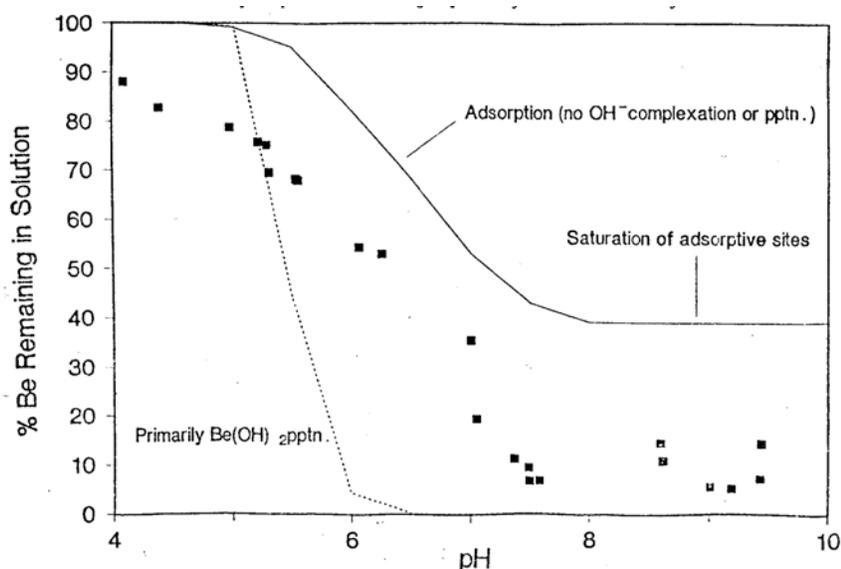observed values (squares).
(After Loux *et al.*, 1989)**

The following two studies concern the same study site: the Pinal Creek area of the
copper mining district near Globe, Arizona. The first study was commissioned by the U.S. EPA
and performed by Battelle Pacific Northwest Laboratories. It was originally suggested in the
model validation feasibility study previously mentioned (Zachara et al., 1988). The second study
at the same site was a collaborative effort by the U.S. Geological Survey (USGS) and the U.S.
EPA. It was published both as a journal article (Applied Geochemistry) and as part of a USGS
Water-Supply Paper. Both publications are cited below.

Title: Geochemical Model "Validation": Reliability of Solubility Equilibria Calculated with
             Field Data from an Acidic Metal-rich Plume Near Globe, Arizona
Authors: Jenne, E.A.
Source: Unpublished report prepared for the U. S. EPA, Office of Research and Development,
             Environmental Research Laboratory, Athens, GA by Battelle Pacific Northwest
             Laboratories, Richland, WA
Date: 1994
Metals: Ca, Fe, Mn, Al, Si
Basis of validation:
The solid phases predicted to exist by MINTEQA2 were compared with solid phases identified
analytically in field samples (e.g., by scanning electron microscopy (SEM), x-ray diffraction
(XRD), or other means).
Description:
MINTEQA2 was used to predict the assemblage of equilibrium solid phases in samples obtained
from wells along a transect in a contaminated aquifer. For each sample, MINTEQA2 predicted
the saturation index (SI) for each possible solid phase. An SI value of zero for a solid phase
indicates equilibrium between that phase and the corresponding solution. The study site
included the area downgradient from tailings piles in the Globe, Arizona copper mining district.

These tailings piles contain sulfide-bearing minerals, the oxidation of which has resulted in infiltration of acidic, sulfate-rich water high in Cu and other metals. The area includes Pinal Creek and a tributary, Miami Wash. This area in underlain by an unconsolidated alluvial aquifer with a high hydraulic conductivity (200 to 300 m/day). This valley aquifer is bounded by cemented formations of much lower conductivity. The pH of the uncontaminated aquifer ranges from 6.4 to 8.4. A zone of neutralization has developed due to intrusion of the acidic water. This zone has moved downgradient at about 0.5 m/yr. Over thirty observation wells that penetrate the alluvial aquifer and transect the zone of neutralization are located in the valley floor. In this study, samples from these wells, both up- and down-gradient from the neutralization front, were used to represent the solution chemistry in MINTEQA2. In each model run., the total concentrations of solutes, including metals, was as measured in the filtered (0.45 μm) well water samples. The pH was constrained at the measured value of each sample. The solid phases predicted to exist by MINTEQA2 (evidenced by SI approximately zero) were compared with the solid phases identified analytically (e.g., by scanning electron microscopy (SEM), x-ray diffraction (XRD), or other means). The MINTEQA2 predictions regarding the existence of calcite and gypsum conformed reasonably with the observed occurrence of these minerals. MINTEQA2 predictions indicated that amorphous iron hydroxide was oversaturated in most samples; Fe(III) oxide coatings were identified by SEM. The authors suggested that their method of quantifying the total Fe(III) for input in MINTEQA2 may have contributed to the calculation of Fe(III) oxide oversaturation. (They assumed that total measured Fe represented Fe(II) and they calculated Fe(III) using the measured E_h value.) They also noted that a broad range of solubility values for amorphous ferric oxide (corresponding to a range in log K) is reported in the literature. Results also suggested that the MINTEQA2 model predictions for rhodochrosite ($MnCO_3$) may correspond to observations. Results for Al and Si were inconclusive due to uncertainty in the actual controlling solid phases at the site.

Title: Geochemical Interactions Between Constituents in Acidic Groundwater and
              Alluvium in an Aquifer near Globe, Arizona
Authors: Stollenwerk, K.G.
Source: *Applied Geochemistry*, 9:353-369
Date: 1994
Metals: Al, Fe, Mn, Ca, Cu, Co, Ni, Zn; also pH and SO_4
Basis of validation:
Comparison of dissolved concentrations of constituents measured in a series of wells with solution concentrations predicted using MINTEQA2 with sorption and precipitation operative.
Description:
MINTEQA2 was used to simulate geochemical reactions between acidic mine drainage and alluvial aquifer material. The study area was the Pinal Creek-Miami Wash area of the copper mining district near Globe, Arizona. (The same study area as in Jenne,1994). At this site, acidic water from tailings piles contains high sulfate concentrations from oxidation of sulfide-bearing minerals. Higher than normal concentrations of trace metals also occur in the leachate. These constituents move down-gradient through an unconsolidated alluvial aquifer that underlies Miami Wash and Pinal Creek. In this study, a conceptual model of geochemical reactions was first evaluated in a laboratory column experiment using aquifer materials. The objective of this column calibration step was to identify the minimum set of geochemical reactions that would explain the concentration of constituents in the column effluent. MINTEQA2 was used to simulate those reactions and predict breakthrough curves for various constituents in the column.

The grains of alluvial material in the column were visibly coated with iron oxides— the hydrous ferric oxide (HFO) database of Dzombak and Morel (1990) was used in the diffuse-layer sorption model in MINTEQA2 to estimate trace metal sorption. Aluminum and manganese oxide sorbents were also known to be present in the alluvial material, but they were not accounted for in the model. The specific surface area and sorption site density were set at values recommended Dzombak and Morel for use with their database (600 m^2/g and 0.2 moles of sites per mole Fe; Dzombak and Morel, 1990). The amount of HFO used was the sum of an amount determined by chemical extraction of the original alluvium and an amount estimated to precipitate as the acidic leachate moved through the alluvium in the column. The equilibrium constants for H, Cu, Ni, and Zn for sorption onto HFO were as specified in Dzombak and Morel (1990). Published equilibrium constants for Co and Mn sorption were adjusted to fit the extent of sorption in the column experiment. After successfully simulating breakthrough curves from the column experiment, MINTEQA2 was used to simulate measured changes in concentration of aqueous constituents in wells disposed along a flow path in the alluvial valley aquifer along Miami Wash and Pinal Creek. The flow path chosen for simulation connected the most contaminated well in each of six observation well nests and two surface water observations so that a continuous progression from most contaminated to least contaminated water was represented. In applying the column-calibrated geochemical model (embodied in MINTEQA2) to the field, it was necessary to account for dilution of constituents in the acidic plume by groundwater from other sources. A chloride tracer experiment was conducted to assess the extent of dilution in the study area. PHREEQE was used to account for dilution of the groundwater along the flowpath. The resulting mixed water chemistry was used as input to the geochemical model represented in MINTEQA2. Results of the simulations were plotted as constituent concentration versus distance with observations from the wells included for comparison. Figures 12-18 present these comparisons for pH, Fe, Mn, Cu, Co, Ni, and Zn. In Figure 12, the simulated change in pH along the flow path is shown. The reactions in the geochemical model that accounted for the pH behavior were initial buffering by calcite and dolomite until these minerals were depleted. After depletion of carbonates, the pH was controlled by adsorption of H$^+$ on oxide minerals and by reactions with aluminum (precipitation of amorphous Al(OH)$_3$ and AlOHSO$_4$). Figures 13 and 14 show the simulation of Fe and Mn concentration with distance compared with observed concentrations. In the model, oxidation of Fe(II) to Fe(III) and subsequent precipitation was the controlling factor in Fe chemistry. The Fe(II) was oxidized by MnO$_2$ dissolution and reduction of Mn. The authors report that others have provided evidence that the dissolution of MnO$_2$ does occur along this flow path (Ficklin *et al.*, 1991). The total amount of Mn dissolved in the column experiment was less that the amount predicted to dissolve in the oxidation of Fe(II). The authors discussed several explanations of this difference. They chose to eliminate some of the Mn(II) predicted by MINTEQA2 because the column experiment data indicated that approximately 65 percent of the Mn reduced by Fe(II) remained in the solid phase (possibly reprecipitating as Mn(FeO$_2$)$_2$). Results for Cu, Co, Ni, and Zn are shown in Figures 15-18. The controlling reactions for these constituents were the sorption reactions onto ferric oxide. There was little sorption of Co, Ni, and Zn predicted along the low pH region of the flow path (first 10 km). The simulated concentrations along this portion of the transect were explained by dilution alone. Sorption of these metals became more important down-gradient from 10 km where the pH increased. Sorption of Cu was important in controlling Cu solution concentrations along the entire flow path and the combination of dilution and adsorption accurately simulated Cu concentrations in the groundwater.
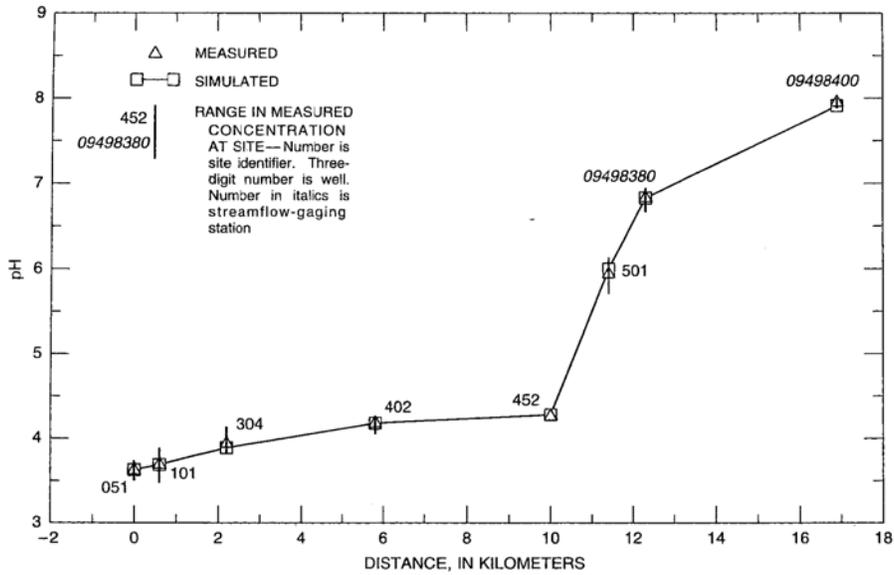
**Figure E-12. Simulated versus measured pH along the flow path.
(Stollenwerk, 1994 and 1996)**

