

GEOCHEM-EZ: a chemical speciation program with greater power and flexibility

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Abstract GEOCHEM-EZ is a multi-functional chemical speciation program, designed to replace GEOCHEM-PC, which can only be used on DOS consoles. Chemical speciation programs, such as GEOCHEM and GEOCHEM-PC, have been excellent tools for scientists designing appropriate solutions for their experiments. GEOCHEM-PC is widely used in plant nutrition and soil and environmental chemistry research to perform equilibrium speciation computations, allowing the user to estimate solution ion activities and to consider simple complexes and solid phases. As helpful as GEOCHEM-PC has been to scientists, the consensus was that the program was not very user friendly, was difficult to learn and to troubleshoot, and suffered from several functional weaknesses. To enhance the usability and to address

the problems found in GEOCHEM-PC, we upgraded the program with a Java graphical interface, added Help files, and improved its power and function, allowing it to run on any computer that supports Windows XP, Vista or Windows 7.

Keywords Chemical speciation · Nutrient solution · Computer software · Plant nutrition · Ion activity

Abbreviations

EDTA Ethylenediaminetetraacetic acid
EDDHA Ethylenebis[2(o-hydroxyphenyl)glycine]

Introduction

Chemical speciation programs, such as GEOCHEM (Sposito and Mattigod 1980; Parker et al. 1987) and GEOCHEM-PC (Parker et al. 1995a), have been excellent tools for scientists to use in designing appropriate solutions for their experiments. Typical results of speciation modeling efforts are the species distributions for all elements, their activity and activity coefficients, the system pH, redox potentials, and saturation indices for all possible minerals. Using speciation modeling programs, the scientist can make a solution in which requisite conditions are satisfied and the design is intelligent. For many years, GEOCHEM-PC has been used to formulate hydroponic solutions for plant growth (Diatloff et al. 1993;

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Hacisalihoglu et al. 2004), including those employing a variety of metal-chelate systems (Fox et al. 1996; Parker et al. 1995b; Schmidke et al. 1999; Shenker et al. 1999; Trostle et al. 2001) to control Fe (II), Fe (III), and Zn status. Likewise, this program has been used for estimating heavy metal (Pb, Hg) activities (Farrell et al. 1993; Ritchie et al. 2001; Vassil et al. 1998) in nutrient and artificial soil solutions. In addition, this program has been an important tool in creating test solutions for plant aluminum (Al) tolerance experiments (Liao et al. 2006; Shen et al. 2004; Silva et al. 2001; Taylor et al. 2000). Thus, one is able to estimate Al^{3+} activities and to create solutions without significantly lowering the activities of the other nutrients, such as phosphate or sulfate. Many of the Al-containing nutrient solutions that are presently in use contain very high Al levels in order to achieve the desired root growth inhibition only because the Al has interacted strongly with anions and thus, is unavailable to the plant.

As helpful as GEOCHEM-PC has been to a number of scientists in their work since its introduction, the consensus among users was that the program was not very user friendly, was difficult for new users to learn and to troubleshoot, and suffered from several functional weaknesses. Indeed the authors of Geochem-PC (Parker et al. 1995a) wrote that part of future development of the program would be a more convenient and intuitive user-interface (i.e. a better “front-end”). For example, there were no “Help” files incorporated into the program to assist those who were new to the program. One learned from others or by trial and error. If there were any errors in creating the “DAT” input file used for the chemical speciation calculations, then the program did not indicate what they were and would not generate an output file. The program was written in FORTRAN to be run in a DOS environment, so file or directory names were limited to eight characters or less. This made naming and finding the proper files more difficult. Data entry involved parsing the salts (e.g. $CaCl_2$, NH_3NO_3) added to the solution into the individual metals and ligands, calculating their respective concentrations, and then entering these concentrations as the negative log of the concentration into a “DAT” input file. This took some time and, at each of these points, there was another opportunity for input error. Some calculations required several iterations to obtain the correct answer. This involved having to save the file, run

the calculation, examine the output file, make appropriate corrections, input the data again, save the file, and make additional calculations. In discussing these issues with the authors of GEOCHEM-PC (Parker et al. 1995a) we were encouraged by them to build upon and to improve the existing program, so that it would work in a Windows XP, Vista, or Windows 7 environment and would have increased power and function. Our aim was to redesign the program so that it would be easier for new users to learn, have interactive components for identifying and for correcting errors, would include Help files, and still include advanced options for experienced users. We also wanted it to be able to open input (DAT) files that have been previously generated using Geochem-PC. In this way, the existing Geochem-PC could be integrated fully into Geochem-EZ.

