

US EPA ARCHIVE DOCUMENT

6.0 Verification and Validation of Chemical Properties Models

The chemical properties for the constituents currently included in the 3MRA modeling system database were developed through modeling and literature search. This section describes the verification and validation for the two models used to develop some of the chemical properties: SPARC (System Performs Automated Reasoning in Chemistry) and the MINTEQA2 Geochemical Speciation Model. Figure 6-1 provides an overview of the steps taken to ensure the quality of the chemical properties models.

6.1 SPARC Chemical Properties Estimator

This section documents the verification and validation activities for the SPARC chemical properties estimator model. Although not incorporated into the 3MRA modeling system as a module, the SPARC model was used to calculate the thermodynamic organic chemical properties required by the various modules, notably solubility, vapor pressure, Henry's law constant, octanol/water partition coefficient, air diffusivity, water diffusivity, and ionization potential. The verification and validation activities described in this section are those conducted for the SPARC model in general, but because they confirm the basic chemical functionality of this model, they are relevant to its application to the 3MRA modeling system.

The SPARC model has been extensively peer reviewed and papers related to the model published in the literature. The SAB also peer reviewed the model in 1991.

For the 3MRA modeling system, SPARC was used to calculate chemical and physical property values for standard conditions (i.e., 25° C, pH of 7). These values are stored in a chemical database accessed by the 3MRA modeling system Chemical Properties Processor (CPP). The CPP contains algorithms that are used to adjust the values developed for standard conditions using SPARC to the specific temperature and pH needed. For example, the Aerated Tank Module calls the CPP during each model realization to get property values adjusted for

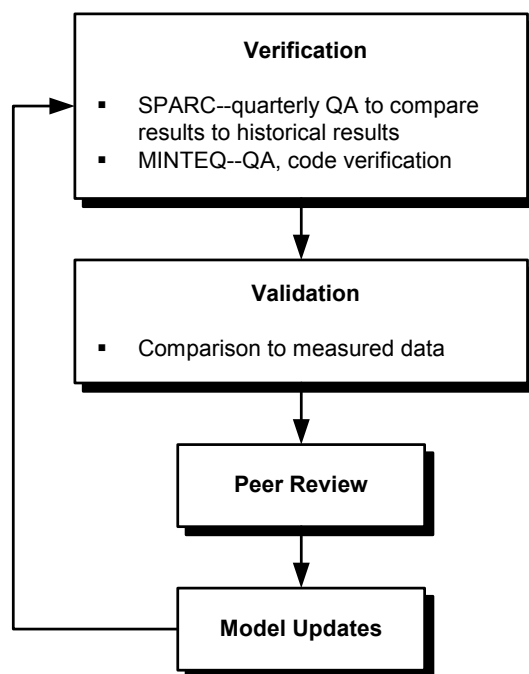


Figure 6-1. Overall approach to ensure the quality of the 3MRA chemical property data.

monthly temperature changes within the tank. For organic chemicals that ionize in the environment, the CPP uses SPARC-generated ionization coefficients (pKa) to adjust partition coefficients to site-specific pH conditions in soil and aquifer materials.

6.1.1 Model Description

EPA developed the predictive modeling system SPARC to help meet the growing need for chemical-specific inputs for risk assessment tools such as the 3MRA modeling system. SPARC calculates values for a large number of physical and chemical parameters from molecular structure and basic information about the environment (media, temperature, pressure, pH, etc.). The ultimate goal for SPARC is to model the chemical and physical behavior of molecules to predict chemical reactivity parameters and physical properties strictly from molecular structure for the universe of organic molecules. Table 6-1 lists the properties calculated using SPARC for the 3MRA modeling system, along with testing status and the reaction conditions that must be specified to calculate a property. Detailed information on SPARC can be found in U.S. EPA (2003a).