**Figure E-13. Simulated versus measured Fe concentration along the flow path.
(Stollenwerk, 1994 and 1996)**

Figure E-14. Simulated versus measured Mn concentration along the flow path. (Stollenwerk, 1994 and 1996)

Figure E-15. Simulated versus measured Cu concentration along the flow path. (Stollenwerk, 1994 and 1996)

Figure E-16. Simulated versus measured Co concentration along the flow path. (Stollenwerk, 1994 and 1996)
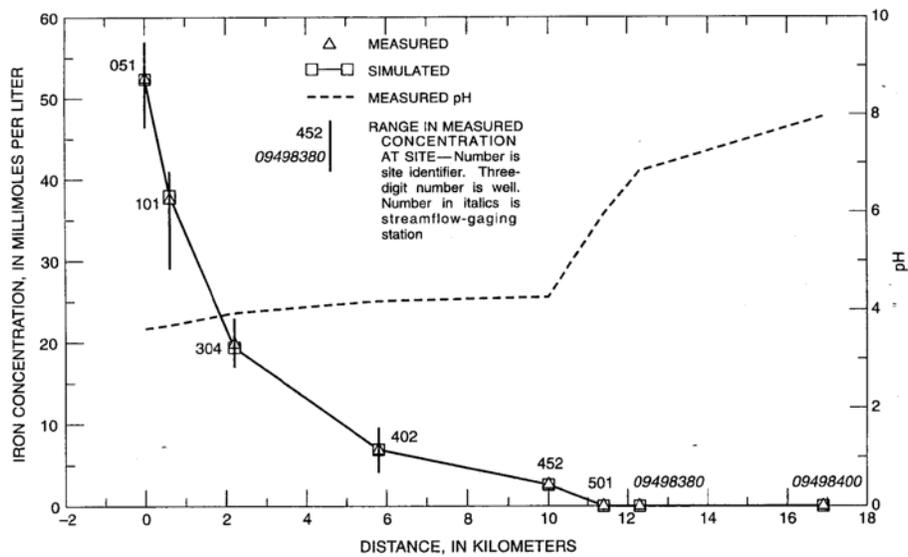

Figure E-17. Simulated versus measured Ni concentration along the flow path. (Stollenwerk, 1994 and 1996)
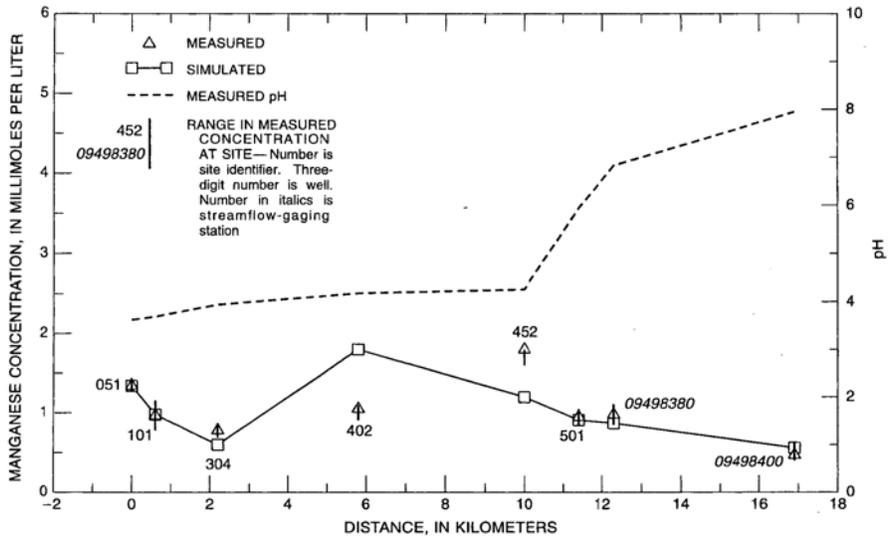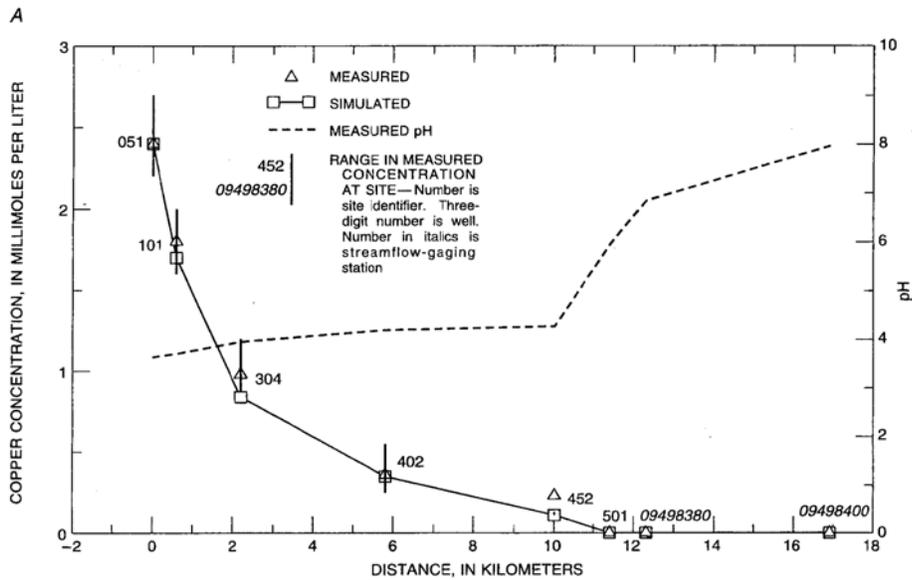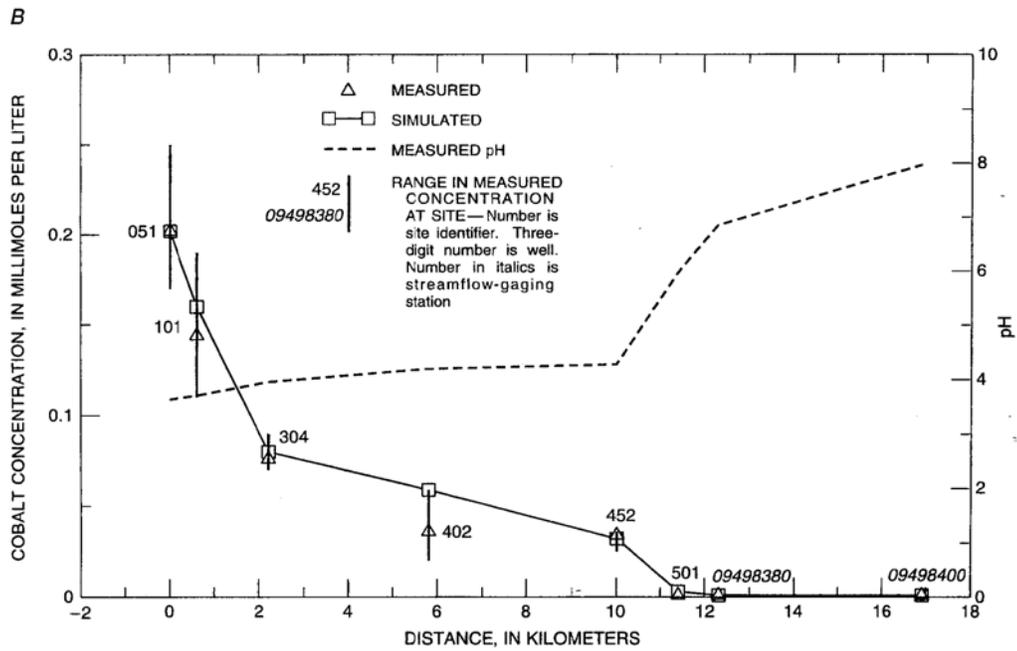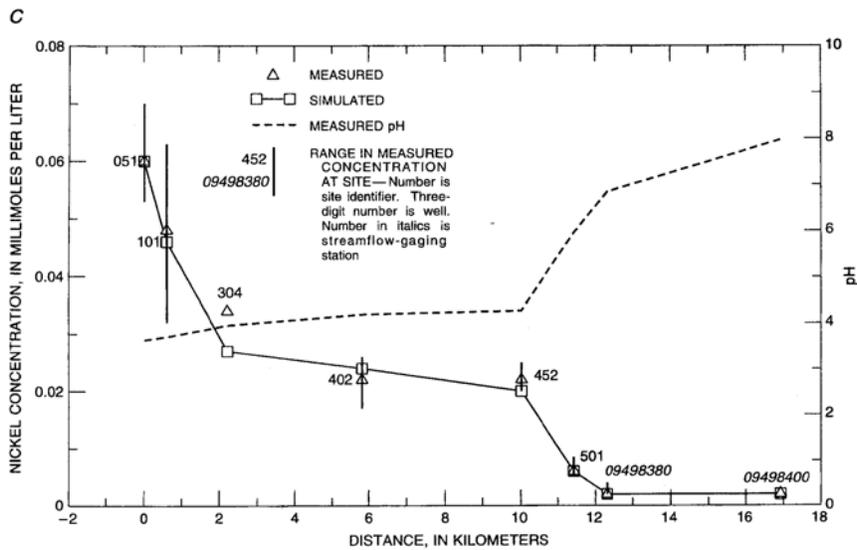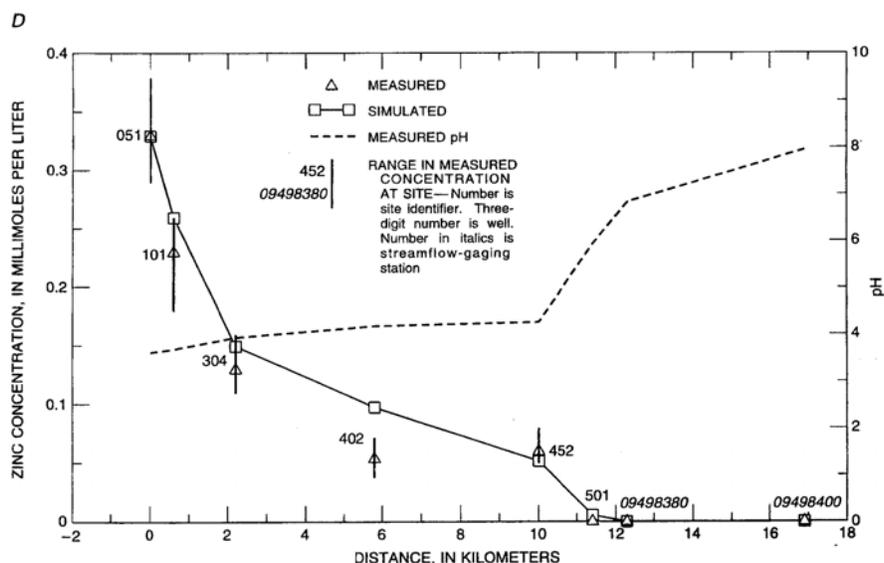
**Figure E-18. Simulated versus measured Zn concentration along
the flow path. (Stollenwerk, 1994 and 1996)**