Methods

All code has been written and compiled using Java Standard Edition 6. All components of the Graphical User Interface (GUI) were created using the Netbeans 6.0's GUI editor. The new GUI updates Geochem-PC to fit the Windows application paradigm. The active interface will be distributed as a precompiled, executable Java Archive (JAR) file wrapped in a Windows executable file. As such, the Geochem-EZ program requires Java SE6 update 7 or higher, which is available for download from Sun Microsystems (<http://www.sun.com/download/index.jsp>). Geochem-EZ contains the GEOCHEM-PC executable file embedded in a simple and clean Java interface. We also have retained the Geochem-PC database of equilibrium constants that can be customized by the user, as well as the numerical algorithm to estimate ionic interactions.

New and basic users can easily negotiate the interface for simple data entry. However, we have retained within the interface the full functionality of GEOCHEM-PC within the new interface, allowing advanced users to perform complex calculations. Geochem-EZ will run on any computer that supports a Windows XP, Vista, or Windows 7 environment. This includes Mac computers running Windows emulation programs (e.g. Parallels Desktop). Help files were developed using Adobe Dreamweaver and scripted in HTML to be viewed through any

conventional Web browser (e.g., Mozilla Firefox, Internet Explorer). These Help files were also incorporated into the program, but can also be viewed outside of the program as a stand-alone feature. Geochem-EZ will be available as free software from our web site: <http://www.PlantMineralNutrition.net>. User support questions can also be addressed to the authors via the program or the web site. The downloaded zip folder will include all of the program elements and help files, as well as example files to illustrate various types of advanced solution analyses.

Results

Included in GEOCHEM-EZ are improvements which would be expected by modern users (customizable user-experience, extensive interactive and illustrated help files, hierarchical organization of options, logical output, real-time error checking), while maintaining complete backward compatibility to the GEOCHEM-PC format.

Users may load input data for calculations from two types of files. The first of which is a Geochem-PC generated DAT file, which provides the backward compatibility. The file is scanned and passed through a number of sets of logic which fill out the Geochem-EZ interface so that this new calculation will generate output identical to the original. The second type of input file is a GEO file which is the primary file type for this program. GEO files are basically, an Extensible Markup Language (XML) print out of the state of Geochem-EZ's interface components and upon being loaded, are simply parsed and the text is restored to its original form.

A customizable database of common salts has been included, which eliminates the need to parse and to calculate the concentration of each metal or ligand. Here, a salt is a previously determined combination of metals and ligands that can be added to the Geochem-EZ calculation. Salts can be created and modified by a user at any time and are stored in a database, which holds their name, molecular weight and list of ionic components. To simplify the creation of salts, a parsing-grammar was created. In this grammar, metals, ligands and old salts are categorized as tokens. Integers immediately following tokens are equivalent to subscripts in standard notation. An asterisk followed by an integer is a pre-multiplier, and a

parenthesis may be used to group ingredients together. This is best illustrated by a few examples.

M., N, L, P are metals/ligands/defined salts.

M2N4 contains 2 M's, 4 N's

M3(L1P2)2 contains 3 M's, 2L's, 4P's

M2N2*2(L1P2) contains 2M's, 2N's, 2L's, 4P's.

The masses of all the metals and ligands are stored in a separate database, and are automatically inserted by the interface. Users can give salts any name they choose, as long as the names begin with a letter and contain only alpha-numeric characters and asterisks. At this time the user may also write a brief explanation of what the salt contains, which will be saved in the salts database. In Geochem-EZ, the interface reads the top section of the database that the user specifies and holds the metal and ligand codes in memory. Each metal/ligand can then be referenced by its name in Geochem-EZ.