Table 6-1. SPARC Physical and Chemical Property Estimations used for the 3MRA Modeling System

Property	Testing Status ^a	Reaction Conditions
Molecular weight	Yes	none
Density	Yes	Temperature
Volume	Yes	Temperature
Vapor Pressure	Yes	Temperature
Boiling Point	Yes	Pressure
Diffusion Coefficient in Air	Mixed	Temperature, Pressure
Diffusion Coefficient in Water	Mixed	Temperature
Solubility	Yes	Temperature, Solvent
Henry's constant (gas/liquid partition)	Yes	Temperature, Solvent
Octanol/Water Partition (liquid/liquid partition)	Yes	Temperature, Solvent
Ionization pK _a in water	Yes	Temperature, pH

^a Testing status:

Yes: already tested and implemented in SPARC

Mixed: capability exists, more testing needed (automated and/or extended)

Mathematical models for predicting the transport and fate of contaminants in the environment require reactivity parameter values; that is, the physical and chemical constants that govern reactivity. Although empirical structure-activity relationships that allow estimation of some constants have been available for many years, such relationships generally hold only within very limited families of chemicals. SPARC avoids this limitation by predicting chemical reactivity strictly from molecular structure for virtually all organic compounds, using computational algorithms based on fundamental chemical structure theory to estimate values for a large array of physical-chemical properties.

EPA has used SPARC for several years to estimate chemical and physical property values for program offices (e.g., Office of Water, Office of Solid Waste and Emergency Response, Office of Prevention, Pesticides and Toxic Substances) and EPA Regions. SPARC has been used in other EPA modeling programs such as LENS3 (a multicomponent mass balance model for application to oil spills) and by state agencies such as the Texas Natural Resource Commission. The SPARC web-based calculators have been used by many employees of various government agencies, academic institutions, and private chemical or pharmaceutical companies throughout the United States. The web version of SPARC performs approximately 50,000 to 100,000 calculations each month (see U.S. EPA, 2003b, for summary web usage statistics).

6.1.2 Major Model Components/Functionality

SPARC analyzes chemical structure to answer a specific reactivity query in much the same manner as an expert chemist would. Physical-organic chemists have established the types of structural groups or atomic arrays that affect certain types of reactivity and have described, in “mechanistic” terms, the effects on reactivity of other structural constituents appended to the site of reaction. To encode this knowledge base, a classification scheme was developed in SPARC that defines the role of structural constituents in affecting reactivity. Furthermore, models have been developed that quantify the various “mechanistic” descriptions commonly used in structure-activity analysis, such as induction, resonance, and field effects. SPARC execution involves the classification of molecular structure (relative to a particular reactivity of interest) and the selection and execution of appropriate “mechanistic” models to quantify reactivity.

The SPARC computational approach is based on blending well known, established methods such as SAR (Structure Activity Relationships) (Lemer and Grundwald, 1965; Lowry and Richardson, 1987), LFER (Linear Free Energy Relationships) (Taft, 1987; Hammett, 1970) and PMO (Perturbed Molecular Orbital) theory (Dewar and Dougherty, 1975; Dewar, 1969). SPARC uses SAR for structure activity analysis, such as induction and field effects. SPARC uses LFER to estimate thermodynamic or thermal properties and PMO theory is used to describe quantum effects, such as charge distribution delocalization energy and polarizability of the p electron network. In reality, every chemical property involves both quantum and thermal contributions and necessarily requires the use of all three methods for prediction.

SPARC’s predictive methods were designed for engineering applications involving physical-chemical process modeling. More specifically, these methods provide:

- An *a priori* estimate of the physical-chemical parameters of organic compounds for physical and chemical fate process models when measured data are not available;
- Guidelines for ranking a large number of chemical parameters and processes in terms of relevance to the question at hand, thus establishing priorities for measurements or study;
- An evaluation or screening mechanism for existing data based on “expected” behavior; and

- Guidelines for interpreting or understanding existing data and observed phenomena.

The basic mechanistic models in SPARC are designed and parameterized to be portable to any type of chemistry or organic chemical structure. This portability affects system validation and verification in several ways. As the diversity of structures and the chemistry that is addressable increases, so does the opportunity for error. However, in verifying against the theoretical knowledge of reactivity, specific situations can be chosen that offer specific challenges. This is important when verifying or validating performance in areas where existing data are limited or where additional data collection may be required. This expanded prediction capability allows one to choose, for exhaustive validating, the reaction parameters for which large and reliable data sets exist. The SPARC models have been validated on more than 10,000 data points.