Title: Simulations of Reactions Affecting Transport of Constituents in the Acidic Plume,
            Pinal Creek Basin, Arizona
Authors: Stollenwerk, K.G.
Source: *U.S. Geological Survey Water-Supply Paper* 2466, pp. 21-49
Date: 1996
Metals: Al, Fe, Mn, Ca, Cu, Co, Ni, Zn; also pH and SO_4
Basis of validation: Comparison of dissolved concentrations of constituents in the effluent from
a column experiment with dissolved concentrations predicted by MINTEQA2 with sorption
operative.
Description: This paper reports on the same study as the preceding entry (Stollenwerk, 1994).
It also includes a new section not present in the 1994 paper. This new section discusses the
application of the same geochemical model (implemented in MINTEQA2) to transport of
contaminants in an aquifer that underlies the originally studied alluvium. This underlying basin-
fill area is characterized by a much lower hydraulic conductivity than the alluvium and by a
higher carbonate content. Some acidic leachate has penetrated this aquifer. The author applied
the same model as used in the valley aquifer to explain contaminant concentrations in this
aquifer. The pH-dependent sorption of Co, Cu, Ni and Zn and the precipitation of Al were
simulated. The basin-fill aquifer data (obtained from a column experiment using basin-fill
aquifer materials) were simulated using MINTEQA2 with the diffuse-layer sorption model with
parameters as described in Stollenwerk, 1994. The model predicted concentrations of Co, Ni,
and Zn that matched the experimental data reasonably well. (The match was described
qualitatively only in this paper.) Cu and Al were not detected in the effluent from the column
and this was consistent with MINTEQA2 predictions that virtually all Cu would be sorbed and
that Al would precipitate as amorphous $Al(OH)_3$.

Title: Modeling the Effects of Variable Groundwater Chemistry on the Adsorption of
                  Molybdate
Authors: Stollenwerk, K.G.
Source: *Water Resources Research*, 31(2):347-357
Date: 1995
Metals: Mo

Basis of validation: Comparison of dissolved concentration of molybdate in the effluent from a
column experiment with dissolved concentrations predicted by MINTEQA2 with sorption
operative.

Description: MINTEQA2 was used to estimate adsorption of molybdate (MoO_4) in column
experiments using sediment and groundwater collected from a shallow alluvial aquifer near Cape
Cod, MA. Two column experiments were performed, one using groundwater from a sewage
contaminated well (F347-46) and one using groundwater from a well not contaminated with
sewage (F347-20). The modeling of the column experiments employed the diffuse-layer model
(Dzombak and Morel, 1990). Surface acidity constants for H^+ sorption and adsorption reactions
for SO_4 and PO_4 were included to account for change in MoO_4 adsorption with pH and with
competition for sorption sites due to changing concentrations of these ions. The acidity
constants and other equilibrium constants were determined in separate batch experiments. The
surface area and surface site density were measured for the alluvial aquifer material. The match
between predicted and measured MoO_4 adsorption for both groundwaters for various pH values
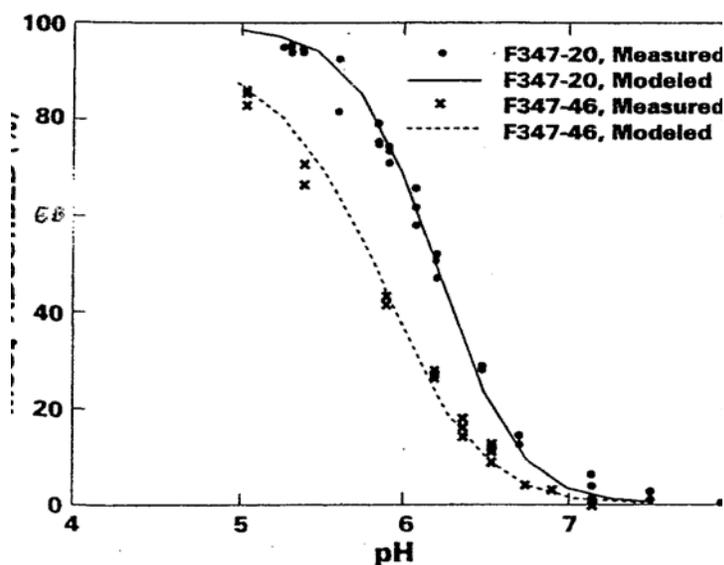

**Figure E-19. MINTEQA2-simulated versus measured
MoO_4 for column experiments using aquifer materials
and water from sewage-contaminated well (F347-46) and
uncontaminated well (F347-20). (Stollenwerk, 1995)**

is shown in Figure 19.

Title: Predicting the Environmental Stability of Treated Copper Smelter Flue Dust
Authors: Doyle, T.A., A. Davis, and D.D. Runnels
Source: *Applied Geochemistry*, 9:337-350
Date: 1994
Metals: As(V)
Basis of validation: Comparison of dissolved concentrations of As in batch and column tests with dissolved concentrations predicted by MINTEQA2
Description: The leachability of As, Cd, Cu, Fe, and Pb from treated copper smelter flue dust was investigated by batch and column tests. Electron microprobe spectroscopy of the treated flue dust identified scorodite ($FeAsO_4.2H_2O$) as the primary As mineral. Modeling of the system using MINTEQA2 also predicted that scorodite controlled the leaching of As from the column. The MINTEQA2 predicted leachate concentration of As (1270 µg/L) compared well with the measured value (1330 µg/L) from the continuously eluted column test. The triple-layer model in MINTEQA2 was used to model sorption of As(V). Including sorption in MINTEQA2 simulations of batch tests resulted in overestimating As removal. However, results for a continuously eluted column test showed good agreement between dissolved As concentration estimated using MINTEQA2 with the triple-layer model for sorption (1120 µg/L) and actual measured As in the column leachate (1330 µg/L). The triple-layer model in MINTEQA2 was used with reactions and parameters from Davis and Leckie (1978, 1980). The equilibrium constant for formation of scorodite used in the simulation was calculated from data provided in Robins (1990).