In addition, the user is no longer limited to enter concentration as *nM*, μM , or *mM*, but he or she can now enter the concentrations as g/L or mg/L, provided the salts of interest are part of the salts database. These last two features will make data input more rapid and help in eliminating the most common user errors. Within the Help menu we have included a Unit Converter which can convert any salt in the database from g/L or mg/L to molar concentrations or vice versa. The program does automatically check for errors in data entry, convergence, and case similarity.

The user can instantly preview input and output files and make necessary corrections (e.g. charge balance the solution, alter ionic components), something that formerly involved having to save the Geochem-PC DAT files and run the calculations a second or third time. Output file content can be modified by choosing the desired output tables prior to saving the file or by initially choosing them in the advanced options mode. Currently, there are a maximum of seven output files that can be generated for each case analysis, six of which can be chosen in the advanced options area and one (infinite dilution table) that is generated by default.

Figure 1 illustrates the GEOCHEM-EZ interface in the advanced entry mode, displaying all of the available options. The default mode for the program is for a basic interface which can analyze solutions at fixed pH, with or without solids or precipitation. For

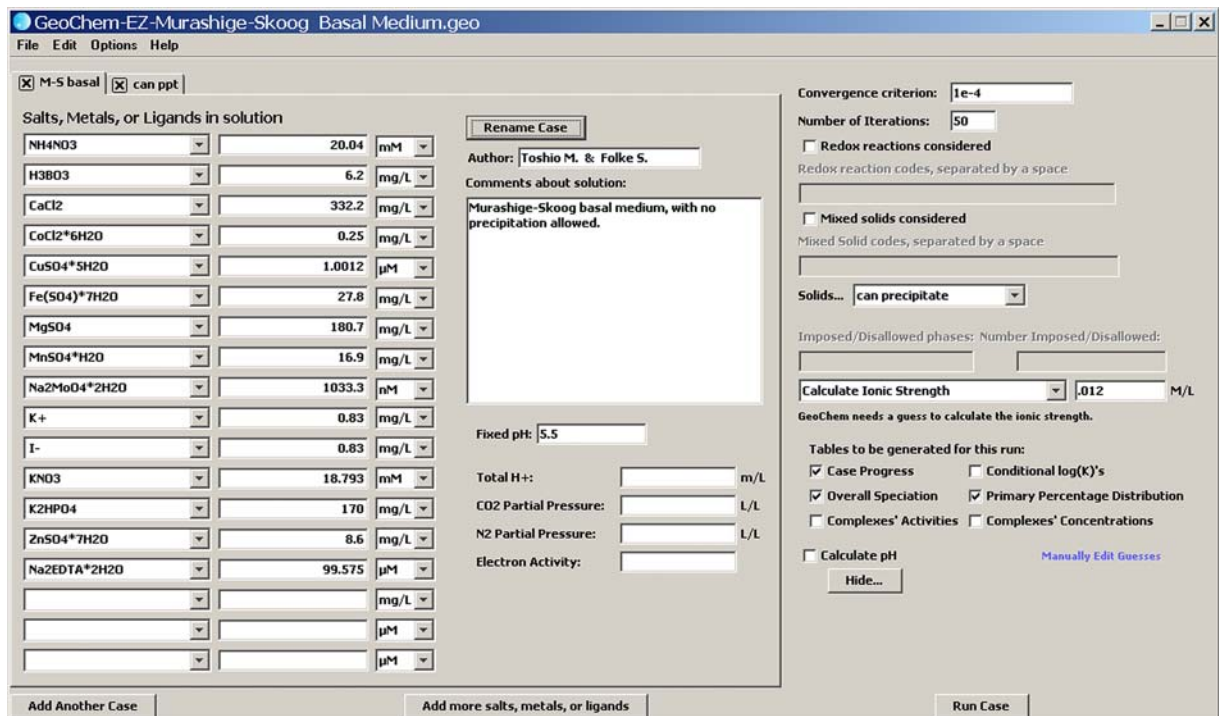


Fig. 1 Geochem-EZ interface showing the basic (*left side and upper center* of the interface) and advanced options (*right side and lower center* of the interface). Solution components of this