Most models that predict a given physical-chemical property (e.g., solubility, boiling point, etc.) are based directly on experimental data for that property for a limited training set of chemicals. Model development involves finding the best correlations between various descriptors of chemical structure and the observed property values. These descriptors are subsequently used to construct a model that adequately “recalculates” the training (or calibration) data set. To validate the model, one must demonstrate that the empirical model also accurately predicts property values for chemicals not included in the training set, but whose experimental values are known. These data are often called the validation set. In order to predict a new physical-chemical property (e.g., octanol/water partition coefficient), the entire process must be repeated, requiring new training and validation data sets for each new property.

With SPARC, experimental data for physical-chemical properties (such as boiling point) are not used to develop (or directly impact) the model that calculates that particular property. Instead, physical-chemical properties are predicted using models that quantify the underlying phenomena that drive all types of chemical behavior (e.g., resonance, electrostatic forces, induction, dispersion, H-bonding interactions, etc.). These mechanistic models were parameterized using a very limited set of experimental data, but not data for the end-use properties that will subsequently be predicted. After verification, the mechanistic models were used in (or ported to) the various software modules that calculate the various end-use properties (such as boiling point).

It is critical to recognize that the same mechanistic model (e.g., H-bonding model) will appear in all of the software modules that predict the various end-use properties (e.g., boiling point) for which that phenomenon is important. Thus, any comparison of SPARC-calculated physical-chemical properties to an adequate experimental data set is a true model validation test—there is no training (or calibration) data set in the traditional sense for that particular property. The results of validation tests on the various SPARC property models are summarized in Section 6.1.4 below and discussed in more detail (by each property) in U.S. EPA (2003b).

6.1.3 Summary of Model Verification

The unique approach to SPARC modeling impacts the strategy for model verification. When a mechanistic model is updated or improved by incorporating new knowledge, the impact on all of the various end-use parameters must be assessed. EPA has developed quality assurance software that is executed each quarter on the current version of SPARC. This software runs the various property modules for a large number of chemicals (4,200 data-point calculations) and compares the results to historical results obtained over the life span of the SPARC program.¹ Because all SPARC property modules are driven by the same verified mechanistic models, this verification approach can be applied after each SPARC improvement to ensure that existing parameter models still work correctly and that the computer codes for all property and mechanistic models are fully operational.

6.1.4 Summary of Model Validation

Each SPARC calculation used to estimate a chemical or physical property has been validated against numerous measured values for the property of interest. A detailed discussion of each of these validation exercises, including graphical results for many, is provided in U.S. EPA (2003b). The following examples illustrate the general processes for some of the more important properties used in 3MRA.

6.1.4.1 Vapor Pressure. The vapor pressure computational algorithm output was initially verified by comparing the SPARC prediction of the vapor pressure at 25° C to hand calculations for key molecules. Because the SPARC self-interactions model was developed initially on this property, the vapor pressure model undergoes the most frequent validation tests. The calculator was trained on 315 nonpolar and polar organic compounds at 25° C. Figure 6-2 presents the SPARC-calculated vapor pressure at 25° C versus measured values for 747 compounds. The SPARC self-interactions model can predict the vapor pressure at 25° C within experimental error over a wide range of molecular structures and measurements (over 8 log units). For simple structures, SPARC can calculate the vapor pressure to better than a factor of 2. For complex structures such as some pesticides and pharmaceutical drugs for which dipole-dipole and/or hydrogen bond interactions are strong, SPARC calculates the vapor pressure within a factor of 3 to 4.

6.1.4.2 Solubility. The solubility calculator spans more than 12 log mole fraction as shown in Figure 6-3. The root mean square (RMS) deviation was 0.40 log mole fraction, which was close to the experimental error. SPARC estimates the solubility for simple organic molecules to better than a factor of 2 (0.3 log mole fraction) and within a factor of 4 (0.6 log mole fraction) for complicated molecules like pesticides and pharmaceutical drugs. The RMS deviation for the solids compounds is three times greater than the RMS deviation for liquid compounds due to the crystal energy contributions.