Title: Modeling of radionuclide and heavy metal sorption around low- and high-pH waste disposal sites at Oak ridge, Tennessee.
Authors: Saunders, J.A. and L.E. Toran
Source: *Applied Geochemistry*, 10:673-684
Date: 1995
Metals: Co, Cd, Pb, Sr, U, and Zn
Basis of validation: Comparison of dissolved concentrations of metals at monitoring wells near a disposal pond with dissolved concentrations of these metals predicted by MINTEQA2.
Description: MINTEQA2 was used to predict the mobility of radioisotopes at low-level radioactive waste disposal sites. Mineral precipitation and metal sorption reactions were included in the simulations. The simulations included estimating the neutralization of both low- and high-pH waste leachates due to interaction with soils. Complexation reactions with EDTA were also included. The sorption model used was the diffuse-layer model with sorption reactions for iron oxyhydroxide with associated sorption site densities and surface area as specified in Dzombak and Morel (1990). The authors compared MINTEQA2-computed dissolved Co, Cd, Pb, Sr, U, and Zn at various pH values with observations in near-source monitoring wells. Although they acknowledged several complicating factors not included in their modeling methodology (presence of additional soil sorbents besides iron oxyhydroxide, kinetics of mineral dissolution and precipitation, effects of flow along fractures, dilution by groundwater), they concluded that "predictions about pH-dependent mineral precipitation and metal sorption reactions from the modeling generally match field observations..." for both the acidic and high-pH disposal sites. (Figures showing model versus measured concentrations for Cd and Zn are included in the original paper, but their quality is too poor to allow reproduction.)

Title: Complexation of Cd, Ni, and Zn by DOC in Polluted Groundwater: A Comparison of
Approaches Using Resin Exchange, Aquifer Material Sorption, and Computer
Speciation Models (WHAM and MINTEQA2)

Authors: Christensen, J.B. and T.H Christensen

Source: *Environmental Science & Technology*, 33:3857-3863

Date: 1999

Metals: Cd, Ni, and Zn

Basis of validation: Concentrations of metal-DOC complexes determined in batch experiments
using a resin exchange method were compared with concentrations of metal-DOC complexes
computed by MINTEQA2

Description: This study compared the extent of metal-DOC complexation measured in a resin
exchange method, measured in batch sorption experiments using actual aquifer materials, and
estimated using the speciation models WHAM and MINTEQA2. Groundwater samples were
obtained from the DOC-rich leachate plume downgradient from a landfill. A synthetic leachate
solution was prepared so as to be similar to each of these leachate samples except that DOC was
not included. The with- and without-DOC solutions were used in the resin exchange method and
in batch experiments with aquifer materials to estimate DOC complexation of Cd, Ni, and Zn.
DOC complexation of these metals was also estimated by simulating the leachate solutions in
WHAM (Tipping, 1994) and MINTEQA2. The authors reported that the resin exchange method
and the batch equilibration with aquifer materials provided similar measures of DOC
complexation of these metals. The ability of the models to predict the complexation of these
metals with DOC varied among the metals and the different samples. Concerning the predictions
by MINTEQA2, excellent agreement with the experimental methods was noted for complexation
of Cd. Agreement of MINTEQA2 results with experimental methods for Zn were described as
"fair." For Ni, MINTEQA2 results were described as in "fair" agreement with experimental
results for one sample, but for a second sample, MINTEQA2 significantly underestimated Ni
complexation with DOC. Several of these comparisons are shown in Figure 20. It was also
noted that the shape of the curves produced by increasing DOC concentration in the experiments
was generally well matched in the MINTEQA2 results. The authors concluded that in leachate
polluted groundwater, the MINTEQA2 model gives a useful first approximation of Cd, Ni, and
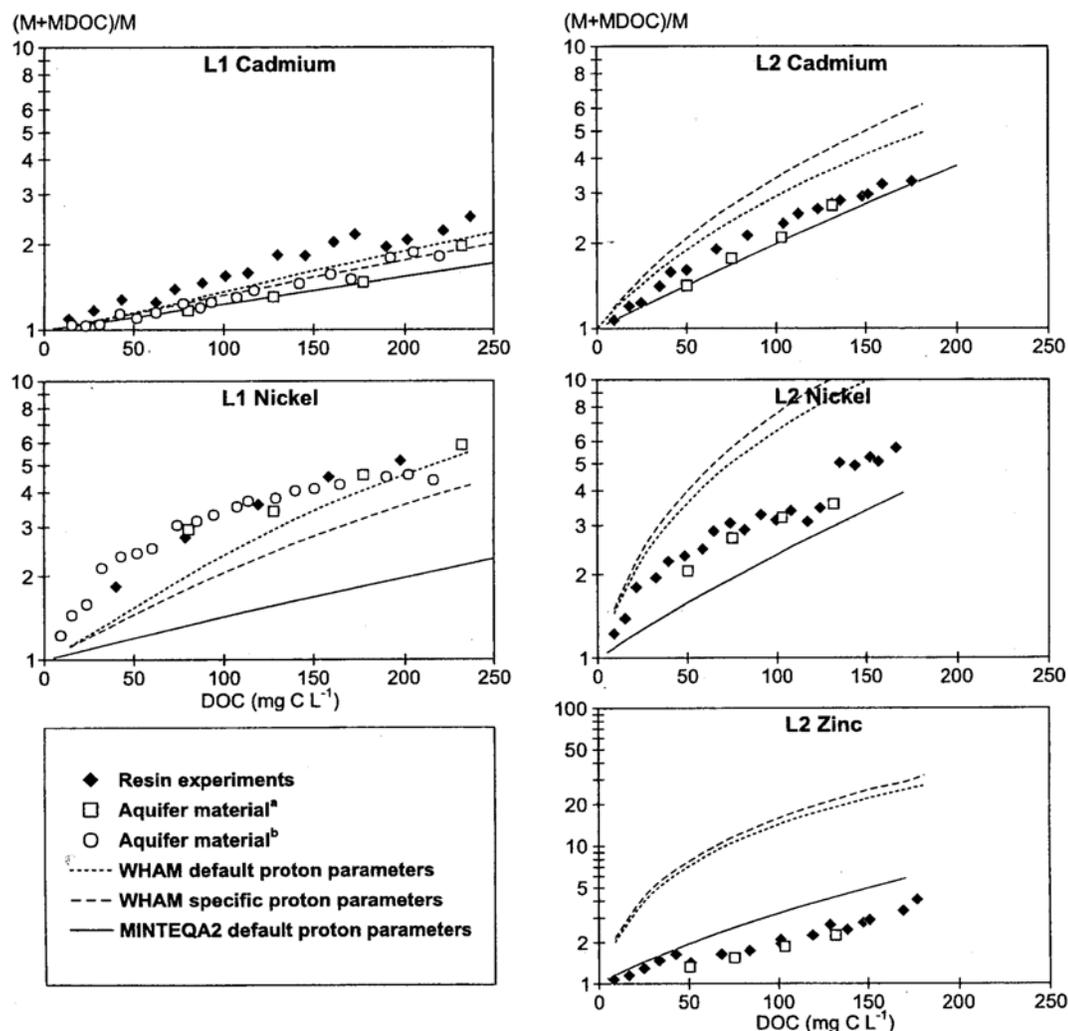Zn complexation by DOC.

Figure E-20. Comparison of MINTEQA2 estimated degree of DOC complexation for Cd, Ni, and Zn versus degree of complexation in resin and batch aquifer material experiments. (Christensen and Christensen, 1999)

Title: Complexation of Cu and Pb by DOC in polluted groundwater: A comparison of experimental data and predictions by computer speciation models (WHAM and MINTEQA2)

Authors: Christensen, J.B., J.J. Botma, and T.H Christensen

Source: *Water Research*, 33(15):3231-3238

Date: 1999

Metals: Cu, Pb

Basis of validation: Concentrations of metal-DOC complexes determined in batch experiments using a resin exchange method were compared with concentrations of metal-DOC complexes computed by MINTEQA2

Description: This study compared the extent of metal-DOC complexation measured in a resin exchange method and estimated using the speciation models WHAM and MINTEQA2. Groundwater samples were obtained from the DOC-rich leachate plume downgradient from a landfill. A synthetic solution was prepared so as to be similar to each of these leachate samples