basal Murashige–Skoog medium are entered via a series of drop down menus on the left, along with their concentrations

this example a basal Murashige–Skoog (M-S) medium, pH 5.5 is shown, with the salt, metal, and ligand concentrations entered, both in mg/L and molar units. Note that the entries are mostly salts (e.g., NH_4NO_3) that are contained within the salts database and are accessed via the drop down lists on the left side of the interface. However, the user may still add individual metals or ligands, if that is preferred. The entry shown for the M-S medium represents a simple calculation (fixed pH, no redox reactions, solids can not precipitate). Note that there are two tabs open (M-S basal, can ppt), representing two separate cases (calculations) that are being run simultaneously. For the second case the solution components are the same as the one shown, except that the calculations allow for solids to precipitate. For cases run at the same time the individual ions in the solution must be the same, but other conditions, such as the respective ion concentrations, solution pH, precipitation, CO_2 and N_2 partial pressures, etc. can be varied. In each case, up to 20 metals and 30 ligands can be considered. A maximum of 10 cases can be run at the same time, another feature that makes solution analyses more rapid.

Further inspection of the Geochem-EZ interface in Fig. 1 shows that there are several advanced options available to the user. Most of these are located on the right side and bottom center of the interface. These can include the analysis of solutions in which the CO_2 partial pressure is important, such as solutions containing inorganic carbonate that are open to the atmosphere. The program can also compute the distribution of redox species if the redox potential of the system is specified. As many as 20 redox reactions can be considered in a single run. Currently, the database contains 29 different redox reactions, but more can be added. Geochem-EZ will calculate the pH of the solution based upon the solution composition and the total proton concentration. In addition, the program allows the user the option to include precipitates and solids formation as part of the calculations. One can exclude or impose particular solid phases, as needed. For all of these advanced options we have included a number of “GEO” files as examples of how to properly input data into the Geochem-EZ interface. As well, there are detailed Help files covering all of the advanced calculations.

For those who are more familiar with solution chemistry and who wish to change the stability constants for selected complexes and simple solids, there is the option to create separate or modified thermodynamic databases for the chemical speciation calculations. Geochem-EZ comes with a default thermodynamic database, Geodat.lig, that has stability constants for 41 metals and 83 ligands, but this can be easily edited and there is the option to add more metals or ligands to the database.

Discussion

Why should one use this program to design experimental solutions? Many scientists have modified standard nutrient solutions for hydroponics-based research or for specific experimental treatments without having analyzed these solutions to see whether any precipitation or solids may form because of these changes to the solution. Geochem-EZ can help predict potential problems in experimental media. This program can also be used to design

sensible chelate buffer systems or to calculate the concentration of a particular ion needed to provide a constant ionic activity. It is also a good way to know whether there is sufficient free activity of important nutrients in the solution of interest. Often, there is the assumption that if the nutrient is part of the solution, then it is readily available to the plant. This is not necessarily true. Interaction with other ions, pH effects, complexation, and precipitation may occur, reducing the free activity of the ion of interest.

An example of the program's strength can be found in analyzing a Yoshida's rice nutrient solution (Yoshida et al. 1971) containing 1.3 mM Al (35 ppm Al), pH 4.0, which is often used to investigate rice Al tolerance (Nguyen et al. 2003; Wu et al. 2000). We employed Yoshida's solution for our initial experiments on rice Al tolerance until we discovered it had some important solution chemistry problems. Many rice lines are fairly Al-tolerant and, thus, require higher activities of Al^{3+} in their test solutions in order to elicit root growth inhibition, the most widely used indicator of Al-tolerance. As with other scientists, we chose to use for our experiments a nutrient solution