¹ During early stage development, the output of all SPARC modules was compared to hand calculations with selected chemicals prior to proceeding with further development.

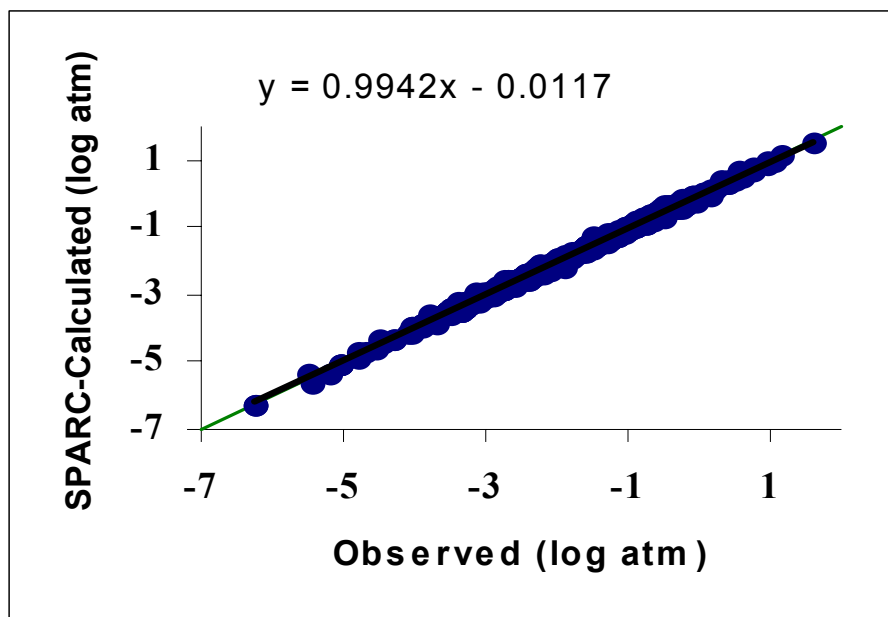


Figure 6-2. SPARC-calculated vs. observed log vapor pressure for 747 organic molecules at 25° C. The figure includes all vapor pressure measurements (real, not extrapolated) found in the literature. The RMS deviation error was 0.15 log atm and R^2 was 0.994.

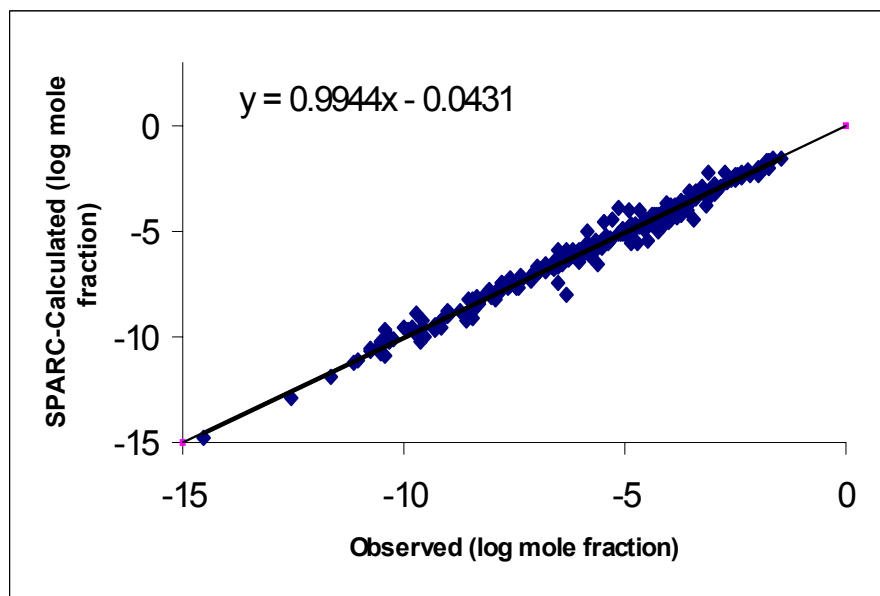


Figure 6-3. Test results for SPARC calculated log solubilities for 260 compounds. The RMS deviation is 0.321 and R^2 is 0.991. For the 119 liquid compounds, the RMS deviation is 0.135 and R^2 is 0.997; for the 141 solid compounds, the RMS deviation is 0.419 and R^2 is 0.985.