except that DOC was not included. The with- and without-DOC solutions were used in the resin exchange method to estimate DOC complexation of Cu and Pb. DOC complexation of these metals was also estimated by simulating the leachate solutions in WHAM (Tipping *et al.*, 1994) and MINTEQA2. The ability of the models to predict the complexation of these metals with DOC varied among different samples. Concerning the predictions by MINTEQA2, agreement between experimental and observed complexation was generally good (see Figure 21). For one sample MINTEQA2 underestimated the degree of Cu complexation by an amount corresponding to a maximum of a factor of two in the free Cu^{2+} concentration. For one sample MINTEQA2 overestimated DOC binding with Pb, again by an amount corresponding to a factor of two in the free Pb^{2+} concentration.
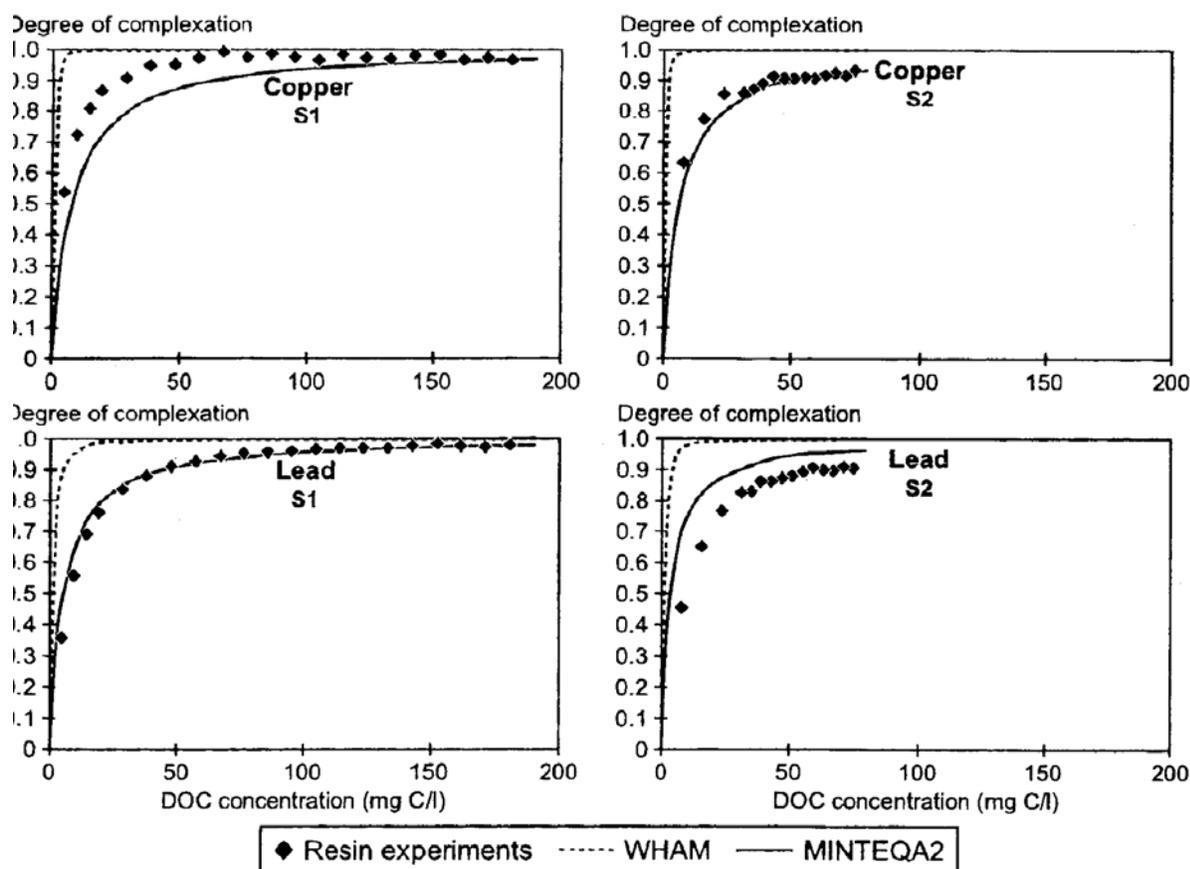

Figure E-21. Comparison MINTEQA2 estimated degree of DOC complexation for Cu and Pb versus degree of complexation in resin experiments.
(Christensen *et al.*, 1999)

Title: The Effect of pH on the Complexation of Cd, Ni, and Zn by Dissolved Organic
           Carbon from Leachate-polluted Groundwater
Authors: Christensen, J.B. and T.H Christensen
Source: *Water Research*, 34:3743-3754
Date: 2000
Metals: Cd, Ni, and Zn

Basis of validation: Concentrations of metal-DOC complexes determined in batch experiments
using a resin exchange method were compared with concentrations of metal-DOC complexes
computed by MINTEQA2 over a range of pH values.

Description: This study compared the extent of metal-DOC complexation measured in a resin
exchange method and estimated using the speciation models WHAM and MINTEQA2 over a
range of DOC concentrations and pH values. Groundwater samples were obtained from the
DOC-rich leachate plume downgradient from a landfill. A synthetic solution was prepared so as
to be similar to each of these leachate samples except that DOC was not included. The with- and
without-DOC solutions were used in the resin exchange method to estimate DOC complexation
of Cd, Ni, and Zn at various combinations of DOC concentration and pH . DOC complexation
of these metals was also estimated by simulating the leachate solutions in WHAM (Tipping *et
al.*, 1994) and MINTEQA2. Concerning the predictions by MINTEQA2, a very poor match with
experimental results was obtained for all three metals because the MINTEQA2 result did not
show appropriate pH response (see Figure 22). The degree of DOC complexation predicted by
MINTEQA2 did not change appreciably as the pH was changed. The authors suggested that
MINTEQA2 predictions of pH dependent complexation by DOC could be improved
considerably by including a second site type (phenolic) in the MINTEQA2 representation of
DOC. The importance of the phenolic site relative to MINTEQA2 predictions has been
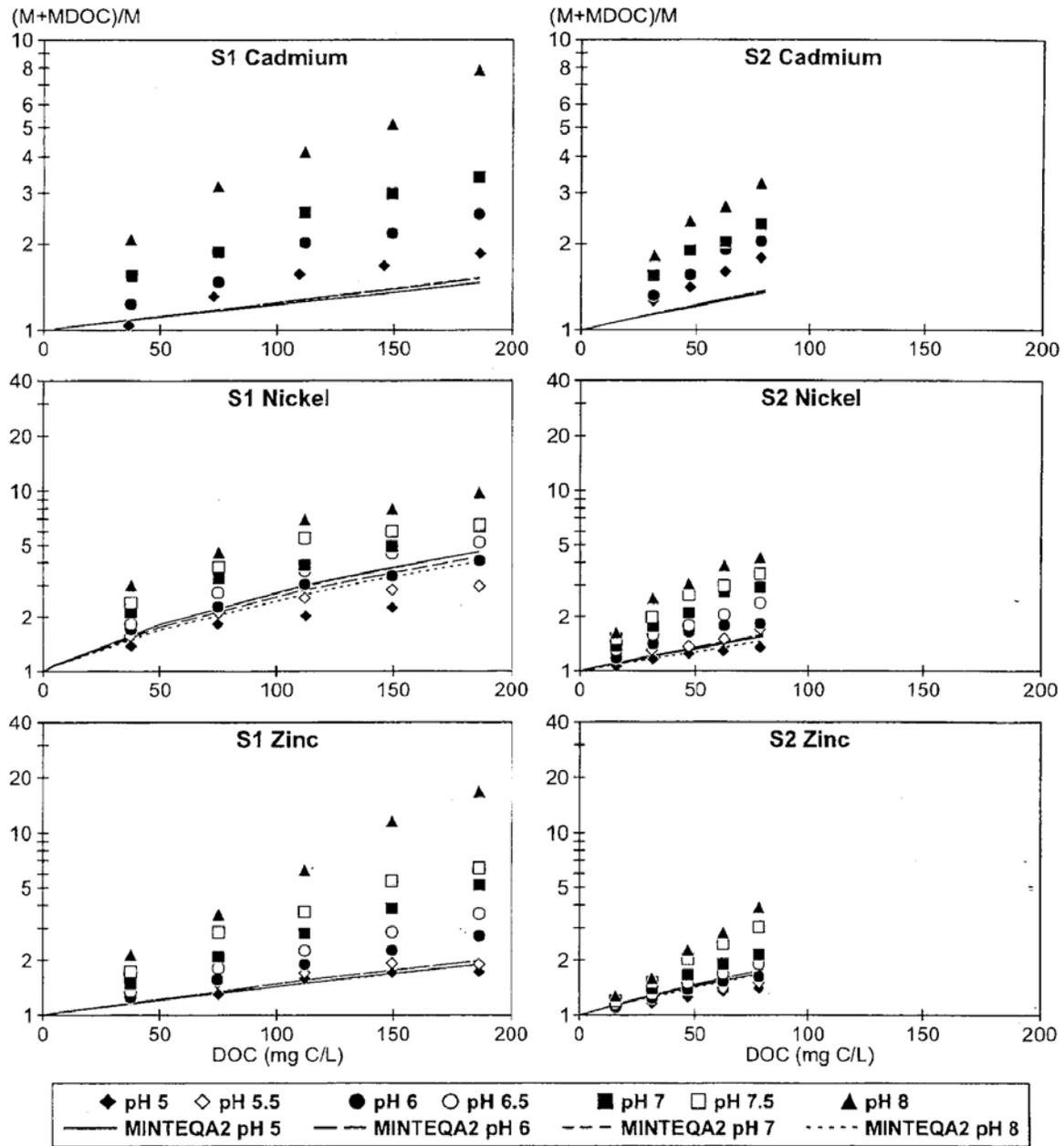discussed previously by Allison and Perdue (1994).