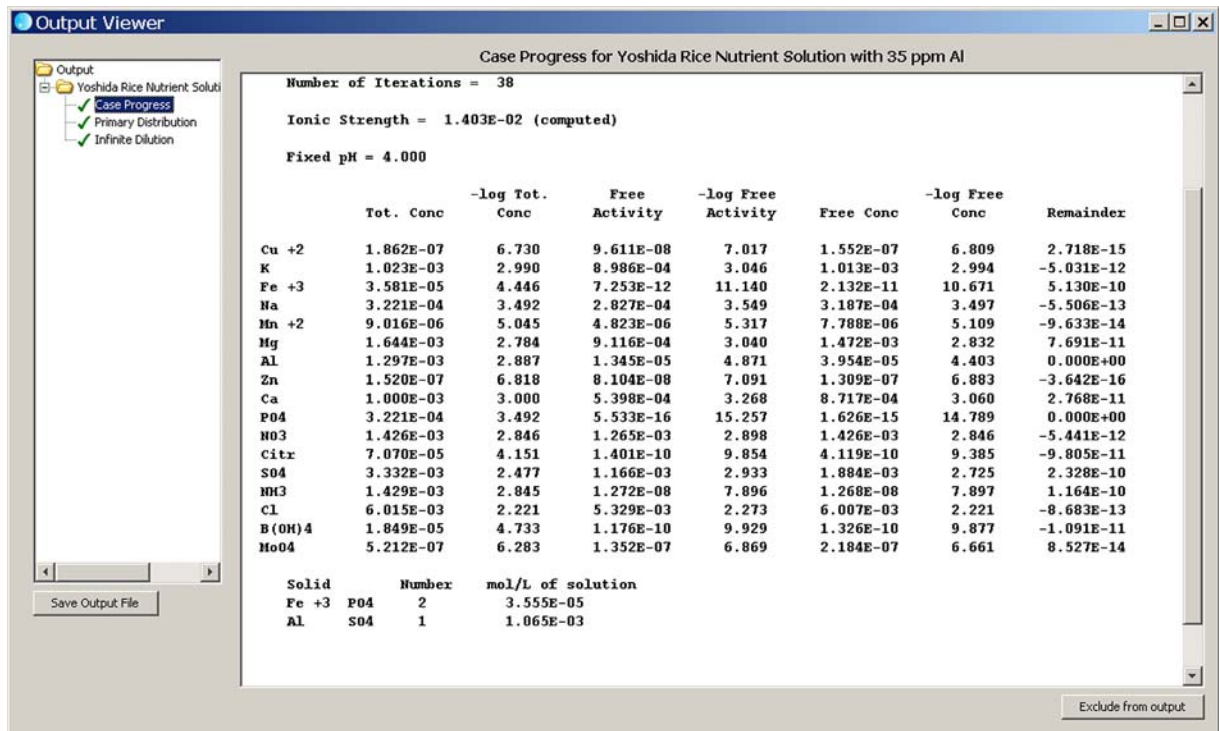


Fig. 2 The Case Progress output table for a Yoshida's rice nutrient solution, pH 4.0, containing 35 ppm Al. This table compares the original concentrations of the anions and cations

added, to their free activities and free concentrations. It also shows any solids or precipitates that are predicted to form

that had appeared previously in the scientific literature. However, when we actually made the solution we soon discovered that there was precipitation in the solution. We analyzed the precipitate and supernatant fractions with Inductively Couple Plasma Emission Spectrometry (ICP-ES) and found that half of the aluminum, 80% of the phosphate, and 87% of the iron had precipitated. Concomitantly, we analyzed the same Yoshida's rice nutrient solution, 1.3 mM Al, pH 4.0, using Geochem-EZ to look at how the program predicts ion activities and precipitation.