6.1.4.3 Octanol/Water Partition Coefficient. The liquid/liquid partitioning models are the most extensively tested partitioning models because a large octanol/water data set is available. Figure 6-4 displays a comparison of the EPA Office of Water recommended observed octanol-water distribution coefficients versus SPARC and ClogP calculated values. The RMS deviation and R^2 values were 0.18 and 0.996 respectively for SPARC and 0.44 and 0.978 respectively for ClogP calculated values (Karickhoff and Long, 1995).

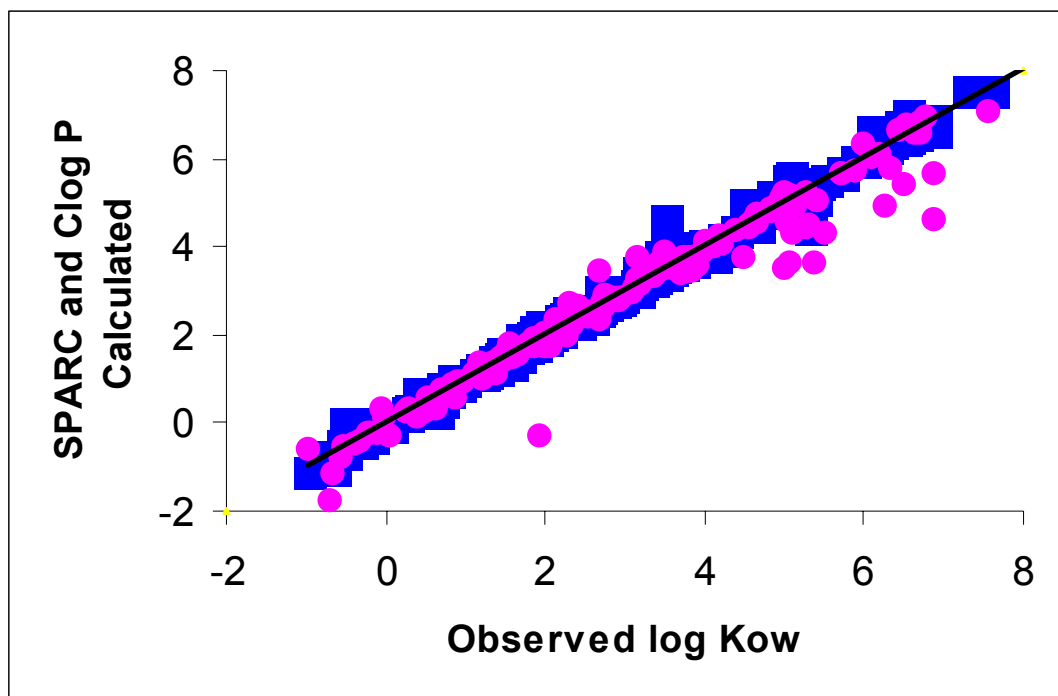


Figure 6-4. Test comparing calculated K_{ow} with measured values. Squares are SPARC calculated values, circles are ClogP calculated values. The RMS deviation and R^2 values were 0.18 and 0.996 respectively for SPARC and 0.44 and 0.978 respectively for ClogP calculated values.

6.1.4.4 Henry's Law Constant. The SPARC gas/liquid models have been extensively tested against observed Henry's constant measurements. In a comparison between measured and SPARC-calculated Henry's law constants for 271 organic compounds, the RMS deviation was 0.1 and the R^2 was 0.997.

6.2 MINTEQA2 Geochemical Speciation Model

This section documents the verification and validation activities for the MINTEQA2 geochemical speciation model. Although not incorporated into the 3MRA modeling system as a module, the MINTEQA2 model is used to develop metal sorption isotherms that are used by the Vadose Zone and Aquifer Modules to provide the pH and concentration- adjusted soil/water partition coefficients needed to estimate sorption of metal contaminants in the subsurface. The verification and validation activities described in this section are those conducted over the past 15 years for the MINTEQA2 model in general, but because they confirm the basic geochemical functionality of this model, they are relevant to its application to the 3MRA modeling system.