Figure E-22. Comparison of MINTEQA2 predictions of DOC complexation of Cd, Ni, and Zn versus experimentally determined values (resin exchange) at various pH values. (Christensen and Christensen, 2000)

Title: Chemical Modeling of the Neutralisation Process for Acid Uranium Mill Tailings
Authors: Khoe, G.H. and G. Sinclair
Source: *Proceedings, Hydrometallurgy and Aqueous Processing Symposium*, 1991 Annual
                   Meeting of the Metallurgical Society of AIME, New Orleans, LA, EP Congress 91
Date: 1991
Metals: Al, Fe, Ca, Mn, Si, PO_4, Pb, U
Basis of validation: Comparison of dissolved metal concentrations predicted by MINTEQA2 versus concentrations measured in neutralization experiments.
Description: MINTEQA2 was used to model the neutralization of uranium mill tailings. The adsorption of UO_2^{2+} via the triple-layer model was included. The acid tailings solution was represented in MINTEQA2 and successive additions of the liming agent were simulated by additions of portlandite. Comparison of the predicted pH and experimental pH measurements were similar. The MINTEQA2-predicted Al, Fe, Ca, Si, and PO_4 solution concentrations versus pH were in good agreement with measured values. The agreement between dissolved Mn concentration versus pH predicted by MINTEQA2 and experimental values was not as good. The authors conducted other experiments which they interpreted as suggesting CO_2 equilibria as the reason for this discrepancy. (The experimental solution did not have time to fully equilibrate with the atmosphere.) This study also included sorption modeling for Pb and U in the neutralized tailings using the triple-layer model in MINTEQA2. This modeling employed sorption reactions and equilibrium constants published by Davis and Leckie (1978) and Payne and Waite (1990). Comparison of model predictions and experimental results are shown in Figures 23 and 24 for U and Pb.
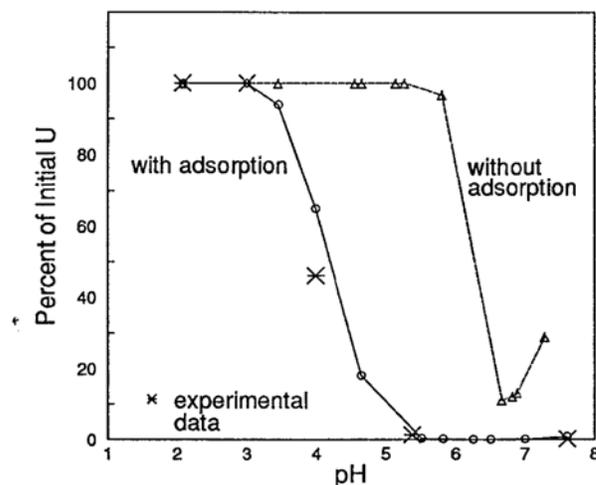

Figure E-23. Percent of UO_2^{2+} predicted as remaining in solution by MINTEQA2 (line) versus measured (X) over range of pH. Circles and triangles denoted model simulations with and without including sorption. (Khoe and Sinclair, 1991)

Title: Arsenic Adsorption from Geothermal Water
Authors: Webster, J.G . and K.S. Webster
Source: *Sixteenth Annual PNOC Geothermal Workshop Proceedings*, Manila, Philippines, pp. 35-42
Date: 1995
Metals: As(III) and As(V)
Basis of validation: Comparison of solution As concentrations measured in batch experiments with dissolved concentrations predicted by MINTEQA2 using the diffuse-layer sorption model
Description: MINTEQA2 was used to predict the sorption of arsenic (As) in batch experiments using As contaminated geothermal bore water and a prepared, freshly precipitated hydrous ferric oxide (HFO) sorbent. The major ion concentrations of the water samples were characterized and entered in MINTEQA2. Experiments were carried out over a range of pH values (3 to 11). Experiments were also conducted using a 0.1 M $NaNO_3$ solution rather than the geothermal bore water. The MINTEQA2 modeling employed the diffuse-layer sorption model and associated database for HFO (Dzombak and Morel, 1990). MINTEQA2 predictions were consistent with experimental observations for the 0.1 M $NaNO_3$ solution, especially for pH < 9.   However, for both As(III) and As(V), MINTEQA2 consistently predicted less As remaining in solution (i.e., more As sorption) than was observed in the bore water experiments. For pH <9, observed As(III) sorption was < 50 percent of the value predicted by MINTEQA2 and observed As(V) sorption ranged from 33 to 95 percent of the predicted value. The authors were unable to explain the discrepancy between the model and experimental results at the time of publication of this paper. However, in a follow-up study they concluded that very high silica concentration in the geothermal bore water samples resulted in sorption of SiO_2 and reduced the sorption of As in the bore water experiments (J. Webster, pers. comm, 1996). Silica adsorption had not been included in the original MINTEQA2 modeling. They repeated the MINTEQA2 modeling of the bore water with sorption reactions for silica onto HFO (equilibrium constants estimated) and obtained a much closer match with experimental results.
Title: Simulating the Response of Metal Contaminated Lakes to Reductions in Atmospheric
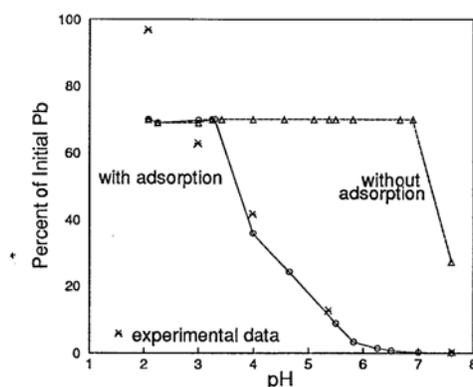

**Figure E-24. Percent of Pb predicted as
remaining in solution by MINTEQA2 (line)
versus measured (X) over range of pH.
Circles and triangles denoted model
simulations with and without including
sorption. (Khoe and Sinclair, 1991)**

Loading Using a Modified QWASI Model
Authors: Woodfine, D.G., R. Seth, D. Mackay, and M, Havas
Source: *Chemosphere,* 41:1377-1388
Date: 2000
Metals: Cu, Ni
Basis of validation: Comparison of QWASI simulation results of average lake water dissolved metal concentrations with observed values when MINTEQA2-predicted partition coefficients are used.
Description: MINTEQA2 was used to simulate the effect of pH, solution chemistry, particulate (sorbent) concentrations and metals loading on metal partition coefficients. The simulated coefficients were used in the QWASI (Quantitative Water Air Sediment Interaction) transport model. This model accounts for metals loading of surface water bodies via atmospheric deposition of metal-laden dust particles originating at smelter sites. Previous versions of the QWASI model had employed constant partition coefficients obtained from the literature or experimentally. The study described here included the use of MINTEQA2 for metal speciation and to calculate partition coefficients for association of metals with suspended particles in two water bodies (Alice Lake and Baby Lake). The lake suspended matter was assumed to be dominated by hydrous ferric oxide (HFO) and the database of sorption reactions for HFO from Dzombak and Morel (1990) was used in MINTEQA2 to quantify sorption. The surface site density for the suspended particles was as determined by Hamilton-Taylor *et al*. (1997) for lake suspended particles (0.8 mmol sites per g). Estimated copper (Cu) and nickel (Ni) deposition rates over a twenty year period beginning in 1972 were used to parameterize the QWASI model. The QWASI simulations produced annual estimated lake concentrations for Cu and Ni using the MINTEQA2-predicted partition coefficients for both lakes. Results are plotted versus measured dissolved metal concentrations in these lakes (Figure 25). Previous studies for metals using the QWASI model employed constant partition coefficients from experiments or from the literature. In this first use of a metal speciation model to predict metal partition coefficients for variable chemical conditions and metal loading within QWASI, the authors concluded that the model simulations were reasonable given uncertainties in the input data.
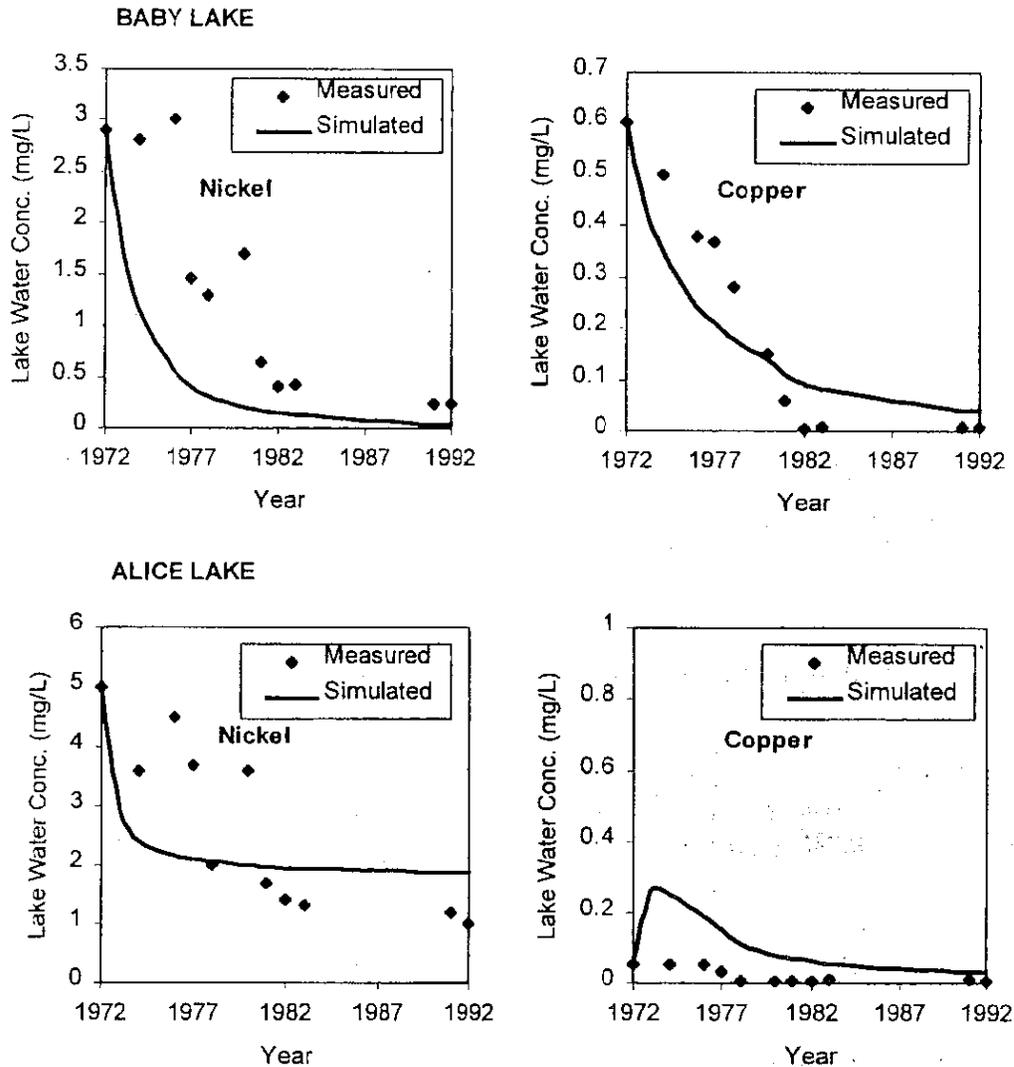
Figure E-25. Dissolved Cu and Ni concentrations simulated by QWASI model using MINTEQA2-generated partition coefficients versus measured metal concentrations. (Woodfine *et al.*, 2000)

Title: Trace Element Geochemistry of Onion Creek near Van Stone Lead-Zinc Mine
                (Washington, USA) – Chemical Analysis and Geochemical Modeling
Authors: Routh, J. and M. Ikramuddin
Source: Chemical Geology, 133:211-224
Date: 1996
Metals: Pb, Zn
Basis of validation: Comparison of MINTEQA2-predicted equilibrium solid phases with solid
phases observed by X-ray diffraction and predicted water concentrations with observed
concentrations.