When Geochem-EZ analyzes a solution it generates several output tables, according to the user's selection. This allows the output data to be presented in a number of ways and it increases the power of the analysis. Consider the ways that the data are shown in the Case Progress (Fig. 2) and the Primary Percentage Distribution (Fig. 3) tables. Figure 2 shows the Case Progress Output Table for a Yoshida's rice nutrient solution, pH 4.0, with 1.3 mM AlCl₃ added. Solids were allowed to precipitate for this solution analysis. This table compares the amount of the ion originally added to the solution, i.e. the total concentration (Total Conc), to what is actually available in solution,

the free activity. Both of these values are presented in "E" scientific notation. For example, the Mn⁺² has a total concentration of 9.016E-6 or 9.016×10⁻⁶ M. Parker writes that "with terrestrial higher plants, the majority of evidence is consistent with the notion that responses correlate best with activities of free, uncomplexed metal ions in solution" (Parker et al. 1995b, 2001) and thus, these activity values are important in crafting a proper experimental or nutrient solution. What one sees from comparing the total aluminum concentration with its free activity is that the majority of aluminum is not free in solution. Much of the aluminum is predicted to react with sulfate, as shown at the bottom of the Case Progress table—Solids. Also, iron (III) is predicted to form a solid with phosphate, so as a result of these two interactions, both sulfate and phosphate are lowered in the nutrient solution. This does not happen in the control solution analysis. Citrate was originally added to the Yoshida's solution to be the ferric iron chelate and acts as such, but only in the absence of Al. The treatment solution (35 ppm Al) and the control solution are not similar at all, with respect to all the other components. When comparing these two sol-

Ion	Species	Percentage
Al	3.05 % as a free metal	3.05 %
	4.76 % complexed with S04	4.76 %
	82.08 % in solid form with S04	82.08 %
	5.41 % complexed with Citr	5.41 %
Fe +3	4.52 % complexed with P04	4.52 %
	.18 % complexed with OH-	.18 %
	.47 % complexed with Citr	.47 %
Na	.25 % complexed with P04	.25 %
	99.28 % in solid form with P04	99.28 %
	98.95 % as a free metal	98.95 %
Cu +2	.58 % complexed with S04	.58 %
	.47 % complexed with Cl	.47 %
	83.35 % as a free metal	83.35 %
Zn	14.99 % complexed with S04	14.99 %
	.23 % complexed with N03	.23 %
	.01 % complexed with NH3	.01 %
	.78 % complexed with Cl	.78 %
	.21 % complexed with Citr	.21 %
	.42 % complexed with P04	.42 %
S04	.01 % complexed with OH-	.01 %
	86.07 % as a free metal	86.07 %
	12.30 % complexed with S04	12.30 %
	.19 % complexed with N03	.19 %
	.80 % complexed with Cl	.80 %
	.09 % complexed with Citr	.09 %
Cl	.54 % complexed with P04	.54 %
	.01 % complexed with OH-	.01 %
	99.87 % as a free ligand	99.87 %
	.02 % complexed with K	.02 %
Citr	.03 % complexed with Na	.03 %
	.08 % complexed with Mg	.08 %
	.24 % complexed with Fe +3	.24 %
P04	99.29 % complexed with Al	99.29 %
	.03 % complexed with Ca	.03 %
	.04 % complexed with Mg	.04 %
	.40 % complexed with H+	.40 %
	.03 % complexed with Fe +3	.03 %
Fe +3	11.04 % in solid form with Fe +3	11.04 %
	18.18 % complexed with Al	18.18 %
	1.05 % complexed with Ca	1.05 %
	.03 % complexed with Mg	.03 %
	69.67 % complexed with H+	69.67 %

Fig. 3 The Primary Distribution Output table for a Yoshida's rice nutrient solution, pH 4.0, with 35 ppm Al. This table shows how a particular ion interacts with its counter ions and to what extent

Table 1 Ionic interactions predicted by Geochem-EZ. Primary Percentage Distribution output tables for Yoshida's rice nutrient solutions, pH 4.0, containing 0 and 35 ppm Al, were combined to show the speciation of the individual metals and ligands as a percentage of the total