6.2.1 Model Description

The metal soil/water partitioning coefficients used by the Vadose Zone and Aquifer Modules are read from sorption isotherms created as a function of pH and metal concentration using the MINTEQA2 model. MINTEQA2 is an equilibrium speciation model that can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. The model can calculate the equilibrium mass distribution among dissolved species, adsorbed species, and multiple solid phases (see Figure 6-5) under a variety of conditions, including a gas phase with constant partial pressure.

The original version of this model (called MINTEQ) was developed in the early 1980s at Battelle Pacific Northwest Laboratory (Felmy et al., 1984). The MINTEQ package was delivered to EPA in 1985 and renamed MINTEQA1, which was distributed with a preprocessor program, PRODEFA1, for the preparation of MINTEQA1 input files. After more significant revisions were made in the late 1980s, the name was changed to MINTEQA2. With further development, version numbers were used to indicate new versions, and the model's formal name continues to be MINTEQA2.

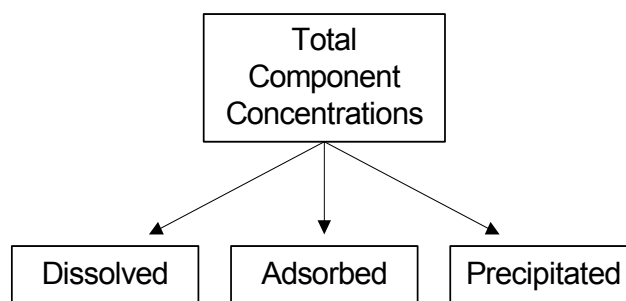


Figure 6-5. MINTEQA2 computes the equilibrium distribution of metals.

6.2.2 Major Model Components/Functionality

The MINTEQA2 model includes a comprehensive database that is sufficient for solving a broad range of problems without the need for additional user-supplied equilibrium constants. The model uses a predefined set of components that include free ions (e.g., Na^+) and neutral and charged complexes (e.g., H_4SiO_4^0 , $\text{Cr}(\text{OH})_2^+$). The database of reactions is written in terms of these components as reactants. The interactive preprocessor (PRODEFA2) produces the required MINTEQA2 input files. As implemented to calculate sorption isotherms for the 3MRA modeling system, MINTEQA2 includes reactions for adsorption of metal ions to hydrous iron oxide and organic matter surfaces. With these reactions, 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. For the 3MRA modeling system, isotherms were generated for a range of pH values and iron oxide and organic matter conditions designed to capture the national variability of these parameters.

The model and modeling procedure used in estimating metal partition coefficients for the 3MRA Subsurface Module were similar to those described in U.S. EPA (1996e, 1998c), with several improvements such as expanded and improved thermodynamic and sorption databases, calculations of isotherms for additional metals, and adjustments to the geochemical modeling conditions (U.S. EPA, 1999f).

6.2.3 Summary of Model Verification

Verification refers to tests and studies that, by design or otherwise, show that the computations performed by the MINTEQA2 computer code representing a geochemical 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. For MINTEQA2, “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. MINTEQA2 verification rests on comparison of the computed answer with hand calculations or results 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.

All parts of the MINTEQA2 code have been verified (U.S. EPA, 2002b). As a quality assurance measure, EPA policy has required testing of all code modifications and additions to MINTEQA1 and MINTEQA2 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.

Early verification efforts compared results with those of similar (verified) models. Zachara et al. (1988) stated that all major code algorithms, including calculation of mass balance, activity coefficients, and equilibrium speciation, were verified by hand calculations during the model’s initial development. Also, speciation results from test executions, some involving adsorption reactions, agreed with identical test calculations using other geochemical models (WATEQ3 and MINEQL). Morrey et al. (1985) compared the results of several equilibrium speciation models, including MINTEQ, and found that the results from these models are the same when identical thermodynamic data and program options are used.