Description: MINTEQA2 was used to predict the concentration of trace elements in surface
waters of Onion Creek. Onion Creek (Washington) receives surface runoff and seepage from
tailings ponds associated with lead-zinc mining activities. The MINTEQA2 modeling included
precipitation reactions for major ions and trace elements and sorption reactions for Pb and Zn.
An experimentally determined amount of ferrihydrite was used to represent the sorbent in
MINTEQA2; its surface parameters were as described by Dzombak and Morel (1990) for
hydrous ferric oxide (surface area 600 m^2/g and site density 0.2 moles of sites per mole Fe).
Sorption reactions also were as specified by Dzombak and Morel (1990). The pH of Onion
Creek water was 7.9. X-ray diffraction analyses of sediment samples confirmed the presence of
dolomite, calcite, Al -oxide, Fe-Mn-oxide, and zinc sulfide as predicted by MINTEQA2. The
model also predicted low dissolved concentrations of Pb and Zn due to sorption onto
ferrihydrite. This finding was supported by high partition coefficients computed for these
elements in Onion Creek waters ($> 10^4$ L/kg).

E.4 Conclusions

The MINTEQA2 validation studies reviewed present a broad spectrum of natural conditions, analytical methods, and metals of interest. The studies also cover most of the important MINTEQA2 sub-models that are important to the use of MINTEQA2 to support rulemaking activities by the U.S. EPA Office of Solid Waste. These activities include the Hazardous Waste Identification Rule (circa 1995-96) and the 3MRA of 1999. In modeling support for both of these activities, MINTEQA2 modeling was performed to estimate metal partition coefficients for use in groundwater transport modeling (US EPA, 1996 and 1999). This modeling involved precipitation of major ions (Al, Ca, Fe, etc.) and sorption of trace metals. The sorption modeling was included by means of the diffuse-layer model with the database of sorption reactions provided by Dzombak (1986) and Dzombak and Morel (1990). The Gaussian DOM model was used to estimate metal binding with dissolved organic matter. The modeling was performed over a broad range of pH, HFO sorbent, and metal concentrations.

The pH range covered among all studies cited is 4 to 12. Some studies were performed using laboratory systems exclusively (e.g., freshly precipitated pure phase HFO as the sorbent) and some involved natural aquifer materials and soils. The analytical methods used included ICP spectroscopy, X-ray diffraction, scanning electron microscopy, speciation using ion exchange resins, and ion-selective electrodes. The metals for which validating comparisons were attempted included Al, Ca, Fe, Mn, PO_4, SiO_2, SO_4, Cd, As, Ba, Be, Cu, Cd, Co, Mo, Ni, Pb, Sr, Tl, U, and Zn (and pH). The studies presented results for MINTEQA2 modeling in which the main process removing metals from solution was assumed to be precipitation as well as studies in which sorption was assumed to be the operative process in reducing dissolved metal concentrations. Most of the studies that focused on sorption employed the diffuse-layer model with the database provided by Dzombak and Morel (1990). The Gaussian DOM model was also included in some modeling studies.

Most of the studies were not undertaken for the specific purpose of validating MINTEQA2, although a few were (e.g., Loux *et al*., 1989, Stollenwerk 1994, 1996). These may perhaps carry more weight in assessing the overall validation status of MINTEQA2 in that both included considerable connection with natural field materials and both place emphasis on the role of sorption. As previously discussed, the 1988 workshop on MINTEQA2 validation presented a broad range of opinions as to what might constitute a validation of this model. The consensus was that a broad range of studies that show some level of correspondence between the model's predictions and actual measurements might be the best that could be hope for. Here, we leave the reader to review the studies cited and form his or her own opinion regarding the validation status of MINTEQA2.

This page intentionally left blank.

E.5 References

Allison, J.D.,1997. *An Implementation of the Competitive Gaussian Model for Metal-humic Binding in a General Speciation Model*, Ph.D. Dissertation, Georgia Institute of Technology, Atlanta, GA.

Allison, J.D., 1996. *Update and Correction of Metal-Organic Complexes for the MINTEQA2 Thermodynamic Database*, prepared for U.S. Environmental Protection Agency, National Exposure Research Lab, Ecosystems Research Division, Athens, GA.

Allison, J.D. and E.M. Perdue, 1994. Modeling metal-humic interactions with MINTEQA2, in *Humic Substances in the Global Environment and Implications on Human Health*, edited by N. Senesi and T.M. Miano, Elsevier Science B.V.

Ball, J.W., D.K. Nordstrom, and E.A. Jenne, 1981. Additional and Revised Thermochemical Data and Computer Code for WATEQ2– A computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibrium of Natural Waters, U.S. Geological Survey, *Water Resources Investigations*, WR1 78-116.

Bard, A.J., R. Parsons, and J.Jordan (eds.), 1985. *Standard Potentials in Aqueous Solution,* International Union of Pure and Applied Chemistry, Marcel Dekker, Inc., New York, 834p.

Christensen, J.B. and T.H Christensen, 1999. Complexation of by DOC in polluted groundwater: A comparison of approaches using resin exchange, aquifer material sorption, and computer speciation models (WHAM and MINTEQA2), *Environmental Science & Technology*, 33:3857-3863.

Christensen, J.B., J.J. Botma, and T.H Christensen, 1999. Complexation of Cu and Pb by DOC in polluted groundwater: A comparison of experimental data and predictions by computer speciation models (WHAM and MINTEQA2), *Water Research*, 33(15):3231-3238.

Christensen, J.B. and T.H Christensen, 2000. The effect of pH on the complexation of Cd, Ni, and Zn by dissolved organic carbon from leachate-polluted groundwater, *Water Research*, 34:3743-3754.

Davis, A., M. V. Ruby, and P. D. Bergstrom, 1992. Bioavailability of arsenic and lead in soils from the Butte, Montana, mining district, *Environmental Science & Technology*, 26(3):461-468.

Davis, J.A. and J.O. Leckie, 1978. Surface ionization and complexation at the oxide/water interface II. Surface properties of amorphous iron hydroxide and adsorption of metal ions, *Journal of Colloidal and Interface Science*, 67:90-107.

Davis, J.A. and J.O. Leckie, 1980. Surface ionization and complexation at the oxide/water interface 3. Adsorption of anions, *Journal of Colloidal and Interface Science*, 74:32-43.

Deutsch, W.J. and K.M. Krupka, 1985. *MINTEQ Geochemical Code: Compilation of Thermodynamic Database for the Aqueous Species, Gases, and Solids Containing Chromium Mercury, Selenium, and Thallium*. Unpublished report prepared by Battelle Pacific Northwest Laboratory for the U.S. Environmental Protection Agency, Athens, GA.

Dobbs, J.C., W. Susetyo, L.A. Carreira, and L.V. Azarraga, 1989. Competitive binding of protons and metal ions in humic substances by lanthanide ion probe spectroscopy, *Analytical Chemistry*, 61:1519-1524.

Doyle, T.A., A. Davis, and D.D. Runnels, 1994. Predicting the environmental stability of treated copper smelter flue dust, *Applied Geochemistry*, 9:337-350.

Drever, J.I., 1997. *The Geochemistry of Natural Waters- Surface and Groundwater Environments* (3rd ed.), Prentice-Hall, New Jersey.

Dzombak, D.A. and F.M.M. Morel, 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley & Sons, New York, 393p.

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

Dzombak, D.A. 1987. *A Practical Guide for Use of the Generalized Two Layer Sorption Model*, prepared for the U.S. Environmental Protection Agency, Athens, GA.

Felmy, A.R., D.C. Girvin, and E.A. Jenne, 1984. *MINTEQ - A Computer Program for Computing Aqueous Equilibria*, prepared by Battelle Pacific Northwest Laboratories for the U.S. Environmental Protection Agency, Athens, GA.

Ficklin, W.H., A.H. Love, and C.S.E. Papp, 1991. Solid phase variations in an aquifer as the solution changes, Globe, Arizona. *U.S. Geological Survey Water Resource Investigations Report* 91-4034, pp.475-480.

Fish, W., D.A. Dzombak, and F.M.M. Morel, 1986. Metal-humate interactions. 2. Application and comparison of models, *Environmental Science & Technology*, 20: 676-683.