	%	0 ppm Al	35 ppm Al		%	0 ppm Al	35 ppm Al
Fe ³⁺	complexed with PO ₄	0.25	0.25	PO ₄ ⁻	complexed with Al	—	18.18
	in solid form with PO ₄	25.71	99.28		complexed with Ca	1.35	1.05
	complexed with Citrate	74.03	0.47		complexed with Mg	0.04	0.03
Zn ²⁺	as a free metal	73.05	86.07	complexed with Fe	0.03	0.03	
	complexed with Cl	0.25	0.80	solid form with Fe	2.86	11.04	
	complexed with SO ₄	16.25	12.30	complexed with H	95.73	69.67	
	complexed with NO ₃	0.17	0.19	Citrate	complexed with Fe	38.51	0.24
	complexed with Citrate	9.65	0.09		complexed with Al	—	99.29
complexed with PO ₄	0.63	0.54	complexed with Ca		4.17	0.03	
Al ³⁺	as a free metal	—	3.05	complexed with H	52.35	0.40	
	complexed with SO ₄	—	4.76	complexed with Mg	4.78	0.04	
	in solid form with SO ₄	—	82.08	SO ₄ ⁻	as a free ligand	86.01	56.53
	complexed with Citrate	—	5.41		complexed with Ca	5.42	3.74
	complexed with PO ₄	—	4.52		complexed with Al	—	2.01
complexed with OH	—	0.18	solid form with Al		—	31.95	
Cu ²⁺	as a free metal	61.26	83.35	complexed with Mg	7.39	5.01	
	complexed with SO ₄	17.16	14.99	complexed with K	0.43	0.28	
	complexed with Citrate	20.77	0.21	complexed with H	0.61	0.39	
	complexed with Cl	0.21	0.78	NO ₃ ⁻	as a free ligand	100.00	100.00
	complexed with PO ₄	0.42	0.42		NH ₃	as a free ligand	100.00
complexed with NO ₃	0.17	0.23	MoO ₄	as a free ligand		41.38	41.90
Ca ²⁺	as a free metal	81.20		87.17	complexed with H	58.62	58.10
	complexed with SO ₄	18.06	12.46	Cl	as a free ligand	99.87	99.87
	complexed with PO ₄	0.43	0.34		complexed with K	0.02	0.02
Mn ²⁺	as a free metal	81.24	86.38		complexed with Mg	0.08	0.08
	complexed with Cl	0.43	1.28		complexed with Na	0.03	0.03
	complexed with SO ₄	18.07	12.34	B(OH) ₄	complexed with H ⁺	100.00	99.45
K ⁺	as a free metal	98.55	98.99		complexed with Al	—	0.55
	complexed with Cl	0.03	0.09				
	complexed with SO ₄	1.42	0.91				
Mg ²⁺	as a free metal	84.71	89.52				
	complexed with SO ₄	14.97	10.16				
	complexed with Cl	0.11	0.31				

utions there are now, in fact, multiple variables (aluminum, sulfate, phosphate, iron) to consider when assessing treatment effects. Table 1 compares the ionic interactions predicted by Geochem-EZ for Yoshida nutrient solutions with and without 35 ppm Al, and illustrates the differences in their chemical speciation.

The Primary Percentage Distribution Table (Fig. 3) shows how a particular ion interacts with the other ions in a Yoshida's solution containing 35 ppm Al. One can see that 82% of the aluminum added is

predicted to be in solid form with sulfate. In addition, citrate (Citr) has complexed almost completely with Al (III). When Al is added, only 0.24% of the citrate is predicted to chelate the Fe, whereas almost 39% of the citrate is complexed with Fe in an Al-free solution. Here, 99.3% of the citrate is complexed with aluminum, leaving very little to react with the iron. As such, the ferric iron is more available to react with phosphate. However, with a basic Yoshida's nutrient solution (no Al) which has no competition for

anions by Al, 74% of the ferric iron is chelated with citrate, rendering it less available to interact with phosphate. These results are not surprising, since citrate is an excellent Al chelator and this chemical interaction allows other interactions (Fe-PO₄, Al-SO₄) to occur. The substitution of a different iron (III) chelate for citrate would help to solve this part of the problem. For example, according to Geochem-EZ calculations, EDTA or EDDHA added in place of the citrate would almost completely eliminate the Fe-PO₄ interaction. This is a good example of how important chemical speciation programs, such as Geochem-EZ, can be in designing the appropriate experimental solutions.

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