EPA performed additional verification tests when new algorithms were added to MINTEQA2. For example, when the diffuse-layer (generalized two-layer) sorption model was added in 1989, test problems presented in Dzombak (1987), including computer solutions (using MICROQL; Westall, 1979) and hand calculated solutions, were used 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 and using a procedure described in Fish et al. (1986). Results from the formally implemented Gaussian dissolved organic matter (DOM) model 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 EPA’s Center for Exposure Assessment Modeling (CEAM) provided a useful clearinghouse function 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 preprocessor PRODEFA2) were discovered and corrected. The confidence that can be placed in MINTEQA2 has been enhanced by its use by the public and the public’s feedback in reporting errors. Modifications made to correct errors were verified prior to release in new versions.

Finally, the MINTEQA2 code has been verified through the use of the model in teaching geochemistry and in textbooks. Several universities (e.g., Lindsay and Ajwa, 1995) and EPA’s MINTEQA2 workshops use MINTEQA2, where simple classroom problems in solution equilibria and redox and sorption reactions use hand calculations to give the student a better appreciation of the nuances of solving geochemical problems. Prior to the EPA workshops, MINTEQA2 results were compared with those of MINEQL for a set of ten instructional problems and were found to agree. In addition, Drever (1997) used MINTEQA2 to illustrate the solution of problems in ground water chemistry in *The Geochemistry of Natural Waters*.

6.2.4 Summary of Model Validation

Validation of MINTEQA2 can be accomplished by conducting tests and studies that show that the geochemical model, 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 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.

Validating geochemical models is difficult 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 with measurements (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, kinetic effects); 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.

Because of these challenges, EPA convened a meeting of geochemists, soil scientists, and other ground water professionals to discuss the best approach to validating MINTEQA2 for 3MRA. Opinions ranged from those who believed that comparisons of MINTEQA2 predictions with measurements made on closely controlled laboratory systems would provide the most relevant validations to those who believed that laboratory systems could not faithfully represent the real

systems that are of interest and preferred a validation exercise closely tied to field sampling. Statisticians pointed out that because of the natural variability in many important MINTEQA2 input parameters, the model should be validated at a host of diverse sites. In the 14 years since that workshop, numerous and varied studies have been performed that reflect these recommendations and directly or indirectly relate to the validation of MINTEQA2.

The validation MINTEQA2 studies summarized in Table 6-2 show where MINTEQA2 model predictions have (and have not) been borne out by measurements in corresponding real systems. Details on these studies and their selection and use for validation may be found in U.S. EPA (2002b). Many of the studies in Table 6-2 were not undertaken specifically to provide validation support for MINTEQA2; however, each study compares results calculated by MINTEQA2 with some measure of reality, and studies were included regardless of whether the comparison was favorable or not.

Table 6-2. Summary of MINTEQA2 Validation Studies

Study Citation [Metals addressed]	Description of Validation	Results
<i>Simple systems (no sorption or dissolved organic carbon [DOC] complexation)</i>		
Unpublished MINTEQA2 workshop problem [pH]	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	Validated for dolomite lime system tested
Frandsen and Gammons (2000) [Zn, Cu, Fe]	Comparison of dissolved metal concentrations predicted by MINTEQA2 with measured values	Lower modeled dissolved metal concentrations than measured attributed to absence of quality metal-sulfide complex data in model database
Marani et al. (1995) [Pb]	Comparison of equilibrium mineral phases predicted by MINTEQA2 with sample mineral phases identified by X-ray diffraction.	Precipitates in keeping with observations
Fotovat and Naidu (1997) [Cu, Zn]	Compares free Cu^{2+} and Zn^{2+} in solution as determined using ion exchange procedures versus computed by MINTEQA2	Speciation measurements and model predictions in close agreement
Jensen et al. (1998) [Fe(II), Mn(II)]	Compares speciation of Fe(II) and Mn(II) in solution as determined using ion exchange procedures versus computed by MINTEQA2	Modeled and measured fractions of Fe(II) and Mn(II) were the same
Yu (1996) [Fe, Al]	Comparison of solid phases predicted to precipitate by MINTEQA2 versus solid phases identified in field samples using X-ray diffraction and other analytical methods	MINTEQA2 predicted different iron and aluminum precipitates than measured; difference attributed to kinetic inhibitions in the field
Palmer et al. (1998) [Cu]	Comparison of Cu^{2+} activity measured using an ion-selective electrode with Cu^{2+} activity computed by MINTEQA2	Good agreement between modeled and calculated Cu^{2+} concentrations for all test solutions
Davis et al. (1992) [As, Pb]	Comparison of MINTEQA2-calculated metal solubilities with measured solubilities	Modeled solubilities compared well with measurements