Fotovat, A. and R. Naidu,1997. Ion exchange resin and MINTEQa2 speciation of Zn and Cu in alkaline sodic and acid soil extracts, *Australian Journal of Soil Research*, 35: 711-726.

Frandsen, A. K., and C. H. Gammons, 2000. Heavy metal complexation with aqueous sulfide in an anaerobic treatment wetland, in *Wetlands and Remediation: An International Conference*, Battelle Press, Columbus, OH, pp. 423-430.

Hamilton-Taylor, J., L. Giusti, W. Davidson, W. Tych, and C.N. Hewitt, 1997. Sorption of trace metals (Cu, Pb, Zn) by suspended lake particles in artificial (0.005 M NaNO$_3$) and natural (Esthwaite Water) freshwaters, *Colloids Surfaces A: Physicochem. Engrg. Aspects*, 120:205-219.

IUPAC, 1998. *Stability Constants Database SC-DATABASE for Windows v2.62 and 3.02*, International Union of Pure and Applied Chemistry (IUPAC) and Academic Software, United Kingdom..

Jenne, E.A., 1994. *Geochemical Model "Validation": Reliability of Solubility Equilibria Calculated with Field Data from and Acidic Metal-rich Plume near Globe, Arizona,* prepared by Battelle Pacific Northwest Laboratories for the U.S. Environmental Protection Agency, Athens, GA.

Jenne, E.A. and E.A. Crecilius, 1988. *Determination of sorbed metals, amorphic Fe, oxidix Mn, and reactive particulate organic carbon in sediments and soils*. Presented at the 3rd International Conference on Environmental Contamination, Venice, Italy, Sept 26-29, 1988.

Jenne, E.A. and K.M. Krupka, 1985. Validation of geochemical models, in *Workshop on Fundamental Geochemistry Needs for Nuclear Waste Isolation*, B.R. Erdal (ed.), pp. 143-152.

Jensen, D.L., J.K. Boddum, S. Redemann, and T.H. Christensen, 1998. Speciation of dissolved iron(II) and manganese(II) in a groundwater pollution plume, *Environmental Science & Technology*, 32(18): 2657-2664.

Khoe, G.H. and G. Sinclair, 1991. Chemical modeling of the neutralisation process for acid uranium mill tailings, *Proceedings, Hydrometallurgy and Aqueous Processing Symposium*, 1991 Annual Meeting of the Metallurgical Society of AIME, New Orleans, LA, EP Congress 91.

Krupka, K.M., E.A. Jenne, and W.J. Deutsch, 1983. *Validation of the WATEQ Geochemical Model for Uranium*, PNL-4333, Battelle Pacific Northwest Laboratories, Richland, WA.

Lindsay, W. L. and H.A. Ajwa, 1995. Use of MINTEQA2 for Teaching Soil Chemistry, in *Chemical Equilibrium and Reaction Models*, edited by R.H. Loeppert, A.P. Schwab, and S. Goldberg, Soil Science Society of America, Special Publication 42, Madison, Wisconsin, pp.241-252.

Loux, N.T., D. S. Brown, C.R. Chapin, J.D. Allison, and S.M. Hassan, 1989. Chemical speciation and competitive cationic partitioning on a sandy aquifer material, *Chemical Speciation and Bioavailability*, 1:111-125.

Marani, D., G. Macchi, and M. Pagano,1995. Lead precipitation in the presence of sulphate and carbonate: Testing of thermodynamic predictions, *Water Research*, 29(4): 1085-1092

Mathur, S. S., 1995. *Development of a Database for Ion Sorption on Goethite Using Surface Complexation Modeling*, Master's Thesis, Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA.

Morrey, J.R., C.T. Kincaid, and C.J. Hostetler, 1985. *Geochemical Models for Solute Migration, Volume 3: Evaluation of Selected Computer Codes for Modeling Aqueous Solutions and Solute Migration in Soils and Geologic Media*, EA-3417, Battelle Pacific Northwest Laboratories, Richland, WA.

NIST, 1997. *Critical Stability Constants of Metal Complexes Database* (CRITICAL, version 2.0 and 4.0), Standard Reference Database 46, National Institute of Standards and Technology, Washington, DC.

Nordstrom, D.K. and J.L. Muñoz, 1986. *Geochemical Thermodynamics*, Blackwell Scientific, Palo Alto, CA, pp. 365-391.

Nordstrom, D.K., L.N. Plummer, D. Langmuir, E. Busenberg, H. May, B,L. Jones, and D.L. Parkhurst (1990) Revised chemical equilibrium data for major water-mineral reactions and their limitations. **In**: *Chemical Modeling in Aqueous Systems II* (D.C. Melchior and R.L. Bassett, eds.), American Chemical Society Symposium Series 416, Chapter 31 pp. 398-413.

Palmer, F.B, C.A. Butler, M. H. Timperley, and C. W. Evans, 1998. Toxicity to embryo and adult zebrafish of copper complexes with two malonic acids as models for dissolved organic matter, *Environmental Toxicology and Chemistry*, 17(8):1538-1545.

Payne, T.E. and T.D. Waite 1990, Surface complexation modeling of uranium sorption data obtained by Isotope exchange techniques, *Radiochim. Acta*,

Robins, R.G., 1990. The stability and solubility of ferric arsenate: an update. Paper presented at the *Metallurgical Society Annual Meeting*, Feb. 18-22, 1990, Anaheim, CA.

Routh, J. and M. Ikramuddin, 1996. Trace element geochemistry of Onion Creek near Van Stone lead-zinc min (Washington, USA) – chemical analysis and geochemical modeling, *Chemical Geology*, 133:211-224.

Saunders, J.A. and L.E. Toran, 1995. Modeling of radionuclide and heavy metal sorption around low- and high-pH waste disposal sites at Oak ridge, Tennessee, *Applied Geochemistry*, 10:673-684.

Sehmel, G.A., 1989. *Cyanide and Antimony Thermodynamic Database for the Aqueous Species and Solids for the EPA-MINTEQ Geochemical Code*, prepared by Battelle Pacific Northwest Laboratory for the U.S. Environmental Protection Agency, Athens, Georgia.

Serkiz, S.M., J.D. Allison, E.M. Perdue, H.E. Allen, and D.S. Brown, 1996. Correcting errors in the thermodynamic database for the equilibrium speciation model MINTEQA2. *Water Research*, 30(8):1930-1933.

Stevenson, F.J. and A. Fitch, 1986. Chemistry of complexation of metal ions with soil solution organics, in *Interactions of Soil Minerals with Natural Organics and Microbes*, P.M. Huang and M. Schnitzer (eds.), Soil Science Society of America.

Stollenwerk, K.G., 1994. Geochemical interactions between constituents in acidic groundwater and alluvium in an aquifer near Globe, Arizona, *Applied Geochemistry*, 9:353-369.

Stollenwerk, K.G., 1995. Modeling the effects of variable groundwater chemistry on the adsorption of molybdate, *Water Resources Research*, 31(2):347-357.

Stollenwerk, K.G., 1996. Simulations of reactions affecting transport of constituents in the acidic plume, Pinal Creek basin, Arizona, *U.S. Geological Survey Water-Supply Paper* 2466, pp. 21-49.

Susetyo, W., L.A. Carreira, L.V. Azarraga, and D.M. Grimm, 1991. Fluorescence techniques for metal-humic interactions. *Fresenius Jour. Analytical Chemistry*, 339:624-635.

Tipping, E. ,1994. WHAM— A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances, *Computers & Geosciences*, 20: 973-1023.

USEPA, 1996. *Background Document for Metals; EPA Composite Model for Leachate Migration with Transformation Products (EPACMTP)*, Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC.

USEPA, 1998. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0*, prepared by HydroGeoLogic, Inc. and Allison Geoscience Consultants, Inc. for the U.S. Environmental Protection Agency, Athens, GA.

USEPA, 1999. *Changes in the MINTEQA2 Modeling Procedure for Estimating Metal Partition Coefficients in Groundwater*, prepared by HydroGeoLogic, Inc. for the U.S. Environmental Protection Agency, Washington, DC.

Webster, J.G . and K.S. Webster, 1995. Arsenic adsorption from geothermal water, *Sixteenth Annual PNOC Geothermal Workshop Proceedings*, Manila, Philippines, pp. 35-42.

Westall, J.C., J.L. Zachary, and F.M.M. Morel, 1976. *MINEQL: A Computer Program for the Calculation of Chemical Equiloibrium Composition of Aqueous Systems*, Technical Note 18, Ralph M. Parsons Laboratory, Dept. of Civil Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Westall, J.C., 1979. *MICROQL. II. Computation of Adsorption Equilibria in BASIC*, Swiss Federal Institute of Technology, EAWAG, Deubendorf, Switzerland.

Woodfine, D.G., R. Seth, D. Mackay, and M, Havas, 2000. Simulating the response of metal contaminated lakes to reductions in atmospheric loading using a modified QWASI model, *Chemosphere*, 41:1377-1388.

Yu, J.Y.,1996. Precipitation of Fe and Al compounds from the acid mine waters in Dogyae area, Korea: A qualitative measure of equilibrium modeling applicability and neutralization capacity?, *Aquatic Geochemistry*, 2: 81-105

Zachara, J.M., D.C. Girvin, R.L. Schmidt, and C.T. Resch, 1987. Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions, *Environental Science & Technology*, 21(6):589-594.

Zachara, J.M., R.L. Schmidt, and E.A. Jenne, 1988. *Feasibility of Field Testing the MINTEQ Geochemical Code*, prepared for the U.S. Environmental Protection Agency by Battelle Pacific Northwest Laboratories, Richland, WA.