(continued)

Table 6-2. Continued

Study Citation [Metals addressed]	Description of Validation	Results
Complex systems (with sorption or DOC complexation)		
Loux et al. (1989) [Ba, Be, Cd, Cu, Ni, Pb, Tl, Zn]	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	Agreement between measured and modeled results sufficient for a number of elements; behavior of Ba, Be, Cu poorly described by model (database subsequently improved)
Jenne (1994) [Ca, Fe, Mn, Al, Si]	Field study where solid phases predicted to exist at equilibrium by MINTEQA2 were compared with solid phases identified using analytical methods	Model predictions reasonably conformed with observed mineral occurrence
Stollenwerk (1994) [Al, Fe, Mn, Ca, Cu, Co, Ni, Zn, pH, SO ₄]	Comparison of dissolved concentrations of metals measured in a series of wells with solution concentrations predicted using MINTEQA2 with diffuse-layer model	Combination of dilution and adsorption accurately simulated ground water concentrations for several metals
Stollenwerk (1996) [Al, Cu, Co, Ni, Zn]	Comparison of dissolved concentrations of metals measured in a column experiment effluent with dissolved concentrations predicted using MINTEQA2 with diffuse-layer model	Model-predicted concentrations matched experimental data reasonably well
Stollenwerk (1995) [MoO ₄]	Comparison of dissolved concentration of molybdate in column experiment effluent with dissolved concentration predicted using MINTEQA2 with diffuse-layer model	Good match between measured and modeled adsorption
Doyle et al. (1994) [As(V)]	Comparison of dissolved concentrations of As in batch and column tests with dissolved concentrations predicted by MINTEQA2	Predicted As leachate concentrations showed good agreement with measured values
Saunders and Toran (1995) [Co, Cd, Pb, Sr, U, Zn]	Comparison of dissolved concentrations of metals at monitoring wells near a disposal pond with dissolved concentrations predicted by MINTEQA2	Model predictions generally matched field observations
Christensen and Christensen (1999) [Cd, Ni, Zn]	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	Excellent agreement for Cd; fair agreement for Zn and one Ni sample; underprediction for one Ni sample. Model gives useful first approximation of Cd, Ni, and Zn complexation by DOC
Christensen et al. (1999) [Cu, Pb]	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	Agreement between predicted and observed complexation was generally good
Christensen and Christensen (2000) [Cd, Ni, Zn]	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	Poor match with experimental results because model did not show appropriate pH response; attributed to lack of lack of phenolic sites in model representation of DOC
Khoe and Sinclair (1991) [Al, Fe, Ca, Mn, SiO ₂ , PO ₄ , Pb, U]	Comparison of dissolved metal concentrations predicted by MINTEQA2 versus concentrations measured in neutralization experiments	Model predictions for pH, Al, Fe, Ca, Si, and PO ₄ agreed well with measured values; agreement not as good for Mn due to CO ₂ equilibria
Webster and Webster (1995) [As(III), As(V)]	Comparison of dissolved As concentrations measured in batch experiments with dissolved concentrations predicted by MINTEQA2 using the diffuse-layer model	Model overpredicted As adsorption; subsequent study included silica adsorption in model and obtained much closer match with experimental results
Woodfine et al. (2000) [Cu, Ni]	Comparison of Quantitative Water Air Sediment Interaction (QWASI) model simulation results of average lake water dissolved metal concentrations with observed values when MINTEQA2-predicted partition coefficients are used	Model simulations were reasonable given uncertainties in the input data
Routh and Ikramuddin (1996) [Pb, Zn]	Comparison of MINTEQA2-predicted equilibrium solid phases with solid phases observed by X-ray diffraction and comparison of predicted water concentrations with observed values	Measurements confirmed model predicted solid phases and dissolved concentrations